

Jean-Pierre de Vera  
Joseph Seckbach *Editors*

# Habitability of Other Planets and Satellites

# HABITABILITY OF OTHER PLANETS AND SATELLITES

# Cellular Origin, Life in Extreme Habitats and Astrobiology

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Volume 28

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*Series Editor:*

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*The Hebrew University of Jerusalem, Jerusalem, Israel*

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# Habitability of Other Planets and Satellites

*Edited by*

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## **DEDICATION**

This book is dedicated to all colleagues of the Helmholtz-Alliance “Planetary Evolution and Life” and in particular to Prof. Tilman Spohn, Dr. Gerda Horneck, Prof. Sieglinde Ott, my wife Elena, my parents and my sister who opened the door to the Universe



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## INTRODUCTION

The main themes of this book are focusing on environmental properties ranging from cosmologic to micro-niche areas. Environmental conditions might play a major role in influencing planetary surfaces and may act on the interior of planets and satellites. The environmental conditions are important for the emergence, maintenance, and enhancement of habitability. In this book, we attempt to give an insight into the nature of planets and their moons or satellites. We discuss their potential to harbor life and the role of life itself as an engine to increase the habitability of planets as well as satellites. Knowledge of different disciplines, such as astronomy, biology, chemistry, geology, physics, and planetology, is the driving force for this book where the question is addressed what might be the clues to classify a planetary body as a habitable object. The role of radiation, magnetism, and the atmosphere on habitability, as discussed in Part 1 in this issue (see chapters of Kane, Grenfell et al., Shaviv et al., Talmi et al., Hengeveld, and by Möhlmann), is one step to address the question what makes a planet habitable.

It is commonly agreed that the three driving forces, which are most important to develop and maintain life, are energy, the presence of a solvent (e.g., water), and preservation and replication of information. These are also the three main themes, which are considered in Part 1 of this book. Earth can be the only reference system, because we have not yet found life anywhere else in the universe. Terrestrial life-forms are therefore references for life in general to get an approximation of the factors, which might be important for classification of a celestial body as a habitable object. The role of crater analysis at the poles of the Moon is also an important way to gain an insight into the early history of the solar system. Furthermore, it is important for finding potential areas of preservation in the lunar ice for possible remnants of early terrestrial life, which might give information on how life looked like in the very early beginning of our planet, which had complete different environmental conditions if compared to present days (Schulze-Makuch in Part 2). The role of tectonics for habitability of a planet (see Noack et al. in Part 4) might give some answers on the necessity of planetary dynamics and the recycle process of probably rocky nutrients for the appearance and maintenance of life on a planetary body.

Results from field studies in planetary analogs (see chapters of Barbieri in Part 3 and Westall in Part 4 of this book) and obtained by laboratory studies in space and planetary simulation facilities on Earth might help to answer the question if some locations on, or in, the planets and satellites of our solar system would be able to create areas where life could originate or be potentially habitable. An approach to answering this question is presented in Part 3, where the analysis

of chemical organic processes in simulated volcanic environments is presented as possible prebiotic processes for the origin of life (see Strasdeit et al.) or given by the example of investigations with life-forms in experiments which simulate the conditions of other well-studied planets of our solar system, such as Mars (Lorek et al.). Further on, the discussion is enlarged in particular to extrasolar planets and their potential to be habitable (see Noack et al. and Kane, in Part 4; Raven and Donnelly, in Part 5).

One of the challenging tasks of the book is to develop less Earth-centric scenarios with developing conditions, which might also be responsible for the origin of life and/or its suitability (see chapters of Schulze-Makuch, Raven and Donnelly in Part 5). Considerations gained by the exclusion of the Earth-centric view might have important implications on the characterization of the habitable zone because the habitable zone around a star, or even a planet, is characterized by a specific zone where the environmental conditions are supporting the existence of liquid water on the surface of a planet. However, this idea does not take into account that solvents other than water might exist under other conditions and a different chemistry might be possible, providing complex organic molecules and probably the formation of life. For example, M-type stars (Raven and Donnelly) or giant stars, which are clearly distinguishable from our star, the Sun, provide different radiation fluxes and have different spectra ranges (Talmi and Shaviv) reaching surfaces of exoplanets and their satellites in the habitable zone. Consequently, the temperature, the atmospheric composition, and the pressure as well as the mineral composition and the liquid solvent on these exoplanets might be completely different to what we know from our home planet, Earth. Are these different worlds completely uninhabitable? Is the likelihood of the formation of life completely excluded on planets and satellites, which are clearly different from Earth? Is the Earth the right model and therefore our Earth-centric view the only universal key to understand habitability, the origin, and maintenance of life? This book tries to give answers on these questions; however, it is a clear understanding that these answers present that would be approximations to reality and would build up new scientific theories. No final answer can be forthcoming until we have shown that there are no other planets harboring life.

For this reason, instruments are needed, which are able to detect life, and new missions with the focus to find out the existence or absence of “life as we know it” are very important in future space exploration enterprises. Part 6 is focusing on recent technologies, which might be suitable for searching remotely (Rauer et al.) or in situ (Edwards et al. and Böttger et al.) for habitable environments and life. Examples of instrumentations, detection devices, space projects, and space mission designs to search for habitable niches and life are given also in Part 7. In this part, the authors give insights into the challenges we might confront if we pursue the main task to detect life. Promising missions to the icy moons of the Jovian and Saturnian system (Chela-Flores, Dachwald et al.) are discussed, and a concrete promising mission might be the project IceMOLE, which plans to land a probe on the icy surface of the polar caps of Mars or on some of the

Jovian or Saturnian icy satellites. The plan is to melt the probe into the thick ice layers and acquire information about the nature of the ice and the absence, or existence, of water pockets as probable habitats or the existence of minerals as nutrients and salts or the presence of organics or even traces of life transported by the tidal movement of the ice to the near surface areas (see Dachwald et al.). In summary, it can be considered that the initial step of these exploration endeavors might be to discover first habitable environments and then to look for organics or life-forms with well-developed and applied life-detecting instrumentation in the discovered habitable niches.

In the very last chapter (Part 8), we will summarize and give some conclusions, which cover the implications on the society if habitable worlds and even extraterrestrial life are discovered. The existence of other habitable worlds and life in the universe would complete the Copernican and Darwinian revolution and would emphasize that life is a universal phenomenon and not an anomaly or particularity. In a provoking further step, we might be able to formulate the thesis that the evolution of life and the formation of intelligence is a usual process in our universe. Discoveries supporting the last thesis could consequently have an important impact on religions, philosophy, and the human society itself.

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December 2012

Biodata of **Dr. Jean-Pierre de Vera**, editor of this book and author of the chapter “*Introduction*” and “*Summary and Conclusions*” (with coeditor and coauthor: **Joseph Seckbach**) and coauthor of the chapter “*Application of Raman Spectroscopy as In Situ Technology for the Search for Life.*”

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## FOREWORD

### Habitability of Other Planets and Satellites: *The Quest for Extraterrestrial Life*<sup>1</sup>

The questions “are we alone?” or “is there anybody out there?” have been often asked in history and currently even more intensely. Billions of planets in our galaxy may have the potential for life following the preliminary multiple discoveries from the Kepler Mission. Today astronomers are developing powerful ways and means to find it. There are efforts by most space agencies to investigate first the solar system neighboring celestial worlds. The search for life and life-supporting environments in the solar system is vital for understanding also the origin of life.

This search for extraterrestrial life has developed with the ability to flyby and with the visit of rovers to some neighboring celestial planets and moons. Knowing the environmental conditions of Earth-like extraterrestrial bodies could assist in the analysis of chances for life on them. The flyby over Mars and Europa (satellite of Jupiter) and the rovers over Mars exposed surficial details and may provide answers to the queries posed above. Europa was discovered in 1610 by Galileo Galilei. It is slightly smaller than Earth’s moon and has a thin atmosphere composed also of oxygen; its surface contains water ice striated by cracks and streaks. The smooth surface has suggested that an ocean exists beneath it that could carry extraterrestrial life. This ocean of liquid water is heated by geological activity similar to plate tectonics.

In the past, the red planet was most probably warmer and wetter, with green coverage. It has been suggested that Mars probably had life at one time. The surface morphology of this planet shows traces of water bodies such as lakes, rivers, canyons, and other water-carved features.

Under the icy layer of the Russian Antarctic research station Vostok lays a large salty lake, which may harbor organisms. The drilling down toward the lake’s surface exhibited various organisms in the icy cores removed out of the boring. This Vostok undersurface lake might be a good analogue or a model for the proposed large, European salty liquid ocean. Life might be possible there, too, as it exists in Vostok’s undersurface lake. A similar subsurface ocean may exist in other bodies of our solar system. The next mission to Europa is the Jupiter Icy Moon Explorer (JUICE), due to be launched in 2022. On planets or on the surface of satellites, there are some chances for life where there is the presence of liquid water, which is a prime requirement for life, along with sources of energy, chemicals, and suitable environment.

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<sup>1</sup>The author thanks Professors Julian Chela-Flores and Francois Raulin for improving this Foreword and appreciates the styling and language fixing by Fern Seckbach.



If, however, there is a possibility for life to exist in nonaqueous area, then theoretically there is a good chance to find life on Titan (moon of Saturn). Titan contains the aliphatic alkanes of ethane and methane that exist there in lakes and rivers in a state of liquid aggregation. In any event, Titan does not have enough heat to support “normal” life.

Venus, the “twin of Earth,” is known as a non-habitable; its physical and environmental conditions (high temperature, radiation, CO<sub>2</sub> atmospheric composition, and high pressure) do not enable any life-form as we know it. Yet, the conditions of the close atmospheric layer over the planet are milder and cooler, and one might expect to find traces of life there. In the past, some suggestions appeared in the literature for terraforming the atmospheres of some close celestial bodies with cyanobacteria (blue green algae) in order to make them inhabitable.

The hypothesis of panspermia (origin of life from “space”) in our solar system, as a result of ancient impacts due to the Late Heavy Bombardment, raises the possibility of exchange of microorganisms between the habitable planets, such as Mars and the Earth, and the spreading life-forms have to consider also the presence of the asteroid belts.

Extremophiles are terrestrial microbes that could tolerate very harsh conditions in their habitats; they have been pointed out as analogues for habitants on extraterrestrial worlds. These organisms live in very severe conditions such as high temperature, elevated pressure, concentrated salt solution, anaerobic habitats, and extreme pH ranges, and they tolerate various gases in their atmosphere (for further information, see volumes 1, 2, 11, and 26 of the Springer series *Cellular Origin, Life in Extreme Habitats and Astrobiology*).

This volume contains **8** parts encompassing **21** chapters contributed by **37** authors from **8** countries. The main purpose of this volume is to investigate the conditions of habitability of extraterrestrial worlds.

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## PREFACE

The history of science is marked by those special moments where completely new ideas, or concepts, emerge out of scientific laboratories to become part of everyday life. A possible way to assess the importance of such turning points is to imagine the answer a parent would give to a young child in reply to questions asked by children for thousands of years. In the early twentieth century, galaxies were not even known to exist. In the 1920s, due to the work of Hubble, the answer to the question “what is the Milky Way?” became clear: “The Milky way is a galaxy of stars, one out of billion such objects in the universe.” The answer to the question “what kind of universe we are living in?” became, in 1998, “an expanding and accelerating universe,” and the answer to the question “what is the moon?” became, in July 1969, “a place that human beings can walk on.” The year 1995 marked yet another turning point of this kind. Since this date, a parent can point to a faraway star and tell his or her child that right there, billions of kilometers away from us, there is likely to be a world, a planet, similar to our own Earth which possibly supports life. There are only a few moments in everyone’s life that the answers to such fundamental questions become clear. We are witnessing one of these moments, and the present book is an attempt to start to provide more detailed answers, involving scientific terms and facts, to questions about such faraway worlds.

The area of extraterrestrial planets and life in the universe has undergone a revolution since 1995. While many studies have been conducted prior to this time, today they are becoming a center stage of science. From pure astronomy (search for extrasolar planets) or geophysics (the structure of solar system bodies), today we are witnessing the formation of a new, interdisciplinary field that includes geophysics and astrophysics, chemistry and biology, ecology, communication, and more. New departments of astrobiology are being opened in many academic centers, and scientists from different fields are joining effort in attempt to build and launch new satellites that will not only measure the size and mass of these remote bodies but also look for signs of life in their atmospheres. This research is likely to shape and reform the twenty-first-century science.

The chapters presented below will help the interested reader to have a glance at the huge progress in this new and developing field. The basic terminology used in some of the articles still resembles the one used in the 1970s and 1980s, but the content has changed significantly. For example, the old concept of “habitable zone” that used to refer to the vicinity of G-type stars (those similar to our Sun) is expanding to include much smaller and cooler M-stars since, as the space mission “Kepler” shows, most Earth-size planets are likely to revolve around such stars. Can Earth-like life be created and evolve in such different environments? Chemist and biologists are looking into this issue using new theories and experimental

tools. Information about the chemical composition of the Earth atmosphere is becoming the basis of new instruments that will be launched on future satellites with the purpose of detecting a signal of life in the atmospheres of faraway planets, hundreds and thousands of light years away from us. The little known properties of some unusual chemical compounds are studied in earth laboratories in attempt to test the feasibility and likelihood of life which is not based on water and carbon. Even those scientists looking for a signal from ET, in the SETI project, are starting to examine their next set of targets.

These are all signs of a true scientific revolution. The unusual aspect of this revolution is that despite its complexity, even a young child can understand its main questions and likely consequences that can lead mankind to change its perspective of the universe.

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**PART I:  
PARAMETERS FOR  
HABITABILITY, HABITABLE  
ZONES AND LIFE: ENERGY,  
LIQUID SOLVENT, INFORMATION**

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# THE HABITABLE ZONE: BASIC CONCEPTS

**STEPHEN R. KANE**

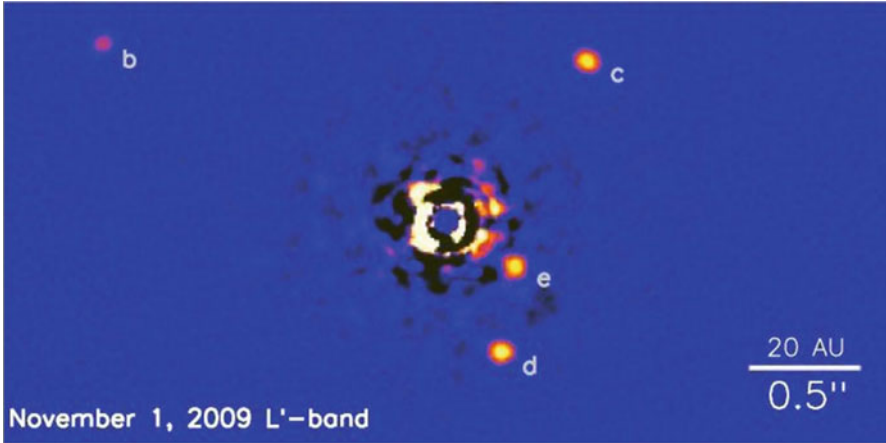
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## 1. Exoplanet Characterization

The detection of exoplanets has undergone extraordinary growth over the past couple of decades since substellar companions were detected around HD 114762 (Latham et al., 1989), pulsars (Wolszczan and Frail, 1992), and 51 Peg (Mayor and Queloz, 1995). From there, the field rapidly expanded from the exclusivity of exoplanet detection to include exoplanet characterization. This has been largely facilitated by the discovery of transiting planets which allows unique opportunities to study the transmission and absorption properties of their atmospheres during primary transit (Agol et al., 2010; Knutson et al., 2007) and secondary eclipse (Charbonneau et al., 2005; Richardson et al., 2007). In addition, studies of phase curves allow insight into the thermal and albedo atmospheric properties (Kane and Gelino, 2010, 2011). These studies are being applied to smaller planets as our detection sensitivity pushes down into the super-Earth regime (Bean et al., 2011; Croll et al., 2011).

Studies thus far have largely been directed toward short-period planets which are expected to have an a priori high effective temperature. This bias results from a relatively high thermal flux required from the planet in order for the signature to be detectable. One exception to this is the planet HD 80606b, with a highly eccentric orbit ( $e=0.93$ ) and an orbital period of 111 days, detected by Naef et al. (2001). Subsequent Spitzer observations by Laughlin et al. (2009), as well as the detection of the secondary eclipse of the planet, were used to measure the out-of-eclipse variations and estimate the radiative time constant at  $8\ \mu\text{m}$ . Interpreting these data to deduce atmospheric patterns is a highly model-dependent process and poorly understood for planets in the short-period regime due to the complex interaction of planetary structure, composition, tidal effects, and incident flux. As pointed out by Barbieri et al. (2007), ambiguous measurements of radiative time constants have prevented a consensus on expected planetwide flow patterns for short-period planets.

Characterization of longer-period planets have been greatly aided by the detection of planets via the imaging technique. The multi-planet system HR 8799 (Marois et al., 2008, 2010) has provided such opportunities since spectra of these planets may be directly acquired. Figure 1 shows data acquired of this system and



**Figure 1.** The HR 8799 system as imaged by Marois et al. (2010).

demonstrates the magnificent resolution which can be achieved in these cases. This has been undertaken using the Keck telescopes, the data of which have revealed strong water absorption which is indicative of a hydrogen-rich atmosphere for the outermost planet (Barman et al., 2011).

Studying the atmospheres of Earths and super-Earths obviously presents a significantly deeper challenge from an observational point of view. The discovery of a super-Earth orbiting the nearby M dwarf GJ 1214 (Charbonneau et al., 2009) has enabled studies of the atmosphere to be performed (e.g., Menou, 2012). This provides our first insight into the structure of these large terrestrial planets for which we have no analogs in our own Solar System. It also motivates further exploration and study of terrestrial size planets around low-mass stars in terms of their frequency, size distribution, and the possibility of their detection in the habitable zones of these stars.

The Kepler mission (Borucki et al., 2011) is expected to detect many transiting terrestrial size planets in the habitable zone of more solar-type (F, G, K) stars. However, the vast majority of the host stars will render the planets undetectable by other methods and certainly beyond the capabilities of traditional characterization. The detections will, however, provide invaluable information as to the frequency of these kinds of planets and inform the target selection for future missions, such as the James Webb Space Telescope (JWST).

## 2. The Habitable Zone

The expansion of exoplanetary science is leading the field toward the question of the frequency of Earth-like planets and, in particular, of habitable planets. The merging of stellar and planetary properties results in a quantitative description

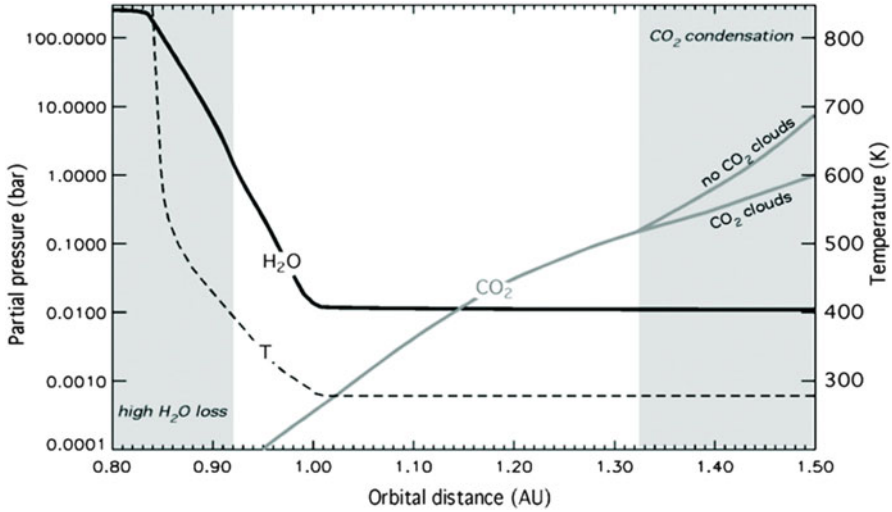
of the habitable zone (HZ), usually defined as that region around a star where water can exist in a liquid state. The HZ is a key concept in our understanding of the conditions under which basic life can form and survive. On our own planet, we find extreme conditions under which organisms are able to not only sustain metabolic processes but thrive and grow. Thus, this understanding informs our precepts on how life formed in our own Solar System and also the possibility of similar processes in exoplanetary systems.

Although the concept of the HZ has been in the literature for some time, it is only within the past 20 years that complex atmospheric models have been developed to allow a rigorous examination of its nature. In particular, the response of different atmospheres to varying amounts of stellar flux allows the determination of HZ boundaries for known exoplanetary systems. Although habitability had certainly been considered before, the concept of HZ first started to appear in the science literature during the 1950s in articles such those by Su-Shu Huang (1959, 1960). However, these were written at a time when atmospheric studies of other planets were in their infancy and the presence of planets outside of our Solar System had not yet been confirmed. The work of Kasting et al. (1993) was instrumental in new advancements in HZ research and in particular quantifying the boundaries in terms of climate models as well as the properties of the host star.

### 3. Habitable Zone Boundaries

The boundaries of the HZ for a particular system are calculated based upon both the stellar properties and assumptions regarding the response of a planetary atmosphere to stellar flux. Calculations for HZ boundaries have undergone considerable change since the published articles of Huang (1959, 1960). Estimates for our Solar System by Dole and Asimov (1964) were in the relatively broad range of 0.725–1.24 AU, compared with the conservative estimates by Hart (1979) of 0.95–1.01 AU. Detailed models for runaway greenhouse implications for Venus were considered by Pollack (1971) and Kasting (1988). For more recent studies regarding the HZ, we refer the reader to the detailed models of Kasting et al. (1993), Kasting and Catling (2003), Underwood et al. (2003), Selsis et al. (2007), and Jones and Sleep (2010). Here we describe the primary factors which influence the boundaries and present examples both in and out of our Solar System.

The premise that remotely detectable habitability requires water to exist on a planetary surface in a liquid state allows a quantitative representation of the HZ to be estimated. This is established by combining the stellar properties with those of a hypothetical planet at various distances from the star. The flux received by the planet is a function of this distance and the luminosity of the star. Kasting et al. (1993) used one-dimensional (altitude) climate models to calculate the response of the atmosphere to the flux by considering conditions whereby the equilibrium would sway to a runaway greenhouse effect or to a runaway snowball effect. The runaway greenhouse cycle is summarized as follows: stellar flux increases,



**Figure 2.** Water vapor and  $\text{CO}_2$  levels in the atmosphere of a habitable planet within the HZ (Kaltenegger et al., 2010).

temperature increases, temperature rise leads to an increase in water vapor, and increased greenhouse gas concentration leads to high temperatures. Note that the increase in water vapor leads to rapid loss of hydrogen due to  $\text{H}_2\text{O}$  photolysis and increased absorption at the wavelengths through which much of the Earth's infrared radiation escapes, thus propagating the runaway warming of the surface. The runaway snowball model is summarized as follows: stellar flux reduces, carbonate-silicate cycle feedback increases the amount of  $\text{CO}_2$  in the atmosphere, and the  $\text{CO}_2$  condenses to form clouds and a maximum greenhouse point is reached. This also results in significant amounts of atmospheric  $\text{CO}_2$  condensing as dry ice, increasing surface reflectivity and further reducing the greenhouse effect. Figure 2 shows one possible scenario for an Earth-like planet within the HZ of the host star which undergoes the carbonate-silicate cycle and is thus able to regulate the temperature within reasonable timescales (Kaltenegger et al., 2010). The sensitivity to semimajor axis is apparent in the levels of  $\text{CO}_2$  present in the atmosphere.

The overall habitability is further complicated by the various other factors inherent to the system. The flux from the host star depends on spectral type and luminosity class but also depends on the age of the star. As the age of the star increases, so does the luminosity, and, thus, the HZ moves outward from the center of the system. One then can consider a continuously habitable zone (CHZ) in which a particular planetary orbit may remain while the star is on the main sequence, since the movement of the HZ continues even after the star leaves the main sequence (Lopez et al., 2005). Figure 3 depicts the location of the HZ as a

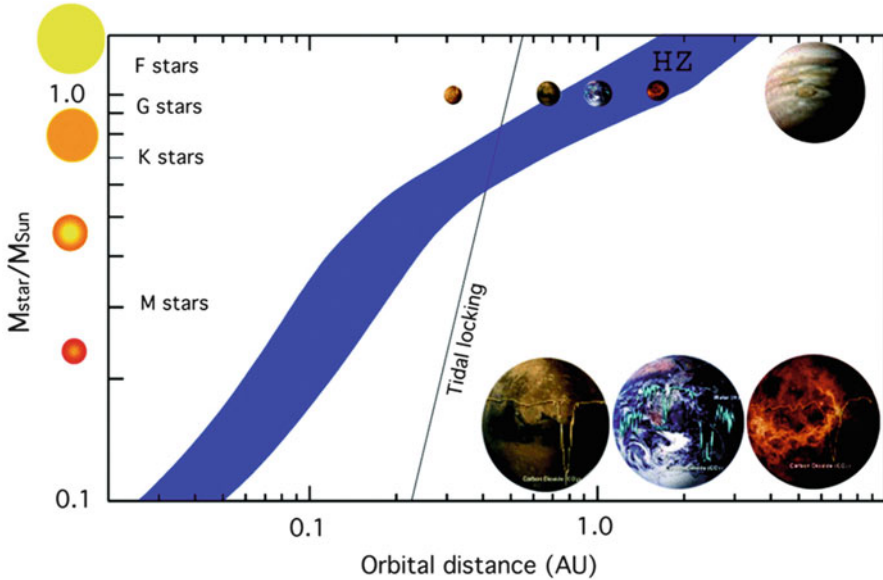


Figure 3. HZ as a function of stellar type (Kaltenegger et al., 2010).

function of the stellar type and semimajor axis of the planet (Kaltenegger et al., 2010). The “spectral fingerprints” of the three major terrestrial planets within our Solar System show remarkable variation considering that they all fall within or close to the HZ of the Sun. As described above, the planetary atmospheric and albedo properties play an important role in controlling the heat retained at the surface. The redistribution of that heat is in turn related to the planetary rotation rate, particularly important for planets in the HZ which may be tidally locked around late-type stars (Williams and Kasting, 1997). In addition, the planetary mass will influence such aspects as the amount of retained atmosphere and the level and continuity of volcanic activity. Too small a mass will likely lead to a lack of these attributes, and too high a mass will lead to a possibly inhospitable thick hydrogen envelope that will further obscure the visibility of biosignatures. Thus, optimal planetary masses exist which result in a more suitable balancing of these effects.

#### 4. Application to Exoplanetary Systems

These techniques may be applied to known exoplanetary systems for which there are a variety of host stars and associated planets. There have been numerous recent discoveries of super-Earth mass planets whose orbits have been found to lie within their stars’ HZ. Examples include Gliese 581 d (von Paris et al., 2010;

Wordsworth et al., 2011) which is in a multi-planet system around an M dwarf and the more recent case of a potentially habitable planet around HD 85512 (Kaltenegger et al., 2011). The investigation of the HZ for Kepler candidates is of particular interest since many of these planets fall in the terrestrial regime (Kaltenegger and Sasselov, 2011).

Many of the known exoplanets are of Jovian mass, and, thus, we do not necessarily consider them as habitable on their own. However, it is worth considering that these planets likely harbor their own systems of terrestrial moons considering the frequency with which we see such occurrences in our own system. Indeed, one may consider how the ecology of the Jovian moons may have evolved, were Jupiter in the Earth's current orbit. The habitability of exomoons has been considered in the literature (Kaltenegger, 2010; Porter and Grundy, 2011) and attempts are being undertaken to detect their presence from Kepler mission data (Kipping et al., 2009, 2012). There are also alternative energy sources for exomoons, such as tides, which may help or hinder habitability and even allow an extension of habitable conditions beyond the traditional HZ (Barnes et al., 2009; Scharf, 2006; Williams et al., 1997).

Although the concept of the HZ has been discussed for some time, it is only recently that sophisticated climate models are allowing concise quantification of this region. The study of exoplanetary atmospheres enables us to apply these concepts to known exosystems, even those with exoplanets in orbits which result in extreme temperature variations. A targeted search for exomoons in these environments may yield more surprises on what we consider "habitable."

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# EXOPLANETS: CRITERIA FOR THEIR HABITABILITY AND POSSIBLE BIOSPHERES

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## 1. Habitability: Historical Context

The word “habitable” is derived from the classical Latin *habitabilis* (to inhabit, to dwell). As early as 1853, William Whewell introduced the notion of a planet orbiting in the “temperate zone” where liquid water (an essential requirement for all life on Earth) on the surface is favored. A century later, astronomer Harlow Shapley (1953) discussed climate conditions for planets orbiting in the so-called water belt in the context of understanding Earth’s climate change. In the same year, Hubertus Strughold investigated the Solar System “ecosphere” (1953) as part of a physiological study of survival on Mars. Huang (1960) discussed the requirements a star should fulfill to support life in its so-called Habitable Zone (HZ). Dole (1964) then discussed the “complex life HZ,” the region where a planet has surface temperatures from 0 to 30 °C over >10 % of its surface, an oxygen (O<sub>2</sub>)-rich atmosphere and <1.5 Earth’s gravity. Hart (1979a, b) applied a numerical climate model to estimate the width of the HZ for liquid water and showed that runaway climate processes implied a thin HZ extending from 0.95 to 1.01 astronomical units (AU). Schneider and Thompson (1980), however, argued that understanding of complex climate feedbacks (e.g., between atmosphere and glaciation) suggested that such climate estimates are only “order of magnitude.” Kasting et al. (1988) showed that including long-term negative climate feedbacks such as the carbonate-silicate cycle could stabilize a planet’s climate and expand the HZ width calculated by the Hart et al. studies. A key study by Kasting et al. (1993) subsequently investigated the HZ width for a range of main sequence stars. In the modern literature, the HZ is widely studied, including models with, e.g., complex climate feedbacks, interactive atmospheric climate-chemistry (e.g., Segura et al., 2003; Grenfell et al., 2007a), radiative effects of clouds (Kitzmann et al., 2011), climate dependence on planetary orbit (e.g.,

Williams and Pollard, 2003), the effect of 3D planetary properties such as ocean mass and albedo (e.g., Abe et al., 2011), and investigation of climate and evolution (e.g., Selsis et al., 2007; Wordsworth et al., 2011).

## 2. The Classical Habitable Zone (HZ)

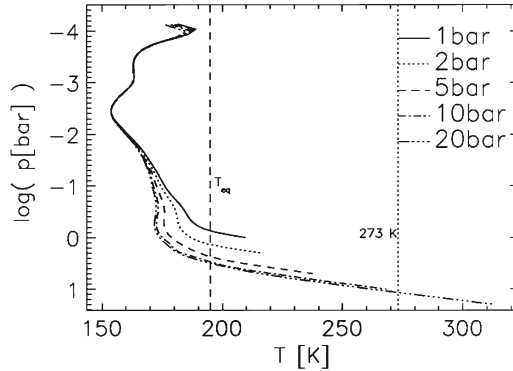
The classical HZ is defined as the region around a star where climate on an Earth-like planet's surface favors the presence of water in its liquid form. This definition arises naturally from the fact that all life on Earth requires liquid water to thrive and survive. Varying planetary parameters such as mass and density influence the extent of the HZ. Also, the nature and mass of a planet's atmosphere critically influence its greenhouse effect, hence also the HZ.

Clearly, life as we know it requires more than liquid water to thrive – it additionally needs, e.g., stable, protected conditions and a steady supply of nutrients. However, in the context of exoplanets, where information is limited, liquid water is taken to be the key criterion for habitability. From the available observables (e.g., the energy input from the star as calculated from the planet-star distance) and assuming a particular atmospheric mass and composition (currently no such information is known for the atmospheres of terrestrial exoplanets), one can apply atmospheric models to calculate the planetary surface temperature, hence determine whether liquid water is thermodynamically stable. Energy input from the star is assumed to be the dominant source at the planet's surface, as on Earth.

Atmospheric model studies of exoplanets typically vary key input parameters such as the spectral type of the central star (e.g., Segura et al., 2003); the planet-star orbital distance (Grenfell et al., 2007a) or the planetary orbital eccentricity (Williams and Pollard, 2003) then discuss the effect on climate hence habitability.

A recent landmark was the discovery of the first potentially habitable planet Gliese 581d (Mayor et al., 2009; Udry et al., 2007), discussed in Selsis et al. (2007). Column radiative model calculations by von Paris et al. (2010) suggested this planet could be habitable assuming about 20 bar of a 5 % CO<sub>2</sub> atmosphere, as shown in Fig. 1. Kaltenecker et al. (2011) suggested ~7 bar of a CO<sub>2</sub>-dominated atmosphere would also suffice to maintain habitability in their radiative column model study. Wordsworth et al. (2011) presented 3D atmospheric climate calculations, suggesting that a 10 bar CO<sub>2</sub>-dominated atmosphere would maintain habitability of Gliese 581d. Thus, a range of current models predict that Gliese 581d could indeed be a potentially habitable planet if it possesses a high-pressure CO<sub>2</sub> atmosphere.

In addition to Gliese 581d, other exoplanetary objects are currently being discussed which could also lie in the HZ, e.g., HD85512b (orbiting a K-star) (Pepe et al., 2011), or Kepler 22b (Borucki et al., 2012). In the text which follows, we first give an overview of the HZ, including its boundaries and time dependence, and then discuss briefly definitions which go beyond the classical HZ concept.



**Figure 1.** 1D radiative-convective model calculations showing temperature (K) on Gliese581d for (1–20) bar atmospheres consisting of 5 % CO<sub>2</sub>, 95 % N<sub>2</sub> (Taken from von Paris et al., 2010).

### 3. Boundaries of the Present-Day Classical HZ

In the modern Solar System, the classical HZ lies somewhere between the orbits of Mars and Venus. The inner boundary is marked first by the “water loss limit” (defined to occur where a planet such as the Earth would lose its mass of ocean within its current lifetime due to escape) and then (further in) where the atmospheric temperature exceeds the critical point of water. Clearly, this limit depends on planetary mass, density, and atmospheric protection. Kasting et al. (1993) (taking into account the carbonate-silicate cycle) suggest the inner HZ would occur at 0.84 AU for the critical point of water and at 0.95 AU for the water loss limit for Earth in our Solar System. Kaltenegger and Sasselov (2011) estimated the inner HZ boundary for exoplanets receiving Venus’ equivalent insolation flux. Abe et al. (2011) considered the effect of varying exoplanetary parameters such as ocean mass upon the inner HZ boundary. Kitzmann et al. (2010) discussed the radiative effect of clouds upon the width of the HZ for Earth-like planets orbiting F, G, and K main sequence stars. They suggested that clouds extend the inner (outer) HZ boundaries by up to 15 % (35 %). At the outer HZ boundary, CO<sub>2</sub> clouds may start to form in the planet’s atmosphere (e.g., Forget and Pierrehumbert, 1997). The radiative properties of CO<sub>2</sub> clouds are challenging to determine, since, e.g., their size and shape is not well defined. The maximum greenhouse effect is defined as the maximum distance of planet-star at which a surface temperature of 273 K can be maintained with no CO<sub>2</sub> atmospheric clouds. Joshi and Haberle (2012) recently suggested that including the spectral dependence of the snow-ice albedo for simulated planets in the HZ of red dwarf stars led to an increase in the outer HZ boundary by up to 30 % due to a weakening in the snow-ice albedo feedback. Pierrehumbert and Gaidos (2011) suggested that collision-induced greenhouse warming of high-pressure (40 bar) H<sub>2</sub> protoatmospheres (which could be retained by super-Earths) could lead to a

large extension of the outward HZ boundary. Their results suggest an outer HZ as far out as 10 AU for solar-like stars.

#### 4. The Changing HZ with Time

Since many nearby stars are young, it is feasible that terrestrial exoplanets in their HZ may resemble the “Early Earth” period (i.e., during the Archaean era, ~3.8–2.5 Gyrs ago) rather than the modern Earth. A key topic in Early Earth science is the following:

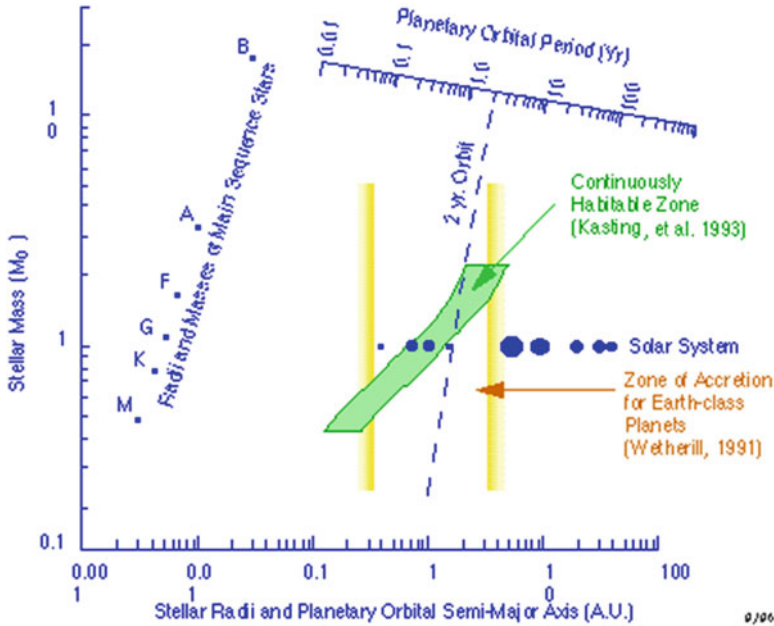
The Faint Young Sun Problem – the Sun’s total luminosity was 20–30 % lower than today on the Early Earth (Gough, 1981). However, despite indications from ancient soils of liquid water being present, many climate model studies (see, e.g., Kasting et al., 1988) suggest a completely frozen planet – this puzzle is termed “The faint young Sun problem.” Various solutions have been proposed, e.g., supplying additional greenhouse gases such as methane ( $\text{CH}_4$ ) (Pavlov et al., 2003) or nitrous oxide ( $\text{N}_2\text{O}$ ) (Grenfell et al., 2011), or improved radiative transfer calculations (e.g., von Paris et al., 2008). In a different approach, Goldblatt et al. (2009) suggested a stronger greenhouse effect on Early Earth due to a possibly stronger atmospheric greenhouse effect arising from enhanced atmospheric  $\text{N}_2$  (they considered up to three times modern levels).

The amount of greenhouse warming on Early Earth is likely, therefore, to be sensitive to surface pressure. Som et al. (2012) suggested Early Earth possessed less than 2 bars of surface pressure, based on inspecting fossilized mud droplets. In an exoplanetary context, lessons learned from the Early Earth are useful to understand potential spectral signals for Earth-like planets, e.g., Kaltenegger et al. (2007) calculated theoretical atmospheric spectra for different epochs of an Earth-like development.

The Continuous Habitable Zone (CHZ) is defined (e.g., Hart, 1979b) as the region of continuous habitability taking into account the increase in luminosity of the star with time. If life requires long timescales (i.e., several billion years) to develop (which is debatable), then CHZs would be the favored regions to study.

Early Venus and Mars – how the climate of early Venus evolved, whether (or for how long) it was habitable and how it diverged to its present-day extreme state are central questions, as reviewed, e.g., in Chassefière et al. (2012). On Mars, modern surface flow features suggest that liquid water probably existed early in its history. How the atmosphere developed from possible habitable conditions to its present state is a challenge for atmospheric, impact, and planetary interior models as summarized in Lammer et al. (2005). In an exoplanetary context, understanding the planetary developments of Venus and Mars offers valuable insight into improving our calculations of the boundaries of the HZ around different stars.

Figure 2 summarizes the extent of the CHZ and its dependence on some key properties:



**Figure 2.** Continuous Habitable Zone (CHZ) shown as a green strip with calculations based on Kasting et al. (1993) as a function of planetary and stellar parameters (Image adapted from the NASA Kepler Mission homepage).

**5. Definitions Beyond the Classical HZ**

There are several concepts under discussion which go beyond the classical HZ model. On Earth, life has proved itself rather resilient – so-called extremophiles can survive under harsh conditions of, e.g., temperature, radiation, salt content, and pH. Definitions which go beyond the classical HZ include:

*Extended liquid water HZ* – for the Solar System, this includes additional habitats beyond the classical outer HZ boundary with, e.g., possible subsurface oceans on bodies such as Europa and Enceladus (e.g., Lammer et al., 2009). For exoplanets, no information on the habitability of analogous bodies, if they exist, is available.

*Floating HZ* – conditions (p, T) in Venus’ stratosphere allow in principle droplets of liquid water to exist, hence in this sense are habitable although not in contact with a solid surface (see, e.g., Irwin and Schulze-Makuch, 2011). Whether life can develop and thrive in such “floating HZs” is debatable. Similarly, Jupiter’s middle atmosphere has been suggested as possessing a possible floating HZ (Sagan and Salpeter, 1976).



*Nonliquid water HZ* – debated is whether life could develop based on non-water solvents such as ammonia ( $\text{NH}_3$ ) or methane ( $\text{CH}_4$ ) or for water-based salt solutions. This could potentially extend the classical HZ, as considered in recent model studies (e.g., Neubauer et al., 2011). The unique physical properties of water however (e.g., universal solvent, high heat capacity, intermolecular H-bonding) may mean that liquid water alone is essential for life. This point is reviewed in Chapter 6 (“Why water?”) of the NASA Committee on the Origins and Evolution of Life Report, 2007.

## 6. Importance of Atmospheres for Habitability

The Earth’s atmosphere is clearly essential for life as we know it. It provides  $\text{O}_2$  needed for respiration, hence directly supports all forms of higher life on our planet. However, atmospheres also favor habitability in a range of other ways. E.g., liquid water cannot exist for long periods at low pressures, being thermodynamically unstable. Also, atmospheres provide protection from incoming radiation – the Earth’s ozone ( $\text{O}_3$ ) layer (International Panel on Climate Change (IPCC) Third Assessment Report, 2001) protects the surface from harmful UV. Atmospheres also transport heat which helps maintain stable conditions in the biosphere. Atmospheres participate in climate feedback cycles, such as the “carbonate-silicate cycle” (Walker et al., 1981) which help stabilize Earth’s climate. In the context of exoplanets, therefore, so-called proposed “water-worlds” and “desertworlds” which do not have subduction zones are expected to lack such a stabilizing mechanism which could impair their habitability. Atmospheres of possibly “tidally locked” planets (i.e., with constant day- and nightsides) orbiting in the HZ of M dwarfs (discussed in the next section) could play a critical role in transporting heat from the planetary dayside to the nightside hence maintaining habitable conditions. Finally, atmospheric spectral signatures can provide information on surface climate conditions and even possible indications of life on exoplanets.

## 7. The Classical HZ Beyond the Solar System

*M-dwarf stars* – These are numerous and long-lived hence favored targets for exoplanet search missions (see e.g., Bonfils et al. 2013). Their potential to host habitable worlds was reviewed by Scalo et al. (2007). The close proximity of their HZ implies that any Earth-like exoplanets could be tidally locked, slow rotators with a constant dayside and nightside. The 3D modeling study of Joshi (2003) suggested that atmospheres of such worlds could effectively transport heat from the dayside to the nightside, hence maintain habitable conditions. Joshi and Haberle (2012) highlighted the potential importance of including the

spectral dependence of ice and snow albedo for planets in the HZ of M-dwarf stars, as already mentioned. Kite et al. (2011) modeled potentially destabilizing climate feedbacks involving weathering and pressure on tidally locked planets. They considered, e.g., the effect of a small decrease in pressure on the dayside; this leads in their model to a warming, since air is less efficiently transported to the nightside. A warmer surface temperature results in a faster weathering rate, which further decreases the atmospheric pressure. The bio-indicator responses are discussed in Sect. 8.

*Cosmic rays (CRs)* – Possible weak magnetosphere protection for Earth-like planets in the HZ of M-dwarf stars could lead to enhanced bombardment of the planet's atmosphere by stellar and galactic CRs. Climate and photochemical effects of CRs in such planetary atmospheres were investigated by Grenfell et al. (2007b) and Segura et al. (2010) – the responses of key species such as O<sub>3</sub> are discussed in Sect. 6.

*K and F stars* – K-stars are also favored targets for exoplanet search missions, being rather cool, but unlike the case of the M-dwarfs, planets in their HZs are unlikely to be tidally locked. Segura et al. (2003) and Grenfell et al. (2007a) modeled the climate and photochemistry of Earth-like planets in the HZ of K and F stars and showed the importance of coupling climate and photochemistry when calculating bio-indicator abundances. E.g., they showed that key bio-indicators, such as O<sub>3</sub>, and important greenhouse gases, such as CH<sub>4</sub>, respond sensitively to the stellar input spectrum and the planet's position in the HZ.

*Exomoons* – Gas giants have been detected which lie in the HZ of their star, e.g., 55 Cancri f (e.g., von Braun et al., 2011). Moons around such objects, if they exist, may therefore also be habitable, that is, with liquid water on their surface.

*Binary systems* – The formation, stability, and potential HZ region of binary star systems was reviewed in Haghighipour (2010). In addition to the HZ around a particular star, binary systems may also possess a “circumbinary HZ,” a region encompassing both stars. Quarles et al. (2012) calculate the binary HZ for the Kepler-16b system.

*Brown dwarfs* – Since these objects (for the most part) do not support fusion, they simply cool in time and their HZ moves inward. Bolmont et al. (2011) suggested a *Brown Dwarf Habitable Zone* (BDHZ) typically extending from (0.007 to 0.02) AU 1 Gyr after formation, based on tidal energy calculations for a BD with typically 4 % of the solar mass. However, little is known about whether planets can form around BDs.

*Red giants* – The Delayed Habitable Zone (DHZ) is defined as the outer disk region which becomes habitable at the onset of the stellar red giant phase (Stern, 2003). Lorenz et al. (1997), e.g., suggested that Titan could lie in the DHZ when the Sun leaves the main sequence ~7 Gyr from now.

*White dwarfs* – Agol (2011) suggested a *White Dwarf Habitable Zone* (WDHZ), e.g., from 0.005 to 0.2 AU for white dwarfs with masses from 0.4 to 0.9 Msun. However, there are serious caveats, e.g., the lack of bright WD targets and the uncertainty of whether life could reestablish subsequent to the supernova.

## 8. Habitability and Possible Bio-indicators

Habitable conditions do not automatically imply the presence of a biosphere. The term “bio-indicator” refers to a criterium (e.g., a particular species’ abundance) which could indicate the presence of life. Clearly, in the ideal case, we would detect the unambiguous signal which proves the presence of life; however, in practice, this is not the case – required in each case is a discussion of the potential biomarker signals and their interpretation. In this context, a *false positive* refers to an erroneous detection of life on a dead planet. This could occur, e.g., due to abiotic production of, e.g., O<sub>2</sub> (produced from CO<sub>2</sub> or/and H<sub>2</sub>O photolysis) or due to spectral band overlap of a biotic with an abiotic species. A *false negative* refers to a missed detection of life. This could occur, e.g., due to thick clouds or high atmospheric optical depths which could mask spectral biosignatures. With the above caveats in mind, Selsis et al. (2002) proposed the so-called triple signature as a more reliable indicator of life. This is based on the simultaneous detection of O<sub>3</sub>–H<sub>2</sub>O–CO<sub>2</sub> since their simulations suggested that only life could produce such signals.

Broadly speaking, there are two types of bio-indicators, namely, *in situ* and *remote*. In situ criteria include chirality (e.g., amino acids favor the left-handed form, Brandenburg et al., 2007), isotopic signals (e.g., photosynthesis favors the lighter carbon isotope, Ohkouchi et al., 2010), carbon number distribution (Lovelock, 1965), as well as the study of bio fossils (e.g., Simoneit, 2004). However, in the context of exoplanets, our main focus here will be on the available remote bio-indicator methods.

*Remote bio-indicator methods* – Clearly, for exoplanet studies, only remote detections are feasible. A main challenge will be to extract potential information from (likely) very low spatially resolved exoplanetary spectral data – sometimes referred to as the “pale blue dot” problem.

*Spectropolarimetry* – Since reflected planetary light has a higher degree of polarization than starlight, this can lead to enhanced (planet/star) contrast ratios (Keller and Stam, 2012). Spectropolarimetry can in principle deliver information on, e.g., atmospheric bio-indicators, dust and planetary albedo, since they influence the wavelength-dependent degree of linear polarization of the scattered light.

*Spectral red edge* – Vegetation features a characteristic increase in reflectance from about 5 to 45 % at 700–750 nm in the visible red region which may help

prevent leaves from overheating. This spectral feature was suggested as a possible indicator of vegetation on remote Earth-like exoplanets (e.g., Seager et al., 2005), although measuring such signals is very challenging.

*Entropy disequilibrium* – The Earth’s atmosphere is far from thermodynamic equilibrium – this condition partly arises due to life. It is however a challenge for atmospheric modeling studies to separate the biotic from the abiotic contributions. Kleidon (2012) provides a review.

## 8.1. ATMOSPHERIC SPECIES ASSOCIATED WITH BIOSPHERES

The modern Earth features an  $N_2$ - $O_2$  atmosphere since its early  $CO_2$ -dominated atmosphere was removed into the crust and since life on Earth generated a large amount of  $O_2$ . Thus, molecules in the atmospheres of exoplanets can be investigated as bio-indicators (see, e.g., Schulze-Makuch et al., 2002) as outlined in the following sections. To illustrate the method, spectra of Earth’s atmosphere can be compiled from so-called earthshine where light reflected from the moon is observed from the ground (e.g., Woolf et al., 2002; Sterzik et al., 2012). Resulting spectral features of key bio-indicators such as ozone  $O_3$  (see also below) are useful for theoretical discussions for compiling and interpreting spectra for Earth-like exoplanets. We now discuss some key atmospheric bio-indicators and their chemical responses.

*Ozone* ( $O_3$ ) on Earth is formed mostly from molecular oxygen ( $O_2$ ) associated with photosynthesis. Although the large abundance of atmospheric  $O_2$  is the direct consequence of life,  $O_3$  has stronger spectral features and likely persists over a wide range of  $O_2$  conditions, so  $O_3$  is a key focus in atmospheric exoplanetary studies.

On Earth, about 90 % (10 %) of  $O_3$  is found in the stratosphere (troposphere). The main source is via the Chapman mechanism (Chapman, 1930) via  $O_2$  photolysis in the stratosphere and in the troposphere via the smog mechanism (Haagen-Smit, 1952) which requires volatile organic compounds (VOCs), nitrogen oxides, and ultraviolet (UV). Loss of atmospheric  $O_3$  in the stratosphere proceeds mainly via catalytic cycles involving hydrogen, nitrogen, or chlorine oxides (e.g., Crutzen, 1970) (designated  $HO_x$ ,  $NO_x$ , and  $ClO_x$ , respectively). Destruction of  $O_3$  in the troposphere occurs, e.g., via wet and dry deposition or/and gas-phase removal via fast reactions with, e.g.,  $NO_x$ .  $O_3$  can be formed from non-biological processes, e.g., in  $CO_2$  atmospheres (e.g., Segura et al., 2007).  $O_3$  layers (although these are very weak) also form on Mars (Fast et al., 2009) and on Venus (Montmessin et al., 2011), so care is needed when interpreting  $O_3$  signals (e.g., Selsis et al., 2002).

In an exoplanet context, Segura et al. (2003) studied  $O_3$  spectral signals as a function of, e.g.,  $O_2$  concentrations for Earth-like planets in the HZ around F, G, and K central stars and confirmed that  $O_3$  remains stable over a wide  $O_2$  range. Grenfell et al. (2007a) studied photochemical responses of  $O_3$  as a function of

star-planet distance in the HZ, showing that  $O_3$  signals were mostly stable over the so-called complex life HZ (where surface temperatures range from 0 to 30 °C). Grenfell et al. (2011) studied the photochemical interactions of  $O_3$  and nitrous oxide ( $N_2O$ ), a species which indicates microbial activity in Proterozoic atmospheres, and suggested a stabilizing mechanism for  $O_3$  (which is otherwise destroyed by  $NO_x$  released from  $N_2O$  photolysis) at high  $N_2O$  abundances. Segura et al. (2010) and Grenfell et al. (2007b) studied the effects of cosmic rays upon atmospheric biomarkers for Earth-like planets in the HZ of M-dwarf stars, finding that photochemical effects could lead to strong  $O_3$  loss under strong flaring conditions.

*Nitrous oxide* ( $N_2O$ ) has almost exclusively biogenic sources on Earth arising from soil microbes as part of the nitrogen cycle (IPCC, 2001). Small abiotic sources include, e.g., the reaction  $N_2 + O(^1D) + M + N_2O + M$  (e.g., Estupiñan et al., 2002). Loss occurs in the stratosphere via photolysis or via reaction with excited oxygen atoms. Various studies, e.g., Grenfell et al. (2011) suggested that the spectral absorption bands of  $N_2O$  may be small for Earth-like exoplanet scenarios.

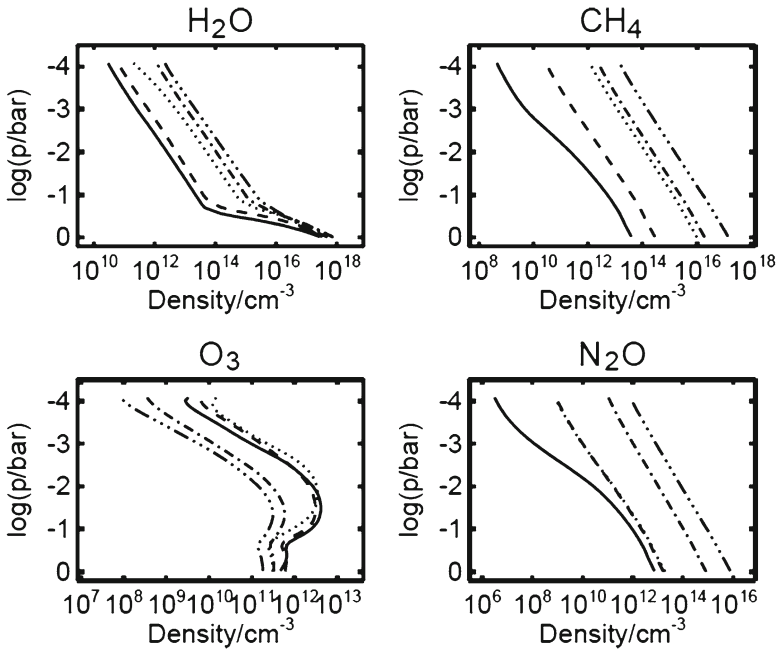
*Methane* ( $CH_4$ ) does not necessarily indicate life since it can be produced abiotically, e.g., by outgassing, although it is mostly produced on Earth by methanogenic bacteria.  $CH_4$  is a key greenhouse gas on Earth and is removed via oxidative degradation from Earth's atmosphere by the reactive hydroxyl (OH) radical. On Mars, earlier claims of atmospheric  $CH_4$  detection (Formisano et al., 2004) have been strongly debated. Recent works (e.g., Mumma et al., 2009) suggest a few ppbv in the global mean with possible spatial variations. Challenges include, e.g., correctly removing the interfering telluric lines from the upper atmosphere when detecting from the Earth's surface. Also, photochemical models overestimate the implied observed  $CH_4$  lifetime by a factor of 100, suggesting that the models could be lacking key atmospheric sources or/and sinks of Martian  $CH_4$ . Zahnle et al. (2011) review the current debate.

*Chloromethane* ( $CH_3Cl$ ) on Earth has important biogenic sources associated with vegetation although its source-sink budget and net anthropogenic contribution is not well known (Keppler et al., 2005). Like  $CH_4$ , its removal is controlled by reaction with OH, although the chlorine atom leads to increased reactivity (with an enhanced rate constant of about a factor 6 for this reaction) compared with  $CH_4$ .

## 8.2. STUDIES OF BIO-INDICATORS IN EARTH-LIKE ATMOSPHERES

Segura et al. (2005) and Rauer et al. (2011) (Fig. 3) modeled atmospheric photochemical and spectral signals for Earth-like planets in the HZ of M-dwarf stars:

Overall, Fig. 3 suggests that key bio-indicator species can vary by up to about two orders of magnitude depending on the spectral class of the M-star.

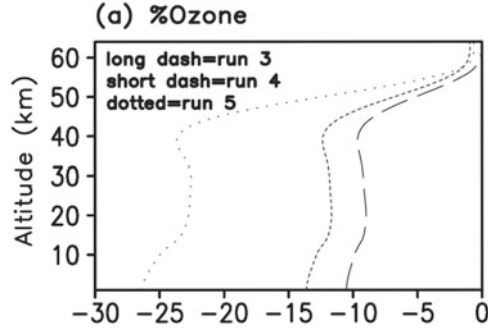


**Figure 3.** Vertical abundances of key atmospheric species for Earth-like planets in the HZ of M-dwarf stars (Earth is shown for comparison) for a range of spectral classes. Earth control (*solid*); M0 (*long dashed*); AD-Leo (*dotted*); M5 (*dot dashed*); M7 (*triple dot dashed*) (Taken from Rauer et al., 2011).

Planetary bio-indicators are sensitive to the level of UV; e.g., for the cooler stars, weaker UV leads to significant photochemical effects in the planetary atmosphere, e.g.,  $\text{N}_2\text{O}$  in Fig. 3 increases with weaker UV since its photolytic sink is weaker. For more details, see Rauer et al. (2011).

Grenfell et al. (2007b) and Segura et al. (2010) simulated the effects of CRs on bio-indicators in atmospheres of Earth-like planets in the HZ of M-dwarf stars. Secondary electron showers from CRs can split molecular nitrogen ( $\text{N}_2$ ) in the planetary atmosphere. Subsequent photochemical reactions with oxygen-containing species form nitrogen oxides ( $\text{NO}_x$ ).  $\text{NO}_x$  can then destroy the protective  $\text{O}_3$  layer of the planet, e.g., under extreme flaring conditions via established catalytic cycles (e.g., Crutzen, 1970) as the two studies above showed. Figure 4 shows this effect for galactic cosmic rays (GCRs) taken from Grenfell et al. (2007b), that is, GCRs in the planetary atmosphere create  $\text{NO}_x$  which destroys atmospheric  $\text{O}_3$ :

Atmospheric chemical disequilibrium – the simultaneous high abundance of oxidant (e.g.,  $\text{O}_2$ ) (mainly from photosynthesis) and reductant (e.g.,  $\text{CH}_4$ ) (mainly from methanogenic bacteria) in Earth’s atmosphere is suggested to be indicative of life (Sagan et al., 1993). Without life on Earth, such high quantities of atmospheric oxidant and reductant would be removed via naturally occurring chemical processes (e.g.,  $\text{O}_2$  via surface removal,  $\text{CH}_4$  via atmospheric in situ oxidation).



**Figure 4.** % Change in atmospheric  $O_3$  for an Earth-like planet in the HZ of the M-dwarf star AD-Leo shown relative to a run with no GCRs. Top-of-atmosphere GCR flux (run 3); Interplanetary GCRs (run 4); Interstellar GCRs (run 5) (Taken from Grenfell et al., 2007b).

## 9. Summary

The context of habitability and its philosophical repercussions have a long history, although scientific discussion has started to make real headway only in the past few decades. Clearly, an increasing sample of rocky exoplanets located near or in the HZ will ultimately better constrain our knowledge of habitability outside the Solar System. At the same time, an increased exoplanet sample will also lead to an improvement in models which, e.g., predict the width of the HZ or which calculate theoretical atmospheric spectra, etc. This, in turn, should influence and guide future observing campaigns. Current notions of habitability and bio-indicators are mostly based on what we know of the Earth with a main focus being liquid water existing for long periods, although more exotic definitions do exist. We are indeed experiencing a golden age not only of exoplanets but also of habitability beyond the Solar System.

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# THE HABITABLE ZONE AND THE GENERALIZED GREENHOUSE EFFECT

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## 1. Introduction

Generally, the habitable zone (HZ) is defined in terms of the mean distance between the central star and the planet in which life-supporting (habitable) conditions exist. Under the assumption that the prevalence of liquid water is a prerequisite for the development of life, at least as we know it, the habitable region around a star is mainly determined by the stellar insolation that is sufficient to maintain liquid water at the planetary surface. Thus, the temperature range which includes the water triple point is a prerequisite for the HZ. The distance between central star and the planet is then the dominant parameter determining whether a planet can be habitable or not (see Stracke et al., 2012). Von Bloh et al. (2009) considered the habitability of super-Earth-like planets during the evolution of the central star. They assumed a specific atmosphere composed of  $\text{CO}_2/\text{H}_2\text{O}/\text{N}_2$  and examined the fate of water in Earth-like atmospheres as the central star evolves. Here we consider a generalized atmosphere, which we characterize by two optical depths rather than the actual chemical composition.

The above line of thought emerges from the fact that it is generally assumed that the atmosphere is transparent in the visible and totally opaque in the far infrared. Among the first to discover that this is not the general case were McKay et al. (1989) who discussed the anti-greenhouse effect (hereafter aGHE) on Titan. Lorenz et al. (1999) developed a semi-empirical gray radiative model to quantify Titan's surface temperature. They found that a volatile-rich Titan is unstable with respect to a runaway greenhouse – a small increase in solar luminosity from the present value can lead to a significant increase of the surface temperature. Kasting and Pavlov (2002) discussed the case when the ratio of  $\text{CH}_4$  to  $\text{CO}_2$  in the atmosphere exceeded unity. At this point, polymerization of  $\text{CH}_4$  by stellar UV radiation causes the formation of an organic haze layer similar to that observed today on Titan. Such a layer of haze cools the climate by creating an aGHE which creates an overall negative feedback loop that may have been responsible for maintaining a stable Archean climate on the Earth. Pujol and Fort (2002) discussed how the aGHE modifies the runaway greenhouse point (the SKI limit). While the above authors discussed mainly the effect of scattering by aerosols, we extend the

discussion to include the effect of molecular absorption and extinction in general. Thus, if the extinction in the visible is significant, we can have on the planet physical conditions which are favorable for life under more general conditions.

The nature of the molecular absorption is that there is frequently no absorption up to a certain wavelength  $\lambda_{\text{cut}}$  and large absorption for longer wavelengths. The range with absorption is treated as a range with uniform properties. However, in many cases, the lower part of this range absorbs solar radiation, while the longer part absorbs the planet's thermal radiation. Consequently, we split the wavelength range into two parts according to the dominant radiation (stellar or planetary)  $\lambda < \lambda_{\text{rad}}$  and  $\lambda > \lambda_{\text{rad}}$ . In doing so, we can better understand the role of each part in the spectrum and generalize the theory to include the regular greenhouse effect (hereafter GHE) as well as the aGHE and appreciate better the effect of a change in the concentration of every type of molecule. Recently, Shaviv et al. (2011) have defined two wavelength domains, one in which the stellar radiation is absorbed in the atmosphere (called the visible range, *vis*) and one in which the Earth's IR radiation is absorbed (called the far infrared, *fir* range). Second, the authors created a unified picture of the GHE and the aGHE, demonstrating how the increase of absorption in the visible range can lead to an aGHE, namely, the temperature is maximal at the top of the atmosphere and decreases toward the surface of the planet. However, most absorbers absorb in the visible as well as in the far infrared and hence most absorbers can exhibit the phenomenon of aGHE or at least reduce the effect of the GHE, namely, mitigate it. An increase in the absorption in the far infrared always leads to a higher surface temperature and, as was proved by Shaviv et al. (2011), eventually saturates. The term visible range means in this context the wavelength range over which the insulating specific radiation intensity is larger than the blackbody emission of the planet.

Let  $\tau_{\text{vis}}$  and  $\tau_{\text{fir}}$  be the total optical depths in the visible and the far infrared, respectively. We assume that the surface temperature is then a function  $T_{\text{surf}} = T(\tau_{\text{vis}}, \tau_{\text{fir}})$ . We solve the radiative transfer problem in the atmosphere and investigate the properties of the function  $T_{\text{surf}} = T(\tau_{\text{vis}}, \tau_{\text{fir}})$ . The calculations in this part are carried out in the  $(\tau_{\text{vis}}, \tau_{\text{fir}})$  plane and do not depend on any linear scale, namely, the physical dimensions of the planet's atmosphere or mass play no role.

The molecular absorption is very complicated and is composed mostly from line absorption as well as a small continuum. Since the optical depths we use are semi-gray over a large range of wavelengths, it is necessary to find the proper average to be used. In other words, if  $\varphi(\lambda)$  is the weight function, then

$$\kappa_{\text{eff}} \equiv \frac{\int \kappa(\lambda, P, T) \varphi(\lambda) d\lambda}{\int \varphi(\lambda) d\lambda}. \quad (1)$$

In principle, the weight function is arbitrary, and hence, an additional condition can be imposed. The weight function  $\varphi(\lambda)$  will be discussed in the appendix. With the proper definition of  $\varphi$  and the scale of the atmosphere, we translate the physical problem to the non-dimensional scale independent form,

in which the present model is formulated. The mathematical details are described in Appendix B.

In the third section, we discuss the region of habitable surface temperatures as provided by the function  $T_{\text{surf}}(\tau_{\text{vis}}, \tau_{\text{fir}})$ . We show that there is a much larger than previously thought region in the plane  $(\tau_{\text{vis}}, \tau_{\text{fir}})$  which can harbor life.

As a planet evolves with time, it changes the composition of its atmosphere and therefore the values of  $\tau_{\text{vis}}$  and  $\tau_{\text{fir}}$  as well. Thus, the planet moves in the  $(\tau_{\text{vis}}, \tau_{\text{fir}})$  plane. As long as the evolution due to chemical changes in the atmosphere leaves the planet within the habitable zone in the  $(\tau_{\text{vis}}, \tau_{\text{fir}})$  plane, life may prevail. However, there are changes in composition which would carry the planet outside the habitable zone and give rise to conditions that may have devastating consequences for life. The inverse is also possible, namely, a planet may reside outside the HZ but evolves temporarily into it and enables the formation of life. However, if the planet will move outside the HZ again, the episode of life will end.

The structure of this chapter is as follows. In Sect. 2, we present the semi-gray radiative model along with its boundary conditions. In Sect. 3, we present the general results of the model. First, we show the existence of a universal saturation for  $\tau_{\text{fir}} \rightarrow \infty$ . Second, we show in Sect. 3.2 the effect of the aGHE due to  $\tau_{\text{vis}}$ . Our main result is presented in Sect. 3.3 in the form of the function  $T_{\text{surf}}(\tau_{\text{vis}}, \tau_{\text{fir}})$  and its sensitivity to the two optical depths. Once the behavior of the GHE as a function of  $\tau_{\text{vis}}$  and  $\tau_{\text{fir}}$  is known, the next question is how to evaluate these optical depths from the basic molecular data. The mathematical details are discussed in appendices. The radiative model is presented in Appendix A. The derivation of the optical depth from the raw molecular absorption is discussed in Appendix B. The actual molecular data and the derivation of the molecular absorption is described in Appendix C. We end with a short discussion.

## 2. Summary of the Radiative Model

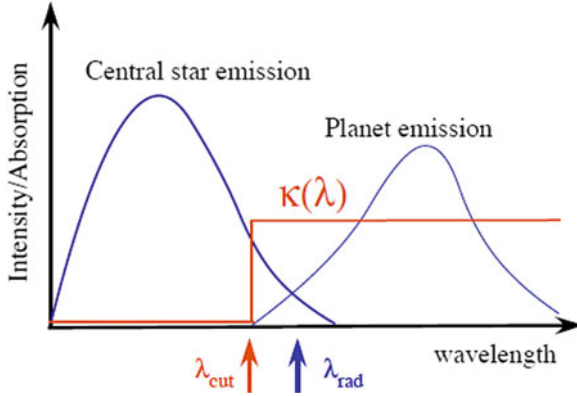
We solve the planetary radiative transfer problem by the two-stream approximation. Our solution is unique since we impose the energy conservation equation at each point in the atmosphere. Namely, we iterate the temperature distribution  $T(z)$  so that

$$\frac{1}{C_v} \frac{dQ}{dt} = \int_0^\infty [B(T(z), \lambda) - J(z, \lambda)] \kappa(z, \lambda) d\lambda = 0. \quad (2)$$

Consequently, the temperature profile obtained is consistent with the radiation field.  $J(z, \lambda)$  is the mean specific intensity given by

$$J(z, \lambda) = \frac{I^+(z, \lambda) + I^-(z, \lambda)}{2}, \quad (3)$$

where  $I^+(z, \lambda)$  and  $I^-(z, \lambda)$  are the outward direction and the inward specific intensities, respectively. The boundary condition at the top of the atmosphere is that the



**Figure 1.** The definition of  $\lambda_{\text{rad}}$  where the specific intensity of insolation equals the specific intensity of the planetary thermal emission. Also shown is the definition of  $\lambda_{\text{cut}}$ , the wavelength above which the molecular absorption becomes significant.

inward specific intensity is given by the stellar insolation. The lower boundary condition assumes that incident radiation is absorbed and reradiated upward. The planet is assumed to be in a steady state at a constant temperature. No day/night variations are considered.

## 2.1. THE SEMI-GRAY APPROXIMATION

The greenhouse problem involves molecular absorption in the range where vibrational and rotational bands are abundant. This gives rise to a very complicated and a highly wavelength-dependent absorption, which consequently imposes numerical problems. Hence, the goal is to simplify the problem of the radiative transfer by assuming that the absorption coefficient is constant over certain ranges, practically a band model. Since our prime goal here is to examine the range of temperatures that the greenhouse effect can yield, we find it simpler to introduce a simple band model which (a) yields the greenhouse effect and (b) is still sufficiently simple so that one can analyze and comprehend the physics with it.

Consider Fig. 1. We define  $\lambda_{\text{rad}}$  as the wavelength for which

$$\frac{(1 - \langle a(\lambda) \rangle) R_*^2}{4 d^2} I_*(\lambda_{\text{rad}}) = I_p(\lambda_{\text{rad}}), \quad (4)$$

where  $d$  is the distance between the planet (or Earth) and the central star (or the sun),  $R_*$  is the radius of the central star,  $I_*(\lambda_{\text{rad}})$  is the intrinsic stellar specific intensity, and  $I_p(\lambda_{\text{rad}})$  is the radiation emitted by the planet's surface.  $\langle a(\lambda) \rangle$  is the mean albedo of the planet (to the stellar radiation) and the factor 4 appears in because



we assume the planet to be a fast rotator. When  $\langle a(\lambda) \rangle = 0.36$  in the “visible,” the central star is the sun and the planet’s distance is 1 AU, the radiative equilibrium temperature is  $T = 288$  K, and one finds  $\lambda_{\text{rad}} = 43,200$  Å. The definition is somewhat vague because it changes slightly with the surface temperature of the planet. As the surface temperature decreases,  $\lambda_{\text{rad}}$  increases. However, the sensitivity is not large and for  $T_{\text{surf}} = 250$  K one finds,  $\lambda_{\text{rad}} = 43,750$  Å. The low sensitivity is due to the exponential decrease of the Wien approximation at short wavelengths.

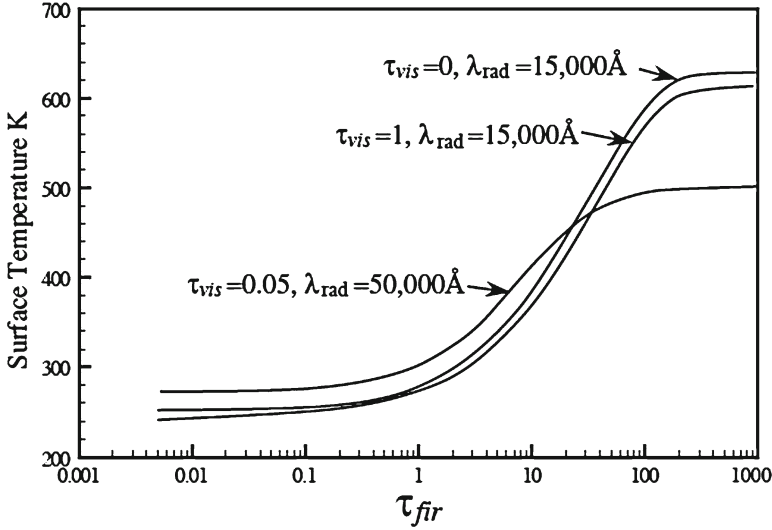
We show also in Fig. 1 a schematic semi-gray absorption as a function of wavelength. The wavelength separating between the short wavelengths, where the absorption is minimal, and the long wavelengths, where the absorption is large, is denoted by  $\lambda_{\text{cut}}$ . However, it is  $\kappa_{\text{vis}}(\lambda) = \kappa(\lambda < \lambda_{\text{rad}})$  and  $\kappa_{\text{fir}}(\lambda) = \kappa(\lambda > \lambda_{\text{rad}})$  which are important for the two bands, respectively. In the semi-gray radiative model, we use effective  $\kappa$ ’s which are wavelength independent. The conversion of the wavelength-dependent highly complicated molecular  $\kappa$ ’s to constants or effective constant optical depths, over certain wavelength ranges, is carried out in Appendix B. We note that  $\lambda_{\text{rad}}$  does not exist in the original Simpson (1927) treatment and many more recent publications; only  $\lambda_{\text{cut}}$  exists. The implication is that the insolation at wavelength longer than  $\lambda_{\text{cut}}$  is ignored.

The role of the absorption changes at  $\lambda = \lambda_{\text{rad}}$ . For  $\lambda < \lambda_{\text{rad}}$  the atmosphere absorbs the direct stellar radiation, which heats the atmosphere. At longer wavelengths,  $\lambda > \lambda_{\text{rad}}$ , the atmosphere absorbs the planet’s radiation and imposes a resistance to the emission into space. When the insolation by the central star is absorbed by the atmosphere at high altitude and is partly radiated to space at high altitudes, a smaller amount reaches the ground and the heating of the ground decreases. The consequence can therefore be an anti-greenhouse temperature gradient, namely, the temperature decreases from the top of the atmosphere downward. Before the aGHE takes over, there is a regime where the temperature is almost constant with optical depth (or equivalently with altitude). We would like to map the function  $T_{\text{surf}}(\tau_{\text{vis}}, \tau_{\text{fir}})$  and find out the domain for which  $T_{\text{surf}}$  is within the limits of the HZ.

### 3. General Results of the Semi-gray Radiative Model

#### 3.1. SATURATION OF THE GHE FOR $\tau_{\text{fir}} \rightarrow \infty$

A typical dependence of the surface temperature on  $\tau_{\text{fir}}$  for a fixed  $\tau_{\text{vis}}$  and  $\lambda_{\text{rad}}$  is shown in Fig. 2. For vanishing absorption, the surface temperature approaches the equilibrium temperature obtained when no atmosphere exists. As the total optical depth  $\tau_{\text{fir}}$  of the atmosphere increases, the surface temperature saturates. The value of the saturation depends on  $\lambda_{\text{rad}}$  and  $\tau_{\text{vis}}$ . As was shown by Shaviv et al. (2011), the saturation occurs primarily due to the leakage of the planetary thermal radiation through the visible range.



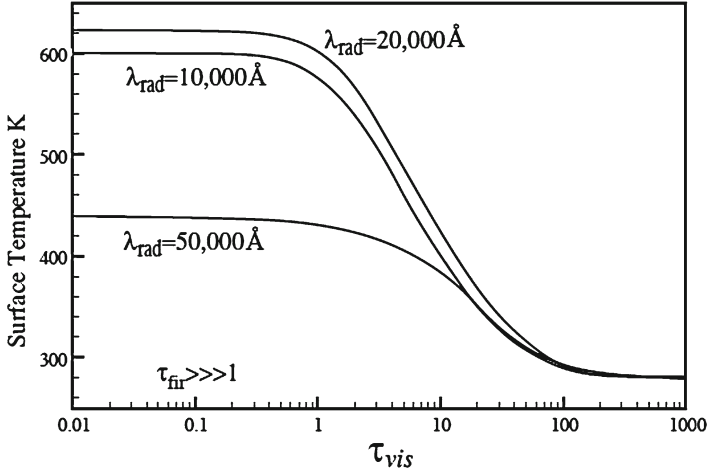
**Figure 2.** The saturation of the surface temperature  $T_{\text{surf}}$  upon the increase in  $\tau_{\text{fir}}$  for three cases.

For a given central star,  $\lambda_{\text{rad}}$  depends on the distance between the planet and the central star. In a way, it is a proxy of the distance of the planet. The closer the planet is to the central star, the smaller is  $\lambda_{\text{rad}}$  and the higher is the saturation temperature.

The optical depth  $\tau_{\text{vis}}$  controls how much insolation energy is absorbed by the atmosphere. The absorbed energy is radiated to space directly from the atmosphere without reaching the surface. Hence, the surface has a smaller energy flux to radiate to space and consequently requires a lower  $T_{\text{surf}}$ . The increase in  $\tau_{\text{vis}}$  leads, therefore, to lower surface temperatures for all values of  $\tau_{\text{fir}}$  and reduces the saturation temperature. A sufficiently high  $\tau_{\text{vis}}$  can reduce the saturation temperature significantly and even bring it into the HZ range. Thus, it has a crucial role on the habitability during the evolution of a planet.

### 3.2. EXAMPLES OF ANTI-GHE

We show in Fig. 3 three examples of the anti-greenhouse effect. In all the three cases shown,  $\tau_{\text{fir}}$  is much larger than unity and effectively in the saturation range. Thus, the effect of  $\tau_{\text{vis}}$  is demonstrated on the maximal effect of the absorption in the IR. As is evident from the figure, most of the effect takes place while  $\tau_{\text{vis}}$  is between 1 and 10, for which  $T_{\text{surf}}$  reduces to a minimal value. It is interesting to note that all three cases converge to the same low temperature, which is 280 K. This is because the central star in all cases calculated in this chapter has an effective temperature of 5,800 K. Thus, irrespective of  $\lambda_{\text{rad}}$ , the minimal temperature is the same. But as was discussed above,  $\lambda_{\text{rad}}$  is a proxy for the distance of the planet



**Figure 3.** The effect of  $\tau_{vis}$  on the surface temperature for constant  $\tau_{fir} = 1$ .

from the central star. Hence, over a significant range in distances, the minimal temperature induced by  $\tau_{vis}$  does not change.

We note that the saturation temperature is not a monotonic function of  $\lambda_{rad}$ , nor of the distance between the central star and the planet. There is a specific distance for which the saturation temperature reaches its maximal value. The distance at which the saturation temperature is maximal depends on the spectral type of the central star and for the case of the sun, it is obtained for  $\lambda_{rad} = 15,000 \text{ \AA}$ .

### 3.3. THE SURFACE TEMPERATURE IN THE $(\tau_{vis}, \tau_{fir})$ PLANE

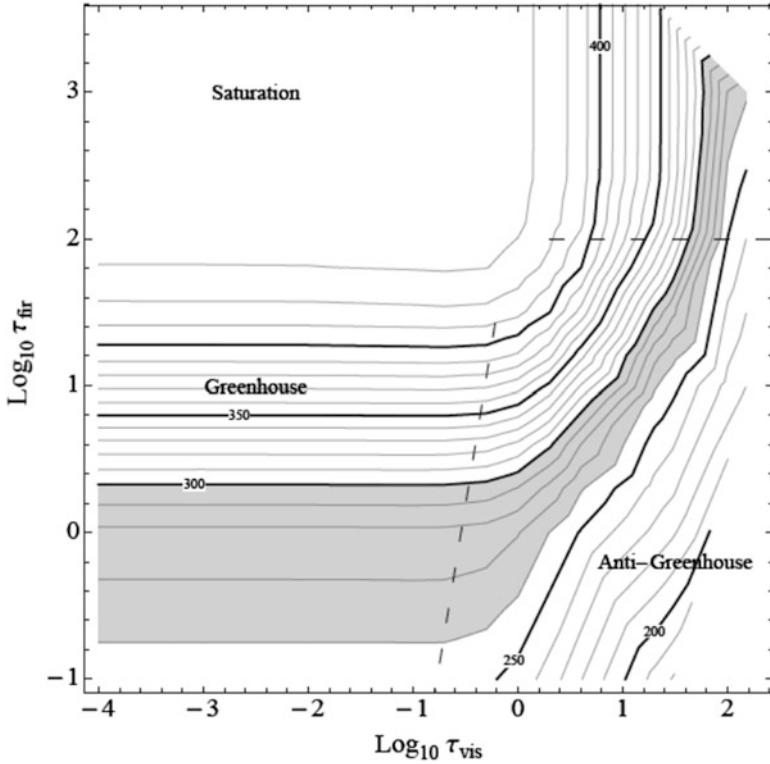
In the previous examples, we demonstrated the effect of  $\lambda_{rad}$  on the surface temperature for different combinations of  $\tau_{vis}$  and  $\tau_{fir}$ . Now we assume a constant  $\lambda_{rad}$  and examine the  $(\tau_{vis}, \tau_{fir})$  plane at a fixed distance from the central star.

The classical case of greenhouse is along the y-axis, namely, for  $\tau_{vis} \ll 1$ . Here  $T_{surf}$  rises monotonically as  $\tau_{fir}$  increases but as  $\tau_{fir} \sim 20$ ,  $T_{surf}$  saturates as long as  $\tau_{vis} < 2$ , where the anti-greenhouse effect of  $\tau_{vis}$  becomes dominant. Quite low surface temperatures are found for sufficiently large  $\tau_{vis}$ . Clearly, in this case, the insolation reaches only the very high heights of the atmosphere.

The calculations were carried out for a specific value of the albedo function (0.36 in the visible and vanishing in the IR). However, if we consider the equilibrium temperature, namely,

$$\sigma T_{equil}^4 = \frac{(1 - \langle a(\lambda) \rangle) R_s^2}{4 d^2} B(T_s), \quad (5)$$

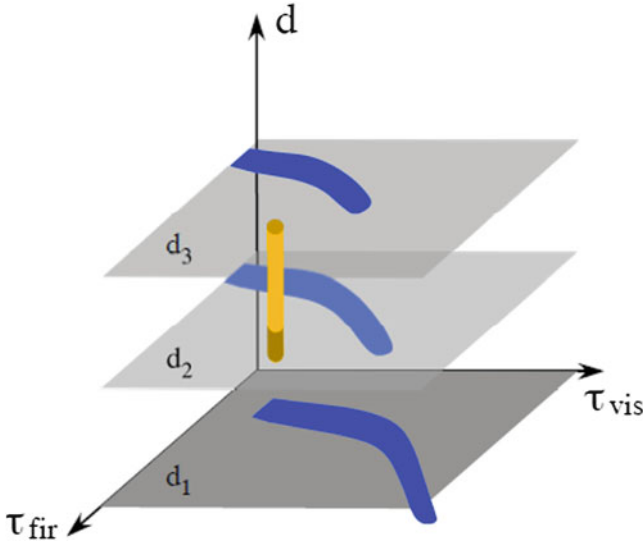
where  $\langle a(\lambda) \rangle$  is the albedo, we find that  $(1 - \langle a(\lambda) \rangle)/d^2$  appear together, and, hence, changing the albedo is equivalent to changing the distance.



**Figure 4.** The constant temperature lines in the  $(\tau_{\text{vis}}, \tau_{\text{fir}})$  plane, for the case  $\lambda_{\text{rad}} = 5 \times 10^4 \text{ \AA}$ , which is consistent with a solar like star at a distance of 1 AU. Different regions are marked according to their different behaviors. The *shaded regions* encompass conditions around the triple point of water.

### 3.4. THE HABITABLE ZONE IN THE $(\tau_{\text{vis}}, \tau_{\text{fir}})$ PLANE

In Fig. 4, we depict the habitable zone in the  $(\lambda_{\text{vis}}, \lambda_{\text{fir}})$  plane. The small gray zone describes the location of the classical greenhouses Earth. Consider now a planet at a distance of 1 AU from the central star and with  $\tau_{\text{vis}} \ll 1$ , namely, it is close to the  $\tau_{\text{fir}}$  axis. The adequate temperature range is found for  $\tau_{\text{fir}} \leq 1.5$ . This is the classical HZ. However, as  $\tau_{\text{vis}}$  increases, we find that  $\tau_{\text{fir}}$  can increase and the temperature remains in the HZ. In other words, there exists a function  $\tau_{\text{fir}}(\tau_{\text{vis}})$  for which the temperature remains equal to 300 K. Thus, there is a continuity of habitable planets all at the same distance from the central star, and each habitable planet has a temperature between  $\tau_{\text{fir},H}(\tau_{\text{vis}})$  and  $\tau_{\text{fir},L}(\tau_{\text{vis}})$ . There can be many habitable planets all having different atmospheres with different optical depths at a distance of 1 AU from the central star. The radiative transfer allows for a range of solutions for every distance.



**Figure 5.** The variation of the HZ with distance from the central star. The *yellow cylinder* describes the standard HZ assuming an Earth-like atmosphere. The *blue* parts describe the HZ in the  $(\tau_{\text{fir}}, \tau_{\text{vis}})$  plane. The  $(\tau_{\text{fir}}, \tau_{\text{vis}})$  plane is shown at three different distances from the central star along with the HZ zone (*in blue*) as a function of the optical depths. The inclusion of the radiative properties of the atmosphere leads to an extension of the HZ to closer distances to the central star and further away as well.

So far, we discussed the HZ at a distance of 1 AU with  $\lambda_{\text{rad}} = 50,000 \text{ \AA}$ . The variation with the distance is shown schematically in Fig. 5. Each plane marked  $d_1$ ,  $d_2$ , and  $d_3$  describes the situation at a different distance from the central star. The yellow cylinder describes the classical HZ. Clearly, a planet at a fixed distance from the central star evolves in such a plane and as its  $\tau_{\text{vis}}$  and  $\tau_{\text{fir}}$  vary, it moves in the plane and may stay or get out of the blue domain which defines the HZ.

The plane  $d_2$  shows that for a fixed distance, the space of  $\tau_{\text{vis}}$  and  $\tau_{\text{fir}}$  is extended. However, planet may migrate due to various effects and in this case change the distance and effectively move from one plane to the other. We find again that the move can keep the planet in the HZ but can also move the planet out of it. The combination of optical depths may bring the planet to distances for which the classical HZ does not exist, but greenhouse effects create habitable conditions.

A similar situation exists when the central star evolves. In this case,  $\lambda_{\text{rad}}$  changes and with it the shape of the HZ.

## 4. Discussion

The HZ is usually considered as a position at a certain distance from the central star. The consideration of the optical properties of the atmosphere reveals that in addition to the distance from the central star, one should consider the optical properties of the atmosphere. These determine the magnitude of the greenhouse effect and control the mean surface temperature on the planet. We find that there exists a strip in the  $(\tau_{\text{vis}}, \tau_{\text{fir}})$  plane where habitable temperatures exist.

The classical consideration of the limits on the HZ is affected by the temperature and not by the parameters affecting the temperature, namely, the greenhouse effect. The consideration of  $(\tau_{\text{vis}}, \tau_{\text{fir}})$  plane leads to a larger distance range of the HZ, namely, distances which were excluded due to improper temperatures can be included in the HZ provided the atmosphere has the proper optical depths (caused by its composition).

The parameter space in which habitable planets can exist is therefore, larger than what was assumed hitherto.

Planets evolve and change their atmospheric composition and optical properties. Hence, planets harboring life can move in the HZ strip. As long as the planet remains inside, the HZ strip life formed under one set of conditions will survive the new set of conditions and vice versa. Any evolution to the outside of the HZ will bring life, if it exists, to an end.

## 5. Appendices

### 5.1. APPENDIX A. THE RADIATIVE MODEL EQUATIONS

The radiative transfer equation including isotropic scattering is given by

$$\mu \frac{dI(z, \lambda, \infty)}{dz} = -\kappa(\lambda)(I(z, \lambda, \mu) - B(T(z), \lambda)) + \sigma(\lambda)(J(z, \lambda) - I(z, \lambda, \mu)) \quad (\text{A.1})$$

with

$$J(z, \lambda) = \oint_{4\pi} I(z, \lambda, \omega) d\Omega \quad (\text{A.2})$$

where  $\omega$  is the solid angle,  $\kappa(\lambda)$  is the pure absorption coefficient, and  $\sigma(\lambda)$  is the isotropic scattering.  $B(T(z), \lambda)$  is the Planck function, and  $T(z)$  is the temperature at height  $z$  above the surface. The temperature is obtained from the energy conservation equation, namely,

$$\frac{1}{C_v} \frac{dQ(z)}{dt} = \int_0^\infty [B(T(z), \lambda) - J(z, \lambda)] \kappa(z, \lambda) d\lambda = 0. \quad (\text{A.3})$$

This condition has to be satisfied at all heights  $z$  of the atmosphere. The radiative transfer equation is solved in the two-stream approximation. For details and mode

of solution, see Shaviv and Wehrse (1991). In this approximation, we have a specific intensity  $I^+$  in the outward direction and a specific intensity  $I^-$  in the inward direction. The intensity vector is then written as

$$I = \begin{pmatrix} I^+ \\ I^- \end{pmatrix}, \quad (\text{A.4})$$

and the radiative transfer equation becomes

$$\pm \frac{dI^\pm}{dz} = -(\kappa(z, \lambda) + \sigma(z, \lambda))I^\pm + \sigma(z, \lambda)J(z, \lambda) + \sigma(z, \lambda)B(T(z), \lambda) \quad (\text{A.5})$$

with the mean intensity defined as

$$J(z, \lambda) = \frac{I_+(z, \lambda) + I_-(z, \lambda)}{2} \quad (\text{A.6})$$

In the present model we do not discuss scattering, only absorption. We actually show that an aGH is obtained even without scattering.

### 5.1.1. A.1. Boundary Conditions on the Radiation Transfer Problem

At the top of the atmosphere, we have  $z = Z$  and  $I_-(Z) = \frac{1}{4} \frac{R_*^2}{d^2} B(T_*, \lambda)$ , where  $T_*$  is the surface temperature of the sun/central star, and we assumed that the planet is a fast rotator. No condition is imposed on  $I_+(Z)$  at the top of the atmosphere, but a consistency check of the calculation is the fulfillment of the condition

$$\frac{R_*^2}{d^2} \int_0^\infty B(T_*, \lambda) d\lambda = \frac{R_*^2}{d^2} \sigma T_*^4 = \int_0^\infty I_+(Z, \lambda) d\lambda, \quad (\text{A.7})$$

namely, the planet is in steady state and does not store or lose energy. At the surface we have

$$\int_0^\infty (1 - a(\lambda)) I_-(0, \lambda) d\lambda = \sigma T_{\text{surf}}^4, \quad (\text{A.8})$$

where  $T_{\text{surf}}$  is the surface temperature which is unknown and is iterated for.

## 5.2. APPENDIX B. THE TRANSITION FROM LINE ABSORPTION TO THE SEMI-GRAY APPROXIMATION

### 5.2.1. B.1. Transition in the Visible Range

Both the Rosseland and the Planck mean are poor approximations in insolated planetary atmospheres and hence require modifications – the first because of the existence of spectral windows which do not exist in stars and the second because in many wavelength domains the total optical depth is much greater than unity.

We observed above that the radiation field changes its nature between the *vis* and the *fir* ranges and consequently the behavior of the specific intensity changes, calling for different forms of averaging the molecular line absorption. Consider first the *vis* range. Since the temperature of the radiation is that of the sun and hence very high relative to the self emission of the atmosphere, the zeroth solution for the transmission of specific intensity  $I(z, \nu)$  is given by

$$I(z, \nu) = I_{*,\nu}^{TOA} e^{-\kappa(\nu)z}, \quad (\text{B.1})$$

where  $I_{*,\nu}^{TOA}$  is the stellar specific intensity at the top of the atmosphere. To secure the energy flux transfer through the atmosphere, we write therefore that

$$\int_{\nu_1}^{\nu_2} I_{*,\nu}^{TOA} e^{-\kappa(\nu)z} d\nu = e^{-(\kappa_{vis})z} \int_{\nu_1}^{\nu_2} I_{*,\nu}^{TOA} d\nu. \quad (\text{B.2})$$

Next we note that the radiation interacts with the atmosphere which is at temperature  $T_{atm}$  and the stellar radiation is to a good approximation that of a blackbody at a temperature  $T_*$ , so we have

$$\ln \langle \tau_{vis} \rangle = - \frac{\int_{\nu_1}^{\nu_2} B(T_*, \nu) e^{-\tau(\nu, T_{atm})} d\nu}{\int_{\nu_1}^{\nu_2} B(T_*, \nu) d\nu}, \quad (\text{B.3})$$

where  $\nu_1$  and  $\nu_2$  are both in the *vis* range,  $T_{atm}$  is the temperature of the atmosphere, and  $\tau_{vis}$  is the total optical depth for this range. It is important to note that the temperature in the weighting function is not that of the plasma through which the radiation passes but that of the insulating star, the sun in the particular case of the Earth or the star in the general case. The optical depth,  $\int_0^Z \kappa(\lambda, T, P) d\lambda$ , however, is calculated with the temperature of the atmosphere.

### 5.2.2. B.2. Transition in the Far Infrared Domain

Consider now the radiative transfer in the *fir* range. Let  $\tau$  be measured from the top of the atmosphere downward. If we write  $I_+(\tau)$  as the thermal flux toward larger optical depths (downward) and  $I_-(\tau)$  as the flux toward smaller optical depths, then the solutions for  $I_{\pm}(\tau)$  under the above approximations are

$$F(\tau) \equiv I_-(\tau) - I_+(\tau) = \text{const.} \quad (\text{B.4})$$

$$E(\tau) \equiv I_-(\tau) + I_+(\tau) = [I_-(\tau) - I_+(\tau)]\tau + \text{const.}$$

or by comparing the conditions at the top ( $\tau = 0$ ) to the bottom ( $\tau = \tau_{tot}$ ), we obtain

$$I_-(\tau_{tot}) - I_+(\tau_{tot}) = I_-(0) - I_+(0), \quad (\text{B.5})$$

$$I_-(\tau_{tot}) + I_+(\tau_{tot}) = [I_-(0) - I_+(0)]\tau_{tot} + [I_-(0) + I_+(0)].$$



The boundary conditions we have are

$$I_+(0) = I_{\dot{a},fir} \quad \text{and} \quad I_-(\tau_{tot}) = I_{p,fir}, \quad (\text{B.6})$$

where  $I_{\dot{a},fir}$  is the insolation for  $\lambda > \lambda_{rad}$  and  $I_{p,fir}$  is the planet's emission at  $\lambda > \lambda_{rad}$ . It is generally assumed that  $I_{*,fir} = 0$ . However, if  $\lambda_{rad}$  decreases significantly, it may no longer be justified to assume the vanishing of  $I_{*,fir}$ .

Next we consider the thermal equilibrium of the surface, that is, total absorption equals the total emission:

$$(1-a(\lambda))I_{\dot{a},vis} + I_{atm,\downarrow} = (1-a(\lambda))I_{p,vis} + I_{p,fir}, \quad (\text{B.7})$$

where  $I_{\dot{a},vis}$  is the insolation for  $\lambda < \lambda_{rad}$ ,  $I_{atm,\downarrow}$  is the emission of the atmosphere toward the surface (at  $\lambda > \lambda_{rad}$ ),  $I_{p,vis}$  is the planet's emission at  $\lambda < \lambda_{rad}$ , and  $a$  is the albedo at the short wavelengths. Our main point is that  $F_{p,vis}$  must be included at relatively high surface temperatures.

