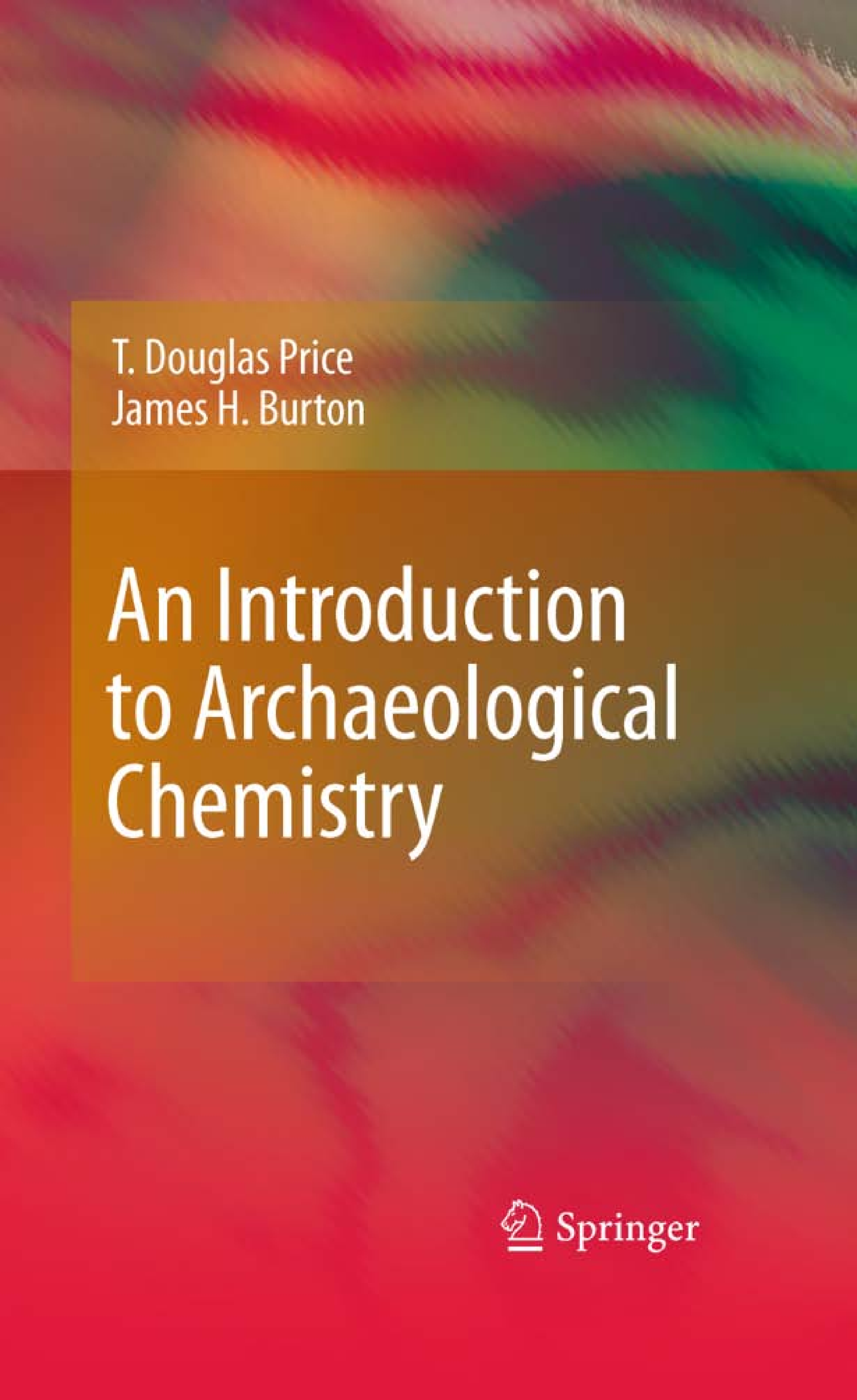

T. Douglas Price
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An Introduction to Archaeological Chemistry

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Preface

Thirty some years ago, one of us (Doug) was excavating Stone Age sites in the Netherlands, trying to learn how small hunting groups survived there 8,000 years ago. All that remained of their former campsites were small stone tools and tiny pieces of charcoal from their fireplaces. Questions like what did they eat, how often did they move camp, or even how many people lived there, were almost impossible to answer from the scant materials that survived. A frustration grew – these were important archaeological questions.

I remembered some research that a fellow student had been doing during my years at the University of Michigan – measuring the elemental composition of human bones to learn about diet. Maybe this was a way to find some answers. I began similar investigations in my job at the University of Wisconsin-Madison. By 1987, that research had provided some interesting results and the National Science Foundation gave us funding for the creation of the Laboratory for Archaeological Chemistry and its first major scientific instrument. Equally important, the NSF money paid for a new position for another scientist. Jim Burton joined the lab as associate director.

Jim was trained as a geochemist, Doug as an archaeologist. This combination of education, background, and knowledge has been a powerful and effective mix for our investigations of the human past through archaeological chemistry. We have worked together for more than 20 years now, analyzing stones, bones, pottery, soils, and other fascinating things in the lab. We have collected deer legs in Wisconsin, snails and chicken bones in Mexico, horse teeth in China, and semi-frozen, oily birds from Alaska, in addition to prehistoric artifacts and human bones from a number of different places on earth. There are many, many stories.

For a number of years we have together taught a course in archaeological chemistry. We have written this book because we believe there is a critical need for more archaeological scientists. The major discoveries in archaeology in the future will come more often from the laboratory than from the field. For this reason, it is essential that the discipline have well-trained scientists capable of conducting a variety of different kinds of instrumental analyses in the laboratory. That means that more college courses in the subject are needed and that good textbooks are essential. We hope to entice students to the field of archaeological science by making the subject more accessible and interesting. Too many students are turned off by scientific courses because they find them boring and/or incomprehensible. That situation needs to change and good textbooks can help.

This book is an introduction to *archaeological chemistry*, the application of chemical and physical methods to the study of archaeological materials. Many of the most interesting discoveries being made in archaeology today are coming from the laboratory. Archaeological chemists study a wide variety of materials from the past – including ceramics, bone, stone, soils, dyes, and organic residues. The methods and techniques for these studies are described in the following pages.

Archaeologists are often found in the laboratory and there are many kinds of labs. There are laboratories for studying animal remains, laboratories for plant materials, and laboratories for cleaning and spreading out artifacts for study. There are other laboratories where archaeologists and physical scientists investigate the chemical properties of materials from the past. These are wet-labs with chemical hoods, balances, and a variety of scientific instrumentation.

Not all kinds of laboratory archaeology are covered in our book. We do not write about the analysis of animal bones or plant remains. We don't talk much about dating techniques, although radiocarbon measurement is mentioned. There is also a case study presented involving the authentication of the Shroud of Turin discussed in Chap. 5. We do not spend a lot of time on ancient DNA studies, although such genetic work will likely be a major part of archaeological discoveries in the future. Genetics in archaeology is the subject for a different kind of book. Our concern is with archaeological chemistry, the study of the elements, isotopes, and molecules that make up the material remains from the past.

This book is intended to introduce both professional archaeologists and students to the principles and practices of archaeological chemistry. We hope this book will be a guide to this exciting branch of archaeology. We have worked hard to keep the text straightforward and clear and not too technical. Chemical tables and mathematical formulas are mostly confined to the appendix.

We have designed the book so that the reader is introduced to the instrumental study of archaeological materials in steps. We begin with vocabulary and concepts, followed by a short history of archaeological chemistry to place such studies in perspective. We provide a brief survey of laboratories that do such studies. An important chapter considers what archaeologists want to know about the past. These questions guide research in archaeological chemistry.