Using the two sets of Eqs. B.5 and B.6, the thermal equilibrium becomes

$$(1-a(\lambda))(I_{\dot{a},vis} - I_{p,vis}) = \frac{2(I_{p,fir} - I_{\dot{a},fir})}{2 + \tau_{fir,tot}}. \quad (\text{B.8})$$

From the above set of equations, we can derive an expression for the average net *fir* flux (per unit frequency) over a finite band  $\Delta\nu$  and define an effective opacity through the following:

$$\begin{aligned} \overline{\Delta I}_{fir} &= \frac{1}{\Delta\nu} \int_{\nu_1}^{\nu_2} \frac{[I_{p,fir}(T_p) - I_{*,fir}]}{1 + 3\tau(\nu)/4} d\nu \\ &\approx \frac{[\overline{I}_{p,fir}(T_p) - \overline{I}_{*,fir}]}{\Delta\nu} \int_{\nu_1}^{\nu_2} \frac{d\nu}{1 + 3\tau(\nu)/4} \\ &\equiv \frac{[\overline{I}_{p,fir}(T_p) - \overline{I}_{*,fir}]}{\Delta\nu} \frac{1}{1 + 3\tau_{fir,tot}/4}, \end{aligned} \quad (\text{B.9})$$

that is,

$$\tau_{fir,tot} = \frac{4}{3} \left[ \frac{\int_{\nu_1}^{\nu_2} B(T_{atm}, \nu) d\nu}{\int_{\nu_1}^{\nu_2} \frac{B(T_{atm}, \nu) d\nu}{1 + 3\tau_{tot}(\nu)/4}} - 1 \right]. \quad (\text{B.10})$$

This expression for the gray absorption has several advantages besides conserving energy. If the optical depth is constant as a function of frequency, we find  $\tau_{\text{fir}} \rightarrow \tau$ . However, when  $\tau \ll 1$ , we also find that  $\tau_{\text{fir}} = \tau$ . Windows in the absorption coefficient, which would cause vanishing values of the absorption and explosion in the mean Rosseland, cause no problem. Similarly, the vanishing of the Planck absorption is taken care of properly.

### 5.3. APPENDIX C. CALCULATION OF THE EFFECTIVE OPTICAL DEPTHS

The HITRAN 2008 (Rothman and Gordon, 2009) compilation provides a list of all molecular lines in the range of interest. The range of interest is determined by the effective temperature of the insulating star and by the temperature of the atmosphere. In our particular case, we considered the range  $10^3$ – $10^6$  Å. We checked that extending the integration to  $2 \times 10^6$  Å affected the results for the surface temperature only in the fourth significant figure.

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# THE INFLUENCE OF UV RADIATION ON EXOPLANETS' HABITABILITY

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## 1. Introduction

The habitable zone (HZ) concept was proposed for the first time by Huang (1959, 1960). Since then, the HZ limits have been calculated by several authors, each imposing his own constraints (see, e.g., Rasool and de Bergh, 1970; Hart, 1978; Kasting et al., 1993; Williams and Pollard, 2002; Pena-Cabrera and Durand-Manterola, 2004; Buccino et al., 2006; Selsis et al., 2007; von Bloh et al., 2007; Spiegel et al., 2009) as he tries to find out what are the characteristics of habitable planets. Nowadays, it is commonly agreed that for main-sequence (MS) stars, the inner HZ boundary is determined by the loss of water via photolysis and hydrogen escape. The outer HZ boundary, however, is not well determined as the formation of CO<sub>2</sub> clouds can either cause further cooling of the planet and thus limit the HZ or give rise to heating as they contribute to the greenhouse effect (Kasting et al., 1993; Forget and Pierrehumbert, 1997; Mischna et al., 2000).

However, others pointed out that life existence not only needs clement temperature but also appropriate ultraviolet (UV) radiation (Kasting et al., 1997; Cockell, 2000; Segura et al., 2003; Buccino et al., 2006; Cuntz et al., 2009). Low level of radiation may prevent life evolution while high level of radiation may prevent habitability (Buccino et al., 2006). Kasting et al. (1997) and Segura et al. (2003) were the first to estimate the danger from UV radiation on Earth-like exoplanets. Based on Segura et al. (2003) and using the Principle of Mediocrity, Buccino et al. (2006) defined the boundaries of ultraviolet habitable zone (UV-HZ).

We assume that the UV radiation does not endanger native life forms as they would have evolved to withstand the conditions of the local environment. However, the UV radiation can be a problem for external life forms, such as Earth-like life, which had migrated to a different planet. In this study, we have concentrated on Earth-like life and on the health risks related to the UV radiation. For this reason, the criteria chosen for the UV radiation were taken from risk analysis of UV on human skin (erythema curve). The conclusions of this study are therefore limited to the habitation of exosolar planets by Earth-like life. However, since we do not rule out the case of migrating life forms, very hot stars with relatively short lifetime are within our scope of interest.

The UV-HZ does not necessarily overlap the standard HZ for MS stars. The comparison between the two regions was carried out by Guo et al. (2010), who found that the regions may overlap only for stars with effective temperatures of

4,600–7,100 K. Therefore, they concluded, any planet which orbits a colder or a hotter star is necessarily inhabitable. We question this conclusion and, in particular, its applications to Earth-like planets.

We argue here that Guo et al. (2010) conclusion has to be revised, as it is based on the UV-HZ definition given by Buccino et al. (2006) which we claim to be oversimplified. More precisely, we suggest that the surface UV flux is not necessarily proportional to the UV flux which impinges the planet's top of atmosphere (TOA). The response of the atmosphere to the incoming stellar radiation has to be accounted for, and it is not uniform. Consequently, detailed photochemical calculations are mandatory.

We have carried out such calculations and found that the surface UV flux never reaches a lethal level and therefore does not limit the HZ. Furthermore, we have found that UV radiation is expected to be most harmful on planets orbiting a MS star with effective surface temperature of 9,000 K. This is in contrast to previous studies (Kasting et al., 1997; Segura et al., 2003) which found that the level of lethal UV is higher in the case of the current Earth than for an Earth-like planet with the same surface temperature around a K and an F stars.

This chapter is organized as follows: The photochemical model and the numerical simulation are presented in Sect. 2 and are tested for accuracy in Sect. 3. In Sect. 4, we define and calculate the UV Index for Earth-like planets and discuss the results and the conclusions in Sect. 5.

## 2. Model Description

In order to produce a realistic estimate of the spectral irradiance at the surface, one should, in principle, perform a fully coupled photochemical-climate calculations. The climate model would predict the temperature profile and the distribution of water vapor, while the photochemical model would predict the species distribution and the local irradiance throughout the atmosphere. These models should take into account the different aspects of the system, among them are the following: three-dimensional scattering, planet's rotation, atmospheric diffusion, and cloud formation.

We do not present such detailed a model here. Rather, we have developed and used a simplified one-dimensional (horizontally averaged) photochemical model which we have applied to Earth-like planets.

### 2.1. MODEL ASSUMPTIONS

The model simulates planets which are similar to present day Earth and orbit MS stars. The atmosphere is assumed to be composed of about 78 % nitrogen, 21 % oxygen, and 1 % hydrogen and carbon dioxide. This atomic composition commensurate to the abundances of the most common species:  $N_2$ ,  $O_2$ ,  $CO_2$ , and  $H_2O$ . While the chemical profiles are calculated by the photochemical model, the

temperature and density profiles are assumed to be constant in time (but not in height) and are taken from the 1976 US Standard Atmosphere (COESA: US Commission/Stand Atmosphere, n.d.).

Our tacit assumption is that the change in composition does not lead to a significant change in temperature.

Since we assume a predefined temperature profile, we can neglect the IR part of the spectrum and, in particular, the thermal emissions. In addition, we assume zero scattering and reflection as they have a negligible effect on the photochemical reactions. Hence, the radiation transfer becomes Beer-Lambert law. However, we note that the scattered photons have a significant contribution to the irradiance at the surface. We will further discuss this contribution in Sect. 3.

In order to simulate an atmosphere of a planet with all the relevant processes, one requires an intimate knowledge of the simulated planet and its atmosphere. We possess such knowledge for Earth, but accurate simulations which reproduce all the features of the atmosphere are yet to be constructed. Since we wish to investigate Earth-like exosolar planets, for which no data is available, we must use some assumptions and approximations. In our opinion, it was better to construct a general and simple model which, on one hand, reproduces the ozone level and the surface UV radiation on Earth-like planet while, on the other hand, involves minimal characteristics that are specific to the Earth. Two examples for such characteristics are wind and chemical emission from the ground. In our opinion, a simpler model would produce more general results. Moreover, as models become more and more complicated, the ability to understand the effect of the different parameters on the result decreases.

We also assume a static atmosphere, therefore neglecting processes of convection, diffusion, chemical emissions, and chemical sinks. As a result, we maintain a local mass conservation. On Earth, the atmosphere contains many compounds which were emitted from the surface, such as  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , and  $\text{NH}_3$ . These compounds, among others, are also affected by downwashing processes such as rain and photosynthesis. In order to model these processes, we would have had to assume the specific details of a hypothetical planet, such as volcano eruptions, ocean's surface, and average precipitation. In our considered opinion, the details of the planet's surface, and their relative effect on the atmospheric composition, are beyond the scope of this study.

Finally, we preferred to calculate the atmospheric column under a clear-sky approximation, when the sun is at the zenith, since under these conditions the surface irradiance reaches its maximum.

## 2.2. PHOTOCHEMICAL MODEL

The photochemical model produces a self-consistent steady-state concentration of all species involved. The solution of the differential system is carried out as a time-dependent system and is followed until a steady state is reached. The initial state includes the concentration profile of all species. The photon flux at each

**Table 1.** Wavelength bins used in the computations.

Region (nm)	$\Delta\lambda$ (nm)	Number of bins
To 50	1.000	50
To 175	0.100	1,250
To 205	0.005	6,000
To 1,000	0.250	3,180

altitude for each of the spectral bins is then calculated using Beer-Lambert law and the chemical profile. Once the radiation field is known, the chemical profile in future time  $t + \Delta t$  is calculated. The iteration cycle which includes the radiation field and the composition ends once a steady state is reached. A steady state is defined as one in which the total ozone differ from the converged value by less than 1 %. The converged value is defined as the asymptotic total ozone amount and approximated by a linear extrapolation.

The altitude grid extends from 0 to 100 km in 1-km increments. At each height, the radiation flux was calculated line by line by Beer-Lambert law. About 10,000 wavelength bins were used to discretize the wavelength spectrum of 1–1,000 nm. The bins' widths were chosen with special regard to the absorption lines width and are listed in Table 1. This spectral resolution was found to produce a reasonable accuracy (few percents) in a reasonable computational time.

The absorption cross sections were taken from MPI-Mainz-UV-VIS Spectral Atlas of Gaseous Molecules (Keller-Rudek and Moortgat n.d.). The quantum yields for the photodissociation reactions were taken from NASA's JPL-15 evaluation (Sander et al., 2006) and from Welge (1974).

The model includes 21 chemical species, as listed in Table 2, which interacts via 65 photochemical reactions. The reactions' coefficients were taken from NASA's JPL-15 evaluation (Sander et al., 2006). For each of the species, a rate equation, which describes the change of the concentration with time, was written.

The chemical composition is calculated by integrating the differential rate equations explicitly in time. We remark that we refrained from dividing the species into short-lived and long-lived groups, and as a result, the set of differential equations is very stiff. However, for the price of this complication, we do not limit ourselves to an assumed solution. In order to overcome the stiffness of the problem, we chose to integrate the equations with a semi-implicit scheme which is a generalization of the Bulirsch-Stoer semi-implicit method, developed by Bader and Deuflhard (1983). The implementation of the scheme was taken from *Numerical Recipes for C*, 2nd edition (1992) (Press et al., 1992).

The initial chemical profile is taken to be similar to the chemical profile on Earth. The chemical composition is specified at the surface and then extended upward using a scale height factor taken from the 1976 US Standard Atmosphere COESA: US Commission/Stand Atmosphere (n.d.) (about 7.17 km, on the



**Table 2.** List of species used in the computations.

	Species	Name
1	O	Monatomic oxygen
2	O(1d)	Excited monatomic oxygen
3	O <sub>2</sub>	Oxygen
4	O <sub>3</sub>	Ozone
5	H	Monatomic hydrogen
6	H <sub>2</sub>	Hydrogen
7	H <sub>2</sub> O	Water
8	OH	Hydroperoxy
9	HO <sub>2</sub>	Hydroperoxy radical
10	H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
11	CO	Carbon monoxide
12	CO <sub>2</sub>	Carbon dioxide
13	HO <sub>2</sub> CO	Hydroxidooxidocarbon
14	N	Monatomic nitrogen
15	N <sub>2</sub>	Nitrogen
16	NO	Nitric oxide
17	NO <sub>2</sub>	Nitrogen dioxide
18	NO <sub>3</sub>	Nitrate radical
19	N <sub>2</sub> O	Nitrous oxide
20	N <sub>2</sub> O <sub>5</sub>	Dinitrogen pentoxide
21	HONO	Nitrous acid

average). The only exception is water vapors which are assumed to concentrate at altitudes lower than 15 km due to water vaporization and rain. At these altitudes, we assume a scale height factor of 2 km for the water vapors and the general atmospheric scale height factor above.

For each steady-state profile, the direct UV irradiance ( $I(\lambda)$ ) at the surface was calculated.

The direct irradiance was then converted into units of UV Index (UVI) by using the erythema curve ( $W(\lambda)$ ) suggested by Mckinlay and Diffey (1987) as the action spectrum. The conversion was carried out according to the definition of the UV Index given by

$$\text{UV Index} \equiv \frac{\int_0^{400\text{nm}} I(\lambda)W(\lambda)d\lambda}{25 \text{ mW m}^{-2}}. \quad (1)$$

We chose to present our results in units of UVI as they are currently the standard units (adopted by the World Health Organization) for measuring the health risks from UV radiation.

### 3. Accuracy and Validation

In order to test the accuracy of our simulation, the following tests were carried out:

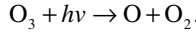
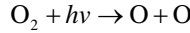
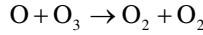
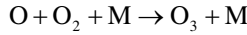
- *Convergence tests:* The simulation converges to an error of  $<10\%$ , relative to spectral, spatial, and time resolutions (i.e., width of wavelength bins, height and number of atmospheric layers and integration period). The calculations were carried out with a resolution which varied with wavelength. Our numerical tests for the numerical accuracy of the model have shown that this rather high resolution is required if the calculation is expected to be accurate to less than  $10\%$ .
- *Same input test:* The simulation converges to the same composition and radiation field with an error of up to  $<1\%$  when a different, but equivalent, initial profile is used. We have also tested the sensitivity of the converged ozone profile to perturbations (changes of few percents) in the species abundances in the initial profile. In all cases, the ozone profile obtained converged quickly to the original one with up to  $10\%$  deviations.
- *Temperature profile test:* We tested the effect of the temperature profile on the solution by comparing a computation with a standard temperature profile and a computation with a constant temperature profile of  $T = 245$  K. The computations' solutions vary by  $\sim 10\%$ .
- *Planet rotation test:* We estimated the effect of the planet's rotation on the total ozone column by comparing computations with a constant stellar flux (a Noon model) and computations with a periodic stellar flux (a Day/Night model) with  $F_{\text{star}}$  proportional to  $\cos((t - \text{Noon}) \pi/12_{\text{h}})$  through daytime and 0 at night (which lasts 12 h). The total ozone columns were found to vary between the two models by up to  $10\%$ . For comparison, decreasing the photochemical rate coefficients by a factor of 2 (as an approximation for the day and night variation) yields about  $3\%$  variation between the models. We wish to emphasize that we have tested the variation between the models and not between the ozone abundances at day and at night. As for the diurnal variations – we have found that the diurnal variations of the ozone are negligible for solar-like or colder stars but can reach up to  $10\%$  for much hotter stars.
- *Verification tests:* The simulation reproduces the analytical solution for pure oxygen atmosphere with an error well under  $1\%$ . This test is discussed in details in Sect. 3.1.
- *Validation test:* The simulation was tested to reproduce the Earth's ozone profile and surface UV irradiance. The simulation reproduces the Earth's ozone layer (altitude and concentration) with an error of about  $20\%$ . The calculated total ozone column is about  $20\%$  higher than measured. Subsequently, the calculated surface UV irradiance is about  $25\%$  lower than measured. The validation test is discussed in details in Sect. 3.2.

From these tests, we estimate the numerical errors to be within the acceptable range of  $20\%$ . For reference, the nonuniformity of the ozone column over the globe

varies by up to 25 % diurnally and from place to place. In addition, we stress that the values of the assumed rate coefficients have an experimental error of about 20 %.

### 3.1. VERIFICATION TEST: PURE OXYGEN ATMOSPHERE

This test simulates the simple photochemical system of oxygen reactions, which yields a semi-analytical solution for all altitudes. The atmosphere is assumed to consist of the following oxygen species: O, O<sub>2</sub>, and O<sub>3</sub> (excitations species/reactions are not included). These species interact via four photochemical reactions:



The rate coefficients for these reactions are  $k_1 [\text{O}][\text{O}_2][\text{M}]$ ,  $k_2 [\text{O}][\text{O}_3]$ ,  $J_{\text{O}_2} [\text{O}_2]$ , and  $J_{\text{O}_3} [\text{O}_3]$ , respectively, with the following reaction coefficients:

$$k_1 = 6 \times 10^{-34} \cdot (T / 300)^{-2.4} n^{-2} \text{ s}^{-1}$$

$$k_2 = 1.2 \times 10^{-12} \cdot \exp\left(-\frac{2060}{T}\right) n^{-1} \text{ s}^{-1},$$

where  $n$  is the number density of molecules. The photolysis coefficients  $J_{\text{O}_2}$  and  $J_{\text{O}_3}$  are given by

$$J_A = \int_0^{\infty} \sigma_A(\lambda, T) \cdot I(\lambda) \cdot \phi_A(\lambda) \cdot d\lambda, \quad (2)$$

where  $\sigma_A(\lambda, T) [\text{cm}^2]$  is the absorption cross section of species A at wavelength  $\lambda$  and temperature  $T$ ,  $I(\lambda) [N_{\text{photons}} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{nm}^{-1}]$  is the spectral photon flux at wavelength  $\lambda$ , and  $\phi_A(\lambda)$  is the quantum yield. These four reactions define the following set of three differential equations for the corresponding species concentrations:

$$\frac{d[\text{O}]}{dt} = -k_1 [\text{O}][\text{O}_2][\text{M}] - k_2 [\text{O}][\text{O}_3] + J_{\text{O}_3} [\text{O}_3] + 2J_{\text{O}_2} [\text{O}_2] \quad (3)$$

$$\frac{d[\text{O}_2]}{dt} = +k_1 [\text{O}][\text{O}_2][\text{M}] + 2k_2 [\text{O}][\text{O}_3] + J_{\text{O}_3} [\text{O}_3] - J_{\text{O}_2} [\text{O}_2] \quad (4)$$

$$\frac{d[\text{O}_3]}{dt} = +k_1 [\text{O}][\text{O}_2][\text{M}] - k_2 [\text{O}][\text{O}_3] - J_{\text{O}_3} [\text{O}_3], \quad (5)$$

where  $[\text{M}]$  equals  $[\text{O}] + [\text{O}_2] + [\text{O}_3]$ . The steady-state solution of this set is given by

$$[\text{O}_3] = \frac{[\text{O}_2]}{2} \cdot \left( -\frac{J_{\text{O}_2}}{J_{\text{O}_3}} + \sqrt{\left( \frac{J_{\text{O}_2}}{J_{\text{O}_3}} \right)^2 + 4 \frac{J_{\text{O}_2} k_1}{J_{\text{O}_3} k_2} [\text{M}]} \right) \quad (6)$$

$$[\text{O}] = \frac{2J_{\text{O}_2} [\text{O}_2]}{k_2 [\text{O}_3]}. \quad (7)$$

As an initial profile for this test, we chose a pure  $\text{O}_2$  with surface concentration of  $5.4 \times 10^{18} \text{ cm}^{-3}$ . The profile was then extrapolated upward with a constant scale height factor of  $\tilde{H} = 7.17 \text{ km}$ . The altitude grid extended up to 80 km in 1-km increments. We simplified the semi-analytic calculation by taking  $[\text{O}_2]$  to be constant, which is a good approximation as long as  $[\text{O}] + [\text{O}_3] \ll [\text{O}_2]$ . The temperature profile was chosen to be constant at  $T = 245 \text{ K}$ , which is consistent with the scale height factor of 7.17 km. The rate coefficients  $k_1$  and  $k_2$  at this temperature are

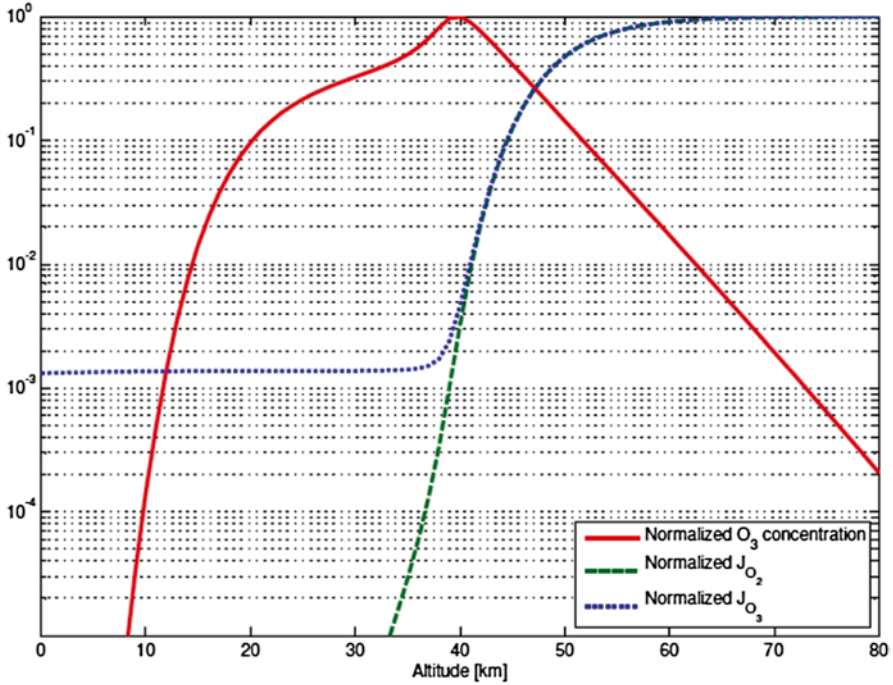
$$k_1 = 9.76 \times 10^{-34} n^{-2} \text{ s}^{-1}$$

$$k_2 = 1.78 \times 10^{-15} n^{-1} \text{ s}^{-1},$$

where  $n$  is the number density of molecules. For stellar radiation, we chose two monochromatic beams of wavelengths 200 and 400 nm. The cross sections and quantum yields for  $\text{O}_2$  and  $\text{O}_3$  for these spectral lines are given in Table 3.

**Table 3.** List of the parameters used in the verification test: photon fluxes, cross sections, and quantum yields.

Wavelength (nm)	200	400
Photon flux at TOA (1 nm bin width) [ $N_{\text{photons}} \text{ cm}^{-2} \text{ s}^{-1}$ ]	$9.93 \times 10^{12}$	$1.25 \times 10^{14}$
$\text{O}_2$ cross section [ $\text{cm}^2$ ]	$2.51 \times 10^{-23}$	$1.27 \times 10^{-26}$
$\text{O}_3$ cross section [ $\text{cm}^2$ ]	$3.15 \times 10^{-19}$	$1.37 \times 10^{-23}$
Quantum yield for reaction $\text{O}_2 + h\nu \rightarrow \text{O} + \text{O}$	1	0
Quantum yield for reaction $\text{O}_3 + h\nu \rightarrow \text{O} + \text{O}_2$	1	1



**Figure 1.** Results of the semi-analytical computation. The  $O_3$  concentration (solid line) and the photon dissociation coefficients  $J_{O_2}$  (dashed line) and  $J_{O_3}$  (dotted line) are plotted as a function of altitude. The graphs are normalized by their respective maximal value.

The coefficients  $J_{O_2}$  and  $J_{O_3}$  cannot be computed independently at each height as they depend on the concentrations at higher altitudes. We calculate, therefore, the coefficients  $J_{O_2}$  and  $J_{O_3}$  and the concentrations of O and  $O_3$  for each layer in descending order, starting with the top layer, using Eqs. (6) and (7). The results of this semi-analytical computation are presented in Fig. 1 (the values of  $[O_3]$ ,  $J_{O_2}$ , and  $J_{O_3}$  are normalized, respectively, by their maximal value). The simulation reproduces the semi-analytical calculation with an error of at most  $10^{-5}$ .

### 3.2. VALIDATION: EARTH'S OZONE

We have validated the simulation by reproducing Earth's atmospheric ozone profile. The simulation is not expected to reproduce the ozone profile to better than 15 %, since the diurnal and seasonal changes in the ozone column are of the same order. The initial profile was defined by the surface composition listed in Table 4. The temperature profile was taken from the US standard atmosphere.

**Table 4.** The initial chemical composition at the surface used for the validation simulation.

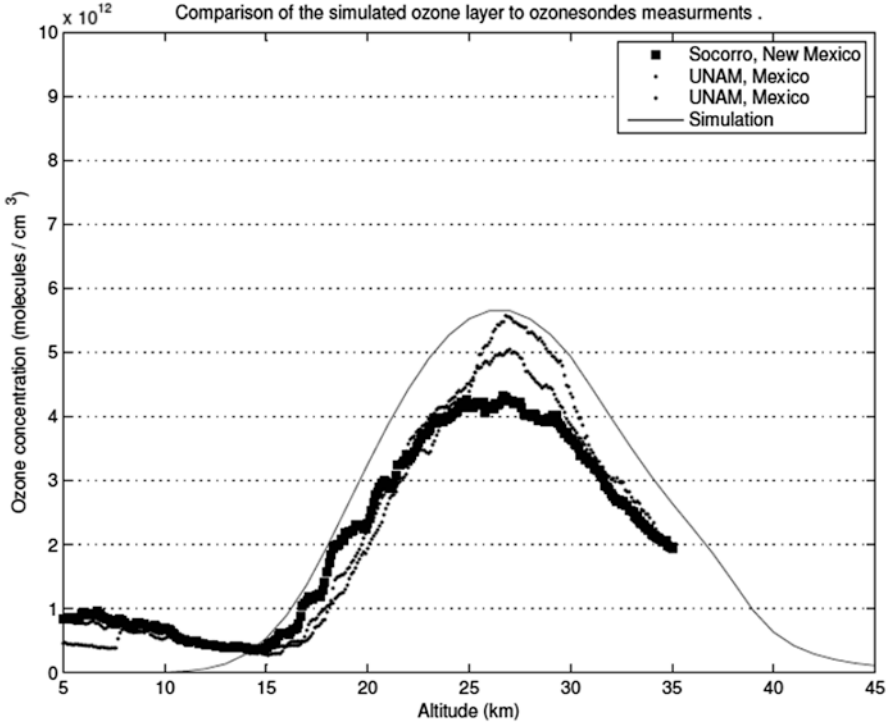
Species	Input concentrations/cm <sup>-3</sup>
O	0
O(1d)	0
O <sub>2</sub>	$5.4 \times 10^{18}$
O <sub>3</sub>	0
H	0
H <sub>2</sub>	0
OH	0
HO <sub>2</sub>	0
H <sub>2</sub> O	$2.5 \times 10^{17}$
H <sub>2</sub> O <sub>2</sub>	0
N	0
N <sub>2</sub>	$2.0 \times 10^{19}$
NO	0
NO <sub>2</sub>	$5.0 \times 10^{11}$
NO <sub>3</sub>	0
N <sub>2</sub> O	0
N <sub>2</sub> O <sub>5</sub>	0
HONO	0
CO <sub>2</sub>	$2.5 \times 10^{17}$
CO	0
HOCO	0

The stellar radiation reaching the Earth was computed with the following stellar parameters:  $R_c = 6.69 \times 10^5$  km,  $T_c = 5,778$  K, and  $D_{\text{Sun-Earth}} = 150 \times 10^6$  km.

The resulting solar constant is  $1,367 \text{ Wm}^{-2}$ . The spectral photon flux was discretized as listed in Table 1. The altitude grid extended up to 100 km in 1-km increments.

The computed ozone profile and a comparison to measured ozone profiles are given in Fig. 2. The computed ozone profile follows the measured profiles in its shape, but it is higher by up to 20 %. This deviation occurs only at the stratosphere and above. Significant deviations take place in the troposphere where the calculated ozone concentration deviates from the measured by one several orders of magnitude ( $10^5$  as compared to  $7.5 \times 10^{10} \text{ cm}^{-3}$ ). We therefore conclude that our model cannot be used to calculate the surface ozone. This is not surprising since the surface affects the atmospheric composition at low altitudes through chemical emissions and sinks, winds, clouds, reflection of radiation, and other processes which we did not take into account.

Moreover, we did not take into account processes responsible for vertical transport such as the eddy diffusion. In our opinion, this approximation contributes the lion share of the discrepancy found. This limitation, however, does not prevent



**Figure 2.** Comparison of the computed ozone profile to the measured profile. Comparison of stratospheric ozone concentration as a function of altitude from full simulation (*solid line*) and as was observed (2006) over U.N.A.M., Mexico (19.3°N), and Socorro, New Mexico (34.6°N).

us from computing the surface UV radiation as over 90 % of the ozone is located above the tropopause.

The computed ozone column is  $8.5 \pm 1.7 \times 10^{18} \text{ cm}^{-2}$ , while the measured mean ozone column is  $6.8 \pm 0.7 \times 10^{18} \text{ cm}^{-2}$  in Mauna Loa, Hawaii, and  $8.9 \pm 1.3 \times 10^{18} \text{ cm}^{-2}$  in Boulder, Colorado. The error in the simulation result is assumed to be 20 %, as discussed above, while the errors in the measured mean columns come from the diurnal and seasonal changes, as can be seen in Fig. 2. We conclude therefore that the computed ozone column reproduces the measured mean ozone columns with an error of <20 %, which is similar to both the computational error and the measured variations. We believe that the disparity between the measured and calculated columns comes both from the model approximations and the errors in the database (cross sections and reaction coefficients).

The UVI calculated from the direct irradiance is  $4.3_{-0.8}^{+1.2}$  units. The result is corrected for the diffusive and reflected irradiance by applying a factor of 2.5 (Caldwell et al., 1980; Piazena, 1996). In this approximation, the total UVI equals  $10.75_{-4.3}^{+2}$  units. The maximal total UVI on Earth, excluding holes in the ozone layer, is 12–13 units which is about 20 % more than calculated.

To summarize, the simulation reproduces the ozone column and the ozone layer with an error of up to 20 %. This error is reasonable as the observed quantities suffer themselves from high errors and fluctuations (Fig. 3).

## 4. Results

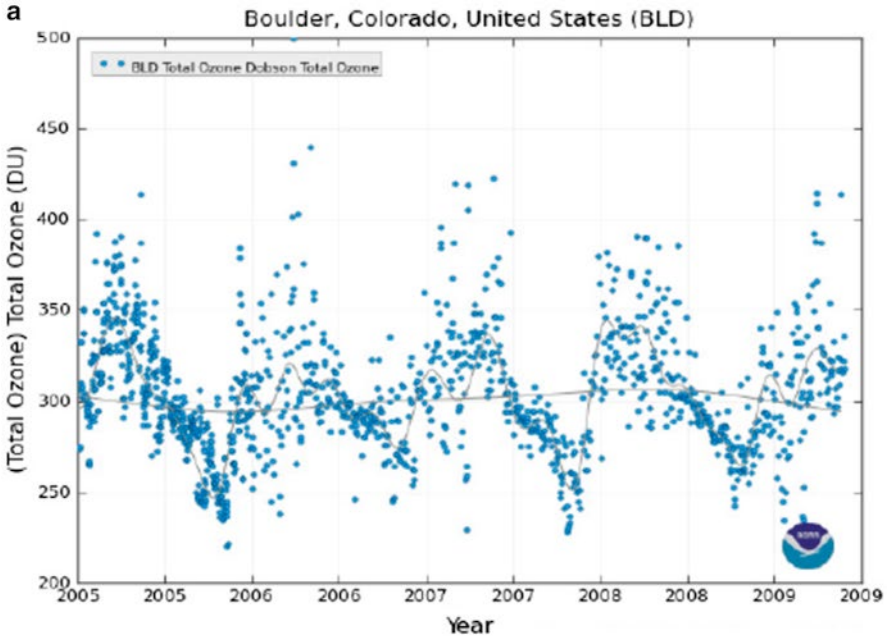
### 4.1. SIMULATED PLANETS

We simulated planets with solar constant of either  $935 \text{ Wm}^{-2}$  (Cold),  $1,367 \text{ Wm}^{-2}$  (Earth), or  $1,895 \text{ Wm}^{-2}$  (Hot). We chose these solar constants, our proxies, as they would yield surface temperatures of 273, 300, and 323 K, respectively, assuming a greenhouse effect of 20 degrees. In general, in order to compute the solar constant of a planet, one needs to know the values of the stellar parameters and the planetary albedo. For simplicity, we wish to obtain the solar constant as a function of only two stellar parameters – the effective stellar temperature ( $T_{\text{eff}}$ ) and the orbit radius ( $R_{\text{orbit}}$ ). For this goal, we set the value of the other parameters as follows: (1) zero albedo, (2) zero age MS star emitting perfect blackbody radiation, and (3) the stellar radius is the sun’s radius  $R_{\text{star}} = R_{\text{e}} = 7 \times 10^5 \text{ km}$ . In this method, we are left with only three parameters –  $T_{\text{eff}}$ ,  $R_{\text{orbit}}$ , and the solar constant – of which two are independent. For our needs, we preferred  $R_{\text{orbit}}$  to be the dependent parameter which is determined by the effective stellar temperature, the required solar constant, and the other stellar parameters. The values of the stellar parameters vary greatly, but it would not affect our results as they depend only on the effective stellar temperature and the solar constant.

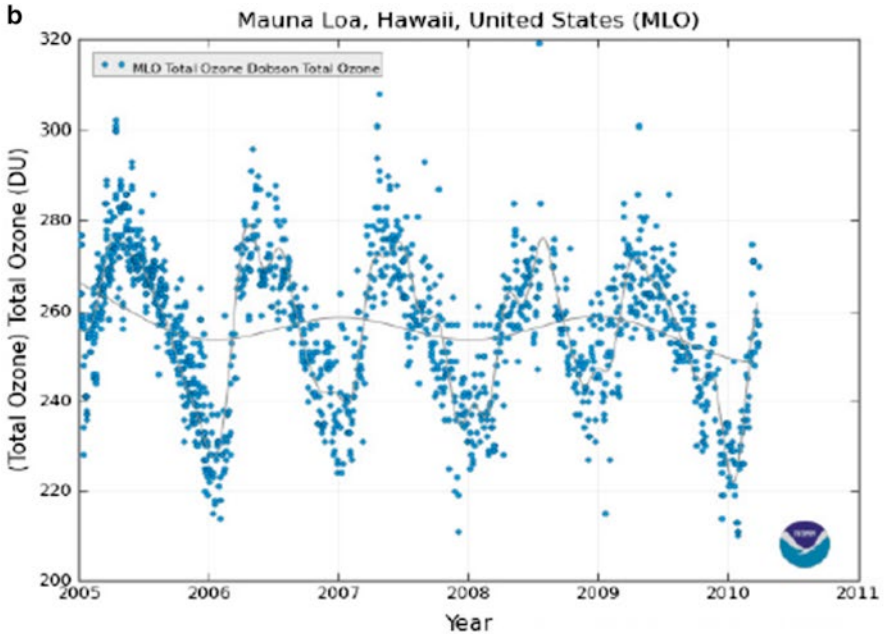
The reference planet for these calculations was the Earth, located at a distance of 1 AU from the sun which has an effective temperature of 5,778 K. The stellar parameters ( $T_{\text{eff}}$  and  $R_{\text{orbit}}$ ) of the simulated planets are listed in Table 5. The parameters vary –  $T_{\text{star}} \cong 3,500 \text{ K}$  to  $T_{\text{star}} \cong 18,500 \text{ K}$  for the stellar effective temperatures and  $D_{\text{planet}} \cong 0.43 \text{ AU}$  to  $D_{\text{planet}} \cong 8.7 \text{ AU}$  for the distance between the planet and the star. Originally, we paired hot and cold planets by choosing similar orbit radius, but we now recognize it to be a mistake. Identical effective stellar temperature should have been used to pair the hot and cold planets.

The simulated planets were divided into two groups – *Hot planets* with solar constant of  $1,895 \text{ Wm}^{-2}$  and *Cold planets* with  $935 \text{ Wm}^{-2}$ . For each of the planets chosen, the atmospheric profile and the UV Indexes at TOA and at surface were computed. The input parameters used are the same parameters used for the Earth validation test (described in Sect. 3.2). The stellar radiation, as mentioned above, was assumed to be a blackbody radiation. It should be noted that the temperature profile for Earth was assumed in all of the calculations. This was necessary as our model does not assumed obtain the actual temperature profile for each planet. Thus, we chose to use the same first-order temperature profile for all planets. This approximation induces a nontrivial error to our results. However, we tested the sensitivity of the ozone composition to the temperature (see Sect. 3) and found it to be of the order of 10 %.





Total ozone column measured above Boulder, Colorado, US (40°N, 105°W, 1630masl)



Total ozone column measured above Manua Loa, Hawaii, US (19.5°, 155.5°W, 3400 masl)

**Figure 3.** Variations of the ozone column above (a) Boulder, Colorado, and (b) Mauna Loa, Hawaii. The altitude difference of 2 km contributes to the total ozone about 10 Dobson units (DU).

**Table 5.** Stellar parameters used for the simulated planets.

Simulated planet	$T_{star}$ (K)	$D_{planet}$ (AU)	Simulated planet	$T_{star}$ (K)	$T_{planet}$ (AU)
<i>Earth</i>	5,778	1.000			
<i>Hot 4</i>	4,112	0.432	<i>Cold 4</i>	3,470	0.436
<i>Hot 5</i>	5,280	0.712	<i>Cold 5</i>	4,455	0.719
<i>Hot 6</i>	6,780	1.173	<i>Cold 6</i>	5,720	1.185
<i>Hot 7</i>	8,706	1.935	<i>Cold 7</i>	7,345	1.954
<i>Hot 8</i>	11,179	3.190	<i>Cold 8</i>	9,432	3.222
<i>Hot 9</i>	14,354	5.259	<i>Cold 9</i>	12,110	5.312
<i>Hot 10</i>	18,431	8.671	<i>Cold 10</i>	15,550	8.758

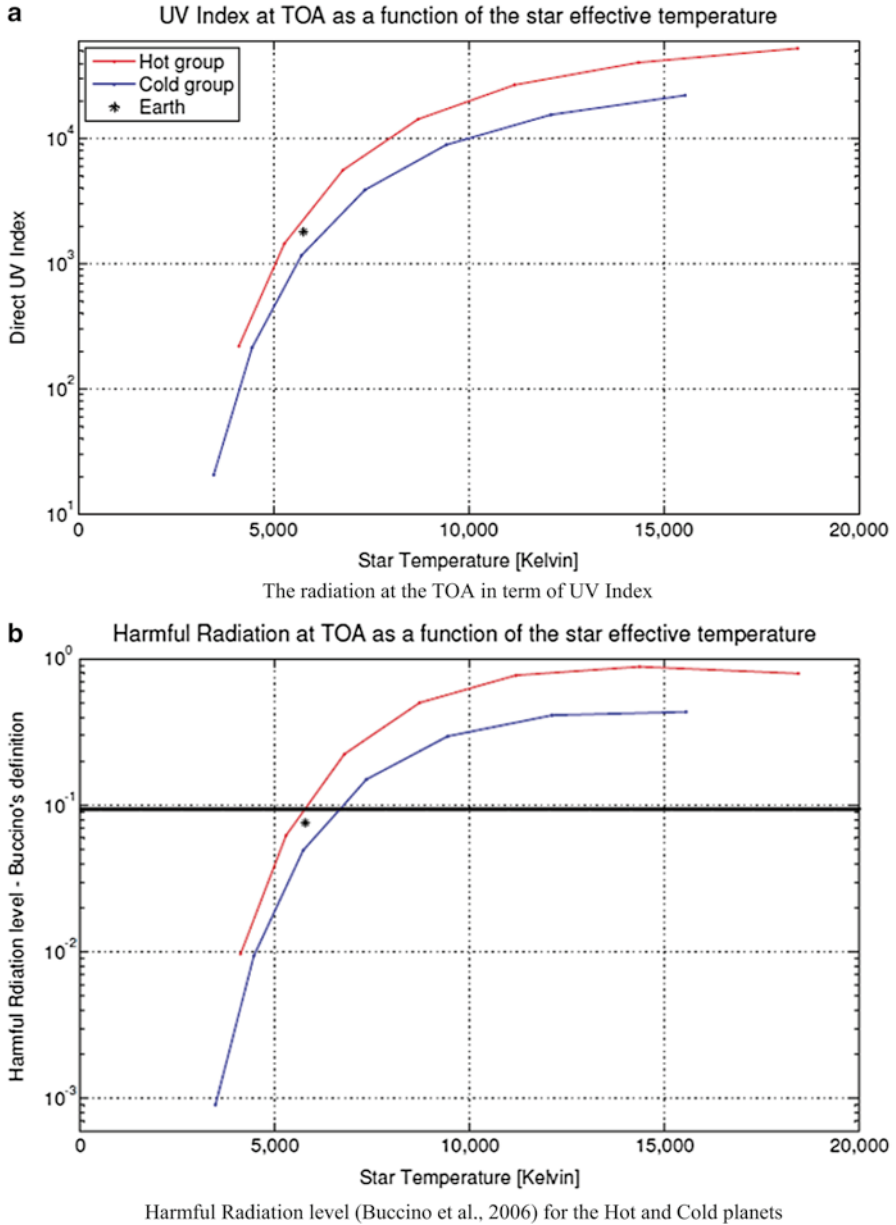
#### 4.2. UV INDEX AT THE TOP OF THE ATMOSPHERE

The harmful radiation reaching the planets' TOA, in terms of UVI, was calculated and is plotted in Fig. 4a. We plot the radiation harmfulness at TOA as it was the base for the definition of the UV-HZ suggested by Buccino et al. (2006). However, Buccino et al. used different units to measure the harmfulness of the radiation (Buccino et al., 2006). In Fig. 4b, we plot the harmful radiation according to the erythema curve used by Buccino et al. (2006). The black horizontal line in Fig. 4b indicates the limit of biologically harmful radiation for the HZ inner boundary, as was defined by Buccino et al. The figures are almost identical in shape, which means that, approximately, only the scaling is different (a scale factor of about 23,500 was found).

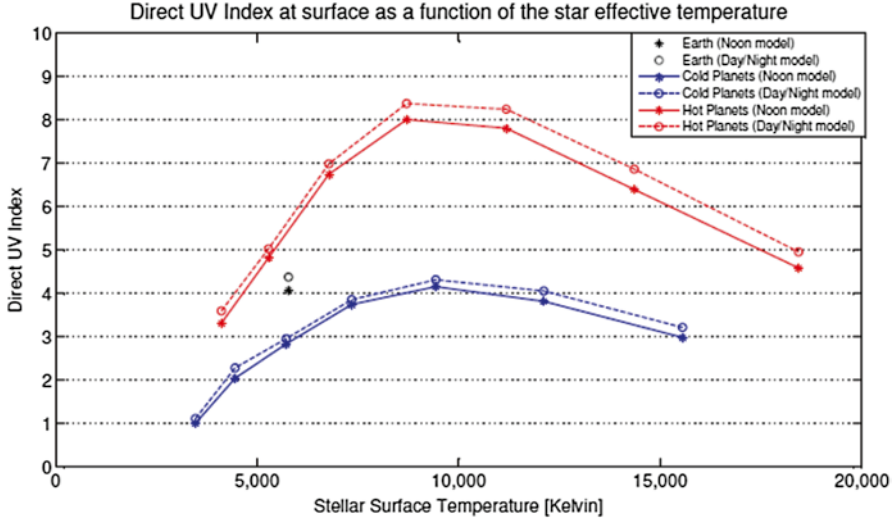
By comparing the harmful radiation level at the TOA for the chosen planets (blue and red lines in Fig. 4b) to the inner UV-HZ limit (black line in Fig. 4b), we see that planets with solar constant of  $935 \text{ Wm}^{-2}$  or higher orbiting stars with  $T_{\text{eff}} > 6,600 \text{ K}$  are expected to be inhabitable due to excessive UV radiation. This comparison is similar to the comparison done by Guo et al. (2010). Guo et al. have calculated the harmful radiation level at the TOA for planets located on the limits of the standard HZ region (Jones et al., 2006), and then compared it to the limits of the UV-HZ region suggested by Buccino et al. (2006). From this comparison, they concluded that the standard HZ region and the UV-HZ region do not overlap for hot MS stars ( $T_{\text{eff}} > 7,000 \text{ K}$ ) as they receive excessive UV radiation.

#### 4.3. UV INDEX AT THE SURFACE

The direct UVI for each planet was calculated in both Noon and Day/Night models. The results are plotted in Fig. 5 and given in Tables 6 and 7 for Noon and Day/Night models, respectively. From these results, we see that (a) the Day/Night model produces at the planet's surface about 5% higher UVI at noon time; (b) the direct UVI is maximal for planets which orbit MS stars with an effective temperature of about 9,000 K; and (c) the maximal direct UVI is about 8.4 units which is about twice the direct UVI calculated for the Earth.



**Figure 4.** The UV Index at TOA for the hot and cold planets as calculated by us (a) and by Guo et al. (2010) (b). The black line in (b) is the inner limit defined by Buccino et al. (2006) for the UV-HZ.



**Figure 5.** The UV Index at surface as computed in both models for the Earth and other planets. The results of the Noon model are marked by \* while the results of Day/Night model marked by o .

**Table 6.** Direct UV Index as computed in the Noon model.

Planet name	Direct UVI	Planet name	Direct UVI
<i>Earth</i>	4.08	<i>Hot 4</i>	3.32
<i>Cold 4</i>	1.01	<i>Hot 5</i>	4.82
<i>Cold 5</i>	2.05	<i>Hot 6</i>	6.75
<i>Cold 6</i>	2.84	<i>Hot 7</i>	8.01
<i>Cold 7</i>	3.75	<i>Hot 8</i>	7.81
<i>Cold 8</i>	4.16	<i>Hot 9</i>	6.40
<i>Cold 9</i>	3.82	<i>Hot 10</i>	4.59
<i>Cold 10</i>	2.99		

A discrepancy of 5 % between the two models was to be expected from the difference in the ozone column density (3).

The appearance of the peak at 9,000 K is a result of our model. This value is not sensitive to the details of the model but rather to the correlation of the ozone abundance and the effective stellar temperature, due to the dependence of the absorption cross section on wavelength. This can be seen from the transmittance of UV radiation through an atmosphere composed of ozone and molecular oxygen. The following integral gives the harmful energy transmitted  $E_{UV}$  (in units of UVI) as a function of the stellar effective temperature:

$$E_{UV}(T_{eff}) = 40_{W^{-1}m^2} \int_0^{400nm} \left( F(T_{eff}, \lambda) \cdot \exp(-L_{O_2} \sigma_{O_2}(\lambda)) \right) \left( \exp(-L_{O_3}(T_{eff}) \sigma_{O_3}(\lambda)) \cdot d\lambda \right) \quad (8)$$

**Table 7.** Direct UV Index as computed in the Day/Night model.

Planet name	Direct UVI	Planet name	Direct UVI
<i>Earth</i>	4.38		
<i>Cold 4</i>	1.12	<i>Hot 4</i>	3.60
<i>Cold 5</i>	2.29	<i>Hot 5</i>	5.03
<i>Cold 6</i>	2.96	<i>Hot 6</i>	6.99
<i>Cold 7</i>	3.86	<i>Hot 7</i>	8.38
<i>Cold 8</i>	4.32	<i>Hot 8</i>	8.25
<i>Cold 9</i>	4.06	<i>Hot 9</i>	6.87
<i>Cold 10</i>	3.22	<i>Hot 10</i>	4.96

where  $F(T_{\text{eff}}, l)$  is the incoming radiation flux (blackbody radiation),  $L_{\text{O}_x} = L_{(\text{O}_x)}(T_{\text{eff}})$  is the column density of  $\text{O}_2$  ( $\text{O}_3$ ), and  $\sigma_{\text{O}_2}(\lambda)$  ( $\sigma_{\text{O}_3}(\lambda)$ ) is the absorption cross section of  $\text{O}_2$  ( $\text{O}_3$ ).

Note that in our calculations,  $E_{\text{UV}}$  peaks at 9,000 K. We have checked the sensitivity of the peak position to  $L_{\text{O}_3}(T_{\text{eff}})$  by doing the following: For each  $T_{\text{eff}}$ , we chose appropriate orbit radius as to produce a constant insolation of  $1,367 \text{ Wm}^{-2}$ , and we set  $L_{\text{O}_2}$  to be  $4 \times 10^{24}$  (similar to Earth's  $\text{O}_2$  total column density). We then calculated the position of the peak of  $E_{\text{UV}}$  for  $L_{\text{O}_3}(T_{\text{eff}}) = 7.5 \times 10^{18} \text{ cm}^{-2} C (T_{\text{eff}}/5,778 \text{ K})^\alpha$  for different values of  $C$  and  $\alpha$ . We found the position of the peak to be sensitive only to  $\alpha$ .  $\alpha=0$  yields peak at 12,000 K,  $\alpha=1$  yields peak at 9,000 K, and  $\alpha=2$  yields peak at 7,000 K.

## 5. Discussion and Conclusions

The present model was verified and validated and found to predict the ozone level to within  $\pm 20\%$ . The accuracy is of the same order of magnitude as the variations in the measured quantities and of the uncertainties in the databases used. However, this precision is more than sufficient for the calculations of the constraints on the UV-HZ.

We have used a new approach to describe the diurnal changes in the solar constant. By multiplying the solar constant with a time-dependent factor, we accounted for the day and night cycle. The impact of this cycle on the atmosphere is not negligible as it predicts about 5% higher UV Index at noon time, as can be seen in Fig. 5.

The response of the atmosphere to the stellar parameters can be seen in Fig. 5. The surface UV Index on the Hot planets is about twice higher than the surface UV Index on the Cold planets. This factor of 2 correlates with the differences in the solar constants of the two groups. The existence of a correlation means that the solar constant has very little effect on the atmospheric ozone and oxygen profiles. The atmospheric ozone and oxygen profiles are affected mainly by the stellar temperature.

Our basic finding is that the higher stellar temperatures cause more oxygen photolysis and ozone formation which in turn results in better protection against UV radiation. In addition, the UV filtering is more efficient due to the higher absorption cross section at shorter wavelengths. The combination of these two trends overcompensates the increased UV radiation emitted from the hotter stars, as can be seen in Fig. 5 and cause the bending and decline in the intensity of the surface UV flux.

The direct UV Index peaks at a stellar temperature of about 9,000 K with a maximal value of about 8.4 units (or total UV Index of 21), which is about twice higher than the direct UV Index calculated for the Earth. This radiation level is high, but it is as dangerous as staying outdoors twice as long. Consequently, the UV radiation emitted by hot MS stars does not prohibit the habitation of any Earth-like planet, as the UV Index never reaches lethal levels. Add to it the fact that no clouds were included in the model. This implies that the search for habitable planets need not be restricted solely to planets which orbit sunlike stars but should also be extended to much hotter main-sequence stars.

Such hot main-sequence stars would suffer from relatively short lifespan, which can be as low as  $10^7$  years. This lifespan is relatively short in comparison to the time scales needed for life evolution. Therefore, habitable planets which orbit such hot stars are more probable to be inhabited by life forms which have originated somewhere else. However, the star's lifespan is relatively very long when compared to history of the human race, and, therefore, the short lifespan does not prohibit habitation of an orbiting planet by external life forms – either being simple life forms (panspermia) or complicated life forms (migration). The short lifespan presents another problem – Can an oxygen-rich atmosphere be produced in the lifespan of such hot star? For comparison, the oxygen in Earth's atmospheres has accumulated over billions of years to reach its present level. Therefore, existence of rich atmosphere on such planets suggests a terraforming process and thus intelligent life forms.

Guo et al. (2010) have stated that no habitable planet can be found around stars hotter than 7,100 K as they emit excessive UV radiation. This conclusion is derived from a calculation of the harmful UV radiation at the top of the atmosphere. However, as we have shown, the harmful UV at the surface is proportional to harmful UV radiation at top of the atmosphere only for relatively cold planets. Therefore, the UV radiation that impinges the planet cannot be used as a criterion for the planet's habitability.

In our calculations, we assumed Earth-like atmosphere. Thicker atmosphere with higher ground pressure will reduce the harmful radiation even more. In our calculations, the UV Index peaks on planets having Earth-like atmospheres orbiting a 9,000 K star. The appearance of a peak is a result of the increased ozone column density on planets orbiting hotter stars. The position of the peak is a result of three competing processes; (a) as the effective temperature rises, the total amount of UV radiation increases, and in particular, the ratio between the shortwave UV and the longwave UV increases. (b) Ozone is created by shortwave

UV radiation and destroyed by the longwave radiation. Consequently, the rise in  $T_{\text{eff}}$  leads to more ozone. (c) The photo cross section for ozone and molecular oxygen increases with frequency. The result of the competition between these three process results in a peak at  $T_{\text{eff}} = 9,000$  K.

However, as was discussed in Sect. 4.3, the position of the peak is not very sensitive to the details of the model but rather to the rate at which the ozone abundance increases with the effective stellar temperature. Previous studies (Kasting et al., 1997; Segura et al., 2003) have found that the level of lethal UV is higher in the case of the current Earth than for an Earth-like planet with the same surface temperature around a K star and an F star. This is a major difference which can be explained by the many differences between the simulations (i.e., physical processes implemented, numerical schemes, databases, and spectral resolutions).

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Biodata of **Rob Hengeveld**, author of “*Factors of Planetary Habitability*.”

**Prof. Rob Hengeveld** worked after his study at the University of Leiden in the Netherlands on various ecological problems, gradually focusing on spatial processes, such as the colonization of large inland polders by carabid beetles. After this, he first turned to biogeography and then to invasion research. He has written two books on these subjects, *The Dynamics of Biological Invasions* (1989), Chapman and Hall, and *Dynamic Biogeography* (1990), Cambridge University Press. Subsequently, he extended his interest to biogenesis on which he published several papers, part of them with Dr. M.A. Fedonkin of the Russian Academy of Sciences. A third book, *Wasted World* (2012), concerns long-term environmental trends causing problems for man’s prolonged existence on Earth (University of Chicago Press). The Dutch translation of this book, *Wildgroei*, is due in 2013. A fourth book with Dr G.M. Walter of the University of Queensland, *Autecology*, on an alternative approach to ecology, is in press (Taylor and Francis).

In 2004, he became Extraordinary Professor at the Vrije Universiteit at Amsterdam, teaching Biogeography and Invasion Research. He is a founding member of the International Biogeography Society. Working in the front line of research of various disciplines, his focus has been on theoretical and methodological aspects in biology. In this connection, he received the Distinguished Statistical Ecologist Award from the International Association for Ecology.

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# FACTORS OF PLANETARY HABITABILITY

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## 1. Introduction

Which factors determine whether life can exist on another planet within or outside the solar system? This question can only be tackled by considering under what physical and chemical conditions life could have begun here on Earth, and how great the freedom is to deviate from those conditions. In the case of complete freedom, information from earthly biogenesis will not give us any clue about factors essential to the existence of extraterrestrial life. When, however, this freedom is restricted, we have to search for the existence of similar conditions elsewhere in the universe. In the first case, we don't know what to look for, but in the second case, our search can focus on the existence of very specific conditions. For example, we may wonder if life began organically or inorganically, then being based on an element such as silicon rather than carbon. Alternatively, would life also be able to start under pressures or temperature conditions higher than those dominating the conditions on Earth today? I will argue that the freedom to deviate from earthly conditions – and occasionally from those existing at present – is rather restricted.

True, the idea of chemically different kinds of life systems evolving, or systems originating and evolving under widely different physical conditions, is not new, but so far, the search has been done only in very general, chemical terms rather than by modeling the buildup of a functioning living system. Which elements present at the start determine its stability, and it is the degree of stability that determines the possibility of an element or compound playing a role in a living system and evolution of life. Silicon, for example, can be ruled out because its bonds are only half as strong as those of carbon, making the compounds it can form less stable and, therefore, less reliable within a complex metabolism (e.g., Ponnampertuma, 1972). Yet, with oxygen, silicon forms the very stable compound  $\text{SiO}_2$ , quartz, but this compound is so stable that it can no longer function as a component. Similarly, arsenic is less stable than phosphorus and is therefore also unsuitable as a component of a complex system. In principle, it could have been present in primitive forms (Wolfe-Simon et al., 2010), but we have no indication of this at all (Hengeveld, 2010).

The emphasis given to the operation of certain factors differs between authors. Common to all, though, is the acceptance of the presence of water, although the reasons given vary from that of determining the temperature range

in which life can exist to that of a general solvent of compounds essential to life. In this context, however, the significance of the interchange of protons in such basic processes as condensation and hydrolysis has not generally been emphasized. Biochemically, hydrogen may be considered more basic to life than carbon (Fedonkin, 2009; Hengeveld, 2012a).

Still, instead of speculating about the biotic or abiotic origin of individual elements or compounds (Hengeveld, 2007), it may be more relevant to know how a well-coordinated system of reactions originated that was able to form the compounds on its own (Hengeveld, 2007, 2012a). How does a system itself begin to produce a compound as a functioning part of a host of interactive and interdependent processes, within a network of biochemical structures? From this perspective, it is of no interest to know the possibility of a certain amino acid, purine, pyrimidine, or adenine, etc., raining down from outer space. Nor is it interesting to know that it can be formed abiotically by strong electric charges (Miller, 1953) or pressure shocks (Hazen, 2005), etc. And it is of no interest either that most molecules found in space are organic: because of their relatively low nuclear ignition temperatures, carbon, oxygen, and nitrogen are formed in all stars of more than one solar mass and are therefore the most abundant atoms in the universe, and they all react with hydrogen (Delsemme, 1998). Yet, a system that depends on receiving some compound from outer space, but apparently cannot produce it itself, will remain unable to do so.

The assumption that a running system can adopt an alien chemical compound successfully accepts the occurrence of chemical Lamarckism. This means that, after passively receiving some compound, the system would be able to develop genetic structures and subsequent biochemical processes for producing this compound itself. And it could do this at exactly the moment, and in the right concentration, when its external supply runs out and the system's internal condition requires it! However, no mechanism is known for inducing genetic and biochemical structures to synthesize the same chemicals as those raining down from space. Chemicals from outer space are therefore of no use to living systems, not in their origin, nor in their operation. We have to understand the origin and development of the biological system as such. The study of biogenesis concerns the evolution of the self-regulated logistics of biochemical systems (cf. Abel, 2011). The problem of the habitability of planets concerns the possibility of the buildup of this kind of logistics under local conditions elsewhere.

This reasoning not only concerns the insertion of alien chemical compounds one by one into a system, but it applies even more strongly when several compounds, or even sets of many compounds, are thought to be put together instantaneously, although just before they were still part of a primeval, unorganized organic soup. According to organic soup models, a great number of preadapted compounds would at some point come together, at the same time excluding a number of apparently nonviable compounds. From then on, they would instantaneously form a complete, functionally differentiated, delimited system operating with its own energy budget, and this within a given physical and chemical environment. Again, no mechanism is known to achieve such an unlikely result

(compare Hoyle, 1983). Historical reasoning attempts to explain how this can happen in small, mechanically understandable, and testable steps.

The operation of a system, moreover, not only requires the supply of chemical materials in tune with each other, but it also requires electrochemical energy; from the start, the system must immediately generate and process this energy. Where and how does it generate it, and how does it flow through the system? How does the system process it? Furthermore, how much has the structure and dynamic of the system been formed by the flow of energy running through it? Systems logistics originates and evolves by means of a bootstrapping process (Hengeveld and Fedonkin, 2007), and it is this bootstrapping process that we need to reconstruct.

To be able to judge the habitability of a planet, we have to know the local occurrence of the physical, chemical, and energetic conditions under which bootstrapping can take place.

## **2. Defining Life Hampers Biogenetic Research**

For reconstructing life's past, definitions based on widely occurring biochemical structures and processes seem at first reasonable research guides. However, giving such definitions introduces circular reasoning into biogenetic research (Hengeveld, 2010b). For example, the presence of DNA in virtually all organisms living at present has been taken as a criterion to define life, meaning that by studying the origin of DNA, we understand the origin of life. However, a molecule of such an extreme complexity, which, moreover, can only operate within a highly complex biochemical context, cannot possibly have been present and functioning right from life's very beginning. It must have had precursors, such as RNA, which however, for the same reason, cannot define life either. Also, carbon compounds, or amino acids, are pivotal to all present-day life. Their discovery in outer space has also been taken to justify considering them as life-giving chemicals on other planets. If, however, the earliest life forms were indeed unable to use carbon or nitrogen compounds, and build them into their biochemistry the Lamarckian way, searching for them points biogenetic research in the wrong direction and, thus, hampers its progress.

Biogenesis concerns the earliest processes that happened within the system itself. This similarly applies in the evaluation of the chemical habitability of planets.

## **3. An Inorganic Beginning of Life**

### **3.1. STARTING UP CHEMICAL RECYCLING**

Biogenetic models assuming that complex life processes began in a warm little pond of organic soup cannot work for another reason as well: reactions would fade to equilibrium before being able to build up a thermodynamically and chemically

independent, and thus continuing, existence. Life must have begun with, and within, an enclosed space which is in continuous thermodynamic disequilibrium with its environment. If the proton and electron concentrations outside are higher than those within, electrochemical energy keeps flowing in, enabling chemical processes to start up and to continue. However, because chemical processing happens within an enclosed space, the elements inside cannot interchange with those outside it, as this requires specialized pumps. This means that, from early on, perpetuation of each process must have depended on chemical recycling. The energy flow through the system will keep this recycling process going as long as the disequilibrium with the environment lasts. Therefore, the barrier that initially separated a distinct chemical compartment from the general environment must also have had a significant thermodynamic function.

Russell and Hall (1997) assumed that fine trickles from the basaltic ocean floor introduced alkaloid material into the acidulous seawater, resulting in the precipitation of a mineral crust around a cavity, which created a charge and proton disequilibrium. Metals dissolved in the water, in turn, created its relative electron-richness, whereas dissolved carbon dioxide resulted in carbonic acid, which could split off protons. Metals available before the Great Oxygenation Event (Keller and Schoene, 2012), such as iron, nickel, vanadium, and tungsten, could have catalyzed the early reactions (Fedonkin, 2009). Over the Precambrian, though, the environment gradually became more oxidizing, which meant that various metals, such as copper and zinc, successively became available and were adopted into the metabolism of various living systems (e.g., Anbar, 2008; Anbar and Knoll, 2002; Fedonkin, 2009; Hengeveld and Fedonkin, 2007; Schoepp-Cothenet et al., 2012; Williams and Fraústo da Silva, 2006).

The assumption that reactions may have occurred between some elements without forming stable compounds implies that molecules formed relatively easily would also have fallen apart easily. This continuous formation and falling apart of compounds would have resulted in the required chemical recycling without material being exchanged with the environment. Hengeveld and Fedonkin (2007) assumed that selenium reacting with hydrogen could have led to primeval cyclic reactions: as the only elements having a metal as well as a nonmetal character, short polymer chains could have alternately formed and broken down.

### 3.2. MOLECULAR HABITABILITY FACTORS

As the system built up, the weakly electronegative selenium would have been substituted by sulfur, a stronger nonmetallic electron acceptor, occurring one period higher in the same group in the periodic table, and, this, in turn, by the strongest electron acceptor of that group, oxygen. These three elements occur in the same group of elements and have similar chemical properties, so that the primeval chemical structures and reaction systems in which they occurred could largely be

conserved. A good example is seen in the two chemically similar Photosystems I and II, which operate in series in cyanobacteria and chloroplasts, the  $\text{H}_2\text{S}$  in Photosystem I being substituted by  $\text{H}_2\text{O}$  in Photosystem II.

de Duve (1995) proposed the existence of an early Thioester World, which presumably existed prior to the RNA World, or even prior to that in which ATP originated, when thioesters supported the formation of phosphate groups. They catalyzed the condensation of monophosphates into diphosphates and triphosphates, which were hydrolyzed back into monophosphates again, with the result of energy transfer (Baltscheffsky and Baltscheffsky, 1997). These oligophosphates first evolved into nucleotriphosphates, NTPs, as ATP, NHDP, and other nucleotide coenzymes, and eventually into a host of RNAs constituting the RNA World, from which eventually DNA evolved, basic to the DNA World of today. Thus, the metabolic and genetic systems would have arisen simultaneously from an enzymatic energy transfer system, ultimately supporting material recycling.

Thioesters were also involved in the synthesis of complex lipids as ancient membrane constituents replacing the mineral crust. Later, too, thioesters participated in the synthesis of fatty acids, peptides, sterols, terpenes, and porphyrins. According to de Duve (1991, 1995), the reductive synthesis of the thioesters itself would have been powered in the iron cycle driven by UV radiation. Energy from UV radiation liberated an electron from the donor  $\text{Fe}^{2+}$ , after which the resulting electron acceptor  $\text{Fe}^{3+}$  released the energy again when taking up an electron. This energy was then used in the endergonic synthesis of the thioester. On the other hand, in the absence of atmospheric oxygen, and therefore of ozone, biochemical structures sensitive to UV radiation were not shielded off from this kind of radiation, as happened later (initially, the stronger UV radiation may also have selected for the large number of double bonds in lipids and other hydrocarbons, as these increase their stability (Pullman, 1972)).

Although UV radiation, driving de Duve's (1995) iron cycle, penetrates deeper into water than radiation of longer wavelengths, it could not have penetrated very deeply into the ancient oceans, the water of which, still being rich in  $\text{SiO}_2$ , was opaque. Instead of the later formed ozone, dissolved silica could have shielded early life forms from UV radiation (Phoenix et al., 2006). In very clear water, UV radiation reaches a depth of some 50–70 m, but in opaque water, it can only penetrate to relatively shallow depths of about 30 m (Cockell, 2000). This implies that life on Earth could only have originated and developed in relatively shallow water.

Therefore, in order to use UV radiation in similar processes early in its development, it is unlikely that life could originate in deep waters with tall smokers or on Jupiter's moon Europa with an ocean 100 km deep. At its distance from the sun, it is improbable that the amount of solar UV radiation would be sufficient anyway. Water composition and depth thus constitute significant planetary habitability factors.

### 3.3. CHEMICAL HABITABILITY FACTORS

The cell contents mainly consist of energy-processing, electron-accepting elements, the nonmetals, and its evolution may have progressed from weak, metalloid acceptors to strong, nonmetallic acceptors, such as carbon, nitrogen, oxygen, sulfur, and phosphorus. The first three elements form the most stable compounds, which have to be synthesized and be broken down catalytically by nucleotide enzymes and the present-day proteins. As the active, prosthetic part of proteins consists either of some metal or of some form of RNA, the ancient metabolic processes are still basic and operating. Because their own synthesis as macromolecules, and their continuous breakdown, depends on a highly complex biochemical machinery in which yet other proteins play a part, proteins could not possibly have been present right at life's beginning. Their operation and recycling will have been based on metals, nucleotide coenzymes, and RNA as catalysts.

Therefore, it makes no sense to speculate about the role amino acids may have played as building blocks of the first living systems based on nitrogen either. Carbon, on its part, is important in the functions of energy storage and mechanical support, both of which require the high stability of its bonds. However, such functions were not yet required at the time of life's very beginning but became functional only during later evolutionary stages. Typically, its macromolecules are built up in multistep pathways and cycles in which energy is added at many of the steps. Thus, the later adoption of these functions fits a trend toward greater biochemical complexity and the chemical stability and reliability resulting from their adoption. Oxygen, in turn, is too reactive to be a part of the biochemistry of the cytosol.

This has to be kept in mind when investigating the chemical habitability of planets and when judging whether primitive life may be present.

## 4. Adaptive Processes Counteracting a Diminishing Disequilibrium

Within a compartment, catalysts and biological enzymes speed up the previously existing processes, thereby increasing the stability of the molecules and the chemical complexity of the system, and at the same time enhancing the energy flow. As outside the compartment the initially reducing conditions grew more oxidizing, the energy-generating disequilibrium between conditions inside and outside lessened, whereas the energy needed increased. At some point, energy shortage could therefore have prevented the system from operating.

The shift toward greater electronegativity of the elements inside the compartment was just one of several adaptive processes. The proton-motive force as a newly added mechanism restored the initial proton disequilibrium by first pumping protons out and by subsequently letting them in again along the pathway probably already existing (Hengeveld and Fedonkin, 2007). Another mechanism was the *Z*-scheme which bridged the redox conditions between the more



recently developing high environmental redox values and the still existing, initially low ones inside, thus maintaining the inflow of electrons. Both mechanisms, though, required energy which had to come from elsewhere than could be obtained from the diminishing disequilibrium with the environment. The new mechanism of photosynthesis offered a solution by converting solar radiative energy as an external energy source to electrochemical energy (Hengeveld and Fedonkin, 2007), as the iron cycle running on UV radiation had done before. Still later, eukaryotic endosymbiosis would again, and in yet another way, have solved the basic need for hydrogen (Martin and Muller, 1998), as life's biochemistry and ecology kept running on a reducing hydrogen economy. Moreover, the cell now contained several energy-processing units, the mitochondria, supplemented in algae and plants by chloroplasts. The system as a whole thus followed the backward compatibility principle known from computer science.

All these adaptive processes have to be duplicated in one form or another on other planets if life is to be sustained there. The probability of such duplications happening is small because even trends that are deterministic on a long term happen through many stochastic processes on a short term. This leaves room for different routes being taken or for failure.

## 5. Habitability as Set by Gravity and Planetary Temperature

Much has been written about the physical suitability of planets to carry life (e.g., Kasting, 2010; see also Hengeveld, 2012b), such as gravitational pressure and (water) temperature.

### 5.1. GRAVITATIONAL PRESSURE

Gravitational pressure, resulting from the elemental composition and size of a planet, relates to those of its star and determines the dissipation rate of gases, such as hydrogen and carbon dioxide; at the low pressures associated with small planetary size, not only hydrogen but also carbon dioxide would dissipate into outer space. Earth kept most of its carbon dioxide, for example (Russell and Kanik, 2010). A different gravitational pressure from that found on Earth therefore would result in a different atmospheric and aqueous composition under which life would have to originate. Larger gravitation also would have its effects on the anatomy, growth form, and size of multicellular organisms (Comins, 1993). In the past, both the initial composition and size of the Earth, though, changed due to a chance collision, first with a Mars-size protoplanet and then with shutoff material from that collision (Jutzi and Asphaug, 2011). These collisions, followed by many other, smaller ones made Earth unique, as their relative sizes, and the timing, location, and angle of colliding relative to Earth's compositional stratification almost cannot possibly be repeated exactly. Also, the size, composition, distance, and rate

of retreat of the moon once it was separated from the Earth were important with regard to the stabilization of the Earth's axis and to that of its consequent seasonality, as well as to the changing intensity of the tidal movements of its crust and its oceans over the eons (Hazen, 2012; Ward and Brownlee, 2000).

Gravitational pressure could also affect reaction rates by determining the density and thus the frequency and intensity of contact between elements and compounds, as well as the compactness and shape of molecules. Therefore, the search for planetary habitability should be for pressures and temperatures roughly identical to those we experience on Earth.

## 5.2. ANCIENT TEMPERATURE

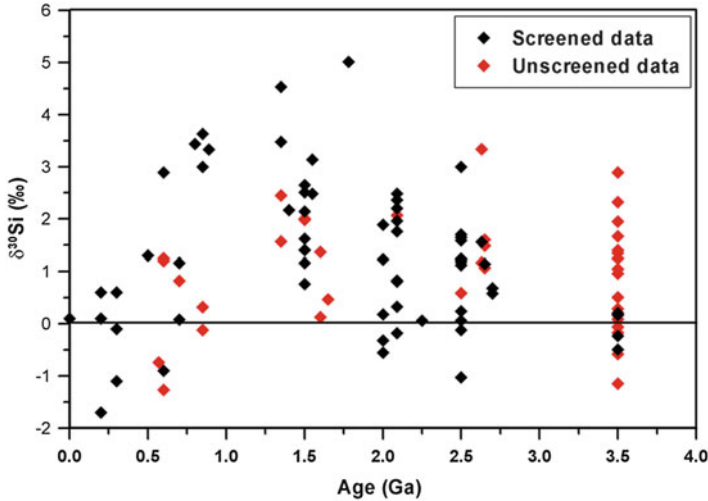
It is commonly assumed that, for some time after the consolidation of the Earth, temperatures remained high and that, therefore, life must have originated under high temperature conditions. Thus, studies on representatives of ancient life forms tend to concentrate on extremophiles and hyperthermophiles, which are still found in hot, volcanic lakes on land, and on black and white smokers in the deep ocean. Yet different temperatures affect the stability of chemical compounds, particularly that of macromolecules, and thus would have determined the possibility of biogenesis, as well as the direction of chemical evolution of living structures. It is therefore essential, contrary to common practice (e.g., Robert and Chaussidon, 2006), to use seawater temperatures away from such smokers (van den Boorn et al., 2007, 2010).

Using silicon isotopes, Robert and Chaussidon (2006) estimated ancient water temperatures from cherts of up to 3.5 billion years old, close to the presumed time of life's origin on Earth. They found that the oldest temperatures must have been high. However, these authors heavily screened their original data, dropping more than one-third of the points (Fig. 1).

Information given by Robert and Chaussidon (2006) refers to data from black and white smokers, whereas those from cooler water away from these were dropped. Using data for oxygen isotopes instead of from silicon means that older data are preferentially dropped, particularly for higher values of  $^{30}\text{Si}$ . This biased their conclusions (van den Boorn et al., 2007, 2010). Instead of a downward trend in the scatter as claimed, the dispersion of all data points together appears to be constant. They do not indicate a temperature decrease with time; instead, temperatures during biogenesis were similar to present-day ones, that is, less than 55 °C, and probably around 20 °C (Vroon, pers. com.).

By analyzing the size and depth of raindrop imprints in volcanic ash, Som et al. (2012) found similar temperatures for 0.8 Ga later, some 2.7 billion years ago. The characteristics of those imprints, determined by air density which, in turn, depends on temperature, are the same as they are today.

The long-term constancy of temperature agrees with my expectation from systems behavior. The fine-tuning of biological molecules, biochemical structures,



**Figure 1.** Variation in isotopic composition of silicon in cherts with age in billions of years. *Black and red dots* according to original data and supplementary information in Robert and Chaussidon (2006), respectively (Figure plotted and kindly supplied by Vroon (personal communication, 2012)).

and processes in a complex system is destroyed under greatly altered conditions, which would destroy the system. Also, the size, stability, and internal structure and dynamic of macromolecules depend on temperature, which should keep stable for them to remain functional. This holds particularly for the quantum tunneling of hydrogen, playing a pivotal role in numerous biochemical reactions (Hengeveld and Fedonkin, 2007; Greener, 2005; Dutton et al., 2006): both temperature and pressure affect the distances to be bridged between molecules.

The idea that life would have originated under high temperatures therefore may need to be revised. This has repercussions for the habitability of other planets, as it has for the classification of all life forms (see Gupta, 1998, 2000): planetary temperatures should be moderate and roughly constant to allow biological stability and a sustainable evolutionary development over billions of years.

### 5.3. A DYNAMIC WORLD

The early world was dynamic: widespread volcanism; a moon circling Earth at high speed and at close distance thus causing intense tidal movements, both in its waters and in the crust; partly inundated plutons, cratons, and protocontinents were growing and drifting; meteorites bombarded the young planet. High smokers like the Lost City could not have been formed. Crisis followed upon crisis, leaving traces in the rate and direction of evolutionary development

behind. All this would need to happen on other planets as well, if life were to be duplicated one way or the other elsewhere.

## 6. Deterministic and Stochastic Processes

All processes both within and outside the compartment of the (proto-) cell have a deterministic component: at the start-up of biogenesis, a certain set of chemical elements would be required and in particular proportions. After this, these elements would gradually be supplemented or substituted in a sequence running from low electronegative ones to those with an increasingly higher electronegativity. We can assume that inside and outside the cavity, these processes, being interdependent, happened at rates that were in tune, the rate of biochemical reduction matching that of the environmental shift toward more oxidizing conditions. The matching of the rates at which elements became available with those of their biochemical supplementation and replacement would determine the probability of life originating, maintaining, and developing on a planet.

Therefore, in identifying the probability of life occurring, originating, and developing elsewhere in the universe, we need to look for a particular, shifting set of elements on the planet concerned. Of course, these probabilities depend on the process as we think it has happened on Earth. If my expectations are correct, on this broad temporal scale, a particular, roughly deterministic sequence occurred, in which inorganic compounds were dominating in the initial stages, whereas organic ones prevailed in later ones. The chance of finding organic compounds or oxygen on another planet, either in living systems or as waste products, depends on the probability of a similar system having developed in the same direction and having reached the same stage.

Contrary to the few, simple, physical rules of the deterministic filling of atomic electron shells on which this trend depended, though, the specific form of life evolving also contained a large historic and stochastic component. The exact route taken on a short term, namely, was stochastic, which means that the number of chemical compounds, processes, and life forms was virtually limitless. The synthesis of a particular molecule was not entirely random but depended deterministically on the conditions of its physical and chemical environment, conditions that themselves varied stochastically. Conditional variability is the basis of biochemical stochasticity, making the direction in which the complex system evolved vary stochastically.

However, the very complexity of processes within the system required that they were tuned right from the beginning. This tuning put constraints on the internal stochasticity, despite the fact that genes were absent. In fact, the present biochemical system, comprising tens of thousands of compounds, is still ruled by a complex of tightly tuned, homeostatic interactions of which DNA is but one component. In this system, DNA is not an independent biochemical ruler handing out instructions, but a conservative standard interacting with processes

happening around it (cf. Keller, 2000). Overall, fine tuning in increasingly complex biochemical systems reduces stochasticity and increases its determinism.

Therefore, how exactly a biochemical system took shape to counteract the deterministic lessening of the disequilibrium does not follow a deterministic but a stochastic process. Moreover, here too, spatial and temporal variation in chemical composition, concentration, and rates of reaction must have occurred. Different life forms, at first microbes, and then, after three billion years, the faster evolving multicellular organisms, all responded and interacted specifically. At any one scale, chance disturbances and opportunities occurred, ranging from local and incidental to global, the latter with astronomical impacts, volcanic eruptions, snowball earth glaciations, and mass extinction events. The stochasticity of metabolic, organismic, and species evolution thus interacted with this huge environmental stochasticity, enhancing the complete unpredictability and non-reproducibility of the process even more.

This basic unpredictability makes it extremely improbable that somewhere in the universe, we can expect life to evolve for a second time and even in the same way, in the same direction, and reaching the same result as it has done here on Earth (compare Gould, 1989). It is even improbable that it might have got going elsewhere at all (e.g., Hengeveld, 2012b; Wallace, 1904). Apart from long-term deterministic conditioning and trends, stochastic variation in environmental conditions and the ways in which life maintains and evolves would decide the habitability of planets. Taking a particular evolutionary route by chance determines the probability that life can be sustained in that particular way.

## 7. The Probability of Occurrence of Similar Conditions

Initially, Earth had a reducing environment, the atmosphere being rich in methane, ammonium, carbon monoxide, and carbon dioxide, and the oceans rich in hydrogen carbonate. Lack of oxygen, and therefore ozone, in the atmosphere meant that the UV radiation released by the young Sun could split water into hydrogen and oxygen. Part of the hydrogen dissipated into the outer space, whereas the oxygen stayed behind. Thus, partly through this and partly through a conversion of atmospheric methane into carbon dioxide, in turn binding metals dissolved in water and by silicate weathering, the reducing environment evolved into an oxidizing one. This lessened the redox disequilibrium which determines the energetics of the early living systems, whereas their own biochemistry, depending on a reducing environment, added to the general trend. As mentioned, to keep the system going, apart from an external energy source, they needed ever stronger electronegative elements for enhancing their metabolic stability, and thus a greater biochemical reliability required by the increasingly complex system.

Apart from the incredible stochasticity over billions of years, the probability of occurrence of these relative amounts of elements – and of the rates at which these amounts become available – being replicated elsewhere in the universe

would determine the chance of life originating and evolving there as well. This probability would determine the habitability of the exo-planet concerned. Moreover, as the composition of this set of factors changed over geological time, one also needs to include the probability that the rate of biological evolution matches that of environmental change. With an increase in the complexity of the biochemistry, organismal structure and development, ecology, and behavior of the evolving systems, as well as the spatial heterogeneity, temporal variability, and longer-term change of their environments, such probabilities soon become exceedingly much smaller than the total number of planets or even than the number of atoms in the universe. In fact, they become incalculably small (Elsasser, 1987; Hengeveld, 2012b; Hoyle, 1983).

Of course, we have to allow for interdependencies between variables, both within the system and over time, as these enlarge the probability values obtained. In heme groups or in photosystems, for example, individual chemical elements can be substituted by functionally similar ones without greatly changing the structure and mechanism. This happened in the hemoglobin of arthropods where copper replaced iron (e.g., Williams and Fraústo da Silva, 2006). Similarly, as mentioned, oxygen substituted for sulfur in Photosystem II. Alternatively, altered chemical conditions in the environment usually demand special mechanisms to be added in order to keep the system functioning in the same way as before. For example, under falling iron concentrations at the end of the Achaean, pumps inserted in the cell membrane kept the internal iron concentration constant, despite a decrease in seawater concentration by a factor of up to ca. 45,000 (Fedonkin, 2009). Sometimes, therefore, new mechanisms had to evolve, whereas in other instances, they adapted from previously existing ones. As with other newly added mechanisms, this resulted in a gradual complexification of the living structure. The evolution of a completely new complex mechanism has a low probability of being repeated, whereas one adopted from a previous one is more likely. Similarly, rather than high (e.g., Conway Morris, 2003), the probability of the evolution of ecomorphs is low.

Particularly for other planets, such interdependencies, though, being empirical, are unknowable for the great number of compounds, cells, organisms, species, and for all environmental factors perpetually influencing them, and this all over a period of billions of years and across a whole, spatially heterogeneous, dynamic planet like Earth.

Usually, single factors treated qualitatively are taken into account to judge a planet's habitability, with the result that many planets seem to be able to carry life. Instead, I suggest that combinations of physical and chemical factors, factor values, plus their interactions determine their habitability. These combinations make planets unique. At present, each of the several tens of millions of species existing on Earth is adapted to such a unique combination. As they represent only between 0.01 and 0.001% of all species that have ever existed, the chance that their origination, continuation, and evolutionary adaptation might be repeated on another planet is negligibly small. The chance of finding another habitable planet, certainly one comparable to Earth, is beyond any reasonable imagination.

## 8. Extraterrestrial Life, Planetary Habitability, and Natural Laws

If my biogenetic model holds true, then the chemical conditions for biogenesis, the adoption of elements, as well as the broad chemical phylogeny of subsequent life forms are determined by the trends in the electronegativity of the elements, expressed by the structure of the periodic table. As these trends pertain to universal physical properties of atoms, they will similarly condition the habitability of exo-planets throughout the universe. The same applies to the principles of systems behavior during the buildup of life forms toward greater complexity: they apply independently of the subject concerned and pertain to all systems, whether they are living systems or computers. The more complex a system, for example, the more conservative it will be and the more deterministically it will operate. Different temperatures or pressures cannot change such laws and principles; they only affect the chemistry concerned. However, conditions can affect the physical properties of macromolecules and thus the way they operate, such as they can in quantum tunneling of hydrogen unfavorably affect, if not destroy, the feasibility of life.

Therefore, the chance of life originating and following the same course of evolution elsewhere in the universe is prohibitively small, whereas the feasibility of life according to dissimilar physical principles can safely be excluded. All exceedingly complex adaptive processes must be duplicated on a planet other than Earth if life is to be initiated and to continue there as well. There too, the rules of physics, systems analysis, and the periodic system must be obeyed.

## 9. The Search for Planetary Habitability and Extraterrestrial Intelligent Life

Ultimately, all arguments in favor of the existence of extraterrestrial life as well as the search for habitable planets reflect an anthropocentric worldview interwoven with scientific reasoning (Basalla, 2006). However, the probability of life developing extraterrestrially – even that evolution will culminate in something like mankind – would be exceedingly small (Hengeveld, 2012b). This is in sharp contrast with the general assumption that the probability is so large that it would be certain that intelligent life exists elsewhere: a probability equal to one has been defended (Aczel, 1998). Life would even be abundant throughout the universe (e.g., Hoyle, 1983; Schulze-Makuch and Darling, 2010).

The motivation of the search for extraterrestrial intelligent life (e.g., Boss, 1998; Sullivan and Baross, 2007) may be based on religious (e.g., Conway Morris, 2003), philosophical and social (e.g., Taub, 1993), or physical arguments (see Kuhn, 1957). Others choose arguments based on astronomical probability (e.g., Shklovskii and Sagan, 1966), the ancient natural-philosophical idea of the Great Chain of Being (Lovejoy, 1965), or orthogenetic reasoning (Conway Morris, 2003).

However, over time, physical and astronomical observations have toned down our anthropocentric worldview. Kepler's Third Law from which the distances within the solar system could be derived destroyed the crystal spheres

surrounding the Earth (Delsemme, 1998), and Galileo equated the Earth circling the Sun with the moons rotating around Jupiter. Copernicus' heliocentric model, combined with Newton's gravitational laws, changed the ancient Earth-centered worldview into the present idea that Earth occupies a position as one of several planets circling the sun. This system is just one of billions existing in one of the arms of the Galaxy, which itself is only one of the hundreds of billions of galaxies, arranged in a multitude of huge superclusters of galaxies that exist in the universe.

Until recently, people thought that Earth was quite young, often basing their opinion on calculations from Biblical accounts, such as those of Ussher, who arrived at the date of 4004 BC that the Earth was born. A contemporary Scottish physicist, Lord Kelvin, however, basing his calculations on physical arguments, extended its age to be between 20 and 40 million years (see Oldroyd, 1996), which was further lengthened by recent data on isotope fractionation to roughly 4.5 billion years. During and after the Reformation in sixteenth-century Europe, doubts were expressed about the singular interpretation of the Bible and the meaning of local experience, of which the fates of Bruno and Galileo are sad examples.

From their local experience, too, people were initially convinced that the Earth was flat, but these opinions were definitively silenced when photos taken from space showed that it is round. Similarly, since ancient Sumerian times (e.g., Hillel, 1994), people had accepted that animals and plants in their immediate surroundings could be assembled on a single ship braving a deluge, a story later represented by that of the Biblical Ark of Noah saving mankind. Particularly during the nineteenth century, this interpretation gradually lost ground as more and more species became known from other continents and geological times (see Browne, 1983). To keep the story alive, they extended the ship, culminating in a multistory, nineteenth-century steam ark! Knowledge of intricate evolutionary processes has further altered our worldview, especially since the 1920s, whereas since the 1950s, a wealth of genetical, biochemical, geochemical, and planetary processes became known. Paleontology, on its part, has taken a distance from orthogenetic reasoning and evolutionary driving forces (e.g., Simpson, 1953; Gould, 1989) – reasonings underlying the idea that life inevitably reaches a climax in intelligent beings like us, that it would do so on other planets as well, beings with which we might be able to communicate (cf. Goldsmith and Owen, 1992; Grinspoon, 2003; Ponnampereuma and Cameron, 1974). Not only would other planets hold forms of (intelligent) life, but ecosystems would have evolved comparable to those found on Earth (Irwin and Schulze-Makuch, 2010). Despite sophisticated technology to detect it, however, so far no sign of life, intelligent or not, has ever reached us from space (Davies, 2010). So far, simplistic models, such as Drake's equation, by mainly taking astronomical arguments into account (e.g., Shklovskii and Sagan, 1966), fall dismally short (Hengeveld, 2012b).

The search continues for exo-planets with properties promising past or future life, inspired by scientifically ungrounded, outdated opinions and speculations, which all fall short in justifying the continued search for extraterrestrial life.



## 10. Conclusions

So far, chemical experiments have focused on the abiotic origin of individual compounds, such as on carbohydrates or proteins, that arguably date from relatively late evolutionary stages. Moreover, such experiments also tend to neglect considerations of energetics or systems analysis (e.g., Miller and Orgel, 1974; Zubay, 2000; but see Morowitz, 1992).

If, however, the model of building and maintaining a functioning system given above holds true, the habitability of an exo-planet depends on shifting combinations of a large number of variables, as well as on many processes happening at many spatial and temporal scales. For thermodynamic reasons, we can only expect elements and compounds to be adopted by the evolving system from that time onward that they obtain a biological function. The sequence of their adoption is bound by the physical properties of the elements and is therefore universal and deterministic. However, the number of molecules and biochemical pathways and cycles that may potentially be formed leaves room for extensive stochastic variation in the evolution of life. Stochasticity also determines the processes of eukaryotization, several previous (Kooijman and Hengeveld, 2005) and subsequent endosymbiotic events, and speciation among the eukaryotes, as well as to geological, climatological, ecological, and behavioral events and processes on all scales in both space and in time. Historical processes complicate the picture further and in the same way. All this stochasticity determines the chance of life originating and evolving and that of it being repeated in some other corner of the universe.

If a planet is to carry life, both the conditions for life originating and maintaining itself, as well as those for it to evolve in a way similar to that here on Earth, would need to be repeated. This is unlikely to the extreme. Its habitability makes the Earth unique.

## 11. Acknowledgments

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Biodata of **Diedrich Möhlmann**, author of “*Bio-relevant Microscopic Liquid Subsurface Water in Planetary Surfaces?*”

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# BIO-RELEVANT MICROSCOPIC LIQUID SUBSURFACE WATER IN PLANETARY SURFACES?

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## 1. Introduction

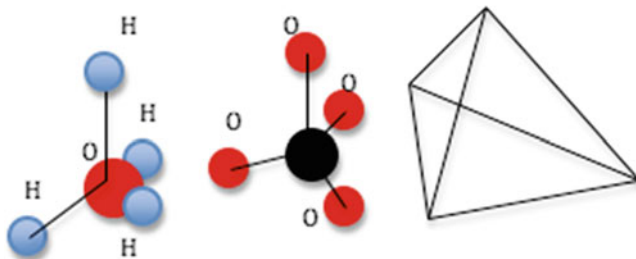
A liquid is *per definitionem* able to flow and to continually deform under an applied force. This implies internal mobility, which is understood in terms of an organized relative motion of units like atoms, molecules or local (internally ordered) domains of them. It is this internal mobility, which makes liquids able to support internal transport of matter down to the atomic and molecular level. Life requires transport processes.

Furthermore, liquids are able to dissolve substances like salts. This property makes them essential to realize a transport of nutrients. Thus, liquids are necessary to make life possible as it is currently known. Transports of nutrients, waste and entropy are key requirements for life to exist. The export of entropy (by high-entropy matter) is a necessary process to stabilize life processes, which are generally of comparatively low entropy (in terms of ordered structures).

Water is liquid in a large range of temperatures and pressure, and it has some further “life-supporting” properties like the solubility of numerous substances, and the thermal balancing in course of a remarkable large specific heat capacity. Therefore, water is of specific importance among the fluids, and this paper is focused on presence and properties of liquid water.

Water is on the molecular level usually understood as a steadily changing network of water molecules, which temporarily are connecting (loosely binding) and separating. The main reason for this internal property is the “hydrogen bond” (H-bond), whereby a proton (hydrogen atom), while by covalent bond “belonging” to one water molecule, temporarily forms “by hydrogen bonding” a bridge to (the oxygen atom of) another water molecule. The timescale of these changes is in the range of picoseconds ( $10^{-12}$  s). In the “normal” covalent bond of a water molecule, the electrons shared by the atoms are for a greater amount of time closer to the oxygen nucleus than to the hydrogen. Thus, the oxygen seems to have on the average an effective negative charge and the hydrogen atoms seem to have a positive charge, what “stimulates” further bonds (the hydrogen bonds). These hydrogen bonds act over a longer spatial scale.

This hydrogen bond is the main reason for the inherent tendency of water molecules to temporarily and microscopically form loosely coupled local substructural



**Figure 1.** *Left:* Tetrahedron-like geometry of hydrogen atoms (hydrogen bond is indicated by a *thin line*, the hydrogen bonds are “longer” than the covalent bonds) in a water molecule with two hydrogen bonds, of the related attachment of neighbouring O-atoms (red) by four hydrogen bonds to the (black) “central” O-atom (two H-bonds by the two H-atoms of the “central” O-atom, two between the H-atoms of the neighbouring O-atoms and the “central” O-atom), and a tetrahedron structure sketch (*right*). Obviously, tetrahedron structures are appropriate to organize the ordered arrangement of water molecules.

units like clusters, similar to flexible and varying dynamical “quasicrystal”-like ordered domains. Of course, and in some similarity to crystal-like arrangements, these substructures exhibit more or less stably ordered structures, which in their whole of numerous different of these forms “built up” water, which obviously is not simply made of interacting water molecules but is determined in its properties also by the presence and interaction of the domains of variable, flexible, nanometre-sized dynamic quasicrystals or domains of, e.g. tetragonal or hexagonal (and other) geometry (cf. Figs. 1 and 2).

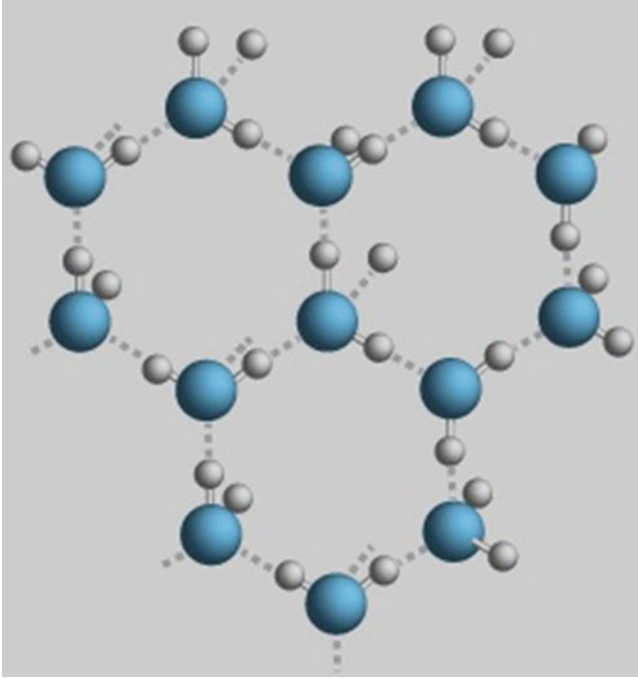
Note that the hexagonal lattice structure (“ice  $I_h$ ”) requires more space than the molecular arrangements in the liquid state. Therefore, ice has a lower density and freezes on top of the liquid. Further 12 crystal forms of ice have been identified (cf. <http://www.lsbu.ac.uk/water/>).

Structure and presence of these domains depend on temperature. In short, the properties of water are determined by two interactions, namely, by the direct internal interactions on the molecular level as on the domain level.