Chapter 3 on archaeological materials outlines the kinds of objects and materials that are discovered in excavations and used in the study of the past. A subsequent chapter deals with the methods of analysis, the kinds of studies that are usually done (magnification, elemental analysis, isotopic analysis, organic analysis, mineral/compound analysis) and the kinds of instruments that are used. These chapters include illustrations and examples aimed at nonscientists – to make clear how the characteristics of materials, the framework of methods, and the capabilities of instruments together can tell us about the past.

A series of chapters then describe and document what archaeological chemistry can do. A brief introduction to these last chapters outlines the strengths of archaeological chemistry. We then consider the kinds of archaeological questions that laboratory science can best address and we discuss the principles and goals of archaeological chemistry. The chapters then move to the heart of the matter. What can archaeological chemistry tell us about the past? These chapters offer description and case studies of these major areas of investigation: identification, authentication, technology and function, environment, provenience, human activity, and diet. Case studies involve stone tools, pottery, archaeological soils, bone, human burials, and organic residues. We will consider some of the more interesting archaeological investigations in recent years including the Getty kouros, the first king of the Maya capital of Copan, the spread of maize agriculture, house floors at the first town in Turkey, and a variety of others. These case studies document the detective story that is archaeology and archaeological chemistry.

The concluding chapter provides a detailed case study which involves a number of different techniques, instruments, and materials. Ötzi the Iceman from the Italian Alps is probably the most studied archaeological discovery of our time. We review some of the investigations that have been conducted to demonstrate how archaeological chemistry can tell us much more about the past. This last chapter also includes a look ahead at the future of the field of archaeological chemistry, what's new and where things may be going in the coming years.

It is our hope that by the end of the book you will have a good grasp of how archaeological chemistry is done, some of the things that have been learned, and a desire to know more about such things.

Practical features of the book appear throughout. New words and phrases are defined on the page where they appear and combined in the glossary at the back of this book. We have tried to have informative and attractive artwork in the book. Illustrations are an essential part of understanding the use of science in archaeology. We carefully selected the drawings and photos to help in explaining concepts, methods, and applications. Tables of information have been added where needed to condense textual explanation and to summarize specific details. The back of the book contains additional technical information about archaeological chemistry, lab protocols, tables of weights and measures, the glossary, references, and a subject index.

There are many people involved in many ways to make a book – our lab, our students, our families, our editors, our reviewers. Theresa Kraus initiated the idea for this volume and has been our senior editor. Kate Chabalko, editorial assistant at Springer, has been our direct contact and done a great job in helping us get the manuscript ready for publication. We would also like to thank the outside reviewers who offered their time and knowledge to greatly improve this book.

Lots of friends and colleagues have helped us with information, photos, illustrations, and permissions. The list is long and includes the following: Stanley Ambrose, Søren Andersen, Eleni Asouti, Luis Barba, Brian Beard, Larry Benson, Elisabetta Boaretto, Gina Boedeker, Jane Buikstra, Patterson Clark, Andrea Cucina, Jelmer Eerkens, Adrian A. Evans, Karin Frei, Paul Fullagar, Brian Hayden, Naama Goren-Inbar, Kurt Gron, Björn Hjulstrom, David Hodell, Brian Hayden, Larry Kimball, Corina Knipper, Jason Krantz , Z.C. Jing , Kelly Knudson, Petter Lawenius, Lars Larsson, Randy Law, David Meiggs, William Middleton, Nicky

Milner, Corrie Noir, Tamsin O'Connell, Dolores Piperno, Marianne Rasmussen, Susan Reslewic, Erika Ribechini, Henrik Schilling, Steve Shackley, Robert Sharer, James Stoltman, Vera Tiesler, and Christine White. No doubt we failed to include one or two individuals in this list. Please accept our thanks as well. Many students have contributed to our thoughts about teaching archaeological chemistry and to the success of our laboratory. Some of the names that come to mind include Joe Ezzo, Bill Middleton, Corina Knipper, Kelly Knudson, David Meiggs, and Carolyn Freiwald. Heather Walder helped produce the artwork for the book and Stephanie Jung worked on obtaining permissions for the use of illustrations. The University of Wisconsin has given the laboratory a good home for many years, along with substantial financial support. The National Science Foundation has provided continuous funding since the lab was created. This volume is one way of saying thank you.

Madison, WI

T. Douglas Price
James H. Burton

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Archaeological Chemistry

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A book on archaeological chemistry must cover a lot of ground. Both subjects, archaeology and chemistry, are large, rich, and dense. At the same time the two are very different. Archaeology belongs to the humanities or social sciences; some would call it an historical science. Archaeology is usually associated with the outdoors, ruins, excavations, piles of dirt, and artifacts of stone, ceramic, or metal. Chemistry, on the other hand, happens indoors, in the laboratory. It's a hard science – the textbooks are weighty, the formulas are complex, the chemical terms endless. Chemistry is associated with beakers and acids, Bunsen burners, strange smells, and lab coats. How can two such different fields fit together?

Archaeological chemistry thus sits at this juncture of two branches of the tree of knowledge. This combination of fields, in fact, provides an exciting interface of science where many extraordinary new discoveries are being made. This combination of academic disciplines is the focus of our book.

This first chapter of the book provides an introduction, of course. Because each realm of scientific investigation has its own vocabulary, it is essential to learn to speak the language in order to communicate and comprehend. The next section, *Archaeological Chemistry*, considers some of those words and their meanings to provide some language training and gain a sense of what the subject is about.

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The subsequent section, *Terms and Concepts*, continues this lesson with a brief discussion of basics – matter, organics, energy, measurement, precision, samples, and data – as these issues relate to archaeological chemistry.

The third section of this chapter, *A Brief History of Archaeological Chemistry*, is intended to place the field in the context of its past. This history helps to better understand how such studies got to the place they are today and what is important and new in the field. The fourth and final section concerns *Laboratories*, the home bases of archaeological chemistry and the folks in white lab coats. We provide an impression of what such labs are like and how they are used. Within this section we offer a detailed description of our own home, the Laboratory for Archaeological Chemistry at the University of Wisconsin–Madison. Let's get started.

1.1 Archaeological Chemistry

It seems best to begin this book on archaeological chemistry with some definitions and concepts to place the subject within the larger field of archaeology. *Archaeology* is the study of the human past through the material remains that survive. Archaeology covers a great range of times, places, principles, and methods. Archaeologists study recent battlefields in Belgium, Bronze Age temples in China, and our earliest ancestors in Africa six to seven million years ago.

There are many kinds of archaeology, including archaeological science. *Archaeological Science* is a general term for laboratory methods in archaeology that includes both instrumental and noninstrumental areas such as faunal analysis, archaeobotany, human osteology, and even some aspects of stone and ceramic analysis. In some cases, these methods can also be applied in the field (Fig. 1.1).

Archaeometry is a specialized branch of archaeological science that involves the measurement of the physical or chemical properties of archaeological materials in order to solve questions about chemical composition, technology, chronology, and the like. Sometimes described as "instrumental" archaeology, archaeometry also includes things like dating methods, remote sensing, and ancient DNA. The term *molecular archaeology* is sometimes used to refer to the organic component of archaeological chemistry and particularly to the investigation of ancient DNA in plant and animal remains, including humans. In terms of scientific pedigree, physicists are usually responsible for dating laboratories and geneticists are often the experts on DNA.

Archaeological chemistry is a subfield of archaeometry and involves the investigation of the inorganic and organic composition – elements and isotopes, molecules and compounds – of archaeological materials. Archaeological chemistry is primarily concerned with (1) characterization – measuring the chemical composition of a variety of prehistoric materials, and (2) identification – determining the original material of an unknown item. Information on identity and composition is used for different purposes such as (1) authentication – verifying the antiquity of an item, often associated with works of art, (2) conservation – determining the optimal means for preserving and protecting archaeological items endangered by decay and

Fig. 1.1 Archaeological science in the field. Excavations in the background supply samples for a Fourier Transform Infrared Spectrometer, center, and microscopic identification, foreground. This project is at Tell es-Safi/Gath, an archaeological site in Israel occupied almost continuously from prehistoric to modern times. Photo courtesy of Kimmel Center for Archaeological Science, Weizmann Institute of Science, Israel

decomposition, and (3) answering archaeological questions about the past. Archaeological questions are the subject of the next chapter.

Much of such research involves elemental and isotopic analyses of inorganic materials or the identification of compounds in the case of organic specimens. These studies can tell us about subsistence and diet, exchange and trade, residence, demography, status, and many other aspects of prehistoric human behavior and activity. In addition, information from the composition of archaeological materials is often useful in the conservation of these items for museum display and storage. The primary goals of archaeological science are to learn more about the human past and preserve its remnants for the future.

The field of archaeological chemistry is an exciting one, combining methods, principles, and ideas from both the humanities and the physical sciences. It is at this interface of disciplines that extraordinary new research often takes place. It is also a place where student and professional involvement can focus to engage nonscience individuals in the sciences. At the same time, because of the two branches of the discipline, there are some different ways of doing things and two groups doing them. These two groups are (1) archaeologists employing the physical sciences and (2) physical scientists interested in archaeology. Archaeologists usually have interesting questions that can be answered by instrumental analysis, but they often don't understand the method. Physical scientists know the instruments and understand the analyses, but often don't grasp the archaeological questions or the complex nature of archaeological data.

It is also the case that the instruments needed to answer questions about elemental concentrations, isotopic ratios, and molecular composition are rare, complex, temperamental, and costly. Archaeologists often collaborate with chemists and other physical scientists who have such instruments in their labs. In many instances, these collaborations are short-lived and focused on a single question. However, scientific instruments are becoming easier to maintain and operate and more accessible in terms of costs. This means that archaeologists are beginning to use this equipment in their own laboratories. Research is now often being done in the context of archaeological knowledge.

Archaeological chemistry is a rapidly growing field for good reason. Today, a number of innovative approaches are revealing exciting new information about the past. Elemental and isotopic analyses of prehistoric objects can tell us about subsistence and diet, exchange and trade, residence, demography, status, and other aspects of prehistoric human behavior and organization. Organic analyses are revealing the contents of pottery and how ancient implements were used. Genetic studies of ancient DNA are outlining the origins and relationships of past human groups.

Many of the major discoveries in archaeology in the future will be made in the laboratory, not in the field. Archaeological chemistry will unlock many new secrets of the past, using methods and instruments that are now only in someone's imagination. For that reason, it is very important that more archaeological scientists are trained, that more archaeological laboratories are constructed and filled with sophisticated instruments.

At the same time, a basic principle must be kept in mind. Archaeological chemistry must be problem oriented, investigating questions about past human behavior and activity that can be answered in the laboratory. The focus must remain on understanding our ancestors, their activities, and their societies in the past. The most important question in any research is "What do you want to know?" On that basis the archaeological scientist can decide on the appropriate methods, samples, instruments, and scale of analysis to try and find the answer. But without the question, without the research problem, the study will simply be an application of method.

1.2 Terms and Concepts

An understanding of some of the basic vocabulary and principles employed in archaeological chemistry is essential to understanding this field of study. In the following paragraphs a brief discussion of matter and energy includes these relevant concepts. This is followed by a consideration of measurement issues and the very small quantities of elements, isotopes, and molecules we often have to measure in the lab. Finally the meaning of accuracy, precision, and sensitivity provide perspective on the results obtained from scientific instruments.

1.2.1 Matter

As we noted at the beginning of this book, archaeological chemistry involves the investigation of the inorganic and organic composition – elements and isotopes, molecules and compounds – of archaeological materials. To understand the composition of materials we have to begin with atoms, the building blocks of matter.

All matter is composed of *atoms* (Fig. 1.2). Atoms have three major components: neutrons, protons, and electrons. *Neutrons* and *protons* make up the core of an atom and have about the same weight. Neutrons have no electrical charge; protons have a positive charge. *Electrons* spin around the core of neutrons and protons with a negative electrical charge and a very small mass. *Ions* are electrically charged atoms that have lost or gained electrons.

Atoms vary in the number of protons and neutrons they contain, resulting in different *atomic weights*; these different weights make up the 92 chemical *elements* in nature and in the *periodic table* (Fig. 1.3). The *atomic number* of an element is the number of protons in the nucleus. The *atomic mass* is the total mass of protons, neutrons and electrons in a single atom, often expressed in unified atomic mass units (AMU).

A lot of important information about the chemical elements is contained in a periodic table. The periodic table is a tabular illustration of the elements. Each element is listed with its chemical symbol and atomic number. The layout of the periodic table demonstrates a series of related, or periodic, chemical properties. Elements are arranged by increasing atomic number (the number of protons). Elements with similar properties fall into the same vertical columns. Elements with atomic numbers 83 or higher (above bismuth) are unstable and undergo radioactive decay over time. There are many examples of this table and some of the interactive versions on the Internet provide many details about the full name of the element, isotopes, atomic mass, and other information.

Eighty of the first 82 elements have stable isotopes. *Isotopes* share the same atomic number, but a have different numbers of neutrons. Ratios of one isotope to another of the same element provide important measures for the study of archaeological materials.

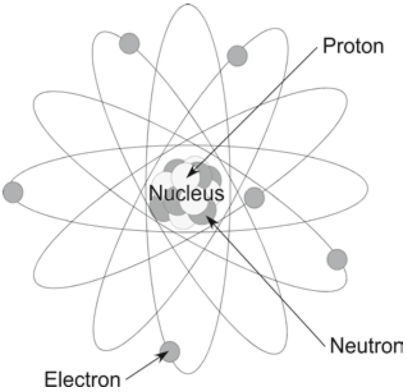
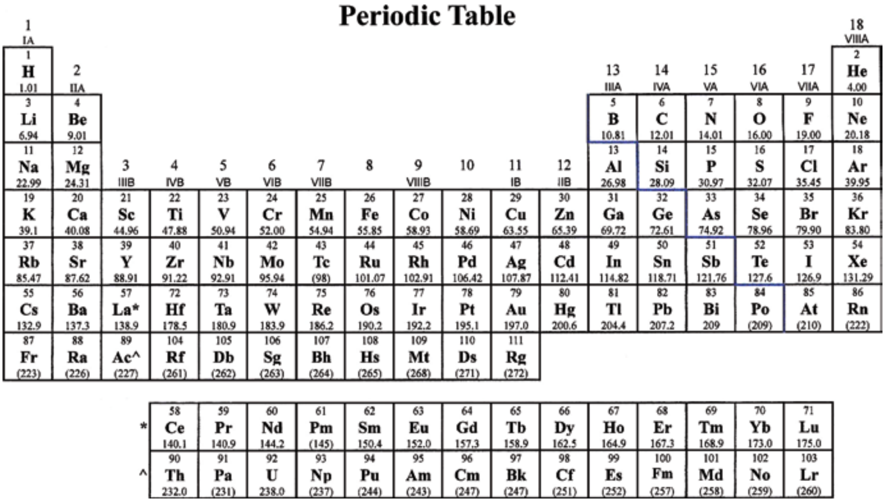


Fig. 1.2 Components of an atom



Periodic Table

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 **H** 1.01																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.1	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.29
55 **Cs** 132.9	56 **Ba** 137.3	57 **La*** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac^** (227)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (264)	108 **Hs** (265)	109 **Mt** (268)	110 **Ds** (271)	111 **Rg** (272)							

*	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
^	90 **Th** 232.0	91 **Pa** (231)	92 **U** 238.0	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)

Fig. 1.3 Periodic table of the elements

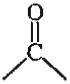
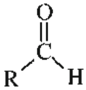
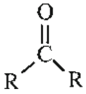
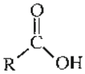
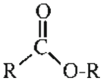
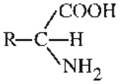
Every substance on earth is made up of combinations of some of the first 92 elements. A *molecule* is a combination of atoms held together by bonds (e.g., water is H_2O). *Compounds* are combinations of two or more different elements chemically bonded together in a fixed proportion in either organic or inorganic molecules. The law of constant composition states “All samples of a compound have the same composition; that is, all samples have the same proportions, by mass, of the elements present in the compound.” *Organic compounds* make up the tissues of living organisms and have the element carbon as a base. *Inorganic compounds* do not normally contain carbon.