It is well known that water exists in different forms like the “high-density mode”, the so-called HDW (high-density water) with a density up to about  $1,170 \text{ kg m}^{-3}$ , and also LDW (low-density water) with a density of about  $920 \text{ kg m}^{-3}$  (similar to ice  $I_h$ , and of lower intrinsic entropy, i.e. in a comparatively higher ordered state). LDW has stronger hydrogen bonds than bulk liquid water.

Therefore, and that seems to be of high biological importance, real bulk liquid water can be described in terms of two biologically differently acting liquids, LDW and HDW. The related biological aspects have intensively been discussed by Philippa Wiggins (1997, 2008, 2009), as mentioned in some more detail in Sect. 2. These HDL and LDL modes of water seem to be related to the observation that different ions can completely change the physical and chemical properties of water, particularly that there are two classes of solutes, those that prefer LDW and others





**Figure 2.** The hexagonal lattice of water ice (Taken from <http://hyperphysics.phy-astr.gsu.edu/hbase/chemical/waterdens.html>).

that prefer HDW. These differences are correspondingly to be followed by a local osmotic pressure gradient, what according to Philippa Wiggins (2008, 2009) may drive biologically relevant dynamic cycles. This biological relevance of “different waters” is a yet open but possibly far-reaching challenge to current biophysics.

Another aspect of the biological relevance of water with respect to life is that it acts to stabilize for proteins by forming an outer covering or shell of water molecules. This has an influence on the properties of the proteins, e.g. with respect to their folding. Polar protein surface areas prefer to be covered by a thin layer of the more dense water while the situation is reverse for the nonpolar surfaces of proteins (cf. Sect. 5). A further challenging aspect is that the two prevailing forms (HDL, LDL) of ordered domains of water of different density also show a different chemical behaviour.

Liquid water is not present in form of bulk water only. Particularly, water may accumulate on solid surfaces due to the interaction of water molecules with molecules or atoms of the solid surface. As described in more detail in Sect. 3.1, adsorption of molecules of atmospheric water vapour on surfaces causes another “source” of liquid water to form, which is of nanometre-sized “films” (or layers) or isolated islands of liquid water on solid surfaces. This process is usually called

“surface condensation” if these accumulations will get macroscopic size. Attractive interactions in the nanometre scale between water molecules by van der Waals forces (dispersion forces) of surfaces are the reason of adsorption of water on these surfaces. It is interesting to note that also at temperatures clearly below 0 °C and depending on the surface properties, water molecules in thin films of adsorbed water can be able to move on the surface in a liquid-like but two-dimensional manner. Adsorption or condensation water is on Earth used by organisms in deserts, where this source can provide more water than local rainfall.

It is to be noted here and will be described below that there is also a freezing point depression related to capillaries. This permits to have liquid capillary water also far below 0 °C.

Interfacial water is *per definitionem* liquid water, which is kept between very near surfaces like those in pores, cracks and fractures or between a mineral surface and water ice. It is described in Sect. 3 that the properties of interfacial water depend on the interaction between the water molecules and the surfaces.

Premelting of ice (cf. Sect. 3.3) is a specific phenomenon near the melting temperature of ice. This is mainly caused by the structural changes from a three-dimensional order in the lattice geometry of ice towards that the two-dimensional surface.

Curvature effects can play an essential role with respect to the formation of droplets. This can be described by Kelvin’s equation (cf. Sect. 4). This equation describes the fact that the saturation pressure of water vapour, which value increases with decreasing curvature, is higher above convex or positively curved surfaces of water and is lower for negatively curved (concave) surfaces, if compared to that of a plane surface. Thus, smaller droplets have a higher saturation pressure and evaporate earlier than their larger counterparts, while the equilibrium water vapour pressure above equally sized menisci in capillaries is comparatively smaller.

The curvature of the concave liquid surface in pores or capillaries is negative, and this is related to a decrease of the equilibrium water vapour saturation pressure above a concave surface of liquid water in volumes of decreasing pore size or diameter of the filled capillary, vein or tip or so (cf. Sect. 4). This explains, e.g. the comparatively high hygroscopic action of small wetted grains with menisci of small radii in between the grains. Furthermore, liquid water with a concave surface already can be in equilibrium with an atmosphere of comparatively low water vapour pressure. That might be of importance for the soil of dry deserts, possibly also on Mars.

Capillary water forms in pores or tubes as a consequence of the attraction (adhesion) between liquid water and solid surfaces (by van der Waals forces). Originally, “capillarity” was meant to describe the ability of a liquid to spontaneously rise in a narrow space such as in pores or narrow tubes. If the diameter of a tube is sufficiently small, then the combination of surface tension due to cohesion of water and of adhesive forces between the liquid and tube wall can act to lift the liquid at the wall. Capillary water and adsorption water are the main reason for keeping granular and porous matter wet also under dry environmental conditions. This is due to the binding of water molecules to the internal surfaces.

This is remarkably strong in case of hygroscopic zeolitic materials. By the way, the bio-relevant wetting of agricultural soils from below is due to capillarity.

Presence and availability of liquid water are therefore necessary preconditions for life, as it is currently known, to stably exist. As will be discussed more in detail in Sect. 6, liquid water may be present under quite different conditions, and it is present not only as the usual bulk water but also at low temperatures in liquid “cryobrines”, and it can be deposited in thin layers or “films” on surfaces and in interfaces. There, and as will be described in some detail in the following, the intermolecular forces between the surface material and the water can remarkably influence the properties of these “sheath or film waters”. These film waters might, from the point of view of physics, well provide or support (by internal cracking driven erosion) the formation of habitable conditions within the surface (incl. rocks), particularly in cold regions in porous soils and rock with cracks and fissures (cf. Sect. 4).

Deliquescence (cf. Sect. 7) is the phenomenon of liquefaction of originally dry salts by accumulating water molecules from the atmospheric water vapour. This may lead to brines, which may remain liquid at temperatures far below 0 °C. Deliquescence is expected to be effective also on present Mars and it may contribute, at least in dependence on location and on season and daytime, to the temporary presence of liquids on and in the upper surface of Mars (Möhlmann and Thomsen, 2011).

It is finally to be noted here that the description of water properties is given in this paper from the point of view of physics but having in mind possibly bio-relevant aspects, and it is also aimed to give a first and rough introduction to properties of liquid interfacial water at temperatures also far below 0 °C to the mainly biologically qualified researchers.

## 2. Biological and Chemical Aspects of Substructures of Water

The well-known “phase diagram” illustrates in the “p-T-space” the conditions for the presence of liquid bulk water. Obviously, to have bulk liquid water, temperature  $T$  and total pressure  $p$  must exceed those at the triple point:  $T > T_t = 273.16$  K,  $p > p_t = 611.657$  Pa.

As described in the introduction, bulk liquid water at ambient temperatures is a mixture of nanometre-sized domains of a local but flexible and varying regular structure. These domains may well interact by the exchange of water molecules. A rough approach to understand (aspects of) the properties of bulk water is based on the assumption of the existence of two prevailing types of temperature-dependent domains, namely, of the mentioned above LDW and HDW, i.e. in form of local nanometre-sized “high-density” and “low-density” domains.

This can plausibly be illustrated by the example of two types of local structures in water ice like those of:

1. The regular “hexagonal ice  $I_h$ ” (cf. Fig. 2) analogue to LDW with larger internal distances and of a density  $\rho_h = 0.92$  kg m<sup>-3</sup>

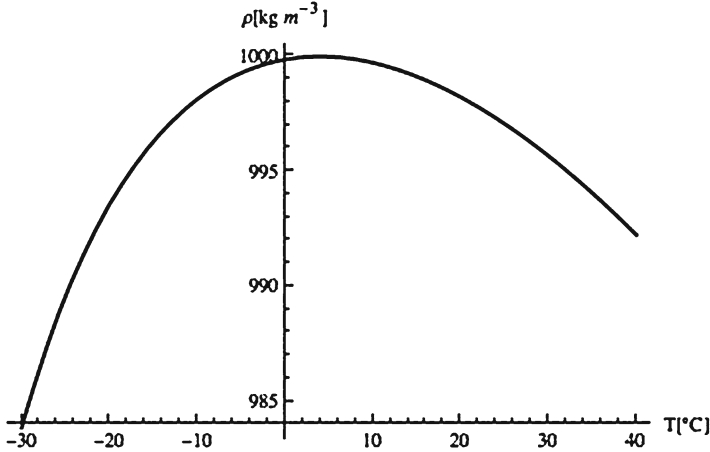


Figure 3. Density of liquid water (Based on data of Kell, 1975).

2. The more dense HDW-analogue “rhombohedral ice II” ( $\rho_{\text{II}} = 1.17 \text{ kg m}^{-3}$ ), which is different in its geometry (having another angle between the O–O–O-atom connection with about  $80^{\circ}$  instead of  $109.5^{\circ}$  for  $I_{\text{h}}$ ) (cf. Petrenko and Whitworth, 1999; Urquidi et al., 1999)

The difference in volume filled by the molecules of these two types of water is with  $36,399 \cdot 10^{-29} \text{ m}^3$  for type  $I_{\text{h}}$  and  $2.5992 \cdot 10^{-29} \text{ m}^3$  for type II. These original “ice structures”  $I_{\text{h}}$  and II can be observed to evolve in liquid water at and around temperatures above  $0^{\circ}\text{C}$ . The relative part of the regular (less dense) water increases in case of cooling towards  $0^{\circ}\text{C}$ , reaching finally the low ice density at  $0^{\circ}\text{C}$ . Thus, Fig. 3 can be understood in terms of a temperature-dependent mixture of two “modes” of liquid water, where the “low-density mode” (i.e. the domains forming this mode) has the minimum participation at temperatures around  $4^{\circ}\text{C}$ .

Meanwhile, numerous models have been developed to describe water in terms of domains of much more complicated geometry and structure like two types of icosahedrons (cf. Chaplin, 2000) and other geometries. For more details with respect to LDL, HDL, and other properties of water, the interested reader is referred to “Chaplin’s Internet water bible” (cf. <http://www.lsbu.ac.uk/water/>).

It is to be mentioned here that there are relations between LDW and HDW and chemical influences on the structure of pore water (cf. Wiggins, 2008): NaCl, LiCl and  $\text{MgCl}_2$  solutions in pore water have infrared spectra similar to  $I_{\text{h}}$  or analogously to the “ordered” LDW, and the spectra of KCl and CsCl solutions are similar to those of the more dense liquid water.

Furthermore, pore water is highly selective to ions. The KCl and CsCl solutions in the pores are accumulated in pore water in case of low external (out of the pores but connected) concentrations. In case of an increase of the external concentration, the in-pore concentration tends to approach that of the external

concentration. This can be understood to indicate that KCl and CsCl are selectively accumulated in pores in the more icelike LDW but revert the LDW to normal water at high concentrations.

Otherwise, NaCl, LiCl and MgCl<sub>2</sub> solutions in pore water are increasingly excluded from the pores, and this exclusion (or decrease of in-pore concentration) increases with increasing external concentration (cf. Wiggins, 2008, 2009). Thus, NaCl, LiCl and MgCl<sub>2</sub> are selectively excluded from the pores for increasing external concentration.

This opposite selectivity with respect to, e.g. K<sup>+</sup> and Na<sup>+</sup> reminds on that of biological cells, which inside have high concentrations of K<sup>+</sup> and low concentrations of Na<sup>+</sup>, what is reverse to the situation in extracellular liquids like blood.

As has been proposed by Wiggins (1997, 2008, 2009), the presence of two different domains (or “modes”) of liquid water may be relatable to biological observations. Neighbouring unlike domains of LDW and HDW will be the cause of local gradients and related gradients of the osmotic pressure. Thus, if there are solutes with separated domains which prefer LDW and others preferring HDW, the local osmotic gradient will tend to transform them into the other. This, in principle, may according to Wiggins (2008, 2009) drive a cycle with and between the two “modes”.

These two classes of solutes can also be seen in the light of the traditional distinction between chaotropes (K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, H<sub>2</sub>SO<sub>4</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, etc.), which tend to include HDW, and kosmotropes (H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>), which tend to include LDW.

The field of the biological relevance of local substructures like internally ordered domains in water is a current challenge to microbiophysics. This challenging field is discussed again in some more depth in Sect. 5.

### 3. Surface Water on Solids

In the small scales of micrometer and nanometre range, surfaces are not “force neutral”. Water molecules can be exposed to attractive forces from the surface (the surface is “hydrophilic”) or to rejecting forces (then the surface is “hydrophobic”). The electrically polar nature of the water molecule and the character of the surface forces play a central role in case of either expelling water or otherwise of the deposition of water layers on surfaces. The process of a direct attachment of water molecules (from the vapour state) on a solid surface is called adsorption of water, while a liquefaction of the uppermost layers of solid ice is called “premelting”.

#### 3.1. ADSORPTION AND LIQUID LAYERS

Adsorption is the deposition of atmospheric water molecules on solid surfaces. This deposition is governed by the attractive interaction between the water molecules of atmospheric origin and the molecules in the upper surface layers

**Table 1.** Hamaker constant in zJ ( $=10^{-21}$  J) for ceramics (medium 1=medium 3) with vacuum, water, and SiO<sub>2</sub> in between (medium 2).

Material	Vacuum	SiO <sub>2</sub>	Water
Muscovite mica	69.6	0.27	2.9
Al <sub>2</sub> O <sub>3</sub>	145	19	27.5
SiO <sub>2</sub>	66	–	1.6
Si <sub>3</sub> N <sub>4</sub>	174	33	45
TiO <sub>2</sub> rutile	181	45	60

of the solid. This can be described in terms of attractive van der Waals forces (dispersion forces) of the mineral surface (cf. Möhlmann, 2008). The van der Waals force  $F_{\text{vdw}}$  per surface area  $S$  between plane surfaces of water ice and a mineral can be described by

$$F_{\text{vdw}} / S = \frac{A_{123}}{6\pi d^3}. \quad (1)$$

Here,  $d$  is the distance between the two surfaces (or between the solid and the surface of the adsorbed film of water), and  $A_{123}$  is the Hamaker constant for the general case of a van der Waals interaction between the surface-media “1” and “3” with medium “2” in between. Ackler et al. (1996) have determined the Hamaker constants for some representative materials (cf. Table 1) with nanometre-sized interfaces of liquid water.

Obviously, these attracting forces acting on water molecules are for these materials and for characteristic distances in the nm range of the order of  $10^7$  N. On the other side, these molecules may more or less freely move in the two dimensions of the adsorbing surface, behaving in this 2D space like a 2D gas, liquid, or solid. The mobility depends on thermal energy of the molecules and on the distribution of the hindering “potential walls” of the atoms or molecules of the surface material. Thus, transport processes can be possible also in case of a few monolayers only.

The physical adsorption of water molecules on hydrophilic surfaces is a known and intensively studied phenomenon. The bond of the (lowest layers of) water molecules by physical forces to a surface is to be characterized by a corresponding surface bond energy. The surface can be covered partially and also totally or also by multiple layers. There are different “adsorption isotherms” to describe the loading of a surface by adsorbed molecules depending on temperature, specific material properties and atmospheric water content (cf. Atkins, 1998). Figure 4 demonstrates that numerous layers may increasingly accumulate near saturation conditions. Then, this process is called “condensation”. Note that the thickness of one “monolayer” of water is of about 0.3 nm only.

The upper layers of adsorbed water can at temperatures  $<0$  °C freeze in case of the presence of numerous layers. As described below, the resulting pressure will cause a freezing point depression, and an interfacial layer of liquid water will form in between the two solid covering surfaces (cf. Eq. 2).

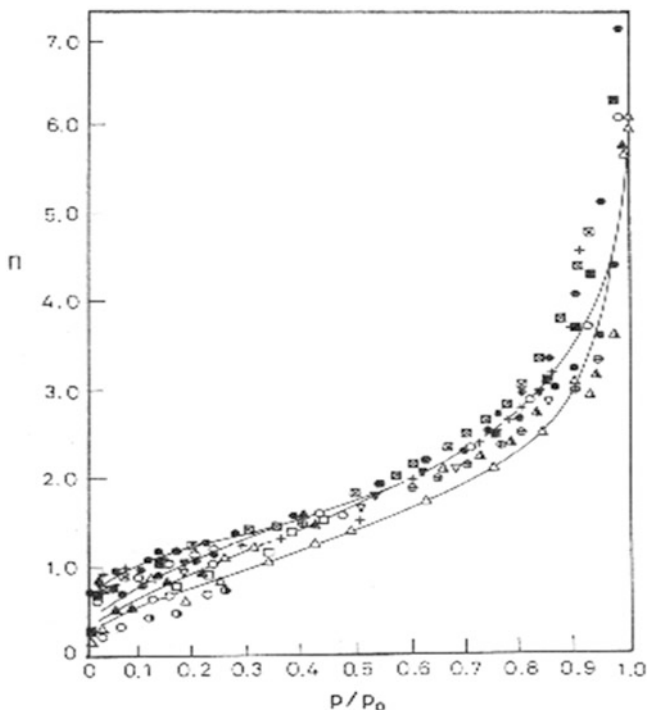


Fig. 2.31  $n$ -Curves for pore structure analysis by water vapour adsorption<sup>92</sup>. The following symbols are used for the experimental points: zirconium silicate ( $C = 4.2$ )  $\odot$   $\ominus$ ; rutile ( $C = 5.2$ )  $\triangle$   $\Delta$ ; silica ( $C = 7$ )  $\circ$   $\ominus$ ; silica gel, Davidson 81 ( $C = 10$ )  $\square$   $\square$ ; zirconium silicate ( $C = 14.5$ )  $\Delta$   $\Delta$ ; silica gel, Davidson 59 ( $C = 23$ )  $\nabla$   $\nabla$ ; quartz ( $C = 23$ )  $\bullet$   $\bullet$ ; anatase ( $C$  about 50)  $\blacksquare$   $\blacksquare$ ; anatase ( $C$  about 60)  $\oplus$   $\oplus$ ; calcite ( $C$  about 70)  $\boxtimes$   $\boxtimes$ ; barium sulphate ( $C$  about 120)  $\blacktriangledown$   $\blacktriangledown$ ; barium sulphate ( $C$  about 160)  $\bullet$   $\bullet$ ; quartz ( $C$  about 200)  $+$   $+$

**Figure 4.** Dependence of the number of adsorbed layers ( $n$ ) on water activity ( $p/p_0$ ) on surfaces of different materials (Taken from Mikhail and Robens, 1983).

The attraction by the solid surface, which causes the adsorption, is equivalent to pressing the water layer towards the solid surface. This pressure causes a related “freezing point depression”. As can be described by the Clausius-Clapeyron relation, this pressure is related to a corresponding freezing point depression  $\Delta T = T_m - T$ .

$$P_{vdw} = \rho_{ice} q \frac{\Delta T}{T_m}, \tag{2a}$$

$$\Delta T = \frac{T_m}{\rho_{ice} q} \frac{A}{6\pi d^3}. \tag{2b}$$

Here,  $T_m$  is the standard melting temperature,  $A$  is the Hamaker constant,  $q = 3.33 \cdot 10^5 \text{ J kg}^{-1}$  is the latent heat of water per unit mass, and  $\rho_{ice}$  is the mass density of water ice. Numerically, a layer of adsorption water of 1 nm thickness will for a Hamaker constant  $A = 60 \text{ zJ}$  ( $1 \text{ zJ} = 10^{-20} \text{ J}$ ) show a freezing point depression



**Figure 5.** Artist's picture of the film of nanometric water covering a grain (or microbe) embedded in water ice. This image is not a direct photo; grain and film sizes are not scaled! (Image: Eigenmann).

of about 2.8 K, and a monolayer will, e.g. on rutile, remain liquid down to  $-77$  °C. Thus, the lower layers of adsorption water on plane surfaces can remain liquid at temperatures clearly below 0 °C. The real value will depend on the Hamaker constant of the respective surface material.

This result indicates that small grains (incl. microbes) in ice must be covered for appropriate conditions by a thin (nanometre sized) “mantle” of (a few) layers of liquid water (cf. Fig. 5). It is a yet open but possibly far-reaching challenge for biophysics if the interfacial water around microbes in solid ice can be of biological importance with respect to life in solid ice at low temperatures (cf. Möhlmann, 2009). It is to be noted that the “liquefaction” at the 2D surface of 3D ice, the so-called premelting of ice, supports this possible biological relevance of interfacial water.

Note that if parts of this nanometre-sized liquid are “captured” (sucked in) by organisms, the liquid sheath will in equilibrium subsequently be delivered from the ice. Thus, the organisms can feel like in an “infinite” ocean.

### 3.2. SATURATION PRESSURE

The attractive interaction of the above described type regulates at the surfaces of liquid water or solid ice the gain or loss of water molecules from or into an atmosphere on top the air-solid or air-liquid surface. The resulting atmospheric



water vapour equilibrium pressure above a plane surface of liquid water or ice of temperature  $T$ , the so-called saturation pressure  $p_s$ , can be described by a “Magnus-type” or “Antoine-type” equation like

$$p_s = Ae^{\frac{B \cdot C \cdot T[K] + T_0}{T[K] + T_1}} \quad (3)$$

(cf. Murray, 1967, for liquid water; Marti and Mauersberger, 1993, for solid ice). Here,  $A = 610.66$  Pa,  $B = 17.26939$ ,  $C = 1$ ,  $T_0 = -273.15$  K, and  $T_1 = -35.85$  K for liquid water, but for solid ice  $A = 3.4435 \cdot 10^{12}$  Pa,  $B = -6132.935$ ,  $C = 0$ ,  $T_0 = 1$  K, and  $T_1 = 0$ .

There are much more sophisticated relations like the Goff-Gratch equation in meteorology, but the following discussion will be based on this much simpler formulation. Equation (2) takes for water ice the form

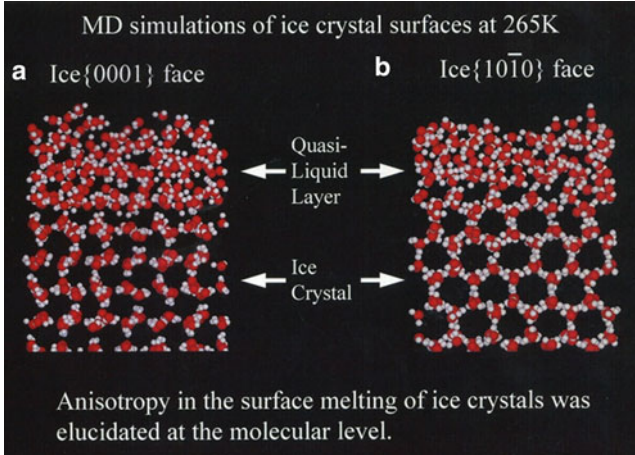
$$p_s = Ae^{\frac{E_w}{kT}} \quad (4)$$

Here,  $k$  is Boltzmann’s constant, and  $E_w = k \cdot B = 8.4668$ , and  $W$  is the bond energy of the water molecules with respect to ice (cf. Möhlmann, 2004). Note that a high saturation pressure indicates that in equilibrium the molecules can easily leave and build up a correspondingly large pressure, while a low saturation pressure indicates that the molecules are more effectively bond to the surface.

Relative humidity and water activity are often used to describe the also bio-relevant content of atmospheric water of a partial water vapour pressure  $p$ . This content is described with respect to the temperature-dependent saturation pressure with the relative humidity (measured in %) by  $\text{rh}[\%] = 100 p/p_s$ . The ratio  $a_w = p/p_s$  is called “water activity”. Note that these ratios depend in real planetary environments on time. Consequently, using only an average value can in the biological context be completely misleading, e.g. in the case of short temporary periods of saturation when organisms can uptake water. This situation of temporary saturation can be given during cold night hours on Mars.

### 3.3. PREMELTING OF ICE

The “liquefaction” of water ice in a thin sheath directly at the surface of ice facing the vacuum or an atmosphere is related to the change from a 3D geometry of the ordered internal bonds of the molecules, fixed in three-dimensional structures in the ice, to the 2D geometry of the surface with different bond structures. Particularly, the uppermost molecules have the new freedom to move on the surface, if compared to the fixations in the solid ice (cf. Fig. 6). Dash and co-workers (cf. Dash et al., 2006) have extensively and in detail described this process of interface melting, which is also called “premelting” of ice. Interface melting starts at a characteristic onset temperature  $T_0$ . Dash et al. (2006) have developed the



**Figure 6.** Ice structure during premelting (computer simulation) according to Furukawa (1997). Premelting can be seen to evolve in the uppermost layers of ice.

related mathematical apparatus to quantitatively describe the implications and consequences of premelting of ice. It is to be mentioned here that premelting of ice is effective on the surface of water ice at temperatures near to but below the melting temperature, but not at much lower temperatures, where the thermal energy of the molecules on the surface is not sufficient to cause appropriate mobility.

According to Dash et al. (2006), the freezing point depression can be described via

$$\Delta T = T_m \frac{2\sigma^2 (-\Delta\gamma)}{\rho_i q d^3} \quad (5)$$

Here,  $\sigma$  is a constant of the order of the molecular diameter, and  $\Delta\gamma (<0)$  is the difference between force coefficients of the dry and the wetted surface.

By the way, it is this process of “premelting” of ice, which is wetting by its own melt, that permits gliding on ice (skating) and analogously on snow (skiing).

The process of “premelting” is expected to have near but below 0 °C, the consequence of filling the micrometric veins between crystallites of solid ice (and snow) with liquid water. These micrometric veins with liquid water are seen as to be of great relevance for life to exist in Arctic and Antarctic ices and snow (cf. Price, 2000) at environmental temperatures below 0 °C.

Note that according to Eqs. (2b) and (5), the thickness  $d$  of the liquid layer is for van der Waals forces proportional to  $(\Delta T)^{-1/3}$ . This thickness is for exponentially with height  $h$  decaying (short range) forces ( $F/S \sim \exp(-h/d_0)$ ) given by the relation  $d = d_0 \ln((T_m - T_0)/\Delta T)$ .

Another challenging aspect of “premelting” around particles or grains in ice is the buoyancy-like driven mobility of these particles and grains (and also microbes) in ice with spatial temperature gradients (cf. Rempel et al., 2001). This remarkable process can cause these particles or grains to move in ice over macroscopic distances.

Hansen-Goos and Wettlaufer (2010) have recently given a more comprehensive description of premelting of ice in porous media by combining interfacial premelting of ice contained in a matrix of porous material, grain boundary melting in the ice, and Coulomb-force-related impurity and curvature-induced premelting. An equation has been derived to describe the resulting possible amount of liquid interfacial water in its dependence on temperature.

#### 4. Curvature and Capillary Water

The saturation pressure of water vapour in equilibrium with liquid water or ice at a plane surface (phase boundary) has been described by Eq. (2). This is to be modified for conditions with curved liquid surfaces, which tend to form a stable surface via a related surface tension  $\gamma$ . The Young-Laplace equation

$$\Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (6)$$

states that the pressure difference at the two sides of the surface (phase boundary) depends on the local radii of surface curvature and on the surface tension of the separating “meniscus”-shaped surface. In other words, the surface acts “stressing” with a pressure on the liquid. Note that the sign of a radius of curvature is per convention positive for convex surfaces and negative for concave surfaces.

The resulting modification of the saturation pressure  $p_{s,c}$  above a curved surface of a liquid of molecule mass  $m_L$  and molecule number density  $N_L = \rho_L/m_L$  is given by the Kelvin equation

$$P_{s,c} = P_s e^{\frac{\gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)}{N_L k T}}. \quad (7)$$

Obviously, the concave surface of the water column in capillaries (of a reduced saturation pressure) hinders the water molecules to leave the vapour through the meniscus into the liquid. On the other side, the convex shape of droplets (with an enhanced saturation pressure) supports their transfer through the meniscus into the atmospheric vapour. Furthermore, smaller droplets evaporate more effectively than the larger ones, while the pressure difference increases for smaller capillary radii due to the decreasing saturation pressure. This pressure, which acts from the surface onto the molecules in the liquid column, can be

related to a freezing point depression. This is with Eq. (7) for a circular tube with  $R = R_1 = R_2$  and in analogy to Eq. (2a, b) described by

$$\Delta p = \frac{2\gamma}{R} = \rho_{\text{ice}} q \frac{\Delta T}{T_m}, \quad (8)$$

or numerically in form of the Gibbs-Thomson equation

$$\Delta T[\text{K}] \approx \frac{50\text{K}}{R[\text{nm}]} = \frac{0.05\text{K}}{R[\mu\text{m}]} \quad (9)$$

Here  $\rho_{\text{ice}} = 916.8 \text{ kg m}^{-3}$ ,  $q = 3.33 \cdot 10^5 \text{ J kg}^{-1}$ , and – according to Van Oss et al. (1992) –  $\gamma = 3 \cdot 10^{-2} \text{ N m}^{-1}$  for ice (cf. Möhlmann, 2008). This agrees with results of laboratory experiments of Liu et al. (2003).

In a more precise version of the Gibbs-Thomson equation, this radius is diminished by the thickness of the water layer at the pore surface (cf. Webber and Dore, 2004; Alba-Simionesco et al., 2006). Nanometric pores can stabilize liquid (“unfreezable”) water down to about 173 K (Alabarse et al., 2012).

Obviously, pores in granular soils or in porous matter can be filled by liquid “capillary” water also at temperatures far below 0 ° C. This important result applies also to micro-cracks and fissures in a nonporous matter like solid basaltic rock. The radius of the capillaries decreases towards the narrow tip in a V-shaped crack, and the related saturation pressure correspondingly decreases. Thus, the tips are prone to get filled by liquid water, also at low temperatures.

The trend to condense increases in an atmosphere for increasing water activity (or relative humidity)  $a_w = p/p_{s,C}$ , where  $p$  is the partial water vapour pressure. In other words, capillary condensation can occur, and liquid water will be present at least in the tip (where  $R = 0$ ) of cracks, fissures, etc. Depending on the real atmospheric water content, cracks and fissures in otherwise solid rocks can that way get filled partially or completely (cf. Fig. 2) by liquid water. Diurnal and seasonal cycles of freezing and melting may cause internal “structural erosion” by producing more and more cracks and fissures. This internal structural erosion may have the consequence of finally forming habitable volumes with access to liquid water for microbes and fungi-like life forms inside rocks and soils.

Of course, this process of structural erosion can be much more efficient in case of ice embedded in a “closed” rock, i.e. without direct exchange with the atmosphere. This ice is at the interface between ice and rock necessarily covered by a film of adsorption water (cf. Sect. 3). This liquid water is under a pressure, as it is described by Eq. (1). Therefore, this liquid water “under pressure” is forced to move into all accessible “free volumes” in cracks, fissures, etc. The cover of the ice by liquid water will in equilibrium be delivered subsequently from the large ice volume.

It is to be noted that this process of “structural erosion” in closed rocks and soils can in case of liquid cryobrine, i.e. a presence of salts in rocks or granulates be effective also at low temperatures (cf. Sect. 6).

Furthermore, the increasing local accumulation of liquid water in the closed subsurface, when repetitively being driven by “structural erosion”, can get released in a gully-like fashion when the cracks reach the surface of the rock. Possibly, gullies observed on Mars may have their origin in this mechanism of “structural erosion” caused by water accumulation and final release.

The described above presence of liquid water in “structural erosion driven” cracks or fissures (and network systems of them) in rocks, and analogously in granular regolith, can be expected to give conditions for habitats (for lithophiles) since these volumina of liquid water are protected below the surface. There they can extend deep into the rock or soil.

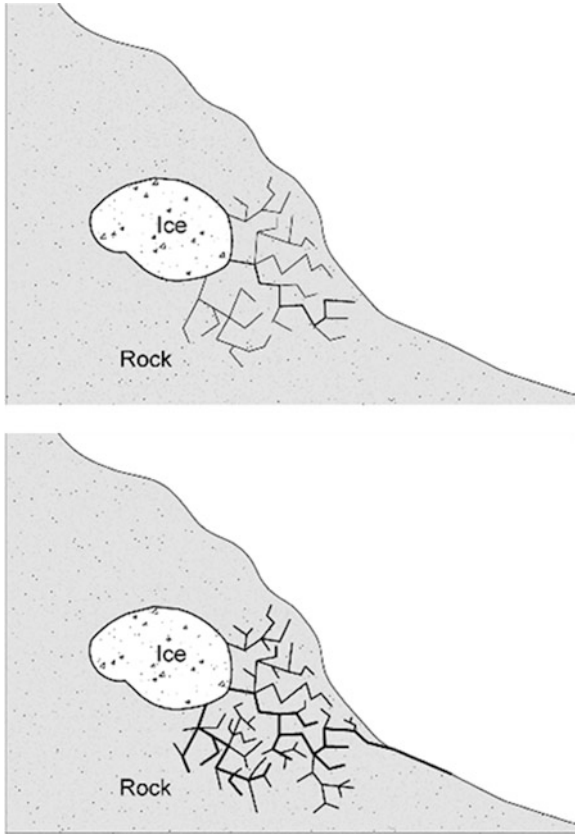
## 5. Interfacial Water and Internal Water Structure

Bulk water is in good approximation a mixture of LDW and HDW, and also the properties of interfacial water are to be described in dependence of these two basic types of water. The molecules of interfacial liquid water between a substrate surface and ice (on top) tend to differently interact with the atoms or molecules of the substrate in case of LDW and HDW. Experimental investigations with silicon as the substrate have shown that there forms a layer of (hydrophilic) SiOH between the silicon and the liquid water layer below the ice (Engemann, 2005). The layers differ in their mass density with a relatively high density of the liquid layer in the range  $1.1\text{--}1.2\text{ g cm}^{-3}$  on top of a 2 nm  $\text{SiO}_2$  layer. The thickness of the liquid layer decreases with decreasing temperature from about 5 nm at  $-0.04\text{ }^\circ\text{C}$  towards about 0.8 nm at  $-30\text{ }^\circ\text{C}$ . Note that the thickness of one monolayer of water is in the range of 0.35 nm. The measured density is close to that of amorphous ice (HDA) and to rhombohedral ice II, what indicates structural similarity (cf. Sects. 1 and 2) (Fig. 7).

With respect to silicon it is to be mentioned that a bare silicon surface (like those used by Engemann) is hydrophobic, but this is not stable and tends to evolve a hydrophilic  $\text{SiO}_2/\text{SiOH}$  layer, as described. So,  $\text{SiO}_2$  (SiOH) is hydrophilic and Si is hydrophobic.

There is experimental evidence (Streitz et al., 2003; Jensen et al., 2003) that interfacial water on hydrophobic substrates is of low density like the comparatively better-ordered LDW with stronger internal hydrogen bonds than in bulk water, while that on hydrophilic surfaces (like on  $\text{SiO}_2$ ) is of a less ordered but “high-density” structure (HDW). Obviously, hydrophobic interfaces stabilize the formation of LDW structures (like  $I_h$ ) with stronger hydrogen bonds than in bulk water and of low intrinsic entropy; however, the formation of HDW-structures (like rhombohedral ice II) is supported at hydrophilic surfaces.

Hydrophilic and hydrophobic interfaces (and molecules) are known to be electrically polar and nonpolar, respectively. Hydrophobic interfaces (and molecules) tend to be nonpolar and to prefer other neutral molecules and nonpolar solvents. Hydrophilic interfaces (and molecules) have a tendency to interact with or to be dissolved (like salts) by water. A hydrophilic interface is typically charge polarized and capable of hydrogen bonding, enabling it to dissolve more readily in water.



**Figure 7.** Structural erosion by stepwise (opening, filling and widening of interfacial volumina by flow and freezing of interfacial water).

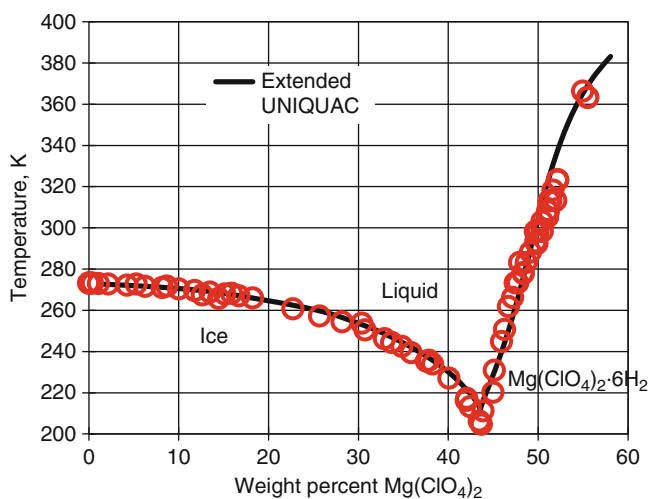
The biologically relevant hydrophobic hydration describes the direct interaction of hydrophobic molecules with water. This causes a changing of the water structure towards an LDW structure. The LDW structure is related to changes in physical properties like density, solubility, viscosity and in chemical properties, and this can directly influence, e.g. protein folding (Wiggins, 1997). It is to be mentioned in this biological context that there are hydrophilic and hydrophobic parts of the cell membrane.

Chaotropic (or structure breakings) substances are chemicals, which tend by breaking the hydrogen bonds to disturb the ordered hydrogen bond structures in water. The decreasing structural order is related to an increase in intrinsic entropy. The more-ordered LDW structure is therefore called to be kosmotropic (or antichaotropic), while HDW is chaotropic.

## 6. Liquid Water in Brines

Real liquid water in nature is normally not “pure”. There are numerous impurities, which can have an influence on the properties of real waters. Brines are the liquid watery solutions of salts. One of the remarkable and possibly also bio-relevant properties of brines is that the involved water can remain liquid at temperatures far below 0 °C (so-called cryobrines). Figure 8 describes this for the example of magnesium perchlorate. There is for all concentrations a solid frozen brine at temperatures below the so-called “eutectic” temperature  $T_E$ . At temperatures  $T > T_E$  but on the side of lower concentrations (left part in Fig. 4) and below the “eutectic curve” exists a mixture of water ice and liquid brine, while below the “eutectic curve” on the side of higher concentrations, a liquid brine and salt particles form the mixture. A liquid brine without embedded solids exists above the “eutectic curve” for  $T > T_E$ .

Raoult’s law approximately describes the water vapour pressure at the liquid–gas surface of brines. The resulting partial water vapour pressure of brines depends on the concentrations of the salts in solution. The evaporation rate is larger for lower salt concentrations. Low vapour pressure indicates a reduced evaporation rate. Raoult’s law expresses the finding that the difference  $\Delta p$  of the water vapour pressure  $\Delta p = p_s - p_r$  is proportional to the concentration  $n_x$  of the



**Figure 8.** Eutectic diagram of magnesium perchlorate. The liquid brine exists in the *upper part* above the curves. A liquid brine and chunks of solid ice are present in the *lower left part*, while a liquid brine and solid salt grains are found in the *right part*. The solid state (frozen brine) exists below the eutectic temperature (here at  $T_E = 212$  K) (Taken from Möhlmann and Thomsen, 2011).

**Table 2.** Properties of LDW and HDW at interfaces.

Property	LDW	HDW
Density (g cm <sup>-3</sup> )	0.92	1.17
Entropy	Lower	Higher
Similar ice structure	$I_h$ (hexagonal)	II (rhombohedral)
“Structuring” interfaces	Hydrophobic	Hydrophilic
Interface electric polarity	Nonpolar	Polar
Substance-solution type	Kosmotropic (stable H-bonds)	Chaotropic (structure breaking)
Preferred chemicals/solutions	H <sup>+</sup> , Li <sup>+</sup> , Na <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup>	K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Cl <sup>-</sup> , Br <sup>-</sup>

dissolved material by  $\Delta p/p = n_x/n$ . Here,  $p_s$  is the water vapour partial pressure of pure water and  $p_r$  is that above the real solution,  $n_x$  is the amount of the solute, and  $n$  is that of the solvent (i.e. water) and the solute.

This pressure difference is according to the Clausius-Clapeyron equation related to a freezing point depression  $\Delta T_f$  (and also an increase of the boiling temperature). This freezing point depression can be described by

$$\Delta T_f = -K_g \frac{m_x}{m} \frac{1}{M_x}. \quad (10)$$

Here,  $x$  stands for the solute,  $m$  [kg] is the mass and  $M$  the molar mass, and  $K_g$  [K kg/mol] is the “cryoscopic constant”, which gives the molar freezing point depression, when adding 1 mol of the to be solved material to 1 kg of the solvent. The cryoscopic constant of water is  $-1.858$  K kg/mol.

To have a liquid solution of Na(ClO<sub>4</sub>) – cf. Table 2 – in water at a temperature of, say,  $-30$  °C requires for 1 kg water and according to Eq. (8) with  $m_x = \Delta T_f \cdot m \cdot M_x / K_g$  and  $\Delta T_f = -30$  K,  $M_x = 122.5$  g/mol a mass of 1,975.8 g Na(ClO<sub>4</sub>). Taking into account that Na(ClO<sub>4</sub>) dissociates into two ions, only an amount of 987.9 g will be needed to have a stable liquid solution of sodium perchlorate at a Mars-relevant temperature  $-243$  K.

The bio-relevance of brines is indicated by the existence of specifically adapted, e.g. halophilic, microbes in caves and salty lakes, which prefer alkaline environments. Generally, life seems to be able to adapt to conditions of nearly all pH values in nature. It is particularly the effect of a low-temperature liquidity what widens the concept of habitability to sites and environments with temperatures lower than the “canonical limit” of 0 °C. In so far, also Mars, salty ice moons and possibly water-rich dwarf planets and ice-rich asteroids may come into the field of view. This conclusion is supported by the fact that life can exist and evolve also in case of only temporarily available liquids during short periods, which have only to be sufficient for the uptake of water and the export of waste (Möhlmann, 2012).

It is to be noted here that there are in nature several hygroscopic salts, which, in presence of water, like to form brines and cryobrines. At low temperatures the



**Table 3.** Possibly Mars-relevant binary and ternary nonorganic cryobrines.

Brine	Eutectic temperature $T_e$ (K)	Eutectic composition (%)
<sup>a</sup> Ice + Na <sub>2</sub> SO <sub>4</sub> 10H <sub>2</sub> O	271	3.8 Na <sub>2</sub> SO <sub>4</sub>
<sup>a</sup> Ice + K <sub>2</sub> SO H <sub>2</sub> O	271	7.1 K <sub>2</sub> SO <sub>4</sub>
<sup>a</sup> Ice + MgSO <sub>4</sub> 11H <sub>2</sub> O	269	17 MgSO <sub>4</sub>
<sup>a</sup> Ice + K <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> O + KCl	261	0.9 K <sub>2</sub> SO <sub>4</sub> , 19.5 KCl
<sup>a</sup> Ice + NaCl 2H <sub>2</sub> O	251	23.3 NaCl
<sup>a</sup> Ice + Na <sub>2</sub> SO <sub>4</sub> 10H <sub>2</sub> O + NaCl 2H <sub>2</sub> O	251	0.12 Na <sub>2</sub> SO <sub>4</sub> , 22.8 NaCl
<sup>a</sup> Ice + NaCl 2H <sub>2</sub> O + KCl	250	20.2 NaCl, 5.8 KCl
<sup>b</sup> Ice + Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	247 <sup>f</sup>	39 Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
<sup>a</sup> Ice + MgCl <sub>2</sub> 12H <sub>2</sub> O	239.5	21.0 MgCl <sub>2</sub>
<sup>c</sup> Ice + MgCl <sub>2</sub> 12H <sub>2</sub> O + KCl	239	21.0 MgCl <sub>2</sub> , 1.2 KCl
<sup>a</sup> Ice + MgCl <sub>2</sub> 12H <sub>2</sub> O + NaCl 2H <sub>2</sub> O	238	22.7 MgCl <sub>2</sub> , 1.6 NaCl
<sup>a</sup> Ice + MgCl <sub>2</sub> 12H <sub>2</sub> O + KCl	238	22.? <sup>g</sup> MgCl <sub>2</sub> , 2.? <sup>g</sup> KCl
<sup>a</sup> Ice + MgCl <sub>2</sub> 12H <sub>2</sub> O + MgSO <sub>4</sub> 7H <sub>2</sub> O	238	20.8 MgCl <sub>2</sub> , 1.6 MgSO <sub>4</sub>
<sup>d</sup> Ice + NaClO <sub>4</sub> 2H <sub>2</sub> O	236 (±1)	52 NaClO <sub>4</sub>
<sup>a</sup> Ice + CaCl <sub>2</sub> 6H <sub>2</sub> O	223	30.2 CaCl <sub>2</sub>
<sup>a</sup> Ice + CaCl <sub>2</sub> 6H <sub>2</sub> O + KCl	221	29.3 CaCl <sub>2</sub> , 1 KCl
<sup>a</sup> Ice + CaCl <sub>2</sub> 6H <sub>2</sub> O + NaCl 2H <sub>2</sub> O	221	29.0 CaCl <sub>2</sub> , 1.5 NaCl
<sup>a</sup> Ice + CaCl <sub>2</sub> 6H <sub>2</sub> O + MgCl <sub>2</sub> 12H <sub>2</sub> O	218	26.0 CaCl <sub>2</sub> , 5 MgCl <sub>2</sub>
<sup>d</sup> Ice + Mg(ClO <sub>4</sub> ) <sub>2</sub>	212 (±1) <sup>i</sup>	44 MgClO <sub>4</sub>
<sup>e</sup> Ice + LiCl	207	24.4 LiCl
<sup>f</sup> Ice + Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	205 (±1)	48 (±2) Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
<sup>g</sup> Ice + LiI	204	48.2 LiI
<sup>h</sup> Ice + LiBr	201	39.1 LiBr

Taken from Möhlmann and Thomsen (2011).

<sup>a</sup>Brass(1980).

<sup>b</sup>This work.

<sup>c</sup>Usdowski and Dietzel (1998).

<sup>d</sup>Chevrier et al. (2009).

<sup>e</sup>Voskresenskaya and Yanat'eva (1936).

<sup>f</sup>Chevrier and Altheide (2008).

<sup>g</sup>, <sup>h</sup>Linke and Seidell (1965).

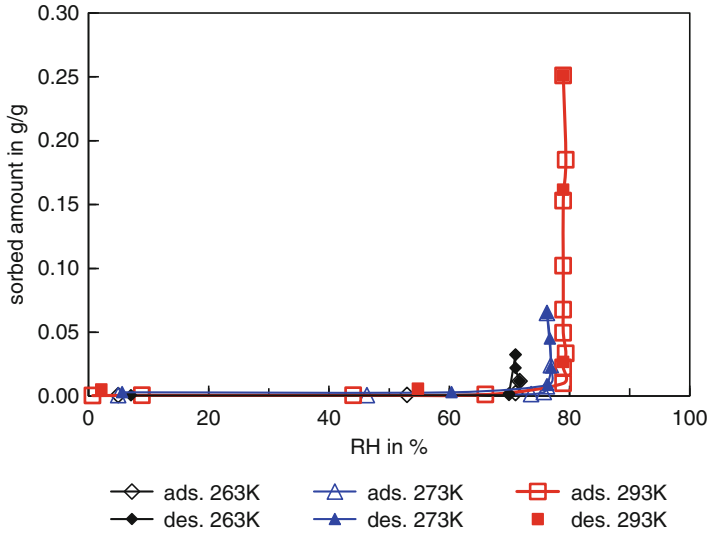
<sup>i</sup>Taken from Chevrier and Altheide (2008).

<sup>j</sup>Based on the UNQUAC-model, Chevrier et al. (2009) use 206 K for the eutectic temperature.

cryobrines may overtake the actions of the liquid water at temperatures above 0 °C. They can support freezing-driven erosion and eventually also life processes at these temperatures. Table 3 gives rough summary of known values of the eutectic temperature and the concentrations of different nonorganic brines.

## 7. Water in Atmospheres and Deliquescence

Water vapour can in planetary atmospheres exist as long as there is liquid water or ice on the planetary surface. This water or ice evaporates or sublimates into the atmosphere. As has been described in Sect. 3.1, the atmospheric water content



**Figure 9.** Water uptake of halite from Atacama Desert (cf. Davila et al., 2010). The salt uptakes at the DRH that much water that it will be liquefied.

in an atmosphere can be related to adsorption of water and adsorptive wetting processes. But there is a further process, which is relevant for wetting of surfaces and porous subsurfaces. This is based on the phenomenon that hygroscopic salts can be able to accumulate that much water molecules that they will get liquefied at a characteristic threshold of the relative humidity (cf. Fig. 9). This process is designated as “Deliquescence”, and the threshold value of a salt to get liquefied is the “DRH” (Deliquescence Relative Humidity), which is a characteristic value for each salt. Thus, salts are able to evolve towards brines in course of the accumulation of water of atmospheric origin. Probably, deliquescence is one of the probably efficient mechanisms, which can locally cause an at least temporary wetting of the surface of present Mars. Davila et al. (2010) have described the life-supporting role of deliquescence-driven brines on Earth for organisms in the Atacama Desert.

## 8. Summary and Conclusion

Liquid water is a key substance to enable life processes to proceed. This liquid can, on and in planetary surfaces, be present not only in form of bulk water but also in form of brines and of different volumina of “microscopic” liquid interfacial water at interfaces in porous planetary surfaces or rocks of cold planets in case of a low content of atmospheric water vapour and in cold surfaces or rocks with embedded water ice.

Freezing and thawing of interfacial water can modify the internal structure of, e.g. rocks by supporting the formation of fissures and cracks. These, at least partially water-filled volumina, may be of high biological relevance.

Interfacial water may consist of a spatially and temporarily varying mixture of different microscopic structures (domains), and these internal structures can be of physical, chemical and biological relevance.

The understanding of the bio-relevance of the types of liquid water of different micro-domains is a yet open challenge to biophysics, and the related bio-relevance of cold but liquid interfacial water even more.

The presence of cold but liquid interfacial water might widen the range of environments for life to exist also in surfaces of icy bodies.

## 9. Acknowledgements

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**PART II:  
IMPACT CRATERS  
AND THE EVOLUTION OF LIFE**

**Schulze-Makuch**

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# ORGANIC MOLECULES IN LUNAR ICE: A WINDOW TO THE EARLY EVOLUTION OF LIFE ON EARTH

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## 1. Introduction and Rationale

The Moon is thought to have formed by a gigantic impact about 4.5 billion years ago (Benz et al., 1986), explaining the inclined lunar orbit, the high spin of the Earth–Moon system, the Moon’s low density compared to that of Earth, and the very low volatile and refractory elemental abundances (Baker et al., 2005). Sputtering by solar wind ions, vaporization of lunar surface materials due to meteoroid impacts and outgassing from the surface produce an extremely thin atmosphere. Due to its lack of water, the Moon is not a likely candidate for the origin or persistence of life. However, the Moon may hold some evidence for the early evolution of life on Earth, since meteorite impacts on Earth may have delivered biogenic material to the surface of the Moon (Armstrong et al., 2002). The ice at the south pole of the Moon may also serve as a relatively easy accessible reservoir to analyze cometary ice and to provide potable water for possible future human habitation of the Moon (Schulze-Makuch et al., 2005). However, the ice would have to be extracted from a few meters below the surface since it is altered by radiation.

## 2. Evidence for Lunar Ice

The possibility of an environment suitable for the preservation of ice deposits or other volatiles over geologic time scales on the Moon has been suggested for a long time (e.g., Watson et al., 1961). Lunar ice may have accumulated from early Moon degassing, and deposition by water-rich meteor impacts near lunar poles may have been preserved for geologic time scales (Arnold, 1979; Lowman, 2000; Vondrak and Crider, 2003). The existence of significant deposits of hydrogen-bearing material at the lunar poles, probably representing several billion years of accumulation, makes investigation of such deposits a matter of high interest for space exploration and astrobiology (Lowman, 2000). Temperatures in shadowed Moon craters, which hold frozen water molecules, have been estimated to not exceed  $-230\text{ }^{\circ}\text{C}$  (40 K) (Stacy et al., 1997). Presence of ice has been verified based on data from the Clementine and Lunar Prospector missions and some radar



measurements with the Arecibo radio telescope located in Puerto Rico, though some argue that a large proportion of the detected hydrogen may be in form of solar wind implanted hydrogen and other volatiles rather than water ice (Lowman, 2005; for discussion, see also Binder, 1998; Feldman et al., 1998b; Nozette et al., 1996; Spudis, 2001; Stacy et al., 1997). Either way, Lunar Prospector instruments indicate unambiguous evidence for concentrations of hydrogen at both poles, especially in permanently shaded areas at the south pole (Binder, 1998; Feldman et al., 1998a, 2000), and in analogy with Mars at least some of this hydrogen should be in the form of water ice. Because polar craters are difficult to observe from Earth, due to indirect illumination, little emitted radiation, and a small viewing angle from the horizon, the Clementine Bistatic Radar Experiment was launched shortly after the 1992 Arecibo observations to test a different method and to clarify any ambiguities (Weidenschilling et al., 1997). The Clementine mission results still were not conclusive in determining the presence of ice at the Moon's poles, but are suggestive of small patches of ice (and/or other frozen volatiles) covered and mixed with rocky material (Nozette et al., 1996). Observations with the Arecibo telescope support this notion and indicate that the crater floors at the poles, which are in permanent shadow from the Sun, likely consist of distributed grains or thin layers (Campbell et al., 2003).

Most of the knowledge of the Moon's composition and complex history is derived primarily from returned Apollo and Luna samples and the lunar meteorites collected, but questions remain about the composition at the poles, especially within the South Pole–Aitken basin (Binder, 1998; Lucey et al., 1995; Spudis, 2001). The South Pole–Aitken basin is the largest basin on the Moon, which at 2,500 km in diameter and over 12 km depth, is the largest, deepest basin known in the Solar System (Spudis et al., 1994). If frozen ice is in fact present in form of dirty patchy ice in the pole's dark craters, the mixed rock material's composition is important for water quality. In 1994, the Clementine mission mapped global multispectral reflectance data that resulted in maps of Fe and Ti concentrations (Elphic et al., 1998; Lucey et al., 1998) and global topography and color (Spudis, 2001). In 1998 the Lunar Prospector mapped compositional abundances of key elements (H, U, Th, K, O, Si, Mg, Fe, Ti, Al, and Ca), with emphasis on the polar ice deposits observed by the Clementine mission and Arecibo radio telescope (Binder, 1998). Lunar Prospector maps also defined three distinct rock types and regions: (1) the Fe- and Ti-rich mare basalts, (2) rocks of intermediate Fe and Ti contents that make up the floor of the South Pole–Aitken basin and the mountainous rims of the nearside circular maria, and (3) Fe- and Ti-poor anorthositic rocks of the highlands (Binder, 1998). In contrast to the iron-rich basin floors (including the South Pole–Aitken basin), much of the highland surface is iron poor and is believed to be composed of the aluminum-rich rock anorthosite. These observations of lunar highlands versus basin floors suggest that a large impact detached the upper aluminous crustal layer exposing the iron-rich material underneath (Spudis, 2001). Table 1 is a summary of known rock types based on previous work.

Table 1. Known rock types of the Moon.

Region on Moon	Crust layer	Rock type	Mission data	References
Highlands	Upper crust	Rich in Al, Poor in Fe and Mg	Apollo Luna	(1)
Mare basalts	Volcanism	High Fe basalts, augite minerals	C	(2, 3)
SPA	Lower crust	Fe abundance, LKFM mafic rock	C	(2, 3)
Highlands	Upper crust	Rich in Al, poor in Fe relative to basalt, anorthosite rich	C	(2, 3)
Mare basalts	Volcanism	Fe- and Ti-rich basalt rocks	LP	(4)
Floor of SPA and mountain rims of nearside circular maria	Lower crust	Intermediate Fe and Ti	LP	(4)
Highlands	Upper crust	Fe- and Ti-poor anorthositic rocks	LP	(4)
Maria basalts	Volcanism	Fe- and Ti-rich, KREEP-rich	C, LP	(5)
SPA	Lower crust	Fe- and Ti-rich	C, LP	(5)
Maria deposits in large nearside basins	Volcanism	Low thermal, high fast neutrons	LP	(6)
Highlands	Upper crust	High thermal, low fast neutrons, feldspathic rock	LP	(6)
Humboldtianum, SPA, and a rim of nearside basins	Lower crust	Intermediate thermal, fast neutrons	LP	(6)
Highlands	Upper crust	KREEP-rich material	LP	(7)
Western maria basalts	Volcanism	High conc. of Th, K, and Fe	LP	(7)
Mare Ingenii in the SPA	Lower crust	High conc. of Th, K, and Fe	LP	(7)
Floor of SPA	Lower crust	Enriched in Fe, Ti	C	(8)
Mare basalts	Volcanism	Fe-rich, varying Ti	C	(8)
Hydrogen in permanently shadowed poles	Hydrogen deposits	Ice (and/or other frozen volatiles) mixed with rock	C, LP, Arecibo	(4), (8–10)

Notes: (1) Heiken et al. (1991), (2) Lucey et al. (1998), (3) Lucey et al. (1995), (4) Binder (1998), (5) Elphic et al. (1998), (6) Feldman et al. (1998a), (7) Lawrence et al. (1998), (8) Spudis (2001), (9) Nozette et al. (1996), (10) Stacy et al. (1997).  
 LP Lunar Prospector, C Clementine, SPA South Pole-Aitken basin, LKFM low-K fraction Mauro basalt, and KREEP potassium (K), rare earth elements (REE), phosphorus (P), and Th thorium.

More recent results also support the presence of lunar ice. Both the Chandrayaan-1 mission and the LCROSS space probe detected water on the Moon via hydroxyl absorption lines in reflected sunlight (Pieters et al., 2009), probably distributed in chunks and within material thrown up near the south pole (up to 5 % weight). Also, the Mini-SAR radar aboard the Chandrayaan-1 detected what appear to be ice deposits at the lunar north pole, at least 600 million tons in sheets of relatively pure ice and at least a few meters thick (NASA, 2010). The Moon is not as desiccated as once believed, but holds water chemically bound to lunar minerals (Lucey, 2009) and in adsorbed form. Clark (2009) calculated that adsorbed water exists on the Moon at concentrations between 10 and 1,000 ppm.

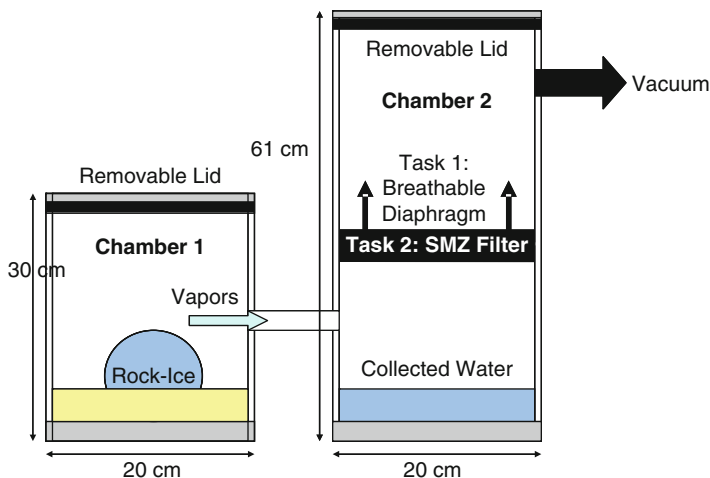
### 3. Lunar Ice Recovery

The feasibility and economics of melting lunar ice for use by explorers or converting lunar ice into hydrogen and oxygen for rocket fuel has been considered in detail previously (Blair et al., 2002; Lowman, 1966; Stump et al., 1988; Vondrak and Crider, 2003). An often discussed method of recovering water from lunar regolith containing ice is by mining it from the permanently shadowed areas by either a transport rover, dragline bucket, or a combination of the two (Gustafson, 1999; Whitlock, 1999). The material is loaded into a sealed vessel and heated by a solar furnace while the released gasses are recovered and condensed into water and stored in a storage tank for later use.

The source of sunlight (solar furnace) could be from areas of uninterrupted solar power popularly known as the “peaks of eternal light.” Examples are the rim of Shackleton and the top of Malapert Mountain (Lowman, 2005). This process, however, is only effective if the ice concentration is 1 % or greater (LCROSS predicted up to 5 %; see above). One obstacle with this approach is conceivably the high power/heat requirements to heat the ice and the inert regolith materials. Selective mining might be a possibility in a water plant setup if the detailed geology and stratigraphy of the ice deposits in the permanently shadowed areas are known. One additional obstacle in mining is that the ice which is intended for drinking water and analysis of organics would have to be extracted from the subsurface as the surface ice has been altered by radiation. The degree of shielding from cosmic radiation is very sensitive to the thickness of the lunar soil cover. Only a thin layer of lunar covering material is needed to protect volatiles (lunar ice) from UV sources (Crider and Vondrak, 2003), but 6 m of lunar material depth is needed to fully protect water ice from galactic cosmic rays and less than 1 m to fully protect it from solar particle events (Angelis et al., 2001).

### 4. Extraction of Organic and Molecules from the Lunar Ice

Here I introduce laboratory experiments that are designed to yield a feasible and practical water extraction system for potable water and to concentrate and analyze organic macromolecules preserved in lunar ice. The compositional analysis of the



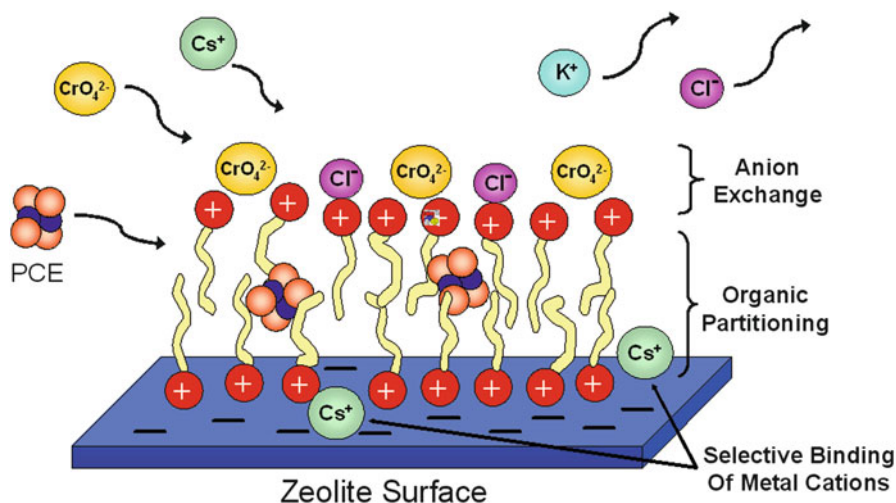
**Figure 1.** Experimental setup for vacuum chamber. Dimensions are given for a laboratory setup and can be scaled up. The sample of rock-ice in *Chamber 1* consists of approximately 1–10 wt% water ice.

organic molecules, which would eventually be performed in the laboratory of a lunar station, will help shed insights on the expected composition of comet ice deposited on the lunar poles and on molecular evidence for the evolution of life on Earth. The introduced designs below have to be still extensively tested to optimize recovery of both organic molecules and water suitable for human consumption.

I propose to extract the water from the lunar soil with a standard vacuum distillation setup, with a few key differences. We will not employ an added heat source or an ice bath condenser (Zubrick, 2000). Since all organic macromolecules are of interest, the ice sample will be allowed to volatilize/evaporate at 25 °C to minimize the volatilization of low-temperature range organic compounds. Two cylindrical vacuum chambers house the regolith–ice analog samples and separate liquid water (Fig. 1).

Samples will be accessed through removable lids sealed by inert “Viton” rubber O-rings. The chambers will be sterilized before and after every experiment by an autoclave and washing with ethanol. Ice samples will be placed in a sterile glass Petri dish in *Chamber 1* and allowed to volatilize under a vacuum at 25 °C (or under sunlit crater conditions on the Moon). Water and low-temperature range organic volatiles will vaporize and move to *Chamber 2*, to be stopped and collected by a breathable diaphragm which will also be made from inert “Viton” rubber. The movable diaphragm is designed to only allow air to pass through, while stopping any water vapor. Most vacuum pumps use oil to create a vacuum, and any water vapor traveling through a pump will become contaminated by the oil and be rendered nonpotable. To avoid this problem, the breathable diaphragm mentioned will be used to limit water contamination.

After all of the ice has been sublimed and condensed in the water collection chamber, the liquid water will be analyzed for overall drinking water quality, using



**Figure 2.** Surface properties of surfactant-modified zeolite.

standard water quality measurements. Any organic macromolecules remaining on the Petri dish and within the diaphragm will be removed with an organic solvent such as hexane, and analyzed for organic macromolecules using a GC/MS.

In a modified setup, a surfactant-modified zeolite (SMZ) filter is used instead of a breathable diaphragm filter to trap the organic components from the condensed vapors (Fig. 2). SMZ was previously tested by us and others and proved extremely efficient removing organic compounds and even organisms from natural waters due to its (1) cage-like porous structure, (2) hydrophobic properties, and (3) charge characteristics (Bowman et al., 1995, 2001; Li and Bowman, 1998; Schulze-Makuch et al., 2002, 2003).

SMZ has a distinct advantage over activated carbon in that regeneration of the sorbent and recovery of the organic compounds is much easier. While activated carbon has to be heated to desorb retained volatile organics, SMZ is readily regenerated by blowing air through the filter (Li and Bowman, 2001; Ranck et al., 2005). Thus, a filter with trapped organic compounds could be taken from the extraction device and analyzed in a future lunar laboratory or transported to Earth for analysis.

Zeolites are naturally occurring hydrated aluminosilicates characterized by cage-like structures, high surface areas (hundreds of  $\text{m}^2/\text{g}$ ), and high cation exchange capacities (hundreds of  $\text{meq}/\text{kg}$ ). Zeolite surface chemistry resembles that of smectite clays. Unlike clays, however, natural zeolites can occur as millimeter- or greater-sized aggregates and are free of shrink–swell behavior. As a result, zeolites exhibit superior hydraulic characteristics and are suitable for flow-through applications. Treatment of natural zeolites with large cationic surfactants (quaternary amines) dramatically alters their surface chemistries. These large organic cations exchange

selectively with native inorganic cations to form a stable, organic-rich coating on the external surfaces of the zeolite. Surfactant modification allows the zeolites to sorb nonpolar organic solutes and anions, for which untreated zeolites have little affinity.

The surfactant is nontoxic. Surfactant-modified zeolites have been extensively studied for removal of neutral and anionic contaminants from water (Bowman et al., 1995, 2001) and *E. coli* and bacteriophages from sewage water (Schulze-Makuch et al., 2002, 2003). This inexpensive (\$0.50/kg) SMZ has hydrophobic properties along with a positive surface charge that bind neutral organics, positively and negatively charged ions, and even organisms.

The maximum surfactant loading of the zeolite sample is attained by treating a known mass of zeolite with an excess amount of surfactant. In a previous study the maximum surfactant loading was measured to be 87.2 mM HDTMA/kg zeolite (Salazar, 2006).

One other possible modification is a nanofiltration device with an applied surfactant coating on the filter. The ice sample would be vacuum filtered through the surfactant-coated filter in order to trap the organic and heavy metal components of interest from the volatilizing vapors. Nanofiltration is a form of physical filtration that uses partially permeable membranes to preferentially separate different fluids or compounds from water. The more economical nanofiltration is not as fine of a filtration process as reverse osmosis ( $<0.001\ \mu\text{m}$ ), but allows filtration of compounds of about 1 nm ( $0.001\ \mu\text{m}$ ) size range. Thus, it filters all organic macromolecules of interest and requires less energy to perform the process.

Suitable nanofilters are ceramic membranes to which the surfactant will easily adhere (Mattson et al., 2000). The nanodevice will separate organic macromolecules and heavy metals from the ice sample, while allowing water to pass. With the addition of surfactant to the filter, we expect to observe a higher filtration rate of organic macromolecules and heavy metals. Once all water has been filtered, both filtered water and filtered compounds are analyzed. Trapped organic molecules can be easily released from the surfactant-coated filter by blowing air through the filter device.

## 5. Discussion and Conclusions

The importance of the possible presence of prebiotic and biological molecules (e.g., amino acids, lipids, oligopolymers) in lunar ices originating from early life on Earth cannot be overestimated. It would allow us to understand the origin of life and open a window on how we came into being. Suggestions are provided in this chapter on how the organic compounds can be harvested from lunar ice. Analysis of the lunar ices would also provide us with a better understanding of cometary compositions. We might even be able to extract sufficient drinking water for a future lunar base. Previous results (e.g., LCROSS) indicate that the lunar regolith holds sufficient water to make this a feasible possibility. However, it may be prudent

to first launch a sample return mission to confirm whether the lunar ice consists of a high-enough amount of water ice (>1 %). Compared to Mars the water weight percentages on the Moon are low but likely be sufficient to extract drinking water from the lunar regolith, both based on scientific and economical reasons, once a permanent human presence on the Moon is established. Others are encouraged to follow up on the research presented here.

## 6. Dedication

This chapter is dedicated to my friends and good colleagues Rob Bowman and Paul Lowman. Particularly, the untimely death of Rob was painful and prevented this project to come to its full fruition. Both will be dearly missed.

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**PART III:**  
**FIELD STUDIES IN PLANETARY**  
**ANALOGS, SIMULATIONS AND SPACE**  
**EXPERIMENTS WITH RELEVANCE**  
**TO HABITABILITY**

**Strasdeit**

**Fox**

**Lorek**

**Koncz**

**Barbieri**

Biodata of **Prof. Henry Strasdeit** and **Dr. Stefan Fox**, authors of “*Experimental Simulations of Possible Origins of Life: Conceptual and Practical Issues.*”

**Professor Henry Strasdeit** holds the Chair of Bioinorganic Chemistry at the University of Hohenheim, Stuttgart, Germany. He studied chemistry at the University of Münster where he received his Ph.D. in 1985. Following a 1-year postdoctoral stay at the University of Leiden, the Netherlands, he established an independent research group at the University of Oldenburg. There he completed his habilitation in 1993 and in 2000 was appointed adjunct professor. After a visiting professorship at the University of Vienna, Austria, he took up his current position in 2002.

Dr. Strasdeit’s research interests lie in the chemical aspects of astrobiology, especially chemical evolution and origin-of-life chemistry. In his laboratory, potentially prebiotic organic molecules are exposed to simulated environmental conditions that are thought to exist on young Earth-like planets. An inorganic chemist by training, Dr. Strasdeit is particularly interested in how metal ions, minerals, and rocks influence the results of such experiments.

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**Henry Strasdeit**



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# EXPERIMENTAL SIMULATIONS OF POSSIBLE ORIGINS OF LIFE: CONCEPTUAL AND PRACTICAL ISSUES

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## 1. Introduction

According to current knowledge, terrestrial life emerged from inanimate matter on a planet or moon in our solar system. The Earth is the most likely place where the key steps of chemical evolution proceeded and the first organisms appeared (Brack, 2004). However, an alternative exists that is worth considering. It is based on the idea of lithopanspermia, that is, the interplanetary transfer of microorganisms in rocks which have been ejected from their parent bodies by high-energy impacts. For example, a natural transfer of viable microbes from Mars to Earth is regarded as highly probable, provided there was life on Mars (Mileikowsky et al., 2000). In fact, the existence of Martian meteorites proves that rocks from Mars can reach the surface of the Earth (Gladman et al., 1996; Hutchison, 2004; McSween, 1994). Some microorganisms are sufficiently resistant to survive in a hostile space environment (Horneck, 2003). This means that life might have originated on another body of the solar system and come to Earth by lithopanspermia. In contrast, the probability of lithopanspermia over interstellar distances, that is, from one solar system to another, appears to be exceedingly low (Adams and Spiegel, 2005; Melosh, 2003; Valtonen et al., 2009). Therefore, it is highly improbable (though not impossible) that the Earth was seeded with life from an exoplanet. This conclusion can be generalized to hypothetical life-bearing planets and moons in other solar systems. Thus, most planetary systems must be regarded as virtually isolated with respect to biological exchange. It follows immediately that potential extraterrestrial life forms in different solar systems will very probably have originated independently of each other and of terrestrial life.

The idea of biologically isolated planetary systems has consequences for the concept of habitability. Namely, it is not sufficient to consider whether a planet or moon was and is suited to sustain biological evolution. Furthermore, there must have been a time when somewhere in the planetary system in question, the chemical and physical conditions allowed life to emerge. In this way, habitability is closely connected to prebiotic chemical evolution. On Earth, the prebiological evolution of organic molecules has left no fossil record. Moreover, we do not know of any celestial body on which evolution near the nonliving to living transition can be observed at work. Research in prebiotic chemistry therefore relies on models

and, ultimately, on laboratory simulations. For experiments to be prebiotically relevant, the environmental conditions which are to be simulated must be adequately known. From this point of view, reasonable simulations are possible at least for the young Earth and Mars (Strasdeit, 2010).

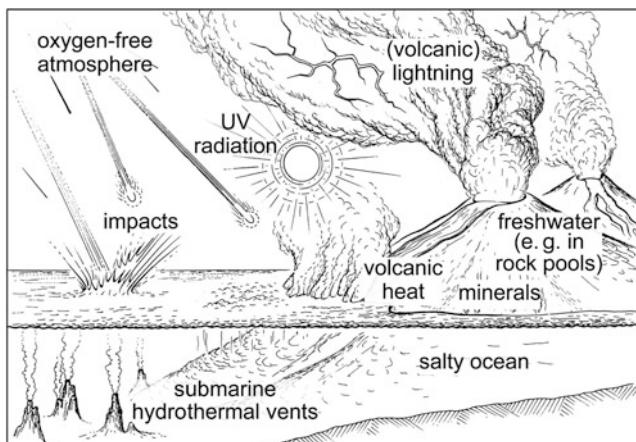
In the following, we discuss some concepts that may be helpful in designing chemical evolution experiments and assessing their prebiotic relevance. In addition, we give examples of the technical challenges associated with laboratory simulations. The discussion is not meant to be comprehensive. Hence, some important aspects such as energy (e.g., Deamer and Weber, 2010), compartmentation (e.g., Martin and Russell, 2003; Meierhenrich et al., 2010; Pohorille and Deamer, 2009), and the origin of biomolecular homochirality (e.g., Klabunovskii, 2012) will not be addressed in detail.

## 2. Concepts

We begin our discussion with the well-known fact that a simulation is merely an approximation to reality. Any theoretical or experimental model is more or less “erroneous” because it inevitably suffers from simplifications and insufficient or even wrong assumptions and data. Such difficulties are particularly pronounced in origins of life research. As mentioned above, only for Earth and Mars, the knowledge of the prebiotic conditions (Fig. 1) is sufficiently advanced to allow meaningful simulation experiments (Strasdeit, 2010). In contrast, our current knowledge of other locations where chemical evolution might have reached an advanced stage or even led to biological evolution is very limited. This includes, for example, the subsurface water oceans that probably exist on Europa and Callisto and possibly also on other satellites in the solar system, such as Ganymede, Enceladus, Titan, and Triton (Saur et al., 2010). Attempts have been made to model the chemical processes that might occur in these oceans (Chyba and Phillips, 2007; Levy et al., 2000; Sohl et al., 2010). Although experimental data constrain the models, key issues nevertheless remain speculative. Thus, there is only a very limited basis for laboratory experiments that aim to simulate prebiotic chemical evolution on icy satellites. This is also true for other non-Earth-like celestial bodies.

Traditionally, synthetic chemists are concerned with inventing and applying procedures for the preparation of target molecules. They also routinely optimize the yields of their products. Experimental prebiotic chemistry, however, requires a different strategy. Here it is not appropriate to modify the conditions until a desired result (e.g., an expected product in high yield and purity) is achieved. Instead, one should simply observe how (small) molecules interact with each other under simulated prebiotic conditions (Shapiro, 2007). “Don’t interfere, don’t look for the results you expect, just let nature teach you, see what nature wants to do...,” as Shapiro (2008) put it.

As a working hypothesis, we assume that the process of biogenesis consists of a very large number of steps (de Duve, 1991) and has no discontinuities



**Figure 1.** The Earth in the late Hadean–early Archean eon: locations and geochemical and geophysical conditions that should be considered in prebiotic simulation experiments. In the late Noachian eon, the surface conditions on Mars might have been similar.

(Morowitz et al., 1988). Under this assumption, it could prove beneficial to regularly view the results of prebiotic experiments in the context of evolution. In this respect, basic concepts of evolutionary biology can be helpful. Before we discuss this issue, we first turn to some aspects of abiotic organic synthesis which are relevant to the design of simulation experiments.

## 2.1. FROM PRIMORDIAL-SOUP TO PROTOMETABOLIC ABIOTIC SYNTHESIS

Darwin, in a private letter, already mentioned that a peptide might have formed abiotically in a “warm little pond” (Darwin, 1871). The conjecture that on the young Earth small organic molecules spontaneously transformed into functional polymers is central to the Oparin–Haldane hypothesis of the origin of life (Haldane, 1929; Oparin, 1924). It was most clearly formulated by Oparin. Haldane speculated that the starting monomers might have accumulated in the ocean until they formed a solution with the consistency of “hot dilute soup,” which later became known as the “primordial soup.” These ideas laid the groundwork for experimental prebiotic research. After several decades of spectroscopic studies of the interstellar medium, analyses of extraterrestrial material, and laboratory experiments – starting with Miller’s famous amino acid synthesis (Miller, 1953, 1955) – it is now beyond doubt that small organic molecules form abiotically from inorganic precursors. These molecules are widespread, occurring in interstellar clouds, circumstellar envelopes, comets, meteorites, and on planets and moons.

In the Murchison meteorite, for example, tens of thousands of different elemental compositions, probably corresponding to millions of different organic compounds, have been detected (Schmitt-Kopplin et al., 2010). Such molecules were almost certainly present on Earth and Mars four billion years ago.

The prebiotic organic inventory probably included amino acids, fatty acids, aldehydes, and various nitrogen heterocycles. Short oligomers might have also existed. In the case of amino acids, simulation experiments have shown that abiotic oligomerization usually does not exceed the trimer stage. The salt-induced peptide formation (SIPF) reaction is a good example. It mainly yields dipeptides (Rode, 1999). Under prebiotically plausible conditions, only glycine condenses to a somewhat higher extent. For example, oligomers up to the hexamer have been observed after the heating of glycine to 200 °C in clay minerals (Dalai and Strasdeit, 2010). The *de novo* appearance of functional *polymers*, however, is highly unlikely. The reasons leading to this conclusion have been discussed elsewhere (Strasdeit, 2010). Relatively long oligomers have been obtained in the presence of minerals (Ferris et al., 1996), but a plausible prebiotic origin of the chemically activated monomers used in these experiments has still to be demonstrated. The volcanic gas carbonyl sulfide has been shown to be an effective and prebiotically plausible condensing agent for amino acids. However, only peptides up to tetramers and traces of penta- and hexamers formed (Leman et al., 2004). In fact, at our present state of knowledge, we are forced to assume that the spontaneous formation of *polypeptides* and *polynucleotides* is improbable on young Earth-like planets.

How then the first functional polymers did come into existence? The “tricks” of synthetic organic chemistry are not particularly helpful in answering this question because, for example, activated molecules, preformed complex building blocks, a clean spatial–temporal separation of reaction steps, and high concentrations and purities of reactants are largely incompatible with prebiotic conditions. The formation of reaction networks of small molecules has been proposed as a solution (Shapiro, 2006). Such a network can be regarded as protometabolic. Its molecules are involved in reactions and catalytic actions in such a way that the network as a whole is autocatalytic. To illustrate this, let us consider the following general example: we imagine the formation of a new molecule AB from the low molecular mass “nutrients” A and B:  $A + B \rightarrow AB$ ; this reaction is catalyzed by another “nutrient” C; the product AB, in turn, catalyzes the reactions  $A + C \rightarrow AC$  and  $B + C \rightarrow BC$ ; AC may catalyze the combination of AB and BC to ABBC etc. In this way, the protometabolism produces increasingly complex molecules. Theories have been developed that describe the behavior of autocatalytic sets of molecule (Dyson, 1982, 1999; Kauffman, 1993). Dyson’s model suggests that polypeptides may form before polynucleotides and related molecules. Without a genetic material such as RNA, replication is, of course, impossible. Instead, the chemical composition may be inherited (Segré et al., 2000; Segré and Lancet, 2000), but the evolvability of “compositional genomes” remains to be shown experimentally.

Early cell ancestors – we follow Pohorille (2009) in using this term instead of “protocells” – possess no polymeric catalysts at the very start of the protometabolism.

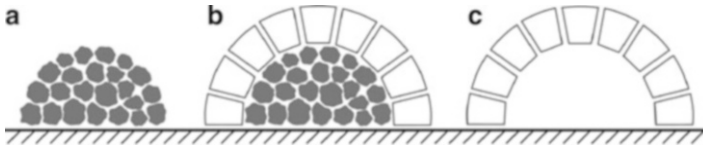
However, this does not pose a fundamental problem since an immense number of reactions are known to be catalyzed by low-molecular-mass organic compounds (Dalko and Moisan, 2004) and their metal complexes (Ward, 2004). Catalytically active prebiotic metal complexes may be regarded as functional precursors of metalloenzymes. Organocatalysis in presumably prebiotic reactions has been demonstrated experimentally. The catalytic influence of nonracemic amino acids on the formation of sugars from glycolaldehyde or glycolaldehyde and formaldehyde may serve as an example (Pizzarello and Weber, 2004).

It was hypothesized very early that the first cell ancestors on Earth were heterotrophs because various carbon compounds were available from spontaneous abiotic syntheses in the primordial soup (Haldane, 1929; Oparin, 1924). Autotrophic protometabolic pathways possibly evolved soon afterward. Autotrophy could have reduced the dependence on an uncertain supply of some “nutrients” and therefore provided an evolutionary advantage. It seems plausible that initially only some of the “biomolecules” were autotrophically synthesized, meaning that individual entities were simultaneously heterotrophic and autotrophic. Furthermore, there was possibly a pronounced exchange of “biomolecules” which more or less obliterated the individuality of the early cell ancestors. Molecular exchange might have accelerated the pace of chemical evolution. A high “evolutionary temperature” was perhaps still present in the universal ancestor, which has been described as a diverse community of cells that evolved as a unit and exhibited intensive horizontal gene transfer (Woese, 1998). A related idea has been discussed by Jacob (1977) who pointed out that the real biochemical novelties must have occurred very early in evolution. It should be mentioned that there is an alternative to the transition from heterotrophy to autotrophy, namely, that autotrophic systems existed from the very beginning (e.g., Wächtershäuser, 1988, 1992).

The transition from primordial-soup to protometabolic synthesis appears to be a fundamental step in biogenesis on Earth-like planets. However, to our knowledge, experiments that tested whether this transition can really occur have not been reported. Laboratory simulations are therefore urgently needed to examine the possible self-assembly of autocatalytic networks from small molecules under prebiotically plausible conditions. In addition to the analytical challenges, the simulations will present a large combinatorial task. Some of the experimental parameters that can be systematically varied are (1) a set of small organic molecules, (2) the temperature, (3) gradients (e.g., of redox potential and pH), and (4) cyclic changes (e.g., hot–cold, wet–dry). Metal salts and minerals, particularly clay minerals (Brack, 2006; Negron-Mendoza and Ramos-Bernal, 2004; Ponnampertuma et al., 1982), may also be important and represent additional experimental parameters. Chemistry has reached a stage where such simulations should be feasible.

The experiments just described are a typical example of the bottom-up approach, which tries to reconstruct chemical evolution in its actual direction, that is, from lower to higher complexity. The alternative top-down approach uses the biochemistry of extant cells as a starting point for backward extrapolations to the origin of life. We think that the latter approach involves a high risk of





**Figure 2.** Building an arch of stones can serve as a metaphor for the evolution of central biochemistry (Cairns-Smith, 1985). A scaffold (a) is needed in the construction phase (b). After removal of the scaffold, the arch is self-supporting (c). It is a seemingly paradoxical structure because, as the central biochemistry, it cannot be constructed by simply adding one building block at a time. The information about the scaffold (the preceding evolutionary step) has been lost.

drawing erroneous conclusions. The main reason for this is that in biochemical evolution add-and-subtract steps probably play an important role. A new structure or function develops by using existing ones as a scaffold; the scaffold eventually disappears (Cairns-Smith, 1982). Little or no information about the nature of the scaffold is then preserved in the new biochemical feature. Figure 2 illustrates this by a simple analogy from architecture. It seems reasonable that add-and-subtract processes similarly occurred in chemical evolution already before the universal ancestor emerged.

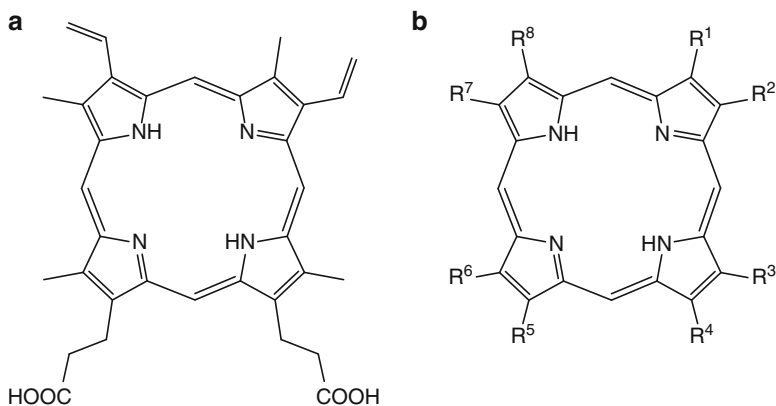
The emergence of a protometabolism is a transition from disorder to order. It may be possible only for systems that tolerate high error rates, for example, in the sequence of monomers in polymers (Dyson, 1999). This imperfection is faintly reminiscent of the imperfect adaptation of organisms. In the following, we examine some possible parallels between chemical and biological evolution and discuss their implications for simulation experiments.

## 2.2. LESSONS FROM EVOLUTIONARY BIOLOGY

The probability that a useful *radical* change in a biological structure or function occurs spontaneously in a single step is exceedingly low. Consequently, biological evolution is regarded as “overwhelmingly gradual” with little or no contribution from sudden saltation (Futuyma, 1998; Mayr, 1976). Assuming that this also holds true for chemical evolution, especially in the protometabolic phase, it should be possible to learn from the basic mechanisms by which biological novelties evolve. In particular, this approach could allow us to tentatively assess the evolutionary plausibility of prebiotic simulation experiments.

### 2.2.1. Intensification of Function

A biological structure can improve its function by gradual change (Mayr, 1976). In this process, no fundamentally new function emerges. The evolution of the eye from a spot of light-sensitive, pigmented cells to the complex vertebrate or octopus eye is a textbook example (Ridley, 2004). One can easily think of analogous examples



**Figure 3.** Structural formulas of (a) protoporphyrin IX and (b) presumably prebiotic porphyrins with variable substitution patterns. For example, hydrogen and alkyl groups are conceivable as substituents R<sup>1</sup> to R<sup>8</sup>.

from prebiotic chemistry, for instance, the evolutionary development of porphyrins. Protoporphyrin IX (Fig. 3) and closely related variants thereof form the organic part of the heme groups whose original function probably was to transfer electrons, which they still do today in cytochromes. The very specific substitution patterns of the heme groups (Voet and Voet, 2011) obviously represent a biological adaptation. We arrive at this conclusion because the ability of a porphyrin to host Fe<sup>2+/3+</sup> ions is not restricted to this particular type of substitution. In fact, most iron–porphyrin complexes should be able to serve as electron-transfer agents. Therefore, it is conceivable that the substitution patterns of the first porphyrins not only differed from those of hemes but were also different from each other (Fig. 3). Nonuniform substitution was probably unavoidable in abiotically formed porphyrins. The initial iron–porphyrin structures were subsequently improved until the heme stage was reached – a typical example of intensification of function. If this picture is correct, then a (proto)metabolism seems absolutely necessary for the evolution of heme groups. Hence, laboratory experiments aiming at the spontaneous self-assembly of protoporphyrin IX would have no prebiotic relevance.

### 2.2.2. Change of Function

In biological evolution, existing structures can often take on new functions without major changes. Such structures are referred to as preadaptations or, especially in the case of biomolecules, cooptions (Ridley, 2004). Initially, the original and the new function coexist, but later the old function may vanish or at least become secondary to the new one. The evolution of feathers is a good example (Hall and Hallgrímsson, 2008; Prum and Brush, 2002). Some dinosaurs already had well-developed feathers, which probably served for thermoregulation

and display. Later on, feathers proved to be useful for avian flight and took on the primary function they have today. The concepts of change of function and cooption/preadaptation may also further our understanding of prebiotic evolution. For example, the sole function of the very first porphyrins could have been the protection against ultraviolet radiation (Larkum, 2006), possibly already in the early cell ancestors. It was only later that they assumed a role in electron transfer and light harvesting. Relatively small changes of the molecular structures, in the beginning mainly the complexation of a metal ion, were sufficient to make these new functions possible. This is a typical case of cooption. Subsequently, the structures were gradually improved (intensification of function (Sect. 2.2.1), see above).

Nucleotides may represent another example of change and intensification of function in prebiotic times. Adenosine triphosphate (ATP), which is found in all organisms, is known as the universal energy carrier of extant cells. ATP is already a relatively sophisticated molecule, which has, for example, four chiral centers. It seems plausible that ATP evolved from much simpler triphosphates (or, more generally, oligophosphates) in a series of gradual structural improvements. Such a process could hardly have taken place in the primordial soup, but would have depended on a (proto)metabolism. Thus, laboratory experiments attempting to mimic a spontaneous abiotic origin of ATP may be prebiotically irrelevant. Dyson (1999) suggested that adenosine monophosphate (AMP) and other nucleotides could have accumulated in what he called primitive cells, where “by accident” they were joined to form RNA. The RNA was self-reproducing and infectious. The cells, however, learned to utilize this initially harmful product. There is a less dramatic alternative to this infection scenario. Short, non-self-reproducing oligomers may have been formed from AMP and other nucleotides [the triphosphates of all nucleosides were probably used as energy carriers (compare GTP in modern biochemistry)]. One can hypothesize that the short oligonucleotides represented an evolutionary advantage because they had new useful properties not seen, for example, in peptides. They gradually evolved into RNA, which became the first genetic material. Both functions of nucleoside phosphates, the original one (energy carriers) and the more recent one (building blocks of informational polymers), still coexist today. In the scenario outlined, there is no necessity for assuming a pre-RNA genetic material such as peptide nucleic acids (Nelson et al., 2000). The scenario illustrates the conceptual appeal of the idea that metabolism precedes replication.

It will probably never be possible to exactly reproduce terrestrial biogenesis since evolution is largely governed by chance. For the same reason life on other Earth-like planets cannot be expected to have the same central biochemistry as life on Earth. On the other hand, one can speculate that molecules such as  $\alpha$ -amino acids for which robust routes of spontaneous abiotic synthesis exist have found their way into alien biochemistries. Certain adaptations in response to evolutionary pressure may also be common, for example, the use of double-stranded informational molecules that are comprised of two complementary chains – but

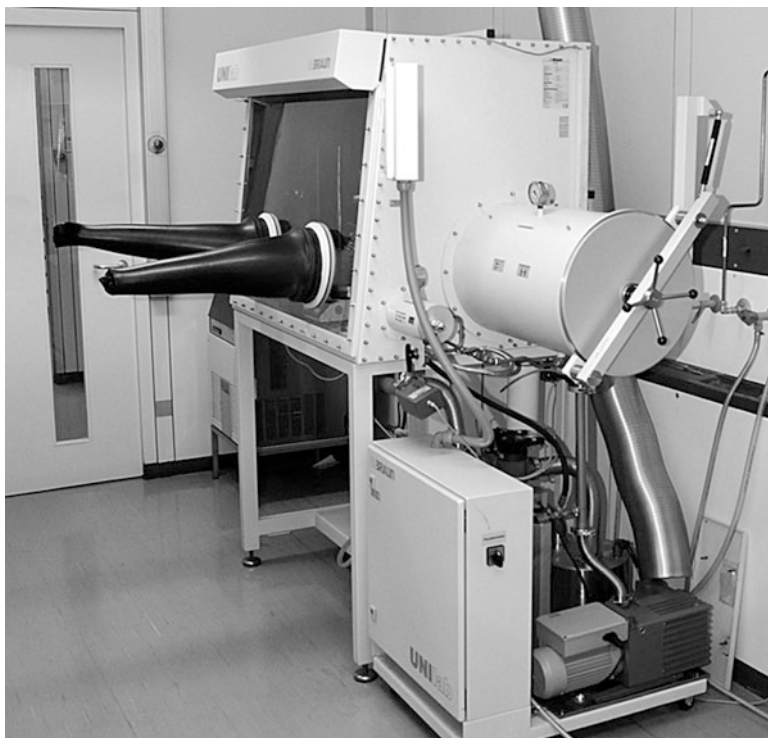
not necessarily in the form of DNA. Again, there is a parallel to biological evolution, namely, to the concept of convergence (homoplasy, analogy). Similar but independently evolved structures such as the vertebrate eye and the octopus eye (Futuyma, 1998) or a bird wing and a bat wing (Ridley, 2004) are examples of convergent evolution.

### 3. Technical Aspects of Prebiotic Simulation Experiments

Here we will focus on selected examples of experimental setups. The discussion will be confined to experiments that simulate prebiotic chemical processes on Earth-like planets. Consequently, certain types of experiments are not considered, in particular simulations of (1) the radiation chemistry in interstellar clouds; (2) processes in small celestial bodies, for example, aqueous alteration in asteroids; (3) chemical evolution on non-Earth-like planets and moons such as icy satellites (see above); and (4) “exotic” chemical evolution, for example, silicon-based or nonaqueous chemistry (Schulze-Makuch and Irwin, 2008).

The abiotic formation of organic molecules from gases of primordial atmospheres was the first issue addressed by experimental prebiotic chemistry (Deamer and Fleischaker, 1994). Miller (1953, 1955) used three versions of a closed Pyrex glass apparatus, in which electrical discharges simulated lightning. The apparatus could be evacuated and filled with the desired gas mixture. This procedure for obtaining oxygen-free conditions is related to conventional Schlenk and vacuum line techniques, which are widely used in chemistry for preparing and handling air-sensitive substances (Shriver and Drezdson, 1986). A special feature of Miller’s apparatus was the unidirectional circulation of water from a heated flask through the electrical discharge, a condenser, and a U-tube back to the flask. The U-tube prevented the water from moving in the opposite direction. This design is somewhat reminiscent of a Soxhlet extractor. A high voltage of 60 kV was used to generate spark discharge between tungsten electrodes (Miller, 1955). The electrodes were situated in a 5-L bulb, which represented the largest single component of the apparatus. The overall size of the setup was not unusual for a chemical laboratory experiment. Schematic drawings can be found in numerous publications (e.g., Voet and Voet, 2011). There is also a simpler experimental design that has been used to simulate the chemical effects of lightning in primordial atmospheres (Cleaves et al., 2008; Schlesinger and Miller, 1983). It consists of a 3-L round-bottom flask equipped with tungsten electrodes and a gas inlet. Standard Schlenk techniques can be used to remove air and fill the apparatus with an aqueous solution and a gas mixture.