Most of the methods and instruments discussed in this book are concerned with the analysis of the composition of organic and inorganic materials. These procedures are designed to identify the elemental, isotopic, or molecular structure of the material. Archaeological chemistry at the organic level is particularly complex and the next section provides some terms and concepts of importance in understanding this subject.

1.2.2 Organic Matter

Organic molecules contain carbon and hydrogen and often other elements such as oxygen, nitrogen, and sulfur. Carbon has an extraordinary property of being able to bond with four other atoms, which can include other carbon atoms, which can in turn link to more carbon atoms. The variety of possible molecules is virtually infinite. The names of these molecules are determined by the number and arrangement of carbon atoms along with other atoms such as oxygen are present and the way they are connected to the carbon atoms. This arrangement of the other atoms is called a “functional group” because they tend to determine the chemical properties of the molecule. Some of the most important functional groups are listed in Table 1.1.

Table 1.1 Functional groups of organic molecules with description, structure, text, and examples

Functional group	Description	Structure	Text	Examples
Alkyl	Hydrocarbon root with only carbon and hydrogen	R—	$CH_3(CH_2)_n$–	Methane CH_4 Propane C_3H_8
Alcohol	Root bonded to an Oxygen atom, which is also bonded to hydrogen	R—OH	R–OH	Methanol $CH_3(OH)$ Glycerol $C_3H_5(OH)_3$ Propanol $C_3H_7(OH)$
Carbonyl	Carbon doubly bonded to oxygen		–CO–	Key functional part of aldehydes, ketones, esters, carboxylic acids and amino acids
Aldehyde	Root bonded to a carbon with a double bond to oxygen and to a hydrogen atom		R–CHO	Propanal $C_3H_7(CHO)$
Ketone	A carbon atom doubly bonded to oxygen between two root groups (which may be different)		R–CO–R	Methyl ethyl ketone
Carboxylic acid	Root bonded to a carbon which is double bonded to oxygen and bonded to an alcohol –OH		R–COOH	Acetic acid $CH_3(COOH)$
Ester	A carboxylic group between two root alkyl groups		R–COOR	Methyl acetate Ethyl acetate
Amine	Root bonded to nitrogen, which is also bonded to two hydrogens	R—NH_2	R–NH_2	Methyl amine Ethyl amine
Amino Acid	Root bonded a carbon that is attached to both an amine and to a carboxylic acid group		R–$CONH_2$	Glycine Tryptophan Proline

These basic organic molecules can react with each other to form larger, more complex "macromolecules." Amino acids can combine to form larger "peptide chains," which in turn can combine to form protein molecules. Likewise, simple sugar molecules can combine to form polysaccharide molecules that combine to form starches and cellulose.

Originally, organic molecules were defined as those associated with living organisms. The organic compounds that remain in prehistoric materials are thus almost by definition complex macromolecular residues of biological materials. Organic residues include things like blood, tissue, food residues, oils, fats, greases, pitches, tars, and resins. A complex variety of molecules make up these organic compounds, including lipids, nucleic acids, amino acids, sugars and starches, and other hydrocarbon compounds.

There are two major areas of current research involving archaeological remains: residue analysis and ancient DNA (aDNA). Organic chemists study the residues; biochemists and geneticists study aDNA. Both of these areas of investigation are discussed briefly below. Ancient DNA is really outside the scope of this book, but its growing importance in archaeological research requires a brief mention. Organic residues, and especially trace organic compounds, are considered in more detail in Chap. 6, Methods of Analysis.

1.2.2.1 Ancient DNA

For the ultimate in specificity, archaeologists are working with molecular biologists to examine traces of ancient *DNA* (deoxyribonucleic acid). DNA is slightly analogous to a long peptide in that it consists of an extremely long chain of nucleotide units, which are composed of a phosphate molecule and a sugar, deoxyribose, to which is attached one of four functional groups: adenine, cytosine, guanine, or thymine. Even though this means there are only four possible units, this simplicity creates DNA, the most complex of all biomolecules. Within this structure is the code for all of the proteins which in turn are responsible for other biomolecules that produce all plants and animals. DNA is distinct not only at the species level, but also permits the identification of individuals.

DNA is the genetic material of life. DNA is a long molecular chain of units called nucleotides, each composed of one of four base units (adenine, cytosine, guanine, or thymine). Genetic information is coded in a sequence of nucleotides in individual genes. Individual genes that determine the growth and characteristics of individuals are segments of DNA molecules. There are some 50,000 genes in the DNA of a human being. Molecules of DNA also have “intergenic” spaces between genes with no biological information that are also important as markers for differences between individuals and between populations.

Two general kinds of studies, on either modern or *ancient DNA*, are being done to investigate the human past. Modern populations are studied to identify genetic differences and the time at which groups of people diverged in the past. These studies generally use DNA in blood or other accessible cells. These studies of modern populations have been used, for example, to estimate the time of the first appearance of modern-looking humans and to examine the spread of Neolithic farmers into Europe.

Ancient DNA (aDNA), preserved genetic material in the nucleus of cells, can sometimes be found in archaeological plant, animal, and human remains (Fig. 1.4). The discovery of DNA preserved in prehistoric human bone was first reported in 1989. Since that time, numerous studies have looked for and found DNA in ancient materials. Samples from human bone, for example, can provide information on sex or genealogy of an individual, or on genetic relationships between populations and migration. In many cases, molecules in ancient DNA have been damaged by decay and degradation over time and are found usually as short segments of the larger original molecule. This breakdown of the molecule makes it more difficult, but not impossible, to reconstruct the original genetic information.

Analysis of ancient DNA has been greatly improved by the development of the technique known as the polymerase chain reaction (PCR) which results in the cloning

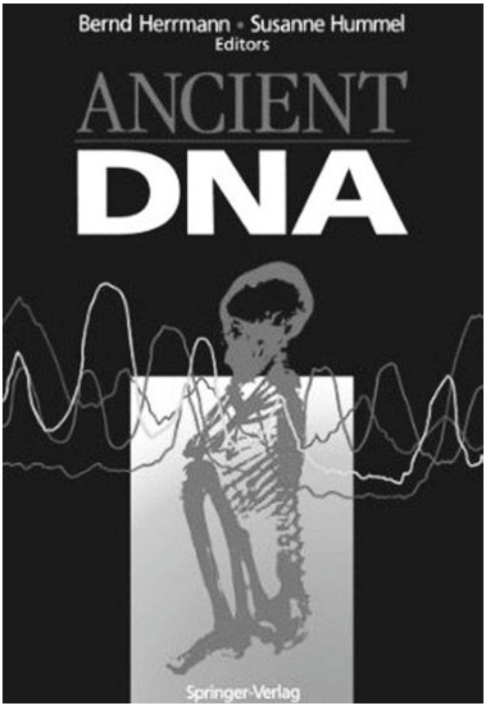


Fig. 1.4 Cover of the book *Ancient DNA* by Herrmann and Hummel, Springer Publications

of large quantities of material for analysis even when only a very small sample is available – often the case with archaeological remains. Theoretically even a single molecule, as well as badly degraded segments of molecules, can be analyzed with the help of the PCR technique.

Contamination is a significant problem in studies of aDNA. Since only small amounts of very fragmentary genetic material are present in samples, any contamination from living humans during excavation or laboratory analysis can mask or hide the prehistoric materials. Researchers must use great caution when removing and preparing samples for such analyses.

1.2.3 The Electromagnetic Spectrum

The discussion above has focused on the identification of matter to help comprehend the composition of archaeological materials. In order to understand how the instrumentation used in archaeology labs works, we need to understand something about energy and how it is used to measure matter. Most laboratory instruments use different kinds of energy in the form of light or other radiation. The best way to describe these different energies is in terms of the electromagnetic spectrum.

The *electromagnetic spectrum* (usually just called the spectrum) covers the range of all possible electromagnetic radiation. Table 1.2 provides information on the types of radiation in the spectrum, their frequency and wavelength, and the type of transition involved in creation of the radiation. One version of this spectrum is illustrated in Fig. 1.5. The type of radiation on the spectrum is defined by wavelength, or frequency, and energy. The light we can see is the visible part of the electromagnetic spectrum

Table 1.2 Radiation in the electromagnetic spectrum, frequency, wavelength, and transition

Type of radiation	Frequency range (Hz)	Wavelength range	Type of transition
Gamma-rays	10^{20}–10^{24}	$<10^{-12}$ m	Nuclear
X-rays	10^{17}–10^{20}	1 nm–1 pm	Inner electron
Ultraviolet	10^{15}–10^{17}	400 nm–1 nm	Outer electron
Visible	4–7.5×10^{14}	750 nm–400 nm	Outer electron
Near-infrared	10^{12}–4×10^{14}	2.5 µm–750 nm	Outer electron molecular vibrations
Infrared	10^{11}–10^{12}	25 µm–2.5 µm	Molecular vibrations
Microwaves	10^{8}–10^{12}	1 mm–25 um	Molecular rotations Electron spin flips
Radio waves	10^{0}–10^{8}	>1 mm	Nuclear spin flips

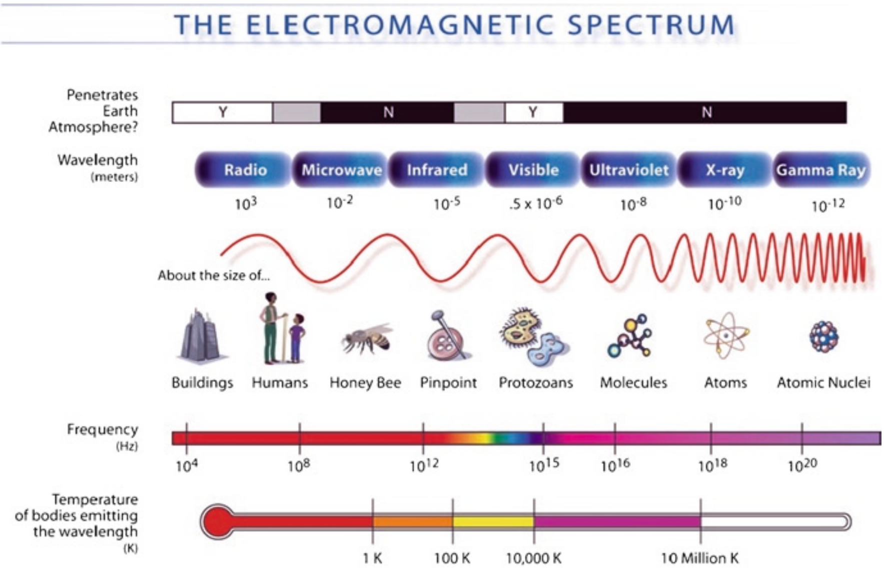


Fig. 1.5 The electromagnetic spectrum: radiation type, scale of wavelength, frequency, and temperature

that ranges from red at the low-energy, long wavelength end through orange, yellow, green, and blue to violet at the high-energy, short wavelength end. The invisible part of the electromagnetic spectrum extends in both directions: from red light into infrared light and microwave and radio waves with wavelengths from meters to hundreds of meters and more. At the other end, the spectrum extends into ultraviolet radiation, X-rays, and into high-energy gamma-rays. The temperature (equivalent to energy) at which these waves and rays are most intense is also shown in the figure and increases to the right side of the spectrum along with shorter wavelength.

The wavelengths involved in the spectrum range from thousands of kilometers to a fraction of the size of an atom. In principle the spectrum is infinite and continuous. Known objects in Fig. 1.5 show the approximate scale of these wavelengths. Just as one cannot measure atoms or molecules with a yardstick, radio waves are too far apart to interact with atoms and cannot be used for compositional analyses of archaeological materials. Microwaves and infrared radiation likewise have wavelengths too large for atomic studies, but they are appropriate for studies of larger organic molecules. The remaining part of the spectrum: visual and UV-light, X-rays, and gamma-rays have wavelengths that can be used for the examination of nature at the atomic scale to determine elemental and isotopic composition. The instruments described in Chap. 4 utilize these different kinds of radiation to examine and measure the composition of archaeological materials.

1.2.4 *Measurement*

To identify the composition of archaeological materials and measure very small quantities of elements, isotopes, and molecules, we need to have appropriate units of measurement and some concept of the amounts we are describing.

Laboratories around the world use the same standardized units of measurements, called the International System of Units, or SI. The SI system has seven base units from which all the others are derived. The base units of this system include a unit of length, meters, and a unit of mass, kilograms. Volume is derived unit and is measured in cubic meters. These units can be described in various sizes. Common divisions of these units are given in Table 1.3. Thus we can measure distance in meters, centimeters or millimeters; we can measure weight in kilograms, or micrograms; we can measure volume in cubic meters, cubic centimeters, and so on.

Table 1.3 Common prefixes used in archaeological chemistry

Mega (M) = 1,000,000× = 10^{6}×
Kilo (k) = 1000× = 10^{3}×
Deci (d) = 0.1× = 10^{-1}×
Centi (c) = 0.01× = 10^{-2}×
Milli (m) = 0.001× = 10^{-3}×
Micro (μ) = 0.000001× = 10^{-6}×
Nano (n) = 0.000000001× = 10^{-9}×

These SI units are absolute measures of distance, mass, volume, and more. It is not always possible to measure absolute amounts in a meaningful way. In such cases, a relative measure of quantity is made reporting the abundance or concentration of an element, isotope, molecule, or compound. Concentrations are reported as a proportion of the total amount of material analyzed or as a ratio to another element, isotope, or molecule. Some of these measures include parts per hundred, or percentages (%), parts per thousand, aka parts per million (‰), parts per million (ppm), or parts per billion (ppb).

Concentrations of small amounts of inorganic matter are often measured in ppm. Such quantities are difficult to comprehend. To understand what this means it might help to imagine an average two-story, three-bedroom house. It would take approximately one million marbles to cover all the floors of the house. One part per million would be one of those marbles in the house. Another way to think about numbers is in terms of volume. Some people like to drink martinis, a mixture of mostly gin and a little vermouth. The less vermouth the drier the martini. A typical martini might contain 2½ oz of gin and ½ oz of vermouth (ca. 17%, or 1.7‰); in metric terms that's about 7.5 cl gin and 1.5 cl vermouth. Throw in an olive, onion, or lemon peel. To make the martini drier we could add only 5 ppm vermouth to the gin. If ½ oz of vermouth were 5 ppm, we would need to add it to almost 800 gallons of gin, enough to fill a very large, 12-person hot tub. Enjoy.

1.2.5 Accuracy, Precision, and Sensitivity

Important reasons for choosing an instrument for elemental analysis are precision, accuracy, and sensitivity. These terms are also important for understanding what our measurements mean. *Accuracy* is the ability of an instrument to provide the correct answer. *Precision* is the measure of how exactly an instrument can reproduce the same measurement, regardless of how correct that measurement might be. An instrument that gave readings of 68, 70, and 72 would be more precise than an instrument that gave readings of 80, 90, and 100, regardless of whatever the true value might be. If the true value in the above example were 100, then the second instrument would be more accurate, although less precise, than the first. An instrument measuring 98, 100, and 102 for the same sample would be both more accurate and precise. The concepts of accuracy and precision are illustrated in Fig. 1.6.