Near-surface O<sub>2</sub> was virtually absent on Earth four billion years ago (Kasting, 1993). Therefore, it is often necessary to conduct simulation experiments under strict exclusion of air. This of course becomes inevitable when oxygen-sensitive compounds are employed or formed or the energy input into the reaction system (e.g., the temperature) is high. The use of a glove box is a convenient way to exclude



**Figure 4.** Glove box for carrying out simulation experiments under an inert atmosphere. The large cylindrical object on the right is the main airlock. The gas purification system and the vacuum pump can be seen below the airlock.

oxygen. The glove box that is operated in our Department at the University of Hohenheim is shown in Fig. 4. It can be regarded as a small laboratory that contains an atmosphere of pure argon instead of air. The  $O_2$  content ranges from  $<1$  to  $5$  ppm, corresponding to  $\sim 0.1 \mu\text{mol } O_2/\text{L}$  or  $\sim 10^{-5}$  of the value in air. The glove box is equipped with an electronic balance, magnetic stirrers, heating plates, etc., and allows standard laboratory operations such as filtration and pipetting to be performed. Conventional glove boxes have two main limitations: firstly, only inert gases can be used, and, secondly, the pressure is fixed at the ambient value of 1 bar. However, glove box, Schlenk, and vacuum line techniques can be combined to overcome the limitations of each individual method.

There are also apparatuses that allow high-pressure–high-temperature and low-pressure–low-temperature conditions to be simulated. Here we will briefly mention two examples. The first one has been used to simulate submarine hydrothermal vents (Imai et al., 1999). It is a flow reactor, in which 500 mL of an aqueous solution circulate under high pressure (230 bar) between a high-temperature (100–350 °C) and a low-temperature zone ( $\sim 0$  °C). The reactor consists mainly of

stainless steel. The other extreme – low pressures and low temperatures – is less relevant to terrestrial prebiotic chemistry, but in the future it may become important for the simulation of chemical evolution on some exoplanets. A low-pressure–low-temperature apparatus is operated at the DLR Institute of Planetary Research at Berlin (de Vera et al., 2010). It is used to conduct biological experiments under simulated present-day Mars conditions (e.g., 6 mbar,  $-75^{\circ}\text{C}$ ). Its central part consists of a cold chamber of dimensions  $80 \times 60 \times 50 \text{ cm}^3$  (cooled volume), which contains the experimental chamber with an inner volume of  $\sim 10 \text{ L}$ . In addition to the control of pressure and temperature, the experimental setup allows controlled mixing of up to four gases and accurate adjustment of the humidity.

The chemical products that are formed in prebiotic simulation experiments are mostly analyzed by standard separation and identification methods. Gas chromatography–mass spectrometry (GC-MS) and high-performance liquid chromatography (HPLC) are usually the analytical workhorses, but in some cases, electronic spectroscopy (UV–vis), vibrational spectroscopy (infrared, Raman), and special mass-spectrometric methods (e.g., high-resolution/high-accuracy MS) are the tools of first choice.

We would like to mention that field research can be a valuable addition to laboratory experiments. So far this opportunity has only rarely been used in chemical evolution studies. In contrast, field research is a common approach in astrobiology-related biological studies and planetary sciences. Some terrestrial field sites (e.g., the Rio Tinto) were formally established as models for surface locations on other planets and moons (Mason, 2009).

#### 4. Concluding Remarks

The next generation of laboratory experiments should tackle the challenge of simulating complex primordial environments, for example, volcanic islands. Instrumental and analytical techniques required for such experiments already exist. The abiotic synthesis of amino acids (i.e., building blocks of key biomolecules) under conditions that at the time were thought to simulate the early Earth's atmosphere (Miller, 1953) raised high expectations. Subsequently, plausible prebiotic syntheses have been discovered for other biologically relevant molecules (Brack, 2004). However, progress has been relatively slow. In fact, the lack of major breakthroughs has been misused by proponents of “intelligent design” as scientific proof that life cannot emerge from nonliving matter by natural means. In response to such antievolutionary views, the use of evolutionary concepts in origin-of-life research should be intensified. The further development of these concepts and their systematic application to prebiotic laboratory experiments can provide a strong framework for a field that currently seems somewhat disoriented. Finally, we wish to stress that education is the most general and most effective means to counter antievolution efforts (e.g., National Academy of Sciences, 1999).

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**Alexander Koncz**



# **SIMULATION AND MEASUREMENT OF EXTRATERRESTRIAL CONDITIONS FOR EXPERIMENTS ON HABITABILITY WITH RESPECT TO MARS**

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## **1. Introduction**

In the early 1960s of the twentieth century when NASA started exploration of Mars with Mariner 4, experiments simulating extraterrestrial atmospheres came into focus of several studies (Hubbard et al., 1971; Mac Cready, 1962). The main purpose of these studies was related to Lander missions, namely, Vikings 1 and 2, which should substantially extend the knowledge about fundamental atmospheric parameters. Until then these parameters had solely been coming from remote (astronomical) sensing data collected since the nineteenth century. Those investigations were mainly designed to detect atmospheric and geological parameters but were also focusing on the question of habitability-related problems and issues (Foster et al., 1978; Anderson et al., 1972). Recent data derived from NASA's Mars exploration rovers Spirit and Opportunity, pictures taken by ESA Mars Express, and in particular the measurements made by NASA Phoenix Lander have boosted our knowledge about the past and current environmental conditions of Earth's nearest neighbor. The data sent back so far enables us to simulate extraterrestrial conditions on Earth much more precisely but also leads to higher requirements on equipment, experiment procedures, and sensors. These challenges have been successfully met by DLR in cooperation with the Dr. Wernecke Feuchtemesstechnik GmbH through newly developed sensors and improved technical capabilities of their Mars Simulation Facility (over the past years). The MSF was built originally for the design and development of a humidity sensor measuring water vapor concentrations similar to those in the near-surface Martian atmosphere. During its development, the laboratory was used increasingly for physical but in particular for habitability-related experiments under Martian environmental conditions. Notably, considerable national and international attention was drawn to the latter experiments (de Vera et al., 2010; Burlak et al., 2011). These experiments document an increase of complexity and accuracy of simulated parameters which reflects the continuous improvement of the laboratory. The water cycle represents, beside CO<sub>2</sub> and dust cycles, one of the planet's most important climatic cycles. Mars is too cold and too dry to allow for bulk water to be stable. Measurements at DLR show that adsorbed water could remain in a liquid-like state even under

the environmental conditions at midlatitudes on Mars. Therefore, it is assumed that a fraction of the water is adsorbed by the soil in the upper layers of the regolith. The soil interacts directly with the diurnally varying atmospheric humidity and, depending on the gradient, water desorbs into the atmosphere or adsorbs onto the regolith. The adsorbed water could have led to several phenomena observed on Mars such as seepage phenomena (Kereszturi et al., 2010) or the formation – in the presence of UV irradiation and catalyzing minerals – of oxygenate molecules (Chun et al., 1978; Möhlmann, 2004). Moreover, laboratory experiments have shown that metabolic activity is still detectable at environmental conditions similar to those on Mars if one or two monolayers of water are present (Rivkina et al., 2000). The availability of water and thus also the interaction between regolith and near-surface atmosphere are key parameters in terms of habitability (Stoker et al., 2010). Since the detection of these low amounts of water in the diurnal range in the Martian atmosphere is of great challenge, the design and development of coulometric sensors, for measuring trace amounts of atmospheric moisture, and capacitive sensors, for detecting relative humidity, have been advanced through several projects, such as MiniHUM (Koncz, 2012), HUMITRACE (Lorek et al., 2010), and SMADLUSEA (Koncz et al., 2010). In addition to sensor development, SMADLUSEA aims at standardizing requirements for experiments those intents to measure under extraterrestrial atmospheres. Thus, we are trying to pass on the experiences made with the MSF over the past years to other researchers who intend to do simulations and measurements under similar environmental conditions.

## 2. Requirements

The MSF simulates the key environmental conditions like pressure, temperature, radiation, gas composition, and primarily also the diurnally varying atmospheric humidity as given in Table 1 in a range similar to those at the near-surface atmosphere on Mars. The data were taken from several missions to Mars that landed on the surface and therefore were able to perform in situ measurements.

**Table 1.** Parameters of the near-surface atmosphere on Mars.

Parameter	Range/value	References
Pressure	Viking Lander (VL)-1 + 2: 680–840 Pa	Hess et al. (1977)
	Phoenix: 720–860 Pa	Taylor et al. (2010)
atm. temperature	VL-1 + 2: 170–220 K	Zurek et al. (1992), at 1.6 m height
	Pathfinder: 197–263 K	Schofield (1997)
	MER: 220–285 K	Spanovich et al. (2006)
	Phoenix: 178–249 K	Taylor et al. (2010)

(continued)

**Table 1.** (continued)

Parameter	Range/value	References
Frost point	VL-2: -107 to 75 °C FP Phoenix: -85 to -53 °C FP	Ryan and Sharman (1981) Zent et al. (2010)
absolute humidity	$1.8 \cdot 10^{-7}$ to $2 \cdot 10^{-6}$ Kg/m <sup>3</sup> $4 \cdot 10^{-7}$ to $3 \cdot 10^{-6}$ Kg/m <sup>3</sup>	Ryan et al. (1982)
Composition of the Martian atmosphere	CO <sub>2</sub> 95.32 %v/v N <sub>2</sub> 2.7 %v/v Ar 1.6 %v/v O <sub>2</sub> 0.13 %v/v	Owen (1992)
Irradiance	200 nm: $1 \cdot 10^{-3}$ W · m <sup>2</sup> · nm <sup>-1</sup> to 400 nm: $1 \cdot 10^{-1}$ W · m <sup>2</sup> · nm <sup>-1</sup>	Rettberg et al. (2004)

### 3. Laboratory Design and Equipment

To simulate the atmospheric environmental conditions (cf. Table 1) in terms of pressure, temperature, and gas composition, the so-called climate chambers can be used. There are many types of climate or simulation chambers available commercially and also tailor-made solutions as can be found, e.g., at Forschungszentrum Jülich and at the DLR Flight Facility Oberpfaffenhofen (Smit et al., 2000; “DLR - Flight Experiments - Meß- und Sensortechnik,” 2012). These facilities are mainly designed to investigate performances of different sensors used for stratospheric measurements on Earth and thus under quite similar conditions (pressure and temperature) as can be found on Mars. The test-room volume of the environmental simulation facility in Jülich can be dynamically regulated within a pressure and temperature range of 5–1,000 hPa and -73 to 27 °C, respectively. Mixing ratios of ozone and humidity can be dynamically regulated as well. The advantage of such a tailored concept is the good accessibility to accommodate sensors and probes within the test-volume being able to use the whole available space. Moreover, the door used to close the chamber is the only vacuum-related interface that decreases possible leakages and reduces errors during the experiments. However, disadvantages of such tailored facilities are the inflexible settings of how experiments within the chamber could be conducted, associated with a large adsorption surface and high costs of their procurement.

More cost-effective are commercially available temperature test chambers such as the one used in the MSF. The chambers can dynamically regulate temperatures down to -75 °C – which corresponds to the expected temperature during the summer season on equatorial latitudes on Mars. Through holes on each side of the chamber cables, gas pipes and vacuum hoses could be fed inside the chamber or connected to the vacuum pump outside, respectively. Dedicated measurement cells are necessary to ensure that pressure, gas composition, and humidity similar

to those on Mars but also for other environmental conditions can be monitored. These cells are designed and developed for each experiment separately and could therefore be adapted to all major requirements. The described modular approach leads to much higher flexibility but also to better accuracies and response times (referring to humidity) compared to the tailored-facility concept. Even though thermal inertia is rather high because the whole equipment has to be cooled down, the climate chamber is able to simulate the diurnal changes in temperature as observed at midlatitudes on Mars.

Even under low and partially medium vacuum conditions (1,000–1 hPa), a careful design of the measurement cells is necessary. This is especially true for temperatures below  $-40\text{ }^{\circ}\text{C}$  where normal gaskets harden and, as a consequence, are causing leakages, leading to unreliable measurement conditions, especially in terms of humidity ( $-85\text{ }^{\circ}\text{C}$  FP =  $173\text{ }\mu\text{g}/\text{m}^3$ ). Thus, all MSF equipment uses vacuum flange standard CF equipment with copper gaskets. The material of the measurement cells shall be made from stainless steel in order to decrease adsorption of water molecules on the walls (Institute of Measurement and Control, 1996) and keep response times low. In this regard, basically all surface areas which are in contact with the carrier gas should be kept as small as possible. Moreover, because of the very high humidity gradient between Mars conditions on the inner side and Earth conditions on the outer side of all tubes, the material should be made from stainless steel as well. Otherwise, water can diffuse through the pipe walls.

Please note: based on their specific functional and experimental requirements, different chambers exist which are using a different approach to simulate the temperature environment on Mars. Most of them are using a temperature-controlled heater + pulsed liquid nitrogen (Jensen et al., 2008; Sears, 2002; Kaufmann et al., 2006) to generate the required temperature regime which in terms of humidity have the substantial drawback of temperature gradients between experiment chamber and probes.

### 3.1. SELECTED DESIGN OF THE MSF

For an adequate simulation over a period of months of the whole variety of environmental conditions starting from those at the near surface of Mars (Sect. 3) up to Earth conditions, the following devices were selected or developed for the MSF:

- Temperature Test Chamber KWP 240 (Weiss Umwelttechnik GmbH)
  - PC controlled in a temperature range from  $-70$  to  $130\text{ }^{\circ}\text{C}$ .
  - Adjustable in 1 K steps with a cooling rate of 1.5 K/min with an accuracy of  $\pm 1\text{ K}$ , cooling rate, and temperature range. They are sufficient to simulate diurnal variations of Mars-like surface temperatures inside the experiment chamber (Sect. 3.1.2).
  - Test volume,  $80 \times 60 \times 50\text{ cm}$ , accessible via two tailored openings (diameter 10 cm) for cables, pipes, etc.

- Membrane vacuum pump MV10Vario with controller and pressure control unit (Vacuubrand GmbH)
  - Pumping capacity 10 m<sup>3</sup>/h, controllable via PC in 1 hPa steps within a pressure range of 1–1,060 hPa (leading to a volume flow within the experimental chamber at 7 hPa of 30 L/h (at 20 °C and 1,000 hPa))
  - Oil free, therefore, no oil emittance into the system during operation
- Gas mixing system (Sect. 3.1.1)
- Experimental chamber (Sect. 3.1.2)
- Measurement cells for calibration and test of humidity sensors (Sect. 3.1.3)
- Photosynthesis Yield Analyzer MINI-PAM (Walz GmbH) (Sect. 3.2.2) with special fiber optics coupled into the experimental chamber to measure in situ the photosynthesis activity of the samples during the experiment
- 150 W Xenon lamp with fiber optics (silica glass) coupled onto the experimental chamber (Sect. 3.1.4)
- High-performance digital multimeter DMM 3706 with 20 channel-multiplexer card
  - Allows the detection of several sensors signals in voltage, current, or resistance, e.g., Pt100; controlled via PC
- LED array for simulation of daylight (power 2 W, supply 12 V)
  - Three spectral channels centered at about 430, 610, and 660 nm, respectively, provided by an array of light emitting diodes (LEDs).
  - The number of colored LEDs is weighted orientated on the daylight spectra. The LEDs are circularly arranged to illuminate the sample on the sample holder homogeneously.
- Rotating disk with provisions for up to eight samples
  - The disk can be used within the experimental chamber to circulate up to 8 different probes to the MINI-PAM and/or to illuminate the samples with Xenon light.
- LabView software for programming of control and analyses software for devices and measured values
- Dew-point hygrometer S8000 Integrale RS (Michell Instruments GmbH)
  - Measurement range 40 °C dew point (TP) to –80 °C FP ( $\pm 0.1$  °C).
  - Optical dew-point hygrometers are generally used as reference devices in humidity laboratories.

With this hardware including all instruments mentioned above and the software (Fig. 1), it is possible to simulate Earth but also Mars-like atmospheric conditions within the experimental chamber. The conditions are like it appears near the surface of Mars. Figure 2 shows an example of collected data of a biological experiment, measured with this equipment. The accuracy, response time,



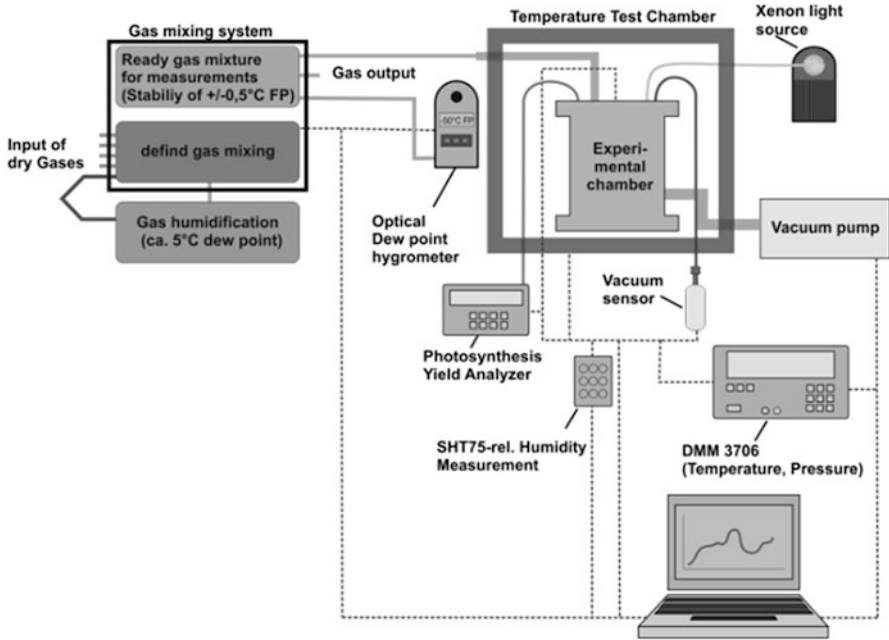


Figure 1. Experimental setup for a biological experiment.

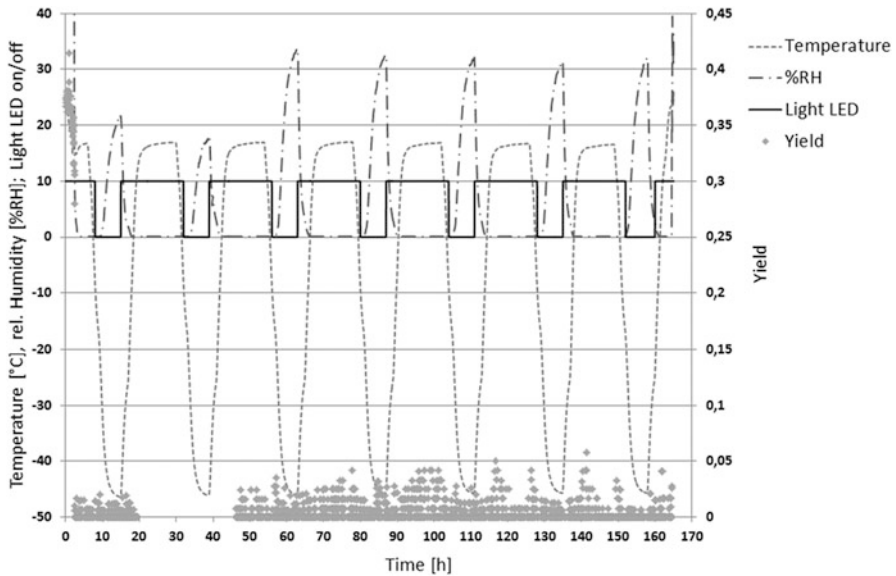


Figure 2. Results of a biological experiment inside the experimental chamber with the equipment shown in Fig. 1; temperature and rel. humidity [%RH] measured above the probe by a PT100 and aSHT75, applied light (LED Array) and photosynthetic activity yield (measured by MINI-PAM).

and in particular the reproducibility of the simulation facility allow to design, develop, and test sensors for trace humidity detection under Earth and Martian conditions.

### 3.1.1. Gas Mixing System (GMS)

The gas mixing system was developed to provide atmospheric humidity as well as gas composition as expected on Mars (Table 1). The central part of the GMS are nine mass flow controllers (one controller per inlet feeding, three outlets in total) which can dynamically apply humidity in a range of 5 °C TP to -73 °C FP at 101,325 Pa (Fig. 1) to a dedicated carrier gas that can be mixed within the GMS as well. When expanded to a pressure of 7 hPa (Table 1), the moisture content inside the experiment chamber amounts to a humidity in a range of -46 to -101 °C FP.

The moist gas is produced in scrubber bottles located in water bath thermostat allowing to maintain the humidity in the carrier gas at  $\pm 0.5$  °C FP.

The GMS can provide a carrier gas with volume flux of 150 L/h at 20 °C and 1,000 hPa that have been mixed from up to five constituents.

### 3.1.2. Experimental Chamber

The experimental chamber (EC) (Fig. 3) can be cooled separately from the Temperature Test Chamber. The EC is made of stainless steel, forming a cylinder with a volume of 10.3 L, and has an inner diameter of 20 cm and a height of 32 cm. There are feedthroughs at the top plate allowing gas inflow and outflow as well as pressure measurements. Moreover, there are two 50-pin D-Sub connectors for electrical signal routing and two openings for the MINI-PAM and Xenon light fiber optics. Two humidity sensors and two PT100 sensors are currently mounted inside the chamber. The gas outlet is connected to the membrane pump, allowing the evacuation down to 100 Pa with a volume flow 30 L/h (20 °C and 1,000 hPa) at 600 Pa.

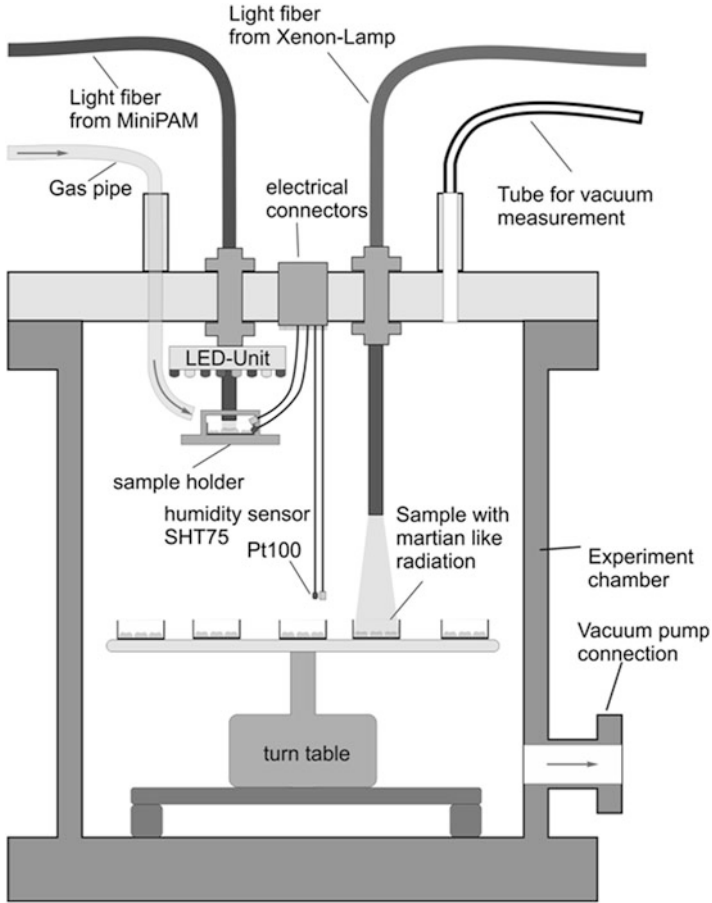
### 3.1.3. Humidity Measurement Cells

The cells are used for test and calibration of humidity sensors in combination with temperature sensors under low and medium vacuum with temperatures down to -70 °C. To improve the accuracy of the calibration, three measurement cells made of stainless steel are used, each providing two adapters for sensor installation (Fig. 4).

The cells are mounted for sensor tests inside the Temperature Test Chamber. Figure 6 shows the response of several humidity sensors accommodated within the described measurement cell.

### 3.1.4. Light Unit with 150 W Xenon Lamp and Light Fiber

The light of the 150 W Xenon lamp is led over optic components and a special light fiber into the experiment chamber. A collimation optic, inside the chamber mounted at the light fiber, creates a light spot with a diameter of approximately



**Figure 3.** Layout of the experimental chamber.

13–25 mm at a distance of 50–75 mm. The irradiation within this spot reaches the highest values in the main wavelength range of 200–400 nm which is similar to that on the Martian surface (Rettberg et al., 2004). This range is of particular interest for biological experiments. All optical components consist of silica glass to ensure the transmission of short wavelengths down to 190 nm through the entire light path. An irradiance calibration of this light system was performed in a range from 250 to 2,190 nm (Fig. 5).

A problem is the reduced irradiance at the same power within the spot over time. A reason could be a reduced transmission ability of the optical components caused by the transmitted light. Therefore, a measurement of the irradiance with an optometer is necessary, before and after an experiment.



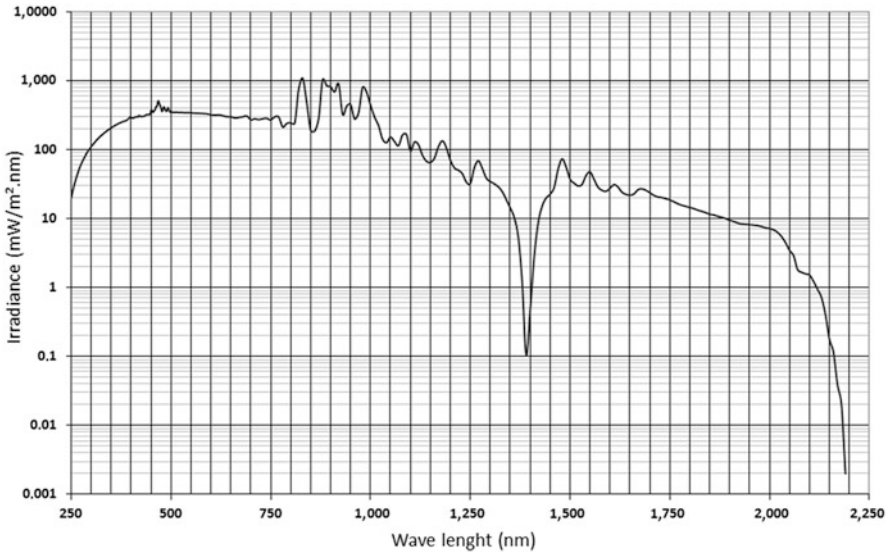
**Figure 4.** Humidity measurement cells inside the Temperature Test Chamber.

### 3.2. SELECTED SENSORS, REQUIREMENTS AND EXPERIENCES

This chapter reviews all the sensors that are used inside the simulation chamber, with a focus on the different types of humidity sensors due to their more stringent requirements in terms of accuracy and therefore to their higher risk of possible errors or failures.

#### 3.2.1. *Pressure Control*

The pressure is regulated by directly controlling the pump rotation and hence the pumping capacity via a dedicated control unit. The pressure inside the chamber is measured with a capacitive diaphragm transmitter CMR 361 in the range of 0.1–1,100 hPa with an accuracy of  $\pm 0.003\%$  of the full scale. The transmitter which is placed outside the climate chamber is connected via 2 mm stainless steel



**Figure 5.** 150 W Xenon lamp with light fiber optic at 6.6 A current and 7.5 cm distance from probe, calibrated at the “Kalibrierlabor für optische Strahlungsmessgrößen der Gigahertz-Optik GmbH” (Test equipment is reducible to national and/or international normal).

tubes (Length 1.5 m) to the EC or dedicated measurement cells. Considering that this configuration leads to a negligible dynamic pressure inside the tube, the induced measurement error can be neglected. A significant advantage of the pressure transmitter used here is its wide measurement range which allows to measure under both Mars and Earth conditions.

### 3.2.2. *MINI-PAM (Photosynthesis Yield Analyzer)*

The MINI-PAM (Walz GmbH) detects several fluorescence values caused by a light pulse on a biological sample. Based on this data, different specific values are calculated by the MINI-PAM. The most interesting one is the quantum yield of photochemical energy conversion (yield value), a degree for the photosynthesis activity of the biological sample and the values  $qP$ ,  $qN$ , and  $NPQ$  (fluorescence quenching parameters) which are measured if stress occurs in the biological sample (“Instruction manual for MINI-PAM,” 1999).

### 3.2.3. *Temperature Thermometers Pt100*

As mentioned in Sect. 3.1, the temperature inside the EC or measurement cells is regulated by the climate chamber. The temperature itself can be measured with 20 different thermistors, which can be accommodated where necessary, e.g., at the walls of the EC, above the samples, or at the inlet of the gas stream. They can be placed in the vicinity of the humidity sensors. The temperature is monitored with platinum resistance thermometers Pt100 (IST AG) because of their high precision,

linearity, stability, and therefore reproducibility over a wide temperature range (Bernhard, 2004). The response time of this sensor type at low gas velocities (0–1 m/s) can take up to several seconds but stays within an acceptable range for correct measurements during diurnal changes such as it occurred and has been observed on Mars.

The temperature measurement is extremely important for correct and precise monitoring of the relative humidity where inaccuracies of 0.5 °C can cause errors of  $\pm 0.3$  %. Temperature measurements with noncalibrated class A Pt100s are basically possible with an accuracy of  $< \pm 0.1$  °C but errors like self-heating, heat conduction, and imperfect connection and therefore variable heat resistances between the element to be monitored and the Pt element itself have to be added to this value. Especially the latter can lead to high inaccuracies if ignored at low pressure. The used DMM 3706 (Sect. 3.1) allows four-wire sensing which allows a precise detection of Pt100 values neglecting impedance contribution and contact resistances of the wires.

#### 3.2.4. Humidity Sensors

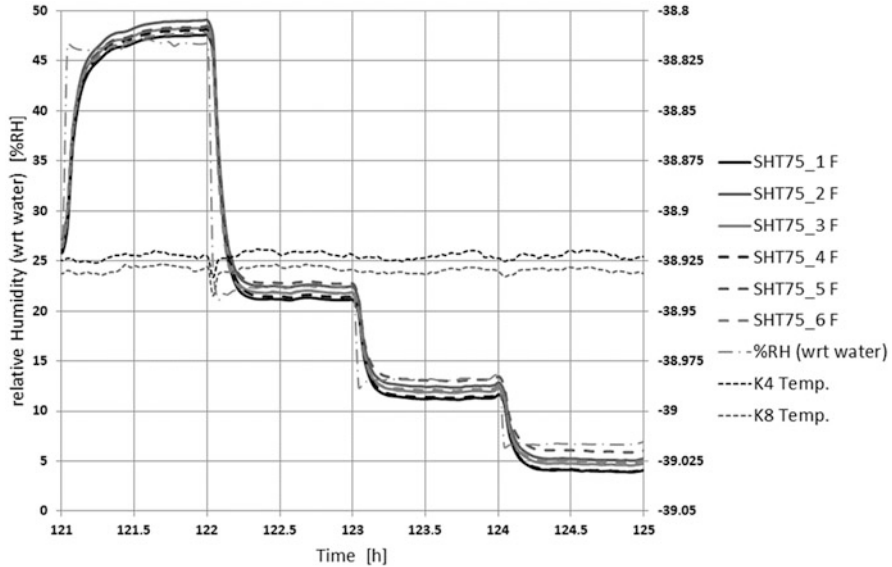
Since water is of extreme importance for habitability, special attention is paid to monitoring humidity within the range given in Table 1. Beside the capacitive and coulometric humidity sensors described hereafter, also hygrometers based on quartz-crystal oscillators or metal oxides and optical systems like dew-point hygrometers and TDLAS (tunable diode laser absorption spectroscopy) sensors are in use for humidity measurements (May et al., 2001).

In respect to requirements like small, “easy-to-use,” long-term stable, all the further-mentioned principles show disadvantages like the following: they need either a reference gas system (quartz-crystal oscillator); have high drifts in sensor characteristics, in particular at low humidity (metal-oxide meter); or require large amounts of space to be accommodated (optical dew-point hygrometer, TDLAS).

#### The Capacitive Humidity Sensor

A commercial off-the-shelf humidity sensor based on the capacitive principle has been used in combination with a coulometric sensor for the ESA ExoMars Project “MiniHUM” (Humboldt payload) for measuring the moisture content of the near-surface atmosphere on Mars. A similar type of this small and lightweight sensor has been used for NASA Phoenix Mars Lander and will be used on the NASA Curiosity rover, respectively (Zent et al., 2009), proving their capability to measure under these extreme conditions. This kind of sensors can measure in the range from 2 % RH to 98 % RH, with the best accuracies being reached between 10 and 90 % RH.

Currently sensor characteristics down to  $-40$  °C at normal pressure are available from the manufacturer though only a few publications are available, which are showing that also measurements were performed under more extreme environments with more applied lower pressures and temperatures (Smit et al., 2008). Measurements with SHT-75 sensors (Sensirion AG) at DLR had shown that these sensors take reliable measurements down to  $-70$  °C at a pressure of 8 hPa



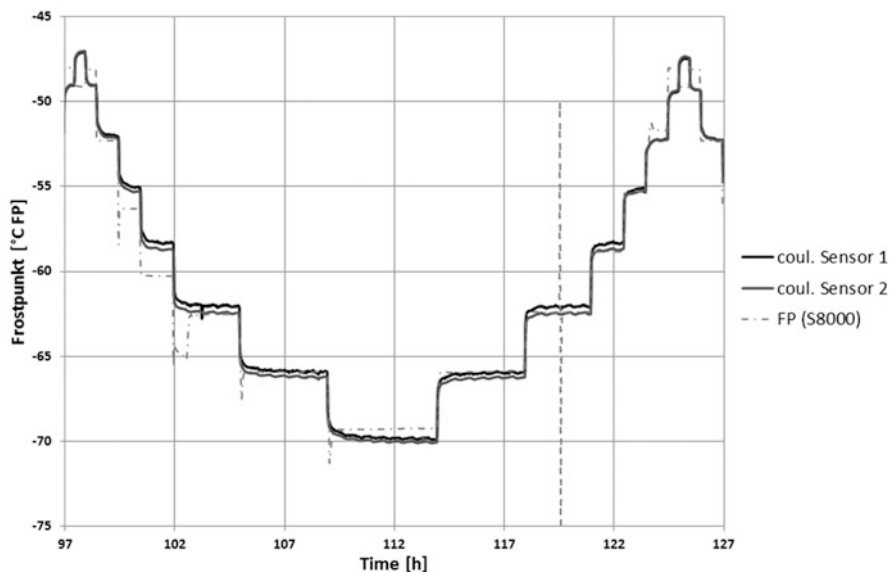
**Figure 6.** Response of six humidity sensors (SHT75) at 5 hPa and  $-39^{\circ}\text{C}$  with test gas air (measurement results from the SMADLUSEA project). Humidity reference was the dew-point mirror (% RH (wrt water) line), K4 K8 temp. lines show the gas temperature inside the measurement cells.

(Koncz et al., 2010). Figure 6 shows the sensor response of six different SHT-75 sensors at  $-40^{\circ}\text{C}$  and 5 hPa to different humidity levels. It can be seen that all the sensors follow almost exactly their implemented sensor characteristics and are therefore applicable to environmental conditions similar to those on Mars. However, these tests have also shown that especially at the lower and upper limits of the measurement range ( $<10$  and  $>90$  % RH), deviations of up to 20 % from the reference are possible, making a dedicated sensor calibration procedure necessary.

An important advantage of the capacitive sensor principle is that it does not affect the measured atmosphere itself. Due to this fact and because of their small overall dimensions ( $|19.5 \times 3.1 \times 5| \text{mm}^3$ ), the sensors are particularly convenient to be accommodated in the vicinity of the samples. Namely, for habitability experiments, the proximity of the sensors to the sample is important since measurements at DLR had shown that differences of up to 6 % RH between different sampling points are detectable due to locally varying temperatures in the EC.

#### Coulometric Humidity Sensor

The coulometric sensor is an electrolytic cell which is based on the very low water vapor pressure over Diphosphorpentoxid (at  $20^{\circ}\text{C} < 10^{-4}$  Pa (Wiberg and Wiberg, 1995)) serving as a trapping agent (Keidel, 1959). Because of its very hygroscopic nature lowest quantities of atmospheric water will be absorbed in the vicinity of



**Figure 7.** Response reaction of 2 coulometric sensors in air at 9 hPa and 23 °C (Measurement results from Koncz, 2012). The dew-point hygrometer (FP (S8000)-line) was used as a reference.

the sensor. When a potential is applied to the electrodes, the trapped water will be electrolyzed and the resulting current is directly related to the amount of absorbed water, as described by Faraday's law.

This sensor type is characterized by a high sensitivity at low water vapor contents in a range from  $-13$  to  $-90$  °C FP (Wernecke, 2003) and low cross sensitivity against other gases. This measurement principle was demonstrated to be functional in low vacuum (Wiedijk, 1980; Koncz, 2012) (Fig. 7) and at temperatures down to  $-50$  °C (Koncz, 2012).

At DLR this sensor principle was chosen in 2003 in order to realize an instrument (project MiniHUM (Koncz, 2012)) for in situ measurements of the near-surface atmospheric humidities in mid- and equatorial latitudes on Mars. In a joint project with an SMB (small- and medium-sized businesses), the spin-off of techniques and technologies has been used for developing a next generation coulometric sensor (HUMITRACE) (Lorek et al., 2010), mainly for industrial applications.

In the current project SMADLUSEA, this sensor is being characterized for applications under low and medium vacuum conditions and temperatures down to  $-70$  °C.

We expected that in the future it should be possible to detect also with this sensor the habitability parameter gas humidity in experiments under simulated Martian conditions.



### 3.3. CURRENT LABORATORY CAPABILITY AND PLANNED IMPROVEMENTS

Table 2 shows all measurement categories and parameters currently controlled in the MSF.

The experiences to date have shown that a relatively complex system, which is necessary to simulate a Mars-like atmosphere (Fig. 1), requires a high degree of technical know-how. The high number of prototypes and software programs controlling various devices and measurement values lead to a numerous sources of errors and require a continuous optimization.

Through our research we found that smaller experiment chambers, optimized for the specific requirements of a dedicated experiment, led to better results. For example, in smaller chambers, the relative humidity equilibrates faster at the same pump capacity because the surface-sorbing water molecules are smaller. Moreover, a change in temperature of the Temperature Test Chamber or in the gas mixture can balance faster.

**Table 2.** Measurement categories and ranges of experimental parameters.

<i>Measurement category</i>	Trace humidity in gases, relative humidity, water activity, material and soil moisture, pressure, temperature, photosynthetic activity, volume flow of gases, current, resistance, voltage, gas analysis
<i>Humidity</i>	Ranges of experiment parameters 5 °C DP to -73 °C FP at 1,023.25 hPa (measured) to -46 to -101 °C FP at 7 hPa (calculated)
<i>Pressure</i>	1 to 1,060 hPa
<i>Temperature</i>	-70 to 130 °C
<i>Gas mixture</i>	Maximum of five gases mixable (e.g., Air, CO <sub>2</sub> , N <sub>2</sub> , Ar, H <sub>2</sub> O, CH <sub>4</sub> ) Max. output 150 NI/h (at 20 °C and 1,013 hPa)
<i>Controlled time profiles</i>	Humidity, gas mixture, temperature, pressure, LED illumination
<i>Irradiation with Xenon lamp via fiber (inside EC)</i>	Spectral range from 0.19 to 2.2 µm with 0–0.4 W/m <sup>2</sup> nm on a 13 mm diameter spot

A further improvement could be made by using tubes with larger diameter for the carrier gas supply to the measuring cells in order to decrease as much as possible a pressure gradient at the inlet of the measurement cell. Therefore, heating of the pipes inside the Temperature Test Chamber would no longer be necessary, and the relative humidity inside the experiment chamber could be controlled much more precisely. In addition, the sorption of water vapor on the pipe and chamber walls could be avoided to a greater extent. As a result, a higher relative humidity could be achieved.

The experiment requirements do often vary. Therefore, a standardization of the measuring requirements is only partially possible. Nevertheless, any of the conducted experiments have a basic procedure in common, especially for temperature and primarily humidity measurements, and could therefore be comprehensively

described in a DIN or ISO standard. This would also enable different institutions or researchers to generally compare their results.

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# THE ROLE OF TERRESTRIAL ANALOGS IN THE EXPLORATION OF THE HABITABILITY OF MARTIAN EVAPORITIC ENVIRONMENTS

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## 1. Introduction

As a result of the US and European space exploration missions of the past and present decades, the geological and (paleo)environmental knowledge of Mars has rapidly increased. Excellent imagery data sets, combined with compositional data derived from land- and spacecraft-based spectrometers, have enabled the investigation of a number of surface areas, geological bodies, and mineralogical compositions through which reliable paleoenvironmental reconstructions have been attempted. In addition, radar equipment, such as the MARSIS instrument, on board the Mars Express Orbiter, and SHARAD, on the Mars Reconnaissance Orbiter (MRO), obtained subsurface stratigraphic data in key areas (e.g., the poles) for life on Mars (Plaut et al., 2007; Phillips et al., 2008). These combined reconstructions enabled the defining periods of the Martian past during which the conditions were remarkably different from those that are observed today on the red planet and, also, allowed determination of whether and when environments suitably habitable for life were established at some time in the history of Mars (Kargel, 2004; Ehlmann et al., 2011). Because life, as it is known on Earth, uses liquid water as a biosolvent, a key aspect for defining the habitability of a Martian environment is the unambiguous presence of liquid water on its surface or in the shallow subsurface. Such evidence also implies a further basic condition: a warmer, ancient Martian climate that is able to maintain liquid water masses (Beatty et al., 2005; Warner et al., 2010). In spite of extensive evidence suggesting that water played a role in shaping the surface of the red planet (Baker, 2001, 2006), however, there is still much debate about the evolution of its climate. Where does the heat come from? Did Mars have a greenhouse atmosphere able to warm the planet enough? Alternative hypotheses, such as impact effects and consequent prolonged rainfall (Segura et al., 2008), have, furthermore, been proposed for keeping sufficient flowing water able to form rivers, alluvial fans, and deltas, rather than a greenhouse-related warm and wet early planet.

Regardless of its origin, evidence of the action of liquid water from the Martian regolith also comes from the compositional data collected so far, including mineral compounds and their alteration phases (e.g., Bandfield, 2002; Bibring et al., 2006; Murchie et al., 2009; McGlynn et al., 2012). These data are crucial

for determining past environmental conditions with special reference to aqueous environments. Hydrated and other salt minerals, such as sulfates and chlorides, detected from different areas of the Martian surface, have been interpreted as the product of evaporite deposition from arid, hypersaline shallow basins (Gendrin et al., 2005; Osterloo et al., 2008, 2010; Murchie et al., 2009; Andrews-Hanna et al., 2010). Together with compositional data, this type of environment fits geomorphologic and stratigraphic evidence (Grotzinger et al., 2005; McLennan et al., 2005) of a transition toward a drier climate during the Siderikian period (Milliken et al., 2010).

The recent dramatic increase in our understanding of terrestrial extreme environments permits a more realistic structure of their biotic components and diversity. Apart from very high temperature materials (molten rock) and settings, any other terrestrial environment can support some form of life. Whereas, until recently, the biodiversity of extreme environments at the Earth's surface—for example, those highly salty, highly acidic, or highly alkaline environments or the environments strongly characterized by arsenic or other “poisonous” compounds—was assumed to be extremely low, direct field and laboratory investigations show that these environments host a wide variety of species. The example of highly salty environments is paradigmatic. In the Dead Sea, for example, one of the most extreme environments for microorganisms on Earth—in spite of the highest salt concentrations of terrestrial natural lakes, the unique ionic composition that is strongly inhibitory even to halophilic microorganisms (Oren, 1999), and the rapidly changing (increasingly harsh) conditions (Bodaker et al., 2009)—a considerable number of representatives of eukaryotes, archaeobacteria, eubacteria, and fungi have been documented (e.g., Oren, 1997, 1999; Kis-Papo et al., 2003; Ma et al., 2010). Continental hypersaline lakes are, therefore, useful for studying (1) diversity, density, and upper tolerance limits of microorganisms toward salt concentrations; (2) unfavorable ionic composition and other extreme environmental factors related to this type of environment; (3) the evidence in the geologic (evaporite rock) record of signatures suggestive of biologic activity and the ways for their detection; and (4) the habitability potential for Martian evaporite-derived environments.

Considering the abundance of salts on the Martian surface and shallow subsurface, salt tolerance should be considered an important requirement for (present or past) survival on the red planet.

The recognized potential of detecting traces of organics in shallow, saline lakes has received a recent confirmation by the landing site selected for NASA's Mars Science Laboratory rover Curiosity, in the Gale Crater, a site whose selection was also based on the potential for placing evidence of habitability in a stratigraphic context. The environmental evolution of the Gale Crater includes a series of processes governed by different aqueous and atmospheric processes and leading to the formation of a thick sedimentary succession inside the crater that also includes sulfate-bearing deposits presumably originated from playa environments (Andrews-Hanna et al., 2010; Niles and Michalski, 2012).

## 2. Continental Evaporite Environments: Physical Settings and Limits of Biotic Tolerance

### 2.1. PHYSICAL SETTINGS

Hydrological systems require adequate ionic concentrations and/or evaporation processes to precipitate evaporite minerals in continental aquatic environments waters. Compared to marine environments, those from nonmarine ones have less predictable ionic proportions (Warren, 2010), and this negatively reflects on the environmental stability and consequent problems of biotic adaptation. The main physicochemical constraints that make athalassohaline environments particularly stressful and challenging for biotic communities, therefore, depend on (1) the salt concentration and its recurrent short-time changes and (2) the ion types and their proportions. In addition, considering that these environments are mainly located in arid regions—most of the salt accumulation is consistent with the two belts of maximum aridity (Warren, 2006)—changes in moisture availability and the heating produced by intense solar radiation are other crucial biotic limiting factors. The interplay of the above factors in the evaporite environments can make the possibility of hosting halophilic communities, which, with few exceptions, are the only inhabitants of these environments, critical.

Research on polyextremophilic microorganisms—that is, those able to simultaneously endure different stressors (Rothschild and Mancinelli, 2001)—is rapidly expanding and shows how extremophiles can develop adaptive mechanisms to colonize and survive environments previously considered off-limits to life. As far as the halophiles are concerned, the definition of polyextremophile applies to the limited (at this stage) number of archaea that require the combined (triple) effect of  $\text{Na}^+$  concentrations of 1.7 M or greater, alkaline pH, and elevated ( $\geq 50^\circ\text{C}$ ) temperatures for their optimal growth (Bowers et al., 2009; Bowers and Wiegel, 2011). The ability of microorganisms to adapt to the high concentration of certain ions is documented in different hypersaline lakes. At the alkaline lakes of the Wadi El Natrun (Egypt), for example, new anaerobic halophilic alkalithermophiles adapted to extremely high ion requirements (e.g., 1.4 M  $\text{Cl}^-$  or greater) have been recently described (Mesbah et al., 2009; Mesbah and Wiegel, 2012).

Among the multiple forms of stress that characterize the nonmarine evaporite environments are sharp changes of salt concentration that appear as an effective factor limiting the environmental habitability. These changes depend on the recurrent phases of persisting aridity and rainfall/flooding (or other hydrological factors influencing the groundwater) that can change the concentration of salts in the water. Drought/rainfall alternations can profoundly alter the physical environments; a striking example is represented by the extremely rugged surfaces (clinkerlike textures, Stoertz and Ericksen, 1974) developed in different *salares* of the Atacama Desert (Barbieri and Stivaletta, 2011) (Fig. 1). Halobacteria use regulation of osmotic pressure to avoid water loss in hypersaline environments





**Figure 1.** Irregular salt flats from *salares* of the Atacama Desert (Chile). **(a)** Southeastern part of the Salar de Atacama: extremely irregular saline surface (clinkerlike texture) produced by repeated periods of drought (precipitation) and rainfall (dissolution). **(b)** Detail of a rugged surface from the Salar de Llamara.

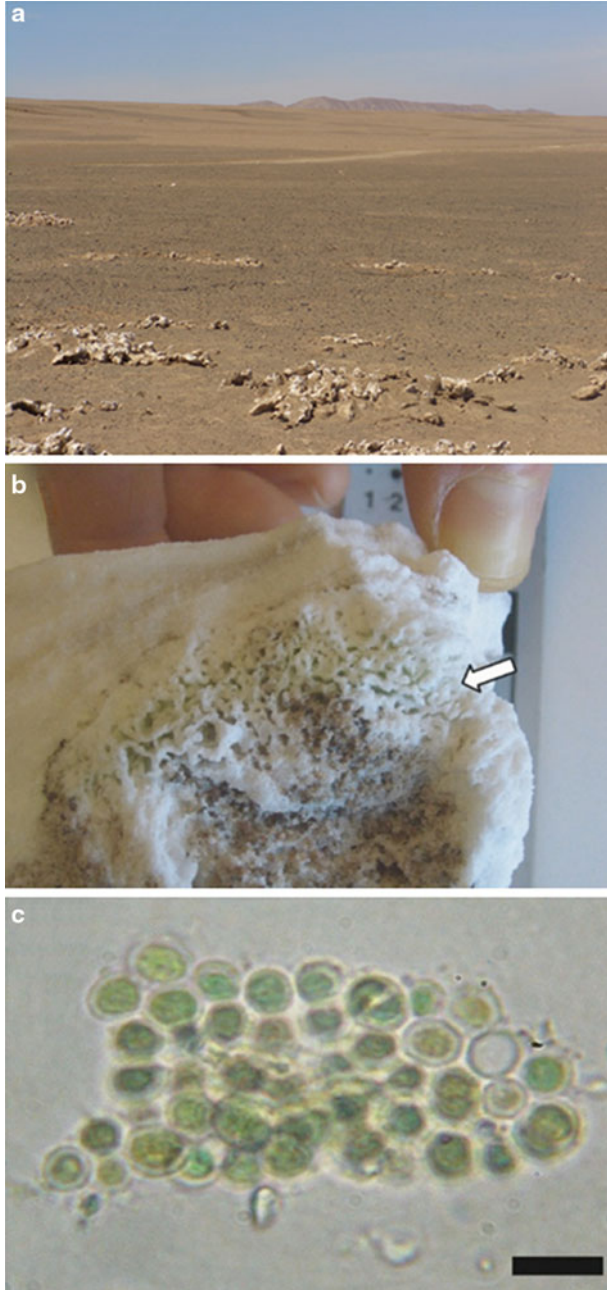
through well-described strategies (e.g., Grant et al., 1998), and, in the case of environmental disturbance caused by quick changes of the salinity, efficient mechanisms of osmoregulation have been described. Examples include the cyanobacterium *Synechococcus* 6311, which accumulates soluble sugar as an osmoregulatory response to increasing salinity (Blumwald et al., 1983) or, more recently, the strategy of the family Halobacteriaceae (such as the extremely halophilic *Halobacterium salinarum* NRC-1) that, in order to compensate for changes in sodium chloride concentrations, can balance the external osmotic pressure through the accumulation of intracellular inorganic cations (Leuko et al., 2009, cum bibl.). Halobacteriaceae dominate the communities of the extremely halophilic environments with high cell densities. They also include the extraordinary square-shaped haloarchaea (Walsby, 1980), first described from sabkhas near the Red Sea, that are characterized by a worldwide dominance where highly saline environments approach saturation.

## 2.2. LIMITS OF BIOTIC TOLERANCE

Research over the last decade indicates a higher biodiversity for halophiles than was previously assumed (Ma et al., 2010), and this largely depends on the broad range of salt concentration on which these microorganisms can grow. Even more surprising is the fact that polyextremophilic halophiles also display a remarkable biodiversity. This is shown, for instance, in the Dead Sea, where documented high archaeal diversity has to face a continuous increase of extreme environmental conditions because of the progressive lake desiccation (Bodaker et al., 2009, 2010).

Hyperhalophiles are far from having entirely revealed their functional secrets, and the following two examples can clarify this point: (1) the unusual finding of acidophilic haloarchaea that colonize alkaline-saline lakes (Minegishi et al., 2008) and (2) the recent, still open controversy over the bacterium from the hypersaline and highly alkaline Mono Lake, eastern California, able to use arsenic instead of phosphorus for constructing DNA and other key biomolecule backbones (Wolfe-Simon et al., 2011). If confirmed by further data, the latter finding could provide a substantial step in expanding the limits of life. Apart from their tolerance to arsenic-rich (thereby extreme) environments, microbes found in the Mono Lake sediments could, in fact, open the door to other forms of organized life different from those traditionally known with still unpredictable implications.

Although the above examples indicate that type and ion concentrations can establish net limits on habitability, the existence of physical environmental conditions that allow flowing water ranks first among the necessary prerequisites for the development of life in any terrestrial environment. With this respect, certain areas of the Atacama Desert (Fig. 2a) are important, and, because of their similarities with sectors of the Martian surface, they have been regarded as a convincing Mars environmental analog (Navarro-González et al., 2003). One further reason that makes Atacama a reliable terrestrial analog for the Martian



**Figure 2.** Salar Grande (Coastal Cordillera, Chile). (a) Panoramic view; the white spots in the foreground are fossil salt deposits. (b) Salt (halite) fresh-cut sample that exhibits the phenomenon of the deliquescence. (c) Transmitted light micrograph of cyanobacterial cells (*Chroococcidiopsis* sp.) colonizing the halite deposits of the Salar Grande. Scale bar 10  $\mu\text{m}$  (Image (c) reprinted with permission from Stivaletta et al., 2012).

environment is the strongly oxidizing chemistry imparted by high UV radiation levels. The combination of the hyperaridity and surface oxidative processes produces challenging conditions not only to the habitability but also for the preservation of the organic compounds.

In the Salar Grande—located close to the western coastal range, in the driest place of the Atacama Desert and, therefore, of the world (Parro et al., 2011; Wierzchos et al., 2011; Stivaletta et al., 2012)—rain is virtually absent. Because the area has been hydrologically inactive since at least the Pliocene, the only available moisture comes from some morning dew that allows for the phenomenon of the deliquescence (Davila et al., 2008; Azúa-Bustos et al., 2010) (Fig. 2b) that has been also detected well below the surface. In spite of its prohibitive conditions, the microbial communities inhabiting the very shallow subsoil of the Salar Grande—where the millimetric thickness of the salt rocks seems sufficient for providing at least minimum protection levels—include the association of bacteria belonging to Actinobacteria, Beta-Gammaproteobacteria and Firmicutes, and to endolithic cyanobacteria (*Chroococcidiopsis* sp., Fig. 2c) (Stivaletta et al., 2012).

The evaluation of the habitability potential in surface/subsurface deposits that formed during high evaporative rates is of particular interest in an astrobiological perspective, by considering the recognized abundance of this type of environments on Mars (Cabrol and Grin, 2010). Moreover, since the Martian surface is largely exposed to the effect of ionizing radiations, with expected severe effects on the preservation of organic molecules, if any (Kminek and Bada, 2006), a subsurface location, rather than the surface, could provide protection or, at least, sufficient radiation dose limits. In the context of subsurface exploration (down to 2 m) planned by ESA's ExoMars Mission (Zacny et al., 2008; McLennan et al., 2012) because of the lack of subsurface hydrology, the Salar Grande was chosen to perform a drilling campaign for testing subsurface life-detection instruments adapted to planetary exploration (Parro et al., 2011). Compared with the communities recovered from the surface of the Salar Grande, the subsurface microorganisms lack the cyanobacterium *Chroococcidiopsis*. This coccoidal, extremely desiccation-resistant cyanobacterium (Friedmann and Ocampo-Friedmann, 1995) is regarded as a polyextremophile because of its adaptability to hypersaline/hyperarid environments, temperature excursions, and the resistance to high doses of ionizing radiation (Billi et al., 2000). Because of its extreme tolerance, *Chroococcidiopsis* has been used as a model in space-condition experiments (Billi et al., 2011) where the species, in form of dried cells, survived simulated Martian UV flux. The ability of this taxon to deploy a special state, known as anhydrobiosis, for surviving long-lasting extreme desiccation (Billi and Potts, 2002), in association with its resistance to Martian analog UV radiation, makes *Chroococcidiopsis* a reliable candidate for tentative colonization of Martian areas in which the surface consists of transparent/translucent rocks as is the case of evaporite minerals.

### 2.3. WATER ACTIVITY: HABITABILITY AND CELL DENSITIES

Environments with higher salinity have reduced water activity. Because water activity has profound implications in the physiology of any living organism (see review by Schiraldi et al., 2012), it should be carefully considered in the evaluation of the habitability of a given environment, rather than the availability of water itself. Lower water activities, such as those induced with increasing salinity, tend to support, therefore, less microbial densities. Prokaryotes do not grow at water activity below 0.75 (Madigan et al., 2003) and this applies to extremely halophilic archaea and bacteria. On Earth, certain hypersaline environments display calculated water activities close to the lowest known levels to support life. In the Dead Sea water, for example, water activity ranges from 0.69 to 0.70, depending on the temperature (Krumgalz et al., 2000), making this environment critical even for extreme halophilic bacteria, such as *Halobacterium* and related organisms. The ecological limits given by water activity has, therefore, the final consequence that cells may experience some desiccation stress even if they still thrive in aqueous milieu.

Since the Martian atmosphere is characterized by very low moisture levels, the low water activity necessary for growth displayed by extreme halophiles has obvious interest. A puzzling and challenging problem in a comparative analysis between the terrestrial salt-bearing deposits and their Martian environmental analogs is the extremely low water activity values for evaporite mineral precipitation that have been calculated on Mars (Tosca et al., 2008). These calculated values are remarkably lower than 0.60, which is the putative lower limit enabling life on Earth (Oren, 2008). Of particular relevance is the ability of the haloarchaeon *Haloquadratum walsbyi* to live in low water activity environments, for which the presence of specific proteins that are able to provide an effective protection against desiccation has been suggested (Bolhuis et al., 2006).

In hypersaline environments rapid changes of their environmental factors profoundly influence the diversity structure and the cell densities of halophiles. Although diversity is necessarily restricted by adaptation requirements forced by the salinity, halophiles are highly diverse (Oren, 2002a), and also densities can rapidly reach high values and exceed  $10^7$ – $10^8$  cells  $\text{ml}^{-1}$  (DasSarma and Arora, 2001; Oren, 2002b). The coloration (e.g., bright pink) that can pervade a hypersaline lake, for example, indicates how intense the bloom of the population can be of halophiles that the lake harbors and, consequently, the increase of microbial cell densities (e.g., Buskey et al., 1998). Cell densities in hypersaline environments can also experience dramatic drops, for example, in case of a complete desiccation. Even in the latter case, however, some information on cell density can still be recovered by fluid inclusions preserved in evaporite crystals, especially in halite (Adamski et al., 2006), or, in the case of species adapted to long-lasting extreme desiccation, such as the cyanobacterium *Chroococcidiopsis*, by endospore accumulation (Billi and Potts, 2002). The sudden density changes and their measurements, including the means of detecting extremely rarefied densities of different categories of biomolecules (Nadeau et al., 2008), can provide useful information

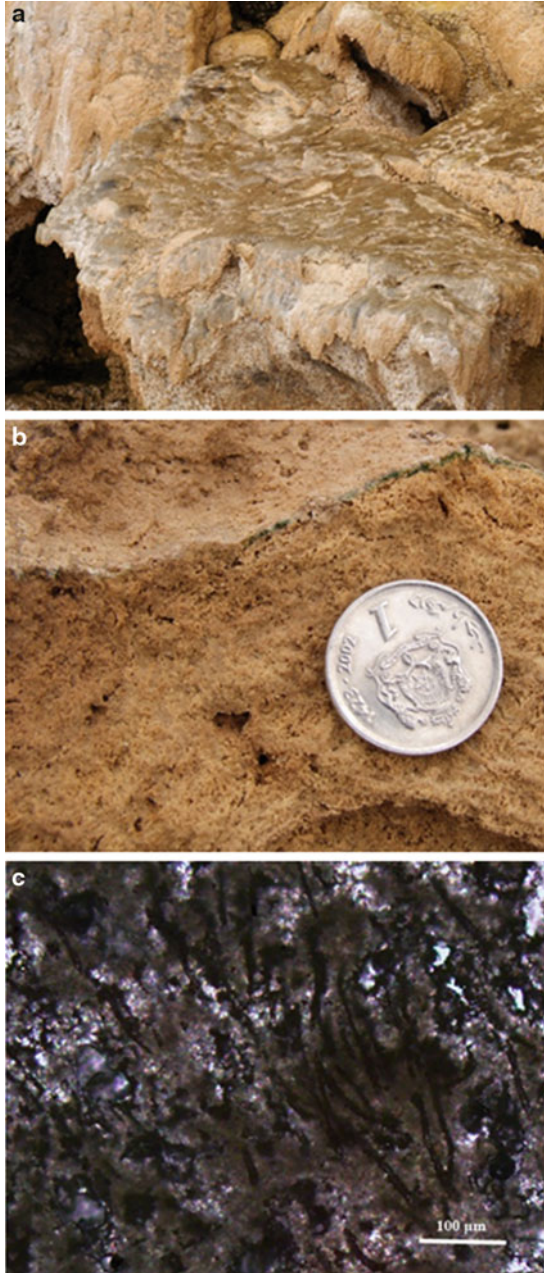
in an astrobiological perspective and in consideration of the type of payload on board the forthcoming new generation of Mars rovers (e.g., NASA's Curiosity of the MSL mission).

#### 2.4. PRESERVATION OF BIOSIGNATURES IN EVAPORITIC DEPOSITS

Since fluid inclusions may persist in the evaporite minerals for geologically significant periods of time and bacterial endospores have generally good preservation potential, both the examples mentioned in the previous section can, at least potentially, deliver to the fossil record some microbial remain. The somewhat controversial issue of the preservation potential of biosignatures in salt deposits, however, has not yet been completely solved. Limits to this potential depend on reasons that are mainly centered on the problems of (1) the evaporite mineral stability and its response to postdepositional changes (Hardie, 1984; Spencer, 2000) and (2) possible postdepositional contaminations and the difficulty of their identification (McGenity et al., 2000). All things considered, fossil evaporites remain a privileged site for the conservation of a variety of biological traces and a recent successful example is the world's oldest known cyanobacterial DNA isolated that comes from Late Miocene primary sulfates of an evaporitic environment (Panieri et al., 2010). Because of its low preservation potential and ease of contamination, however, recovery of fossil DNA is often ambiguous (Hebsgaard et al., 2005). Contrary to DNA, because of their high preservation potential principally due to the high thermodynamic stability (Love et al., 2008), lipid biomarkers are used with much greater degree of reliability to determine the source organisms even in very ancient rocks (Brocks et al., 1999) including evaporites.

### 3. Earth Versus Mars Evaporite Environments: Limits to Detecting Habitability

Similarly to the Earth, sulfate- and other salt-bearing deposits seem widespread on Mars, and, as previously stated, their stratigraphic settings and composition suggest a strong relationship with ancient aqueous environments. For example, layered rocks such as those encountered by the NASA rover Opportunity at Meridiani Planum seem to represent salt-bearing (eolian?) sandstones (Squyres et al., 2004) that abound on Earth in arid regions (e.g., Fig. 3). Martian salts, however, were presumably formed under different chemical conditions compared to the Earth, with aqueous alteration possibly related to high temperature and, as a consequence, differences in the ionic balance. For explaining the origin of mobile ions in the Martian regolith, Moore et al. (2010) suggested that the following possible explanations should be considered: alteration of basalts by hot hydrothermal fluids, precipitation of volcanic-derived aerosol/gas compounds, groundwater/igneous rock interactions, and, lastly, the falling of meteorites. Experiments on evaporite salts in simulated modern and ancient Martian conditions (e.g., Bullock



**Figure 3.** Sebkhat Oum Dba (Western Sahara, Morocco). (a) Mineral (carbonate and evaporites) precipitation in modern microbial mats that develop in shallow pools of groundwater (width of field of view is approx. 1 m). (b) Fresh-cut of eolian sand deposit cemented by carbonate, chloride, and sulfate salts derived from the evaporation of groundwater. Note the colonization (the upper horizon of green color) by endolithic cyanobacteria just beneath the surface of the rock. Coin equals 24 mm. (c) Cyanobacterial filaments with ongoing micrite impregnation induced by photosynthesis. Cross-section with normal stratigraphic orientation (Micrograph courtesy of Barbara Cavalazzi, The University of Bologna, Italy).

et al., 2004; Moore et al., 2010) have shown that ions and their abundance are different from those of Earth's marine and continental waters, suggesting, therefore, different mechanisms of salt formation in which the interactions between liquid water and igneous rocks (basalts) may have had a primary role.

On Earth, as well as on Mars, hydrous Mg sulfates abound in marine and continental evaporite environments. At Meridiani Planum Mg and Fe sulfates were estimated to reach more than 30 wt% (Vaniman et al., 2004; Christensen et al., 2004; Clark et al., 2005). The habitability of a site such as Meridiani Planum is assumed to be controlled by arid and acidic conditions (Knoll et al., 2005), which are two environmental requirements that are effective as biological limiting factors on Earth. The inference of an arid environment comes from the abundance of evaporite minerals, whose formation requires evaporation to dryness, whereas formation in acidic and highly saline ambient water is indicated by the presence of sulfate components that include jarosite, a potassium iron sulfate. Several terrestrial environmental analogs of the salt-rich strata of Meridiani Planum have been proposed for comparative investigation and one of the most convincing examples are Permian rocks from Kansas (Benison, 2006) deposited in and around acid saline lakes. The abundance of Mg sulfate is a common feature shared by Meridiani Planum, other Martian localities, and terrestrial saline environments, and this is another effective limiting factor to life because of the low water activity associated with the precipitation of this salt (Tosca et al., 2008). It should, therefore, be considered when interpreting the habitability of a Martian site. At Valles Marineris and other Martian locations, Mg sulfates (kieserite) have also been detected in association with gypsum (Bibring et al., 2005; Gendrin et al., 2005). A common genesis has been proposed for sulfate-rich deposits of Valles Marineris and Meridiani Planum, for which an origin from evaporite and diagenetic processes, largely governed by groundwater upwelling (Andrews-Hanna et al., 2010; Roach et al., 2010), contrasts with hypotheses involving icy weathering and atmospheric sources (Niles and Michalski, 2009; Michalski and Niles, 2012), such as sulfuric acid and H<sub>2</sub>O volcanic emissions, in which smaller volumes of liquid water are involved. This second hypothesis, although it envisages a different scenario, has a similar impact on habitability because the environment, as well as in the first hypothesis, remains acidic and highly saline.

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**PART IV:**  
**SEARCH FOR HABITABLE WORLDS**  
**IN THE SOLAR SYSTEM AND BEYOND**

**Westall**  
**Noack**  
**Breuer**  
**Kane**

Biodata of **Dr. Frances Westall**, author of “*Microbial Scale Habitability on Mars.*”

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# MICROBIAL SCALE HABITABILITY ON MARS

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## **1. Introduction: Habitability on Mars**

Ever since Schiaparelli's (1887) identification of channel structures on Mars and his later reflections on life on Mars (Schiaparelli, 1887), there has been an almost philosophical "need" for a companion form of life on another planet, Mars appearing to be the most likely candidate. Percival Lowell, who mistook the Italian "canali" for channels or artificially made "canals," as well as numerous other fiction authors, such as H.G. Wells and R. Bradbury, contributed to the popular perception of a sister planet teeming with life. Nevertheless, from a more scientific point of view, it is widely accepted that Mars has been habitable in the past, at least on a microbial scale, and may still be habitable under specific circumstances.

### **1.1. WATER**

Central to this view is the evidence for water on the surface of the planet since it is one of the main ingredients of life (together with carbon, bioessential elements including H, N, O, P, S, and energy), and the presence of water is, therefore, a defining criterion for habitability. On a planetary scale, the zone of habitability about a star is defined as the distance from the star at which water can exist in the liquid phase (Frank et al., 2000; Kasting and Catling, 2003). This distance varies throughout the lifetime of the star. Both Earth and Mars, during their early evolution, were outside the theoretical habitable zone, Earth just on the cold outer edge and Mars even further afield. However, high heat flow from the hotter mantles of the early planets (Buffet, 2003), fueled by the decomposition of short-lived radiogenic elements, such as potassium or aluminum, contributed to heating of the outer envelope of volatiles. As they cooled down, other phenomena are required to keep the surfaces of the planets above freezing. On Earth, a higher CO<sub>2</sub> pressure in the atmosphere or the presence of greenhouse gases, such as methane, has been invoked (Kasting, 1993; Haqq-Misra et al., 2008), although Rosing et al. (2010) suggest that the low-albedo conditions on the early Earth would have been sufficient to warm the atmosphere. The distance from the Sun was even more problematic for Mars. On the one hand, there are numerous geomorphological and mineralogical indications of liquid water existing at the surface of the planet



**Figure 1.** Planet-scale habitability. View of the Earth (*left*) from space centered on the Pacific Ocean – the early Earth was an ocean planet (NASA). Artist's impression of early Mars (*right*) with an ocean covering the northern plains (Free Software Foundation).

in its early history (the 6 mbar  $\text{CO}_2$  surface pressure of the present atmosphere precludes the continuous presence of liquid water on its surface; however, the early atmosphere may have been much more massive, with surface pressures up to several bars, sufficient to have created a modest global greenhouse (Kasting, 1997)). An ocean covering the northern plains has been proposed (Clifford and Parker, 2001) (Fig. 1), although if present was likely to have been short lived (Carr, 2006). However, there are a wide variety of other features, such as layered sediments, channels, gullies, and lakes (e.g., in Hellas Basin and the northern plains) that are strongly indicative of either flowing water or standing bodies of water on the planet's surface, potentially fed by rainfall and/or snowmelt (Carr, 2006 and references therein). These features are generally restricted to the Noachian (>3.7 Ga) and especially the Late Noachian (~3.7–3.82 Ga) period (Carr and Head, 2010). Layered material in some craters may represent, at least partly, sediments deposited in long-lived lakes, such as Gale Crater, the landing site for Mars Science Laboratory mission (Andrews-Hanna et al., 2012) or Mawrth Vallis (e.g., Loizeau et al., 2007, 2010). Numerous detections of hydrated minerals in Noachian materials attest to the alteration of volcanic lithologies by water, for example, phyllosilicates (e.g., Bibring et al., 2005, 2006; Carter et al., 2009), sulfates (e.g., McLennan et al., 2005), carbonate (Ehlmann et al., 2008; Morris et al., 2010), hydroxides (Klingelhöffer et al., 2004), and amorphous silica (opal, Squyres et al., 2008; Ruff et al., 2011). Modeling of the early Martian atmosphere is, however, proving problematic. These phenomena exist despite the

difficulties of modelers to find ways of warming the early atmosphere sufficiently to maintain liquid water at the surface. Additional greenhouse gases have also been proposed for the Martian atmosphere (Squyres and Kasting, 1994), but neither they nor the scattering effect of CO<sub>2</sub> ice clouds (Forget and Pierrehumbert, 1997) are adequate to keep the atmosphere warm enough. Recent attempts at taking the modeling into the third dimension (including the effect of a strong early adiabatic lapse rate) are equally unsuccessful (Forget et al., 2013). This has implications for the state of water on the surface of the early planet, and Clifford and Parker (2001) suggest that bodies of standing water may well have been ice covered.

If habitability is defined partly on the basis of liquid water, then the geomorphological and mineralogical evidence shows that the surface was habitable in its early history but became uninhabitable at the end of the Noachian/Early Hesperian (Carr and Head, 2010). Thus, the aqueous history of Mars is characterized by enormous spatial and temporal heterogeneity, extending even into younger epochs, the latter controlled perhaps by short-term climatic forcing (Andrews-Hanna and Lewis, 2011).

The importance of water for life led to water being the leitmotif of exploration for Mars. The NASA missions of the last decade have had the objective of “follow the water.” Hence, the enormously successful Mars Exploration Rovers (MERs) searched in particular for minerals formed in the presence of water and for sedimentological features providing evidence for aqueous activity. From their data and including the spectral data from the orbital missions (Mars Odyssey, Mars Express, Mars Reconnaissance Orbiter), it has become increasingly apparent that the mineralogical signature of aqueous activity has followed the changing climatic regimes on Mars throughout its history (Bibring et al., 2006). The earlier, more water-rich period of the Noachian is characterized by Fe and Mg phyllosilicates, the sulfates of the Hesperian record more acidic, dryer conditions, while the presence of metastable minerals on the surface, such as olivines, reflects extremely dry conditions in the later Amazonian period.

## 1.2. ORGANICS

Liquid water is just one of the main ingredients of life. Carbon and carbon molecules are also important ingredients. The two Viking landers that landed on the planet in 1976 analyzed Martian surface materials at two locations, searching for evidence of life on the basis of its expected organic constituents and metabolism. The results of the different experiments were conflicting. One experiment designed to provide evidence of microbial metabolization produced an enigmatic positive response (Levin and Straat, 1979), but the other experiments (one to detect gases potentially given off by microorganisms – the gas exchange experiment – and the pyrolytic release experiment to detect for metabolizing photosynthetic microorganisms (e.g., Horowitz et al., 1976)) gave negative

results, while the gas chromatograph-mass spectrometer did not measure any organic carbon in the Martian soil at all (Biemann et al., 1976). This latter result was all the more surprising because there is a continual rain of extraterrestrial materials containing organic molecules (from meteorites, comets, and cosmic dust particles) onto all the inner planets. For example, Maurette et al. (2001) calculate a flux of 20,000 tons/year of micrometeorites accreting on Earth at the present day. It was concluded that the labeled release experiment result was an artifact (Klein and Levin, 1976), and that the lack of organics in the surface soils indicated by the other two experiments was due to a combination of the presence of a strong oxidant (perchlorate was discovered by the Phoenix mission in 2008, Cull et al., 2010) and the long-term effects of UV radiation. However, more recent analogue investigations have demonstrated that the Viking GC-MS may not have been able to detect low levels of organics in soils (Navarro-Gonzales et al., 2006), and/or that, if organics had been there, they would have been destroyed during the experiment because of the interaction between perchlorates in the soil and the reagents of the experiment (Navarro-Gonzales et al., 2010). Thus, the question of whether the Viking experiments did or did not detect organics in the soils at the landing sites remains open. On the other hand, modeling of the combined effects of oxidant and ionizing radiation over very large periods of time by Kminek and Bada (2006) shows that, over periods of 3–4 billion years, organics in soils and rocks will be degraded to depths of up to at least 1.5 m.

Moving on from simply searching for signs of water as a signature of habitability, the current Mars mission, the Mars Science Laboratory (MSL) with its rover Curiosity, is searching for environments that may have been habitable in the past. Habitability has now become the leitmotiv of Martian exploration. This new slant takes into account all the criteria needed to define habitability (Grotzinger, 2009); that is, in addition to water and carbon, sources of energy and evidence for chemical disequilibria that can be tapped by microbes, as well as the presence of potential nutrients (Hoehler and Westall, 2010). Thus, the MSL mission seeks information on the geological context of the rocks and soils analyzed in order to better interpret the potential for habitable conditions, as well as any evidence for past life (Grotzinger et al., 2012).<sup>1</sup>

## 2. Scales of Habitability

The habitability of a planet or satellite can be considered on a wide range of scales. On a global to regional scale, habitable environments tend to be long lived, whereas local to microbial scales of habitability are short term (Fig. 1). The scales

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<sup>1</sup> Note in press: NASA has just announced that the landing site at Gale Crater was habitable since they have evidence for water, the bioessential elements C H N O P S, and the possibility of chemical energy.

of habitability are important when considering whether life could have emerged, whether conditions were only habitable for established life, or simply the survival of life. Whereas established life can exploit a short-lived habitable environment, such as a playa lake or hydrothermal spring, the appearance of life requires habitable conditions on longer time scales.

## 2.1. HABITABILITY SCALES FOR THE ORIGIN OF LIFE

Orgel (1998) estimated that the prebiotic processes leading to the formation of simple living cells took place on timescales ranging from hundreds of thousands of years to a few million years. On the geological timescale, this is fast, the kinetics of the succeeding reactions needing to be rapid so that the assembling molecules did not break down. Most likely a scenario of trial and error, the first cellular life probably appeared and became extinct many times over, depending on the environment, until it became efficient and established. Although the environment of the early Earth was extreme in comparison to the present-day planet (hot, highly volcanic, CO<sub>2</sub> atmosphere, overall neutral to slightly acidic seawater; Westall, 2005), it was covered by an ocean. It has been hypothesized that, between 4.0 and 3.85 Ga, the Earth was probably impacted by between 0 and 6 impactors large enough to completely vaporize all the oceans and thus sterilize its surface (Sleep et al., 1989). This period is known as the Late Heavy Bombardment (LHB), the cause of which is yet uncertain but may have been related to destabilization of the asteroid belt due to late-stage migration of the outer planets (Gomes et al., 2005). Recent modeling by Abramov and Mojzsis (2009) has shown that, at least for the period after planetary accretion, complete sterilization of the Earth's surface would not have been possible. Indeed, evidence for the Earth's record of life supports continuous habitability. If the Earth had been sterilized, life could not have appeared until after about 3.85 Ga. However, the rock record contains clear evidence for photosynthesis dating back to at least 3.5 Ga (Allwood et al., 2009; Westall et al., 2011a), if not by 3.8 Ga, when Rosing (1999) and Rosing and Frei (2004) postulate that the existence of oxygenic photosynthesizers is a strong counterargument to Sleep et al.'s (1989) hypothesis.

Thus, with a global ocean, there was global connectivity of the habitats in which life appeared, whether it was in a hydrothermal vent setting (Russell et al., 2010) or in the foamy swash on a volcanic beach (Deamer et al., 2002). This global connectivity was important because it permitted reestablishment of life after a major catastrophe, such as an asteroid impact, of which there were many during the LHB. This consideration is important because Mars was also influenced by the LHB. Once life is well established on a planet or satellite, it is very difficult to extinguish, at least on relatively short geological timescales (10s to 100 My). This is because chemotrophic life forms that obtain their carbon from organic substrates or CO<sub>2</sub> and their energy from the oxidation of organic carbon or redox reactions related to mineral/rock alteration can colonize fractures in the crust via

aquifers and low-temperature hydrothermal circulation. Obviously the depth to which the crust can be colonized depends on water availability and temperature. On Earth, the subsurface teems with life and metabolizing cells have been documented at depths down to 4 km in the continental crust (Onstott et al., 2006) and down to 2 km in deep-sea sediments (Ciobanu, 2012). If the cells can continue to metabolize in the subsurface, they will be the stock from which newly habitable surface environments can be colonized after catastrophes.

Thus, for life to emerge on Mars, the necessary environmental conditions need to be united over timescales of only up to a couple of million years. This implies the existence of bodies of water of a minimum size of  $\sim 100$  km or perhaps smaller if the bodies of water are continuously fed from a subterranean source (Westall et al., 2013a, b, submitted). As noted above, from a geological point of view, these timescales are very short and the spatial scale is small. A priori such habitats could have existed on early Mars. However, it is becoming increasingly evident that the planet has probably always been relatively dry. In a recent review, Ehlmann et al. (2011) note that, for much of its pre-Noachian-Noachian history, the water cycle on Mars was controlled by subsurface systems and that water existed at the surface in an episodic fashion. Nevertheless, based on geomorphological considerations, Carr (2006) considers that bodies of standing water must have existed in the larger basins, such as Hellas or in the northern plains. Moreover, dendritic river channels (Craddock and Howard, 2002) testify to precipitation, and there may even have been a northern ocean (Clifford and Parker, 2001). We can thus reasonably envisage that life could have appeared on Mars. Surface habitats would, however, have been heterogeneously distributed in time and space and would not have been connected. Thus, because of the limited or nonexistent connectivity of potential habitats on the surface of Mars, it is also reasonable to envisage the appearance of life in a number of different habitable locations on the planet at individually different points in time during the pre-Noachian-Noachian period. As on Earth, it is also possible that life appeared and became extinct before it could become well established in one locality because of degradation in the habitable conditions.

## 2.2. HABITABILITY SCALES FOR ESTABLISHED LIFE

Scales of habitat for well-established life are much shorter and smaller than those necessary for the emergence of life, of the order of 100s microns, cm, and even km for well-developed microbial mats and days to sometimes years (the latter again for microbial mats). Established life could colonize a newly available habitat, if it could be transported to that habitat, for instance, by flowing water through an upwelling aquifer or a low-temperature hydrothermal system that tapped into subsurface habitats, or in impact ejecta. Note that on Earth, subsurface permeability, while low, allows global scale circulation on timescales of  $10^8$ – $10^9$  years (Clifford, 1993). The number of potential habitats available in time and space will

be much larger than those required for the emergence of life, but the fact that they exist does not necessarily mean that they were (or still are) inhabited. As pointed out by Cockell et al. (2012), uninhabited habitats must be frequent on Mars because of the lack of connectivity between them. This has a practical implication for the choice of landing sites and the potential success of missions searching for traces of life, such as MSL. MSL may not find traces of life in Gale Crater, as carefully underlined by Grotzinger et al. (2012), despite its apparent habitability. Westall et al. (2013b) have recently evaluated the different scenarios regarding the possible presence of life at a particular landing site. Any potentially habitable area may not contain traces of life because life may never have emerged on Mars or it may have appeared but not in the landing site area. On the other hand, if life had emerged and had, at some stage, inhabited the landing site area, it may still not be detected because of heterogeneous preservation, or lack of preservation, of the biosignatures (cf. Summons et al., 2011), or the scale of the potential habitat, and, consequently, serendipity. The biosignatures may be undetectable because (1) they have been destroyed by postdiagenetic processes including UV and ionizing radiation; (2) they may have been destroyed by physical processes, such as erosion; (3) they may be below the limit of resolution of the instrumentation; or (4) they may exist but not in the locations examined by the rover.

MSL will be searching primarily for complex organic molecules that could only have been manufactured, to our understanding, by living cells. Other signatures that may be present include morphological features, such as microbially induced sedimentological structures (MISS, Noffke et al., 2003), biofabrics, and isotopic signatures (Summons et al., 2011). Westall et al. (2011b, 2013a, b) argued that microbial life on Mars is likely to have remained at a very small and primitive evolutionary stage because of the lack of continuous habitability and connectivity between the habitats. This has implications for the kinds of biosignatures preserved and for their potential detection in in situ instrumentation in a planetary mission. For instance, on Earth, many larger-scale biosignatures (mm, cm to m), such as MISS or biofabrics, or even large cells and/or colonies of cells, are produced by microorganisms that have developed photosynthesis. Photosynthesis on Earth evolved on a continuously habitable planet (not affected on a microbial scale by the LHB; cf. Abramov and Mojzsis, 2009) and was flourishing by 3.5 Ga. It may have been present by 3.8 Ga, as suggested by Rosing (1999) and Rosing and Frei (2004). But life on Earth could have appeared at any time after habitable conditions had been established, possibly by 4.4 Ga when there is evidence of water and hydrothermal circulation by 4.4 Ga (Wilde et al., 2001). These long-lived and continuously connected habitats did not exist on the surface of Mars. Moreover, in addition to the time factor, there is a strong likelihood that bodies of standing water on the planet were ice covered (Clifford and Parker, 2001), especially in the shallow water regions close to the edges of the basin, thus blocking access to sunlight. Photosynthesis and the mat-forming, sediment-controlling features that characterize photosynthetic microbial mats may not have appeared on Mars.

The environmental restrictions on Mars and their consequences for the evolution of life on the planet suggest that Martian life may have been (or may still be) surface bound and strictly chemotrophic (cf. Westall et al., 2011a, b). These life forms would have been initially associated with volcanic/hydrothermal substrates and minerals associated with these substrates. Further evolution may have permitted them to diversify to take advantage of other habitats and other ecological niches, such as evaporite environments.

### 2.3. HABITABILITY AND SURVIVAL

The limiting conditions of the Martian environment, especially at the surface of the planet, will be challenging to any life form. Knoll and Grotzinger (2006) and Tosca et al. (2008) note that, at the MER landing sites, the mineralogical indications of water activity indicate that there was too little water to sustain life in those locations. In addition, the oxidizing and radiation conditions at the surface are not conducive to the preservation of organic molecules, especially the lighter, more volatile molecules. Could life survive under these conditions? Numerous investigations of life in extreme environments and in laboratory simulations have vastly increased our understanding of the physicochemical limits of life. Life appears to be able to thrive or survive in the most extreme environments known. The upper temperature limit for thriving life is 121 °C (Kashefi and Lovely, 2003), and the lowest for viable cells is reported to be –20 °C (D’Amico et al., 2006). Life can survive in extremely acidic and extremely alkaline environments, in very saline environments, under high pressure (e.g., at depth under the sea), under arid conditions, and under high UV fluxes (Cox and Battista, 2005). However, in each situation, various survival strategies have been evolved. Sometimes the extremophile microorganisms can cope with more than one constraint (polyextremophiles), for example, both saline and acidic conditions (DasSarma and DasSarma, 2008). UV-resistant microbes, such as *Deinococcus radiodurans*, on the other hand, need full access to sources of carbon and nutrients, as well as water, because they need to continuously repair their genes and rapidly divide (every 30 min; DasSarma and DasSarma, 2008), all resource-intensive activities, in order to survive.

### 2.4. ANALOGUE STUDIES

There are many investigations documenting flourishing or surviving life forms in extreme environmental conditions of relevance to Mars. All of these investigations are related to the possibility of life forms being able to exploit a particular – microbial scale – habitat on Mars at some time in its past history and, even, in present-day conditions under certain circumstances. This presupposes that the ephemeral surface habitats could be colonized by viable life forms, that is, that a subsurface reservoir exists in which microbes could continue to metabolize and

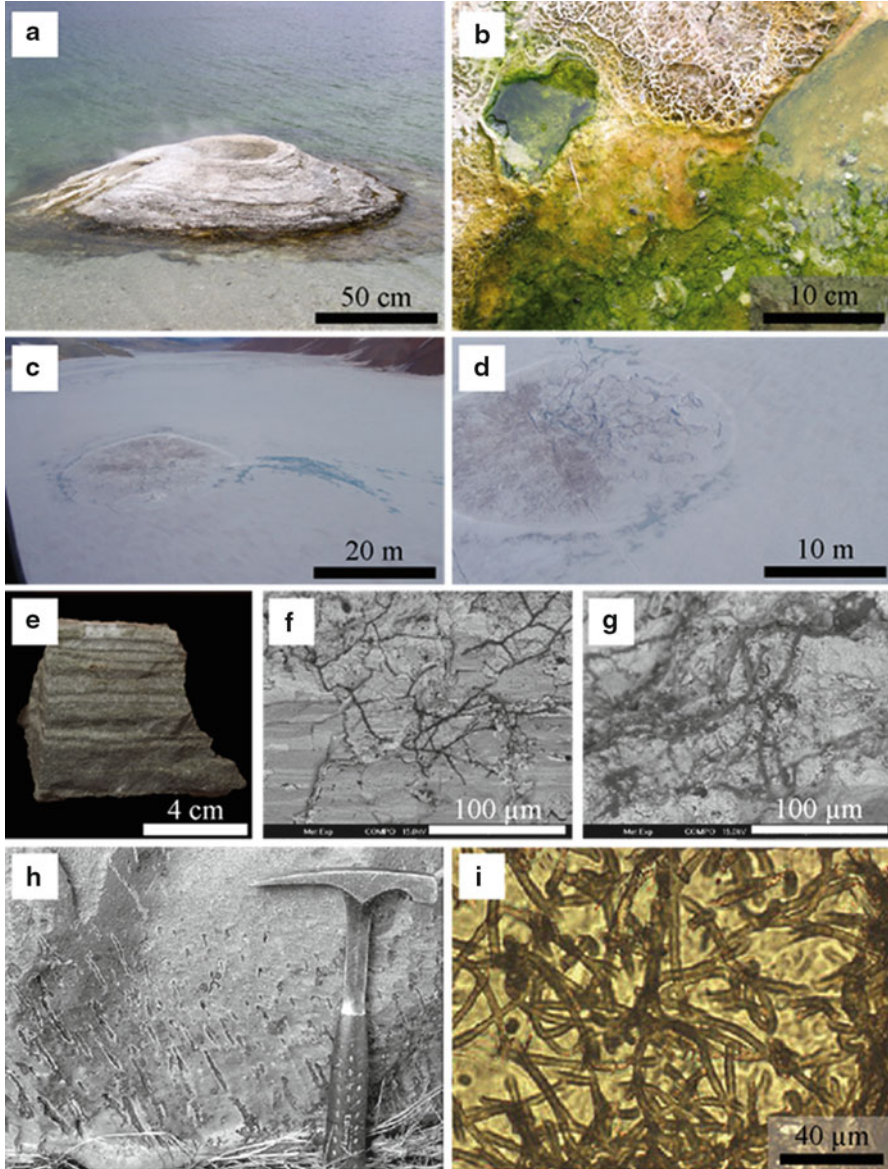


that, as noted above, the viable microbes could be transported into the short-lived habitat. Long-term survival of viable microorganisms for up to 5 My has been documented in Antarctic permafrost (Gilichinsky et al., 2007). If the subsurface were indeed the only habitat available to microorganisms after surface conditions became uninhabitable (about 3.5 Ga) (cf. Friedmann and Koriem, 1989), these same life forms would have to cope with a frozen water table, the cryosphere, as well as low-grade background radiation on timescales of up to billions of years, although liquid water could exist at greater depths in the crust. Indeed, evidence for liquid water in relatively recent times (Burr et al., 2002) indicates that subpermafrost groundwater persisted on Mars for a considerable length of time. We do not know the maximum length of time that a microorganism can survive without renewal and cell division, but it seems that 5 My is a minimum. However, 5 My is a very short time on the geological scales we are looking at on Mars, and the microorganisms would have needed regular access to liquid water, carbon, nutrients, and chemical energy, at least every 5 My. This could have been achieved by warming of the subsurface by hydrothermal circulation in association with volcanic, or impact activity. Under these circumstances, chemotrophs could not only survive but also periodically flourish if they were able to remain in a viable state until the environmental conditions improved. And the spatially habitable scales necessary would be microbial to local, not regional or global. Although there are a large number of constraints on the continued survival of life in the subsurface of Mars, the astonishing biomass in the subsurface of the Earth (Onstott et al., 2006) suggests that this scenario as a real possibility.

Accepting the possibility that ephemeral habitats could have been colonized by viable opportunists, there is a wide variety of investigations of analogue environments and microorganisms that are relevant to the survival of life on Mars throughout its history. The examples presented below and illustrated in Fig. 2 are just a few of a vast array of analogue studies to give an idea of the huge variety of habitats and the metabolic strategies the microorganisms have developed to cope with resource and environmental challenges.

Cockell et al. (2000) calculated the UV dose that would affect microorganisms on Mars and found that the DNA-weighted effect of UV radiation at the surface of the planet today would be 3.5 times higher than during the Noachian (the latter calculated at  $\sim 54 \text{ Wm}^2$ ). As noted above, microorganisms, such as *Deinococcus radiodurans*, not only survive but also flourish at much higher doses of UV but only when they are not limited by any other parameter, such as water or nutrient/carbon availability. On the other hand, a number of factors could counteract the effects of UV radiation on the Martian surface, including iron-containing soils, halite encrustations, polar snows, or protection by crystalline rocks (Cockell and Raven, 2004). This was also demonstrated in an experiment in which *Bacillus subtilis* spores exposed to UV radiation died except when they were coated with a protective layer of analogue Martian soil (Wassmann et al., 2012).

Many of the analogues studied concern the xerophilic conditions reigning on the planet for much of the last 3.5 Ga. In analogue terrestrial environments,



**Figure 2.** Extreme environments microbial habitats. (a) Geyser at Yellowstone Park. (b) Hydrothermal photosynthetic microbial mats in a spring at Yellowstone Park. (c, d) Hot spring under a glacier, Svalbard. (e) 3.8 Ga Banded Iron Formation (BIF) from Isua, Greenland (Westall and Folk, 2003). (f, g) Endolithic fungal hyphae in cracks in the BIF. (h) Vesicles in basalt can be habitats for chemolithotrophic microorganisms (B. Cavalazzi). (i) Fossilised chasmolithic microorganisms in basalt (Schumann et al. 2004).

for example, hot and cold deserts, resistance to UV is a considerable advantage to such organisms. Liquid water can exist at grain contacts in snow in polar environments at temperatures down to  $-20^{\circ}\text{C}$  (Price, 2000), and microorganisms isolated from the Siberian permafrost can metabolize at these temperatures (Gilichinsky et al., 2007). Jakosky et al. (2003) therefore conclude that the polar regions of Mars could be habitable under high-obliquity conditions. Other survival strategies in such regions include endolithic behavior whereby the rocks themselves protect the organisms from excess radiation and where water activity levels in the protected microhabitats can be maintained, for example, in cold deserts (cf. Westall and Folk, 2003) (Figs. 2e-g) or the impact-fractured crystalline rocks on Devon Island in the Canadian Arctic (Cockell et al., 2002).

Endolithic habitats occur not only in deserts or at high altitudes. Volcanic rocks can also host endolithic organisms. Chemolithotrophs inhabit lava tubes and caves in recent basalt flows (Léveillé and Datta, 2010) or vesicles in the surfaces of cooled pillow lavas (Cavalazzi et al., 2011) (Figs. 2h, i). In hot deserts, the surfaces of nutrient-rich volcanic rocks can host colonies of xerophilic epilithic organisms, including fungi, whose traces can be preserved by precipitations of Fe and Mn, known as desert varnish (Taylor-George et al., 1983; Allen et al., 2004).

Evidence for groundwater seepage in an arid environment at the landing site of the MER Rover Opportunity led to a spate of studies of similar terrestrial environments. Playa lakes on Mars were not only saline but also acidic, with sulfate as the dominant anion (Clark et al., 2005). Terrestrial saline lakes may become acid due to the presence of iron leached from the surrounding rocks, although the anions in these lakes are Cl-1 (Marion et al., 2008). These lakes host a diverse array of microorganisms (Mormile et al., 2009) demonstrating that such environments on Mars may be habitable. The microbial content of the iron-rich, acidic Rio Tinto River has also been extensively investigated as a Mars-analogue environment (Amils et al., 2007).

Salt-rich environments, such as brines, evaporites, or saline sediments, are extreme environments that are characterized by a rich diversity of halophilic microorganisms that have developed strategies to cope with the osmotic challenge of reduced water activity (Mancinelli, 2005). Salt-impregnated soils associated with playa lakes, such as in the Atacama Desert, the driest region on Earth, host diverse communities of microorganisms that are thus protected from UV radiation (Stivaletta et al., 2012).

Microorganisms can also live within fluid inclusions in salt crystals, the crystals providing UV protection and the organisms themselves having efficient gene repair mechanisms (McGenity et al., 2000). These and additional factors point toward the possibility of long-term survival of halophilic microorganisms entombed in salt. Moreover, the morphological plasticity of salt (encouraging the movement of fluid inclusions and the eventual replenishment of nutrients and

substrates for the microorganisms) and their physiological versatility helps adaptation to changing nutrient levels.

At the other end of the temperature scale, hydrothermal habitats are favored environments for potential Martian microbial life, not only because they are sources of energy and nutrients, and possibly carbon, but also because of their association with liquid water (Lederberg and Sagan, 1962). Prieur (2005) reviewed the microbiology associated with deep-sea hydrothermal vents, noting that anaerobic lithotrophic organisms inhabiting these environments could be useful analogues of Martian organisms. At the surface of the Earth, hot spring environments are often considered to be analogues for Mars, although here phototrophic organisms tend to compete for nutrient resources (Figs. 2a-d). However, study of the preservation of hot spring microbiota within siliceous sinters (Cady and Farmer, 1996) and calcareous deposits (Allen et al., 2000) is relevant for Mars.

Although acidic environments are commonly considered to be representative of Mars, especially from the Hesperian onward, alkaline-rich environments in relation to alteration of basic volcanic rocks have been postulated for early Mars (Bibring et al., 2006). Alkaline springs in similar terrestrial environments are proposed as mineralogical and microbial analogues for Mars. For example, Blank et al. (2009) have investigated the preservation of microbial biosignatures associated with the precipitation of Mg-Ca cements in methane-producing cold-water alkaline springs.

The previous overview considered modern terrestrial extremophiles and analogue environments. Early Mars, however, has an excellent terrestrial analogue in the sediments deposited on the Earth during the Archaean period. Environmental conditions, from a microbial point of view, were identical on both planets during their early histories (Westall, 2005). Volcanic sediments were deposited in water on a hotter, anaerobic, and hydrothermally very active planet Earth. Although life was already diversified by 3.5 Ga and included anaerobic photosynthesizers, the heterotrophic organisms and their traces are very similar to what could be found on Mars (Westall et al., 2011b). These organisms were small, <1  $\mu\text{m}$  in size, and formed monolayer colonies on the surfaces of the volcanic substrates. The Archaean seawater was saturated in silica, and, thus, the microorganisms were preserved through silicification. There was a very close relationship between life and hydrothermal activity at that period (Westall et al., 2006; van den Boorn et al., 2007). These are the kinds of life forms that could have appeared on Mars and whose signatures might have been preserved. The techniques adopted to study these traces are of relevance for those being used in the search for life on Mars. Indeed, although organic carbon is still associated with the physical traces and as disseminated organic matter sedimented with the detrital grains, the molecules are so ancient that they have lost their functional groups and become nothing more than PAHs. Nevertheless, although no “biomarker” molecules remain, the complexity of the remnant molecule fragments is evidence of their biogenic precursors (Derenne et al., 2008; Westall et al., 2011b).

### 3. Conclusions

The various temporal and spatial scales of habitability on Mars have strong implications for the emergence of life and its survival. Mars has always been relatively dry on a global scale, but in its early history, the presence of bodies of standing water containing the carbonaceous ingredients of life, as well as hydrothermal systems and water in contact with reactive minerals, on timescales up to a couple of million years suggests that life could have appeared. Once established, life could have acceded to the subsurface through fractures in the crust and groundwater circulation. However, the haphazard geographical and temporal distribution of these habitats, especially those on the surface, must have hindered the possibilities for evolution. It is thus unlikely that Martian life could have developed photosynthesis, for example. Nevertheless, the range of potentially habitable environments on Mars during the Noachian and even in younger periods is large. For example, spring environments, such as those identified in Arabia Terra (Allen and Oehler, 2008; Pondrelli et al., 2011) or even in Gale Crater (Schwenzer et al., 2012), where water from the subsurface has reached the surface, could be suitable locations to search for Martian life. Investigations of terrestrial microbes inhabiting the kinds of environments that could have occurred on Mars greatly enhance our understanding of the nature of that life and the preservation of its traces.

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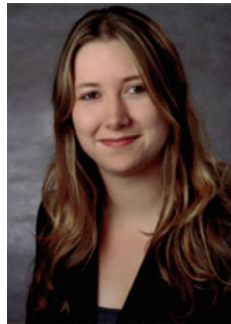
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# INTERIOR AND SURFACE DYNAMICS OF TERRESTRIAL BODIES AND THEIR IMPLICATIONS FOR THE HABITABILITY

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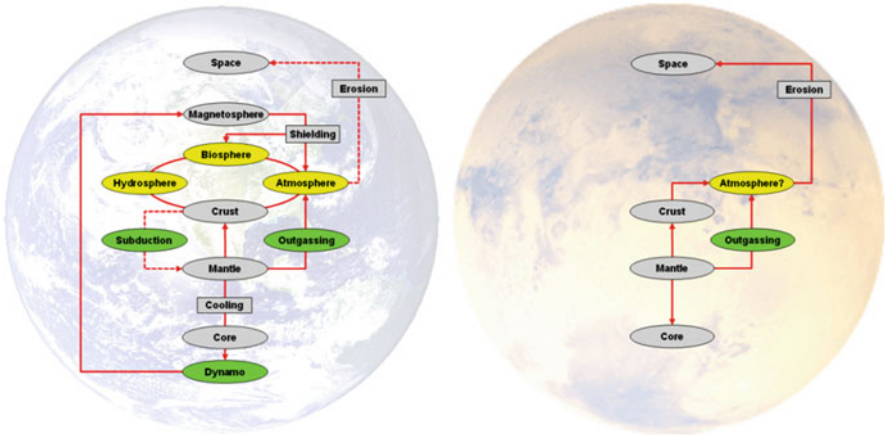
## 1. Plate Tectonics and Habitability

It has often been argued that plate tectonics may be strongly linked to the habitability of the Earth. In particular, the *Gaia hypothesis* proposes that life and the planet itself are closely connected to form a self-regulating complex system, maintaining the conditions for life on the planet (Lovelock and Margulis, 1974). This sensitive and complex system, however, depends on several feedback mechanisms coupling the atmosphere with the surface (oceans and continental surface) and the interior.

Figure 1 (after van Thienen et al., 2007) visualizes the potential role of plate tectonics for the origin and evolution of life (see e.g. Parnell, 2004; Ward and Brownlee, 2000). The left panel shows a simplified sketch that includes main processes on Earth, which are described in detail below. The sketch on right panel represents the processes on Mars on which plate tectonics is not active. The lack of plate tectonics may reduce the ability of a planet to become or remain habitable.

Starting from the inside out, subduction of the cold surface layer leads to a strong cooling of the interior and hence to a larger heat flux at the core-mantle boundary compared to a one-plate planet as Mars (Breuer and Spohn, 2003). This way, a magnetic dynamo generated in the fluid outer core of Earth may be maintained on long timescales (e.g. Stevenson, 2003). A magnetic field (i.e. the magnetosphere) protects the atmosphere against erosion from the solar wind (e.g. Dehant et al., 2007) and life from radiation. In case of the Earth, the magnetic field together with a strong gravitation protects the atmosphere from being strongly eroded – on Mars the weaker gravity and the missing magnetosphere at least since the last ~4 Ga may have resulted in the thin present-day atmosphere of only 6–10 mbar (compared to 1 bar on Earth); see, for example, Haberle et al. (2001).

The Earth's atmosphere contains greenhouse gases like carbon dioxide, water or methane which are fed into the atmosphere by outgassing during volcanic activity. On Venus, these greenhouse gases lead to high surface temperatures of about 460 °C (e.g. Taylor and Grinspoon, 2009), which makes life as we know it impossible at the surface of our sister planet. On Earth with its plate tectonics, the partial pressure of carbon dioxide in the atmosphere is buffered over geological



**Figure 1.** Visualization of the feedback cycles between interior and atmosphere for Earth and – in contrast – the limited coupling for a one-plate planet like Mars. Plate tectonics seems to be important for life due to regassing of volatiles, replenishing of nutrients and stabilization of the atmosphere due to the long-term carbon cycle. Furthermore, surface recycling cools the mantle efficiently, which leads to a high heat flux at the core-mantle boundary and can be helpful in maintaining a magnetic field (After van Thienen et al., 2007).

timescales by a negative feedback mechanism in which the rate of weathering of silicate minerals (followed by deposition of carbonate minerals) depends on the surface temperature. The occurrence of the so-called global carbon cycle as a consequence of plate tectonics saved the Earth from sharing the same fate as Venus with its dense atmosphere and high surface temperatures. Almost the total amount of carbon, which is present in the atmosphere of Venus, exists on Earth as well – but is deposited in chalkstones. Carbon is extracted from the atmosphere and incorporated into sediments via the silicate-carbon cycle. The extraction rate depends on the strength of rainfall and the area of land masses. If the atmospheric temperature increases for instance due to an increase in volcanic activity, enhanced rainfall washes the carbon out of the atmosphere resulting in a decrease of the surface temperature – decreasing surface temperatures on the other hand leads to a reduction of rainfall and weathering, and hence more  $\text{CO}_2$  remains in the atmosphere, resulting in a temperature increase (Kasting et al., 1988). This negative feedback mechanism of the silicate-carbon cycle keeps the surface temperature constant over a long time period.

The biosphere is expected to play a substantial part in the short-term carbon cycle due to both storage of carbon in shells and skeletons and by enhancement of the carbon-silicate cycle (e.g. Sundquist, 1993). Weathering leads to solution of carbon into water (carbonic acid) and possibly to an enrichment of the carbon concentration in the oceans. Dissolved carbon in the surface layer of the oceans can be exchanged with the atmosphere, such that the ocean can be seen as short-term regulating system of the carbon concentration in the atmosphere. However,

the buffering mechanism of the oceans has its limitations. Since life is a main factor of the buffering mechanism of the oceans (i.e. organic carbon, carbon-silicate cycle and photosynthesis), an increased oceanic acidity due to an increasing carbon concentration may slow down the precipitation of calcium carbonates and thus decrease the amount of carbon that the oceans can absorb. Here, plate tectonics sets in. On long, geological timescales, the oceanic crust including its carbon-rich upper layer (e.g. limestone built from organic carbon reservoirs) is subducted into the mantle. At the same time, new oceanic and continental crust (including replenished nutrients) is formed. It is questionable if an enhanced Earth-like CO<sub>2</sub> cycle can exist without the interaction of life.

The subduction of oceanic crust further transports water into the mantle, which is stored as hydrated minerals in the subducted material, leading amongst others to a reduced melting point of the silicate. At shallow depths, subducted basaltic crust is therefore remelted and forms the continental crust consisting of light granitic material. Parnell (2004) argued that this process was necessary for life to evolve in the way it was the case on Earth by influencing surface mineralogy. Furthermore, the existence of (proto-) continents may have been essential for the evolving complexity of life (e.g. Ward and Brownlee, 2000).

An interesting connection between the origin of life and the rise of continents has been suggested by Rosing et al. (2006) in arguing that the energy needed for the formation of light granite has been provided by photochemical-active microbes. Therefore, plate tectonics would be important for the development of life, which then would help to form the continents that are needed for more complex species to develop. Another process indicating the importance of plate tectonics for the origin of life may be found at the hydrothermal vents, where it has been suggested that life may have originated (e.g. Martin and Russell, 2003). These hydrothermal vents – so-called black and white smokers – are regions of volcanic activity in the oceans, mostly located directly at the plate boundaries, for example, at the mid-ocean ridges. Even though the temperature of the water streaming out of the vents is much larger than in the surrounding oceans (up to ~400 °C; e.g. Martin and Russell, 2003), several early life forms can be detected around the smokers, and chemical reactions lead to a sufficient energy source (to be used instead of photosynthesis). This environment reflects the conditions expected for early Earth and led to the idea that life may have originated in hydrothermal vents. Without plate tectonics, these smokers that originate at the plate boundaries would most likely not exist. The only volcanic activity to be expected would be hotspots, which are magmatic plumes in the mantle, from which melt may be erupted to form island chains like, for example, the Hawaiian Islands (due to the movement of the oceanic plate over the hotspot, several islands evolve with time).

The arguments listed above suggest that plate tectonics might be important for the habitability of the Earth and the evolution of Earth-like life. In the Solar System, plate tectonics is a rare phenomenon; the Earth is the only planet showing evidence of long-term plate tectonics. Thus, special conditions seem to exist on Earth, and it can be shown that this surface recycling depends on a series of factors,

for example, planetary mass, age of the planet (i.e. mantle temperature), water content in the interior, surface temperature (compare e.g. Earth and Venus), mantle rheology (reference viscosity and phase transitions), partial melt (crust development, density variations in the mantle and dehydration) and the possible influence of life on the mechanism of plate tectonics and continent forming.

## 2. Plate Tectonics on Earth

The planet in the Solar System that we know by far best is our own planet, which has been inhabited for several billions of years. Before space observations became available, the Earth in its wholeness was only difficult to observe. However, several centuries ago, travel reports and maps of the coastal lines of the different continents have been compared to each other, and astonishing similarities in the coastal lines of Africa and South America have been found (Ortelius, 1570); see Fig. 2a.

It was speculated at this time that the continents once belonged together and that the oceans may have formed due to a catastrophic flood. In the beginning of the last century, Alfred Wegener found not only a geophysical accordance (of geological deformations like shear zones) but also similar fossils and glacial traces on the costal lines separated by the Atlantic ocean (i.e. mainly between South America and Africa). He concluded that all continents may have belonged to one supercontinent some time ago (Wegener, 1912) and drifted away from each other.

Several explanations have been suggested for the continental drift at that time, ranging from planetary expansion of the Earth (Mantovani, 1889) or contraction (Suess, 1885) over polar flattening (Taylor, 1910) to assuming that the Moon once filled the pacific ocean before it separated from the Earth (Pickering, 1907). Wegener (1912) concluded that more investigations are needed to identify the driving mechanism behind the continental drift but already suggested that arbitrary flows in the interior could be the cause of the continental drift. A few decades later, Holmes (1944) speculated that convection in the mantle may have separated South America and Africa.

In the 1960s, several studies investigated the floor of the oceans and detected a correlation between age and distance of oceanic crust to a mid-ocean ridge (MOR), as well as remnant magnetization of the oceanic floor with regularly reversed polarity – indicating both a steady movement of the oceanic crust away from the MOR as well as regular reversed polarity of the magnetic field of Earth. These observations led to the idea of a steady sea-floor spreading (Dietz, 1961). The subduction of the oceanic crust beneath the less dense continental crust (see Fig. 4a for the simulation of subduction on Earth) is a logical consequence and has meanwhile been observed via seismic tomography (Grand, 2002). Plate tectonics is now a widely accepted fact on Earth as well as the supercontinent cycle, due to which in the past regularly supercontinents formed just to be ripped up again.

One of the main questions still to be answered – next to the questions about the mechanisms that trigger plate tectonics – concerns the age of plate tectonics





**Figure 2.** (a) Historical map of Earth which led to first thoughts about a possible continental drift from Ortelius (1570). (b) Modern map of Earth revealing the present-day continental sizes and their estimated ages, where *blue* is the youngest and *orange* the oldest (Archean) area (USGS, 2012).

on Earth. Ages ranging from the Cenozoic era (66 Myr to present) to the Archean era (~3.8–2.5 Gyr) have been determined for the continental crust; see Fig. 2b. The oldest minerals that have been found on Earth are zircons with an age of up to 4.4 billion years (e.g. Wilde et al., 2001) – with a chemistry pointing towards

granitic melt (e.g. remelted subducted basaltic crust) and a hydrosphere (i.e. liquid water at the surface). This suggests that plate tectonics as well as the oceans are at least 4.4 billion years old – just 150 Ma after the formation of Earth and 100 Ma after the Moon-forming impact (e.g. Arndt and Nisbet, 2012). However, it is speculated that on early Earth, a different resurfacing occurred, leading to remelting of basaltic crust without the need for plate tectonics. Also, several numerical studies conclude that plate tectonics was not very likely on early Earth due to a larger amount of radioactive heat sources and hence larger mantle temperatures at that time (e.g. O’Neill et al., 2007). Their results suggest that Earth’s mantle first had to cool sufficiently to be able to shift into the plate tectonics regime. Rosing et al. (2006) correlated the occurrence of life with a possible rapid increase in continent formation – which could indicate that plate tectonics started around 2.5 Gyr ago (and maybe was triggered by the additional energy obtained by surface microbes with photosynthesis); see Sect. 1.

## 2.1. MECHANISM OF PLATE TECTONICS

The crust and the oceans build the envelope of our planet, where the crust is separated in an oceanic crust (basaltic crust obtained by melting of mantle material) and continental crust (felsic crust, which forms due to multiple remelting of subducted oceanic crust and for which plate tectonics or a similar mechanism is needed). Plate tectonics is part of the convective system in the mantle, where thermal buoyancy leads to stirring of the mantle material on long timescales. One important criterion for plate tectonics to occur suggests that the upper rigid layer (lithosphere), which forms due to the cool surface temperature, needs to be deformed strongly such that it can be further dragged down by the mantle flow. This situation is given when the convective stresses are higher than the yield strength of the plate, the latter being a measure for the strength of rocks against deformation. Note, however, that this is a necessary criterion but not sufficient for plate tectonics.

To model the mantle flow and plate tectonics, it is assumed that the silicate mantle behaves like a fluid on geological timescales. For the simulation of the convective streams, the Navier–Stokes equation describing the fluid motion is used together with an energy equation (e.g. radioactive heat sources in mantle and crust). These partial differential equations are solved under several simplifying assumptions (e.g. incompressibility of the mantle) with modern numerical codes (mostly finite volume, finite element or spectral codes; see Noack and Tosi, 2013) on supercomputers.

In the convection models, for example, 2D or 3D geometry (either in a sphere or – to reduce the complexity of the problem – in a convection box), one then can trace local convective stresses. These stresses lead to a local deformation (weakening) of the lithosphere. In the simulations, this weakening is assumed to occur in a pseudo-plastic regime, where the local viscosity (which is the resistance of a material against motion) is reduced due to brittle deformation. The viscosity is reduced in the pseudo-plastic regime subject to the yield strength  $\sigma_{ys}$  of the

material, which depends on a friction coefficient  $\mu$  and the hydrostatic pressure  $p_h$  that increases linearly with depth (Byerlee, 1978).

$$\sigma_{YS} = 50 \text{ MPa} + \mu p_h \quad (1)$$

The yield strength is compared to the second invariant of the convective strain rate  $\dot{\epsilon}_{II}$ . The effective viscosity (for Newtonian material) is calculated via

$$\eta_{eff} = \min \left\{ \eta(T, p), \frac{\sigma_{YS}}{2\dot{\epsilon}_{II}} \right\} \quad (2)$$

Deformation therefore only occurs if the strain rate is large enough, such that the quotient of yield strength and twice the strain rate is smaller than the actual viscosity. Note that in the Newtonian rheology, the viscosity directly depends on temperature  $T$ , pressure  $p$  and grain size  $d$  (e.g. Karato and Wu, 1993). In the lithosphere of the Earth, however, the viscosity of the rock is better described by a non-Newtonian flow law, which depends on temperature, pressure and convective stress. For non-Newtonian materials, the effective viscosity is calculated in a similar way. However, since the Newtonian rheology has been observed to be the dominant rheology in several shear zones (e.g. Mehl and Hirth, 2008; Foley et al., 2012), Newtonian rheology is often used in plate tectonics simulations. Note also that the buoyant crust may also have an important influence on the existence of plate tectonics but is typically neglected in global convection models. Furthermore, elasticity of the lithosphere is rarely considered in plate tectonics simulations.

Once the convective stress ( $\sigma = 2\eta\dot{\epsilon}_{II}$ ) exceeds the yield strength such that the viscosity is reduced, local deformation in the lithosphere may lead to a separation of the upper conductive layer into several small plates. Additional convective forces are needed to drag surface material downwards into the mantle and push oceanic plates away from the mid-ocean ridges (or separating continents as is happening presently with Africa, which is split up due to a super-plume formed beneath the continent) – and therefore leading to subduction and ongoing plate tectonics. This view of plate tectonics on planets is a simplified model and may not consider all relevant aspects discussed so far – for example, the influence of protocontinents (e.g. Yoshida, 2010; Rolf and Tackley, 2011; Cooper et al., 2006), the influence of layered convection (e.g. Condie, 1998) or the effect of initial conditions on the resulting surface regime (Weller and Lenardic, 2012). This approach can be used, however, to study first-order effects on the initiation of plate tectonics such as the influence of the surface temperature and the mass of a planet.

Some of the main results of these basic investigations can be summarized as follows:

- Water in the lithosphere, for example, as hydrated minerals, reduces its yield strength and may favour the existence of plate tectonics (e.g. Korenaga, 2010).
- High surface temperatures lead to a fast healing of (plastically) deformed material (Landuyt and Bercovici, 2009) as well as to reduced convective stresses (O'Neill et al., 2007), both making plate tectonics less likely than assuming lower surface temperatures by comparison.

- An increasing amount of radioactive heat sources or a warmer mantle reduces the likeliness of plate tectonics (e.g. Crowley and O’Connell, 2012; Stein et al., 2011).
- Larger so-called Rayleigh numbers (being a measure for the thermal buoyancy against resistance and therefore correlated to large convective velocities) lead to larger convective stresses (e.g. Stein et al., 2004).

Several studies have been published in the recent years concerning the likelihood of plate tectonics on exoplanets. Depending on the parameters used (which are mostly not well constrained for large exoplanets), plate tectonics has been found to be either more likely than on Earth (a larger planet suggests an increased Rayleigh number and thus increased convective stresses (Valencia et al., 2007; van Heck and Tackley, 2011)), less likely than on Earth (a larger planet is hotter due to increased heat production rate number and thus shows reduced convective stresses (Stein et al., 2011)) or equally likely (Korenaga, 2010). In the latter case, it is suggested that other factors such as the presence of water play a larger role in the existence of plate tectonics.

For planets smaller than Earth, the above-mentioned trends concerning the likelihood of plate tectonics are also self-contradictory. The smaller planet would lead to smaller Rayleigh numbers than on Earth and should therefore lead to a one-plate planet with an immobile lithosphere. However, an expected lower mantle temperature – since the total amount of radioactive heat sources in the mantle is smaller than on Earth – should foster plate tectonics. Note that the observed trends have been obtained for steady-state simulations (e.g. heat sources are constant and core cooling is neglected) and can be different if the thermal evolution of a planet is considered. We therefore simulate the thermal evolution of Earth-like planets (see Sect. 3) assuming either a smaller radius, a higher surface temperature or a larger core radius compared to Earth values; see Table 1 for the applied parameters and initial temperatures. The results of these findings will then be discussed and used to argue why the Earth is the only planetary body in our Solar System acting in the plate tectonics regime.

### 3. Plate Tectonics and Habitability of Other Terrestrial Bodies in the Solar System

#### 3.1. MARS

For a long time, scientists speculate about life and oceans on Mars. Based on telescope observations, Giovanni Schiaparelli published a map of the Martian surface in 1877 (republished in Schiaparelli, 1893) showing not only riverlike structures but also a dichotomy of the northern and the southern hemisphere. The smooth and shallow surface in the North was interpreted as a water ocean (named *Mare Australe*), and the visible *canali* (channels) (see Fig. 3a) gave way to wild speculations about intelligent life on Mars (e.g. Mumford, 1909), since they

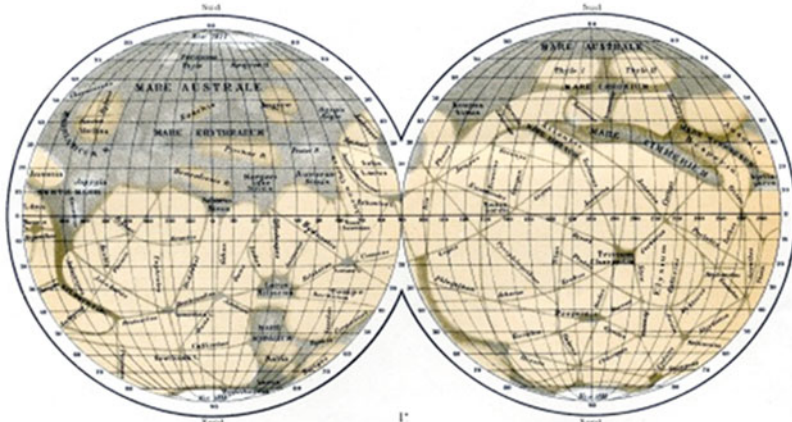
looked like artificial constructed channels. The *canali* have alternatively been interpreted to be either rivers connecting the poles with each other or “lines of vegetation” (Pickering, 1926).

The first detailed photographs of Mars (Mariner 4 in 1965 and Mariner 6 and 7 in 1969 (Collins 1971)) instead revealed a red (oxidized) surface without any evidence for water or life at all – and no large canals could be observed. The view of the Martian surface, however, changed again with the Viking mission (e.g. Toulmin et al., 1977 and later with Mars Express Poulet et al., 2005). Data of these missions indicate a wet past of the planet from its surface morphology and hydrated minerals, even though stable liquid water does not exist at the surface due to the present-day surface temperature of  $-55^{\circ}\text{C}$  (locally the temperature can rise above the freezing point during summer (Haberle et al., 2001)). Later the NASA rover Phoenix excavated a water ice layer beneath the red sand cover (Smith et al., 2009) – until then ice has only been detected at the poles.

How much water was present on the Martian surface is extensively debated. Some studies suggest an early ocean (e.g. Baker et al., 1991; Head et al., 1999), but others argue that Mars was wet only for a short (and maybe only episodic) time (e.g. Craddock and Howard, 2002) and maybe only liquid water in the subsurface occurred (e.g. Ehlmann et al., 2011). The latter models are also favoured by coupled atmosphere and interior models (Lammer et al., 2013) which predict that the atmosphere has never been dense enough to allow for liquid water at the surface for a longer time period. If – from the earliest times on – most water was indeed present in the subsurface of Mars, the implications for a possible habitability of Mars are severe. It might restrict the place where life could possibly have formed, survived and developed over the last billions of years to the subsurface (analogous to the deep biosphere on Earth; see Gold, 1992; Farmer and Des Marais, 1999), where liquid water may still exist.

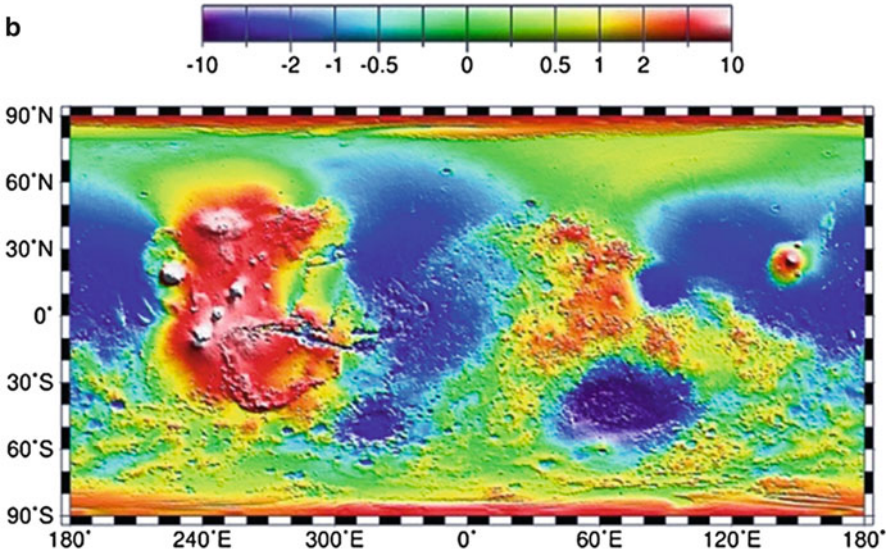
The space missions also revealed the so-called crustal dichotomy (see Fig. 3b) with a smooth northern hemisphere that seems to be several hundreds of million years younger than the southern, heavily cratered part and the remnant magnetization mostly of the oldest crust (Frey, 2006). The latter suggests the existence of an early magnetic field in Mars (e.g. Connerney et al., 1999; Zuber, 2001) and led to the speculation of early plate tectonics on Mars (Sleep, 1994; Nimmo and Stevenson, 2000; Lenardic et al., 2004). Early plate tectonics allows a strong cooling of the mantle and could be a likely driver of a thermal dynamo, where a large (superadiabatic) heat flux out of the core can lead to strong convection in the core and can induce a magnetic field – consistent with the findings. However, plate tectonics seems to be less realistic since no geological evidence of, for example, subduction zones could be found (e.g. Nimmo and Tanaka, 2005). Furthermore, it is difficult to explain the observed crustal evolution with early plate-tectonics-induced mantle cooling (Breuer and Spohn, 2003). Alternative scenarios for the crustal dichotomy are for instance an impact-induced differentiation process (Golabek et al., 2011) or low-degree convection (Roberts and Zhong, 2006; Keller and Tackley 2009).

a



Carta generale del Pianeta Marte  
secondo le osservazioni fatte a Milano  
dal 1877 al presente

b



**Figure 3.** (a) Historical map of Mars by Giovanni Schiaparelli showing not only the dichotomy of the planet but also several *canali*; Schiaparelli (1893). (b) A MOLA topographic map of Mars showing the northern lowlands and the heavily cratered southern highlands (NASA, 2012) with elevation in km.

To investigate if plate tectonics should, in general, be possible on a small planet like Mars, we simulate a Mars-sized planet in comparison to an Earth-sized planet with a radius of 6,371 km and use half the radius of Earth for the Mars case. The ratio of core radius to planet radius is kept Earth-like with 0.55; the average mantle density was reduced from 4,500 to 3,000 kg/m<sup>3</sup>, and the gravity

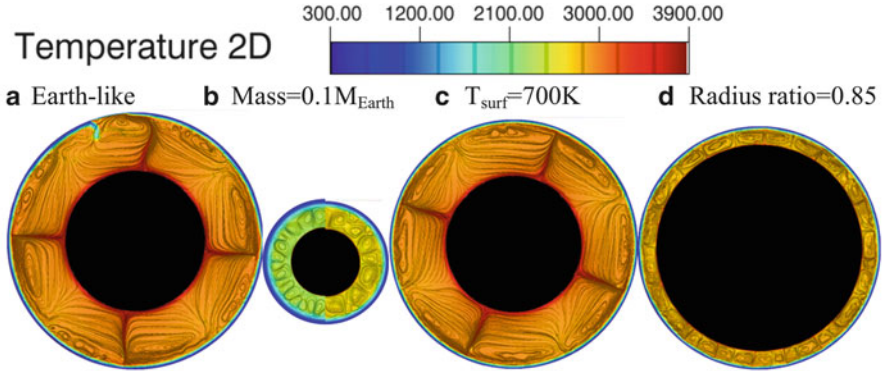
acceleration is 3.4 instead of 9.81 m/s<sup>2</sup>. For both simulations we apply an Earth-like composition and use a pseudo-plastic rheology (e.g. Tackley, 1998), such that the viscosity is reduced if large convective stresses are applied. We use Earth-like parameters in our model but assume an increased reference viscosity of 10<sup>23</sup> Pas for numerical reasons. To compensate the effect of weaker convection on plate tectonics due to the increased viscosity (which may also lead to weaker convective stresses), we had to reduce the friction coefficient obtained by laboratory experiments (Byerlee, 1978) to  $\mu = 0.06$  (compare Eq. 1), such that plate tectonics initiates for the Earth model. We assume a wet olivine-dominated rheology using the Arrhenius law and employ an activation energy of  $E^* = 240$  kJ/mol and an activation volume of  $V^* = 2.5$  cm<sup>3</sup>/mol (Karato and Wu, 1993). We neglect compressible effects and use a constant surface temperature, a cooling boundary condition (i.e. the core temperature decreases with time due to mantle cooling) and decaying radioactive heat sources to assess the thermal evolution of the planets. To investigate if the initial core-mantle boundary (CMB) temperature has an effect on the likelihood of plate tectonics on the smaller planet, we either assume an initial core temperature of 3,900 K (analogous to the applied CMB temperature for the Earth case following Kawai and Tsuchiva, 2009) or use a lower CMB temperature of 2,000 K. For detailed information on the initial parameters for all simulations, confer Table 1.

Figure 4 shows a comparison of the convection pattern of an Earth-sized body and a Mars-sized body after 4.5 Gyr of evolution corresponding to the age of the terrestrial planets in the Solar System. While for the Earth-sized planet subduction locally initiates (Fig. 4a – at 3.3 Gyr), the Mars-sized planet instead forms a thick stagnant lid (Fig. 4b; the left half of the panel shows the case with initially 3,900 K at the CMB, and the right half shows the case with initially 2,000 K, both after 4.5 Gyr).

**Table 1.** Initial conditions and parameters used for the 2D convection simulations in Fig. 4.

Case	a	b	c	d
Radius planet	6,371 km	3,185 km	6,371 km	6,371 km
Radius core	3,504 km	1,752 km	3,504 km	5,415 km
Surface temp.	300 K	300 K	300 K	700 K
Initial mantle temp.	2,000 K	2,000 K	2,000 K	2,000 K
Initial CMB temp.	3,900 K	2,000/3,900 K	3,900 K	3,900 K
Density mantle	4,500 kg/m <sup>3</sup>	3,000 kg/m <sup>3</sup>	4,500 kg/m <sup>3</sup>	4,500 kg/m <sup>3</sup>
Gravity acceleration	9.81 m/s <sup>2</sup>	3.4 m/s <sup>2</sup>	9.81 m/s <sup>2</sup>	9.81 m/s <sup>2</sup>
Ref. Rayleigh number	$7.6 \times 10^5$	$1.0 \times 10^4 / 2.2 \times 10^4$	$7.6 \times 10^5$	$2.8 \times 10^4$
Initial heat sources	$2 \times 10^{-11}$ W/kg	$2 \times 10^{-11}$ W/kg	$2 \times 10^{-11}$ W/kg	$2 \times 10^{-11}$ W/kg
Heat sources at 4.5 Gyr	$4.4 \times 10^{-12}$ W/kg	$4.4 \times 10^{-12}$ W/kg	$4.4 \times 10^{-12}$ W/kg	$4.4 \times 10^{-12}$ W/kg

The reference Rayleigh number is defined at the reference viscosity, which is 10<sup>23</sup> Pas in our simulations



**Figure 4.** Convection simulations for four different planets with Earth-like composition at 4.5 Gyr (apart from the first case, where plate tectonics is initiated at around 3 Gyr): (a) Earth-sized planet, (b) Mars-sized planet with an initial CMB temperature of 2,000 (*left half*) or 3,900 K (*right half*), (c) Earth-sized planet with Venus-like surface temperature and (d) Earth-sized planet with a Mercury-like interior structure.

Convection takes place in the deep interior of the smaller planet, but plate tectonics is not initiated – convection is too weak and convective stresses too small for localized plastic deformation. Independent of the initial mantle or CMB temperature, the planet cools very fast compared to the Earth-sized case and therefore produces the thick stagnant layer. To compensate the strong cooling, a much larger amount of radioactive heat sources than realistic would be needed to obtain a thin and “breakable” lithosphere on a long timescale. For both initial CMB temperatures, after 4.5 billion years, convection is still active in the mantle of Mars – consistent to the study of Platz and Michael (2011), who argue for recent hotspot volcanism on Mars and ongoing mantle convection as an explanation for the observed volcanic history.

According to our results, we conclude that with decreasing planetary mass (with adapted decreased gravity acceleration and mantle density), the likelihood for plate tectonics decreases, assuming all other parameters being constant. Our simulations suggest that even for a water-rich early Mars, plate tectonics is rather unlikely, even though it may be possible that short-term mobilization of the surface occurs during the magma ocean overturn (Debaille et al., 2009).

### 3.2. VENUS

Venus is the planet in our Solar System, which is most similar to Earth – at least with respect to mass and size. With a radius of 6,052 km (Lodders and Fegley, 1998), Venus has almost the same size as the Earth and also the same average density (and hence, probably almost the same core size as Earth). Venus is therefore often called Earth’s sister planet. A thick opaque cloud layer, however,



does not allow the direct observation of its surface, and speculations existed at the beginning of the last century about possible intelligent life on Venus (e.g. Mumford, 1909).

For a long time, it was believed that the surface temperature on Venus is similar to the Earth's surface temperature (e.g. Buscombe, 1952), until space missions such as Venera 4 and Marina 5 (e.g. Wood et al., 1968) revealed that the dense atmosphere, with a surface pressure almost 100 times the pressure on Earth's surface, leads to very high surface temperatures of around 730 K (e.g. Taylor and Grinspoon, 2009). The closeness to the Sun but in particular the gases in the atmosphere are mostly responsible for the efficient heating of the surface – an effect known as greenhouse effect (Pollack et al., 1980). The most important greenhouse gases in Venus' atmosphere are CO<sub>2</sub> (95 % of the atmosphere) and H<sub>2</sub>O (currently only 30 ppm) which lead to a present-day temperature effect of 423 and 70 K, respectively (e.g. Taylor and Grinspoon, 2009). It is believed that the young Venus may have had water oceans, which evaporated as solar luminosity increased in the past billions of years as a consequence of a runaway greenhouse effect (Ingersoll, 1969; Kasting, 1988). Following this hypothesis, early Venus may have been habitable. On present-day Venus, however, neither the surface nor the subsurface has temperatures low enough for life to survive. A possible habitable environment would therefore only be restricted to the dense clouds (Schulze-Makuch and Irwin, 2002).

The surface shows a significant difference to the other terrestrial planets: few impact craters can be found on Venus, and the age of Venus' surface is therefore assumed to be rather young with about 300 Myr to 1 Gyr on average (e.g. Schaber et al., 1992). Several attempts have been made to explain the young surface using geodynamic models and assuming, for example, the cessation of (maybe episodic) plate tectonics (Schubert et al., 1997; Armann and Tackley, 2012), mantle overturn due to lithosphere thickening (Turcotte, 1993; Schubert et al., 1997), influence of phase transitions leading to a change in mantle convection (Steinbach et al., 1993) or exclusively magmatic resurfacing (e.g. Reese et al., 1999). All these models assume that a catastrophic global resurfacing of the planet occurred several hundreds of millions of years ago. However, there are some specific areas like the tessera regions, which may be much older than their surroundings (Hansen and López, 2010). The average surface age may therefore be better explained by episodic local resurfacing over time instead of a global catastrophic resurfacing (e.g. Smrekar et al., 2010; Noack et al., 2012). The tessera terrains may in addition have a felsic and not basaltic composition (Mueller et al., 2008) – an observation which would show a resemblance with Earth, where the continents are in general of felsic composition.

Venus lacks a detectable planetary magnetic field, and no evidence for a crustal magnetization could be observed (Russell, 1981). This seems to be in contrast to the observations made for the other terrestrial planets, which show either evidence of an active magnetic dynamo (Earth and Mercury) or early remanent magnetization (Earth, Mars and the Moon). Dynamo theory predicts that in the early

thermal evolution of a terrestrial planet, a short-lived dynamo (so-called thermal dynamo) due to strong cooling of the core is not unlikely – depending on the initial core temperature and electrical conductivity (e.g. Stevenson, 2003). It should be noted that the slow rotation of Venus is in general sufficient to generate a dynamo and not the explanation for its present non-existence. The non-finding of a crustal magnetization may instead be explained by the high surface temperature, which is roughly the Curie temperature, above which the surface material (e.g. magnetite with 850 K) can be demagnetized (Luhmann and Russell, 1997). Some studies of Venus even suggest that higher surface temperatures existed in the past hundreds of million years (Basilevsky and Head, 1998; Ruiz, 2007; Phillips et al., 2001; Noack et al., 2012), and, therefore, no evidence of an early magnetic field may have survived on Venus – independent of any possible resurfacing mechanism.

The reason why Venus does not have plate tectonics under present-day conditions can be explained by its high surface temperature. In Fig. 4 we compare an Earth-sized planet assuming a pseudo-plastic rheology with a surface temperature of either 300 (Fig. 4a) or 700 K (Fig. 4c). While for the Earth-like surface temperature plate tectonics occurs (as discussed in the last section), no real subduction occurs for the higher surface temperature. In the latter case, the lithosphere is weaker in comparison to the Earth's case, and no large convective stresses can build up – a stagnant lid forms (e.g. Lenardic et al., 2008). If the surface temperature would increase to 800–900 K or more, the situation might be different. At these high temperatures, the viscosity would be significantly reduced, such that mobilization of the lithosphere might again be possible (Noack et al., 2012). However, this would not resemble an Earth-like plate tectonics state but rather a convective surface mobilization regime. Other explanations for the lack of plate tectonics on Venus include the fast healing of deformed rock (Landuyt and Bercovici, 2009) or the absence of liquid surface water, which increases the yield strength of the lithosphere and may lead to a stagnant lid or episodic plate tectonics (Moresi and Solomatov, 1998).

Note that even though our study may explain why present-day Venus lacks plate tectonics, it does not explain why and how Venus evolved to obtain these high surface temperatures. One possible explanation, however, is that Venus experiences a larger solar luminosity due to the smaller distance to the Sun as compared to the Earth, which led to a vaporization of the surface ocean (if it ever existed) and hence to a runaway greenhouse effect (Kasting, 1988).

### 3.3. MERCURY

Mercury, the planet closest to the Sun, has an atypical interior structure in comparison to the other terrestrial planets of our Solar System. Its average density of  $5,430 \text{ kg/m}^3$  is comparable to the density of the Earth, which has almost three times the size of Mercury; see Table 2. However, due to compressibility, the average density of a planet strongly increases with increasing planetary mass and size.

**Table 2.** A comparison of the size, average density, resurfacing mechanism (PT, MC, MR), water occurrence and possible present-day habitability of the discussed terrestrial bodies in the Solar System.

Body	Radius (km)	Density (kg/m <sup>3</sup> )	Large-scale resurfacing	Water	Habitability
Earth	6,371 <sup>a</sup>	5,515 <sup>a</sup>	PT	Surface	Surface/subsurface
Mars	3,390 <sup>a</sup>	3,934 <sup>a</sup>	Early PT?	Ice/subs. water?	Subsurface?
Venus	6,052 <sup>a</sup>	5,243 <sup>a</sup>	PT? MC? MR?	–	Cloud layer?
Mercury	2,438 <sup>a</sup>	5,430 <sup>a</sup>	–	–	–
Moon	1,737 <sup>a</sup>	3,344 <sup>a</sup>	–	–	–
Ganymede	2,634 <sup>a</sup>	1,936 <sup>a</sup>	–	Subs. ocean?	Subsurface?
Europa	1,560 <sup>a</sup>	3,018 <sup>a</sup>	–	Subs. ocean?	Subsurface?
Io	1,821 <sup>a</sup>	3,529 <sup>a</sup>	MR	–	–
Enceladus	252 <sup>b</sup>	1,610 <sup>b</sup>	PT? MC? MR?	Subs. ocean?	Subsurface?

References: <sup>a</sup>Lodders and Fegley (1998)

<sup>b</sup>Grott et al. (2007)

*PT* plate tectonics, *MC* mobile convection, *MR* magmatic resurfacing

The high density of Mercury therefore can only be explained with a large iron core with a radius of about 2,000 km and a thin silicate mantle with a thickness of about 400 km (e.g. Smith et al., 2012) – the other terrestrial planets have a core radius that is approximately half the planetary radius. To explain this structure, it has been suggested that Mercury’s interior either emerged from a giant impact (or several impacts) which removed the largest part of the silicate mantle (Benz et al., 1988), an early vaporization of the silicate shell (Cameron, 1985), or can be explained by a high-temperature formation of Mercury (condensation model (Lewis, 1973)). However, recent data of Mercury from MESSENGER reveal surprisingly a relatively volatile-rich surface and interior (e.g. Peplowski et al., 2011) and question these formation models, since all suggest a volatile-poor composition.

Even though Mercury is a small planet (smaller even than Mars), a weak magnetic field is generated in its iron core (e.g. Russell, 1981; Stanley et al., 2005). Dynamo models can explain a magnetic field for Mercury if an inner solid core forms and light elements (like sulphur) lead to chemical convection in the core, resulting in a so-called chemical dynamo (as on Earth) – even if the mantle is not convecting (Christensen and Wicht, 2008). The problem, however, is to explain the observed weakness of the field, and so far, various models exist that also predict different characteristics of the degree and time dependence of the magnetic field (see review in Wicht et al., 2008). Future missions are needed to investigate the magnetic field in more detail to distinguish which of the possible explanations are more or less likely (Anderson et al., 2010).

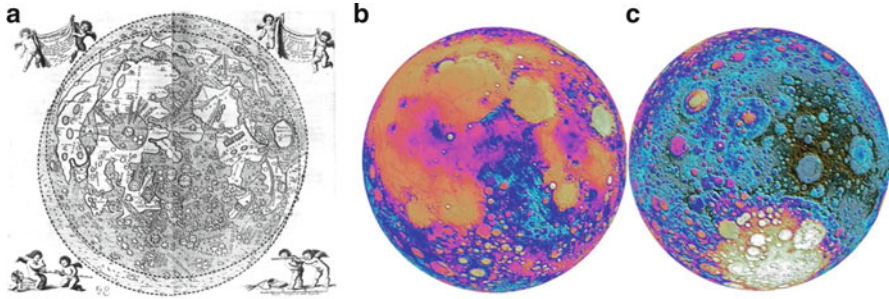
Even though Mercury has a magnetic field to shield the surface from solar wind, the surface is not habitable. Due to the closeness of the Sun, large surface temperatures (up to 700 K, Lodders and Fegley, 1998) can be observed at the dayside of the planet. Also, an Earth-like atmosphere cannot survive due to both

the small mass of Mercury and the solar wind, which leads to a fast loss of the atmosphere – the surface pressure on Mercury is therefore less than  $10^{-12}$  bar compared to 1 bar on Earth (Lodders and Fegley, 1998). Therefore, Mercury is an inhabitable world, and the occurrence of plate tectonics for example would not change that. In fact, plate tectonics seems not to have operated on Mercury. No evidence can be found at the surface – only tectonic features which indicate significant contraction during the last billions of years. This is in accordance to the finding that with decreasing planetary radius, plate tectonics is less likely (cp. Fig. 4b). However, not only the size explains why Mercury does not show any evidence of plate tectonics. Mercury’s large core further makes plastic surface mobilization unlikely. In Fig. 4d, we show an Earth-sized planet with a Mercury-like interior structure (i.e. with a large iron core). For the sake of simplicity and to concentrate solely on the effect of mantle thickness, we neglect changes in planetary mass, gravity acceleration and average mantle density; see Table 1. The thin mantle does indeed lead to smaller scale and weaker convection than in the Earth’s case and therefore does not shift into the plate tectonics regime – independent of the mass and surface temperature, which would both alone argue against plate tectonics. Note that an Earth-sized planet with a Mercury-like interior structure and hence a large iron core would have a higher mantle density and an increased gravity acceleration, which may have a further effect on the occurrence of plate tectonics and is subject to a separate study.

### 3.4. THE MOON

The Moon is the first Solar System body next to the Sun that humans investigated, since its inhomogeneous surface is visible for the eye. In 1647 Johannes Hevelius mapped the visible nearside of the Moon in detail including all larger craters as well as several black spots (the Mare); see Fig. 5a. These regions have been interpreted as oceans, and life on the Moon was thought to be a possibility. This idea, however, was disproven when more information became available, showing that surface life cannot survive on the Moon due to the missing atmosphere and water and the low surface temperatures at the nightside. The dark Mare can be explained by a basaltic composition of the surface material and correspond to the low terrains on the nearside of the Moon (Fig. 5b).

During the Apollo missions 1969–1972, the Moon has been studied intensively. In addition to the collection of surface samples, for example, seismometers allowed to look inside our closest neighbour. Even though the quality of the data is not comparable to the ones obtained by seismic measurements on Earth, scientists gained new information about the interior structure of the Moon. It has a rather small core with a radius of few hundreds of kilometres, that is, between 15 and 25 % of the planet’s radius (1,737 km). Weber et al. (2011) re-evaluated Apollo-era seismic data and obtained even a terrestrial interior structure with an inner solid iron core (~240 km), an outer liquid iron core (~330 km), a partial melt layer above the CMB and a silicate mantle with a basaltic crust on top.



**Figure 5.** (a) Historical map of the Moon by Johannes Hevelius including the Mare (*white areas*), which have initially been interpreted to be water-rich lakes – from Hevelius (1647). (b) Near- and (c) farside of the Moon after LOLA (2012). *White and orange* represent shallow areas; *blue and black* are high terrains.

Based on the Apollo rock samples, it has been speculated that the interior of the Moon is relatively volatile poor, which also seemed to fit to the evolution of the Earth-Moon system – assuming that a Mars-sized impactor collided with Earth and formed the Moon (Canup and Asphaug, 2001; Hartmann and Davis, 1975) instead of a co-accretion scenario (e.g. Morishima and Watanabe, 2001). However, the view on the volatiles content in the Moon has changed significantly due to new spacecraft data, reinvestigations of Apollo samples and indication of aqueous alteration of lunar granite, suggesting that a volatile-richer interior is more likely (e.g. Lawrence, 2011). Still, even though the Moon is not as dry as previously thought, it can hardly be defined to be habitable due to its lack of an atmosphere. Also, plate tectonics is not very likely on such a small body (see Sect. 3.1). The Moon does not have an active dynamo but shows remnant magnetization of surface rocks. The favourite explanation is an early dynamo generated in the small iron-rich core (e.g. Stevenson, 2003; Garrick-Bethell et al., 2009) but also an impact-induced transient magnetic field that leads to an antipodal magnetization has been suggested (Hood and Artemieva, 2008).

### 3.5. SATELLITES OF THE GIANT PLANETS

Apart from the terrestrial planets and the Moon in our Solar System, life may also exist in one of the moons orbiting the gas giants like Jupiter or Saturn. However, the conditions for life are different than on a terrestrial planet. For example, life on Earth needs solar light as an energy source and would probably become extinct without the closeness to the Sun. On Europa, an icy moon of Jupiter, an ocean layer of about 100 km is believed to exist beneath an icy crust (Hand et al., 2010). Assuming an energy source in this ocean layer (e.g. Reynolds et al., 1983), then life could have developed on a moon orbiting a non-habitable gas giant, where almost

no solar light is available. In that case, the most suitable conditions for life require that the subsurface ocean layer is in contact with the silicate shell of the terrestrial body (Lammer et al., 2009) to provide energy and nutrients with potential suboceanic volcanoes. In fact, interior models (e.g. Zolotov and Kargel, 2009) suggest that the ocean layer in Europa is in direct contact with the silicate mantle. One can speculate that plate tectonics of the silicate layer may help to sustain long-standing volcanic activity. However, for the habitability of these bodies, at least plate tectonics is not necessary to stabilize the atmosphere.

A substantial energy source in the Jupiter moon is tidal dissipation that helps to prevent the interior ocean from freezing and possibly to sustain volcanic activity. Thus, the habitable zone – which is defined in its classical version as the zone where liquid surface water may exist – should be generalized to include moons (and also planets in other planetary systems) which are covered by ice but allow for liquid water underneath.

Another example for subsurface habitability is Enceladus, a moon of Saturn with a radius of 252 km. On Enceladus, the area around the South Pole is young in age, and few craters can be found in the southern hemisphere. Regular eruptions of new, fresh material (cryovolcanism) cover the surface (Squyres et al., 1983). Furthermore, long parallel fractures of tectonic origin (sometimes referred to as “tiger stripes”) can be observed. The ongoing activity at the South Pole may be best explained by an underlying plume (e.g. Grott et al., 2007), even though active (and possibly episodic) plate tectonics (O’Neill and Nimmo, 2010) or mobile lid convection being reminiscent of plate tectonics (Barr, 2008) has been suggested as well. Early surface mobilization may be seen as an important factor for habitability in a subsurface ocean. Prebiotic compounds delivered to the surface by cometary impacts (Blank et al., 2001; Mumma and Charnley, 2011), which are the building blocks for life, may have been transported to the subsurface by plate tectonics or a different surface mobilization mechanism in the early evolution of the Moon. In addition, a habitable subsurface ocean would need to include weathering of interior rocks resulting in a geochemical cycle and energy provided by chemical redox gradients (Parkinson et al., 2007) similar as one can expect for Europa.

Although Ganymede, the largest moon of Jupiter, has a much thicker ice water layer than Europa (~900 km compared to 120–170 km, Sohl et al., 2002), it is less likely to be habitable. The subsurface ocean is sandwiched between two ice layers; thus, it is not in contact with the silicate mantle, and it seems to be more difficult to obtain sufficient energy and nutrients in the fluid layer. Ganymede on the other hand generates a magnetic field in its iron core (Schubert et al., 1996). Due to its radius of 2,634 km and the associated lower pressure increase in comparison to the Earth, a classical Earth-like chemical dynamo is unlikely where freezing of the iron core starts in the centre. Instead, the Fe-snow principle is more likely the mechanism for the dynamo generation (e.g. Hauck et al., 2006; Breuer et al., 2010). As a consequence of the low pressure in the core, the adiabatic temperature gradient with pressure is steeper than the melting temperature, such that the core starts to freeze from CMB towards the inside. Solid iron particles

would then fall down, remelt on its way downwards and induce this way chemical convection and a magnetic field. Note that this type of core freezing is also likely for the Moon, Mercury and Mars due to their respective small central pressure. Understanding the different ways of how a magnetic field can emerge in the Solar System helps also to predict magnetic fields on extra-Solar Systems (see Sect. 4), which is one of the factors that may influence the surface habitability of a planet, as has been discussed in Sect. 1.

Jupiter's silicate moon Io is differentiated and has an iron-rich core as also suggested for Europa and Ganymede but does not have an ice layer – subsurface habitability in an ocean can therefore be excluded. Instead, Io seems to be more comparable to the other terrestrial planets in the Solar System – at least concerning the interior structure. The satellite is with an average radius of 1,821 km comparable to the Moon, even though the planet's density is higher, suggesting a larger iron core. However, Io's surface experiences constant resurfacing, probably due to magmatic eruptions (Carr et al., 1998), and even active lava lakes have been observed by the Galileo mission in 2000. This global volcanic activity shows a resemblance to Venus, where a (maybe partly) magmatic resurfacing is assumed to have formed the young surface. The cause for the strong present-day volcanic activity on the relatively small body is – in contrast to Venus – tidal heating due to gravitational forces of Jupiter and the other three large moons (Europa, Ganymede and Callisto).

#### 4. Plate Tectonics and Habitability Outside the Solar System

Two decades ago, several groups started to investigate the light curves of bright stars and pulsars. In 1991 a regular diminishing of a pulsar's light has been observed – the first exoplanet system had been detected (Wolszczan and Frail, 1992), soon followed by the first confirmed exoplanet transiting the star 51 Pegasi (Mayor and Queloz, 1995). This exoplanet is a gas giant with almost one Jupiter mass detected by the radial velocity method, where the wobbling of the star due to gravitational forces of the planet is measured. Since then, newly discovered exoplanets are typically given in relative Jupiter masses, even though several small planets of Earth size have already been detected in the last years due to improved observing techniques.

The first Earth-like planet was discovered in 2007 (CoRoT-7b, Queloz et al., 2009) and opened the research field of exoplanets to simulations of the interior dynamics (O'Neill and Lenardic, 2007; Valencia et al., 2007). This new branch of study expanded over the last years, and studies focus on specific properties of rocky exoplanets with up to ten Earth masses – so-called super-Earths (Valencia et al., 2006) – ranging from magnetic field generation (e.g. Gaidos et al., 2010; Tachinami et al., 2011) to plate tectonics simulations (Valencia et al., 2007; O'Neill and Lenardic, 2007; van Heck and Tackley, 2011; Korenaga, 2010; Stein et al., 2011) and atmosphere models (Wordsworth et al., 2011; Selsis et al., 2008;

Lammer et al., 2010). However, all these studies employed simplifying assumptions into their models starting with the poorly constrained interior structure. Typically, the information available for detected exoplanets are mass, radius and age of the star, measured with some inaccuracy due to observational limits. To assess the possible interior structure of exoplanets, the mean density is compared to the mean density of, for example, an Earth-like, Mercury-like or ocean planet to estimate the main components of the planet – for example, in terms of water, silicate rocks and iron (e.g. Wagner et al., 2011). The variation of density due to changes in composition, however, is not unique – for instance, a purely silicate planet can have the same density as a planet with a thick global ocean layer and a small iron core. Furthermore, the density of an iron core may decrease if light elements as sulphur are present in the core. To complicate matter, some exoplanets may never have been capable of forming an iron core (Elkins-Tanton and Seager, 2008).

The terrestrial planets in our Solar System can be investigated in more detail, and additional information as the moment of inertia factor and the surface composition give better constraints on the interior structure. For instance, the existence (or non-existence) of a global surface ocean can be easily detected on planets in our Solar System. This is a difficult task for exoplanets so far – only if an exoplanet is close to its proximity and hence has high surface temperatures, a surface ocean can be excluded. However, these are planets that are probably not habitable, since liquid water is assumed to be a prerequisite of life. Due to the uncertainties mentioned above, convection models of exoplanets usually perform generalized parameter studies.

In the last years, an increasing number of numerical studies has worked especially on the influence of the planetary mass on the likelihood of plate tectonics, with different conclusions drawn (Valencia et al., 2007; O'Neill and Lenardic, 2007; Korenaga, 2010; van Heck and Tackley, 2011; Stein et al., 2011; Haghighipoura, 2011). These studies used different approaches to simplify the numerical solving process of the underlying partial differential equation system. We speculate that this may be the reason for the different tendencies of plate tectonics likeliness observed (i.e. making plate tectonics on larger exoplanets more, less or equally likely than on Earth). Also, the treatment of the rheology (e.g. using viscosity approximations for the simulations) may have a strong impact on the numerical results (Noack and Tosi, 2013), and more studies are required here.

In addition to the numerical approaches and approximations, one effect on mantle dynamics, which is typically neglected in the latter studies, is the strong pressure dependence on the viscosity (Karato, 2008; Stamenkovic et al., 2011). The viscosity increase due to pressure may even lead to a stagnant lower mantle, and this so-called CMB-lid (Stamenkovic et al., 2012) can have an important impact on the convection pattern in the mantle and the thermal evolution: it can repress a magnetic dynamo due to inefficient cooling of the core and may have a negative effect on the occurrence of plate tectonics. Assume the presence



of a thick CMB-lid is dynamically similar to a planet with a large iron core (i.e. a Mercury-like interior structure). In Fig. 4d a simulation is presented where the planetary radius is similar to Earth, but the inner structure is similar to Mercury. In that case, the thin mantle leads only to weak and small-scale convection, and plate tectonics is not likely.

The existence and thickness of a possible CMB-lid, however, strongly depend on the initial core and mantle temperatures, that is, it depends on the resulting viscosity profile. For high initial temperature, a CMB-lid is most likely not present – high temperatures reduce the viscosity and thereby compensate the effect of pressure that increases the viscosity. Furthermore, the pressure dependence of viscosity is controversially discussed. While Stamenkovic et al. (2011) argue for a strong pressure dependence, Karato (2011) suggests even a possible decrease of viscosity with depth due to a change in the diffusion mechanism. For the plate tectonic behaviour, however, even a decrease of the viscosity in the lower mantle may have a negative influence on the likeliness of plate tectonics (Stein et al., 2011). High-pressure laboratory experiments for pressures up to at least 1TPa (corresponding to the CMB pressure for a ten Earth-mass exoplanet) as well as detailed simulations of accretion and differentiation resulting in reliable initial temperature profiles in large exoplanets are needed to understand the physics in the deep interior of super-Earths.

Next to the planetary mass, the influence of surface temperature and internal heating rate on the occurrence of plate tectonics has been investigated in parameter studies. Some general trends can be found in most of these studies, namely, that an increasing Rayleigh number leads more easily to plate tectonics (Valencia et al., 2007; Stein et al., 2004; van Heck and Tackley, 2011), but an increasing internal heating rate decreases the likeliness of plate tectonics (Stein et al., 2011; O'Neill et al., 2007). A higher surface temperature at some point leads to stresses too low for plate tectonics to occur (Lenardic et al., 2008, see Sect. 3.2) and to a larger healing of the deformed rocks (Landuyt and Bercovici, 2009). Furthermore, water may play an important role for the initiation of plate tectonics (Korenaga, 2010; Regenauer-Lieb et al., 2001). In particular, water in the lithosphere reduces the yield strength of the material and thus favours plate tectonics.

## 5. Summary and Conclusions

In the past decade, increasing attention has been paid to simulations of global processes on terrestrial planets including the atmosphere-interior interactions, surface processes, mantle convection and the dynamics in iron cores. Studies try to understand how the likelihood of plate tectonics and therefore the habitability of a planet – and thus the ability to harbour Earth-like life – may depend on the size of a planet (e.g. Mars and Mercury) or on the thermal evolution (e.g. Venus vs. Earth). Especially since more and more Earth-like exoplanets (i.e. with averaged densities

suggesting an Earth-like interior structure) have been detected, the question about limiting factors for plate tectonics becomes increasingly important. With the models that we have summarized above, we can meanwhile explain why Mars, Mercury, Venus and the Earth evolved in a different way – at least concerning the occurrence of plate tectonics. The question about the likelihood of plate tectonics and moreover a possible habitability on exoplanets, however, is still open.

When searching for a habitable world outside of the Solar System, we typically search for a planet (or moon) in the so-called habitable zone, which is defined as the distance from the star at which liquid water may exist at the surface for an Earth-sized planet (Kasting et al., 1993). A moon, however, needs in addition a strong magnetic field to shield its atmosphere from the planet's magnetosphere (Williams et al., 1997). In any case, a planet or moon located in the habitable zone does not necessarily have habitable conditions. For instance, the Earth without plate tectonics probably would not be habitable, since the end of the long-term CO<sub>2</sub> cycle would eventually lead to a runaway greenhouse effect with much higher surface temperatures (Berner, 1999; Ward and Brownlee, 2000). The actual habitable zone for a planet or moon is therefore not one specific zone around a star but strongly depends on the atmospheric composition and atmospheric pressure of the planet. The latter depends on the geological activity of that planet, for example, plate tectonics versus stagnant lid convection, which on the other hand depends amongst others on the planet size and composition. In the course of the chapter, we have argued that plate tectonics is necessary for long-standing surface habitability, but one should also consider the possibility for short-time habitability. As mentioned in the case of Mars, habitable conditions may have been possible for a stagnant lid planet, but the stability of its atmosphere to keep these favourable conditions is much more unsecure – possibly life can expand in these cases into the subsurface. Furthermore, icy moons or planets, which have an ocean layer beneath an ice crust and are located outside the typical habitable zone, may be habitable as well (as is discussed for Europa and Enceladus). Unfortunately, it is even more challenging to have a look inside of an exomoon or exoplanet, and only surface habitability can possibly be detected in the near future.

In addition to plate tectonics, one other resurfacing mechanism exists in our Solar System that can transport efficiently surface material into the mantle, that is, mobile convection of the silicate crust (maybe on past Venus). This mechanism is, however, linked to high surface temperatures that do not allow fluid water at the surface and thus cannot be associated with a habitable body. The case is different for a moon or planet with an icy crust and an underlying water ocean. Mobile surface recycling of ice occurs at much lower temperatures and may bring prebiotic material of cometary origin (e.g. Blank et al., 2001) from the surface into the subsurface ocean – which would influence the habitability during the early evolution of the icy body in a positive way.

Some studies focussed already on the simulation of plate tectonics on exoplanets. However, we are far from understanding all physical processes that may appear in larger terrestrial planets than Earth. To make numerical predictions

whether a detected large planet has plate tectonics or not, we have to deal with three main problems:

1. Present measurements of mass and radius can give only a rough constraint of the interior structure and composition, and several assumptions have to be done in order to simulate the dynamics of exoplanets.
2. The high-pressure physics in the deep mantle of large rocky planets is not well known, and new experiments and ab initio calculations are needed. Furthermore, the dominating mineral in the mantle of large terrestrial exoplanets can be different to what we presently assume.
3. The initial thermal state of planets (as well as the amount and type of internal heating sources) is not known but appears to be of particular importance for the dynamics and thus the occurrence of plate tectonics in large planets.

Thus, plate tectonics simulations of exoplanets should only be seen as parameter studies and not as actual simulations of terrestrial planets. The case is different, however, for the terrestrial planets in the Solar System. Even though the exact initial condition of the planets is not known, thermal evolution models can be used to investigate different possible scenarios, and initial parameters can be constrained by comparing the present-day state of the terrestrial planets with simulation results.

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# EXOPLANETS AND HABITABILITY

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## 1. The Diversity of Exoplanets

The discovery of planets outside of our Solar System has been accompanied by numerous surprises. The field of exoplanets has undergone enormous diversification over the past 20 years. The reasons for this include (but are not limited to) new detection techniques, longer period baseline, smaller mass/radius sensitivity, and atmosphere detection and modeling. As a result of these developments, we are able to accurately characterize the orbits of exoplanets and infer properties of their atmosphere's surface conditions. Figure 1 demonstrates the rapid rate at which the field has grown and the new techniques, most particularly the transit method, which have greatly enriched both the number and diversity of the discoveries. The sensitivity of radial velocity and transit surveys to planets at longer periods is fundamentally limited by the survey duration. Many of the radial velocity surveys are now pushing this detection threshold beyond orbital periods of 10 years and with upgraded instruments are sensitive to masses only a few times that of the Earth.

The result of this continuing expansion of orbital parameter space is that we are discovering the diversity of planetary orbits, particularly in comparison to our own Solar System. The increased sensitivity toward giant planets of the detection techniques means that we have primarily discovered these ones first, many far more massive than Jupiter and extremely close to their host stars. A snapshot of the masses and orbital periods is shown in Fig. 2 which not only demonstrates this diversity but also highlights the sensitivity of different techniques to different kinds of planets. The range of terrestrial bodies, both in independent orbits around the host stars and in possible orbits around the known giant planets, is opening a new area of considering habitable conditions outside that of what we are typically used to seeing.

## 2. What Makes a Planet Habitable?

In order to search for a habitable planet, then one must first clearly understand what it is we are searching for. Life on Earth is carbon-based (DNA, RNA, and proteins) and requires liquid water to serve as a stable solvent in which biochemical reactions can take place. We thus require conditions under which liquid water could be

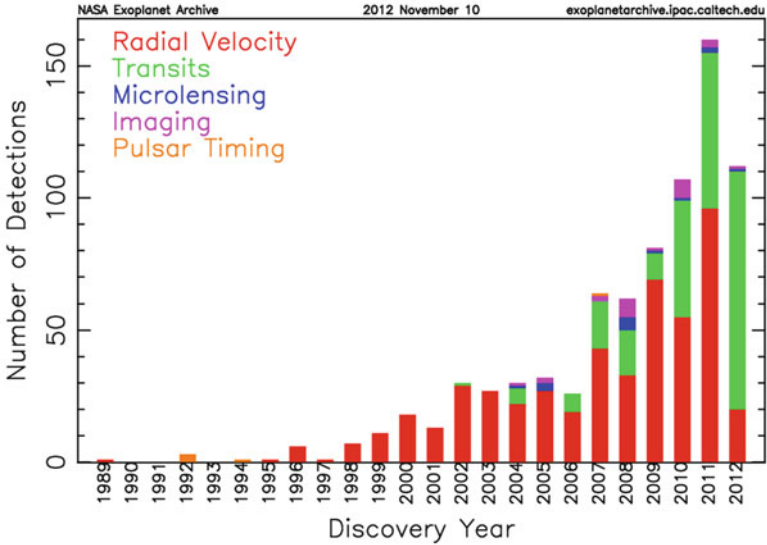


Figure 1. Histogram of exoplanet discoveries color-coded by detection method.

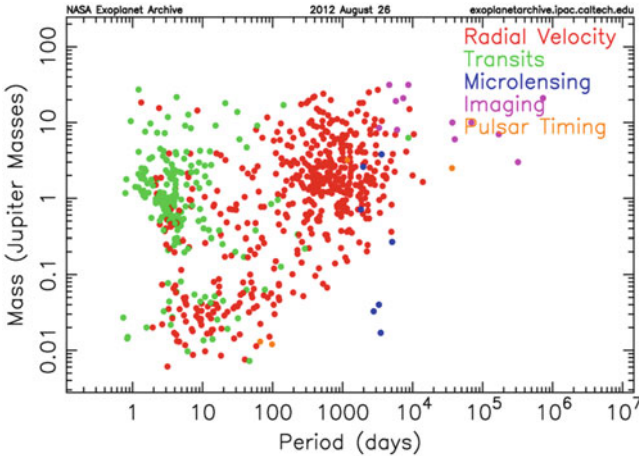


Figure 2. The mass of confirmed exoplanets as a function of orbital period.

present as a condition for habitability. There are various factors which contribute to a planet's having habitable qualities. The first is the amount of flux which is received by the planet from the host star. This depends on the location of the planet and the properties of the host star. Externally received energy is not limited to the star however and may be received also from tidal effects due to eccentric

orbits and interactions with other bodies in the system, such as a terrestrial body interacting with a giant planet it is orbiting.

Most other determining factors are due to the properties of the planet itself. The planetary mass plays a key role since it affects aspects such as atmospheric mass and plate tectonics. The atmospheric mass will affect, for example, the pressure at the surface which will in turn determine the temperatures at which water undergoes phase transitions. As pointed out by Spiegel et al. (2008), the climate dynamics of a planet plays a key role in achieving a climate balance and determining the response of the atmosphere to changes in flux and the probability of entering a “snowball” phase. The regulation of carbon dioxide in the atmosphere, a major greenhouse gas, is aided by achieving equilibrium with the carbon-silicate cycle which is a geochemical exchange of carbon between the atmosphere, geosphere, and hydrosphere. The atmospheric composition also determines the reflectivity (albedo) of the upper atmosphere. A low albedo will result in the absorption of most of the incident flux whereas a high albedo will result in the flux being reflected back into space.

Here we concentrate our discussion on the external influences which aid in determining the location of the Habitable Zone (HZ) around a star.

### 3. Quantifying the Habitable Zone

In the following sections, we apply the equations of Underwood et al. (2003) and Jones and Sleep (2010) which relate the HZ boundaries to stellar luminosity and effective temperature for reasonable models of planetary atmospheric responses. As described earlier, a comprehensive treatment of the HZ for a particular planet and star requires detailed knowledge of the climate dynamics of that object which, for exoplanets at least, is unfortunately unavailable at the present time. The calculations presented here can be treated as a robust first-order approximation for the HZ boundaries.

#### 3.1. EFFECT OF STELLAR PROPERTIES

We begin with the luminosity of the host star, which is approximated as

$$L_* = 4\pi R_*^2 \sigma T_{\text{eff}}^4$$

where  $R_*$  is the stellar radius,  $T_{\text{eff}}$  is the stellar effective temperature, and  $\sigma$  is the Stefan-Boltzmann constant. In cases where the radius of the star is not available from direct measurements, we estimate the radius from the derived values of the surface gravity  $\log g$  using the relation

$$\log g = \log\left(\frac{M_*}{M_\odot}\right) - 2\log\left(\frac{R_*}{R_\odot}\right) + \log g_\odot$$

where

$$\log g_{\odot} = 4.4374$$

according to Smalley (2005).

We can approximate the effective temperature of a planet,  $T_p$ , as a blackbody. This approximation will deviate slightly from the true temperature depending upon albedo, atmospheric properties, and internal heating. Assuming that the atmosphere is 100% efficient at redistributing heat around the planet, the planetary equilibrium effective temperature is given by

$$T_p = \left( \frac{L_*(1-A)}{16\pi\sigma r^2} \right)^{\frac{1}{4}}$$

where  $A$  is the spherical (Bond) albedo and  $r$  is the star-planet separation. In this case the surface is uniformly bright and thus there will be no observable phase function at infrared wavelengths. However, if the atmosphere is inefficient with respect to heat redistribution, this will lead to a hot dayside for the planet where the effective temperature is

$$T_p = \left( \frac{L_*(1-A)}{8\pi\sigma r^2} \right)^{\frac{1}{4}}$$

where there will be a resulting phase variation as the planet orbits the star. The generalized form for the planetary effective temperature is thus

$$T_p = \left( \frac{L_*(1-A)}{(1+\eta)8\pi\sigma r^2} \right)^{\frac{1}{4}}$$

where  $\eta$  is the atmospheric heat redistribution efficiency with a value ranging between 0 and 1.

For a typical hot-Jupiter scenario, the star-planet separation is assumed to be the same as the semi-major axis,  $a$ , since these are usually circular orbits. However, the star-planet separation for eccentric planets has the following form:

$$r = \frac{a(1-e^2)}{1+e\cos f}$$

where  $e$  is the orbital eccentricity and  $f$  is the true anomaly. Thus, the eccentricity of a planetary orbit introduces a time dependency to the effective temperature of the planet.

Using the boundary conditions of runaway greenhouse and maximum greenhouse effects at the inner and outer edges of the HZ, respectively, the stellar flux at these boundaries is given by

$$S_{\text{inner}} = 4.190 \times 10^{-8} T_{\text{eff}}^2 - 2.139 \times 10^{-4} T_{\text{eff}} + 1.268$$

$$S_{\text{outer}} = 6.190 \times 10^{-9} T_{\text{eff}}^2 - 1.139 \times 10^{-5} T_{\text{eff}} + 0.2341$$

The inner and outer edges of the HZ are then derived from the following:

$$r_{\text{inner}} = \sqrt{L_{\star} / S_{\text{inner}}}$$

$$r_{\text{outer}} = \sqrt{L_{\star} / S_{\text{outer}}}$$

Thus, we are able to determine the inner and outer edges of the habitable zone from basic stellar properties. For main sequence stars, this results in a narrow HZ range which is relatively close to the host star for low-mass stars, whereas a high-mass star will have a broad HZ much further away. This has significant implications for determining which planets lie in the HZ of their stars and can influence the target selection of planet-hunting surveys which may be optimized toward detecting planets around stars of a certain spectral type.

### 3.2. TIDAL INFLUENCES

Another source of energy for a planet is that from tidal effects. We have a well-known example in our own Solar System which is Jupiter's moon Io. Io is the innermost of the Galilean moons and is on a slightly eccentric orbit due to perturbations from the other moons in the system. The proximity to Jupiter along with the time-dependent distance from the giant planet produces enormous tidal pressures within the moon resulting in Io's being the most volcanically active object in the entire Solar System.

The diversity of exoplanetary orbits discussed earlier has revealed planets which may have very similar tidal effects which would have drastic consequences for the atmospheric evolution and habitability in general. Terrestrial planets in the traditional HZ of low-mass stars will be subjected to tidal forces similar to that of Io (Barnes et al., 2008, 2009; Heller et al., 2011). Tidal effects can produce a complex evolution of internal, spin, and orbital properties but greatly depend on the stellar and planetary properties. For example, one outcome is that the planetary spin will alter such that it is synchronous with the orbit or the planet (i.e., one side of the planet always faces the star). This may result in a rotation period which is much slower than that of modern Earth and will hence affect the climate dynamics (Kasting et al., 1993). Tidal heating is expected to have a much greater effect for planets in eccentric orbits, especially when the orbit is close to the host star. The relevance to the HZ is that planets in short-period orbits



around low-mass stars (M dwarfs) may be in the HZ but still suffer the effects of severe tidal heating. This means that it is possible for a wide range of very different worlds under a variety of heating conditions to exist around M dwarfs. Given that several potentially habitable planets have been discovered orbiting M dwarfs such as Gl 581 d (Udry et al., 2007) and Gl 667C c (Anglada-Escude et al., 2012; Bonfils et al., 2013; Delfosse et al., 2012), tidal effects are an important consideration for this class of planets.

### 3.3. FURTHER CONSIDERATIONS

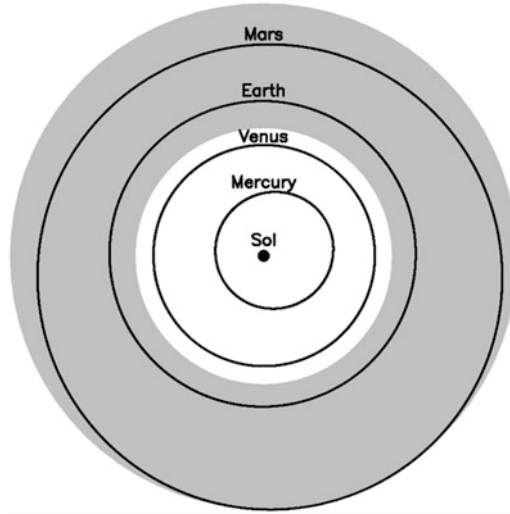
There are other energy sources which could feasibly contribute to the total energy budget of a planet. Planets of Earth mass and higher will often maintain a source of geothermal heating resulting from a combination of heat left over from the formation processes (accretion) and radioactive heating. However, for an age similar to that of the Earth, this kind of heating has minimal effect at the surface of the planet. For terrestrial-sized bodies that orbit giant planets, the flux from the planet itself can be substantial. The giant planets in our Solar System tend to have relatively fast rotation periods and generate large magnetic fields. These magnetic fields trap radioactive ions in radiation belts which will produce an additional source of incident flux on the moons within that system.

One further consideration is the identification of exclusion zones within an HZ. These are regions where a planet of terrestrial mass cannot exist in a stable orbit due to the presence of other planets in the system (Kopparapu and Barnes, 2010). The application of such a stability analysis to the known exoplanetary systems will help to identify those systems which cannot have terrestrial-mass planets in the HZ and thus lower their priority as candidate host stars for habitable worlds.

## 4. Application to the Solar System

By way of demonstration, we first apply the HZ models to our own Solar System. For a solar-effective temperature of 5,778 K, we find the inner and outer boundaries of the HZ to be 0.836 and 1.656 AU, respectively. Figure 3 shows the HZ depicted as a gray disk with the orbits of the terrestrial inner planets overlaid.

An estimate of the equilibrium temperatures for the inner planets can be calculated by using their known orbital parameters and Bond albedos and treating them as blackbodies, as described by Kane and Gelino (2011). This calculation is further explored by considering two cases: one in which the heat is evenly redistributed throughout the surface and the other where there is no heat redistribution and so the heat is constrained to a hot dayside. The results of this are shown in Table 1, where Temp 1 is the former and Temp 2 is the latter. This shows that the model of complete heat redistribution works reasonably well for Solar System



**Figure 3.** The inner Solar System showing the orbits of the terrestrial planets. The HZ is indicated by a *gray disk*.

**Table 1.** Calculated blackbody temperatures for the terrestrial planets assuming complete heat redistribution (Temp 1) and no heat redistribution resulting in a hot dayside (Temp 2).

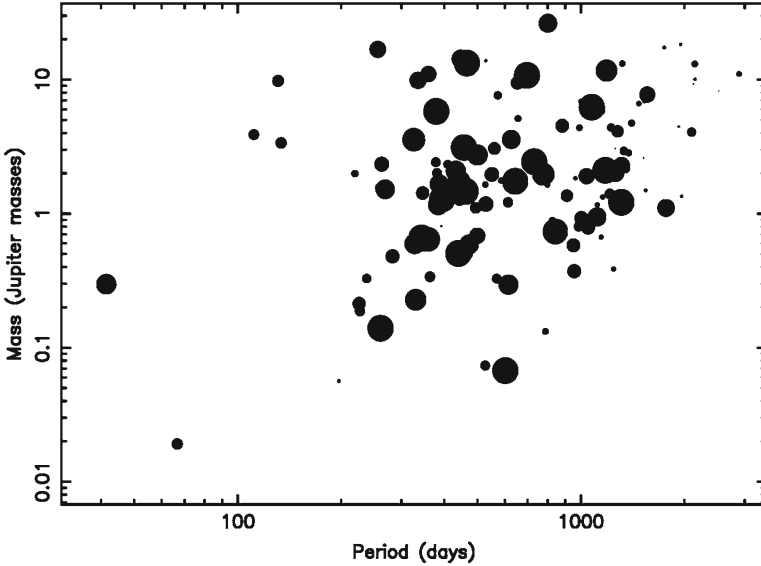
Planet	Temp 1 (K)	Temp 2 (K)	Actual temp (K)
Mercury	448	532	440
Venus	327	389	737
Earth	279	331	288
Mars	226	268	210

For comparison, we show the actual measured mean surface temperatures

terrestrial planets. The major exception to this is Venus whose temperature has become dominated by the climate changes which have resulted in a runaway greenhouse effect, as described earlier. For Mercury, the actual surface temperature varies enormously and is positionally dependent on the planetary surface due to tidal locking and the lack of any substantial atmosphere.

## 5. Application to Exoplanets

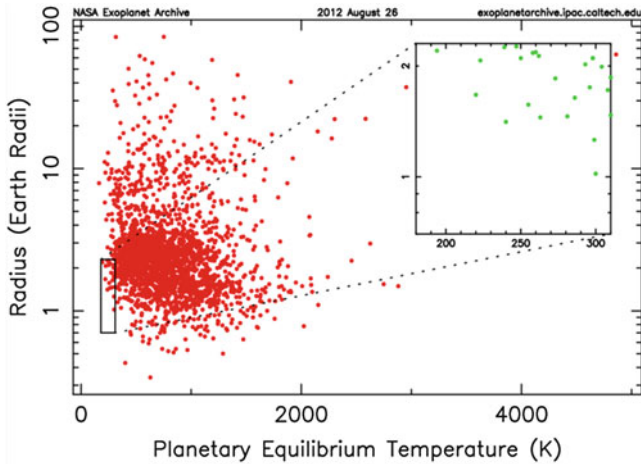
Over the past 20 years, we have entered an extraordinary era of human history when we are routinely discovering new planets around other stars. The sensitivity of exoplanet surveys is spreading in various directions, to lower masses, to longer



**Figure 4.** The mass and orbital periods of discovered planets that enter the HZ of their star. The size of the point is proportional to the fraction of the orbit in the HZ.

periods, and to later and earlier spectral types. This broadening of the field opens up new areas to explore in terms of the Habitable Zones of these configurations. Although we are currently unable to directly characterize the atmospheres of terrestrial exoplanets, we are able to use the properties of the host star and the Keplerian orbital solution of the planets to obtain a first-order approximation of the energy budget received by the planet. We are thus able to apply the previously described calculations to many of the discovered planets. Shown in Fig. 4 are the masses and orbital periods of confirmed exoplanets. This is similar to what is shown in Fig. 2; however, this time we only plot those planets which enter the HZ of their star, and the size of the points is proportional to the percentage of the orbit which it spends there. The mass sensitivity of radial velocity surveys results in most of these planets' having masses close to a Jovian mass. However, a new area of habitability being explored is that of terrestrial moons of giant exoplanets which lie within the HZ of their parent stars. Based upon the statistics from our own Solar System, it is natural to expect that many of the planets discovered via the radial velocity method do indeed harbor moons of various size and composition. For the moons in these systems, the habitability prospects will depend largely upon the conditions under which the primary planet is subjected to.

The topic of the HZ has become even more relevant in the wake of the results from the Kepler mission. Figure 5 shows the radius and temperature estimates from the Kepler candidates with a zoomed panel focusing on terrestrial-sized

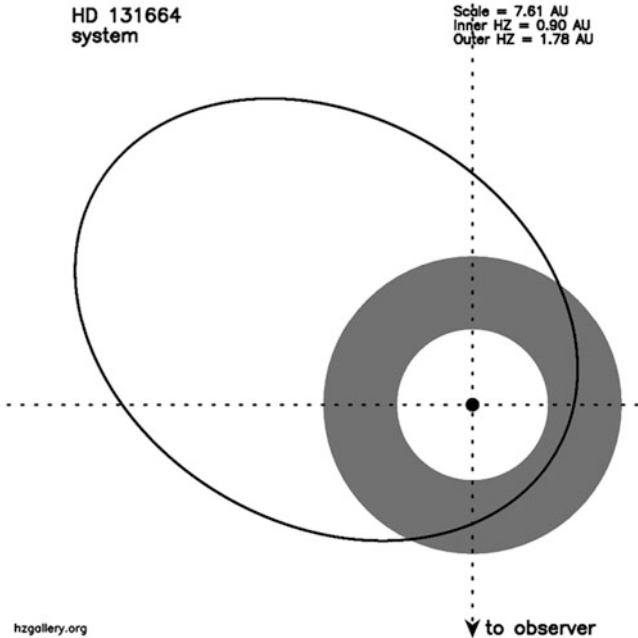


**Figure 5.** Radius and estimated temperature for Kepler exoplanet candidates. The zoomed panel shows terrestrial-sized planets in the HZ.

planets within the HZ. Although these results illustrate the frequency of habitable terrestrial planets, the relative faintness of the Kepler sample makes more detailed follow-up difficult.

## 6. Eccentric Orbits and Habitability

Amongst the surprises included in exoplanet discoveries is that of planets in highly eccentric orbits. Due to dynamical stability considerations, most of the very eccentric planets occupy single-planet systems. There have been several interesting studies regarding the habitability of terrestrial-mass planets in eccentric orbits, such as that by Dressing et al. (2010). Kita et al. (2010) show the possible detrimental effects of terrestrial planet habitability when excited to an eccentric orbit by another companion in the system. Spiegel et al. (2010) consider the effect of transiently eccentric orbits on planet habitability. In particular, the work of Williams and Pollard (2002) considers an orbit-averaged flux as a habitability diagnostic for eccentric orbits. We diverge from this metric since the time-averaged distance of the planet from the star is significantly farther than the difference between apastron and periastron, and, thus, we use the percentage of time spent in the Habitable Zone where metabolic processes could proceed rather than relying on sustainable temperatures. However, the calculated equilibrium temperatures make implicit assumptions regarding the response of the atmosphere to changes in flux. In reality, planetary temperatures at the surface and upper atmosphere are complicated functions of surface and atmospheric composition and dynamics as well as the long-term climate history and so can only be treated as a first-order approximation.

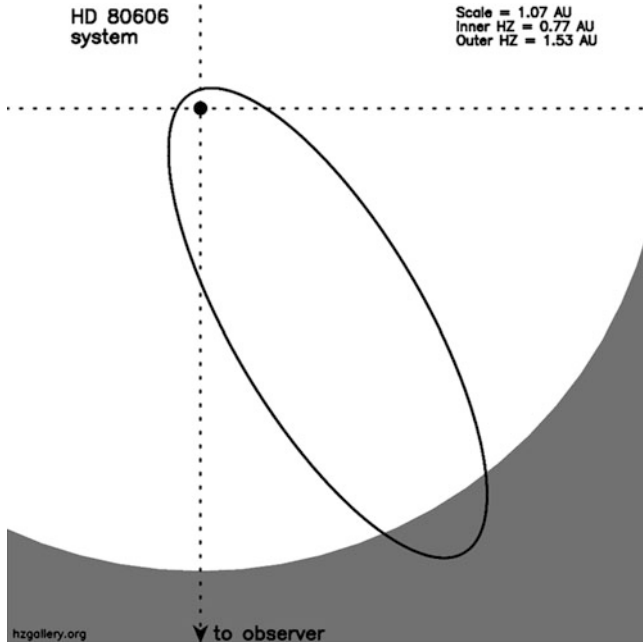


**Figure 6.** The planetary orbit and HZ for the HD 131664 system.

See, for example, Williams et al. (1997), Spiegel et al. (2008, 2009), Kane and Gelino (2011), and references therein. Here we briefly discuss two examples and we refer the reader to Kane and Gelino (2011, 2012) for more detailed information.

One important consideration is the orbital stability of exomoons as the parent planet passes through periastron. Hamilton and Burns (1992) showed that the Hill radius at periastron is a good representation of the stability zone for satellites of planets in highly eccentric orbits. The giant planets discussed here will have Hill radii which extend beyond Galilean moon analogs and thus could retain similar moons under these conditions.

In Figs. 6 and 7 we present two examples, one with periastron in the HZ and the other with apastron in the HZ (shown in gray). The planet orbiting HD 131664 is in a 1951-day orbit and has an eccentricity of 0.64. The minimum mass of the planet is 18 Jupiter masses resulting in a Hill sphere radius of 0.2 AU (416 Jupiter radii) at periastron. The planet only spends 11 % of the orbital period in the HZ since it moves slowly near apastron. The calculated equilibrium temperature is 271 K at periastron and 127 K at apastron assuming a Bond albedo of 0 meaning that the planet and moons absorb 100 % of the incident flux. Thus, the planet and possible moons undergo long periods of hibernation conditions broken regularly with warmer habitable conditions. In fact the situation is improved for eccentric orbits through the extension of the outer HZ boundary as



**Figure 7.** The planetary orbit and HZ for the HD 80606 system.

found by Williams and Pollard (2002) and Dressing et al. (2010). In contrast, the planet orbiting HD 80606 is in a 111-day orbit with an eccentricity of 0.93 and is known to both transit and be eclipsed by its host star (Laughlin et al., 2009). This planet has a mass of 3.9 Jupiter masses leading to a Hill sphere radius of 0.0032 AU (6.7 Jupiter radii). In this case, it is the apastron which lies within the HZ where it spends 40 % of the orbital phase. The temperature at apastron is predicted as 286 K; however, the close encounter with the star at periastron causes temperatures to reach a scorching 1,546 K. This results in flash-heating of the upper atmosphere which doubles in temperature in only 6 h as it passes through periastron. Thus, organisms could only survive such environments if deeply buried under sufficient protective layers. For both of these examples, regular intervals of habitability for the moons depend strongly on the surface conditions and their response to the change in temperatures. For example, a water-rich moon will require sufficient time to melt out of a snowball state to allow metabolic processes to continue.

One may well question how even extremophiles could survive these environments. A transition from liquid to frozen water and back again does not present an obstacle for most Earth-based microorganisms. It has been shown by de la Torre et al. (2010) that organisms such as lichens and bacteria can survive for periods of at least 10 days when exposed to the harsh conditions of outer space.

Foucher et al. (2010) presented the results of atmosphere re-entry experiments which demonstrate that microfossils can survive entry into Earth's atmosphere within sedimentary rock but that microorganisms require protection by at least 5 cm of rock for adequate shielding. During the time an exoplanet or exomoon spends exterior to the HZ, similar organisms can undergo metabolic slowdown for a period of hibernation without any immediate biological harm. The daily and annual biological clock we see exhibited by plants and cells on Earth could be adapted to different orbital durations to optimize time spent in favorable (habitable) conditions. Since we know that several terrestrial organisms can withstand substantial periods of time under extreme temperature conditions in combination with vacuum, UVC irradiation, and cosmic rays, then it is conceivable that such organisms could survive periastron flash-heating at a sufficient protective depth beneath the surface.

## 7. The Anthropic Viewpoint

Although the concept of the HZ has been discussed for some time, it is only recently that sophisticated climate models are allowing concise quantification of this region. The study of exoplanetary atmospheres enables us to apply these concepts to known exosystems, even those with exoplanets in orbits which result in extreme temperature variations. Even so, we consider very seriously that all the discussions and calculations performed when attempting to quantify what we mean by habitable conditions all take place within the context of what we understand to be habitable conditions on Earth. It is difficult to escape from this anthropic viewpoint when assessing the potential for habitability in exosystems. The diversity of exoplanets that we have described here may also be reflected in the diversity of environments in which organic chemistry is able to undergo the necessary reactions for sustainable life conditions. For example, a targeted search for exomoons in relatively extreme environments may yield surprises on what we consider "habitable." Thus, one must keep an open mind when considering the habitability of potential ecosystems in exoplanetary systems.

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**PART V:  
ALTERNATIVES TO EARTH-LIKE LIFE**

**Schulze-Makuch  
Raven  
Donnelly**

Biodata of **Prof. Dr. Dirk Schulze-Makuch**, author of “*Extremophiles on Alien Worlds: What Types of Organismic Adaptations Are feasible on Other Planetary Bodies.*”

**Prof. Dr. Dirk Schulze-Makuch** is Professor in the School of the Environment at Washington State University. He obtained his Ph.D. from the University of Wisconsin-Milwaukee in 1996. Afterward he worked as a Senior Project Hydrogeologist at Envirogen, Inc. and took in 1998 a faculty position at the University of Texas at El Paso. During that time he was also a summer faculty fellow at Goddard Space Flight Center. Since 2004 Dr. Schulze-Makuch is a faculty member at Washington State University. His interests are in astrobiology, planetary sciences, and evolutionary and cancer biology. He published five books and more than 100 scientific articles in these fields.

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# **EXTREMOPHILES ON ALIEN WORLDS: WHAT TYPES OF ORGANISMIC ADAPTATIONS ARE FEASIBLE ON OTHER PLANETARY BODIES**

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## **1. Introduction**

At the time of this writing, Earth is the only planetary body on which we know for sure that life exists. Although we only have one example, life on Earth shows a remarkable diversity and creativity. Organisms exist ranging in complexity from being relative simple such as microbes to being highly specialized such as dolphins and humans, occupying a variety of habitats extending from the Arctic to the equator and the dry deserts such as the Atacama Desert in Chile to the lush African jungle. And even though the phenotypes of life on Earth are incredibly diverse, the underlying building blocks of life on Earth are remarkably uniform. All life on Earth appears to be based on a rather uniform set of amino acids and a handful of macromolecules such as DNA (or RNA) for replication, uses light or chemical energy as energy source, and appears to utilize the same type of solvent (water) for molecular exchange. The question then arises: what does constitute a specific adaptation to the environmental conditions as they are exhibited on Earth and what are general features of life? The more generic definitions of life are independent of mentioning certain types of particular molecules but focus on the processes involved. For example, Irwin and Schulze-Makuch (2011) defined living entities as (1) consisting of discreet beings enclosed by physical boundaries that separate their highly organized interiors from the surrounding environment, (2) consuming energy from their environments to maintain their high level of organization and carry out intrinsic activity, and (3) reproducing themselves by a process of nearly exact replication that is totally autonomous. Using this definition as a starting point, I speculate on the adaptations that organisms on other planetary bodies in our Solar System could have evolved – as a function of the environmental history and conditions existing there.

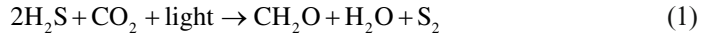
## **2. Habitats and Possible Life on Venus**

Current conditions on the surface of Venus are extremely desiccating and hot, thus prohibitive for life. However, Venus formed in the same general region of the Solar System as Earth, and thus abundant solar energy and primordial waters on

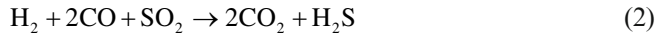
early Venus can be assumed to have been present (Schulze-Makuch et al., 2005). There is evidence for an early ocean on Venus which was likely a hot sea (Kasting, 1989) that eventually evaporated during a runaway moist greenhouse effect. It is unclear how long the ocean or oceans were present. However, given the apparently rapid rise of life on Earth due to abundant surface water along with dynamic endogenic-driven activity, there is the possibility that life originated on Venus (Schulze-Makuch and Irwin, 2008). Alternatively, organisms delivered by meteorites from early Earth or Mars could have found a suitable habitat on early Venus. However the case may be, there is a good chance that microorganisms were present in oceans or surface water pools on early Venus. Originally, these organisms may have been very similar to life on Earth given similar environmental conditions. Once these conditions changed and Venus was subject to a runaway greenhouse effect, life on Venus would have needed to adapt in order to survive. The only possible refuge and habitat is the lower atmosphere of Venus. Current environmental conditions in the lower atmosphere can be summarized as follows: (1) The clouds of Venus are much more continuous and stable than the clouds on Earth; (2) the atmosphere is in chemical disequilibrium, with  $H_2$  and  $O_2$  and  $H_2S$  and  $SO_2$  coexisting; (3) conditions in the clouds at 50 km in altitude are relatively benign, with temperatures of 300–350 K, pressure of 1 bar, and a pH of about 0; (4) the super-rotation of the atmosphere enhances the potential for photosynthetic reactions; (5) an unknown absorber of ultraviolet energy has been detected in the Venusian atmosphere; and (6) while water is scarce on Venus, water vapor concentrations reach several hundred ppm in the lower cloud layer (Schulze-Makuch et al., 2004).