Sensitivity is the measure of the smallest amount that can be reliably measured. An instrument that can measure microgram (0.000001 g) quantities is much more sensitive than one that can only measure milligrams (0.001 g). Precision is thus an important limit to sensitivity. If the uncertainty, or imprecision, of a measurement is ±0.0005 g, then the instrument is incapable of reliable microgram (0.000001 g) measurements, but can easily measure milligram (0.001 g) quantities.

Although it might seem paradoxical, precision is generally the most important criterion of all three, because sensitivity is limited to the level of precision. Moreover, if the measurements are precise, an analysis can be made of standard samples of known composition, and errors can be quantitatively determined and

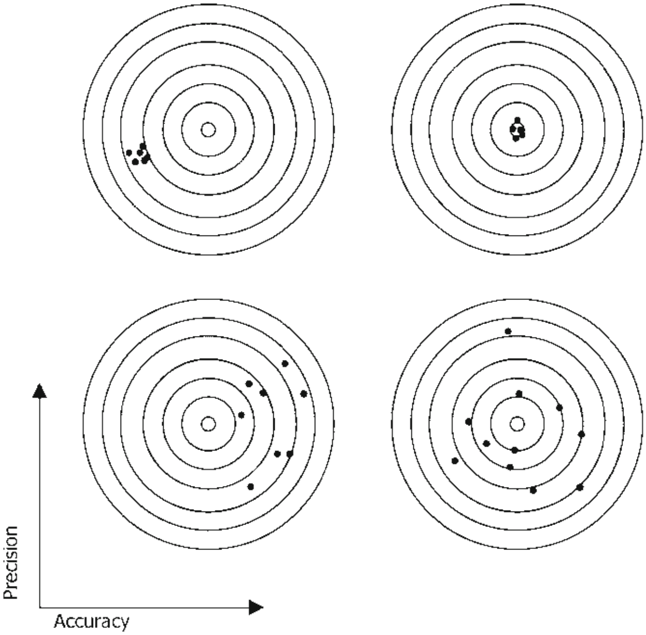


Fig. 1.6 A graph of increasing accuracy (horizontal axis) versus precision (vertical axis). When both are low, the data do not fall close to the correct value (center of target) nor do they cluster. As precision increases the data points become more clustered. As accuracy increases they become closer to the center. When both accuracy and precision are high, they cluster at the correct value

adjusted. If the results were not precise to begin with, then such a correction factor would be limited by the imprecision. In cases where one needs to know the actual amount in a sample, especially when comparing data to similar analyses from other instruments, then accuracy and precision are both important. In some cases, results are only for comparative purposes. The question is whether one sample differs significantly from another, in which case the accuracy of the measurement is less important than the precision.

1.2.6 Samples, Aliquots, and Specimens

There are a few other important terms that require consideration before we move on to the history of archaeological chemistry in the next section. Sampling is the process of collecting materials for analysis. Decisions about what to sample and how are important and help determine the outcome of any research. Usually it is impossible to analyze all the items or material under study and only a part of the whole can be investigated. The portion of the whole population or mass that is sampled is called the *sampling fraction*. For example, we might sample 10% of the burials in a cemetery for analysis. In many cases, however, it is impossible to know or select a specific sampling fraction and the sample that is taken can be described as grab bag.

The archaeological chemist samples what is available. For example, there are thousands and thousands of pottery fragments, or sherds, at many archaeological sites. It is simply not possible to select a specific fraction of the sherds to analyze.

The most commonly used term for a piece of material that is analyzed is *sample*. The word is used in many ways in archaeology and archaeological chemistry. A sample is a part of a larger quantity selected for analysis, but is not necessarily a fixed quantity. For our research on tooth enamel, we use the first molar from the lower jaw of a human skeleton. In one sense, the tooth itself is a sample (Fig. 1.7). We then take a sample of the enamel or crown portion of a tooth. Initially that means roughly 0.1 g of small flakes and powder from the tooth. After some cleaning and other preparation we weigh out a 5 mg portion for analysis. That 5 mg part is also a sample of the tooth enamel.

Aliquot is a more specific term, used less commonly in archaeological chemistry. Aliquot refers to an equal, measurable part of a large whole. For example, an aliquot of 5 ml of HCl (hydrochloric acid) from a large bottle of acid would be a known amount that could be repeatedly measured out. The term *specimen* normally is used to refer to units of a population and is often applied to biological materials. A frog could be a specimen for a study of the ecology of amphibians. The term specimen is not commonly used in archaeological chemistry.

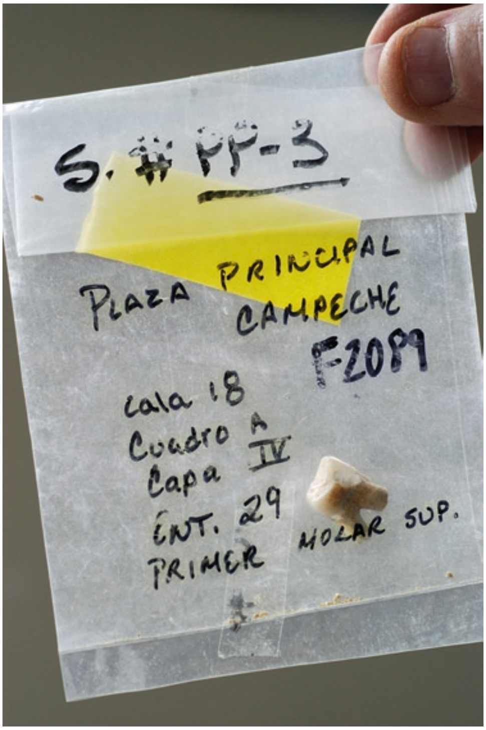


Fig. 1.7 Labeled sample bag with a first molar from the site Campeche, Mexico

1.2.7 Data, Lab Records, and Archives

Data is another term that is used widely with many meanings and applications. To most people, data means numbers, but in fact data includes many kinds of information including text and images. Data is a plural word, to emphasize the fact that they are multiple kinds of information – i.e., these data are important.

Laboratory records are kept very carefully in order to follow the progress of any study and to be able to repeat any steps that are necessary. Detailed records include all the information about samples, preparation methods, analysis results, and storage. These records provide the documentation necessary to prove that the research was done and how it was completed. All of this information together is data and there are two major places these data are kept: a notebook and computer database. The Laboratory Notebook is an essential part of lab activities and the first record of all information. A laboratory notebook is needed to explain lab procedures, write down all lab data, show how calculations are made, and discuss the results of an experiment. A record of lab work is an important document, which will show the quantity and quality of the lab work that you have done. The laboratory database is the digital archive of information from the activities, experiments, and measurements of the laboratory.

1.3 A Brief History of Archaeological Chemistry

In order to better understand archaeological chemistry, some history of the field is essential. We can begin with a quick glance at both chemistry and archaeology. The early history of chemistry goes far back in time and is difficult to trace. Before written history, only a few of the basic elements that occur in nature were known. Elements such as copper (Cu), gold (Au), silver (Ag), lead (Pb), and tin (Sn) were utilized in their native state thousands of years ago in different parts of the globe. Some of these elements began to be mixed, or alloyed, at the beginning of the Bronze Age around 5,000 years ago as their chemical properties were recognized and manipulated. Copper and tin (sometimes arsenic) were mixed to make bronze. It wasn't until the middle of the seventeenth century, however, that the first element, phosphorous (P), was discovered through scientific inquiry. By 1860, a little more than 100 years later, 63 elements had been described.