How could Venusian life have adapted to these kinds of conditions? The major problems for any possible microbial life in the Venusian atmosphere would be the lack of water, the low pH, and the large amounts of UV radiation that the Venusian atmosphere receives. The lack of water could be overcome by microbial organisms if they had developed a mechanism by which to assimilate water vapor from hydrated sulfur compounds or from the atmosphere, similar to the assimilation of carbon from  $CO_2$  by microbes in the atmosphere of Earth (Schulze-Makuch et al., 2005). Although a pH of about 0 in the lower cloud layer may seem extreme, Schleper et al. (1996) isolated microorganisms on Earth that thrive at this pH level (see also the alga *Cyanidium caldarium*; Seckbach, 2013). Certainly, the physiology of those putative microbes would be similar to thermoacidophiles on Earth. With regard to the high amount of UV radiation in the Venusian atmosphere, cyclooctasulfur ( $S_8$ ) could be used by microbes for protection (Schulze-Makuch et al., 2004).  $S_8$  has the capability of shielding organic macromolecules such as DNA and protein at wavelengths most susceptible to UV damage. A somewhat analogous process is observed on Earth, where some purple sulfur bacteria, green sulfur bacteria, and some cyanobacterial species deposit elemental sulfur granules outside of the cell (e.g., Pierson et al., 1993; Tortora et al., 2001).

Schulze-Makuch and Irwin (2002a) suggested the possibility of phototrophic life at Venus based on Photosystem I:



In addition, or alternatively, chemotrophic organisms could exist that under the prevailing environmental conditions would use the following metabolism:



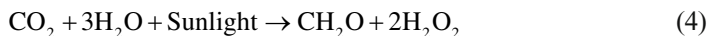
This would close the loop of a microbially based “primitive” ecosystem. Future space mission should test the hypothesis for the possible existence of microbial life in the lower atmosphere of Venus as summarized above.

### 3. Habitats and Possible Life on Mars

Mars is currently cold and dry, and it is difficult to imagine that organisms from Earth could make a living on or near the surface of Mars. However, several lines of evidence (e.g., Malin and Edgett, 2003; Fairén et al., 2003; Schulze-Makuch and Irwin, 2008) point to a much warmer and wetter Mars and the presence of a hydrological cycle and oceans (or at least large surface water bodies) in the early history of Mars. It seems reasonable to argue that under these circumstances, life could have originated on early Mars or was brought in from Earth via meteorites (or vice versa). The Martian climate changed through the eons to its current state, and one can only wonder what would have happened to life on early Mars if it ever existed. There would be two possible evolutionary trajectories for it to survive: (1) retreat to the deep subsurface or other environmental niches such as hydrothermally active areas and live on the scant nutrient sources that are available in these potential habitats or (2) adapt to the near-surface environment of Mars with the possibility to harvest light as an energy source. Here I will focus on the latter possibility.

Various types of adaptations are known by organisms from Earth to adjust to extreme environments including adaptation to some of the same stresses that occur on current Mars such as cold temperatures, low pressure, lack of liquid water, and an intense radiation environment. However, since the combination of stresses on Mars is quite unique and is not exhibited in any Earth environment, it is reasonable to expect that a novel adaptation mechanism could evolve. One possible solution would be the inclusion of hydrogen peroxide into the intracellular fluids of those organisms, which would have the advantage of (1) lowering the freezing point significantly (the eutectic is at  $-56.5\text{ }^\circ\text{C}$ ), (2) mixtures of high  $\text{H}_2\text{O}_2$  concentrations supercool and don't form ice crystals (thus would not

pierce cellular membranes upon freezing), (3) providing a source of oxygen, and (4) exhibition of hygroscopic properties thus allowing to scavenge water directly from the atmosphere in an otherwise very dry environment (Houtkooper and Schulze-Makuch, 2007). Furthermore, both photosynthetic and chemosynthetic metabolic reactions would theoretically be feasible such as



and



The compatibility of  $\text{H}_2\text{O}_2$  with biological processes might seem questionable. However, certain microbial organisms produce hydrogen peroxide (e.g., *Streptococcus* and *Lactobacillus* sp., Eschenbach et al., 1989), while other microbes utilize  $\text{H}_2\text{O}_2$  (e.g., *Actinomyces viscosus* and *Staphylococcus epidermidis*, Ryan and Kleinberg, 1995). The microbe *Acetobacter peroxidans* even uses  $\text{H}_2\text{O}_2$  in its metabolism (overall reaction  $\text{H}_2\text{O}_2(\text{aq}) + \text{H}_2(\text{aq}) \leftrightarrow 2\text{H}_2\text{O}$ ; Tanenbaum, 1956). Organisms control the high reactivity of  $\text{H}_2\text{O}_2$  usually with the help of stabilizing compounds.

While the so-called hydrogen peroxide-water hypothesis for life on Mars would explain the Viking biology experiments well (see Houtkooper and Schulze-Makuch, 2007 for details), perchlorate solutions, more recently discovered by the Phoenix mission, have similar properties to a hydrogen peroxide-water solution. Perchlorates are also hygroscopic and act as an antifreeze down to a temperature of  $-70$  °C (e.g., a water-magnesium perchlorate mixture). Perchlorate-reducing bacteria are ubiquitous on Earth. They generally grow by the complete oxidation of organic carbon or various alternative inorganic electron donors coupled to the reduction of perchlorate in anoxic environments. Coates and Achenbach (2004) likened the reported microbial perchlorate reduction of *Dechloromonas aromatica* to rocket-fueled metabolism. Most perchlorate bacteria are  $\alpha$ - or  $\beta$ -proteobacteria. Members of both the *Dechloromonas* and *Azospira* genera have been identified and isolated from nearly all environments that have been screened, including soil and lake samples collected from Antarctica. A third group – the *Dechlorospirillum* species – is closely related to the magnetotactic *Magnetospirillum* species, a subgroup of the Proteobacteria. The *Magnetospirillum* genus has been described for its ability to form magnetosomes – an intracellular form of magnetite – when grown microaerophilically on iron-based media, which confer a unique magnetotactic characteristic on these microorganisms. A (highly speculative) link may exist to the magnetites and magnetic chains discovered in Martian meteorite ALH84001 (Friedmann et al., 2001). Could the magnetic chains discovered in ALH84001 possibly be the product of Martian microbes that use a perchlorate metabolism?

This opens up the possibility that Martian organisms may be similar to halophilic xerophiles on Earth that thrive in hypersaline solutions, under conditions which would be expected on Mars and at temperatures well below the freezing point of pure water (Schulze-Makuch and Houtkooper, 2010). Xerophilic adaptations

would allow microbes to grow at very low water activities. Even *E. coli* cells are able to generate up to 70 % of their intracellular water during metabolism rather than from extracellular sources (Kreuzer-Martin et al., 2005). The antifreeze and hygroscopicity properties would make perchlorate and  $\text{H}_2\text{O}_2$ -water solutions ideal adaptation tools for life in the Martian cold desert. Adaptation to highly oxidizing compounds would also convey adaptation advantages to deal with high radiation doses on the Martian surface. Evolution on Earth favored (salt) water as an internal solvent, but in dry and cold conditions, a mixture of water with hydrogen peroxide as intracellular solvent and/or an adaptation to perchlorate-water mixtures would be much more favorable (Schulze-Makuch and Houtkooper, 2010). Microorganisms use the resources of their environment optimally – a lesson learned from life on Earth – and this is to be expected in the case on Mars as well.

#### 4. Habitats and Possible Life in Europa

Europa is one of the priority targets for finding life in the Solar System. The reasoning is simple. Europa has water in abundance, almost surely in liquid form beneath a layer of ice that protects its subsurface ocean from radiation. An oft-cited analog are the hydrothermal vents on the ocean floor on Earth that exhibit diverse microbial life and even multicellular life forms. However, light cannot penetrate to the depth where liquid water could exist (Reynolds et al., 1983); thus, only chemical energy would be left of those types of energy used for metabolism on Earth. The question is whether light and chemical energy are fundamental sources for life in general, or whether they are only used on Earth, because they are so abundantly present and easily available on our home planet. Thus, I will discuss the latter possibility here and point to some energy sources that could be used by organisms in a subsurface ocean, as likely existing within Europa.

Hydrothermal vents on the ocean bottom are used by life on Earth for metabolism via redox reactions, but in principle thermotropic life forms that may exist in the oceans of Europa may harvest the energy provided from hydrothermal vents by using thermal gradients or heat directly. Muller (1985, 1993, 1995, 2003) and Muller and Schulze-Makuch (2006) suggested the use of thermal gradients, which they termed thermosynthesis, as a plausible metabolic pathway. Thermosynthesis, just as a steam engine, would make use of a phase transition. Membranes undergoing the thermotropic phase transition would increase the mobility of the molecules within the membrane (Muller and Schulze-Makuch, 2006). This kind of transition could plausibly result in a change in potential across the membrane due to a change in dipole potential (Muller, 1993). Very similar potential changes that undergo the thermotropic phase transition have been measured across monolayers of lipids at the water/air interface. Since these changes can easily reach 100 mV, they would be high enough to drive ATP synthesis (Muller and Schulze-Makuch, 2006). If this reasoning is correct, thermosynthesis could also



be a basic pathway of metabolism for organisms on early Earth, possibly a progenitor of bacterial photosynthesis (Muller, 1985, 1995, 2003), and an option for possible life in Europa's ocean (Schulze-Makuch and Irwin, 2002b).

Alternatively, "thermotrophs" could harvest energy from the high heat capacity of water, which is about 4 kJ/kg under a wide range of temperature and pressure conditions. If we assume a cell mass of  $10^{-12}$  g, comparable to that of microbes on Earth (Madigan et al., 2000), and also assume that one tenth of the cell mass is a vacuole of water from which the thermotropic organism could extract energy, about  $2.5 \times 10^6$  eV would be obtained from cooling the vacuole by 1 °C. The organism could extract about 9,000 eV of usable energy for a temperature change from 5 to 4 °C (using the Carnot cycle; Schulze-Makuch and Irwin, 2002b, 2008). High-energy metabolites within the organism could be produced via conformational changes if a temperature gradient between vacuole and cell plasma is present. For a cell as large as the giant pantropical alga, *Valonia macrophysa* (Shihira-Ishikawa and Nawata, 1992), with a water vacuole of approximately 10 g, the potential energy yield could be close to 1 J (Schulze-Makuch and Irwin, 2008).

Inefficiency is a potential drawback to the use of thermal energy, because the most efficient thermodynamic system known is the Carnot cycle. Thus, most of the energy in a thermal gradient would be dissipated as heat without being captured by chemical bonds and would also degrade the thermal gradient itself. A possible adaptation by the thermotropic organism would be to shuttle back and forth across fairly sharp environmental gradients or to possess an elongated body and make use of convection to dissipate the unusable entropy-related energy. The reader is referred to Schulze-Makuch and Irwin (2008) for further details and scenarios.

Life in a European ocean could also be based on osmotic energy. If life arose on Europa early, it would likely have originated in water of low salinity since it is unlikely that the ocean would have been in chemical equilibrium with the rocky mantle (Schulze-Makuch and Irwin, 2002b). Life could have maintained that hypo-osmotic cellular state as the ocean became progressively saltier. An analogous event occurred among the marine teleosts (bony fish such as sharks) on Earth. When they invaded the oceans from their freshwater origins, they retained a strong osmotic differential of roughly 0.7 osmoles between their intercellular fluids and their surrounding environment (Wilmer et al., 2000), where 1 osmole is 1 mol of osmotically active particles. Using this osmotic pressure gradient as a first assumption for osmotic pressure autotrophs on Europa, the energy yield can be calculated by (Schulze Makuch and Irwin, 2002b, 2008)

$$\Pi = cRT \quad (6)$$

where  $\Pi$  is osmotic pressure (atm),  $c$  is the molar solute concentration (mol/L),  $R$  is the universal gas constant (0.08206 L atm/mol K), and  $T$  is the absolute temperature (K). At a temperature of 25 °C (298 K), the osmotic pressure would

be 16.9 atm ( $1.7 \times 10^6$  Pa). The force that acts on one water molecule along its concentration gradient is then

$$F = \prod A \quad (7)$$

where  $A$  is the cross-sectional area of one water molecule. This force is about  $10^{-13}$  N. Further, assuming this force moves the water molecule through a membrane channel that couples the movement to formation of a high-energy covalent bond, the energy available for bond formation is given by

$$W = Fs \quad (8)$$

where  $s$  is the distance the water molecule moves down its density gradient (assumed to be  $10^{-8}$  m for a biomembrane; Schulze-Makuch and Irwin, 2008). The calculated potential energy yield is then 0.007 eV. Thus, one ATP could be phosphorylated from ADP for about every 45 water molecules entering the cell by osmosis. This is about two orders of magnitude below the energy yield for chemoautotrophs or photoautotrophs on Earth. However, the 0.007 eV is a conservative estimate, because the osmotic differential calculated here is based on those of fish that have adapted from their freshwater origin to their marine environment rather than microbes adapted to use osmotic gradients. Halophilic microbes adapted not only to tolerate but to use osmotic gradients should easily be able to more than quadruple this energy yield. For example, some halophilic strains of cyanobacteria are known to tolerate salt concentrations of up to 2.7 M NaCl (Hagemann et al., 1999).

The direct coupling of water movement to phosphorylation reactions is not known for living systems on Earth. However, evolution could have favored the origin of membranes in which water movement yields energy, given that osmotic gradients were available – particularly in a subsurface ocean environment such as within Europa. A plausible mechanism would involve tertiary structural changes in a channel-associated protein that catalyzes formation of high-energy bonds, much as ligand-induced conformational changes in membrane receptors lead to a series of steps culminating in the synthesis of high-energy cyclic AMP (Schulze-Makuch and Irwin, 2002b). As in the case of thermal gradients, degradation of the osmotic gradient is a potential disadvantage to their use for generating free energy. Also, the influx of many water molecules would either significantly increase the cell volume or increase counteracting pressure in rigid cells that cannot expand in volume. This could be mitigated, however, by a compensatory loss of solutes, such as efflux of  $\text{Na}^+$  (and  $\text{Cl}^-$  for electrical balance) powered by the rise in intracellular pressure. Either the extrusion of solutes or the pressure itself could be coupled to conformational changes that could catalyze high-energy bond formation. Or a membrane water channel could be coupled to a reaction that forms a high-energy bond inside the cell as the water moves inward from hypotonic surroundings, while a similar channel oriented in the opposite direction could harvest

energy when water leaves the cell in hypertonic surroundings. The hypothetical organisms could thus move between two layers of different salinity, using both to harvest energy.

## 5. Habitats and Possible Life on Titan

Titan is one of the highest-priority targets for astrobiology in our Solar System (Shapiro and Schulze-Makuch, 2009). In general, environmental conditions are thought to be conducive for life if (1) an energy source, (2) polymeric chemistry, and (3) a liquid solvent in high enough quantities are present on a planetary body (Irwin and Schulze-Makuch, 2001). This is the case for Titan. Further, what makes Titan so interesting is that it may be hosting exotic life, meaning life that is dependent on some other solvent than water. Methane/ethane lakes have been confirmed on the surface of Titan (Stofan et al., 2007; Brown et al., 2008) and in situ measurements indicate the presence of methane rain on Titan (Tokano et al., 2006). Hydrocarbon compounds may be used as an alternative solvent for life based on theoretical work by Bains (2004), Benner et al. (2004), and Schulze-Makuch and Irwin (2008) and based on microbial organisms extracted from a natural liquid asphalt lake in Trinidad and Tobago (Schulze-Makuch et al., 2011), which is studied as an analog site for Titan.

Despite the frigid temperatures of about 95 K on Titan's surface, it has been suggested that putative life might be present on Titan and use acetylene (Schulze-Makuch and Grinspoon, 2005), heavy hydrocarbons (McKay and Smith, 2005), or even radical compounds (Schulze-Makuch and Grinspoon, 2005) for metabolism. Although temperatures are low, solid acetylene, having formed in the atmosphere, would settle down on the surface and sink in the hydrocarbon lakes. These lakes themselves may be heated from below and promote prebiotic reactions involving the high-energy acetylene molecule, which accumulates on the lake bottom. Schulze-Makuch and Grinspoon (2005) proposed the following metabolic reaction that also would explain the high amounts of methane in the Titan atmosphere:



Acetylene is an explosive under Earth surface conditions. However, under Titan conditions it may provide enough energy to propel a feasible metabolic strategy in an extremely cold environment. Alternatively, radical reactions could provide sufficient energy. For example, the following radical reactions may be feasible under a Titan scenario:



or



All the radical reactants listed above have been detected in the Titan atmosphere. Moreover, the resulting compounds are biologically interesting. HCN is often invoked in origin of life scenarios, particularly since it can combine with itself in alkaline solutions with the help of UV photons to form amino acids such as glycine. There may even be certain environmental conditions that would allow the formation of the all important biomolecule (for Earth life) adenine from HCN. Also,  $\text{CN}_2\text{H}_2$ , cyanamide, “glues” amino acids together to form proteins in Earth’s biochemistry.

Silicon could play a larger role in a Titan biochemistry. Silane is a liquid and polysilanes would be solid under Titan’s very reducing conditions and could be involved in the makeup of biomembranes similar to the functions that lipids have in Earth’s biochemistry. Silicon also interacts chemically well with hydrocarbons as solvent and would not be immobilized (e.g., oxidized to silicates) under Titan conditions (because of the lack of molecular oxygen and liquid water). However, given the prevalence of carbon on Titan and the generally more favorable properties of carbon to form polymers, carbon would be expected to be a dominant element for any life on Titan. However, even life on Earth does use other elements frequently for biological purposes (particularly N, P, and S), including silicon such as in diatoms and in plants (to give them the required rigidity).

## 6. Conclusions

The few examples given here are only a small summary of potential organismic adaptations possible, even within the confines of our Solar System. Based on the creativity and diversity of life on Earth, we surely underestimate the diversity of life elsewhere in its ability to use various building blocks, energy sources, and solvents. The objective has to be to conduct the search for life with an open mind and without preconceived notions of how life ought to be. Only that way we will not miss it when we “stumble” on it along our path of exploring the universe.

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Biodata of **Emeritus Prof. John A. Raven** and **Sean Donnelly**, authors of “*Brown Dwarfs and Black Smokers: The Potential for Photosynthesis Using Radiation from Low-Temperature Black Bodies.*”

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**John A. Raven**



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# BROWN DWARFS AND BLACK SMOKERS: THE POTENTIAL FOR PHOTOSYNTHESIS USING RADIATION FROM LOW-TEMPERATURE BLACK BODIES

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## 1. Introduction

Apart from having a colour in their name and being somewhat politically incorrect terms, what do brown dwarfs have to do with black smokers as energy sources for photosynthesis?

Brown dwarfs are bodies larger than the largest known planets and smaller than M stars (red dwarfs) with a mass greater than 0.075–0.8 of the mass of the sun. Brown dwarfs are too small to sustain nuclear fusion and emit black-body radiation resulting from heating caused by gravitational contraction (Burgasser, 2008) and, to a much smaller extent, radioactive decay. They may be shorter-lived (but may continue to radiate energy for up to 2–10 Ga) and are cooler (effective surface temperature,  $T_{\text{eff}}$ , in the range 600–2,500 K) than typical red dwarfs (M stars), the smallest objects which can sustain nuclear fusion (Andreschchev and Scalo, 2004; Burgasser, 2008; Biller et al., 2011; Luhman et al., 2011). The distinction between late M red dwarfs and what are clearly brown dwarfs in spectral classes L and T brown dwarfs is a contentious matter (Basri et al., 1996; McLean et al., 2003; Lodders, 2004). Here we follow Kirkpatrick et al. (1999) and Kirkpatrick (2005) in considering red dwarfs to run as late as M9V, whereas Joergens et al. (2003) consider spectral classes as early as M5V as brown dwarfs. Luhman et al. (2011) suggest that a spectral object with a surface temperature of only 300 K is a brown dwarf, although it could also be classified as Hot Super-Jupiter. The mean surface temperature of Earth is about 289 K.

Brown dwarfs can host planets: Andreschchev and Scalo (2004) based this conclusion on the properties of their ‘solar’ discs (see also Apai et al., 2005). Considerable effort has been expended in the search for planets orbiting brown dwarfs (Chauvin et al., 2004; Bennett et al., 2008; Todorov et al., 2010; Biller et al., 2011). Bennett et al. (2008) obtained preliminary information as to the occurrence of a planet of several times the Earth’s mass orbiting what appears to be a brown dwarf, while Todorov et al. (2010) have found a planetary-mass companion (five to

ten times the mass of Jupiter) of a brown dwarf. It is possible that brown dwarfs could host Earth-like planets (ELPs) in their continuously habitable zones (CHZs), i.e. the zone of planetary orbits which permits the occurrence of liquid water on the surface for millions to billions of years. While Andreeschchev and Scalo (2004) suggest an upper limit on the duration of 1 Ga, the detailed analysis by Barnes and Heller (2013) suggests a much shorter CHZ duration, and also point out significant problems with the occurrence of the astronomical and geological factors leading to habitability of an ELP orbiting a brown dwarf. However, in this Chapter we assume that there are situations in which brown dwarfs can host habitable ELPs in a CHZ of sufficient duration to allow the evolution of life.

Black smokers are found at some submerged hydrothermal vents which are fissures in the Earth's crust in tectonically active areas, emitting acidic water at 620–670 K (Jupp and Schultz, 2000) containing reductants such as ferrous iron and sulphide whose combination gives a black precipitate. Jupp and Schultz (2000) present reasons based on the thermodynamic properties of water as to why the water does not become hotter than 620–670 K even though the solidifying magma which heats it is at 1,500 K. Black smoker water temperatures are thus at the bottom of the range of temperatures for brown dwarfs. Life supported by chemolithotrophy based on the reductant in the vent water and  $O_2$  from oxygenic photosynthesis as the oxidant is well characterised for black smokers; chemolithotrophy is discussed in more detail below. A green photosynthetic bacterium has been found at one of them at a depth at which essentially no solar radiation penetrates (Beatty et al., 2005). The significance of this for the occurrence of photosynthesis at black smokers is that the green sulphur bacteria are obligate photolithotrophs: they can only grow with electromagnetic radiation as their energy source,  $CO_2$  as their carbon source and some reduced sulphur compound or  $H_2$  as the reductant, strongly indicating that photosynthesis can occur at black smokers (Beatty et al., 2005).

The  $T_{\text{eff}}$  of a black body is related to the wavelength at which the emitted photon flux is highest by Wien's law; this relationship is used to give the wavelengths of maximum photon emission for brown dwarfs in Table 1.

**Table 1.** Wavelengths of maximum photon flux from late M stars and L and T brown dwarfs.

Spectral type	$T_{\text{eff}}$ (K)	Wavelength of maximum photon flux based on $T_{\text{eff}}$ and Wien's law (nm)
G2V (sun)	5,700	644
Late M (M7, M8)	2,500–3,500	1,050–1,470
L	1,400–2,500	1,470–2,620
T	600–1,400	2,620–6,120

The values are calculated using Wien's law which states that the wavelength of maximum photon emission from a black-body radiator is  $3.67.10^6/T_{\text{eff}}$ , where wavelengths are in nm and  $T_{\text{eff}}$  is absolute temperature (K) of the surface of the body (Burgasser, 2008; Nobel, 1999)

The values in Table 1 show that the wavelengths of maximum photon emission from brown dwarfs are further into the infrared than the longest wavelength at which photochemistry occurs in any known photosynthetic organism on Earth (of about 1,050 nm) and also at longer wavelengths than photochemistry is thought to be likely based on the absence of appropriate electronic transitions detectable by spectroscopy (Kiang et al., 2007a, b). An additional problem for photosynthesis, especially for aquatic organisms, is the decreasing transmittance of water for electromagnetic radiation as wavelength increases (Wolstencroft and Raven, 2002; Raven and Wolstencroft, 2004; Kiang et al., 2007a, b; Stomp et al., 2007). Both of these constraints on photosynthesis apply especially to black smokers with their  $T_{\text{eff}}$  values at the low end of the range for cooler, i.e. spectral type T, brown dwarfs.

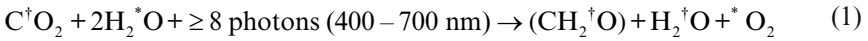
The objective of this chapter is to explore the possibilities of photosynthesis using radiation from brown dwarfs and black smokers as two natural sources of black-body radiation with wavelengths of maximum photon emission in the range 1,500–6,000 nm, in the context of the two constraints discussed in the preceding paragraph. The emphasis on photosynthesis in the astrobiological, brown dwarf, context derives from two related considerations of detectability. The general consideration is that, on current knowledge, photosynthesis using radiation from the body round which an Earth-like planet (ELP) is orbiting provides much more energy for biota than the sum of all other possible energy sources combined (Raven et al., 2012a; see also: Canfield et al., 2006; Raven and Cockell, 2006; Cockell et al., 2009a, b). This means that spectroscopic detectability of life is more likely for a planet with photosynthesis since the energy and chemical flux through biota is greater, giving more likelihood of finding spectroscopic signatures, e.g. photosynthetic pigments (cf. Cockell et al., 2009a, b) and atmospheric gases. The more particular consideration is that there is the possibility of detecting the unique product of oxygenic photosynthesis, i.e.  $\text{O}_2$  either directly as  $\text{O}_2$  or via its photochemical product  $\text{O}_3$ . For black smokers, the interest is in the possibility that obligately photolithotrophic organisms, i.e. those only able to grow with electromagnetic radiation as their energy source and inorganic chemicals as their source of essential elements, which evolved using solar radiation near the surface of water bodies can grow using radiation from black smokers in the absence of solar radiation or whether such additional radiation sources as sonoluminescence, chemiluminescence from abiological oxidation of  $\text{S}^{2-}$  by  $\text{O}_2$  or bioluminescence (Raven et al., 2000, 2012a; Beatty et al., 2005; Cockell et al., 2009a, b). To set the scene, we first briefly discuss photosynthesis and the related autotrophic process of chemolithotrophic metabolism on Earth.

## 2. Photosynthesis on Earth Using Solar Radiation

Photosynthesis using solar radiation supplies almost all of the metabolic energy used by life on Earth, and there are a variety (geochemical, spatial distribution, thermodynamic) of quantitative limits on how solar energy and more particularly

other possible energy sources can be used in biology (Kleidon, 2012; Raven et al., 2012a). The arguments of Kleidon (2012) are based on thermodynamic disequilibrium in the Earth system, and Kleidon points out that Lovelock (1965, 1975) had suggested that the spectroscopic detection of such disequilibrium in the atmosphere of exoplanets could be used as an indicator of life. In particular, the occurrence of the very oxidising gas  $O_2$  (detectable directly or as its photochemical (UV) product  $O_3$ ) with the very reducing gas  $CH_4$  could be used to indicate the presence of oxygenic photosynthesis.

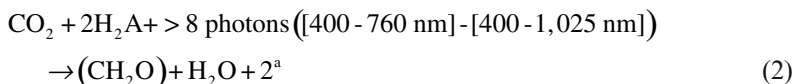
The great majority (>99 %) of photosynthesis on Earth today is oxygenic (Raven, 2009a), proceeding (Falkowski and Raven, 2007) according to the generalised Eq. (1):



where the superscripts on the O indicate the source of the O in the  $O_2$  product.

The range of wavelengths used, i.e. 400–700 nm (with some use of UVA, 320–400 nm, and in a very few organisms 400–730 nm), can be rationalised in terms of the emission spectrum of the sun. Using Wein's law for a black-body radiator (Nobel, 1999; Wolstencroft and Raven, 2002), the wavelength at which the sun emits the greatest number of photons is given by  $3.67.10^6/T_{\text{eff}}$ , where wavelengths are in nm and  $T_{\text{eff}}$  is absolute temperature (K) of the surface of the body. For the sun, a G2V star,  $T_{\text{eff}}$  is 5,600 K, so the maximum emission of photons is at 655 nm, which is shifted to slightly shorter wavelengths after passage through the Earth's atmosphere. The upper wavelength limit for oxygenic photosynthesis is apparently set by the energetics of the photochemical and subsequent reactions involved in the use of two photons, each consumed in a separate photochemical reaction, for each electron transferred from  $H_2O$  to  $CO_2$  (e.g. Bjorn et al., 2009; Milo, 2009; Raven, 2009b). Even with this constraint, over half of the photons reaching the Earth's surface can potentially be used in photosynthesis by photochemical reactions with energy inputs corresponding to photons at 680 nm for photosystem II and 700 nm for photosystem I. Photons of shorter wavelength, i.e. higher energy per photon, absorbed by the photosynthetic pigments are transferred to the photochemical reaction centres with some of their energy dissipated as heat. Water absorbs photons, and even in the waters with minimal content of solutes and particles which cause further attenuation, the maximum depth at which growth of oxygenic photosynthetic organisms using solar radiation as their energy source can occur is less than 300 m (Raven et al., 2000). Maximum transmittance of pure water is in the blue-green region of the spectrum at about 470 nm, so with increasing depth, the wavelength at which the most solar photons are incident on organisms is progressively moved to shorter and shorter wavelengths than the 655 nm value at the surface. In many coastal and inland waters, terrestrially derived organic matter absorbs in the UV and blue regions, further constraining the rate at which photons reach submerged organisms as well as further constraining the range of wavelengths of the photons, at a given depth (Falkowski and Raven, 2007; Kiang et al., 2007a, b; Stomp et al., 2007).

Well under 1 % of photosynthetic CO<sub>2</sub> assimilation on Earth today is carried out by anoxygenic photosynthetic bacteria (Johnston et al., 2009; Raven, 2009a) which are only able to carry out autotrophic CO<sub>2</sub> assimilation in the absence of O<sub>2</sub>. This anoxygenic photosynthesis can be represented by the generalised Eq. (2):



where H<sub>2</sub>A is a generalised reductant (including the case of A = 0, i.e. H<sub>2</sub>) and A is the product of oxidation of H<sub>2</sub>A. Reductants are frequently sulphur compounds with a range of redox states, as well as Fe<sup>2+</sup> (Widdel et al., 1993). The wavelength ranges shown result from the spectral diversity of the bacteriochlorophyll antenna pigments used in photochemistry in the different anoxygenic photosynthetic organisms (Trissl, 1993; Blankenship et al., 1995; Scheer, 2003; Kiang et al., 2007a, b; Stomp et al., 2007). Photochemistry occurs at 798–870 nm, depending on the organism, so that the use of the longest wavelengths harvested by the antenna pigments involves uphill excitation energy transfer to the reaction centre (Blankenship et al., 1995; Kiang et al., 2007a, b; Stomp et al., 2007). These organisms are of particular interest in the context of brown dwarfs and black smokers because of their use of photons in photochemistry at longer wavelengths than oxygenic photosynthesis (Eq. 1).

The anoxygenic photosynthetic autotrophic bacteria have only one kind of bacteriochlorophyll-based photochemical reaction in each organism: suggestions that there was more than one kind of reaction centre in a given genotype of purple photosynthetic proteobacteria (Frenkel, 1970; Karapetyan, 1975) have not been substantiated by subsequent studies. This reaction centre operates only once in moving an electron from H<sub>2</sub>A to CO<sub>2</sub> in the simplest case of the Chlorobiaceae (green sulphur bacteria) where the oxidant generated by the photosystem can oxidise H<sub>2</sub>A and the reductant can reduce CO<sub>2</sub> (Falkowski and Raven, 2007). However, the observed photon requirement given in Eq. (1) is well above the minimum of four needed to transfer four electrons from H<sub>2</sub>A to CO<sub>2</sub>, even when the electron donor is H<sub>2</sub> (i.e. there is no A in H<sub>2</sub>A) which thermodynamically is able to reduce CO<sub>2</sub> without the intervention of photochemistry (Larsen et al., 1952). In the Chlorobiaceae this presumably reflects the need for additional photons for ATP synthesis (Falkowski and Raven, 2007; Okuno et al., 2011) for CO<sub>2</sub> assimilation by the reverse tricarboxylic acid cycle leading to compounds at the redox level of carbohydrate (Raven, 2009a; Raven et al., 2012b), as well as for the synthetic and transport processes required for growth using photosynthate and inorganic nutrients from growth medium (Falkowski and Raven, 2007). For the proteobacterial purple photosynthetic bacteria, the photochemical reaction can oxidise reductants of higher redox potential than is the case for the Chlorobiaceae but cannot generate reductants which are able to reduce CO<sub>2</sub> (Falkowski and Raven, 2007). The requirement for reversed electron transport (the reverse of the reactions considered by Wikström and Hummer (2012)), energised by a

photochemically generated proton gradient (Falkowski and Raven, 2007), in assimilating  $\text{CO}_2$  using high-potential reductants is another factor in increasing the photon cost of anoxygenic photosynthesis. As with the Chlorobiaceae, the use of  $\text{H}_2$  as the electron donor by the purple photosynthetic bacteria still requires at least 8 photons per  $\text{CO}_2$  assimilated (data in Larsen et al., 1952, with a reinterpretation of the data of French, 1937; see also Gobel, 1978). The data available for anoxygenic photosynthetic bacteria suggest that their quantum yield of growth in their natural habitat is certainly not higher than that of oxygenic organisms (Schanz et al., 1998).

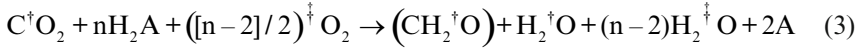
The ability of anoxygenic photolithotrophic organisms to use photons of lower energy, generally corresponding to wavelengths of 798–870 nm in the infrared, in the photochemistry of their single photoreactions than are used in either of the two photoreactions of oxygenic photosynthesis reflects the lower energy requirements for the redox reactions carried out than is the case for oxygenic photosynthesis. The autotrophic anoxygenic photosynthetic organisms are all aquatic, and their growth is increasingly constrained in deeper and deeper waters by the preferential absorption of the longer wavelengths of solar radiation by water (Kirk, 1994; Pope and Fry, 1997; Wolstencroft and Raven, 2002; Kiang et al., 2007a, b; Stomp et al., 2007). The reductant for photosynthesis in these anoxygenic photosynthetic autotrophs comes largely from anoxic oxidation of organic matter produced by oxygenic photosynthetic organisms, using oxidants such as  $\text{SO}_4^{2-}$  to produce the reductant  $\text{S}^{2-}$  (Raven, 2009a). The anoxygenic photosynthetic bacteria are provided with the stronger (lower redox potential than  $\text{H}_2\text{O}$ ) reductant  $\text{S}^{2-}$  because the consortium of organisms oxidising organic matter have run out of the strong (high redox potential) oxidant  $\text{O}_2$  and resort to using the weaker oxidant  $\text{SO}_4^{2-}$ . Earlier in Earth's history, and especially before the global oxygenation event some 2.3 billion years ago, the primary productivity of anoxygenic photosynthetic bacteria has been modelled to be much higher than it is today, with an upper limit of about 10 % of present marine photosynthetic net primary productivity of about 50 Pg C per year by oxygenic photosynthetic organisms (Kharecha et al., 2005; Canfield et al., 2006; Olson, 2006; Johnston et al., 2009; Raven, 2009a). Before 2.3 billion years ago, the regeneration of the reductant  $\text{H}_2\text{A}$  from the oxidant A would have occurred by respiration of photosynthate with A (rather than  $\text{O}_2$ ) as the electron acceptor. Other anoxygenic photosynthetic bacteria grow in aerobic conditions, but do not carry out the autotrophic reaction indicated in Eq. (2). These organisms generate transmembrane proton gradients which can be used to energise solute transport or ADP phosphorylation in otherwise heterotrophic (chemo-organotrophic) organisms, using bacteriochlorophyll-based reaction centres and antenna pigments and photons in the range 400–900 nm (Blankenship et al., 1995). The use of photochemically generated energised intermediates could spare the respiration of organic substrates in the light to energise the two categories of endergonic reactions (Raven, 2009a). The same applied to organisms using bacterio-, halo- or proteo-rhodopsins in their energy-conserving photochemistry

(Raven 2009a, b). Their impact in the global carbon cycle is to decrease the flux of organic carbon back to  $\text{CO}_2$ . Fuhrman (1999) suggests that 80 % of marine net primary productivity (about 50 Pg C per year) flows to bacteria and archaea in the microbial loop, i.e. 40 Pg organic carbon. Of this (Fuhrman, 1999) 20 Pg carbon becomes bacterial biomass and the remaining 20 Pg carbon is lost as  $\text{CO}_2$  in growth and maintenance of these organisms. From Fig. 14.7 of del Giorgio and Williams (2005), allowing for respiration by primary producers, about 80 % of bacterial production and respiration occurs in the epipelagic (euphotic) zone so that about 16 Pg carbon can be allocated to each of archaeal and bacterial chemo-organotrophic productivity and respiration. Zubkov (2009) finds that 10 % of archaeal plus bacterial biomass is contributed by aerobic anoxygenic bacteria, with a rather larger contribution (perhaps 15 %) to productivity, i.e. a productivity of 2.4 Pg organic carbon. Again following Zubkov (2009), not more than 20 % of the energy needed for growth and maintenance comes from photochemistry, while the rest comes from respiration of externally derived organic substrates. Without photochemistry a productivity of 2.4 Pg carbon would involve respiration of a further 2.4 Pg organic carbon to  $\text{CO}_2$ . With photochemistry providing a replacement for the role of respiration in transforming energy, as opposed to providing carbon skeletons for biosynthesis, the global respiration of organic carbon by anoxygenic bacteria might be decreased to as little as 1.92 Pg carbon, i.e. a decrease in C loss of up to 0.48 Pg carbon. While the aerobic anoxygenic bacteria cannot carry out autotrophy, they could prevent the global loss in respiration of up to 0.48 Pg carbon per year, or rather less than 0.5 % of the global net primary productivity of about 110 Pg carbon per year (del Giorgio and Williams, 2005; Raven, 2009a). This upper limit is similar to the estimated sum of anoxygenic photolithotrophy plus chemolithotrophy (Johnston et al., 2009; Raven, 2009a).

In addition to the aerobic anoxygenic bacteria, there are also many aquatic archaea and bacteria with energy-transducing rhodopsins with absorption maxima in the 490–527 nm range (Man et al., 2003; Sabeji et al., 2007) and so of less interest in relation to organisms using radiation from low-temperature black bodies. As with the aerobic anoxygenic bacteria, the organisms with energy-transducing rhodopsins but no other energy-transducing photochemistry lack autotrophic  $\text{CO}_2$  assimilation but have an ecological role for the energy provided by photochemistry involving rhodopsins in surviving periods of starvation (Gómez-Consarneau et al., 2010) and occasionally stimulating growth when organic substrates are available (Giovannoni et al., 2005; Gómez-Consarneau et al., 2007). The global saving of organic carbon loss in respiration in the organisms using rhodopsin-based photochemistry is probably less than that of the bacteriochlorophyll-based aerobic anoxygenic photosynthetic bacteria, so the combination of these two sorts of photochemical energy-transducing organisms is probably about 0.5 Pg carbon per year.

Oxygenic photosynthesis ultimately provides the energy, directly or via biotic provision of one or more inorganic substrates, for almost all life on Earth,

including almost all chemolithotrophy. Chemolithotrophy proceeds according to the generalised Eq. (3)



where  $H_2A$  is a generalised reductant (including the case of  $A=0$ , i.e.  $H_2$ ) and  $A$  is the product of oxidation of  $H_2A$ . The superscripts on the  $O$  indicate some mechanistic aspects of the reaction, in which some of the reductant is oxidised to generate a proton gradient which can be used to transport solutes and phosphorylate ADP and, in the general case when  $H_2A$  is too weak a reductant to reduce  $CO_2$ , to generate a  $CO_2$ -reducing reductant from  $H_2A$ . As with anoxygenic autotrophic photosynthesis, the reductant  $H_2A$  generally comes from anaerobic respiration of organic C produced by oxygenic photosynthesis by other biota; the oxidant  $O_2$  is also a product of oxygenic photosynthesis (Raven, 2009a). Even the chemolithotrophs supported by reductants emitted by black smokers in ocean-floor-spreading regions depend on  $O_2$  from oxygenic photosynthesis as their oxidant (Raven, 2009a). Chemolithotrophs compete for the reductants denoted as  $H_2A$  with anoxygenic anaerobic photosynthetic bacteria (Eq. 2) in illuminated oxic–anoxic interfacial habitats at the surface of water bodies, with habitat partitioning such that the photosynthetic bacteria live in anoxic yet illuminated regions, while chemolithotrophs can grow in the dark but need  $O_2$  or some other oxidant at a significantly higher redox potential than  $H_2A$ . As will be seen below, there is also very limited competition with chemolithotrophs for reductant from green photosynthetic sulphur bacteria at black smokers.

### 3. The Possibility of Photosynthesis on ELPs Orbiting Brown Dwarfs

For main sequence stars, the main source of energy sustaining their high surface  $T_{\text{eff}}$  values is thermonuclear fusion. These stars produce more energy and become hotter with time, so their habitable zone (HZ) at a given time is further from the star than it was when the star was younger. The CHZ of stars is thus at the outer edge of the HZ when they were younger and the inner edge of the HZ when the star is older. Brown dwarfs lack nuclear fusion as an energy source and so cool and produce less radiation with time, so the HZ becomes closer to the brown dwarf with time. The CHZ for brown dwarfs is at the inner edge of the HZ early on and later is at the outer edge of the HZ. For the oldest brown dwarfs, the HZ would involve a planetary orbit within the Roche limit, which is impossible since the Roche limit is the closest that a moon can orbit a planet, or a planet can orbit a star or brown dwarf, without undergoing gravitational disruption to become a ring system of much small particles. These considerations notwithstanding, Andreeschchev and Scalo (2004, p.117) suggest an upper limit on CHZ duration of 1 Ga, with much shorter times suggested by Barnes and Heller (2013). For comparison, the duration of the Earth's ELP is estimated at about 5 Ga (O'Malley-James et al., 2013)



The CHZ of a brown dwarf is, like that of red dwarf (M) stars, within the tidal lock limit. Tidal locking involves a 1:1 or 3:2 (Correia and Laskar, 2004) ratio of number of rotations of the planet per planetary year, while outside the tidal lock zone, there is no such constraint on the ratio of planetary rotations per planetary year and a considerable range of such ratios is seen on the solar system. While tidal locking poses a number of problems for life on a planet, these are not a fatal problem: for example, the atmosphere would not necessarily freeze out on the cold side of a tidally locked ELP, especially for a 3:2 planetary rotation to planetary year ratio.

In considering the radiation environment of an ELP in the CHZ of a brown dwarf, it is clear that delivering radiant energy at the same rate as to an ELP orbiting, say, a G star like the sun in its CHZ would involve a higher rate of photon input in inverse proportion to the lower energy content of each photon than is the case for a G star (see Wolstencroft and Raven, 2002). If there was no constraint on the minimum energy per photon (maximum wavelength of the photon) usable in photochemistry, then more individual photochemical reactions could, in principle, be employed in series to carry out a chemical reaction requiring a minimum. In their classic paper, Hill and Bendall (1960) suggested the now accepted ‘Z scheme’ of two different photochemical reactions in series, each using one photon, co-operating in the transfer of one electron from  $\text{H}_2\text{O}$  to  $\text{CO}_2$  as the best fit to the data available for oxygenic photosynthesis. However, these authors point out that both two-photon and three-photon schemes had previously been proposed, and Heath et al. (1999) and Wolstencroft and Raven (2002) suggest that a three-photon mechanism for oxygenic photosynthesis might be used on an ELP orbiting a red dwarf (M) star with photochemistry using photons at about 1,050 nm rather than 680 and 700 nm for the two-photon mechanism used on Earth, with the same total energy input per electron transferred from  $\text{H}_2\text{O}$  to  $\text{CO}_2$ . Such schemes could be elaborated to involve four or even more photons but would suffer increasingly from two problems mentioned above as wavelengths increase, i.e. the long-wavelength (low-energy) limit on photochemistry and the large attenuation of long-wavelength radiation by water.

Kiang et al. (2007b) propose 1,100 nm as the upper limit for photochemistry since ‘optical’ sensors cannot measure radiation at longer wavelengths, which is termed ‘thermal’. Kiang et al. (2007b, p.256) point out that this is not a strict upper limit, though Blankenship et al. (2011) use this limit for their interesting proposal for how photosynthesis on Earth could use or make more use of solar radiation than either the anoxygenic or the oxygenic organisms do on their own. Such a mechanism might be useful on a planet orbiting a close binary composed of a G and an M star (O’Malley-James et al., 2012 and see Doyle et al., 2011; Orosz et al., 2012 for the occurrence of planets orbiting close binaries). With a 1,100 nm limit, a mechanism involving three photons in the transfer of one electron from  $\text{H}_2\text{O}$  to  $\text{CO}_2$  in oxygenic photosynthesis could be envisaged, with three as the maximum required number of photochemical reactions and a photon requirement of at least 12 in Eq. (1). Relaxing the upper wavelength limit for photochemistry would in principle permit four photon mechanisms for a

**Table 2.** Calculations for an ELP orbiting stellar bodies with various  $T_{\text{eff}}$  values (Column 1), the fraction of photons 400–100,000 nm emitted by the stellar object (and incident on the ELP) which are in the photochemically active range 400–1,110 nm (Column 2), the number of photons incident on the various ELPs needed to give the same radiant energy as on Earth (Column 3) and the number of photons 400–1,100 nm incident on the various ELPs relative to those incident on Earth for the same radiant energy input 400–20,000 nm (Column 4).

$T_{\text{eff}}$ of the black body	Photons emitted 400–1,100 nm/ photons emitted 400–100,000 nm	Relative number of incident photons giving the same energy input to an ELP as occurs on Earth	Number of photons 400–1,100 nm incident on an ELP relative to those reaching the Earth for the same total radiant energy 400–20,000 nm reaching each planet
5,700 (sun: G2V)	$6.1 \times 10^{-1}$	1	1
2,500 (late M red dwarf, early L brown dwarf)	$8.9 \times 10^{-2}$	2.3	$3.41 \times 10^{-1}$
1,400 (late L brown dwarf, early T brown dwarf)	$4.0 \times 10^{-3}$	4.1	$2.7 \times 10^{-2}$
600 (black smoker, late T brown dwarf)	$7.52 \times 10^{-8}$	9.5	$1.3 \times 10^{-6}$

1,400 nm limit, with the limit on adding further photochemical reactions for even longer upper wavelength limits for photochemistry then set by side reactions (Kiang et al., 2007b). Assuming 1,100 nm is indeed the long-wavelength limit for photochemistry, Table 2 presents calculations of the potential photosynthesis on ELPs orbiting the cool stellar bodies considered in Table 1.

Column 2 gives the fraction of total photons emitted which are below 1,100 nm for a range of black-body  $T_{\text{eff}}$  values, using the Blackbody Calculator for a number of stellar bodies and for a black smoker (GATS, Inc.). The lower wavelength limit was set at 400 nm to exclude UV radiation which on Earth has a limited role (as UVA, 320–400 nm) in energising photosynthesis and a predominant role (UVB, 280–320 nm) in causing photodamage. Cockell and Airo (2002) show that the possibility of a UV-transparent metabolism is negligible, so UVB at least is likely to be damaging to organisms on exoplanets rather than a source of energy for photosynthesis.

Column 3 gives the number of incident photons 400–20,000 nm needed to give the same radiant energy input to an ELP which gives the same radiant energy input as on Earth, using the energy content of photons at the photon emission maximum (Table 1) for each stellar body.

Column 4 gives the number of photons 400–1,100 nm incident on an ELP relative to those on Earth for the same total radiant energy input 400–20,000 nm for all ELPs as on Earth, derived from the values in columns 2 and 3.

For estimates of potential photosynthesis on the various ELPs, the important values in Table 2 are those in column 4, i.e. the number photons 400–1,100 nm incident on an ELP relative to those on Earth for the same total radiant energy input

400–20,000 nm. With the conservative estimate of net primary productivity on Earth of 110 Pg C per year (Raven, 2009a), values in column 4 of Table 1 give an upper limit on primary productivity on ELPs orbiting stellar bodies with  $T_{\text{eff}}$  values of 2,500, 1,400 and 600 K are, respectively, 37, 3.0 and 0.00013 Pg C per year. Very little of Earth's productivity (well under 1 %: Johnston et al., 2009; Raven, 2009a) is based on the photosynthetic use of photons in the 700–1,100 nm range: even the anoxygenic photosynthetic bacteria, which are the only photosynthetic organisms on Earth with photosynthetic pigments absorbing in the 700–1,100 nm range, have significant absorption in the 400–700 nm range from the Soret band of bacteriochlorophyll and from carotenoids. Essentially all of the productivity of anoxygenic photosynthetic bacteria on Earth uses reductants generated from the anaerobic oxidation of the organic products of anoxygenic photosynthesis (see discussion of Eq. 2), and a similar situation would occur on an ELP with predominant oxygenic photosynthesis. Since 3, rather than 2, photons per electron transferred from  $\text{H}_2\text{O}$  to  $\text{CO}_2$  are needed for any oxygenic photosynthesis at 700–1,100 nm on brown dwarf and late M red dwarf ELPs, the capacity of such photosynthesis is overestimated by a factor of 3/2 in column 4 of Table 2.

The discussion of the effect of an 1,100 nm upper wavelength limit for photochemistry on the potential for photosynthesis on ELPs orbiting brown dwarfs did not consider the effects of absorption of radiation by water. As discussed by Wolstencroft and Raven (2002), Kiang et al. (2007a, b) and Stomp et al. (2007), there is significantly greater absorption of 700–1,100 nm photons than of 400–700 nm photons by water. This means that photosynthesis by aquatic organisms with photochemical reactions involving energy inputs corresponding to photons in the 700–1,100 nm range would, if their pigments resembled those of such organisms on Earth, rely largely on absorption by photosynthetic pigments absorbing in the 400–700 nm range.

#### 4. Detectability of Photosynthesis on ELPs Orbiting Brown Dwarfs

The methods for detecting photosynthesis on planets orbiting brown dwarfs are the same as those for other extrasolar ELPs, i.e. the spectroscopic detection of products of photosynthesis and the spectroscopic detection of photosynthetic pigments. For oxygenic photosynthesis, the detectable product is  $\text{O}_2$  and/or its photochemical product  $\text{O}_3$  (Lovelock, 1965, 1975; Cockell et al., 2009a, b; Kleidon, 2012). While there is the possibility of abiotic  $\text{O}_2$  production (Kasting et al., 1997), this appears to be limited to waterless planets, i.e. not those on which oxygenic photosynthesis (or life as we know it) could occur (Selsis et al., 2002). Detection of photosynthetic pigments is usually thought of as the long-wavelength cut-off absorption by the pigments: for Earth this corresponds to the 'red edge' at about 700 nm where chlorophyll absorption (<400–700 nm) ceases, corresponding to an increased reflectance beyond 700 nm (Cockell et al., 2009a, b). For ELPs orbiting cooler bodies than our sun (M red dwarfs, L and T brown dwarfs), it is likely that

there would be an ‘infrared edge’ rather than a ‘red edge’ (Wolstencroft and Raven, 2002; Kiang et al., 2007a, b; Stomp et al., 2007; Cockell et al., 2009a, b). The red edge applies to terrestrial vegetation; aquatic vegetation does not show a clear ‘red edge’ and more complicated, and probably less generic, spectral signatures would have to be used (Cockell et al., 2009a, b).

## 5. The Possibility of Photosynthesis at Black Smokers

The finding by Beatty et al. (2005) of molecular genetic evidence and cell culture evidence of a green photosynthetic sulphur bacterium at a black smoker too deep to receive significant solar radiation provided considerable impetus to considerations of the possibility of photosynthesis supported by black-body radiation from the 600 K water emitted by the vent. The green sulphur bacterium occurs at irradiances of a few  $\text{nmol photon m}^{-2} \text{ s}^{-1}$  at  $760 \pm 50 \text{ nm}$  (760 nm being the absorption peak for the ‘red’ (actually infrared) absorption band of the green sulphur bacterium), i.e. about the same as the irradiances at which other green photosynthetic sulphur bacteria grow in the Black Sea (Beatty et al., 2005). Green sulphur bacteria are well equipped for photosynthesis at very low irradiances. Not only do they use a photosystem I-like photosynthetic reaction centre, which has higher efficiency of conversion of excitation energy reaching the reaction centre than at least the  $\text{O}_2$ -evolving variant of the photosystem II-like photosynthetic reaction centres (Raven et al., 2000), but they have very large photosynthetic unit size (antenna pigment molecules per reaction centre) which further minimises energy losses in photochemistry (Raven et al., 2000; Beatty et al., 2005; Kiang et al., 2007a, b; Stomp et al., 2007).

Irradiances of  $1\text{--}10 \text{ nmol photon m}^{-2} \text{ s}^{-1}$  are similar to other reported values for photosynthesis and growth of very low light-adapted photosynthetic organisms, including an oxygenic coralline red alga (Raven et al., 2000; Raven and Cockell, 2006; Cockell et al., 2009b).  $1\text{--}10 \text{ nmol photon m}^{-2} \text{ s}^{-1}$  is also similar to the irradiance from moonlight at the land or sea surface on Earth at full moon at night (Raven and Cockell, 2006). Beatty et al. (2005) very reasonably assumed that the irradiance they measured came from the short-wave tail of 600 K black-body radiation from the black smoker. Further work is needed to quantify possible inputs of radiation from bioluminescence, chemiluminescence from inorganic oxidation of  $\text{S}^{2-}$  from the black smoker by  $\text{O}_2$  and sonoluminescence (Raven and Cockell, 2006; Raven et al., 2012b).

## 6. Conclusions

Even with a long-wavelength cut-off for photochemistry at 1,100 nm, hypothetical ELPs orbiting early L brown dwarfs and which host photosynthetic organisms could have significant photosynthetic primary productivity, i.e. more than 1 % of the present

primary productivity on Earth. This is similar to what is predicted for late M red dwarfs. The potential for photosynthesis declines as the  $T_{\text{eff}}$  decreases from late L and early T brown dwarfs to late T brown dwarfs where photosynthetic primary productivity is predicted to be about one millionth of that on the present Earth. For black smokers, with the same  $T_{\text{eff}}$  as late T brown dwarfs, the photon flux below 1,100 nm is similar to that found in green photosynthetic sulphur bacteria habitats in the Black Sea, to the habitat of a coralline red alga of the Bahamas and also to the light of the full moon at the sea or land surface and could allow slow photolithotrophic growth of the green photosynthetic sulphur bacterium found at a black smoker.

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**PART VI:  
APPLICATION OF EXISTING  
TECHNOLOGIES FOR THE DETECTION  
OF HABITABLE PLANETS  
AND THE SEARCH FOR LIFE**

**Rauer  
Cabrera  
Gebauer  
Grenfell  
Edwards  
Hutchinson  
Ingley**

**Böttger  
de Vera  
Hermelink  
Fritz  
Weber  
Schulze-Makuch  
Hübers**

Biodata of **Prof. Dr. Heike Rauer**, **Dr. Juan Cabrera**, **Stefanie Gebauer**, and **Dr. John Lee Grenfell**, authors of “*Detection of Habitable Planets and the Search for Life.*”

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# DETECTION OF HABITABLE PLANETS AND THE SEARCH FOR LIFE

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## 1. Introduction

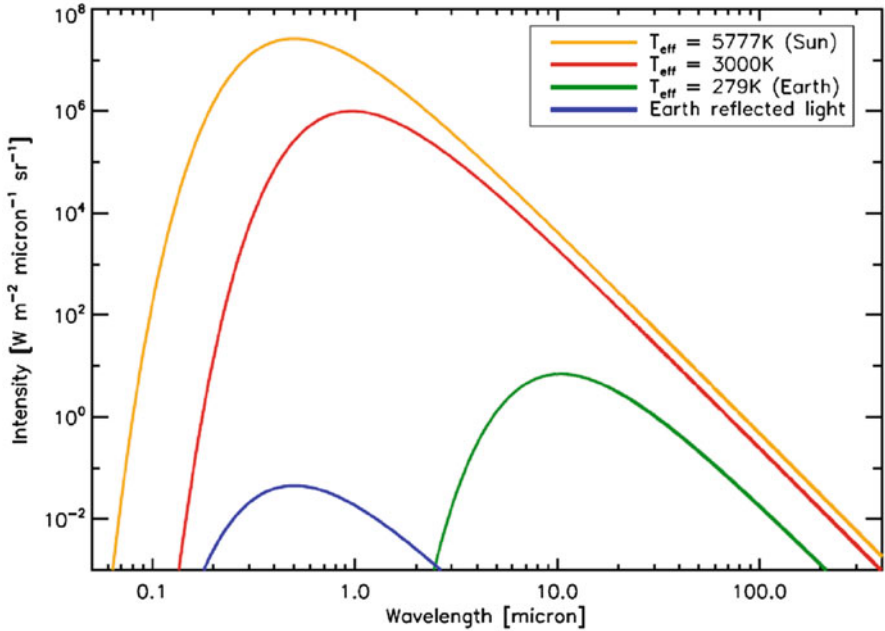
One of the main scientific drivers for extrasolar planet research is the search for terrestrial planets in the habitable zone (HZ) and subsequently the detection of biosignatures indicating the presence of life. This goal is of fundamental importance to answer the question whether the Solar System is the only place in our universe that developed life, or if life is actually common in our galaxy and the biosphere on Earth is just one among many.

However, detecting life outside the Solar System is challenging, because we are far from being able to perform any kind of in situ analysis. Current telescopes on ground and in space can provide us with detected exoplanets in the HZ of cool host stars, cooler than the Sun. Detected small, low-mass planets have to be identified as terrestrial with a rocky surface, and the presence of an atmosphere has to be established. Then, finally, atmospheric biosignatures can be searched for remotely from Earth. Techniques become even more challenging if we consider the option of habitable moons around, for example, gas giant planets.

In this section we describe the various detection methods used for exoplanets and discuss the current status of detection in particular with regard to potentially habitable planets. We then describe the methods to detect atmospheres and finally biosignatures in such planets.

## 2. Detection Methods of Extrasolar Planets

The detection of extrasolar planets is a challenging task since planets orbit stars which are several orders of magnitude brighter than the planet itself (Fig. 1). Due to their different temperatures, stellar and planetary emission fluxes are shifted in



**Figure 1.** Overview of the intensity contrast from central stars of different types (Sun, M dwarf with  $T_{\text{eff}} = 3,000$  K) to an Earth-like planet with surface temperature of 288 K. For simplicity the reflected stellar light and emission fluxes are approximated as Planck curves.

their peak wavelength when considering planets in the HZ. In the visible, the star is much brighter than the planet by  $\sim 10$  orders of magnitude, and in the thermal infrared (IR) spectral range, the contrast ratio of planet/stellar flux is still in the range of  $10^{-6}$ – $10^{-7}$  for an Earth-like planet orbiting a solar-like star. For planets orbiting cool M dwarf stars with effective temperatures as low as 3,000 K, the flux ratio improves in the IR range, although the star is nevertheless much brighter than an orbiting terrestrial planet.

Furthermore, most planets orbit too close to their host to be able to spatially resolve them from the star using current technology. Therefore, modern detection methods, with the exception of direct imaging, use indirect indicators to infer the presence of extrasolar planets. We provide here an overview of the main detection methods used. Recent textbooks describing detection techniques for further reading are, for example, *The Exoplanet Handbook* (Perryman, 2011) and *Transiting Exoplanets* (Haswell, 2010).

## 2.1. RADIAL VELOCITY METHOD

The orbital motion of the planet around its host star causes periodic wobbling of the star around their common center of mass. This wobble can be measured from the periodic Doppler shift of stellar absorption lines using stable high-resolution

spectrographs. Since the orientation of the planetary orbital plane toward us is unknown, we can only detect the radial component of the motion pointing toward Earth. The method is therefore called the *radial velocity method*. For example, Jupiter in our Solar System induces a radial velocity (RV) signal of about 12 m/s, whereas Earth leads to an RV signal in the order of 10 cm/s only, which is below current detection limits (Mayor and Queloz, 2012). The orbital period,  $P_p$ , is directly obtained from the measured radial velocity component of the stellar motion. Using Kepler's Third law,

$$a_p^3 = GM (P_p/2\pi)^2,$$

the planet's orbital distance,  $a_p$ , can then be determined. The shape of the RV curve, when plotting over time, provides the eccentricity,  $e$ , of the planetary orbit. The amplitude of the RV Doppler shift variation is related to the planet's mass,  $m_p$ , but also to the inclination,  $i$ , which is the angle of the projected orbital plane of the planet to the sky plane. Therefore, RV measurements provide a lower limit of the mass only, namely, the quantity:  $m_p \sin i$ . In the case of planetary systems with several planets, their induced RV components overlap and are disentangled during data reduction. Planetary systems with up to seven planets have already been detected so far (Lovis et al., 2011). Current detection limits of the RV method already include planets with masses in the terrestrial regime (so far mainly around stars that are lighter than the Sun). The detection of a planet with about Earth's mass around the bright ( $V \sim 1$  mag) KIV-type star  $\alpha$ -Centauri B marks a recent milestone for RV detections. It shows also the huge effort needed for such detections, since observations lasting 4 years were needed to detect this low-mass planet on a 3-day orbit (Dumusque et al., 2012).

Here, we summarize the quantities which can be derived from the RV signal. We point out that the planetary mass is measured in relation to the stellar mass, which therefore must be derived by other means.

Measured quantity: Doppler shift of stellar radial velocity component

Derived planetary parameters:  $P, a, e, m_p \sin i$

Required stellar parameters:  $m_s$

## 2.2. ASTROMETRY

Another method to follow the wobbling motion of the central star induced by an orbiting planet is to follow its projected spatial motion on the sky. By using high-accuracy astrometric methods to measure the position of the host star in relation to reference stars, its periodic motion can be detected down to, for example, milli-arcseconds in the data of the Hipparcos satellite (Mignard, 1997; van Leeuwen, 2010). Unfortunately, accurate astrometric data with sufficient time sampling are sparse so far, and no planets have been discovered by this method yet. This picture is expected to change with the *Gaia* satellite which is anticipated to detect a large quantity of Jupiter-mass planets (Casertano et al., 2008). It needs to be pointed

out that the astrometric method is particularly well suited to detect planets at intermediate orbital distances of around 1 AU. However, even *Gaia*'s accuracy is insufficient to detect terrestrial planets, and this detection method therefore will be limited to Jupiter-mass planets for a long time until dedicated astrometric space missions are designed (e.g., the NEAT project, Malbet et al., 2012).

Measured quantity: spatial motion of the star on the sky

Derived planetary parameters:  $P, a, e, m_p, i$

Required stellar parameters:  $m_s$

### 2.3. TRANSIT METHOD

This method obtains high-precision photometric data of the stellar flux. When a planetary system is seen edge-on, the planet will periodically pass through the line of sight from Earth to its host star. During such transits, the planet occults part of the stellar disk. The stellar flux,  $F_s$ , received is then reduced in proportion to the occulted area, hence in proportion to the size of the planet:

$$\Delta F \propto (r_p/r_s)^2.$$

The amplitude of the transit signal is around 1 % flux reduction for a Jupiter-sized planet in front of a solar-like star and in the order of 0.01 % for the Earth. The transit method is the only method which allows the measurement of the radius,  $r_p$ , of an extrasolar planet directly.

Since transits can be detected only for systems seen edge-on, the probability to see systems in such geometry reduces the detection efficiency of this method. For example, the geometrical probability to see a Jupiter-sized planet on a short-period orbit of a few days is around 10 % and reduces to about 0.5 % for an Earth at 1 AU. Furthermore, the duration of the transit is short in comparison to the orbital period of the planet. For example, a close-in Jupiter on a 4-day orbit transits in 3–4 h, but an Earth at 1 AU transits in 13 h only during its 1-year orbit. Thus, continuous high-precision measurements are needed not to miss such a short transit event. After detection of transit-like signals, it has to be ensured that these are not caused by other sources, for example, eclipsing binary stars and spots; hence, follow-up observations are required. The secure detection of a planet requires the determination of its mass, for example, by the RV method. If this cannot be done, for instance, if the star is too faint, at least upper limits need to be placed to separate planets from binary stars. The difficulties of the transit method are, however, more than counterbalanced by the huge potential of transiting planets for further characterization of their nature, as will be outlined below.

Measured quantity: photometric dimming of the stellar flux

Derived planetary parameters:  $P, a, r_p$

Required stellar parameters:  $r_s$

## 2.4. TIMING METHOD

There are several ways to use timing measurements as planet indicators:

*Transit Timing Variations (TTVs):* The orbit of an observed transiting planet can be perturbed by additional planets in the system. Under certain circumstances, such perturbations will lead to variations in the time of the observed transit events. From such TTVs, it is possible to put constraints on the mass even of unseen perturbing planets based on numerical studies of the long-term gravitational stability of the system (see Fabrycky et al., 2012). In principle, even terrestrial-sized planets can produce observable perturbations (Csizmadia et al., 2010). In coplanar planetary systems where several planets show transit events, orbital periods and masses can be better constrained. An example is the Kepler 11 system with 6 transiting planets (Lissauer et al., 2011).

*Pulsation timing:* The first extrasolar planets were detected around a pulsar (Wolszczan and Frail, 1992). Their presence was inferred from periodic variations in the arrival times of pulses from the neutron star. In a similar way, periodic variations in the signal of pulsating stars can be used to infer the presence of planets. However, only the orbital parameters and an upper limit to the mass of the planet can be derived. The host pulsar is too faint to make any other characterization possible.

Measured quantity: central time of transit events (TTV) or pulse arrivals

Derived planetary parameters:  $P$ ,  $a$ ,  $e$ ,  $m_p \sin i$  or upper limit on  $m_p$

Required stellar parameters:  $m_s$

## 2.5. MICROLENSING

The gravitational lensing effect (Mao and Paczynski, 1991) leads to an amplification of the stellar flux when two stars are oriented along the line of sight. If the lensing star is orbited by a planet, this again leads to an additional amplification of the background star flux, but with much shorter duration. From the properties of this amplification, the main parameters of the star and the planet acting as a lens can be derived. However, because of the relative configuration of the background and the lens star with respect to the observer, the stellar system hosting the planet is in most of the cases not observable directly (Bennett et al., 2006) and hence is not suitable for any further characterization.

Measured quantity: stellar flux amplification

Derived planetary parameters:  $a$ ,  $P$ , constraints on  $m_p$

Required stellar parameters: (lens star is unknown, constraints in  $m_s$  obtained)



## 2.6. DIRECT IMAGING

Imaging of planets next to their host stars is the most direct method to detect them. However, as outlined above, it is restricted so far to planets with large orbital distances due to the limited spatial resolution of instruments and the unfavorable planet/star flux ratio (Chauvin et al., 2004; Janson et al., 2010). To improve the contrast, usually young stars are observed in the IR wavelength range, because young planets emit more strongly at these wavelengths. Models of the emitting planets then allow their mass to be derived, which is however often model dependent, in particular for very young objects. The orbital parameters are difficult to obtain because these planets typically have very wide orbits, far beyond the HZ (Chauvin et al., 2012). There are several planned projects for direct exoplanet detection (SPHERE, Beuzit et al., 2010; SPICES, Boccaletti et al., 2012).

Measured quantity: planet flux and spatial separation to star

Derived planetary parameters:  $m_p$  (model dependent), in some cases  $P$ ,  $a$ ,  $e$

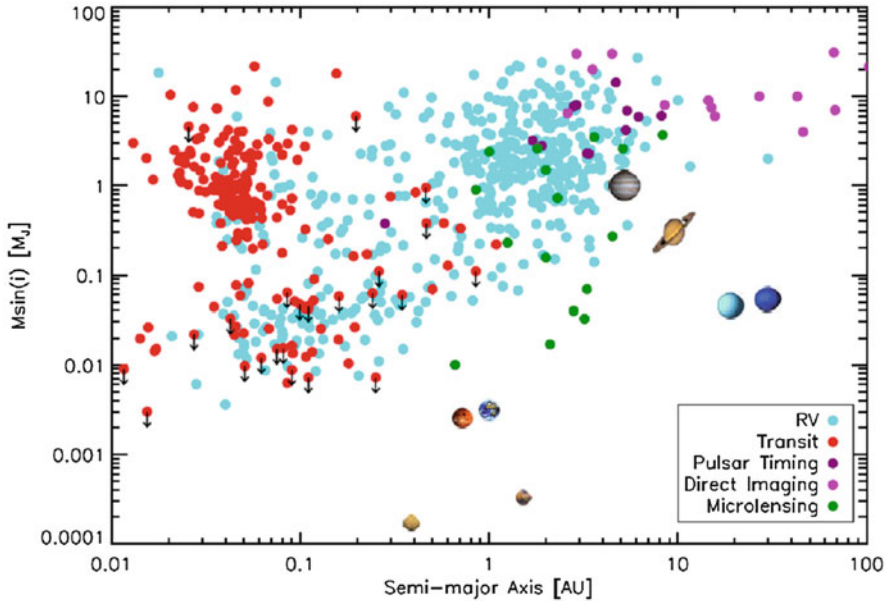
Required stellar parameters:  $m_s$ , distance

## 3. Detection Status and Future Prospects for Habitable Planet Detections

Figure 2 shows the current (April 2013) status of exoplanet detections. For comparison, the planets in our Solar System are also shown. Exoplanets discovered by the main detection techniques are indicated by different colors. Data are taken from [www.exoplanet.eu](http://www.exoplanet.eu).

As outlined above, current direct imaging techniques (light purple) detect predominantly planets at large orbital distances ( $>2-3$  AU) and are restricted to large planets in the regime of gas giants such as Jupiter. This method is therefore not yet suitable to detect planets in the HZ.

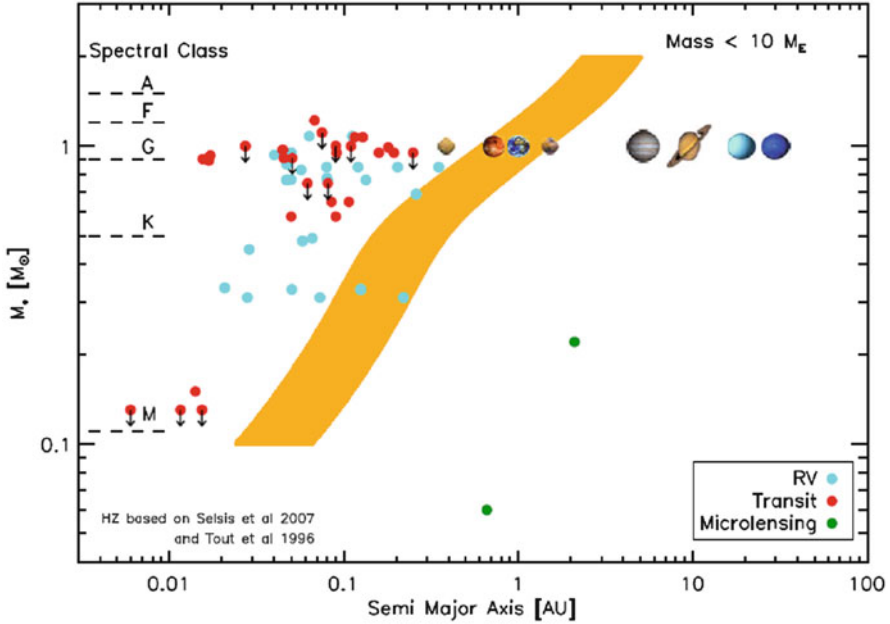
The RV measurements (light blue) provide the largest sample of planet detections so far. This technique has a long tradition in planet hunting (Walker, 2012). For distances very close to the star, RV techniques are already able to detect planets with  $m_p \sin i$  down to Earth mass (Pepe et al., 2011; Dumusque et al., 2012). Since these planets may be of rocky nature, they have been termed “super-Earth” up to about  $10 M_{\text{Earth}}$ . These close-in, hot super-Earths are a new class of objects, not found in our Solar System, similar in this respect the so-called hot Jupiters. Part of the currently known very low-mass super-Earth planets have been detected around low-mass M dwarf stars, where the more favourable mass ratio favors detections (Bonfils et al., 2013). Due to their reduced luminosity, these stars emit less flux and hence their habitable zone is closer (see Fig. 3). Thus, planets in their HZ have shorter orbital periods, again facilitating detection. For planets at 1 AU around solar-like stars, we have to await future instruments, for example, ESPRESSO (Pepe et al., 2010) and an improved data analysis treating the noise induced by stellar activity. Even with such instruments, the observational load for such detections by the RV method will be huge.



**Figure 2.** Confirmed planet detections (March 2013). No planet candidates are included here. *Red dots* with *downward arrows* indicate planets detected by the Kepler mission, but with only upper limits on their mass available.

The second largest group of known planets has been detected by the transit method (red dots in Fig. 2). As expected, these detections show a clear bias toward shorter orbital distances due to the increased transit geometrical probability. However, transiting planets out to 1 AU have already been detected, demonstrating the feasibility of the method to detect planets even in the HZ of solar-like stars. More such detections are expected in future as transit searching space missions (CoRoT and Kepler, Baglin et al., 2006; Borucki et al., 2008) continue. The first detected terrestrial super-Earth with known radius and mass was CoRoT-7b ( $r_p = 1.6 \pm 0.1 r_{\text{Earth}}$ ,  $m_p = 7.4 \pm 1.2 m_{\text{Earth}}$ , Hatzes et al., 2011), and the smallest confirmed planet detected by Kepler (Kepler-10b,  $r_p = 1.416 \pm 0.03 r_{\text{Earth}}$ ,  $m_p = 4.6 \pm 1.2 m_{\text{Earth}}$ , Batalha et al., 2011) is even smaller and lighter. Both planets orbit solar-like central stars, although on very close-in orbits with periods  $< 1$  day.

The Kepler mission has also published a list of candidate planets (detected transits, but no RV measurements are yet available), showing that the detection of photometric transit signals corresponding to Earth-sized planets and even smaller is possible. However, confirming Earth-sized planets in the HZ of solar-like stars by RV follow-up still provides a challenge. Unfortunately, most stars observed by the Kepler mission are too faint to allow for efficient RV observations and therefore for independent confirmation of the signal and planet mass determination. Even in those cases where follow-up observations are sufficient to exclude false alarms by,



**Figure 3.** Known super-Earth planets with respect to the position of the HZ which follows the scaling proportional to the solar insolation flux given by Kasting et al., 1993. Red dots with black downward arrows indicate planets detected by the Kepler mission, but with only upper limits on their mass available.

for example, binary stars, only upper limits for the mass can be given if planets orbit such faint stars (e.g., red dots with downward arrows in Figs. 2 and 3). These upper limits usually do not allow one, however, to securely differentiate between a Neptune-like ice planet and a rocky, terrestrial object. Characterization of the radius and mass for such small planets around solar-like stars has to await future space missions (e.g. the PLATO mission, Catala, 2009).

Transiting planets around small M dwarfs, however, show a favorable radius ratio  $r_p/r_s$ , leading to larger transit depths for a given planet size. In such cases, the detection of super Earth planets comes into reach even for ground-based transit surveys. Since M dwarfs also allow for an easier detection of the RV signal, it is furthermore easier to determine their mass.

The microlensing method is most effective over a range of orbital distances from about 0.5 to 5 AU, thus covering the HZ of solar-like stars. As seen in Fig. 2, super-Earth planets have already been detected in this range (green dots). The derived planet parameters are somewhat model dependent, and detailed follow-up characterization of the detected planets and host stars is usually not possible. The main potential of the microlensing technique is to provide a large sample of low-mass planets, as well as planetary system architectures including Jupiters in

relatively distant orbits for statistical planetary population considerations (Cassan et al., 2012).

The transit timing method is very interesting because it can complement the RV and transit methods, and it can potentially find very small planets in particular orbits (such as resonances). But the proper characterization of such planets requires long baselines and photometric precisions only achievable from space. At present we lack suitable candidates for terrestrial planets in the HZ discovered by this method which can be characterized with present or near-future instrumentation.

Figure 3 summarizes our current status on the detection of super-Earth planets in the habitable zone. The position of the HZ is indicated for different central star types, following Kasting et al. (1993). Known planets with  $m_p \leq 10 m_{\text{Earth}}$  are indicated. As expected from the already discussed detection biases, most super-Earth planets are found inward of the HZ, too close to their star to be habitable. However, some super-Earths at larger distances have already been found.

The first detected potentially habitable planet is Gliese 581d. The planet was detected by RV measurements, together with three additional planets in this system (Udry et al., 2007; Mayor et al., 2009). Since this planet does not show transits, only  $m \sin i$  data are available. The  $m \sin i = 7.09 M_{\text{Earth}}$  implies that the planet may fall into the range of super-Earth planets and might be rocky. The planet is too close to its star to allow for direct imaging, and since it does not transit, spectroscopy of its atmosphere is not possible with current instrumentation. We therefore have no information on its atmospheric composition. To assess whether the planet could be habitable or not, assumptions on its atmospheric composition have to be made. Several authors have studied the potential for habitability by assuming a  $\text{CO}_2$ -dominated atmosphere. This assumption is based on the atmospheres of Venus and Mars, which are  $\text{CO}_2$  rich, as well as the composition of early Earth which was probably  $\text{CO}_2$  rich for long time periods, although the detailed composition of early Earth's atmosphere and its development with time is still debated. While the approaches of various authors differ from mere scaling to self-consistent climate modeling of the surface temperature, all conclude that Gliese 581d could be habitable for high-pressure and  $\text{CO}_2$ -rich atmospheres (e.g., von Bloh et al., 2007; Selsis et al., 2007; Wordsworth et al., 2010; von Paris et al., 2010; Kaltenegger et al., 2011).

Gliese 581 is an M dwarf star ( $T_{\text{eff}} = 3,200 \text{ K}$ ). Therefore, its HZ lies relatively close to its star. Planets around such stars with more favorable viewing geometries, allowing for transits, would readily be detectable. A recent example is the detection of a super-Earth well within the HZ around GJ667C, an M dwarf which is part of a triple star system (Anglada-Escudé et al., 2012; Delfosse et al., 2012). Thus, the detection of super-Earth planets in the HZ of cool M dwarfs is certainly feasible with current techniques in the near future.

Another recent example of planets transiting in the HZ is the planet Kepler-22b. This planet was detected in the HZ of a solar-like star (Borucki et al., 2012).

Unfortunately, due to the faintness of its host star, proper characterization of the mass of the planet (needed to constrain its internal structure) and its atmosphere provides a challenge for current and near-future instrumentation. With an upper mass limit of  $<35 m_{\text{Earth}}$  and a radius of  $2.4 R_{\text{Earth}}$  determined from transit photometry, Kepler-22b is most likely Neptune-like rather than a terrestrial planet. Nevertheless, the detection shows that planets in the HZ of solar-like stars can indeed be achieved by the photometric transit method, despite its geometry bias toward short-period planets.

#### 4. Detection of Habitability

Before deciding whether a detected extrasolar planet could be habitable, we have to define criteria for habitability (which is discussed in detail elsewhere in this book). Most commonly, the word “habitable” refers to surface life as we find it on Earth today, but we know from extremophiles on Earth that suitable habitable conditions can differ widely, depending on which species we are looking at. Detecting habitable conditions and life on exoplanets is challenging. The criteria for habitability of exoplanets, therefore, must be simple and robust. For these reasons, usually the presence of liquid surface water is taken as a minimum requirement. This argument is based on the assumption that life cannot develop without liquid surface water. In addition, water-based life, as we find it on Earth, is the only life form for which we reasonably know what biosignatures to expect and to search for. The criterion of liquid surface water constrains the physical surface conditions on a planet: Surface temperatures must remain above freezing for sufficiently long time periods to allow for the development of life. We emphasize that liquid surface water does not necessarily imply that life actually develops. It is merely a minimum requirement, in addition to the requirements of energy sources and nutrients.

Whether a planet can support liquid surface water depends on the heating from incoming stellar energy flux and the presence of an atmosphere including greenhouse gases. The incoming stellar radiation flux at the planet can be computed once the stellar type, hence effective temperature, and the orbital parameters of the planet are known. To constrain the surface temperature, however, requires additional knowledge about the composition and structure of the planetary atmosphere. The latter is much more challenging and beyond current detection limits for terrestrial planets in the HZ of Sun-like stars, as further outlined below.

The orbital distance of a planet to its host star is used as a first indicator for potential habitability. Kasting et al. (1993, Fig. 3) determined the orbital limits of the HZ for Earth-like planets. The orbital position of the HZ scales mainly with the incoming stellar energy flux and the HZ moves closer to the host for cooler stars. For a particular terrestrial extrasolar planet, its orbital distance can be compared to these HZ limits. If the planet is within these limits, it is often called potentially habitable. However, this implies the assumption of a terrestrial planet with a suitable atmosphere. As an example, we note that the Earth’s moon is also in the HZ of the Sun, but is certainly not habitable.

To better constrain the potential habitability of planets, atmospheric models are used. For this approach assumptions on the atmosphere of the terrestrial planets have to be made. Often, Earth-like atmospheres are assumed, but also CO<sub>2</sub>-rich atmospheres are considered (e.g., Segura et al., 2003, 2005, 2010; Grenfell et al., 2007a, b; Kitzmann et al., 2010; Rauer et al., 2011). Should atmospheric compositions of terrestrial exoplanets be detected in future, such model scenarios obviously can be much better constrained and predictions for particular exoplanets be made. Such predictions form the basis of the search for biosignatures on such planets, but also for the interpretation of measured atmospheric signals.

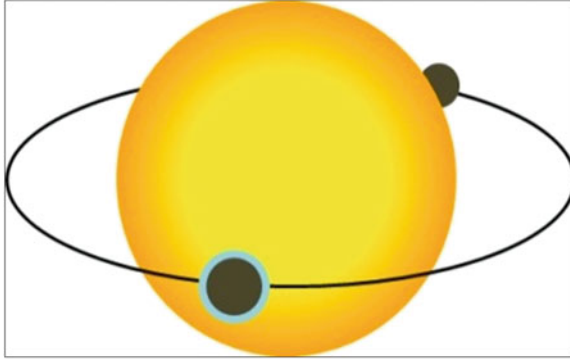
The detection of an ocean glint, the forward reflected stellar flux on an ocean, has been proposed as a way to detect surface water on exoplanets directly (Williams and Gaidos, 2008; Robinson et al., 2010; Barry and Deming, 2011). However, again this detection will be extremely challenging and difficult to disentangle from other planetary features and stellar activity.

In summary, the main criteria for the potential habitability of an extrasolar planet are its orbital distance, the central star type, determining the stellar energy input to the planet, and the composition and structure of its atmosphere, determining the greenhouse heating effect at the planetary surface.

## 5. Detection of Atmospheres and Biosignatures

A biosphere on extrasolar planets can only be detected if it produces a sufficiently large signal in the atmosphere. Due to the large distance to Earth, only planetary disk-integrated fluxes can be observed on exoplanets. A further complication arises from the nearby host star whose emission flux has to be separated from the faint planetary signal. Extrasolar planets orbiting at a sufficiently large distance to their host star can be detected through high-spatial resolution imaging methods, and their emitted infrared (IR) flux can be observed directly. Unfortunately, so far only large gas giants orbiting at distances outside the habitable zone can be detected by this method (see Fig. 2). Plans in Europe and US have been made over the past decades to obtain images and spectra from nearby terrestrial exoplanets, for example, with the Darwin (Leger et al., 1995) and TPF (Beichman et al., 1999) missions. Both projects were identified as too complex to achieve at present, although similar missions are likely to be re-proposed in the future as the need to search for biosignatures increases with the increasing number of terrestrial exoplanet detections.

The detection of atmospheres is so far limited to planets transiting in front or behind their host star (Fig. 4), or via the variation of the reflected stellar light with orbital phase of the planet. When the planet transits in front of its star, the stellar flux passes through the optically thin parts of its atmosphere. When comparing spectral measurements of the (planet + star) flux to those times when the planet is not in the line of sight, the stellar spectrum can be separated from signatures of the planet atmosphere. These measurements are usually performed in the optical wavelength range where the stellar flux is largest and high signal-to-noise

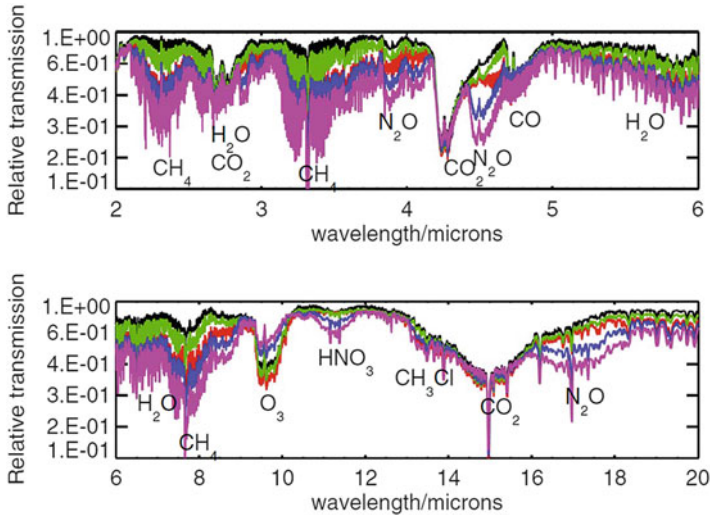


**Figure 4.** Geometry of transiting extrasolar planets. The atmosphere of the planet can be probed during primary transit, when the stellar light passes through the optically thin parts of the atmosphere, and during secondary eclipse, when the emitted infrared flux of the planet can be detected. During the orbit, reflected stellar light varying according to the orbital phase of the planet can be observed.

ratios (SNRs) can be obtained. The planetary atmosphere can also be detected by its IR emission flux. For this purpose, the (planet + star) flux is observed just before the planet vanishes behind the star during secondary eclipse (Fig. 4). Comparing to measurements during the planetary eclipse (obtaining only the stellar flux) again allows us to separate the stellar and planetary flux. Both methods have already successfully been applied to gas giant and Neptune-sized planets (e.g., Deming et al., 2005; Richardson et al., 2007; Tinetti et al., 2007; Knutson et al., 2008; Pont et al., 2008; Redfield et al., 2008; Swain et al., 2008; Bean et al., 2010; Beaulieu et al., 2011; Croll et al., 2011; Crossfield et al., 2011; de Mooij et al., 2012).

Chapter 5 discusses which biomarker signals in planetary atmospheres can be interpreted as indicators for habitability and life. The presence of water (a mandatory ingredient for life), carbon dioxide, oxygen, and ozone is taken as indicator for life on our planet. However, we also have to be aware of false positives or negatives, e.g. via abiotic sources mimicking the signatures of life, or masking the presence of biomarker signals which then remain undetected in exoplanets. Since the interpretation of atmospheric biosignatures is therefore challenging, most studies to simulate the spectral appearance of exoplanets assume an Earth-like biosphere as a first approximation whose parameters we know best (e.g., Selsis et al., 2002; Segura et al., 2003; Kaltenegger et al., 2007, 2011; Kaltenegger and Traub, 2009; Kaltenegger and Sasselov, 2010; Kitzmann et al., 2011a, b; Rauer et al., 2011).

The detection of biosignatures in atmospheres of terrestrial planets orbiting in the HZ around solar-like stars is a highly important goal of exoplanet research, aiming at a better understanding of our Solar System in comparison to other similar systems. However, in view of the diversity of planetary systems found and because of the more favorable contrast ratio between planet and host star (Fig. 1),



**Figure 5.** The “relative transmission,” hence the additional absorption during transit due to the planetary atmosphere, is shown. The modeled atmospheric transmission spectrum of the modern Earth passing in front of the Sun is shown in black. In addition, models of the same planet around the active M dwarf AD Leo (*red*) and two quiet M dwarfs of type M5 (*blue*) and M7 (*magenta*) are shown (From Rauer et al., 2011).

terrestrial planets orbiting cool M dwarfs have gained interest in recent years. Furthermore, the probability of detecting transiting planets in the habitable zone is larger for planets orbiting M dwarfs, because the HZ is closer to the star and the star is smaller compared with the Sun. This further strengthens the interest in M dwarfs. Figure 5 shows as an example the modeled transmission spectrum of the Earth passing in front of the Sun during primary transit (black line). The typical atmospheric spectral absorption bands of several molecules in the Earth’s atmosphere are seen: for example, H<sub>2</sub>O, CO<sub>2</sub> and CO, CH<sub>4</sub>, N<sub>2</sub>O, and O<sub>3</sub>. The figure also illustrates how the spectral appearance of the same planet changes when it orbits in the HZ of different M dwarf host stars. M dwarfs are small, cool stars which emit their energy spectrum more to the red spectral range (maximum flux around 1–2  $\mu\text{m}$ , Fig. 1) when compared to the Sun. Quiet M dwarfs have very low UV emission fluxes, in particular at wavelengths where atmospheric chemical processes are relevant. However, active M dwarfs, like AD Leo in Fig. 5, can also emit the same or even more UV spectral flux as the Sun due to their strong activity. The different spectral energy flux distribution of M dwarfs has an effect on the chemical processes in the atmosphere of the orbiting planet, even though the total stellar energy received by the planets from the different host stars is the same for all examples shown. As a result, a planet with an atmosphere like modern Earth placed at an orbital distance around an M dwarf where it receives the same total energy as Earth can appear spectroscopically very different. This can even



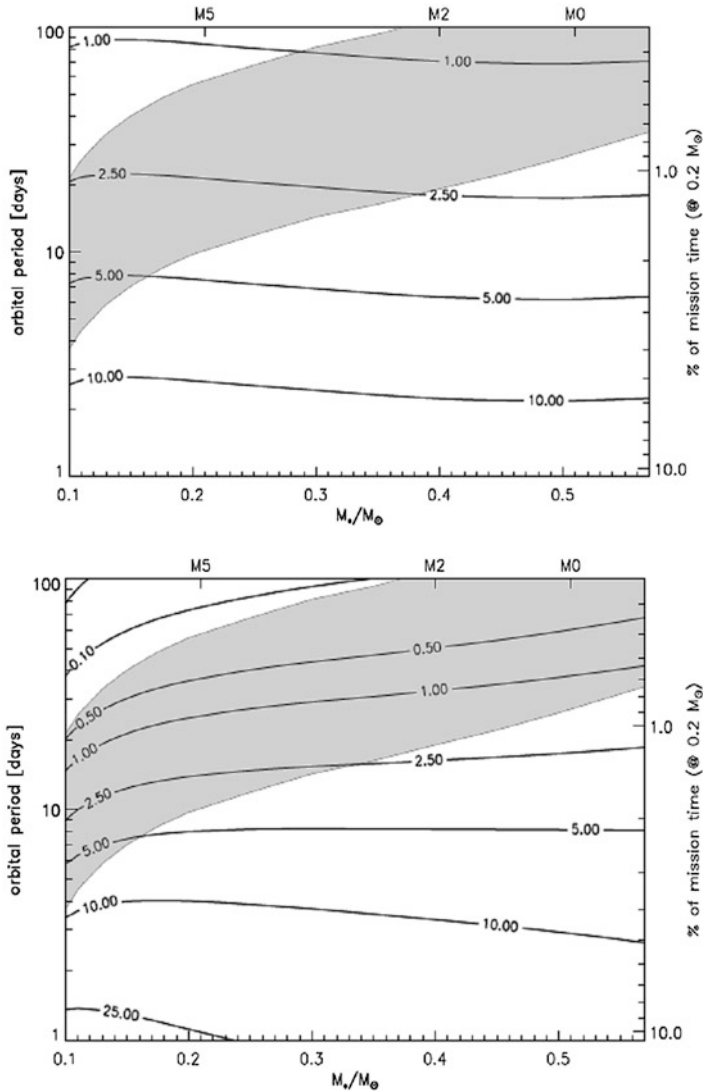
mean that spectral signatures of the biosphere disappear, leading to false negatives (Rauer et al., 2011). This example shows that interpretation of observed spectra of terrestrial planets has to be made with care.

To estimate whether the detection of such atmospheric absorption bands on terrestrial super-Earth planets is actually feasible, one has to consider the stellar and planetary flux received on Earth and the instrument used for detection. In particular in the near IR, where many interesting atmospheric absorption bands appear, the intensity contrast ratio between planet and star is relatively high. In addition, beyond about 2  $\mu\text{m}$  intensities drop significantly, again forming a challenge for instruments.

Biosignatures have also been suggested when observing light reflected by the planet in the visible wavelengths range (Fig. 1) where, for example, the signature of the *red-edge* indicating chlorophyll on Earth has been proposed as biosignature also for exoplanets (e.g., Arnold et al., 2009; Briot, 2010). Some studies suggest using polarization to improve the contrast between star and planet (e.g., Seager et al., 2000; Saar and Seager, 2003; Stam, 2008), but again the low flux levels represent a challenge.

Several SNR estimates have been made in the literature for instruments on the future James Web Space Telescope (JWST) (e.g., Kaltenegger and Traub, 2009; Shabram et al., 2011; Belu et al., 2011; Rauer et al., 2011). A straightforward approach was taken, for example, by Belu et al. (2011) using Planck functions to approximate the stellar and planetary flux and assuming reasonable absorption band strengths derived from consistent atmospheric model calculations (as, e.g., in Fig. 5). This work considered transmission and emission spectra during primary transit and secondary eclipse observed with two instruments on JWST, namely, *NIRSpec* and *MIRI*. Noise introduced by these instruments and from the zodiacal light background of the sky (scattered light on interplanetary dust particles in our Solar System) was considered. Model simulations included a wide range of central stars, from Sun-like to M dwarfs. It was shown by this study that transiting habitable super-Earths can be characterized at low spectral resolution with a significant SNR only in the most nearby systems ( $<10$  pc) and when hosted by a cool M dwarf star ( $<0.2 M_{\text{sun}}$ ) (e.g., Fig. 6 for SNR of the 9.6  $\mu\text{m}$  ozone band). Similar results were also obtained by Rauer et al. (2011) and Kaltenegger and Traub (2009), again showing that many transit observations of terrestrial planets in the HZ have to be co-added to reach a reasonable SNR, even with the 6.5 m mirror JWST telescope. These modeling studies provide an example. Actual absorption strengths of atmospheric bands depend on mixing ratios, temperature profiles, incoming stellar flux, and chemistry. However, all studies show that the detection of atmospheric absorption bands in terrestrial exoplanets is indeed challenging, already for the main atmospheric constituents, and even more so for less abundant biosignatures.

Further complications for the detection of atmospheres arise when clouds are present in the atmosphere. The recently detected mini-Neptune-like planet GJ1214b orbiting an M dwarf star (Charbonneau et al., 2009) can serve as an example here since it is large enough to actually allow for atmospheric signature



**Figure 6.** Modeled signal-to-noise ratio (SNR) for detection of the  $9.6 \mu\text{m}$  ozone band for a terrestrial planet orbiting M dwarf host stars located at 6.7 pc from Earth (From Belu et al., 2011). SNRs are given for transmission observations during transit with the *MIRI* instrument at the JWST. All observable transits during the planned 5-year mission lifetime of JWST have been co-added to obtain the SNR shown. The *gray band* indicates the position of the HZ. *Top*, primary transit; *bottom*, secondary transit.

detections with current instruments. However, all data points obtained over a wide wavelengths range from visible to IR show a featureless spectrum which is interpreted as cloud cover in the planet's atmosphere masking spectral absorption bands that could otherwise indicate the composition of the atmosphere (Bean et

al., 2010). Similar problems can occur for terrestrial planets with significant cloud cover (Kaltenegger et al., 2007; Kitzmann et al., 2011a).