Although it is hard to believe, at the beginning of the nineteenth century, most people did not know that the earth and their ancestors had a deep past in time. Church dogma dictated that the earth had been created in 4004 BC. It was not until the middle of the nineteenth century, when natural scientists discovered the association of human artifacts with the bones of extinct animals, that an acceptance of human antiquity took root. Archaeology became an academic discipline only toward the end of the nineteenth century. Archaeology as a profession is less than 150 years old.

A combination of these two fields, archaeological chemistry also has a significant history. Several useful discussions of this history have been published (e.g., Pollard et al. 2007; Tite 1991; Trigger 1988). Early investigations in archaeological chemistry were carried out by chemists and from a modern perspective appear as rather simple applications of chemical principles to archaeological questions. Initial studies focused on one or a few elements to resolve problems about chronology, the authentication of artifacts of questionable antiquity, and site discovery.

In the mid-nineteenth century, an Austrian chemist pointed out that the chemical composition of archaeological materials could be used to identify their origins. In the 1860s a French geologist argued that the sources for Neolithic stone axes could be determined by their composition. Otto Helm, a Polish pharmacist, began the study of the composition of amber beads from excavations at the Greek site of Mycenae in the 1890s to determine their place of origin. One of the first studies of the chemistry of prehistoric pottery was published in the *Journal of the American Chemical Society* in 1895.

The first half of the twentieth century saw a series of new studies, often using technologies that resulted from the military research driven by world wars. The introduction of instrumental methods such as optical emission spectroscopy (OES) initiated several major research programs concerned with the origins of bronze in Europe. The new instruments meant a large number of samples could be measured. Thousands of bronze objects in Europe were analyzed in these studies (e.g., Caley 1964; Junghans et al. 1960).

In the 1930s, the Swede Arrhenius published a series of articles about the use of phosphate analysis to identify archaeological sites. Phosphate accumulates in places of human habitation because of accumulations of bone, feces, and other organic materials in the soil. Arrhenius used this knowledge and a rapid analysis technique to take samples of soils over a large area and determine their phosphate concentrations. High levels of phosphate usually revealed the location of an ancient settlement. His work was followed by the use of other elements as indicators of past human activity. Lutz (1951) observed enhanced concentrations of phosphorus, nitrogen, potassium, and calcium in soils from archaeological sites in Alaska. Natural occurrences of these elements are enriched by human excrement, bone, and other refuse. Cook and Heizer (1965) investigated calcium, nitrogen, and phosphorus as important indicators of past activity at California sites.

Another early example of archaeological chemistry involved the Piltdown discovery in England from the first part of the twentieth century. A human skull and ape jaw were joined together and stained to appear ancient. The forgery was passed to experts as the “missing link” between apes and humans. It took almost 40 years for new techniques to expose the deceit. Kenneth Oakley and his colleagues at the British Museum of Natural History reanalyzed the Piltdown materials in the late 1940s. They used a new “Fluorine Absorption” test and measured concentrations of fluorine as well as iron, nitrogen, collagen, organic carbon, organic water, radioactivity, and crystal structure in the bones.

Fluorine absorption can provide a kind of relative age for bone samples. Teeth and bones absorb fluorine from groundwater environment. The fluorine reacts with phosphate hydroxyapatite (the mineral component of teeth and bones) to form fluorapatite. This reaction is assumed to be relatively constant in nature. Thus, the amount of fluorine present in the fossils from the same locality should be the same if they were deposited at the same time. Oakley's work showed different levels of fluorine between the skull and the jaw of Piltdown man. The results were published in 1953 and Piltdown was finally removed from the list of our ancestors.

About the same time, a breakthrough in archaeological dating came with the discovery of radiocarbon. Willard Libby, a member of the Manhattan project entrusted with the creation of the atom bomb, recognized the nature of radioactive carbon and the significance of its short half-life (Fig. 1.8). Carbon occurs in all living things. When those things die, the radiocarbon in their bodies begins to decay. After some 5,730 years, half of the ^{14}C has disappeared and that disintegration continues until the radioisotope is gone. That process allows archaeologists to determine the age in calendar years of wood and charcoal, bone and fiber, seed and from the present until almost 40,000 years ago. For the first time, archaeologists could be fairly confident that they knew the age of what they were finding. Libby received the Nobel Prize for his discovery of radiocarbon in 1960.

Much significant work in archaeological chemistry has been done in the last 50 years. A multitude of new ideas, instruments, and procedures have been added to the tool chest of what is now called archaeological chemistry. The evolution of both methodology and instrumentation in quantitative chemistry has permitted more detailed descriptions of the composition of a variety of materials – geological,

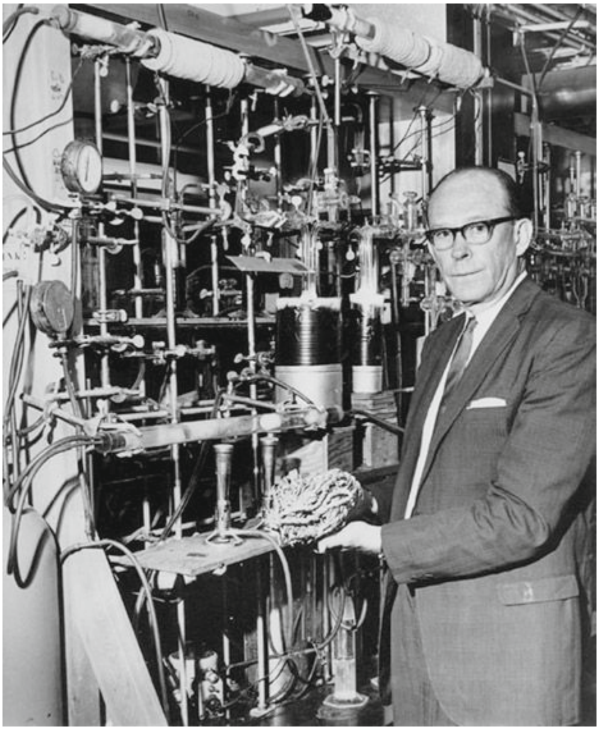


Fig. 1.8 Willard Libby, discover of the principles of radiocarbon dating, received the Nobel Prize for his efforts in 1960

biological, and archaeological. Today, a number of innovative approaches and techniques provide exciting new information about the past. The first specialized journal in the field, *Archaeometry*, appeared in 1958, followed by the *Journal of Archaeological Science* in 1974.

All the research on atomic reactions and the construction of numerous reactors around the USA led to the development of the technique of Neutron Activation Analysis (NAA) after the Second World War. NAA and other methods were used for the chemical characterization of copper, tin, obsidian, and other raw materials. Two groups began to study the sources of obsidian using its chemical composition. Obsidian is a black, volcanic glass highly prized in prehistory for its sharp cutting edge. Obsidian is only found in a limited number of places on earth. The obsidian at these sources has distinctive chemical signatures that can be identified using NAA. All the obsidian from a particular source will contain that distinctive signature. One research group in North America was interested in the long-distance trade of obsidian from Western North America to the east across the Mississippi. Another group in Britain was studying the sources of obsidian in the ancient Near East. This research on Near Eastern obsidian provides one of the cases described in Chap. 8, Provenience.

Some of the most spectacular examples of archaeological chemistry in action in recent years have come from the study of unusual human remains. Ötzi the Iceman from the Italian Alps and Kennewick Man from the State of Washington are two dramatic cases. The Iceman is the name given to the remains of a body frozen for 5,000 years in a glacier in the Italian Alps. A warm summer in 1991 melted the glacier and exposed his icy corpse. Since that time almost every known kind of archaeological science has been applied to his remains to learn about the man and his activities before he died. One of these investigations is summarized in Chap. 9, Conclusions.

A similar situation has arisen with the human skeleton found along the Kennewick River in Washington in 1996. The discovery is very important because its radiocarbon age of 9,300 years before the present makes the skeleton one of the oldest in the North or South America. The skeleton is also important because it is the focal point of a debate between archaeologists, who want to study these remains, and Native American groups in the state of Washington, who want to rebury this individual. Recently, the courts have ruled that the archaeologists could study the skeleton; the full range of archaeological science is now being applied to the bones and teeth of Kennewick Man. The ethical questions regarding the Kennewick controversy are discussed in the concluding chapter.