Planetary systems around M dwarfs are nevertheless very interesting to investigate, since the habitable zone is close to the star (Fig. 3) hence planets there can be more easily detected, as already outlined. Furthermore, the population of stars in our neighborhood is in general dominated by M stars. However, model simulations of expected SNRs have shown, as discussed above, that only the nearest M dwarfs (within 10–20 pc) are feasible for detections of spectroscopic atmospheric signals. Only a small number (~300) of M dwarf stars can actually be found within 10 pc from Earth, limiting the potential number of target stars. Based on a recent RV survey of M dwarfs (Bonfils et al., 2013), about 100 of them are expected to have planets orbiting in the HZ. With a geometrical probability of 1–3 % for transits of such planets (Kaltenegger and Traub, 2009), only 1–3 planets transiting around nearby M dwarfs within 10 pc are expected to be detected in future. Therefore, the number of detected transiting terrestrial planets suitable for atmospheric characterization around such nearby M dwarf host stars will unfortunately remain limited.

Future space mission plans include dedicated telescopes for exoplanet atmosphere detections during planet transits, for example, EChO (Tinetti et al., 2012). Such missions concentrate on Jupiter- and Neptune-like planets and focus for terrestrial planets on M dwarf host stars to take advantage of the improved flux ratio between star and planet and the close-in HZ. However, due to the limited number of very nearby stars, the potential target number for terrestrial planets around these stars will be small.

Finally, we point out that stellar activity and related energetic radiation fluxes of M dwarfs may be a challenge for planets in their close-in habitable zones. It is by no means clear that terrestrial planets around cool M dwarfs exhibit an Earth-like biosphere. The next step along the detection of biospheres therefore is clearly to target Solar System analogues where interpretation of atmospheric signals in terms of biosignatures will be facilitated, and furthermore allow us to put our system into the context of similar systems in our galaxy. But this will require space-based, direct imaging telescopes that are currently not within projected mission plans for either ESA or NASA.

## 6. Summary

The detection of habitable planets outside our Solar System is a challenging goal. However, recent years have shown that it is feasible to find terrestrial super-Earth planets in and near the habitable zone of M dwarfs and even solar-like stars in the near future. This search is facilitated for cool M dwarfs because their HZ is close to the star which makes the detection of planets easier, for radial velocity detections as well as for planetary transits. Furthermore, the improved planet/star flux contrast in principle helps the detection of atmospheric signatures. On the other hand,

model simulations have shown that biosignatures of Earth-like planets can only be detected for planets transiting very nearby M dwarfs ( $<10$  pc), which are unfortunately sparse. In addition, it is by no means clear whether active M dwarfs would allow for the formation of a biosphere on planets in its HZ. Searching for planets more similar to Earth requires that we first detect terrestrial planets in the HZ of solar-like stars. Such detections are in principle feasible for near-future radial velocity instrumentation, albeit extremely time consuming. As a result, their numbers will remain small. Future transit surveys targeting terrestrial planets in the HZ of bright solar-like stars, like the PLATO mission, have the potential to significantly increase these statistics. Other methods targeting planets in the HZ in future are direct imaging, astrometry and microlensing. Detecting biosignatures on any suitable terrestrial planets found is an even more challenging goal. With current instruments, this seems feasible only for the brightest and nearest stars. To obtain a sufficiently high SNR, such instrumentation will need a large aperture telescope with the means of separating the planet from the star, for example, by coronagraphs, starshades, occulters, or interferometry, and forms one of the main challenges for future exoplanet research.

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Biodata of **Prof. Dr. Howell G.M. Edwards**, **Dr. Ian B. Hutchinson**, and **Dr. Richard Ingley**, authors of “*Raman Spectral Signatures in the Biogeological Record: An Astrobiological Challenge.*”

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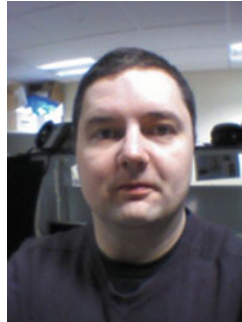
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# RAMAN SPECTRAL SIGNATURES IN THE BIOGEOLOGICAL RECORD: AN ASTROBIOLOGICAL CHALLENGE

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## 1. Introduction

The application of Raman spectroscopic techniques to the characterisation of the protective biochemicals and their geological niche matrices used in the survival strategies of extremophilic organisms in terrestrially stressed environments (Wynn-Williams and Edwards, 2000a, b), coupled with the palaeogeological recognition that early Mars and Earth had maintained similar environments under which Archaean cyanobacteria could have developed, has driven the acceptance of the proposal for the adoption of Raman spectroscopy as novel analytical instrumentation for planetary exploration (Edwards and Newton, 1999; Ellery and Wynn-Williams, 2003; Dickensheets et al., 2000). The European Space Agency (ESA) has announced that a miniaturised Raman spectrometer would form part of the Pasteur analytical life-detection protocol in the ExoMars-C mission for the search for traces of life on Mars in the Aurora programme to be launched as a joint two-rover mission with NASA in 2018. The Raman spectrometer will provide a key role in the first-pass analytical interrogation of powdered rock specimens from the Martian surface and subsurface aboard the ESA ExoMars-C rover vehicle.

It is undeniable that the most important scientific discovery in a future space mission would be the furnishing of indisputable evidence for life signatures on another planet and whether they have arisen from extant or extinct sources; however, this statement itself generates two very important philosophical questions, namely, how do we define life and how would we then recognise it or its residues in the planetary geological record? We must also address the possibility that any extraterrestrial organism identified in space exploration could have originated on Earth and have been transported to our planetary neighbours either by our own intervention, reinforcing the need for planetary protection protocols for our spacecraft and landers, or through *panspermia* processes, which could include the deposition of chemical building bricks through delivery by meteorites, comets and asteroids. The precise definition of life is actually rather

elusive, and many attempts to do so have been eventually deemed unsatisfactory (Shapiro and Schulze-Makuch, 2009; Tirard et al., 2010; Benner, 2010; Bedau, 2010); the NASA definition of life as “a self-sustaining system capable of Darwinian evolution” incorporates a molecular genesis with replicative procedures and avoids several pitfalls of alternative definitions based upon an ability of the system to reproduce (Cleland and Chyba, 2002).

### 1.1. WHAT IS ASTROBIOLOGY?

In an elegant article, Cockell has explored the origins of astrobiology and the literary confusion arising between exobiology and astrobiology (Cockell, 2001); an early exponent, Tikhov enlarged upon his concept of astrobotany to describe an anticipated vegetation on Mars and Venus under the envelope of astrobiology. It is interesting that Tikhov was the first to suggest that spectral signatures from other planets could be used to assess their biotic potential (Tikhov, 1953), which today lies at the heart of remote space exploration, with special relevance here to the ExoMars mission. Tikhov’s suggestion was reinforced the same year in a book by Strughold (Strughold, 1953) and the birth of astrobiology can be said to have occurred, giving rise to Soffen’s description of astrobiology as “the study of the chemistry, physics and adaptations that influence the origin, evolution and destiny of life” (Soffen, 1999).

Fundamentally, the three basic questions of astrobiology are: How did life begin and evolve? Does life exist elsewhere? What is the future of life on Earth and beyond? It is also clear that astrobiology has a very different brief from astrochemistry, astrogeology and astrobotany; it is, therefore, the function of *analytical astrobiology* to apply the principles of chemical, biomolecular, morphological and microbiological analysis to the three baseline questions as outlined above. Here, we shall endeavour to examine the terrestrial criteria for chemical biomolecular analyses associated with living organisms and apply these to extra-terrestrial exploration envisaged by the inclusion of analytical instrumentation on remote planetary spacecraft and landers. The key question here, of course, is what biochemical species truly define the presence of extinct or extant life, be this terrestrial or extraterrestrial.

It is equally appropriate to consider some of the scientific parameters that will need to be evaluated for the detection of life using remote robotic analytical instrumentation, specifically in the ExoMars project; primarily, the selection criteria for an analytical astrobiological mission such as ExoMars need to consider the following questions:

- What organisms could have existed and possibly survived the current and past extremes of environment on Mars?
- What types of geological niches are to be found which may conceal the traces of relict or extant life on Mars?

- What signatures would these organisms have left in such environments as indicators of their presence and how are we going to recognise them?
- What molecules could be considered as constituting a proof of life on Mars?
- Are there terrestrial scenarios or putative Mars analogue sites which could be used as “models” for the evaluation of these scientific questions?

## 1.2. THE HISTORICAL MARS

From the birth of our Solar System some 4.6 Gya, the terrestrial geological record suggests that microbial autotrophic ecosystems already existed on Earth from 3.5 to 3.8 Gya. There is now much evidence that early Earth and early Mars were indeed very similar in their physicochemical composition; since Mars is significantly smaller than Earth, it is very likely that planetary cooling occurred more rapidly and that Mars was able to sustain an aqueous environment on its surface earlier than was possible on Earth. In the Epoch I (ca. 4.65–3 Gya) period of Mars proposed by McKay (1997), the planet was probably more temperate and wet, and since there is geological evidence that life had already started on Earth during this period, it seems reasonable to conclude that life had also started on Mars too; by Epoch IV (ca. 1.5 Gya to present), however, catastrophic changes on Mars would have compromised the survival of organisms on the Martian surface, and it is possible that the Martian analogues of terrestrial extremophiles would have been the last survivors of life on Mars through their environmental adaptation in Martian geological niche sites.

## 2. Analytical Astrobiology of Mars

The detection of biomolecular markers in geological substrates or the subsurface regolith of Mars is a primary goal for astrobiology (Edwards, 2004; Edwards et al., 2005); however, the evolutionary pressure of environmental stress on Mars, especially the high levels of low wavelength ultraviolet radiation insolation, low temperatures, extreme desiccation and hypersalinity would have demanded appropriately severe protective strategies to promote the origin, survival and evolution of microbial life (Cockell and Knowland, 1999). The ultraviolet radiation protection afforded to subsurface organisms by the iron (III) oxide surface regolith acting as a filter has been proposed as a key factor for the maintenance of biomolecular activity at the Martian surface (Clark, 1998), but the same ultraviolet and low wavelength electromagnetic radiation insolation generates hydroxyl radicals and peroxides in the surface regolith which would most certainly inhibit the survival of complex biomolecules in the surface oxidation zone. In this respect the diagenesis, catagenesis and biodegradation of terrestrial Mars analogues to give the materials recognisable in our own geological record would not be directly transposable to a Martian scenario. Hence, the complex chemical systems comprising terrestrial

soils, bitumens and kerogens found in our own planetary lithology (Jehlicka et al., 2010a, b; Edwards et al., 2010; Marshall et al., 2010; Pullan et al., 2008) and which provide much valuable information about their sourcing processes could not be expected to occur to the same extent on Mars except perhaps in special geological niches.

However, it is believed that Mars might still preserve a chemical record of early life in rocks from the Noachian era, which overlaps the terrestrial Archaean geological history, from about 3.8 Gya. The search for extinct or extant life on Mars must therefore centre upon the identification and recognition of specially protected niche geological sites in which the biomolecular signatures would be preserved; the fundamental approach must then consider the detection of key molecular biomarkers, probably within rocks and certainly subsurface, perhaps even in ancient lacustrine sediments (Bishop et al., 2003; Doran et al., 1998), which will necessitate the deployment of remote analytical sensors with preset protocols and an established database recognition strategy for minerals, biologically modified geological strata and biomolecular residues. Examples from terrestrial analogue sites include carbonates, carbonated hydroxyfluoroapatite, gypsum, calcium oxalates, porphyrins, carotenoids, scytonemin and anthraquinones (Edwards, 2010; Wynn-Williams and Edwards, 2002).

Clearly, the identification and selection of terrestrial Mars analogue sites (Pullan et al., 2008; Bishop et al., 2003) will be a critical step in the development of an analytical astrobiology for Mars in two respects: firstly, the understanding of the type of geological formations that have been colonised by extremophilic organisms in terrestrial “limits of life” situations and habitats, and, secondly, the deployment of novel analytical instrumentation which can reveal the presence of the key signatures of extinct and extant life in micro-niches in the geological record (Bishop et al., 2003; Doran et al., 1998; Edwards, 2010; Wynn-Williams and Edwards, 2002; Wynn-Williams, 1999; Wynn-Williams, 1991; Edwards et al., 1997; Treado and Truman, 1996). The gathering of data from such terrestrial Mars analogue sites is therefore the first step to be taken in the search for extraterrestrial life signatures; in this, the application of Raman spectroscopic techniques has already been proved successful through the direct characterisation of the molecular and molecular ionic signatures of biomolecules and their modified structures situated in the geological record which does not involve either the physical or chemical separation of the organic and inorganic components. Some of these terrestrial Mars analogue sites are described below, and the data obtained using laboratory-based Raman spectroscopic techniques have advanced our understanding of extremophile behaviour significantly.

In a recent special issue of the *Philosophical Transactions of the Royal Society*, in a year that celebrated its 350th anniversary as the longest running scientific journal, several articles highlighted the role of Raman spectroscopy in the characterisation of biosignatures of extremophilic colonisation of geological substrates in a range of stressed terrestrial environments (Edwards et al., 2010; Edwards, 2010; Brier et al., 2010; Carter et al., 2010; Jehlicka et al., 2010a, b;

Jorge-Villar and Edwards, 2010; Marshall and Olcott Marshall, 2010; Rull et al., 2010a, b; Sharma et al., 2010; Varnali and Edwards, 2010; Vitek et al., 2010); these articles address the detection of geological and biogeological spectral markers that are relevant to space missions and give a very good appreciation of the spectroscopic requirements that will be essential for the construction of a relevant spectral database (Jorge Villar and Edwards, 2006) for the ExoMars mission and forthcoming space missions which will have a Raman spectrometer aboard their rover vehicles. Some selected examples of the data which can be provided by the Raman spectroscopic interrogation of terrestrial Mars analogue sites will therefore be highlighted here.

## 2.1. BIOMARKERS

A biomarker can be defined as a chemical species or topographical pattern which is uniquely derived from living organisms; thus, from the standpoint of analytical spectroscopy it is not sufficient to simply embrace an organic or bioinorganic molecule that is used or synthesised by life forms, as several of these can also be synthesised abiotically. Examples of the latter include amino acids and proteins. A further complication arises in that organic molecules degrade under stressed environmental conditions, forming derivatives and eventually carbon. The realisation that methane, calcium carbonate, carbon and polyaromatic hydrocarbons can be synthesised by geological processes as well as through the degradation of biomolecules means that these molecular carbonaceous materials are not strictly suitable for classification as biomarkers – even though the detection of methane, carbon or polyaromatic hydrocarbons on Mars would be an exciting discovery in itself, this would not result in the conclusion that life did once exist or may even still be extant on Mars!

It is crucial, therefore, that we can identify a suite of molecular biomarkers, whose detection would positively and unambiguously indicate the presence of extinct or extant life; here, we need to also narrowly permit the definition of life as cyanobacterial, which represents the earliest identifiable Archaean life forms on the emerging planetary and oceanic Earth, some 3.8 Gya. From spectroscopic and microbiological analytical studies of terrestrial cyanobacteria, it has been possible to isolate several biomolecules which truly can be considered as key spectroscopic biomarkers, from which we can safely construct a Raman spectroscopic database that will act as a true standard of assessment for the presence of life in the biogeological record. A list of potential biomarkers is provided in Table 1.

It is interesting to compare this list of potential biomarkers with those mentioned in two key publications which have also proposed biomarkers for extraterrestrial analytical astrobiological missions: firstly, a paper by Perry et al. (2007), which set out to define biominerals and organominerals as direct and indirect indicators of life. Secondly, in the same year, Parnell et al. (2007),



**Table 1.** Biomarkers for analytical spectroscopic astrobiology.

<b>Bioorganic molecules</b>	<b>Bioinorganic molecules</b>
Scytonemin	Whewellite
Carotenoids	Weddellite
Carotenes	Aragonite
Chlorophyll	Vaterite
Trehalose	Mellite
Phycocyanins	
Hopanoids	
Oxalates	
Organic minerals (amber, idrialite, etc.)	

described a very comprehensive list of biomarkers for study as selective targets for the ExoMars mission specifically addressing the antibody requirements for the Life Marker Chip instrumentation to be carried on that mission. It can be appreciated that the range of biomarkers selected in these papers is large and there will be a necessity to perhaps focus on a more prescriptive list of definitive molecular species.

The longevity of survival of the selected biomarkers in the geological record will effectively dictate the usefulness of any selected biomarker target for remote astrobiological analysis, and much work is required in terrestrial scenarios to assess this important and fundamental parameter.

### 3. Raman Spectroscopy and Analytical Astrobiology

It is beyond the scope of a book of this length to describe in detail the merits of the Raman spectroscopic method that lend themselves so well to analytical astrobiology on remote space missions, but some of the important factors will be summarised here.

A very important requirement fulfilled by Raman spectroscopy in the analysis of biomarkers is the ability to differentiate between the key molecular species on the basis of their characteristic spectral signatures; this is not only manifest in the discrimination between the relevant organic components of the complex protective biochemicals comprising the stressed biological colonies and the minerals of the geological host matrix but also the identification of the different types of molecular biomarker, such as those specified in Table 1. It should be appreciated that Raman scattering arises from molecular bonds and not atoms themselves; hence, sodium chloride, a monatomic ionic solid, will not have a first-order Raman spectrum – this can be put to excellent use in searching for residual molecular inclusions in halite crystals, where the salt matrix is effectively spectroscopically “silent” in the Raman effect.

### 3.1. RAMAN SPECTROSCOPIC INSTRUMENTAL PARAMETERS OF IMPORTANCE FOR ANALYTICAL ASTROBIOLOGY

Raman spectroscopy is an analytical technique which provides information about the molecular structures and chemical environments of organic and inorganic molecules and molecular ions. The generation of Raman spectra requires the illumination of target specimens with laser radiation, which can be focused or non-focused and for which the “footprint” can range from about 1  $\mu\text{m}$  to several hundred microns in cross-sectional diameter depending upon the optical design of the sample illuminator. Raman spectra are observed as two sets of wavelength-shifted bands from the Rayleigh line, which occurs at the frequency of the incident laser radiation: the long wavelength set of Raman bands comprise the Stokes Raman spectrum and the low wavelength set that of the anti-Stokes Raman spectrum, which is relatively weaker in intensity compared with the Stokes Raman spectrum. Raman spectra are generally measured as wavenumbers ( $\text{cm}^{-1}$ ) which are shifted from the laser excitation wavenumber, namely, that of the Rayleigh line. Since Raman spectra are significantly weaker in intensity compared with the Rayleigh line intensity, it is important that the irradiance of the incident laser being used for the observation of the Raman spectra is high, consistent with the requirement that sample damage does not occur. Because the Raman effect has an inverse dependence upon the fourth power of the laser wavelength, hitherto much Raman spectroscopy has been carried out in the visible region of the electromagnetic spectrum using blue and green wavelengths. However, the advent of non-visible wavelength diode lasers operating in the ultraviolet and the near-infrared regions has provided some novel sources of excitation of Raman spectra; currently, there are reports of Raman spectra being excited at wavelengths of 240 nm in the deep ultraviolet and at 1,330 nm in the near-infrared region, and with all other instrumental factors being equal, power for power, the Raman spectrum excited in the ultraviolet will be some 950 times more intense than that recorded in the near-infrared region over this wavelength range.

Despite the advantage of greater intrinsic Raman-scattered intensity at low excitation wavelengths, there are several good reasons for the adoption of Raman laser excitation at longer wavelengths, not the least of which is the sensitivity of the materials under study to the high laser energies in the ultraviolet and the onset of fluorescence to the associated with the presence of low-energy molecular electronic states that are more likely to be probed using exciting radiation at low wavelengths. Fluorescence emission is several orders of magnitude greater than the corresponding Raman scattering generated by the same laser wavelength, and relatively intense, broadband fluorescence backgrounds can generally swamp the much weaker Raman bands from the same sample. An example of this is provided in the Raman spectra of an extremophilic *Caloplaca saxicola* epilithic lichen from Crater Cirque, Northern Victoria Land, Antarctica, excited using 633 and 785 nm radiation, respectively, and in both cases the broadband fluorescence emission dominates the spectrum over the wavenumber range 300–1,300  $\text{cm}^{-1}$ . In contrast,

the spectrum excited using 1,064 nm radiation in the near-infrared region shows Raman bands which can be used as biomolecular diagnostics of the protective biochemicals that are being produced by the extremophile in response to the stressed environmental conditions prevailing in the Antarctic site. Hence, the selection of the optimum instrumental requirements and experimental conditions for the generation of Raman spectra is not a trivial task.

### 3.2. RAMAN SPECTRAL INTENSITY

Because Raman spectra are generally weak, special techniques are required for their generation and observation, but the information which can be derived from Raman spectra amply repays the special attention given to their study. Raman spectra will routinely cover the wavenumber shift region from about 50 to 3,500  $\text{cm}^{-1}$ , which will contain all the important vibrational spectroscopic information relating to organic biomolecules and their inorganic counterparts. An example of the Raman spectrum obtained from the extremophilic endolithic cyanobacterial colonisation of Beacon sandstone by *Chroococciopsis* sp. demonstrates this aspect very clearly. Generally, the CH stretching modes of organic aliphatic and aromatic hydrocarbon derivatives will occur in the wavenumber region 2,800–3,150  $\text{cm}^{-1}$ , amide stretching bands of proteins near 1,650  $\text{cm}^{-1}$ , the C=C modes of unsaturated lipid chains and carotenoids between 1,500 and 1,640  $\text{cm}^{-1}$ , quadrant ring stretching bands of aromatic polycyclic hydrocarbons near 1,600  $\text{cm}^{-1}$  and various characteristic modes belonging to C-C, C-O, C-N, C-P and C-S moieties at lower wavenumbers down to 500  $\text{cm}^{-1}$ , including the uniquely observable S-S modes of cysteine residues in keratotic molecules in the region 460–520  $\text{cm}^{-1}$ . At the same time the vibrational modes of molecular inorganic materials and ions such as the Fe-O in haematite, P-O in hydroxyapatite, S-O in sulphate, N-O in nitrate, Si-O in quartz and silicates such as pyroxene and olivine, C-O in carbonates, Ti-O in rutile and anatase and Fe-S in pyrites can all be characterised and identified in the wavenumber range 100–1,100  $\text{cm}^{-1}$ . In the particular example of *Chroococciopsis* sp., the information that is contained in the Raman spectrum and the vibrational spectroscopic assignments that can be made of the Raman bands to the biological and geological features give a valuable and powerful analytical advantage over many other analytical techniques since now not only the presence of organics in a geological environment can be assessed but the interaction between the organics and the inorganic matrix can be examined without the necessity of extraction or separation of the phases being undertaken. Such an example illustrates the application of Raman spectroscopy to the detection of organic molecules of relevance to life in terrestrial geological environments, which clearly has a fundamental application as a test-bed for future planned Raman analytical experiments on Mars. Other useful factors which can advocate the adoption of Raman spectroscopy as an analytical technique for potential life-detection experiments in stressed terrestrial environments relate to the low-Raman-

scattering cross-section for water and hydroxyl groups which immediately has importance for the detection of organics near deep-sea hydrothermal vents, the use of a Raman probe for molecular detection in the subsurface of glaciated lakes, the detection of life signatures in permafrost, the analysis of lacustrine sediments and the detection of micrometeorites in Arctic and Antarctic ice cores. In none of these examples would there be a need for specimen desiccation to record the Raman spectra, which would realistically be extremely difficult to achieve for several of the scenarios mentioned here.

### 3.3. CONCENTRATION OF MOLECULAR SPECIES

Raman band intensities are dependent upon several factors which include the irradiance of the laser ( $\text{Wm}^{-2}$ ) and a linear dependence on the concentration of the molecular scattering species (Wynn-Williams and Edwards, 2000b). The former factor necessitates the use of a reasonably high-powered, focused laser beam incident upon the specimen consistent with the survival of the molecular integrity, whereas the latter factor can be extremely useful for quantitative and semiquantitative analysis of the Raman spectra. The result is that Raman spectra are relatively easy to quantitate, and, for example, to a very good approximation, ten times the amount of material in the scattering volume will give ten times the intensity of the observed Raman band; however, this linearity of response means that there is a threshold for the observation of Raman spectra below which the observation of Raman bands is impractical. This sensitivity will be different for every molecular system and will depend upon molecular Raman-scattering coefficients, which effectively describe the response of molecules to laser Raman scattering. Normally, a minor species concentration in a molecular system which represents about 0.01–0.1 % (about 100–1,000 ppm) of the major component will be at the lower limit of detection in the Raman spectrum. However, as will be demonstrated below, there are several ways in which the detection of minor components in a system can be enhanced, for example, using surface-enhanced Raman spectroscopy (SERS), resonance Raman spectroscopy (RRS) and a combination of these, surface-enhanced resonance Raman spectroscopy (SERRS).

Perhaps a more practical application for remote exploration of an increased sensitivity toward the minor components in heterogeneous specimens is provided by the adoption of Raman microscopy, where the laser is focused into a very small spectral “footprint” which may be of the order of only several microns diameter and individual particles can be examined preferentially from the surrounding matrix; the Raman-scattered intensity from these particles or small aggregates, which only represent effectively nanogram or picogram quantities of material, is enhanced by the high irradiance used in the sample illumination. Hence, good quality Raman spectra can be achieved from apparently low laser powers at source of about 1 mW, which imaged into a specimen particle of one cubic micron

gives an irradiance of more than  $1 \text{ MWm}^{-2}$ , resulting in a Raman spectrum being obtained from only 1 pg of material at a “concentration” in its matrix of less than 1 ppb.

### 3.4. MOLECULAR EFFECTS

The concept of molecular scattering coefficients and the sensitivity of molecules toward excitation in Raman spectroscopy has already been raised, and it is appropriate here to examine the practical consequences that these parameters have upon the ability to record the Raman spectra of different materials. The sensitivity of Raman spectroscopy for the observation of Raman bands depends upon the polarisability change in electronic charge density of the chemical bonds within a molecular system on excitation with laser irradiation. Generally, bonds between large, polarisable atoms can give rise to strong Raman spectra where the number of Raman bands observed is dictated by the molecular symmetry; the more symmetric a molecule, the fewer the Raman bands that are obtained in the spectrum. Most molecules, however, are of low symmetry or have no symmetry at all – hence, they have relatively rich Raman spectra in terms of the number of bands displayed. The wavenumber positions of the Raman bands are also dictated by the type of molecular bond that is being irradiated; Raman bands originating from bonds between heavy atoms will occur in a low wavenumber shift region of the spectrum, for example, mercury sulphide has a very strong and characteristic Raman band at  $253 \text{ cm}^{-1}$ , whereas a carbon-hydrogen bond in an aliphatic hydrocarbon will occur near  $2,950 \text{ cm}^{-1}$ . This gives rise to the *molecular specificity* of Raman spectra, whereby it is possible to recognise the presence of molecules or chemical moieties from the wavenumber positions of their Raman bands.

As a diagnostic device, the presence of key features in the Raman spectra of molecules is a very important process. Hence, the presence of a band in the Raman spectrum of keratotic proteins at about  $500 \text{ cm}^{-1}$  is a diagnostic verification of S-S bonding; furthermore, the change in wavenumber of this feature occurs in a verifiable way with conformation about the C-S-S-C linkage in the protein, and localised *cis*, *trans* and *gauche* conformational structures can be identified diagnostically between  $480$  and  $520 \text{ cm}^{-1}$ .

The low molecular scattering coefficient of water in Raman spectroscopy is useful for cases where desiccation of the specimen is not practicable, such as field applications in ice-laden environments or in contaminated groundwaters, such as polar glaciated regions and volcanic geysers, respectively. The presence of water molecules in different chemical or physical sites in crystal structures is an important parameter and can be recognised through the environmental molecular effects on other neighbouring molecular ions, such as mineral hydrates, for example. Raman spectra of two key biogeological materials that are possible signatures of extinct or extant life, whewellite (calcium oxalate monohydrate) and weddellite (calcium oxalate dihydrate) provide such an example. Although the water bands are not

visible per se in these Raman spectra, the effect of the coordinated water in different sites in the crystal matrix upon the vibrational modes of the oxalate molecular ion is apparent in the wavenumbers of the stretching and bending bands of the  $C_2O_4^{2-}$  ions. The recognition of these two materials in the geological record is significant for life-detection experiments since these materials remain even after the life processes which have produced them have ceased to exist.

It should be noted that Raman spectroscopy depends upon the interactions of electromagnetic radiation with chemical bonds for the production of a spectrum. Hence, a Raman spectrum would not be expected from monatomic ions, such as  $Ca^{2+}$ ,  $Na^+$  and  $Mg^{2+}$ . However, as has been noted in the case of the molecular electronic environments in the vicinity of water molecules, the electronic environmental effects of monatomic cations upon molecular anions can also be observed diagnostically in the Raman spectrum even when these cations themselves have no Raman spectrum. This is generally the basis of mineral diagnostic differentiation in Raman spectroscopy, for example, the Raman spectra of calcite and aragonite, two polymorphs of  $CaCO_3$ . Here, the Raman C-O symmetric stretching band of the  $CO_3^{2-}$  ion which is common to these two minerals occurs at  $1,086\text{ cm}^{-1}$ . It is interesting that although calcite and aragonite have an identical stretching band wavenumber of  $1,086\text{ cm}^{-1}$ , which effectively means that this is not diagnostically useful for discriminating between these two polymorphs and can merely serve to identify calcium carbonate in a mineral matrix, the two polymorphs can be distinguished from the different wavenumbers exhibited by the other bands in their spectra, namely,  $712/704$  and  $283/206\text{ cm}^{-1}$ , respectively, for calcite and aragonite. A similar situation exists for the two magnesium carbonate minerals dolomite,  $CaMg(CO_3)_2$  and magnesite  $MgCO_3$ , where the  $CO_3^{2-}$  stretching band occurs at  $1,094\text{ cm}^{-1}$  for both minerals and it is now essential to use the other Raman-active bands for differentiation purposes, for example,  $713/738\text{ cm}^{-1}$  and  $300, 177, 156/330, 120\text{ cm}^{-1}$ , respectively, for dolomite and magnesite. This highlights a very important point in diagnostic spectroscopy, namely, that it is often not practicable to rely on just one defining band for characterisation purposes, and that sometimes up to three features need to be considered. The rich diversity of chemical information that is provided by the micro-Raman spectra exemplifies the geological applications of Raman spectroscopy to Martian materials.

The construction and effective use of automatic database comparison for the recognition of Raman band signatures will therefore need to address this issue of multiple band occurrences. Although the change in vibrational band wavenumbers in the Raman spectrum can be used to provide some definitive diagnostic applications in many areas of chemical science, it does create a problem for the construction and operation of databases and especially for automated recognition of molecular entities from established databases – essentially, there is no single wavenumber position that characterises every molecule with respect to its Raman bands. For example, a “free” C=C is found in the Raman spectrum at  $1,625\text{ cm}^{-1}$  for ethylene, but substitution of chemical groups on the adjacent C–H bonds in the alkenyl molecule will change the wavenumber of this band,

especially if the groups concerned have the ability to strongly influence the electronic environment of the isolated C=C bond through conjugation, in which the electronic density on the C=C bond is affected. A C=C-C=O moiety, therefore, will exhibit a C=C Raman band at  $1,605\text{ cm}^{-1}$  and a C=O band at  $1,695\text{ cm}^{-1}$ , both shifted down from their respective wavenumber positions in their “free” molecules. Although this is expected theoretically from molecular dynamics, it would be quite difficult to design a suitable database that would immediately recognise these bands as arising from individual C=C and C=O vibrations. Taking this discussion further to the important case of carotenoids, biomolecules based upon the chemical structures of beta-carotene and its congeners with extended chain conjugation of C=C units with each other through a C=C-C=C type coordination, the C=C vibration now appears in the Raman spectrum between  $1,510$  and  $1,534\text{ cm}^{-1}$  depending upon the length of the chain and end substituents (Bedau, 2010); this should be compared with the case of a free, isolated C=C in ethylene at  $1,625\text{ cm}^{-1}$ . Clearly, some sophistication in the automatic database for recognition of this spectral signature and its attribution as a C=C mode diagnostically would be required – and carotenoids are identified as very significant biomolecules, having a major role in prebiotic chemical evolution discussions of the origin of life in the Solar System.

### 3.5. SPECTRAL RESOLUTION

The effect of the instrumental spectral resolution upon the appearance of the resultant Raman spectra with regard to the capability of discrimination between the biological and geological band signatures is a critical one. Although the spectral resolution, measured in  $\text{cm}^{-1}$ , is operator adjustable in laboratory instrumentation, it will normally be a fixed parameter consequent upon the design features in the case of miniaturised instruments. The effect of changing the spectral resolution for  $1,064\text{ nm}$  laser excitation upon the Raman spectrum can be illustrated for olivine; the characteristic doublet at  $820$  and  $860\text{ cm}^{-1}$  using a spectral resolution of  $4\text{ cm}^{-1}$  provides a key diagnostic indicator for this mineral. However, at a spectral resolution of  $32\text{ cm}^{-1}$ , this doublet collapses to a broader singlet band with a peak wavenumber of  $844\text{ cm}^{-1}$ . The result of the recording of the Raman spectrum of olivine at this lower resolution of  $32\text{ cm}^{-1}$  is that a database search mechanism would probably fail to assign the specimen to olivine. An even more serious situation can now be envisaged than was the case for the geological specimen of olivine, in that many more key biological signatures that are essential for the identification of the complex biomolecular composition of the organism are now obscured at low resolution, for example, the key features due to rhizocarpic acid at  $1,664$ ,  $1,595$  and  $1,001\text{ cm}^{-1}$  for which the spectrum with poorer resolution provides data at  $1,663$  and  $1,599\text{ cm}^{-1}$  only. The sharp band at  $1,001\text{ cm}^{-1}$ , a key feature for mono-substituted aromatic ring compounds, is now totally absent at lower resolution. Similarly, the quadruplet in the neighbourhood of  $1,300\text{ cm}^{-1}$  has now collapsed

to two broader bands at 1,346 and 1,287  $\text{cm}^{-1}$ , from 1,347 and 1,280  $\text{cm}^{-1}$  in the spectrum recorded at higher spectral resolution. The bands at 1,159 and 1,520  $\text{cm}^{-1}$  from a carotenoid component are also absent at lower resolution, as are features at 944 and 787  $\text{cm}^{-1}$ .

Clearly, the operating resolution under which the Raman spectra are being recorded will be vital for the effective database discrimination capability that will be an essential component of miniaturised spectrometer design. Instrumental evaluation of proposed miniaturised spectrometers must be an integral part of their incorporation into planetary landers. As the instrument size is diminished physically, each pixel in the diode array detector covers a larger wavenumber range, and a choice facing instrument constructors is the compromise between wavenumber shift range and the spectral resolution – the former will decrease the spectral coverage for materials of interest, whereas the latter can distort the observed spectra which may result in a misattribution of the data or even missing features, the presence of which may be vital particularly for the biological assignment.

Another consequence of a diminished spectral resolution is the analytical “smoothing” effect apparent in the observed spectral quality at a decreased noise level. Normally, Raman spectra are acquired from the spectral accumulation of single-scan spectra which may take only 1–2 s or less to achieve individually; however, weaker spectral features are better observed after the accumulation and co-addition of 10–2,000 spectral scans, depending on the instrument available. The real acquisition time of a Raman spectrum is dependent on the number of spectral co-additions undertaken, for which the signal-to-noise ratio is increased as the square root of  $N$ , where  $N$  is the number of spectral scans accumulated. Hence, the achievement of a tenfold improvement in the signal-to-noise ratio in a Raman spectrum over that observed in a single scan will require 100 scans accumulated – and this will take approximately 3–4 min at 1,064 nm using an FT-Raman system compared with 1–2 min using a visible wavelength CCD system. An increased speed of data acquisition can be achieved by decreasing the spectral resolution to decrease the effective accumulation time, but this can compromise the analytical assignments as seen above, especially for biologically relevant molecules.

### 3.6. MINIATURISED INSTRUMENTATION

Several miniaturised prototype Raman spectrometers have been constructed and are being developed and evaluated by groups for possible space mission adoption by NASA and ESA. The ExoMars/Pasteur and Aurora projects are currently targeting the inclusion of novel miniaturised Raman spectroscopic instrumentation in mineralogical and life-detection suites on robotic planetary landers and rovers for the exploration of Mars.

Several prototype advanced field instruments for mobile remote Raman spectroscopy have been constructed; one of these from JPL/University of Washington,



St. Louis, delivers green radiation at 532 nm (frequency-doubled Nd<sup>3+</sup>/YAG laser radiation) onto a specimen through the probe head of a sensing device. Another miniature Raman instrument that has been constructed as a joint venture between NASA and the University of Montana (Prof. David Dickensheets) uses 852 nm radiation in the near-infrared region to excite the Raman spectra of organic molecules, with an operational spectral resolution of 12 cm<sup>-1</sup>. This arrangement did not compromise the retrieval of quality spectral data in the lower wavenumber region in comparison with the spectra that were excited at 1,064 nm with the laboratory-based FT-Raman system on the same sample. However, the decreased response and sensitivity of the miniaturised instrument in the higher wavenumber region was noticeable; nevertheless, the identification of the protective biochemicals produced by the extremophile lichen from these standards in the database can be accomplished successfully using 852 nm radiation.

The importance of the evaluation of miniaturised Raman prototypes using terrestrial Mars analogues, particularly of extremophilic biological organisms, is stressed so that the advantages and limitations of parameters such as laser excitation wavelength, spectral wavenumber range, spectral resolution, scan characteristics and the speed of data acquisition can be properly quantified in the design of future experimental spectrometers for space mission adoption.

### 3.6.1. Carotenoids

Because the Raman spectral signature wavenumbers of any molecule or molecular ion are dependent upon the electronic and geometric composition of the particular bonds giving rise to the molecular scattering of radiation, the wavenumbers observed in the spectra of a group of closely related compounds such as carotenoids are found to occur over a wavenumber range rather than at a single, precise wavenumber. For example, the biogenetic synthesis of carotenes from the parent lycopene structure involves cyclisation, producing alpha- and beta-carotenes, and further hydroxylation in the aliphatic rings gives lutein and zeaxanthin (Weesie et al., 1999); despite the latter both being centrosymmetric molecules and having a conjugated 11-ene system with three methyl groups in each ring and a further four pendant methyls situated along the unsaturated -C=C-C- backbone chain, these very similar structures can normally be readily differentiated by Raman spectroscopy. More troublesome, however, is the observation of wavenumber-shifted fundamental bands that occur because of external molecular environmental changes – and these are more difficult to quantify, hence, the importance of constructing reference databases of biomolecules in admixture particularly with minerals. Finally, it is not merely sufficient to identify the Raman spectral signatures of biomarkers that also have parallels for abiotic organic compounds as this will in itself create an ambiguous interpretation of the spectral data from a remote planetary interrogation; hence, the observation of CH stretching Raman wavenumbers associated with aliphatic organic compounds in the 2,800–3,000 cm<sup>-1</sup> region on the ExoMars mission would not be exclusively indicative per se of life signatures on Mars as this functionality also occurs widely in abiotic organic compounds, although this result would be the

first direct evidence that organic compounds can survive the hostile Martian environment – itself a major step forward in current knowledge.

### 3.6.2. Carbon

The degradation of biomolecules in hostile geological environments eventually produces carbon (Edwards et al., 2005) whose signatures in the Raman spectrum have been well described in the laboratory. The idea that it is possible to differentiate between biotic and abiotic carbon formation from the shape of the so-called D and G Raman bands, characteristic of  $sp^3$  and  $sp^2$  hybridised carbon, effectively represented by structures typical of diamond and graphite, has had a long and rather controversial history in the literature which is still raging today; a summary of the extensive literature on this subject is provided by Marshall et al. (2010; Marshall and Olcott Marshall, 2010), who attempt to define a possible methodology for rigorously discriminating between these different carbon sources. However, if we consider the requirements of such finely tuned spectroscopic work that has to be undertaken in the field using portable miniaturised instrumentation with all the sacrifices that have had to be made from laboratory versions, additionally performed under extremely hostile conditions that are mirrored nowhere else terrestrially, then one must pose the question whether it is possible with current instrumentation to be able to differentiate abiotic and biotic carbon? The result then is that the observation of characteristic carbon signatures themselves does not constitute the presence of extinct life, so in our definition, carbon cannot be a true biomarker. The same analogy applies to a host of other biochemicals, which have been synthesised abiotically in the laboratory, such as amino acids, sugars, porphyrins and proteins. This is the reason that these molecules are not presented as true biomarkers in Table 1.

## 4. The Raman Laser Spectrometer on the ExoMars 2018 Mission to Mars

The science objectives of the ESA rover on the two-rover NASA/ESA 2018 mission to Mars are to search for signs of past and present life on Mars, the characterisation of water in a geochemical environment in the surface and shallow subsurface (down to approximately 2 m depth); to investigate the planetary subsurface; and to identify hazards to the future human exploration of Mars. The Raman Laser Spectrometer (RLS) will contribute to two of these objectives, namely, the search for past or present life through the identification of biomarkers and the identification of minerals produced as a result of biological activity and the characterisation of mineral phases produced by fluid-rock interactions and their alteration products. As one of the first-pass, non-destructive analytical procedures on the rover's Pasteur instrument suite, RLS will interrogate the target powdered material from surface rocks and subsurface drill cores and will provide an evaluation for the tactical incorporation of sequential and destructive analytical procedures.

The RLS instrument (Rull et al., 2011) with a dedicated mass of only 1.8 kg will have laser diode excitation at 532 nm into a target footprint of 50  $\mu\text{m}$  diameter with an effective irradiance at the sample of between 0.8 and 1.2  $\text{kWcm}^{-2}$ , which is set to below the threshold for thermal grain damage in target oxides and hydroxides and associated organic biomarker molecular residues. The laser operation has an anticipated 400 individual sets of measurement cycles each of 10 min maximum duration, with an operating spectral resolution of approximately  $6\text{ cm}^{-1}$  over a spectral wavenumber shift range of 150–3,800  $\text{cm}^{-1}$ , which encapsulates the fundamental vibrations of molecular anions (e.g., sulphates, carbonates, silicates, phosphates, oxides and hydroxides) in minerals, functional groups in organic biomarker molecules and the water and OH stretching and bending bands in salt hydrates. Although originally it was planned that the RLS instrument would have a dual role in interrogating samples via an external arm and optical head as well as an internal optical head, stringent mass limit considerations have now reduced this capability to the internal head only. The scattered Raman radiation is imaged onto a holographic grating, and several diffracted orders are focused onto a thermoelectrically cooled  $2,048 \times 512$  pixel CCD detector. There are two operational spectral scanning modes: in the automatic mode the RLS will take at least 20 spectral replicates across a line transect on the sample, whilst a smart mode operation will examine the spectra and deduce regions of potential scientific interest, aided by MicrOmega IR camera imaging.

Several flight-like prototypes (FLPs) are in construction which will facilitate the ground tests and spectral evaluation procedures necessary for the setting up of suitable protocols for spectral differentiation and database recognition that will be required for remote observational exercise on the Martian surface, including testing in Earth-based Mars chambers using biogeological extremophilic specimens such as several of those described above.

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# APPLICATION OF RAMAN SPECTROSCOPY AS IN SITU TECHNOLOGY FOR THE SEARCH FOR LIFE

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## 1. Introduction

Raman microscopy is a nondestructive in situ technology appropriate to identify organic compounds and mineral products. It is a well-established technology and applied in various areas like pharmacy, biology, and mineralogy. Measurements could also be taken on other planetary bodies of our Solar System via future spacecrafts. The range for application reaches from acquiring discriminating bands (e.g., Raman reporter molecules like pigments) to the complex evaluation of spectral fingerprints. For the chemical characterization of biological samples as well as biomaterial-containing samples, chemometrical methods and pattern recognition need to be used for a reliable identification. Databases of Raman spectra established beforehand support the identification of the observed material.

The ExoMars Mission in 2018 is the first mission for which a Raman spectrometer is part of the planned payload. In preparation to this and further missions, it is necessary to study the circumstances one could be faced with when performing Raman measurements in a non-Earth-like environment. The differences and difficulties compared to the established measurement approaches on Earth



(Sect. 2) need to be recognized, and solutions must be found. As an example for a space application in Mars exploration, the identification of  $\beta$ -carotene in cyanobacteria on Mars-analogue material by Raman spectroscopy is presented (Sect. 3, based on Böttger et al., 2012). A procedure was developed to optimize the detection of cyanobacteria embedded in different types of martian soils.

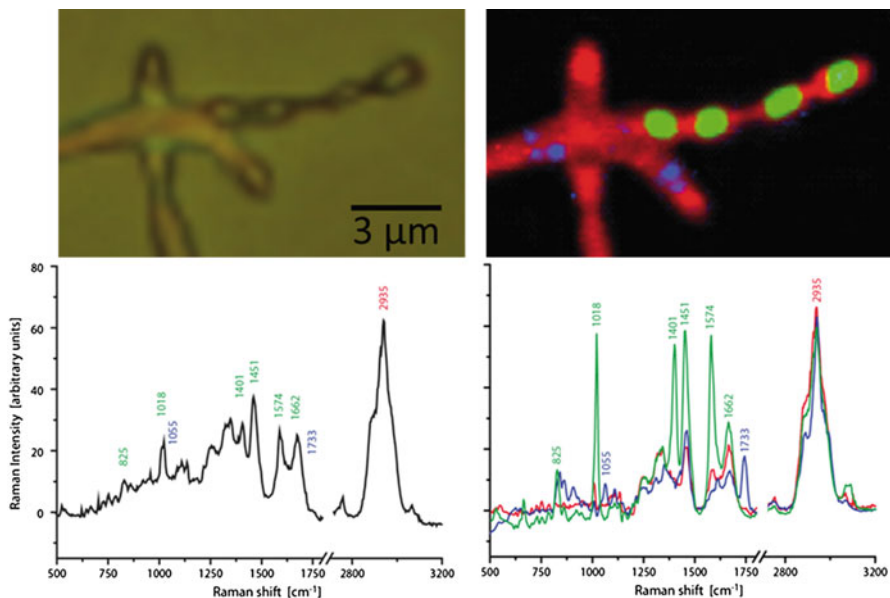
## 2. Raman Spectroscopy for Detection of Life

### 2.1. RAMAN SPECTROSCOPY OF MINERALS

Raman spectroscopy is a technique, where the inelastic scattering of the incoming photons produces a spectrum depending on the molecular and crystal vibrations of the observed matter. In mineralogy it is applied to distinguish between different minerals, such as mineral dissolutions on a micrometer scale. Appropriate databases allow the identification of different minerals. The Raman spectrum is influenced by temperature and pressure the mineral experienced and can be used to identify the degree of structural order or disorder (McMillan et al., 1996). As a nondestructive method Raman confocal microscopy is used to in situ investigate the mineral structure under different environmental conditions. Available databases do not provide this information in a systematic manner. With regard to space application, this is important. Furthermore, mineral mixtures can be found more likely in a natural environment instead within single minerals. Raman spectra of mineral mixtures are difficult to interpret. The superposition of the spectra of the individual minerals is not a simple area weighted sum of the individual spectra, but also depends on the absolute intensities of the spectrum. Some minerals are strong Raman scatterers. Even with a low volume percentage in the sample, their spectrum can be dominant and mask the spectral feature of the other minerals. Such effects need to be investigated prior to missions to other planetary bodies in our Solar System. To demonstrate the problems associated with such missions, martian regolith simulants are investigated as an example for extraterrestrial application of Raman spectroscopy.

### 2.2. RAMAN SPECTROSCOPY OF MICROBES

In microbiology, vibrational spectroscopy and especially Raman spectroscopy is widely used for the chemical characterization of biological samples (Naumann et al., 1991; Maquelin et al., 2002; Hermelink et al., 2009). Even more, it is used for subtyping down to the strain level since it is fast and non-disrupting and needs – in the case of microspectroscopy – a very low sample volume. Figure 1 shows a typical Raman spectrum of a microbial cell (average of *B. cereus*) and a high-resolution chemical map of a cell cluster (part of a colony). Single cells in genetically homogeneous microbial cultures exhibit marked phenotypic heterogeneity that

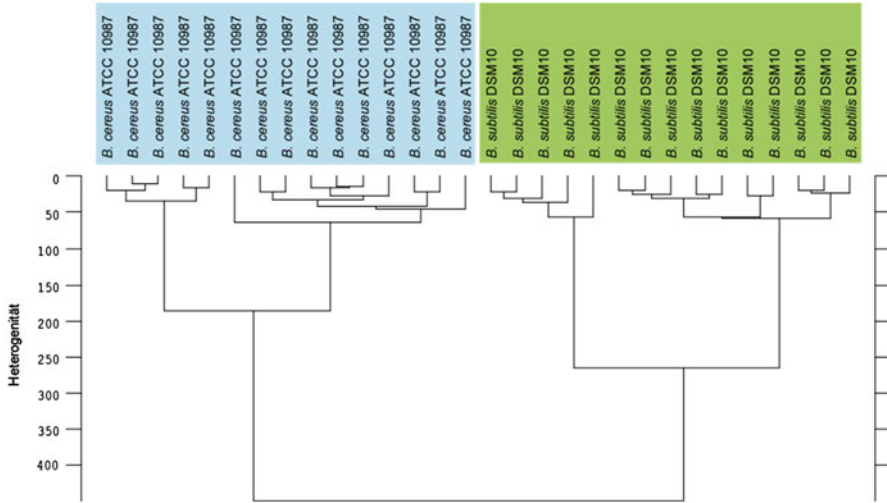


**Figure 1.** Bright field image of *Bacillus cereus* dried onto a CaF slide (top left) and in corresponding areal averaged Raman spectrum. High-resolution chemical map of the same culture (top right). Corresponding spectral signature shown in the same color as chosen in the image.

is considered to support the fitness of the whole population. Heterogeneity on a single-cell level is typically masked in conventional studies of microbial populations, which rely on the data averaged across thousands or millions of cells in a sample. Figure 1 shows the spectral output for two different values of spatial resolution using Raman microspectroscopy.

The *Bacillus* strain displayed here provided the possibility to separate three different components if investigated in high-resolution (diffraction limited) experiments. The three different Raman spectra (Fig. 1 bottom left) depict the three main compounds in the sample and its spatial distribution in the image above. The blue spectrum represents the Raman fingerprint for bacterial poly hydroxyl butyric acid (PHB) (Hermelink et al., 2009).

Its intensity in the image in the chemical map is illustrated by the intensity distribution of the  $\nu$  (C=O) ester stretching vibration band at  $1,733\text{ cm}^{-1}$ . The vegetative cells were visualized by mapping the Raman intensity of the CH stretching region (broad band between  $2,800$  and  $3,000\text{ cm}^{-1}$ ) and are shown in red in the chemical map with the corresponding red spectrum below. Containing bacterial endospores are shown in green in the chemical map and spectrally described with the green spectrum below. The major compound of bacterial endospores is calcium dipicolinic acid (CaDPA), which is a strong Raman scatterer. For a Raman band mapping the symmetric ring “breathing” of CaDPA at  $1,018\text{ cm}^{-1}$  was chosen.



**Figure 2.** Cluster analysis (Ward's algorithm) of confocal Raman spectra from two different strains of close relatives within the *Bacillus cereus* group. Cluster analysis was performed using the 1st derivatives and a combination of spectral ranges (3,000–2,800; 1,200–900; and 900–700  $\text{cm}^{-1}$ ). All spectra were equally weighted.

In this way Raman spectroscopy can be used for both identification (averaging) and chemical characterization of biological material (high-resolution imaging). By using chemometrical methods spectral libraries are successfully used for a fast and non-disrupting subtyping of microbes. Figure 2 shows – as an example – a hierarchical cluster analysis of two different bacterial strains using confocal Raman spectra (Naumann et al., 1995).

### 3. Cyanobacteria on Martian Regolith Analogue for Demonstration of Raman Spectroscopy as an In Situ Technology in Space Research

#### 3.1. MARTIAN REGOLITH SIMULANT

To demonstrate the application of Raman spectroscopy for in situ space research, we produced analogue materials by mixing terrestrial igneous rocks, phyllosilicates, carbonates, sulfates, and iron oxides (Böttger et al., 2012). Two different mineral and rock mixtures, (1) Phyllosilicatic Mars Regolith Simulant (P-MRS) and (2) Sulfatic Mars Regolith Simulant (S-MRS), represent the current understanding regarding environmental changes on Mars: weathering or hydrothermal alteration of crustal rocks and of secondary mineralization during part of the Noachian and Hesperian epoch followed by the prevailing cold and dry oxidizing conditions with formation of anhydrous iron oxides.

Both P-MRS and S-MRS contain igneous rocks with a mineral composition similar to those of martian meteorites, which enclose mainly pyroxene, plagioclase, and olivine. In addition to quartz, hematite was added to both mixtures. Hematite presents the only thermodynamically stable iron oxide under present-day martian conditions (Gooding, 1978).

The phyllosilicatic MRS is analogue to igneous rocks altered by pH-neutral hydrous fluids to clays of the smectite group, including montmorillonite and chamosite (Poulet et al., 2005), and the clay mineral kaolinite (Mustard et al., 2009). Siderite and hydromagnesite are included and account for carbonates that formed by either precipitation or interaction between a primitive CO<sub>2</sub>-rich atmosphere/hydrosphere and the basaltic subsurface rocks (Chevrier and Mathé, 2007; Morris et al., 2010).

The sulfatic MRS represents an analogue for a more acidic environment with sulfate deposits. In addition to igneous rocks and anhydrous iron oxides, goethite and gypsum are included.

The materials were crushed to obtain a grain size distribution for mechanically fragmented regolith with fragments smaller than 1 mm. The different components of the analogue were stirred thoroughly to ensure adequate mixing.

### 3.2. CYANOBACTERIA

Prokaryotes like archaea and bacteria appeared on early Earth at least 3.8–3.5 billion years ago (Gya) (Stackebrandt, 2004). At that time the climate on Mars likely was more temperate and wet compared to today (Poulet et al., 2005; Morris et al., 2010) as indicated by evidence of liquid water on the surface. Life might have developed under similar conditions on Earth or might have been transferred from Earth to Mars (or vice versa) (Schulze-Makuch et al., 2008; Meyer et al., 2011). Cyanobacteria were chosen for our investigations as direct descendants of early autotrophic life forms on early Earth and as an example for potential life on Mars even though it is still under debate if such photosynthesizing organisms appear very early in Earth's history and can be expected on the surface of Mars (Böttger et al., 2012, and Westall, 2013, in this issue). Cyanobacteria and prokaryotes using Photosystem I belong to the most ancient microbes, which still use pigments such as carotene or carotene derivatives for UV protection (Lichtenthaler, 2004). Especially  $\beta$ -carotene has been used as an accessory pigment for the photosynthesis apparatus enhancing the electron transfer after sun irradiation. We therefore concluded that cyanobacteria are good model organisms to start our investigations on the detection of biosignatures in Mars-like environments. In this case Mars-like environment means in particular that cyanobacteria are embedded in Mars-analogue mineral mixtures as described in Sects. 3.1 and 3.3.

The focus of our investigation is  $\beta$ -carotene. With regard to the chosen instrumental parameters (e.g., for ExoMars),  $\beta$ -carotene is well detectable by

Raman spectroscopy because of resonance effects. The Raman technique is used for detection of  $\beta$ -carotene in the coccid, chain, and biofilm forming cyanobacteria *Nostoc commune* strain 231-06 (Fraunhofer IMBT CCCryo) embedded in the described Mars-analogue mineral mixtures (for more details, see Böttger et al., 2012).

### 3.3. SAMPLE PREPARATION

Spectral characterization of cyanobacteria was performed in a more realistic martian mineral environment by Raman measurements on (1) pure cultures of cyanobacteria, on (2) the pure mineral mixtures P-MRS and S-MRS, and on (3) cultures of cyanobacteria on these Mars-analogue substrates.

In case (3) the colonies of a culture of *Nostoc commune* strain 231-06 were streaked on the Mars-analogue mineral mixtures obtaining different stages of single-cell and cluster distribution to be close to natural biofilm conditions.

Additionally, Raman measurements on thick sections of the mineral components of the mixtures were provided for comparison.

## 4. Raman Measurement Procedures

A confocal Raman microscope conducted measurements at room temperature under Earth atmospheric conditions. The Raman laser excitation wavelength used was 532 nm and the spectral resolution of the spectrometer was  $4\text{--}5\text{ cm}^{-1}$ . The laser was focused to a  $1.5\text{ }\mu\text{m}$  spot. The surface laser power was set at 1 mW. A spectral calibration was performed by using Raman measurements of a pure silicon test sample. To obtain optimal spectra, different periods of acquisition time and number of spectra per sample point were performed. This was done so the signal-to-noise ratio is sufficient to identify characteristic Raman peaks of the minerals. With acquisition times in the range of 1 and 100 s per spectrum from 1 to 100, repeating measurements were performed on one spot of the sample and then averaged in the final spectra. The following procedure was applied based on Böttger et al. (2012):

1. Measurements were carried out on the polished thick sections. Spectra of the constituent minerals were derived for later comparison.
2. Single measurements and line scans were taken on each martian analogue material without bacteria and on pure cyanobacteria separately. In this way the constituent minerals and the optimal measurement parameters for the mineral mixtures and the cyanobacteria were determined and serve as reference peak positions for the combined sample in the next step.
3. Measurements were performed on pellets with cyanobacteria. This set of measurements was carried out to distinguish the cyanobacteria from the mineral background and to investigate the influence of each involved material and the cyanobacteria.

Before interpretation, spikes originating from cosmic radiation were removed from the spectra. Further, a baseline correction was applied to the spectra. No further calibration of the spectra was applied. The derived peak positions were used for interpretation and determination of the mineral constituents and of  $\beta$ -carotene.

## 5. Results

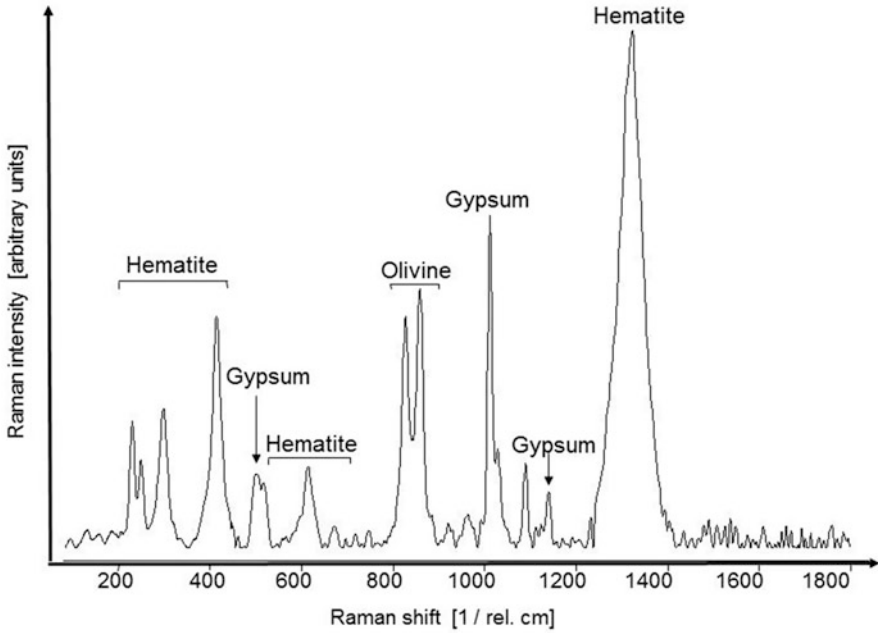
### 5.1. MINERAL SAMPLES

First, Raman measurements were carried out on polished thick sections to obtain the reference spectra of the minerals that make up the Mars regolith simulants. The spectra were obtained with an acquisition time chosen between 5 and 10 s. The measurement time per spectrum and the number of spectra per sample point ranged between (1 s, 5 $\times$ ) and (100 s, 5 $\times$ ). At points on the sample where fluorescence was not dominant, spectra with a signal-to-noise ratio sufficient to obtain the characteristic Raman peak positions were achieved with averaging 5 measurements with an acquisition time of 20 s per spectrum:

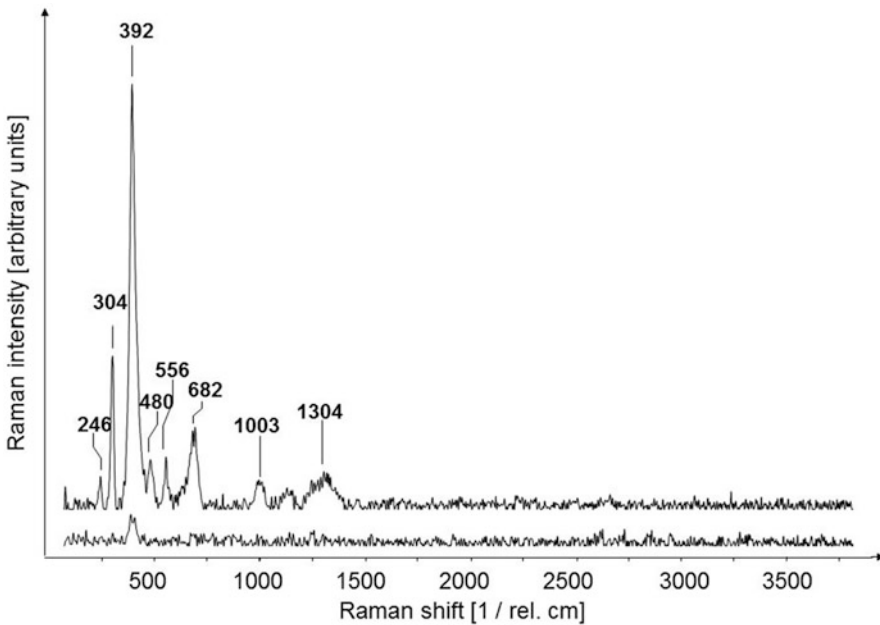
- Raman spectra on P-MRS exhibited strong fluorescence. Raman spectra of quartz, hematite, hydromagnesite, and amorphous carbon were measured on selected points of the sample. The carbon originated from the chamosite sample. Fluorescence was dominant in most of the measurements and no measurement parameters were derived in this case.
- S-MRS Raman spectra were measured at different points on the sample. The acquisition time and number of spectra at each point were (100 s, 5 $\times$ ). The minerals, which were identified within the mixture, are given in Fig. 3. Spectra with variation in acquisition time values (1 s, 5 $\times$ ) and (20 s, 5 $\times$ ) are shown in Fig. 4. The spectra show clearly the improvement obtained by increasing the measurement time per spectrum from 1 to 20 s. However, the main spectral line of goethite at 392  $\text{cm}^{-1}$  can still be recognized in the Raman spectrum with the shorter acquisition time of 1 s (lower curve).

### 5.2. MINERAL SAMPLES WITH CYANOBACTERIA

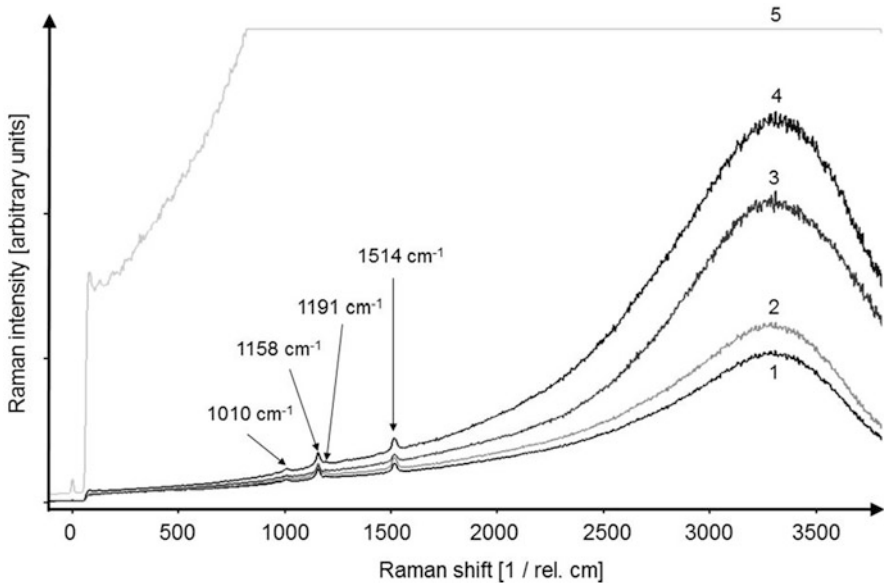
The Raman spectrum of  $\beta$ -carotene present in cyanobacteria can be identified within the applied Mars-analogue mineral mixtures. This is in good agreement with the literature (Vitek et al., 2009; Edwards et al., 2004, 2005; Wynn-Williams and Edwards, 2000). The specific Raman peaks were at 1,010, 1,158, 1,191, and 1,514  $\text{cm}^{-1}$  (Fig. 5). Fluorescence, characteristic for the spectrum, originates from the chlorophyll of cyanobacteria above 620 nm. The measurement time per Raman spectrum is expected to be short as a consequence of the fluorescence and resonance Raman effects. The acquisition time per spectrum was varied between 1 and 100 s, and the number of repetitions was varied between 5 $\times$  and 200 $\times$  per measured spot



**Figure 3.** Raman spectrum obtained from Sulfatic Mars Regolith Simulant (S-MRS) without cyanobacteria. Acquisition time and number of spectra per point on the sample were (100 s, 5×). The spectrum was obtained by integrating the spectra from 100 points along the white line (From Böttger et al., 2012).



**Figure 4.** Raman spectra obtained from Sulfatic Mars Regolith Simulant (S-MRS) without cyanobacteria for different values of acquisition time: lower curve, (1 s, 5×) and upper curve, (20 s, 5×) (From Böttger et al., 2012).



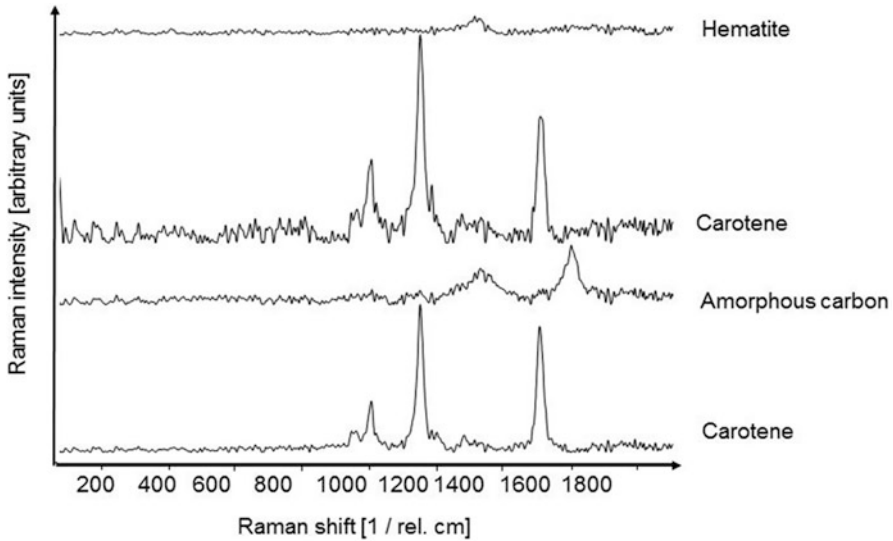
**Figure 5.** Uncorrected final spectra of pure cyanobacteria with 532 nm laser excitation for the following combinations of acquisition time and number of repetitions per measured spot: 1, (1 s, 5×); 2, (5 s, 5×); 3, (1 s, 100×); 4, (1 s, 200×); and 5, (100 s, 5×). The fifth curve shows saturation of the signal (From Böttger et al., 2012).

(Fig. 5). The higher values of acquisition time up to 100 s (curve 5) led to a saturation of the signal. Thus, little improvement is reached by increasing the acquisition time. Therefore, a short acquisition time and few repetitions of the measurement are sufficient to detect the characteristic spectrum of  $\beta$ -carotene.

The spectrum of  $\beta$ -carotene from cyanobacteria is dominant compared to the spectra of the S-MRS and P-MRS substrate:

- Raman spectra obtained from P-MRS with cyanobacteria are shown in Fig. 6. Most spectra exhibit strong fluorescence. In some spectra  $\beta$ -carotene, hematite and amorphous carbon could be identified. For fluorescent mineral mixture it is advisable to choose a rather short acquisition time to discriminate  $\beta$ -carotene of the cyanobacteria from the background.
- Raman spectra obtained from S-MRS with cyanobacteria are displayed in Fig. 7. The illustration of the intensity range of the uncorrected Raman spectra on a sample spot with cyanobacteria in the upper graph clearly shows that the  $\beta$ -carotene from cyanobacteria together with the fluorescence bulge of chlorophyll dominates the spectra. The mineral spectra are not distinguishable. The intensity of the mineral spectra is too low and vanishes in the noise of spectrum due to the strong  $\beta$ -carotene signal. The lower flat spectrum, however, belongs to a point on the same sample where only minerals were present. Here, the minerals can be identified.





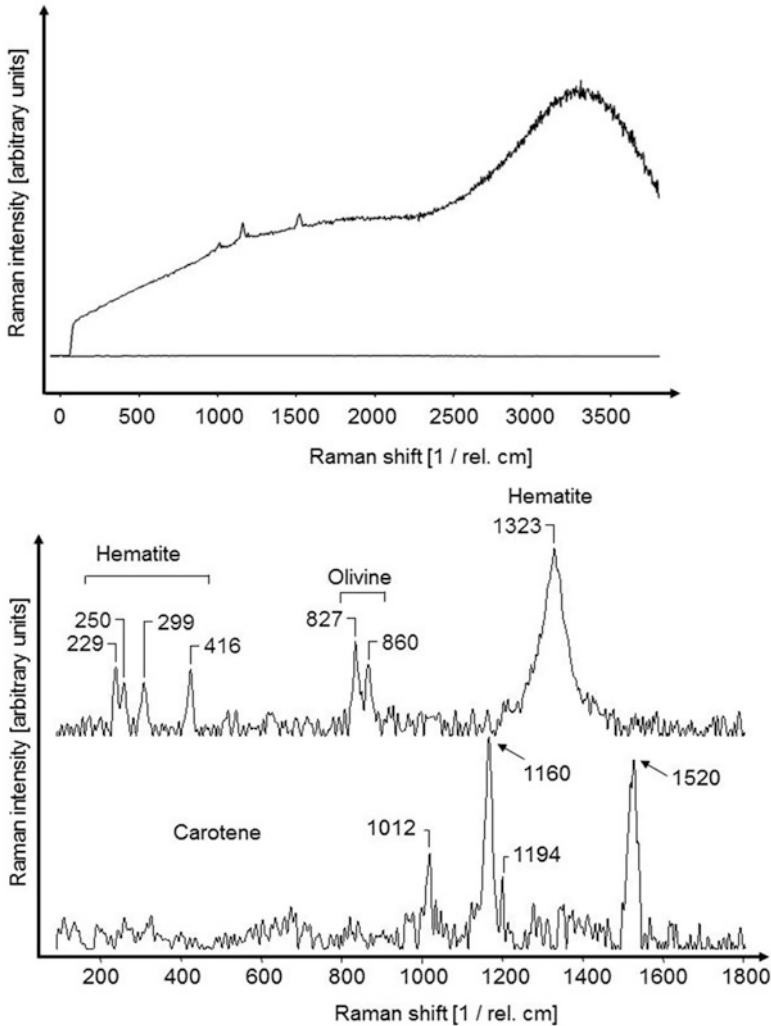
**Figure 6.** Raman spectra after baseline correction obtained from Phyllosilicatic Mars Regolith Simulant (P-MRS) with cyanobacteria from the line scan. The acquisition time and number of repetitions per measured spot were (20 s, 5×) (From Böttger et al., 2012).

The lower plot of Fig. 7 shows baseline-corrected spectra collected with a specified acquisition time and number of repetitions set to 1 s and 5×, respectively. With this measurement conditions  $\beta$ -carotene was clearly identified (lower curve) in the spectra. The spectra collected on sample spots without cyanobacteria and without fluorescence were used for mineral identification (upper curve). In this case the same acquisition time and number of repetitions (1 s, 5×) provide usable final spectra.

## 6. Discussion and Conclusion

The Raman spectrum is dominated by the Raman signal of the cyanobacteria and differs much from the mineral background. For cyanobacteria  $\beta$ -carotene and fluorescence are the predominant features in the spectrum.

According to the measurement procedure, acquisition times have to be adjusted to identify both the cyanobacteria and the substrate of either P-MRS or S-MRS with the same measurement routine. Measurements performed with various values of acquisition time and numbers of accumulated spectra show the improvements of increasing the time per spectrum from 1 to 20 s. Fine tuning is required to optimize the detection of minerals and biological markers and to reduce the disturbing effect of cosmic rays, because a long measurement time leads



**Figure 7.** Raman spectra obtained on Sulfatic Mars Regolith Simulant (S-MRS) with cyanobacteria. *Top:* two different values of acquisition time: upper curve, (1 s, 5 $\times$ ), and lower curve, (20 s, 5 $\times$ ). *Bottom:* averaged spectra from a line scan acquisition time and number of repetitions per measured spot of (1 s, 5 $\times$ ). Spectra with carotene (*lower curve*) and without carotene (*upper curve*) are averaged separately (From Böttger et al., 2012).

to more radiation spikes in the spectrum originating from the interaction of cosmic rays with the detector. Compared to Earth, this is substantially more important for Raman investigations on Mars, because Mars has no strong protecting magnetic field and a lower atmospheric density (Nymmik, 2006; Ferrari and Szuszkiewicz, 2009).

Short acquisition times should be used to avoid the saturation of the spectrum of  $\beta$ -carotene. The fluorescence of chlorophyll from cyanobacteria above 620 nm disturbs the spectrum between 500 and 2,000  $\text{cm}^{-1}$ . The resonance effect of  $\beta$ -carotene gives a very strong signal for the excitation wavelength of 532 nm and is, thus, detectable regardless of the strong chlorophyll fluorescence.

If cyanobacteria are absent, a longer acquisition time should be applied, which is necessary to identify the different mineral constituents of the sample.

The minerals in the P- and S-MRS need an acquisition time of about 20 s for identification of mineral components of the mixture, although the shorter time of 1 s can give an indication, which minerals are involved.

A procedure on a Mars mission is proposed to start with an acquisition time of only a few seconds to identify both biosignatures and minerals. If no biomarkers can be identified, the time and number of repetitions need to be increased until the minerals can be identified in the final spectra. The acquisition time should be selected between 1 s (for  $\beta$ -carotene) and 20 s (for minerals) for a laser power of 1 mW (spot diameter  $<2 \mu\text{m}$ ).

In the future investigations of Raman measurement, parameters should consider as well the different environmental parameters on Mars like atmospheric pressure, composition, temperature, and the heterogeneity of cells which might lead to different spectra, but which could all belong to one strain of a living species.

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**PART VII:  
FUTURE SPACE MISSIONS  
FOR LIFE DETECTION**

**Chela-Flores  
Dachwald  
Ulamec  
Biele**

Biodata of **Julian Chela-Flores**, author of “*Habitability on Kepler Worlds: Are Moons Relevant?*”

**Professor Julian Chela-Flores** was born in Caracas, Venezuela, and studied in the University of London, England, where he obtained his Ph.D. in quantum mechanics (1969). He was a researcher at the Venezuelan Institute for Scientific Research (IVIC) and Professor at Simon Bolivar University (USB), Caracas, until his retirement in 1990. During his USB tenure, he was Dean of Research for 6 years. He is a Fellow of the Latin American Academy of Sciences, the Academy of Sciences of the Developing World and the Academy of Creative Endeavors (Moscow) and a Corresponding Member of the Venezuelan “Academia de Fisica, Matematicas y Ciencias Naturales”. His current positions are Staff Associate of the Abdus Salam International Center for Theoretical Physics (ICTP), Trieste, Research Associate, Dublin Institute for Advanced Studies (DIAS), and Professor-Titular, Institute of Advanced Studies (IDEA), Caracas. His particular area of expertise is astrobiology, in which he is the author of numerous papers. He organized a series of conferences on Chemical Evolution and the Origin of Life from 1992 till 2003. In 2001 he published the book *The New Science of Astrobiology: From Genesis of the Living Cell to Evolution of Intelligent Behavior in the Universe*, reprinted as a paperback in 2004. Its second edition was published with Springer in 2011 as *The Science of Astrobiology: A Personal Point of View on Learning to Read the Book of Life*. He is also the author of *A Second Genesis: Stepping Stones Towards the Intelligibility of Nature* with World Scientific Publishers.

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# HABITABILITY ON KEPLER WORLDS: ARE MOONS RELEVANT?

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## **1. A New Approach for the Kepler Worlds: An Analogy with Systems Biology**

This chapter is based on an extension of previous work and a book review, where additional information has been provided for the interested reader (Chela-Flores, 2011a, b, 2012a, b). We extend our discussions due to the relevance of the question regarding instrumentation would be suitable for achieving further insights into habitability when we explore satellites from the solar system, especially our Moon (Smith et al., 2012) and Europa (Gowen et al., 2011), as well as planets and satellites of other solar systems.

We are considering the question of possible relevance of not only the exoplanets that are currently being searched in over one hundred thousand stars in our galactic neighbourhood with the Kepler mission (the “Kepler worlds”) but also their eventually detectable satellites on the bases of the insights we have gathered in our own solar system. Astrobiology is a science overlapping the life and physical sciences, but it has surprisingly remained largely disconnected from recent trends in certain branches of both life and physical sciences. We have discussed potential applications to astrobiology of approaches that aim at integration rather than reduction.

Aiming at discovering how systems properties emerge has proved valuable in many fields, including engineering, chemistry and biology. In the case of biology, a good definition of systemics—studying systems from a holistic point of view—considers functional genomics in an attempt to characterize the molecular constituents of life: By discovering how function arises in dynamic interactions, this approach to biology addresses the missing links between molecules and physiology (Bruggeman and Westerhoff, 2006). The systems approach should also yield insights in astrobiology, especially concerning the ongoing search for habitability in alternative abodes for life, although at present we have not been able to document sufficiently this approach. However, taking the set of known exoplanets *as a system* is not only feasible but desirable since new data banks in the case of astrobiology—considering its considerable overlap with the science of biology—are of a geophysical/astronomical kind, rather than the molecular biology data that



is used for questions related, firstly, to genetics in a systems context and, secondly, to biochemistry for solving fundamental problems, such as protein, or proteome folding. By focusing on how systems properties emerge in astrobiology, we raise the question whether habitability can be interpreted as an emergent phenomenon and what role can play exoplanets and exomoons. In the search for potential habitable worlds in our galactic sector with current space missions, extensive data banks of geophysical parameters of exoplanets are rapidly emerging. We suggest that it is timely to consider life in the universe as an emergent phenomenon that can be approached with methods beyond the science of chemical evolution—the backbone of previous research in questions related to the origin of life.

## **2. An Analogy Due to the Difficulties of Habitable Zones for Allowing Evolution of Life**

New approaches to biology such as systems biology still have to make a full impact on all branches of biology. This is especially the case for astrobiology, one of the most recent and exciting branches that have a considerable overlap with the life sciences. Research in astrobiology, especially in the origin of life in the universe, does not focus on systems as a whole (systems biology); rather it pursues the organic chemical approach of attempting to synthesize DNA or protein monomers. An approach analogous to systems biology can take advantage of current technological progress to maintain and enlarge the growing fleet of space missions for the exploration of both our solar system and the cosmos at large and profiting from the broad experience in handling data in both proteomics and genomics.

The related work in complex systems from the point of view of chemistry serves as an additional input to support to the thesis that the systems approach to astrobiology should be explored (Chela-Flores, 2012; 2013). The work of P. W. Anderson implies that in chemistry, as well as in biology, the laws that govern its component parts do not regulate exclusively complex systems. In this case, collective behaviour is relevant (Anderson, 1972). This approach has been amply demonstrated subsequently in questions related, firstly, to genetics in systems biology (Sauer et al., 2007); secondly, for solving fundamental problems that physicists and computer scientists have faced, such as protein folding (Dobson, 2003; Wolynes et al., 1995), or proteome folding (Hartl et al., 2011; Frydman, 2001; Vendruscolo et al., 2011); and thirdly, to chemistry in relation to questions closer to aspects of chemical evolution on the early Earth (Szostak, 2009). The well-established areas where systems biology has succeeded are the regulatory networks and mechanisms, amongst other applications.

The catalogue of known exoplanets is expected to increase rapidly beyond those obtained by astronomical means, such as stellar eclipses, also known as the transit method (Fridlund et al., 2010). Observing a very large number of stars simultaneously where, assuming a random orientation in space, between 0.5 and 10 % of the objects will experience an eclipse of a portion of the stellar surface,

which will cause a temporary drop in the stellar flux (Mayor et al., 2009). Amongst these new worlds there is a considerable number of possible Earth-sized planets, as well as in super-Earths, which are still likely habitable bodies. In the coming years, careful consideration of these putative solar systems will be followed up for definite confirmation.

The data has been retrieved in two stages. Firstly, the French Space Agency (CNES) mission CoRoT (CONvection ROTation and planetary Transits) was launched in 2006 in a Sun-synchronous polar orbit around the Earth (Auvergne et al., 2009). The method used is specifically designed to search for transiting super-Earths (1–2 Earth radii) in short-period orbits (<15–20 days, though larger planetary radii are detectable up to periods of 50 days). Secondly, the NASA Kepler mission was launched with a larger telescope. Kepler can remain focused on the same sector in the sky for years, and its funding allows it to make observations for a period of 3–4 years having the potential to detect small long-period planets.

The star field that Kepler observes is constrained to the constellations Cygnus and Lyra. The production of data is truly astounding: At the time of writing Kepler had identified 2,326 exoplanet candidates of which 207 are approximately Earth size (both Earth-like and super-Earths), 1,181 are Neptune size, 203 are Jupiter size, and the remainders 55 are larger than Jupiter (Borucki et al., 2011b). The earlier Kepler estimate (Borucki et al., 2011a) had identified 5.4 % of stars hosting Earth-size candidates, 6.8 % hosting super-Earth-size candidates, 19.3 % hosting Neptune-size candidates, and 2.55 % hosting Jupiter-size or larger candidates. Multi-planet systems are common: 17 % of the host stars have multi-candidate systems, and 33.9 % of all the planets are in multiple systems.

### 3. The Moon and Its Water Content as a Mirror of the Early Earth

Returning to our solar system the primary scientific importance of the Moon is fundamental, being the closest large body near our habitable planet. On the Moon there is a record that may preserve some signatures of early terrestrial evolution, and of the near-Earth cosmic environment in the first billion years, or so of solar system history (Chela-Flores, 2011b). This record may not be preserved anywhere else (Crawford, 2004). The manned Moon project was abruptly interrupted only 5 years after the initiation of the Apollo Missions. However, an enormous boost to astrobiology was given especially due to the lunar samples from six of the Apollo missions during the 4-year time interval from 1969 till 1972. Altogether the lunar astronauts brought back about 382 kg of lunar rocks. In addition, three Soviet Luna Missions added a valuable 300 g from 1970 till 1976. But as we shall see later, Antarctica has proved to be a source of meteorites, some of which have a lunar origin. From these sources we have a considerable insight that can be described in terms of a lunar surface that is igneous. In other words, the cooling of lava has formed the rocks. By contrast, the most prevalent rocks exposed on the Earth's surface due to the presence of water and wind are "sedimentary".

These include basalts and anorthosites. We know that Moon basalts are in the mare. In the highlands the rocks are mostly anorthosites. Some other rocks in these lunar regions are breccias, namely, fragments produced during collisions in an earlier era and reagglomerated by subsequent impacts. In addition, the Apollo missions returned excellent images, which have been completed with subsequent missions of solar system exploration.

Although the programme of human exploration was cancelled at the beginning of the second decade of the twenty-first century by the USA, other leading nations have not ruled out the objective of sending astronauts to our satellite in the foreseeable future such as China and India. A principal achievement of the American Apollo Program was being the first “sample-return mission”.

Renewed interest in the Moon included the Japan Space Agency JAXA with the 1990 Hiten spacecraft in orbit around the Moon. The spacecraft released a probe into lunar orbit, but the transmitter failed. In September 2007, Japan launched the SELENE spacecraft, with the objectives of obtaining data of the lunar origin and evolution and to develop the technology for the future lunar exploration.

NASA launched the Clementine mission in 1994 and Lunar Prospector in 1998. ESA launched a small lunar orbital probe called SMART 1 in 2003, in order to take imagery of the lunar surface (X-ray and infrared). SMART 1 entered lunar orbit on November 15, 2004, and continued to make observations until September 3, 2006, when it was decided to crash the spacecraft into the lunar surface to retrieve information on the impact plume. More recently, however, a widespread interest in the exploration of our own natural satellite is increasing. The Lunar Reconnaissance Orbiter (LRO, cf., Vondrak et al., 2010) spacecraft has orbited the Moon on a low 50 km polar mapping mission simultaneously with the Lunar Crater Observation and Sensing Satellite (LCROSS), a robotic spacecraft that succeeded in discovering water in the southern lunar crater Cabeus.

LRO is a precursor to future manned missions to the Moon by NASA and other space agencies; for instance, ESA is expected to launch a lander near the Moon’s south pole around 2018. Some new technologies will be tested for future exploration. The difficult terrain of the south pole region is still attractive due to access to solar power and water ice. The aim of ESA’s proposed precursor mission to visit the Moon’s south polar region is to probe the moonscape’s unknowns and test new technology to prepare for future human landings. To these efforts we should add the Chinese and Indian space agencies successes.

#### **4. Habitability on the Kepler Worlds and Their Moons**

Satellites of planets and those of exoplanets have been gradually taking the centre stage in habitability. Our satellite was not the exceptional feature of the planets orbiting around our own star, the Sun. It has been suggested that moons in other

solar systems—exomoons—are observable (Kipping, 2009a, b). This startling possibility has been realized after the discovery of exoplanets. We must rely on close observation of the motion of potential host planets, because moons themselves are too small to see directly. For example, as the Earth orbits the Sun, it exhibits a slight wobble due to the presence of the Moon. But although we cannot see an exomoon directly, we can still see the effect it has on the host planet. If this planet transits across its star, the planet passes in front of it once every orbital period and a dip in the amount of observed starlight takes place. For every transit, the planet's wobble makes the motion appear slightly differently. These differences would be signatures of a moon due to two changes: firstly, a change in the planet's position, and, secondly, a change in planet's velocity (Fossey et al., 2009).

From what we have learnt about the Galilean moons since the appropriately named “Galileo Mission”, it is no longer evident that the habitable zone (HZ), in which planets and their satellites may develop life, need be found in a limited region near the star. In the case of the solar system, the HZ has been taken to lie outside the orbit of Venus (0.7 AU) and beyond the orbit of Mars (1.5 AU). What we have learnt about Europa, one of the four Galilean moons, suggests that moons in principle not only can be habitable in our own solar system, but suites of extrasolar satellites around exoplanets can in principle also be abodes for life.

We should underline that all that is relevant for life to emerge is the presence of exoplanets, not that an exoplanet be near its companion star. Traditionally the only concept that has led to estimating the boundaries of the HZ has been the reasonable distance of the Earth-like planet from its corresponding star. But the search for life on Europa has exposed the startling possibility that habitability may depend on other factors beyond its appropriate distance from its companion star: For instance, even though Jupiter lies outside the HZ 0.7–1.5 AU, we should consider whether the satellites may be close enough to this giant planet. For these large bodies may induce ecosystems around hydrothermal vents that are sources of an adequate inventory of organic elements that may be metabolized by extremophilic-like chemosynthetic microorganisms. Following Kipping and coworkers, we know that a change in a satellite position means that the transit light curve seems to shift about, in what is known as transit time variation, TTV (Sartoretti and Schneider, 1998). The duration of a transit is inversely proportional to the velocity of the planet. So since velocity is changing, then transit duration is changing. This manifests itself with the transit duration variation, TDV.

TTV and TDV always exhibit a 90-degree phase shift, and this essentially gives astronomers a very unique signature to identify exomoons. If you try to use TTV by itself, you will run into the problem that a plethora of different physical phenomenon can cause TTV, not just moons. By using TTV and TDV together, you can finally say, that signal is definitely a moon. Combining the two approaches just described (TTV or TDV) allows the calculation of both the mass of the moon and the orbital distance of the moon. Consequently, though Earth-like planets have not yet been detected, and even though giant planets are not evident environments

that may support life, the new extrasolar planets are already indicators of possible environments favourable to the origin of life. This conclusion follows from the generality of the arguments of the formation of Jovian planets from their corresponding subnebulae. The mechanisms for the formation of satellites suggest that in the star cradles in the Orion nebula, we should have a similar situation. New instruments will be needed that will improve on the current technology.

The state of the art in detecting the reflex motion began by allowing the detection of star motion due to the presence of a Jupiter-like planet. Indeed, the early examples were all Jupiter-like planets. It is remarkable that the planets themselves that have been detected up to the present are the least likely to be habitable. However, these Jupiter-like planets could have Europa-like satellites—exomoons—possibly candidates for harbouring life. This opens the debate as to what are habitable zones, a subject of great interest that we shall not develop in detail here. A habitable zone was understood as one in which the amount of stellar energy reaching a given planet, or satellite, would be conducive to the process of photosynthesis. (Clearly, the amount of greenhouse gases, are relevant too.) Water contributes to the dynamic properties of a terrestrial planet, permitting convection within the planetary crust that might be essential to supporting Earth-like life by creating local chemical disequilibria that provide energy (Schneider et al., 2009). Water absorbs electromagnetic radiation over a broad wavelength range, covering part of the visible and most of the near-IR, and has a very distinctive spectral signature. The search for water at radio wavelengths (1.35 cm) started already in 1999 (Cosmovici et al., 2008). Water was also detected in absorption by the Spitzer IR Space Telescope. Abundant water may be likely on some planets since it was detected around the star HD 189733 b (Tinetti et al., 2007; Swain et al., 2008).

## **5. Data Needed for a Universe as a Complex System with Evolutionary Convergence**

Stars evolve as nuclear reactions convert mass to energy. In fact, stars such as our Sun follow a well-known pathway along a *Hertzsprung–Russell* (HR) diagram. They observed many nearby stars and found that in the plot of their luminosity (i.e. the total energy of visual light radiated by the star per second) and surface temperatures, a certain regularity emerges: The stars lie on the same curve in the HR diagram, whose axes are the two parameters considered by the above-mentioned early-twentieth-century astronomers. Such stars are called *main sequence* stars that lie on a diagonal from the upper left of the HR diagram (represented by bright stars) to the lower right (cool stars). We may ask questions that are relevant for our objective of formulating appropriately our concept that the universe may be considered to be complex system: How do stars move on the HR diagram as hydrogen is burnt, and what does it tell us about stellar ages?

Extensive calculations show that main sequence stars are funnelled into the upper right hand of the HR diagram, where we find red giants of radii that may

be 10–100 times the solar radius. Stellar evolution puts a significant constraint on terrestrial habitability and, in general, on habitability in an exoplanet. For estimating stellar ages, the shapes of the HR diagrams are useful. Stars more massive than about 1.3 solar masses have evolved away from the main sequence at a point just above the position occupied by the Sun. The time required for such a star to exhaust the hydrogen in its core is about 5–6 Ga, and the cluster to which the Sun belongs must be at least as old. More ancient clusters have been identified. In our galaxy, globular clusters are all very ancient objects, with ages measured in Ga. Exact ages, however, cannot yet be assigned to globular clusters. The details of the evolutionary tracks depend on hydrogen–metal ratios, helium–hydrogen ratios and the precise theory of stellar evolution. We may expect that the sector of our galaxy that is being probed in the next few years will yield useful data. This forthcoming information can be fed into our model of a universe as a complex system with evolutionary convergence. The data can arise from:

- Kepler astronomical data (KAD). This parameter is related with the age and size of the stellar host of the exoplanets, especially for Earth-like planets in habitable zones that will emerge from Kepler and subsequent missions when such planets are confirmed, following their preliminary identification (Borucki et al., 2011a).
- Kepler spectroscopic data (KSD) of anomalous fraction of biogenic atmospheric gases. This parameter is measurable, not only in hot exo-Jupiters that have already been detected by precision infrared spectroscopy with the Hubble Space Telescope, HST, but eventually it is also measurable in super-Earths and Earth-like planets (Tinetti et al., 2007; Swain et al., 2008). But eventually we will have some information available on the atmospheres of Earth-like planets in habitable zones. These worlds will begin to emerge from Kepler and in due course from subsequent missions.

These two types of data are intimately related. One aspect of astronomical data concerns the size of the stellar host of exoplanets. This is relevant since stars with mass similar to that of the Sun remain at the red giant stage for a few hundred million years. In the last stages of burning, the star pushes off its outer layers forming a large shell of gas much larger than the star itself (a planetary nebula). The star itself collapses under its own gravity, compressing its matter to a degenerate state. The laws of quantum mechanics eventually stabilize the collapse. This is the stage of stellar evolution called a white dwarf. The stellar evolution of stars more massive than the Sun live a shorter life span than stars in the main sequence of the HR diagram. Possibly such stars are not old enough to bear an evolutionary line that will produce the gradual atmospheric anomalies that will mean the evolution of life on the exoplanet, or the exosatellite. In the case of the Earth, the theory of stellar evolution tells us that the Sun is a middle-aged star. Even though in the first 4–5 Ga of its existence the Earth has been able to evolve in the Sun's HZ and to preserve a biota, the Kepler astronomical data is relevant for understanding solar evolution. The radius of the Sun is bound to increase, as it moves

away from the main sequence on the HR diagram, reducing the habitability of the once-habitable planet.

The Sun's expected radial growth will be such that its photosphere will reach the Earth's orbit. This will eventually alter radically habitability on Earth. Likewise in exoplanets, the spectroscopic data will have to be correlated statistically for early-evolved exoplanets with gradual variations of the atmospheric data.

## **6. Biology Other Than Biochemistry and Genetics Viewed from a Systems Approach**

### **6.1. ASTROBIOLOGY FROM AN ANALOGY WITH THE SYSTEMS APPROACH**

In our theory of life in the universe, we have underlined several stages that are analogous with the standard systems biology, namely,

1. *The theory*: The universe is treated as a complex system with evolutionary convergence, although this is not an intrinsic property of biology, such as heritability; evolutionary convergence is rather a consequence of certain genetic and ecological constraints.
2. *The computational modelling*: Statistical correlations of astronomical data are needed from Kepler and subsequent missions and spectroscopic data from the Hubble Space Telescope and the next generation of space telescopes.
3. *A testable hypothesis*: The Earth-like exoplanets in habitable zones of main sequence stars will yield anomalous fractions of biogenic gases in the spectroscopic analyses of their atmospheres.
4. *Experimental validation*: We need to expand the rapidly growing data banks of exoplanetary searches in the present Kepler and in the future post-Kepler era that will yield sufficient data that is required in our systems astrobiology approach.

In other words, a clear prediction from the present work can be tested in the foreseeable future with feasible instrumentation (to prove or falsify the theory). We have assumed the universe can be treated as a complex system. Space probes continue to gather large amounts of data concerning measurable parameters from their search for exoplanets. Amongst the forthcoming data there will be the identity of the elements present in the exoplanet atmospheres by spectroscopic means.

To plot at least some point in a figure that shows the correlation between KAD and KSD is a type of quantitative information that would strongly support the idea that the life may originate naturally from the composition of the environment. These correlations will be forthcoming in due course. But at the present time, we can begin to illustrate how the data may be handled. As a working hypothesis we have assumed that there will be evolutionary convergence when biology is considered at a cosmic scale. In those planets that are Earth-like and placed within the star's

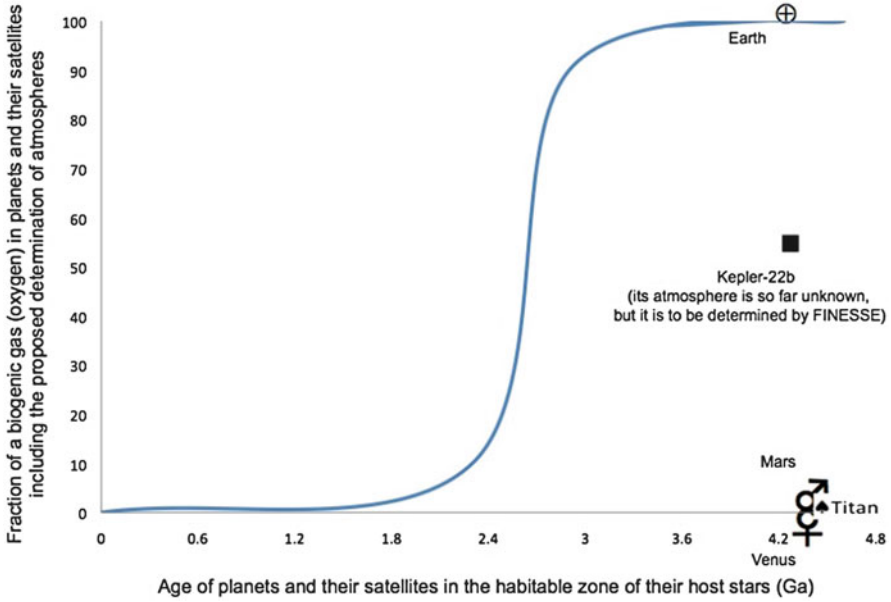


Figure 1. For habitability of planets and satellites: towards an eventual correlation of KAD and KSD.

habitable zone, the evolution of biota will produce atmospheres that will have an anomalously large fraction of biogenic gases, for example, oxygen and methane.

The Kepler Mission data is still gathering in the data banks corresponding to the Earth-like planet candidates that have already been tentatively identified and published (Borucki et al., 2011a). In anticipation to the confirmation of these results, we can illustrate the significance of the hypothesis of the universe as a complex phenomenon by referring to an Earth-like planet that we already know with its host star, namely, our own planetary system. When more reliable results are obtained in the near future with Kepler and its successors, we will know the anomalous fraction of biogenic gases whenever they are present in the list of Earth-like planets in their own HZ.

In due course we will have a series of graphs, one of which is already available and illustrated in Fig. 1. We should take some time to understand what is meant.

6.2. REMARKS ON THE MEANING OF THE HZ OF A G2V STAR

For a sample of planets and satellites in the HZ of a G2V star (cf., the Morgan–Keenan system the stellar spectra), we can return to Fig. 1 in which the atmospheres are known. Even though the satellite with atmosphere that is known to us in our solar system (Titan) lies outside the HZ, it could still be a potential habitable body from internal heat sources triggered by its giant planet.



We have inserted an additional exoplanet in the HZ of its own star, whose atmosphere is to be determined in due course. The abbreviations KAD and KSD denote, respectively, the Kepler astronomical data and the Kepler spectroscopic data. We have suggested plotting the age of the star's confirmed Earth-like planets in its habitable zone (HZ) against the anomalous atmospheric fraction of a biogenic gas (in the present case it is oxygen).

In the familiar case of the G2V planetary system, there are three planets in the star's HZ, but the only appreciable presence of biogenic gas (oxygen) corresponds to the planet at 1 AU from its host star (the Earth). Those at 0.7 AU (Venus) and 1.5 AU (Mars) have a mainly CO<sub>2</sub> atmosphere, 96.5 and 95 %, respectively, with negligible biogenic gases; hence, they were inserted in Fig. 1, where we have chosen oxygen as the most relevant biogenic gas in our solar system. To take into account the vital topic of the satellites of the Kepler worlds, we have inserted the one satellite of our solar system that has a considerable atmosphere, but with negligible biogenic gas. The abundant biogenic gas in the planet at 1 AU (Earth) is oxygen. But in other stars the exoplanets in their HZ, such as Kepler-22b (an exoplanet whose age is undetermined, orbiting a G5 dwarf star in the same class as the Sun, cf., Borucki et al., 2012), could have an anomalous fraction of any of the biogenic gases. Since the time of the origin of the Earth, we have the benefit of knowing even the evolution of the anomalous biogenic gas (oxygen).

For drawing the curve we have assumed that the large increase in oxidation of the atmosphere occurred at 2.45 Ga after the planet's origin (Kump, 2008). By focusing on Sun-like stars of similar age and class in the main sequence of the HR diagram, the data banks will begin to provide evidence for life. For younger stars this illustration (and the corresponding data banks) will not exclude transient episodes of life-bearing exoplanets in their HZ, as may have been the case of Mars at an earlier epoch (Formisano et al., 2004). We have used the standard astronomical symbols for the planets of the solar system. The black square represents a typical exoplanet in its HZ. We have taken Kepler-22b, whose atmosphere, including any biogenic gas, will be determined in due course by NASA's FINESSE.

Later on the anomalous fractions of biogenic gas in other Earth-like planet atmospheres (oxygen, methane) will be available for a number of star planetary systems that are within the scope of Kepler, namely, over one hundred thousand stars a sample that we have called KAD. The forthcoming results will contain a subset of Earth-like planets, whose KSD will also be available in the near future with the remarkable present pace of progress in instrumentation. The proportion of anomalous biogenic gas (oxygen) by volume in the atmosphere in the single case of Fig. 1 is some 21 %.

Earlier estimates of biogenic gas in other planets—methane—were attempted with the help of the Hubble Space Telescope for a Jupiter-like planet. For other Earth-like planets, such as the recently confirmed Kepler-22b, the identification of chemical elements in their atmospheres is still a challenge being faced by the Kepler team. But for a Jovian-like planet HD 189733b (Swain et al., 2008), methane was

tentatively identified. Subsequent research, based at the Keck Telescope, has not confirmed this result (Mandell et al., 2011). The confirmation of the preliminary Kepler data of Earth-like planets (KAD) will allow the next step in building of the data banks for the anomalous biogenic gases. In other words, the KSD data could grow into substantial data banks if the present tendency is confirmed (Sect. 2): 5–6 % of the preliminary sample of exoplanets are Earth-like. In turn, this implies that some of these will lie in the host star's zone of habitability.

## 7. Life's Fingerprints in the Atmospheric Gases of the Kepler Worlds

Our work is part of a larger body of papers that have discussed biogenic gases as signatures for life. Not only has this topic been advanced in the past, but a new mission is under consideration by NASA (JPL)—FINESSE (Fast INfrared Exoplanet Spectroscopy Survey Explorer)—that would measure the spectra of stars and their planets in two alternative situations that would correspond, firstly, to the spectra of both the star and their exoplanets when both are visible, and, secondly, when the exoplanet is hidden by its star (Swain, 2010). This will allow FINESSE to analyse the planetary atmospheric components (to provide the data that is missing in graphs such as the preliminary one shown in Fig. 1). Indeed, this JPL proposal would use a space telescope to survey more than 200 planets around other stars. This would be the first mission dedicated to finding out the fraction of biogenic gases in exoplanet atmospheres and how the solar system fits into the family of planets in the galactic neighbourhood being explored by the Kepler mission.

But returning to recent efforts in the discussion of biogenic indicators of the origin and evolution of life in exoplanets in the context of this chapter, it is worth highlighting:

1. The development of better models has been suggested for the Earth's early atmosphere, including the presence of biosignatures like oxygen ( $O_2$ ), water ( $H_2O$ ), ozone ( $O_3$ ), methane ( $CH_4$ ), methyl chloride ( $CH_3Cl$ ) and nitrous oxide ( $N_2O$ ), in order to be able to select between geophysically produced atmospheres and those that have received an input from biosystems (Kiang, 2008; Darling, 2001).
2. In addition to atmospheric biogenic gases such as oxygen, another gas bio-signature scientists have already considered is the surface reflectance spectra of vegetation, or the amount of light reflected off plant matter at different wavelengths (Kiang et al., 2007). This work is based on an extension to Earth-like planets in their star's HZ of the events that led to the emergence of oxygenic photosynthesis on Earth (Wolstencroft and Raven, 2002).

We are at an early stage, but in an inexorable route towards the first verification of life elsewhere, microbial or multicellular, either in our own solar system (microbial), as emphasized repeatedly in our earlier research focused on

the outer solar system (Chela-Flores and Kumar, 2008; Chela-Flores, 2010), or (microbial, or multicellular) in other solar systems (Kiang, 2008; Schneider et al., 2009, 2010).

As we have discussed above, the large number of exoplanets being discovered will probably be followed up by a suite of exomoons (cf., Sect. 5). From the hints that have been granted to us by the habitability potential of the Jovian Moon Europa in our planetary neighbourhood (Chela-Flores and Kumar, 2008), the range of habitability will be much enhanced.

The implications for the distribution of life can be searched in the potentially habitable planets—Earth-like and placed within the star's habitable zone (HZ). The hypothesis leads to a prediction for a radical change from the atmospheric fractions compared to companion planets (super-Earths and Jovian-like and other planets) in the same stellar planetary systems being explored by the space probes (Kepler and successors, HST and its successors and by the HARPS spectrograph).

We are at the very beginning of this search. Earth-like planets in habitable zones of their stars only begin to be known with certainty. At the time of writing, Kepler-22b that is 600 light years away and is 2.4 times the Earth's radius becomes the first in a list of 207 approximately Earth-sized planets to have been confirmed, with a subset of 48 actually lying in the HZ of their corresponding stars (Borucki et al., 2011b).

Life in the universe will emerge from statistical analysis of large data banks that are now beginning to accumulate. Our combined assumptions of convergence and the cosmos as a complex system imply that all the Earth-like exoplanets that will be in the HZ of their corresponding star will have an identifiable bioindicator (anomalous production of biogenic gases). The signs of life are predicted to be a biologically produced atmosphere, largely fractionated towards one of the biogenic gases (in the case of the Earth, the large fractionation triggered by biosystems is the 21 % of oxygen). Such atmospheres would not be the result of natural accretion processes in the processes that give origin to the planets, but instead, the emergence of the biogenic atmospheres would be the result of the innate phenomenon of life that the laws of biochemistry will allow in brief geologic times.

Systems astrobiology is analogous to systems biology, but it has to wait for its full implementation until after we have gathered enough data from the sector of our galaxy that is being probed by the CoRoT, Kepler and subsequent searches. The practical reason why systems biology is a promising frontier for the future of astrobiology is that it is not easy to have access to information on these planets, except through the now incipient data banks of observable geophysical data, such as methane and oxygen atmospheres, as well as information on the presence of liquid water beyond the present data that has already been searched for (Seager and Deming, 2010; Tinetti et al., 2007; Cosmovici et al., 2008).

The search for exoplanets can be viewed as the first step in an eventual discovery of life as a complex cosmic system. Following the lines outlined above, we expect that a rationalization of life will eventually emerge from the data banks of a very large number of stars in our galactic sector. The geophysical data, rather

than data banks of biological information, will provide a gradual emergence of the living phenomenon. The geophysical (atmospheric) bioindicators point towards ecosystems that have evolved around stars producing measurable biomarkers in our galactic sector. Subsequently, with better missions and with improved instrumentation, this identification of life as a complex system can be extended from a sector of the galaxy now being probed to other more distant parts of the universe.

To sum up, we have suggested that one evident advantage of viewing the cosmos as a complex system (and life as an emergent phenomenon) is to anticipate, organize and interpret the data that is provided by Kepler, as well as the data that is to come in the post-Kepler/FINESSE era. We have described how the hypothesis of life as a complex system will lead to relevant insights into the whole cosmic system (life and its intimate relation with matter).

## 8. Retrieving Insights into Habitability from the Lunar Surface

Increasing experience that is being provided by the penetrator technology will become gradually a more compelling instrument that will prove its worth as a complement to human exploration of the Moon. The solar wind (SW) is a set of particle expelled from the Sun isotropically at supersonic speeds (several hundred km/s close to the Earth). The SW has irradiated the lunar regolith for over 4 Ga. But more significant still is the fact that an indication of isotopic fractionation of the light biogenic elements on the Moon was already evident from analyses of the lunar samples retrieved by the Apollo and Luna Programme sample-return missions. This geochemical phenomenon is illustrated by the  $^{34}\text{S}/^{32}\text{S}$  rates, and the isotopic fractionation in lunar soils is further evidenced in terms of the  $^{13}\text{C}/^{12}\text{C}$  rates. Data from the Apollo 11 lunar bulk fines, breccias and fine-grained basalts excluded biogenic origin, but demonstrated that S and C isotopic fractionation had occurred due to SW impinging on the lunar soils (Kaplan, 1975).

Additional and significant progress in our knowledge of the Moon and the rest of the solar system will depend on the adoption of new space technologies. One particularly relevant example is the kinetic micro-penetrator technology. The UK Lunar Penetrator Consortium is preparing to demonstrate the penetrator versatility with the potential identification of biomarkers robotically. Two possibilities are being followed up: an eventual return to the Moon (Smith et al., 2012) and the exploration of the Jovian Moon Europa (Gowen et al., 2011). We have argued that support would not only be economically more feasible with penetrators, but that the reward of increasing our data of the lunar regolith and its paleoregolith is full of promising astrobiological returns that are no longer accessible on terrestrial locations.

We have argued that significant relevant data for astrobiology may remain accessible on the Moon soils, due to the total lack of lunar erosion or plate tectonics. Since the predictions that Earth wind (EW) may have implanted relics

of the earliest terrestrial atmosphere exclusively on the nearside of the Moon, the case for returning to the farside of our natural satellite with penetrator technology is compelling. In other words, EW is a set of interplanetary particles that impinge on solar system bodies (including the Moon), whose origin is the Earth, in contrast to SW. The chief motivation for the renewed lunar exploration from what we have discussed above is to ascertain that no traces of EW were ever implanted on the Moon's farside. This task of exploring the lunar surface is feasible by the emplacement of kinetic micro-penetrators bearing a suite of instruments. These would include miniaturized mass spectrometers and miniaturized mass analysers.

These instruments are already available for in situ elemental analysis of a variety of solar system bodies in the next generation of planetary missions (Rohner et al., 2004; Tulej et al., 2011). The exciting forthcoming new age of space exploration is expected to probe the S patches on Europa's icy surface, in analogy with terrestrial S patches (Chela-Flores, 2006, 2010; Gleeson et al., 2010; Gowen et al., 2011). Secondly, as we have argued persistently in this chapter, the next generation of space exploration (Smith et al., 2012) should give a high priority to characterizing the geochemistry of Moon soils, especially the N abundances on the lunar farside, which should have remarkable implications on overlapping areas of the early Earth geophysics and the science of astrobiology.

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# CLEAN IN SITU SUBSURFACE EXPLORATION OF ICY ENVIRONMENTS IN THE SOLAR SYSTEM

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## 1. Introduction

A key aspect for understanding the astrobiological potential of the icy environments in the Solar System is the scientific analysis of material embedded in or underneath the surface ice layers. The icy environments that are considered to have the highest potential to harbor life are the polar caps of Mars, the icy crust of Jupiter's moon Europa (with a putative water<sup>1</sup> ocean below), and the icy crust of Saturn's moon Enceladus (also with putative reservoirs of water or even a global ocean below). Although the subsurface environments of those bodies are scientifically extremely interesting, they are also extremely difficult to access. From the astrobiological perspective, Europa is probably the most interesting target, but access to subsurface material might be easier on Enceladus. Subsurface material from Mars' polar caps is even easier to access, and therefore, Mars might be the best choice for a first extraterrestrial subsurface ice exploration mission. Self-steering robotic ice melting probes are considered to be the best method to cleanly access those environments, in compliance with planetary protection standards. Before such a space mission can be undertaken, however, the required technology must be tested at analogue terrestrial environments, for example, in Antarctica. This chapter focuses on the technology that is required for the clean in situ subsurface exploration of the potentially habitable icy environments in the Solar System.

Section 2 gives a brief overview of these environments and their potential to harbor life, as well as Antarctica as a terrestrial analogue. Section 3 then describes why ice drilling cannot be considered as the best method for clean subsurface ice access on other celestial bodies; ice melting probes are much better suited for such missions. Before the melting probes that have been developed in the past by various research institutions are introduced in Sect. 5, together with their achievements, the thermophysical fundamentals that are required to understand their operations

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<sup>1</sup>In this chapter, we will use the term “water” also for salt water or brine.

are briefly covered in Sect. 4. Section 6 then discusses the main technological issues and challenges for ice melting probes. Afterwards, Sect. 7 describes the “IceMole,” a novel self-steerable probe that is currently developed and tested under the direction of one of the authors at FH Aachen University of Applied Sciences.<sup>2</sup> The main points of this chapter are finally summarized in Sect. 8.

## 2. Potentially Habitable Icy Environments in the Solar System

Because life can thrive in the icy environments on Earth (Bidle et al., 2007; D’Elia et al., 2008; Deming and Eicken, 2007; Karl et al., 1999; Price, 2000; Priscu and Christner, 2004; Priscu et al., 1999), it is now widely discussed that extraterrestrial life may also exist in environmental niches in the ice or in aquatic environments below the ice of other Solar System bodies. The ones which are considered to have the highest potential to harbor life are Mars (Jakosky et al., 2007; Tokano, 2005), Europa (Chyba and Phillips, 2007; Greenberg, 2005; Pappalardo et al., 2009), and Enceladus (Parkinson et al., 2007; Postberg et al., 2011).

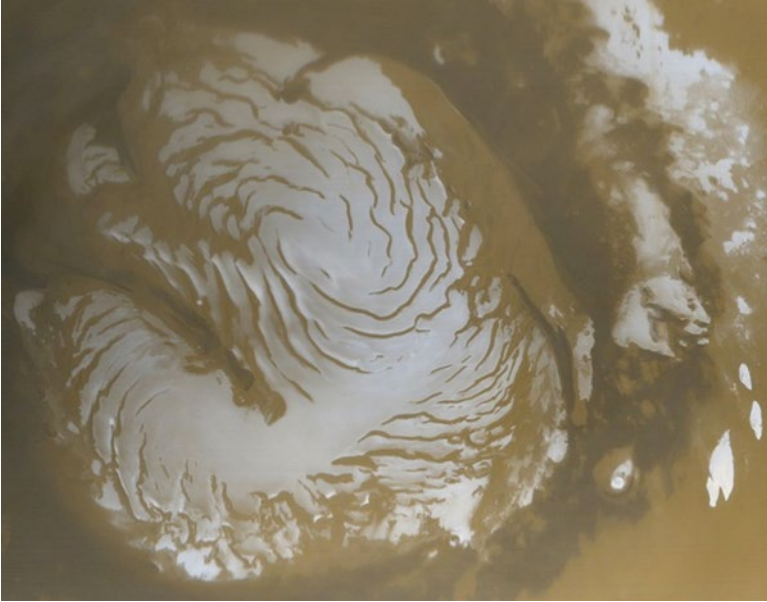
### 2.1. THE POLAR ICE CAPS OF MARS

Being already visible through an ordinary telescope, Mars’ polar ice caps have been observed already in 1666 by the French astronomer and mathematician Giovanni Domenico Cassini (more recent images of Mars’ northern and its smaller southern polar ice cap are shown in Figs. 1 and 2, respectively, as observed by NASA’s Mars Global Surveyor (MGS) spacecraft). The question, whether or not the Martian polar caps are made of water ice, remained unanswered until the dawn of the space age. During its 1965 flyby, Mariner 4 was the first spacecraft to transmit 22 images of the Martian surface back to Earth. More images were obtained by the following flybys of other spacecraft, and the first compositional data of the Martian soil were transmitted to Earth by the two Viking landers in 1976.

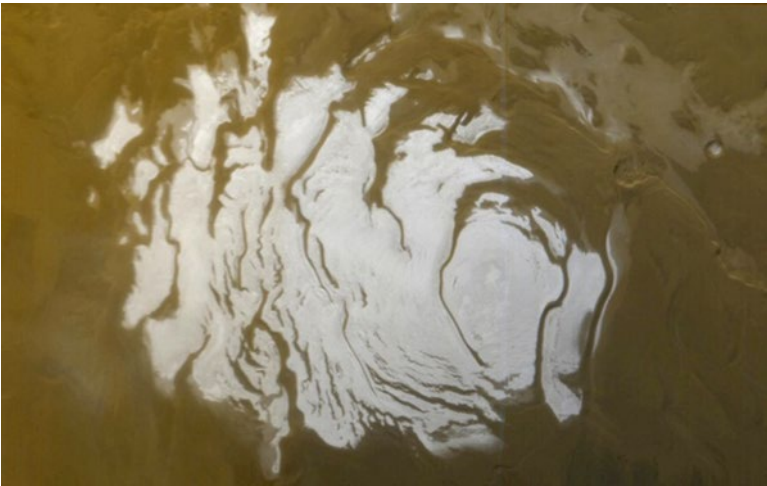
Although both landers were equipped with instruments for the detection of microbial life in the Martian soil, no clear evidence for extant or extinct life was found (Ballou et al., 1978). The most interesting places on Mars, however, where microbial life-forms could still exist, have not yet been explored. These places should contain water and shelter microorganisms from the harsh Martian surface environment. The average temperature on the surface is  $\approx -60$  °C, with a maximum temperature of  $\approx +20$  °C at the equator during summer and a minimum temperature

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<sup>2</sup>The reader may forgive this bias, but the IceMole solves many of the discussed challenges in a unique and seminal way, and reliable information about the current development status of other ice melting probes is difficult to obtain.



**Figure 1.** Mars north polar ice cap, as imaged by MGS in 1999 (Image credit: NASA/JPL/MSSS).



**Figure 2.** Mars south polar ice cap, as imaged by MGS in 2000 (Image credit: NASA/JPL/MSSS).

of  $\approx -140$  °C at the poles in winter. The Martian atmosphere is rather thin, with a surface level pressure of  $\approx 6$  mbar, and is mainly composed of  $\text{CO}_2$ .

Today, no liquid water can be found on the surface, but the existence of old outflow channels and canyons points to the existence of surface water in the

**Table 1.** Europa's and Enceladus' physical and orbital properties.

Parameter	Europa	Enceladus
Radius (km)	1,561	252
Mass (kg)	$4.80 \times 10^{22}$	$1.08 \times 10^{20}$
Equatorial surface gravity (m/s <sup>2</sup> )	1.314	0.114
Mean density (g/cm <sup>3</sup> )	3.01	1.61
Escape velocity (km/s)	2.025	0.239
Surface temperature (K)	$102^{+23}_{-52}$	$75^{+70}_{-42}$
Semi-major axis (km)	670,900	237,948
Orbital period (d)	3.5512	1.3702
Eccentricity	0.009	0.0047
Inclination w.r.t. planet's equator (°)	0.470	0.019

Data from NASA's National Space Science Data Center, (<http://nssdc.gsfc.nasa.gov/>).

geological history of the planet. If life has ever been present on Mars, it is possible that it still exists in environmental niches, sheltered from the surface UV radiation beneath rocks, inside the Martian soil, or inside the polar ice caps, where large amounts of H<sub>2</sub>O are present. The polar ice caps cover an area of  $\approx 10^6$  km<sup>2</sup>, with a thickness of as much as 3–4 km (Clifford et al., 2000); the northern ice cap alone contains several million cubic kilometers of water ice. With a supposed age of  $\approx 10^5$ – $10^7$  years (Fishbaugh and Head, 2001), these layered ice deposits appear to be surprisingly young. Nevertheless, they contain a record of the seasonal and climatic cycling of atmospheric CO<sub>2</sub>, H<sub>2</sub>O, and dust over this period. Therefore, the polar ice caps of Mars are a prime target for in situ subsurface exploration.

## 2.2. THE ICY MOONS OF JUPITER AND SATURN

Both gas giant planets in our Solar System possess an icy moon that is extremely interesting from an astrobiological perspective, Jupiter's moon Europa and Saturn's moon Enceladus. Table 1 lists their main physical and orbital properties.

### 2.2.1. Europa

From an exobiological point of view, Europa is one of the most fascinating bodies in the Solar System. Europa is nearly the size of Earth's Moon. The images provided by the Galileo probe have revealed a surface that shows almost no craters and is covered by a very young layer of water ice. The surface structures indicate geologically recent movements of the ice crust and allow speculations about a global subsurface ocean (Greenberg and Geissler, 2002) whose volume is about twice that of Earth's oceans (Chyba and Phillips, 2007). The surface temperature of Europa is  $\approx 100$  K. Tidal flexing due to Jupiter's gravity, being sustained by an orbital resonance (Laplace resonance) with Io and Ganymede, results in significant heat dissipation within Europa (Chyba and Phillips, 2007), which explains the

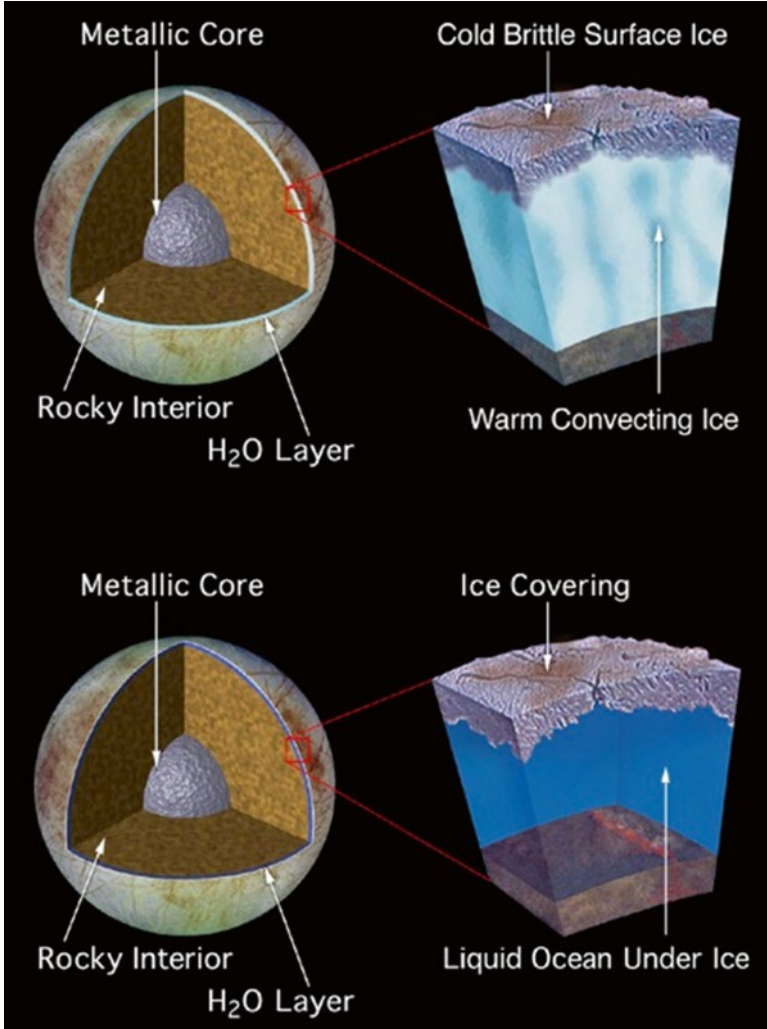


Figure 3. Two possible scenarios for Europa’s internal structure (Image credit: NASA/JPL).

presence of a (probable, but not proven) liquid ocean. There is no generally accepted model for the thickness of the ice crust available yet. Values vary between >50 km and only a few kilometers (Cassen et al., 1979; Ojakangas and Stevenson, 1989; Ross and Schubert, 1987; Squyres et al., 1983). In addition, a model that explains Europa’s surface and magnetic field features with an underlying sheath of viscous icy material (and no liquid water at all) was proposed by Pappalardo et al. (1998). Figure 3 shows two possible scenarios of the internal structure of Europa. The most widely accepted model of the interior of Europa assumes a liquid ocean,

warmed up by the heat from tidal flexing. The idea to find on the bottom of this ocean an environment that is comparable to the “black smoker” environment at the bottom of the terrestrial oceans can be seriously considered. Of course, this is a speculative, but fascinating, idea. The ability to support life, however, does not guarantee its origin or its presence. Answering these questions will require further exploration. An intrinsic problem of the exploration of Europa’s ice crust and its putative ocean is the penetration of the ice with a device suitable for a planetary exploration mission. Drill rigs appear far too heavy and complex to be implemented into currently considered lander missions to the Jovian system.

An ice melting probe, powered with radioisotope heater units (RHUs), seems to be a relatively low-cost, low-mass option to reveal some of the information that is hidden underneath the thick ice layers (Di Pippo et al., 1999; Ulamec et al., 2005). For a simple short-range melting probe, a Li-ion battery may be sufficient to reach a depth of several meters (Biele et al., 2011). Even if the average thickness of Europa’s ice crust may be high, and thus, the liquid water difficult to reach, there may be areas where the ice is much thinner, for example, at the ridges, where fresh water is thought to be upwelling when the plates open, or in the chaotic terrains, where melt-through may occur (Greenberg, 2005; Greenberg et al., 1999; O’Brien et al., 2000). In such areas, melting through the thin ice may be possible within an acceptable time frame. At the same time, rather fresh material from the global ocean might be found at or close to the surface at these places. Once a melting probe is below the top surface layers ( $\approx 10\text{--}40$  m), which are penetrated by Jupiter’s destructive ionizing radiation, frozen ocean material might be sampled without actually accessing open water.

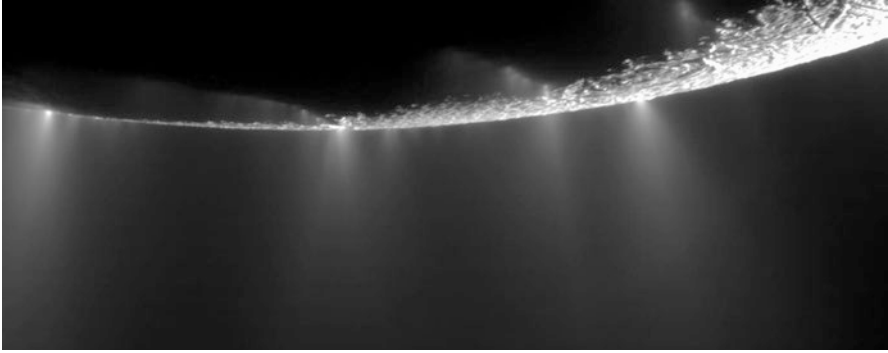
### 2.2.2. *Enceladus*

Enceladus is much smaller than Europa, only  $\approx 500$  km in diameter. Once believed too small to be active, Enceladus has been found to be one of the most geologically dynamic objects in the Solar System (Kargel, 2006). Calculated from Enceladus’ measured mass and density, models assume a rock core with a radius of  $\approx 169$  km (density  $3\text{ g/cm}^3$ ) and a volatile crust with a thickness of  $\approx 83$  km (density  $1.01\text{ g/cm}^3$ ) (Kargel, 2006).

Despite its small size, it has a wide range of terrains, including old and young surfaces. The high albedo of Enceladus results in a colder surface than most of the other Saturnian satellites, with a calculated subsolar<sup>3</sup> temperature of  $75 \pm 3$  K and an average temperature of  $\approx 51$  K (Cruikshank et al., 2005). The spectrum of Enceladus shows that its surface is almost completely dominated by  $\text{H}_2\text{O}$  ice, with small amounts of  $\text{NH}_3$  and a tholin (Hendrix et al., 2010), except near its south pole. At the south pole, the Cassini spacecraft has identified a geologically active province, circumscribed by a chain of folded ridges and troughs (Porco et al., 2006). The terrain southward of this boundary is distinguished by

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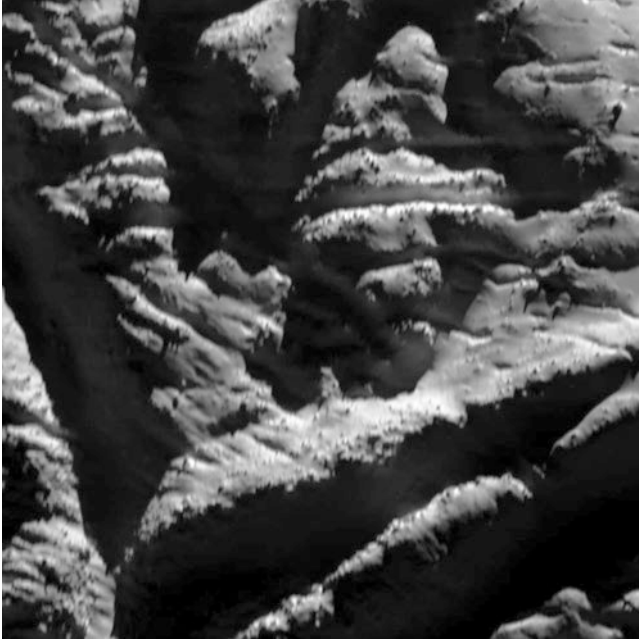
<sup>3</sup>where the Sun is at zenith.



**Figure 4.** Plumes spray water ice out from many locations along the “tiger stripes” near the south pole of Enceladus (Image credit: NASA/JPL/Space Science Institute).

its albedo and color contrasts, elevated temperatures, extreme geologic youth (possibly as young as  $5 \times 10^5$  years), and narrow tectonic rifts that coincide with the hottest temperatures (145 K and more) measured in the region (Porco et al., 2006; Spencer et al., 2006). Much ongoing research deals with the origin and explanation of this puzzling thermal “anomaly” (Abramov and Spencer, 2009; Ingersoll and Pankine, 2010; Tobie et al., 2008). The most prominent features at the south pole are four linear depressions, dubbed “tiger stripes” because of their appearance in the infrared. Particularly in this region, simple organic compounds and  $\text{CO}_2$  are found (not as free  $\text{CO}_2$  ice, but rather complexed, probably with water ice). This high abundance of complexed  $\text{CO}_2$  suggests active replenishment, probably from ongoing geophysical activity (Brown et al., 2006). Multiple flybys of Cassini at Enceladus have shown that plumes of  $\text{H}_2\text{O}$ , including simple organic compounds (Waite et al., 2009), emanate via cryovolcanism from those “warm” fractures at the tiger stripes (Fig. 4). Salt-rich ice particles are found to dominate the total mass flux of ejected solids (more than 99 %) (Postberg et al., 2011). Analysis of the plume material strongly implies that it originates from a body of liquid salt water (Postberg et al., 2011) or even a global ocean (Patthoff and Kattenhorn, 2011) below its icy crust. The unique chemistry found in the plume has fueled speculations that Enceladus may harbor life (McKay et al., 2008; Parkinson et al., 2007), but this question can probably not be resolved by the Cassini mission. A lander mission that is equipped with a subsurface ice melting probe, however, might be able to answer this question. Because it is considered too risky to land close to the cracks from which the plumes emanate (see Fig. 5), a lander would have to land at a safe distance away from a crack and melt its way to the inner wall of a crack to analyze the plume material in situ. This way, subsurface liquids may be much easier to access than on Europa. Nevertheless, such a mission is still considered very challenging, given the current state of the art in space technology.





**Figure 5.** Rough terrain at Enceladus' south pole with boulders resting along the tops of high frozen ridges (edited from the original raw image to enhance detail) (Image credits: NASA/JPL/Space Science Institute, Universe Today).

### 2.3. OTHER ICY ENVIRONMENTS IN THE SOLAR SYSTEM

There are, of course, other very interesting icy bodies in the Solar System, where subsurface in situ exploration can be considered. Besides technical feasibility, the priority and order of their exploration, however, should follow their expected potential to harbor life.

Therefore, they have currently not the highest exploration priority and no midterm missions are defined, where such investigations could be performed. When life cannot be found on Mars, or Europa, or Enceladus, the prospects to find it on or in any other body in the Solar System grow dim. Nevertheless, their subsurface exploration would yield chemical and mineralogical data that would advance our understanding of the origin and evolution of those bodies as well as the Solar System as a whole. Among the other targets for subsurface exploration is Jupiter's moon Ganymede. Ganymede (as well as Jupiter's moon Callisto) might also have a subglacial ocean (Spohn and Schubert, 2003), but it would be covered by a much thicker ice layer. Titan, Saturn's largest moon with a dense atmosphere, does also have an icy surface with a high content of hydrocarbons.

The spectacular results after the entry and landing of the Huygens probe (Lebreton et al., 2005; Zarnecki et al., 2005) indicate that penetrating the surface, which may be a crust on liquid ethane/methane, by melting, could well be appropriate. Looking even further out into the Solar System, one may ponder on missions to Neptune's moon Triton, to Kuiper belt objects, and to the numerous small ice bodies like comets and the small icy satellites.

#### 2.4. ANTARCTICA, A HABITABLE ICY ENVIRONMENT AND A POTENTIAL EARTH ANALOGUE FOR EXTRATERRESTRIAL ICY ENVIRONMENTS

Deep underneath the Antarctic ice sheet, there are tremendous concealed lakes of water kept in the liquid state by the enormous pressure of the overlaying ice on the one hand and the continuous heat flux from the Earth's interior on the other hand. These lakes have been isolated from the atmosphere for up to millions of years (Lorenz et al., 2011; Priscu et al., 1999). Until today, more than 140 of such lakes have been detected (Siegert, 2000; Siegert et al., 2005). The lakes are of enormous scientific interest as a potential and unique habitat for life that has evolved in such secluded environments, whose conditions are considered to be similar to the conditions that may exist in extraterrestrial cases (Lorenz et al., 2011; Marion et al., 2002). There are many physical, chemical, and biological properties of ice that have a bearing on their suitability as icy moon analogues. The relationship between surface chemistry and subsurface brine composition, for example, on Europa (and Enceladus), is best studied with perennial ice-covered saline lakes in Antarctica such as Lake Vanda, Lake Bonney, and Lake Vida (Marion et al., 2002; Matsumoto, 1993). The largest and one of the most interesting lakes is Lake Vostok, lying  $\approx 4$  km below the surface of the central Antarctic ice sheet. It is 250 km long and up to 50 km wide. As a result of the special and isolated environment of the lake, it can be expected that life-forms have developed in an unprecedented way (Siegert et al., 2001). Because of this particularity, any investigation of the lake needs to guarantee minimum contamination with both bacterial life from the surface and any potentially toxic material. Thus, conventional drilling appears problematic. For its clean investigation, it would be necessary to use methods that satisfy the strict requirements of planetary protection, as applied, for example, for the exploration of Mars, and foreseen for any future mission to the icy moons (see Sect. 2.5) by the Committee on Planetary Protection Standards for Icy Bodies in the Outer Solar System (2012). A sterilized melting probe would be an adequate solution for the clean in situ investigation of Antarctica's subglacial lakes with minimal risk of contamination. Another good analogue to test the technology that is required to access material from deep inside Enceladus fractures is the Blood Falls in the McMurdo Dry Valleys, Antarctica, an outflow of a subglacial brine pool of unknown depth, trapped  $\approx 400$  m underneath the glacier, that provides unique access to a subglacial ecosystem (Mikucki et al., 2009; Mikucki and Priscu, 2007).

## 2.5. PLANETARY PROTECTION ASPECTS

An important aspect of space exploration is the prevention of human-caused biological cross contamination between Earth and other Solar System bodies. A growing awareness about the possible “infection” of other places in the Solar System by so-called “hitchhiker” bacteria from Earth found its expression in many discussions among the scientific community. These hitchhiker bacteria could colonize on a spacecraft and its equipment, leading to a contamination of an extraterrestrial environment.

Such a scenario could cause irreversible and dramatic changes to such alien environments. Furthermore, these alterations could also interfere with scientific exploration and consequently could spoil the measured data. Consequently, the design of all missions to other potentially habitable bodies of the Solar System has to consider this aspect of planetary protection. The measures for planetary protection are defined by international law, based on the outer space treaty of 1967 (Rummel, 2001; Rummel et al., 2002). Techniques applied for the sterilization of spacecraft (Engelhardt, 2006) could well be applied for a melting probe that is designed for the clean exploration of Antarctic aquatic environments. For any lander mission to Mars, Europa, or Enceladus, sterilization is obligatory.

### 3. Suitability of Drilling for Clean In Situ Subsurface Ice Exploration

With respect to ice melting, ice drilling has the clear advantage of a much higher energy efficiency (0.5–5 kJ/kg instead of >334 kJ/kg) (Ulamec et al., 2005). Ice drilling methods can be classified into coring drills (e.g., rotary drills, wireline drills, electromechanical drills, and electrothermal drills) and “hole-only” drills (e.g., hot water drills, steam drills, and coiled tubing drills) (Bentley et al., 2009). Sometimes, ice melting probes are also classified as drills, but we will not follow this classification here. An extensive treatment of ice drilling and coring is given in Bentley et al. (2009) and NSF’s Long Range Drilling Technology Plan (2011), and of extraterrestrial drilling – however, not into deep ice – in Zacny et al. (2009). Ice core drilling is the most mature technology to access subsurface ice environments on Earth. It maximizes the recovery of ice samples and allows the application of sophisticated geophysical and geochemical logging methods at the surface, which allow a high temporal resolution of the ice core. What is still needed, however, is a reliable lightweight portable drill system capable of reaching from several hundreds to a thousand meters (Bentley et al., 2009). Also, large quantities of drilling fluids are required to keep the hole open. Those fluids are based on hydrocarbons and hydrochlorouorocarbons (Bentley et al., 2009). They are not inert and do therefore not allow clean access according to planetary protection standards. For ice drilling in the  $\approx$ 1-km range, relatively small hot water drilling (HWD) devices can be used (Engelhardt et al., 1990). Because HWD also results in a relatively low contamination, a potential ice melting probe application on Earth needs to be

carefully compared with HWD technology for any advantages and disadvantages. HWD is very fast (drill rates in the order of tens of m/h are possible), but the energy expended for reheating the water (typically to  $\approx 80\text{--}90\text{ }^\circ\text{C}$ ) is considerable (in the order of MW). Because of their high power demand, a typical several-kW ice melting probe will have very clear advantages for extraterrestrial applications (also, there is no obvious solution for how to use HWD under vacuum conditions). The major disadvantages of all drilling methods for extraterrestrial applications are as follows: (1) the mass and the power requirements of the equipment are currently not compatible with the mass and power constraints for missions into the outer Solar System; (2) drills are not steerable – they can only penetrate vertically downwards; (3) they can therefore not bypass rock inclusions that might exist in the ice; and (4) for deep drilling, their required operational effort on the surface excludes probably their application on robotic missions. Ice melting probes, which will be discussed in the remainder of this chapter, are considered to be a much better method for the clean in situ exploration of icy environments in the Solar System.

#### 4. Thermophysical Fundamentals for Ice Melting Probes

The typical shape of an ice melting probe is that of a cylinder with length  $L$  and diameter  $D=2R$ . In a simple energy balance approximation that neglects all losses, the heat needed to progress a distance  $\ell$  in compact ice via melting is

$$Q = A\ell\rho(c_p\Delta T + \Delta H) \quad (1)$$

where  $A = \pi R^2$  is the probe's cross section,  $\rho$  is the ice density, and  $c_p$  is the specific heat capacity of ice. Above the triple point, the phase change of the ice is from solid to liquid (melting) and the phase change enthalpy  $\Delta H$  (i.e., the specific energy (in J/kg) needed for the phase change, also termed latent heat) is the enthalpy of fusion,  $\Delta H_f = 334\text{ kJ/kg}$  for  $\text{H}_2\text{O}$  at  $0\text{ }^\circ\text{C}$ . Below the triple point, the phase change of the ice is from solid to gaseous (sublimation) and  $\Delta H$  is the enthalpy of sublimation,  $\Delta H_s = 2,836\text{ kJ/kg}$  for  $\text{H}_2\text{O}$  at  $0\text{ }^\circ\text{C}$ , which is more than eight times larger than  $\Delta H_f$ .  $\Delta T = T_{pc} - T$  is the difference between the phase change temperature  $T_{pc}$  of ice and the local ice temperature  $T$  (the phase change temperature is the melting temperature,  $T_m$ , or the sublimation temperature,  $T_s$ , respectively). Because the triple point of  $\text{H}_2\text{O}$  is at a temperature of  $273.16\text{ K}$  ( $0.01\text{ }^\circ\text{C}$ ) and a pressure of  $6.1173\text{ mbar}$ , the operating mode of melting probes under vacuum conditions is sublimation, unless the closing of the hole (by refreezing or covering) raises the pressure in the hole above the triple point pressure, which happens quite rapidly (Treffer et al., 2006). Therefore, only melting is considered from now on. If the heating power is  $P$ , then the penetration velocity  $v$  for melting is

$$v = \frac{P\ell}{Q} = \frac{P}{A\rho(c_p\Delta T + \Delta H)} \quad (2)$$

Note that the penetration velocity scales inversely with the probe's cross-sectional area and is independent of the probe's length. This is why the typical design is a tube with a large aspect ratio ( $L/D > 10$ ), being limited by the volume required for subsystem, payload, and tether integration. Note also that  $\rho$  and especially  $c_p$  are temperature dependent. For low temperatures, one has to use averages over the temperature range  $[T, T_m]$ . Also,  $T_m$  depends (weakly) on ambient pressure and on salinity (freezing point depression). Because Eq. (2) does not consider losses, it gives only a rough estimate of the penetration velocity; in fact, it relates the minimum power requirement  $P_0$  to a given penetration velocity  $v$  via

$$P_0 = A\rho(c_p\Delta T + \Delta H)v \quad (3)$$

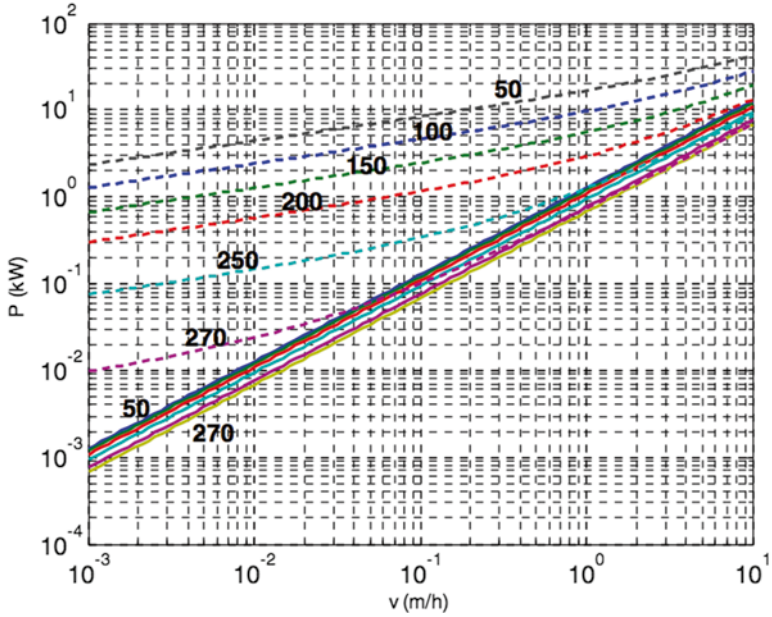
In fact, insufficient heat causes the probe to freeze in and excessive heat produces an oversized hole and wastes power by raising the meltwater temperature far above  $T_m$ . To obtain a more accurate result, losses need to be considered, most importantly the losses due to lateral heat conduction into the ice. The lateral conduction losses have been estimated by Aamot (1967a) for a cylindrical probe with the constraint that the meltwater stays liquid all around the probe's hull. According to Ulamec et al. (2007), the resulting equation for the lateral conduction losses  $P_{lc}$  can be approximated by

$$\frac{P_{lc}}{\Delta T v R^2} = 932 \frac{\text{Ws}}{\text{K}\cdot\text{m}^3} \cdot x^{0.726} \quad (4)$$

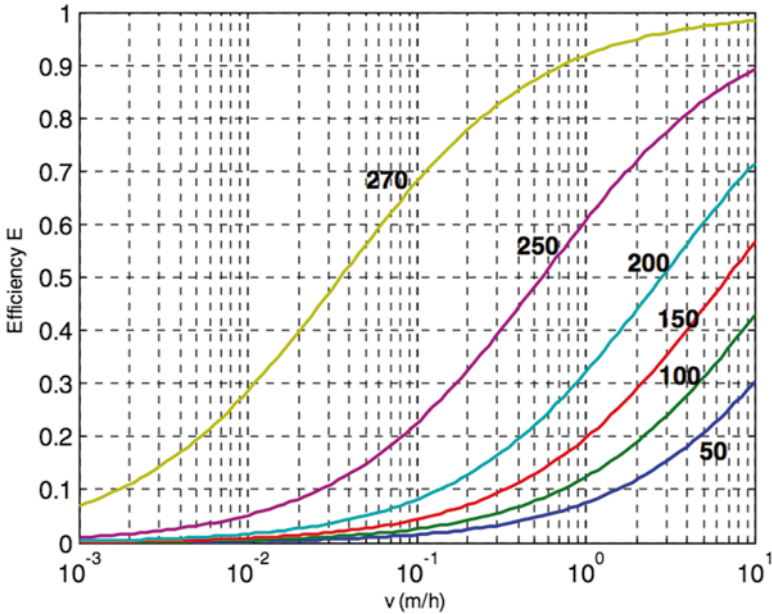
where  $x$  is the numerical value for  $L = (vR^2)$ , being made dimensionless by multiplying it with  $1 \text{ m}^2/\text{s}$ . Hence, the total power required by the probe to penetrate the ice with a velocity  $v$  is given by

$$P = P_0(A; v; T) + P_{lc}(A; L; v; T) \quad (5)$$

Figure 6 shows the required heating power of a typical melting probe ( $L = 1 \text{ m}$ ,  $D = 10 \text{ cm}$ ) as a function of penetration velocity for ice temperatures  $50 \text{ K} \leq T \leq 270 \text{ K}$ . The solid lines show the minimum power requirement according to Eq. (3), while the broken lines depict the total power including losses according to Eq. (5). Figure 7 shows the efficiency  $E = P/P_0$  as a function of penetration velocity. It can be seen that  $E$  becomes very small for penetration velocities  $< 1 \text{ m/h}$  and very cold ice. For example, in moderately cold 250-K Antarctic ice, the efficiency drops below 50% for penetration velocities  $< 0.55 \text{ m/h}$ , while in extremely cold 100-K European ice, the efficiency at this penetration velocity is below 10%. To obtain an even more accurate result, the following losses would also have to be considered: (1) friction losses between the ice wall of the melted channel and the surface of the probe, (2) radiative losses, and (3) losses in the tether. Because these losses are small as compared to the lateral conduction losses, they are omitted in this chapter and the interested reader is referred to Ulamec et al. (2007).



**Figure 6.** Required heating power  $P$  as a function of penetration velocity  $v$ , without (*solid lines*) and with conductive losses (*broken lines*), from Ulamec et al. (2007).



**Figure 7.** Efficiency  $E = P/P_0$  as a function of penetration velocity  $v$ , from Ulamec et al. (2007).

## 5. Past Ice Melting Probe Developments

The application of ice melting probes for subsurface ice exploration is not a new idea. This section describes the melting probes that have been built and used for terrestrial applications and first experiments to test their suitability for space applications in very cold ice and under vacuum conditions.

### 5.1. PROBES DEVELOPED IN THE 1960S

The idea of a melting probe for the investigation of ice layers can be traced back to the beginning of the 1960s (Kasser, 1960; Philberth, 1962; Shreve, 1962). Philberth (1962) designed a non-recoverable, instrumented melting probe for measuring temperatures inside a glacial ice sheet, consisting of a cylindrical hull with an attached conically shaped head (known thereafter as the “Philberth probe”). The probe was connected to an external power supply via a cable (tether), unwinding from a coil within the hull. To protect the probe from damage caused by refreezing meltwater, after turning off the heating elements for ice temperature measurements, a significant part of the hull was filled with silicone oil of density  $>1 \text{ g/cm}^3$  (Aamot, 1967c). A detailed description of the first Philberth probe can be found in Aamot (1967b). Aamot (1970b) reports four US field experiments with early melting probes. In 1965, the first probe reached a depth of 90 m in Greenland ice before contact was lost. One year later, the second probe ran smoothly for 4 days and reached a depth of 259 m after which it was stopped to observe temperature and pressure variations during the refreezing of the meltwater. During the first day, this melting probe, operated at 3,380 W, achieved a penetration velocity of 2.72 m/h. A detailed description of these first two field applications of melting probes, their instrumentation, and the scientific results is given in Aamot (1967c). During a Greenland expedition in 1968, Philbert used two probes which reached depths of 230 and 1,000 m, respectively (Aamot, 1970b). A new concept of a pendulum attitude stabilization for thermal probes was first introduced by Aamot (1967a, 1970a), with additional heating elements in the top part of a melting probe. In the 1980s, the Polar Ice Coring Office (PICO) of the University of Nebraska constructed a similar probe with a telemetry link in its tether (Hansen and Kersten, 1984). The PICO probe allowed constant temperature/ice flow measurements during the ice penetration phase as well as measurements of the meltwater conductivity, and penetration depths between 100 and 200 m were achieved. More recent work of the University of Nebraska on a probe for terrestrial applications is described by Kelty (1995).

### 5.2. PROBES DEVELOPED AT AWI

In the 1990s, the Alfred Wegener Institute (AWI) for Polar and Marine Research, Germany, has developed new melting probes for the investigation of Antarctic

shelf ice. AWI's "SUSI II" probe<sup>4</sup> was successfully tested on the Austrian Rettenbach glacier in 1990 and achieved a penetration depth of 60 m. The probe could be retrieved from the glacier because the melting hole did not refreeze within 8 h. Two years later, during winter 1992/1993, the probe was able to penetrate  $\approx 220$  m of Antarctic shelf ice near the Neumayer station and accessed the open water below the ice (Tüg, 2002, Personal communication, 2003). SUSI II had a length of 2.25 m, a diameter of 10 cm, an effective heating power of 3.4 kW in the head, a supply power of 600 V/8 A, a penetration velocity in the shelf ice of 2.93 m/h (220 m in 75 h), and a wire-tension-controlled stabilization. A further development of this probe, named SUSI III, was built for a penetration depth of 800 m, with a length of 3.6 m, a diameter of 14 cm, a power of 9 kW (head), and a supply power of 1,000 V/12 A. This probe failed, however, because of tether overheating in its winch compartment. Another "routine" probe for lesser depths was patented (Tüg, 2003). Parallel to the technical advancement of melting probes, a more sophisticated instrumentation of the probes took place (see Ulamec et al. (2007) for further details).

### 5.3. PROBES DEVELOPED AT JPL – THE CRYOBOT

Without doubt, the most advanced melting probe design is that of the Cryobot, initiated by the Jet Propulsion Laboratory in 1998 as an in situ exploration and sample return vehicle for a future application on Europa (Zimmerman et al., 2001a, b). The Cryobot is allotted with integrated radioisotope thermoelectric generators (RTGs), providing 1 kW of direct thermal melting power. The probe is 0.8–1 m long with a diameter of 12 cm and a mass of 20–25 kg in the "flight version." Fluid thermal modeling and testing revealed that, with a power of 1 kW, a melting rate of 0.3 m/h can be achieved in very cold (100 K) ice; the water jacket maintained around the probe is 1–2 mm in width and the melt plume would not refreeze until 1.25 m behind the vehicle. An active heater system (warm water jet in front of the probe) allows faster penetration in dense ice. The Cryobot is designed as a fully autonomous robotic mole penetrator system for melting through an ice pack of 3–10 km thickness.

### 5.4. MELTING PROBE EXPERIMENTS AT IWF AND DLR

Experiments performed at IWF Graz and DLR Cologne with simple melting probe prototypes showed that their penetration behavior in a low pressure environment is quite different from the one under atmospheric pressure (Kaufmann et al., 2009; Treffer et al., 2006; Ulamec et al., 2005). Also, it is different for compact water ice

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<sup>4</sup>"SUSI" is the abbreviation for "Sonde Under Shelf Ice."



and porous water ice with a snow/firn-like structure. While in the porous sample the ice is only subliming, the phase changes in the compact ice are much more complex, with alternating phases of melting and sublimation. According to those experiments, the absence of the liquid phase has severe consequences on the melting performance under vacuum conditions. With almost a vacuum between the tip and the ice, heat can only be transferred via radiation, which is very ineffective at low temperatures. Therefore, only a low fraction of the generated heat is used to melt or sublime the ice at the tip of the probe, leading to a high thermal resistance between the probe and the ice. The bulk of the melting power was transferred towards the rear end of the probe, which was particularly a problem in the initial phases of an ice penetration experiment, when the probe had not yet penetrated the ice over its whole length (Kaufmann et al., 2009).

## 6. Main Technological Issues for the In Situ Subsurface Exploration of Icy Environments in the Solar System

The design and operations of any human-made robotic exploration device that has to work at (and below) the icy environments in the Solar System raises several technological challenges, especially for the remote icy moons of the giant planets. Their large distance from the Sun has implications for power supply and their large distance from the Earth has implications for the communications architecture and the required autonomy of the subsurface probe (see Table 2 for the engineering key parameters). The communications between the deployed probe and the Earth requires at least a lander on the surface and, for high data rates, probably also an orbiter. After deployment in the ice, the probe encounters a largely unknown environment that may contain areas with obstacles, which should be bypassed. This is only possible if the probe is steerable and able to sense obstacles in its closer environment. To navigate in the ice, a steerable probe also has to know its position and orientation, probably without external references like stars, a magnetic field, or a global navigation system. Another key driver for the engineering of the probe is the pressure that is acting on it in deep ice.

### 6.1. POWER SUPPLY

Due to their large distances from the Sun, the solar radiation flux,  $S$ , in the outer Solar System is very low (it decreases inversely with the square of solar distance  $r$ , that is,  $S(r) \propto 1/r^2$ , see also Table 2). This has fundamental implications for the power supply of the surface station and the subsurface probe. For Europa, solar electric power systems are infeasible, not only because the solar radiation flux is very low but also because the extremely large charged-particle radiation flux inside Jupiter's radiation belt ( $10^7$ – $10^8$  rad/month (Chyba and Phillips, 2007)) would destroy solar cells within hours to days. Solar thermal systems might be more

**Table 2.** Engineering key parameters for Mars, Europa, and Enceladus.

Parameter	Mars	Europa	Enceladus
Mean solar radiation flux (W/m <sup>2</sup> )	589	51	15
Max. distance from Earth (AU)	2.68	6.48	11.09
Max. signal roundtrip time (h)	0.74	1.80	3.07

suitable, but also they cannot operate during the European night, so that the energy required to survive the night would have to be stored in huge batteries. The charged-particle radiation flux on Enceladus is much lower, but at this solar distance the solar radiation flux is too low to favor a solar power system. Therefore, it is probably impossible to avoid radioisotope units or even small nuclear reactors for the operations of devices with high power demands, such as ice melting probes, in the outer Solar System. The traditional space application RHU (Radioisotope Heater Unit) technology is based on <sup>238</sup>Pu (specific thermal power is 0.57 kW/kg, half-life is 87.74 years). For an Antarctic application, <sup>45</sup>Ca may be an alternative because it is not explicitly excluded by the Antarctic Treaty, it is a beta radiator (specific thermal power is 27 kW/kg, half-life is 162.7 days) that does not require gamma-shielding, and its decay product is <sup>45</sup>Sc, which is stable and nontoxic. The availability of <sup>45</sup>Ca, bearing in mind its short half-life, needs to be investigated or other isotopes with similar properties need to be found. In conclusion, a depth of  $\approx 4$  km (or more) can apparently only be reached with RHUs or a small nuclear reactor (or by launching the probe from the bottom of an already existing borehole). For a small Mars polar ice cap probe, however, where much less heating power may be sufficient during polar summer, a solar power generator may be feasible (see also Kömle et al., 2002). Because both RHUs and nuclear reactors generate direct heating power and because the conversion efficiency to electric power is small, they should be located inside the subsurface probe. For RHUs, however, it has to be considered in this case that the probe cannot be stopped on its way down because RHUs cannot be switched off. For terrestrial ice melting probes, the traditional power transmission between the surface station and the probe is by cable, paid out from a coil stored in the aft of the probe. The delivery of heating power via a cable to great depths is challenging due to both mechanical and electrical constraints. Typically, high voltages (up to several kV DC) are considered for the power supply of several kW to minimize resistive losses in the tether. The tether is also useful for the communications between the probe and the surface station because the housekeeping and science TMTC (telemetry and telecommand) stream can be multiplexed onto the DC supply voltage. Clearly, the thickness of the cable, along with the available total volume for its storage, is the limiting factor for the maximum possible penetration depth. For AWI's SUSI probes, a maximum depth of the order of 1–2 km has been estimated (for an optimized design) (Tüg, 2002, Personal communication), while the Philberth probe concept considers a feasible depth of 3 km or more (Aamot, 1968).

## 6.2. GRAVITY DEPENDENCE AND ATTITUDE CONTROL

Traditional melting probes require the force of gravity to set the direction of penetration, which is unfortunately only vertically downwards. To the first order, however, the weight of the probe does not influence the penetration velocity as long as the weight force is larger than the – possibly non-negligible – friction force between the probe and sediments (gravity exerts, however, a second-order effect on the penetration velocity because the efficiency of the idealized hot point is weakly dependent on the contact pressure of the melt surface on the ice (Shreve, 1962)). Thus, traditional melting probes would not function under microgravity environments. Even if their vertical orientation is only to be maintained, they require some means of attitude control. Such probes are inherently unstable, so that the slightest deviation from the vertical direction results in an increasing tendency of the probe to “lean” and finally to “topple over” (Ulamet et al., 2007). This is almost inevitable in inhomogeneous ice (with voids, cracks, dust layers, etc.). This instability must be counteracted or eliminated. Aamot (1967b) describes “Mercury steering” and “pendulum steering” and reports mixed results. The successful SUSI II probe (Tüg, 2002, Personal communication, 2003) used a simple mechanism based on information of the hot nose temperature and the tilt of the probe to control the friction clutch of the probe’s tether/cable payout mechanism. Active attitude control can also be based on differential melting, that is, by controlling the heating power in the head and along the side walls of the probe. Using an ice screw at the tip, as in the IceMole (see Sect. 7), neither the direction of penetration nor the contact pressure between the melting head and the ice depends on gravity. This allows gravity-independent operations under zero gravity conditions and even melting upwards against gravity (at least on Earth). The ice screw stabilizes the direction of penetration, and by differential melting, the probe can also drive in curves. To support such attitude maneuvers along a long trajectory, however, a simple inclinometer is not sufficient, but the probe requires a sophisticated attitude control system and an attitude determination system that is based on inertial navigation (see Sect. 6.4). In a RHU-heated probe, the required heat distribution could be controlled by means of heat pipes with mechanical valves.

## 6.3. PREVENTION OF BLOCKING

Great care has to be taken, particularly in cold ice, to ensure that the refreezing of ice alongside and behind the probe is slow compared to the melting velocity, in order not to jam the probe. While this is not an issue for temperate terrestrial glaciers, it is critical for cold ice, as experiments have shown (Treffer et al., 2006). Therefore, low-temperature melting probes must foresee heating elements distributed alongside of the probe and careful heating control. Another problem regarding the melting into natural ices is the emplacement of components that cannot be molten, like dust or salts, because the dust concentrates underneath the melting tip, building up

an insulating layer, and increasing the friction. To solve this problem, mechanisms in addition to “pure melting” need to be applied. So far, few satisfactory solutions have been demonstrated to melt into dusty ice. In context with the JPL Cryobot, an active water-jet system is proposed, splashing/pumping away the debris accumulating at the melt head (Zimmerman et al., 2001a, b). Another solution is an ice screw at the tip of the probe, as used by the IceMole (see Sect. 7), where the penetration of up to 4-cm thick “dirt” layers has been demonstrated on an Alpine glacier.

#### 6.4. OBSTACLE AVOIDANCE, STEERABILITY, AUTONOMY, AND NAVIGATION

The large distances from the Earth to Jupiter and Saturn yield signal roundtrip times of  $\approx 2\text{--}3$  h (Table 2), which require any robotic exploration system to operate as autonomously as possible. Autonomy is especially challenging for the exploration of extraterrestrial subsurface environments. In the ice, the probe encounters a largely unknown environment that may contain obstacles, such as inclusions of rocks and liquids, layers of dust, and cracks, crevasses, and voids, especially close to the surface. Therefore, the probe should be steerable and able to sense and bypass potential obstacles in its close environment. Depending on the mission objective, it should also be able to sense potential targets for scientific investigation, for example, liquid-filled pockets and/or crevasses. To navigate in the ice, a steerable probe also has to know its position and orientation, probably without external references like stars, a magnetic field, or a global navigation system. As it will be shown in Sect. 7, steering is possible with an ice screw at the tip of the probe and differential heating of the melting head. Other elaborate techniques for active steering of the probe around obstacles, involving an acoustic obstacle detection sonar and a steerable probe pushing device, have also been proposed by Di Pippo et al. (1999).

#### 6.5. COMMUNICATIONS

Having a probe that is able to melt upwards, against gravity, it may be considered to bring a sample back to the surface. In this case, one may also consider avoiding communications between the surface station and the subsurface probe until it has returned to the surface. This, however, would require a very large degree of autonomy and would be associated with a high risk. It would also be very disappointing to lose the probe without knowing the reason for it and without having gained some data before. Therefore, we consider a communication link between the probe and the surface station as essential. From the surface station, all data (science and housekeeping telemetry) will then be transmitted to Earth, probably via an orbiting spacecraft. The link between the surface station and the Earth can be based on

standard space communications technology. Tethered probes can employ the power cable with intermediate repeaters for data transmission. Although such tethered systems have been examined for planetary ice melting probes, they are likely to be limited to exploration depths in the order of a few kilometers. For untethered probes, the communications between the probe and the surface station becomes challenging, because the data has to be sent through many kilometers of impure water ice. An advantage of using radioisotope sources, however, is that the vehicle is relatively “power rich” and radio communication methods may be viable between the probe and the surface station. Unfortunately, the presence of salts in water ice can radically increase the attenuation experienced by microwave signals, to the extent that studies have considered deploying relay transceiver pods behind the probe as it melts through the ice. Typical propagation figures indicate that microwave links could pass 10 kbit/s over a few hundred meters with powers of around 200 mW. Realistically, lower rates will be achieved when the effect of adding salts and scattering ice inclusions is considered. Other methods of avoiding the high losses faced by high-frequency signals could involve using much longer wavelengths, which would yield lower bit rates and would require a mass memory for data buffering. Acoustic waves can be transmitted through layers of liquid and solid water; the achievable data rate would be very low and strongly influenced by the unknown characteristics of the ice (density, porosity, layering, mechanical discontinuities, varying attenuation, multiple paths, ambient noise, thermal cracking, reverberation, etc.). Therefore, at the moment, the use of a tether appears to be the most reliable solution, despite the great tether length, which also requires storage containers and a technique to manage its safe deployment. It could be based, however, on the mature technologies that exist in wire-guided missiles, subsea torpedoes, and remotely operated submersibles, with the necessary improvements due to the particular environment and operating conditions concerned.

## 6.6. PRESSURE

The usual approximation of the ambient pressure  $p$  in bulk ice (valid if the ice is in a secular hydrostatic equilibrium) is  $p = \rho gh$ , where  $\rho$  is the ice density and  $g$  the local gravitational acceleration ( $g = 9.81 \text{ m/s}^2$  on Earth,  $g = 3.73 \text{ m/s}^2$  on Mars,  $g = 1.31 \text{ m/s}^2$  on Europa, and  $g = 0.11 \text{ m/s}^2$  on Enceladus). This gives, for example, a pressure of  $\approx 400$  bar in 30 km depth on Europa as well as in 4 km depth at Lake Vostok. The probe must not only survive this pressure but also the pressure transient when reaching the ice/water interface. This pressure jump, which would not occur if ice and water were in hydrostatic equilibrium, has already been observed (Tüg, 2002, Personal communication). Aamot (1968) also reported measurements of pressure jumps during stopping or restarting the probe (by freezing or melting of surrounding material with associated volume and pressure changes) up to 88 bar. Two basic system architectures with respect to operational pressure may be considered: (1) a “dry” system architecture, based on a pressure-tight vessel,

capable of structurally withstanding the maximum external pressures and housing all system components with sealed windows and openings (e.g., for instrument access to the environment and tether payout), or (2) a “wet” system architecture, where at least parts of the probe either can be ooded with meltwater or are immersed in, for example, silicone oil. The latter concept has been used, for example, in the Philberth and AWI probes (for the tether storage section of the probes).

## **7. IceMole – A Steerable Probe for Clean In Situ Subsurface Exploration of Icy Environments**

The “IceMole” is a novel steerable subsurface ice melting probe for clean in situ sampling and analysis of subsurface ice and subglacial water/brine (Dachwald et al., 2011; Mann, 2010). Since 2009, it is developed and built at FH Aachen University of Applied Sciences’ Astronautical Laboratory. A first prototype, “IceMole 1,” was successfully tested on the Swiss Morteratsch glacier in September 2010. Clean sampling is achieved with a hollow ice screw (as it is used in mountaineering) at the tip of the probe. Steerability is achieved with differential heating of the melting head. The current design of the IceMole is adapted to the subsurface investigation of terrestrial glaciers and ice shields, but in the long run, the probe should also be adapted to extraterrestrial ice research.

### **7.1. ICEMOLE DESIGN AND ADVANTAGES**

As it has become clear in the previous sections, traditional melting probes have three main drawbacks: (1) They penetrate only vertically downwards and it is difficult to (intentionally) change direction; (2) they cannot penetrate dust/dirt layers; and (3) they cannot be recovered from greater depths. To remedy these drawbacks, the IceMole design is based on the novel concept of combined melting and drilling (or – more precisely – screwing) with a hollow ice screw (see Fig. 8). The probe has the shape of a rectangular tube (15 cm × 15 cm cross section) with a ≈3-kW melting head at the tip. The quadratic cross section is required to counter the torque of the ice screw. The required electric power is generated by a surface aggregate and transmitted via a cable that is uncoiled from the probe. The power cable is also used for communications and data transfer to the surface via a power-line modem. The driving force of the ice screw presses the melting head firmly against the ice, thus leading to a good conductive heat transfer. The ice screw is also able to drag the probe through moderately thick layers of dust/sand/grit. However, it can probably not cope with obstacles that are larger than the diameter of the screw. The IceMole can change direction by differential heating of the melting head, which generates a torque that forces the IceMole into a curve. Therefore, it can also melt upwards, against gravity, to be recovered from the ice.



**Figure 8.** IceMole 2 (Image credits: FH Aachen).

## 7.2. ICEMOLE 1 FIELD TEST RESULTS

In September 2010, three penetration tests have been successfully conducted on the Swiss Morteratsch glacier (Fig. 9) (Dachwald et al., 2011):

1. Melting 45° upwards for  $\approx 1.5$  m, against gravity (Fig. 10).
2. Melting horizontally for  $\approx 5$  m (Fig. 11).
3. Melting 45° downwards for  $\approx 3$  m, thereby penetrating three obstructing non-ice layers (made from material found on the glacier) and driving a curve with a radius of  $\approx 10$  m (Figs. 12 and 13).
4. The penetration velocity was  $\approx 0.3$  m/h (but is planned to be increased to  $\approx 1$  m/h for the next prototype, “IceMole 2”).

## 7.3. POTENTIAL FOR CLEAN IN SITU ANALYSIS AND SAMPLING

Up to now, the test results show that the IceMole concept is a viable approach for the clean delivery of scientific instruments into deep ice (and recovering them afterwards), as well as for clean sampling. Contrary to conventional ice-core drilling methods, the IceMole does not utilize any drilling fluid and may be sterilized according to planetary protection standards before its subglacial deployment (additionally, an optional module for in situ chemical decontamination of the probe during its melting through the ice is under development). In any case, because the material is sampled by the hollow ice screw at the tip of the probe, it does not come into contact with the exterior of the IceMole. Because the ice screw is thermally isolated from the melting head, the ice is ingested into the probe’s interior, where it may be analyzed in situ. For the alternative clean sampling of subglacial liquids instead of ice, the liquids are pumped through the hollow ice screw into sterile bags, from where they can be recovered after the probe has returned to the surface. Additionally, the direct pumping of water to the surface is an option.



**Figure 9.** Deployment of IceMole 1 on the Morteratsch glacier (Image credits: FH Aachen, [www.forschungsfotos.de](http://www.forschungsfotos.de)).



**Figure 10.** First channel, 45° upwards, ≈1.5 m.





**Figure 11.** Second channel, horizontal,  $\approx 5$  m.



**Figure 12.** Third channel,  $45^\circ$  downwards,  $\approx 3$  m, penetration of  $\approx 4$  cm of “dirt” (dust/sand/grit found on the glacier).

#### 7.4. FUTURE ICEMOLE DEVELOPMENT

Between 2010 and 2012, an advanced IceMole prototype, named “IceMole 2,” was developed at FH Aachen University of Applied Sciences. IceMole 2 contains an attitude determination system and should achieve an increased melting velocity



**Figure 13.** Third channel, 45° downwards,  $\approx 3$  m, curve with a radius of  $\approx 10$  m (channel was opened afterwards).

of  $\approx 1$  m/h. In September 2012, IceMole 2 should be tested on the Icelandic Hofsjökull glacier. Between 2012 and 2015, a consortium funded by DLR and led by FH Aachen University of Applied Sciences develops a much more advanced IceMole probe, which includes a sophisticated system for obstacle avoidance, target detection, and navigation in ice. The main technical objective of this project, which is termed “Enceladus Explorer” or “EnEx,” is to test navigation in deep ice in preparation of the IceMole and its navigation technology for extraterrestrial applications. The EnEx probe will also feature a clean mechanism for the sampling of subglacial brine from a crevasse. In the 2014/15 season, it is intended to use this probe in cooperation with a US team for taking clean samples of subglacial brine at the Blood Falls (McMurdo Dry Valleys, East Antarctica) for chemical and microbiological analysis (Mikucki et al., 2009; Mikucki and Priscu, 2007). For this sampling, the forward contamination shall not exceed the concentration of microbes in the surrounding glacial ice ( $\approx 2,000$  cells/ml (Mikucki and Priscu, 2007)). Before the deployment of the probe at the Blood Falls, two intermediate field tests are foreseen to validate the cleanliness of the sampling method.

## 8. Summary and Conclusions

The exploration of Mars’ polar ice caps, the subsurface water reservoirs at Enceladus’ south pole, and the putative water ocean below the icy crust of Europa are seen as prime scientific targets for the fields of planetology and astrobiology. Ice melting probes have already demonstrated their potential suitability for such applications.

For maximum scientific return, however, they should be autonomous and steerable. Considering technical maturity and expected scientific return, it is proposed to develop steerable melting probes, first for the clean exploration of Antarctic subglacial aquatic environments, then for Mars' polar ice caps, then for Enceladus, and finally for Europa. While the first probes explore Antarctica and Mars, orbiters around Enceladus and Europa should explore these icy moons and look for the most promising landing sites. Already the next steps in the development of clean in situ subsurface ice exploration technology, the exploration of Antarctic subglacial aquatic environments (like Lake Vostok and Blood Falls) would result in important scientific advances.

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**PART VIII:  
SUMMARY AND CONCLUSIONS**

**de Vera  
Seckbach**

Biodata of **Dr. Jean-Pierre de Vera** and **Prof. Joseph Seckbach**, authors of “*Theoretically Possible Habitable Worlds: But Will We Get Soon Answers by Observations?*”

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## THEORETICALLY POSSIBLE HABITABLE WORLDS: BUT WILL WE GET SOON ANSWERS BY OBSERVATIONS?

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### 1. The Likelihood of Habitable Worlds

Based on the chapters presented within this volume, one of the conclusions might be, that there is no doubt, that habitable worlds exist. Even in our neighborhood, in our own solar system, it is not improbable that planets like Mars, with some limitations Venus and the satellites or the so-called moons in the Jovian and Saturnian systems (e.g., Europa and Titan resp.), are habitable. The question, which is hidden behind this argument, is if implications are suggested that “there is no life – no life as we know it in the universe” (see chapter “[Factors of Planetary Habitability](#)” by Hengeveld) – could it be possible that our terrestrial inhabitants, the big varieties of present microorganisms on our home planet Earth, could probably live on these extraterrestrial worlds? Could they be able to find habitats, where they would be able to survive? In that case, it seems mainly a question of presence of liquid water and an energy source. However, we also have to be aware that for the classification of a planet or moon as a habitable object, we have to take into account which reference groups of organisms might survive in such conditions. Some of the potential species are described in this book (chapter “[The Role of Terrestrial Analogs in the Exploration of the Habitability of Martian Evaporitic Environments](#)” by Barbieri, chapter “[Microbial Scale Habitability on Mars](#)” by Westall, chapters “[Organic Molecules in Lunar Ice: A Window to the Early Evolution of Life on Earth](#)” and “[Extremophiles on Alien Worlds: What Types of Organismic Adaptations Are Feasible on Other Planetary Bodies](#)” by Schulze-Makuch, and see Seckbach et al., 2013). Examples which have been discussed are mainly focusing on Earth-like life as a reference system. Some problems might be obvious if we try to think about alternative life forms, which appear to be much different from our Earth-centric view. An approach was given in particular in Part 5 with the title “Alternatives to Earth-like Life.” An option to gain energy besides photosynthesis and chemolithotrophic processes, which are known as conservative main power source due to the effective use of redox potentials, has also been given by two innovative examples. The proposed idea of “thermosynthesis” by imaginable thermotrophic life forms is dealing with the idea of thermal phase

differences and transitions in the natural environment from which alternative life forms might gain the needed energy comparable to the charge differences at membranes which are necessary for the synthesis of ATP in the previously mentioned synthetic pathways of photosynthesis and chemoautotrophic synthesis (Schulze-Makuch). The “osmosynthesis” is another postulated alternative (see chapters “[Extremophiles on Alien Worlds: What Types of Organismic Adaptations Are Feasible on Other Planetary Bodies](#)” by Schulze-Makuch), where a cell can be hypo-osmotic and a surrounding saltier ocean can act as a counterpart. This osmotic pressure gradient is again a potential engine to generate energy for life’s requirements of self-preservation, maintenance of reproduction capacities, and life cycle properties.

Raven and Donnelly proposed another life form, which uses alternative photosynthesis to gain energy from brown dwarfs, a kind of star, where the nuclear fusion has not been realized to produce enough light, which might have similar properties as our sun. The energy source would be expected more in spectrum ranges of the infrared. If the photosystem apparatus of the proposed life forms can be excited by such kind of energy sources and start its energy storage mechanisms as it is known by the normal photosynthesis, radiation of black smokers, chemiluminescence, and bioluminescence can also be used by such kind of reaction, and even such kind of metabolism can also be expected in the dark deep oceans of the icy moons in our solar systems and may be beyond.

Taken all these previously mentioned alternative options into consideration and if we have a closer look on these very promising and challenging alternatives, it becomes obvious that water is needed as a liquid. There are some ideas that involve liquids like methane, ethane, acetylene, and other hydrocarbons as probable substitutes, replacing water as the main liquid to be important for life. This would enlarge the number of habitable worlds in our solar system and even on extra solar locations significantly. If this is true, (to be one of probable alternative options), the Moon Titan in the Saturn system would be a very good candidate to search for *life as we do not know it*. But water is differing in many ways from these organic molecules because of its bipolarity, which allows most efficient solutions of salts and erosions of minerals and can provide much easier ions to cells as it might be by the organic liquids. We have to search for other molecules, which might have at least similar capacities to act as an efficient dipole. Perhaps the molecule  $H_2S$  could be an option. However, even here it is dependent on the entire environmental conditions, which might allow its abundance, its stability, and its liquid aggregate phase. There are indices that this is much more limited as it is for water. Nevertheless, liquid water is from a scientific point of view still the most important substance which is needed for life and which makes a planet to be a habitable world.

Based on liquid water, it must also be emphasized that the aggregate phase as a liquid is not just limited to the low temperature limit of 0 °C (chapter “[Bio-relevant Microscopic Liquid Subsurface Water in Planetary Surfaces?](#)” by

Möhlmann in this volume). Even at a temperature far below 0 °C, water can be stable in its liquid aggregate phase, what depends on capillarity, absorption properties, pressures, the presence of a solid greenhouse effect, or the presence of a salty environment which produces brines and what can be observed on the surface of Mars. Therefore, we have to conclude that the numbers of possible habitable worlds increase. Even Mars, as a very cold planet, can be classified as a habitable candidate.

Because of tidal heating (chapters “[The Habitable Zone: Basic Concepts](#)” and “[Exoplanets and Habitability](#)” by Kane) or a heating source from the inner side of the planets or moons, water can be also expected in its liquid phase on the Jovian satellites Europa and Ganymede as well as on the Saturnian satellites Enceladus and Titan (see chapter “[Habitability on Kepler Worlds: Are Moons Relevant?](#)” by Chela-Flores and chapter “[Clean In Situ Subsurface Exploration of Icy Environments in the Solar System](#)” by Dachwald et al.). The heating source itself might be a good energy source for life. Therefore, it is not excluded that such kind of planetary icy systems might be a reservoir of habitable worlds.

## 2. The Probability to Find Life, as We Know It, in the Universe

As a big challenge we can also consider the enterprises to find life as we know it in our solar system or in other stellar systems. First of all according to Hengeveld (chapter “[Factors of Planetary Habitability](#),” this volume), it seems to be improbable that the same evolution as on Earth is occurring twice in the universe. This is because the coordination of so many physical and chemical rules, factors, values, and their interactions determine first the appearance of life on a planet and secondly the habitability of planets (see also chapter “[Experimental Simulations of Possible Origins of Life: Conceptual and Practical Issues](#)” by Strasdeit and Fox) as well as the evolution of life itself, if it has been formed anywhere else in the universe. The fact, that the frequencies of local to global catastrophes (e.g., volcanic events and asteroid impact events) which were exterminating big groups of organisms but also might have triggered the further evolution of the surviving species on Earth in the past can happen a second time in our universe, has a very low likelihood.

Strasdeit and Fox (chapter “[Experimental Simulations of Possible Origins of Life: Conceptual and Practical Issues](#),” this volume) also supported the idea that the quest of habitability is closely connected to the prebiotic chemical evolution. This prebiotic world seems to be unique. However, with a closer look, it seems that before the formation of the first cells, a certain rule of network catalysis (even auto-cyclic network catalysis) enlarges a multi-reaction modus where the possibilities to start a generation of building blocks of life might be relieved. These building blocks of life could differ in a certain range from molecules with relevance to life, as we know it, because in these network reactions alternative pathways are possible. One example by Strasdeit and Fox (chapter “[Experimental](#)

*Simulations of Possible Origins of Life: Conceptual and Practical Issues*,” this volume) is given that metal complexes as metalloenzymes might be able to change the molecule conformations because of an exchange of the metal with another, one allowing similar or completely different functionalities. Just these co-options might enhance chemical evolution and evolve in different planetary environments differently, because the selection of functionality increases the way to form life and its further evolution. As a conclusion the same biochemistry as it appeared on Earth cannot be expected on other Earth-like planets. Co-options of forming the building blocks of life are minimizing a complete same evolution. But further work by an experimental way using simulation facilities to simulate, e.g., the conditions of early Earth or other planets would give better answers to these questions. Therefore, a number of complex simulation facilities were created by engineers in different universities and planetary science institutions and started a number of experiments, to get insights on the geobiochemistry under different conditions if compared to present Earth (see chapter “[Simulation and Measurement of Extraterrestrial Conditions for Experiments on Habitability with Respect to Mars](#)” by Lorek and Koncz and chapter “[Experimental Simulations of Possible Origins of Life: Conceptual and Practical Issues](#)” by Strasdeit and Fox). The design of simulation facilities to enable the simulation of planets like Mars is besides their complex technical realization phases (Lorek and Koncz), a challenging enterprise to perform the in situ observation of chemical evolution or the observation of interactions of bio-samples in a complete different environment. But first experiments are promising. First answers can be given for the habitability status of, e.g., Mars. Mars seems to be carefully expressed as a habitable planet for some of the tested microorganisms (de Vera et al., 2010; Morozova et al., 2007; Morozova and Wagner, 2007, and Schirmack et al., 2013).

The near future might give further answers on still open questions of habitability, which seem to be answered by different model calculations but have to be proven also by such kind of simulation experiments as mentioned above.

## 2.1. STUDIES ON PLANETARY ANALOGUE FIELD SITES AND BIOSIGNATURE DETECTION

To find *life as we know it* in our own solar system, there are other scientific attempts to reach this goal. Research in planetary analogue field sites like in the Dry Valleys in Antarctica, in the Arctic environments, or in high altitudes is in the focus since the last decade. In particular, due to the icy planets in the solar system being classified as potential habitats, the specific high latitudes in the polar zones or dry and elevated deserts of our home planet (e.g., Atacama in Chile) are considered as the best planetary analogues. The presence of evaporate-rich and therefore salty environments are favored to be investigated. In context of cryobrine (such as supposed to be on Mars, according to Möhlmann, see chapter “[Bio-relevant Microscopic Liquid Subsurface Water in Planetary Surfaces?](#)” in this volume), salty environments are

harboring a big variety of microorganisms, the so-called halophiles, which are including species from the two big domains of the tree of life, as there are the Bacteria and the Archaea (see, e.g., chapter “[The Role of Terrestrial Analogs in the Exploration of the Habitability of Martian Evaporitic Environments](#)” by Barbieri). Another advantage is obvious, if the salty environments on Earth are studied: the evaporitic deposits are predestined to preserve biosignatures. Tests with instruments developed for the search of bio-traces in such kind of environments are prerequisite. Some examples, describing instruments which can be used for these specific detection purposes, are mainly concentrating on spectroscopic nondestructive methodologies (chapter “[Raman Spectral Signatures in the Biogeological Record: An Astrobiological Challenge](#)” by Edwards et al. and chapter “[Application of Raman Spectroscopy as In Situ Technology for the Search for Life](#)” by Böttger et al., both in this volume). The Raman technology was given as one example, and the advantages as well as the pitfalls of this methodology were discussed extensively. The difficulties of the definition of biosignatures were obvious. What kind of life form or what kind of biosignatures do we expect? What type of geo-niches do we have to investigate? What are real planetary analogues on our planet so that we would be as close as possible to the environmental conditions as they appear on the other planets and moons? Previous studies with this kind of proposed instrument had their focus on cyanobacteria as one example of possible halophiles with their origin dating back to the Early Earth (3.5 Ga ago). The problem with that is that we do not know, if for the case of Mars, this planet had a longer extended time scale where habitable environments would have been possible in the past, so that life becomes into existence or evolved to let say in a “cyanobacteria-like” life form if compared to the expected short habitable time ranges of just a few thousand to a million years which are recently postulated for the red planet (see chapter “[Microbial Scale Habitability on Mars](#)” by Westall, this volume, and Ulrich et al., 2012). Cyanobacteria might be excluded from the list of potential life forms on Mars (chapter “[Microbial Scale Habitability on Mars](#)” by Westall, this volume). However, perhaps the molecules produced by cyanobacteria, which can be detected by the presented Raman technology, might be used also by other potential life forms. An approximation to find life on Mars might be the use and study of Archaea from permafrost regions (chapter “[Application of Raman Spectroscopy as In Situ Technology for the Search for Life](#)” by Böttger et al., this volume and Morozova et al., 2007; Morozova and Wagner, 2007; Schirmack et al., 2013; Serrano et al., 2013; Ulrich et al., 2012), which would be also a source of methane in Mars’ atmosphere (Formisano et al., 2004; Lefèvre and Forget, 2009; Mumma et al., 2009). But first experiments with these organisms make it obvious that life in general will definitively have a set of different spectra which have to be used in sum for classification of a well-detected biosignature. When the spectroscopic detector is detecting life-related spectra, these biosignature spectra just appeared differently from phase to phase according to their actual position in their life cycle (chapter “[Application of Raman Spectroscopy as In Situ Technology for the Search for Life](#)” by Böttger et al., this

volume and Serrano et al., 2013). Fluorescence and probable disturbing background produced by the mineral background (chapter “[Raman Spectral Signatures in the Biogeological Record: An Astrobiological Challenge](#)” by Edwards et al. and chapter “[Application of Raman Spectroscopy as In Situ Technology for the Search for Life](#)” by Böttger et al. (both in this volume) and Böttger et al., 2012) can influence significantly the detection procedure as well. Therefore, very good databases of biosignatures are needed before the future space exploration missions with the target of “life detection” are launched (de Vera et al., 2012).

## 2.2. DO WE SEARCH A SECOND EARTH?

The search for habitable worlds in extrasolar systems is closely related also to our Earth-centric view. Kane (chapters “[The Habitable Zone: Basic Concepts](#)” and “[Exoplanets and Habitability](#),” this volume) and Lee Grenfell et al. (chapter “[Exoplanets: Criteria for Their Habitability and Possible Biospheres](#),” this volume) made approximations taken care for the habitable zone and the stability of conditions of the early Earth-like as well as of present Earth-like atmospheres and presented this as reference model system to be the basics to find habitable worlds in surrounding other stars, even brown dwarf stars and binary systems. The role of the optical density of atmospheres to enlarge the range of habitable worlds was also further discussed by Shaviv et al. (chapter “[The Habitable Zone and the Generalized Greenhouse Effect](#)” this volume). The optical properties of atmospheres are besides the irradiation properties by the central star (chapter “[The Influence of UV Radiation on Exoplanets’ Habitability](#)” by Talmi and Shaviv, this volume) mainly responsible for the climate of a planet. They determine the magnitude of a potential greenhouse effect or vice versa cooling effect, which means that they control the mean surface temperature of the planet and last but not least the previously chemical reaction regimes (see chapter “[Experimental Simulations of Possible Origins of Life: Conceptual and Practical Issues](#)” by Strasdeit and Fox). Because the temperature might significantly influence chemical reactions, consequently the appearance of life and the direction of its evolution are also influenced. The distance and eccentricity of planetary orbits (chapters “[The Habitable Zone: Basic Concepts](#)” and “[Exoplanets and Habitability](#)” by Kane, this volume) are playing an additional role on the time scales where an exoplanet might be habitable.

Finally, the role of plate tectonics is not to be underestimated (see chapter “[Interior and Surface Dynamics of Terrestrial Bodies and Their Implications for the Habitability](#)” by Noack and Breuer, this volume). The presence of plate tectonics can only be observed on planet Earth in our solar system, and we ignore the presence of such dynamic processes on the detected exoplanets in the last decade. Therefore, the question still remains, if this might be one of the most important planetary habitability indices and biosignatures besides the presence of atmospheric biosignatures of ozone, oxygen, and methane. The relevance of plate

tectonics can be realized, if we consider the common scientific agreement that it is supposed that due to these planetary dynamics, the planet's surface can be recycled providing continuously fresh minerals, nutrients, and energy sources for life. The dynamics are also responsible for certain amounts of CO<sub>2</sub> outgassing processes besides the outgassing of other gases and are therefore influencing the formation and composition of the atmosphere what has again an important influence on the climate, on the presence of water, and therefore on the habitability of the planet itself (as previously mentioned).

But the presence of plate tectonics seems to be dependent on the size of the planet. Due to model studies of Noack and Breuer (chapter "[Interior and Surface Dynamics of Terrestrial Bodies and Their Implications for the Habitability](#)" this volume), the occurrence of plate tectonics are postulated just for Earth-sized planets. Bigger or smaller planets have different thermal properties of the mantle that do not allow the same convective scenarios as it can be observed on our own planet. But this theory can also be rejected, if differences of the elemental compositions of core and mantle (including the amount of water) of other planets might again change the dynamics significantly and approach the conditions of the Earth. A lot of further work has to be done, to find the truth.

So, we have to conclude that the question – if we search for a second Earth – still remains open. The Earth is the only proven habitable environment and may serve at the beginning of the search for habitable worlds as the reference system. Maybe, that if further experimental approaches can investigate the calculated models, we would be able to find alternative habitable options. But actually the search for a second Earth would be the most successful scenario to peruse in future.

### 2.3. WHICH MISSIONS ARE PLANNED TO FIND HABITABLE WORLDS?

Finally this chapter is focusing on missions, which are planned in the near future. The missions, which have high priority, can easily be identified by the quantity of proposed and still accepted projects. Many of the projects are focusing on the detection of extrasolar planets (see chapter "[Detection of Habitable Planets and the Search for Life](#)" by Rauer et al. and chapters "[The Habitable Zone: Basic Concepts](#)" and "[Exoplanets and Habitability](#)" by Kane, both this volume). There are six proposed methods to continue or improve the detection of extrasolar planets approaching the detection of Earth-size planets. They are as follows: (1) the radial velocity method, (2) the astrometry, (3) the transit method, (4) the timing method, (5) microlensing, and (6) direct imaging.

The ESPRESSO mission might detect planets around sunlike stars by the radial velocity method. The CoRoT mission, EChO mission, and Kepler mission are searching for planets by the transit and radial velocity method. A further proposed mission, which is foreseen to look after Earth-like planets, is PLATO.



But none of these missions are able to get information on the presence or absence of an atmosphere and therefore are not really able to give evidence of its habitability. These detection methods have to be developed and improved. One solution might give the IR-flux spectroscopy. Some proposals by NASA/JPL like a new mission called FINESSE would like to fill this gap of remote sensing exploration missions (see “[Habitability on Kepler Worlds: Are Moons Relevant?](#)” by Chela-Flores in this volume).

The search for habitable planets or moons in our solar system seems to be much more promising. The NASA Curiosity Mission has just started on the surface of Mars, and a variety of other Mars exploration projects are foreseen in the near future (e.g., ExoMars) to find out if Mars is or was habitable and if we will be able to detect traces of extant or extinct life.

The IceMole Study is also a very interesting project which might realize in the near future an exploration mission to the polar caps of Mars, Enceladus, or Europa (see chapter “[Clean In Situ Subsurface Exploration of Icy Environments in the Solar System](#)” by Dachwald et al., this volume). A semi- or complete autonomous system within a cryo-lander device will land in areas near chaotic terrains, ridges, and cracks and will drive a screwing melting probe into the ice for exploration of the ice, possible minerals, or water pocket within the ice and organic material. Perhaps this mission might show, if the icy moons might be an alternative option of habitable world to our blue little dot in the universe, our home planet Earth.

### **3. A New (R)evolution After the Copernicanian and Darwinian (R)evolution**

Some words are needed to be expressed: we have to think about the impact of the discoveries of habitable worlds and possibly extraterrestrial life in the universe on mankind’s society. It is clear that such kind of discoveries will have a significant influence on the existing Earth-centric view about the appearance and existence of life. If life exists elsewhere in the universe, life cannot be only classified as a hazardous event but as an inevitable consequence of all physical and chemical processes in the universe.

The uniqueness of life is compromised and after the Copernicanian and Darwinian (R)evolution a new mode of thinking might start in the mankind’s society. Religions and Philosophy might revise again their holy scriptures and have a closer look if this would be consistent with their tradition and their way of thinking and believing.

Again also the centered role of humans in general because of the only known “intelligent” life form can be compromised. Because question will arise: If we find extraterrestrial life, even if it is just microscopic life, could it be that other intelligent beings also exist in one of the corners of our universe? The search for intelligent life will then be in focus and a start of such new projects is just a question of time.

Maybe, that by curiosity, we as human beings will be triggered to increase the exploration of the new discovered worlds and new life forms, and that in particular our own conscience will feel comfortable and not abandoned in such a life-friendly universe.

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