Today, the evolution of both method and instrumentation in quantitative chemistry is providing more detailed descriptions of the composition of a variety of materials – geological, biological, and archaeological. Today, a number of innovative approaches and techniques promise exciting new information about the past. Elemental and isotopic analyses of prehistoric objects can inform us about subsistence and diet, exchange and trade, residence, demography, status, and other aspects of prehistoric human life. Organic studies are revealing the eating habits, raw materials, agricultural fields, dyes and oils, and much more about the past. Examples of such investigations will be discussed in detail in Chap. 8, Technology and function, to document these important principles and methods.

1.4 Laboratories

Laboratories for archaeological chemistry are found in various parts of the world, usually associated with either universities or museums. Table 1.4 lists some of the facilities where such research is conducted. In addition, there are a number of commercial laboratories that do analyses for archaeologists for a fee. Laboratories often have a particular specialty or focus on a particular kind of analysis. Some labs do isotopic research; other labs do elemental analyses or organic chemistry. Some labs focus on particular materials such as obsidian, or concentrate on dating methods or food residues. Some places conduct a variety of different kinds of studies. Our Laboratory for Archaeological Chemistry in Madison investigates stone, pottery, bone, and soil using elemental and isotopic methods. We are interested in the application of inorganic chemistry to all kinds of materials for the investigation of archaeological questions.

Archaeological chemistry is done in laboratories that have the equipment, instruments, and facilities necessary for such research. The instruments range from microwave- to room-size and require elaborate electrical, plumbing, gas, cooling, and ventilation installations. Needless to say the instruments, their installation,

Table 1.4 Selected list of archaeological chemistry facilities

Aghia Paraskevi Attiki, Greece – Laboratory of Archaeometry
Alexandria, Egypt – Laboratory of Archaeometry
Amsterdam, Netherlands – Institute for Geo- and Bioarcheology
Ankara, Turkey – Archaeometry Program, Middle East Technical University
Beijing, China – Department of Scientific History and Archaeometry
Bradford, England – Department of Archaeological Science
Cagliari, Italy – Dipartimento di Scienze Archeologie e Storio-Artistische
Cambridge, England – MacDonald Institute for Archaeological Research
Cambridge, Mass – Center for Archaeological Materials
Columbia, Missouri – Archaeometry Laboratory
Knoxville, Tennessee – Center for Archaeometry and Geochronology
Leuven, Belgium – Centre for Archaeological Sciences
Liege, Belgium – Centre Européen d'archéometrie
Madison, Wisconsin – Laboratory for Archaeological Chemistry
Mannheim, Germany – Curt-Engelhorn-Centre for Archaeometry
Mexico City, Mexico – Archaeometry Laboratory
Oxford, England – Research Laboratory for Archaeology and the History of Art
Orlean, France – Institut de Recherché sur les Archéomatériux
Philadelphia, Pennsylvania – Museum Applied Science Center for Archaeology
Rehovot, Israel – Kimmel Center for Archaeological Science
Stockholm, Sweden – Archaeological Research Laboratory
Tampa, Florida – Archaeological Science Laboratory
Tempe, Arizona – Archaeological Chemistry Laboratory
Urbana, Illinois – Environmental Isotope Paleobiogeochemistry Laboratory
Zaragoza, Spain – Research Laboratory for Cultural Heritage

Table 1.5 Some equipment used in the Laboratory for Archaeological Chemistry

Ratio mass spectrometer	ICP/AE spectrometer
Chemical hood	Ultrasonic water bath
Drying oven	Vacuum pump
Petrographic microscope	Repipet dilutor
Electronic balance	Ultrapure water still
Muffle furnace	Micro electrobalance
Electronic pH meter	Desiccating cabinet
Air abrasive cabinet	Air compressor
Ultrasonic cleaners	Analytical mill
Freeze dryer	
Hot plate	

support, and maintenance are not cheap. At the same time, the research that results is priceless.

In addition to the instruments, laboratories require a complex of equipment for sample preparation, involving extraction, cleaning, washing, weighing, burning, powdering, and dissolving. This requires work places (lab benches), very pure water (water stills and filters), fume hoods, furnaces, drills, mills, balances, and much more. Samples to be powdered require drying ovens and grinding mills. Samples that must be dissolved require strong acids and heating equipment. Samples to be converted into a gas require vacuum lines and a series of pumps, filters, heaters, and frigid liquids to extract the sample for analysis. Some of the equipment used in our laboratory in Madison is listed in Table 1.5 to provide an indication of the range of equipment in a laboratory for archaeological chemistry.

Safety is of course a major consideration in any laboratory. There are extensive local and federal regulations regarding laboratory operations and the use and disposal of toxic materials. Good safety procedures involve regulations, training, and constant attention. Laboratories require the use of safety goggles and acid-resistant lab clothing for personal safety (Fig. 1.9). Most labs will be required to have emergency eye wash facilities and showers in case of accidental spills and splashes. Disposal of toxic materials is an important part of laboratory safety and federal regulations require that these liquids and gasses be treated with special care. A few of the more important safety regulations in chemical laboratories are listed in Table 1.6. Most university manuals for laboratory safety run to hundreds of pages. Safety is essential in the lab.

1.4.1 A Tour of the Laboratory for Archaeological Chemistry

The Laboratory for Archaeological Chemistry at the University of Wisconsin–Madison, founded in 1987, is a center for research and training in the chemical analysis of archaeological materials, one of a few such facilities in the USA. The laboratory and its continuing operation are made possible by grants from the US

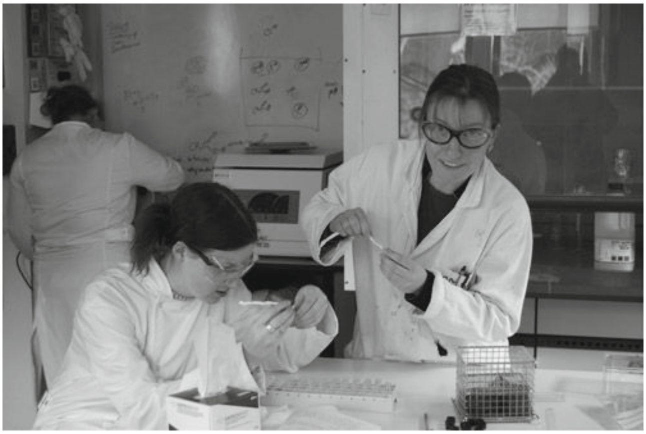


Fig. 1.9 Tamsin O'Connell and students preparing samples of bone and hair for carbon and nitrogen isotopes analysis in the Dorothy Garrod Laboratory for Isotopic Analysis at Cambridge University

Table 1.6 Basic chemistry laboratory safety regulations

Wear appropriate protective clothing, lab coats and goggles required
Never handle chemicals with your bare hands
Know where safety equipment is located and how to use it
Contain spills as quickly as possible
Use the fume hood with all volatile materials
Ensure that your work environment is clear and free of debris
Do not eat, drink, or smoke in the laboratory
Dispose of sharp waste properly
Report any safety issues or violations that you are aware

National Science Foundation and the support of the University of Wisconsin–Madison. Dedicated instrumentation provides the focus of analytical procedures, involving the elemental and isotopic characterization of prehistoric materials. The following description is a composite of the activities of the lab over the last 10 years or so.

Entering the lab first thing in the morning is always an experience. Nearing the front entrance, a low hum and mild vibration alerts one's senses. The door opens, the overhead fluorescents flicker on – there is an immediate feel of energy in the room. The sounds and textures of the lab are vivid. The hum of the instruments becomes a loud drone, the motors of the vacuum pumps, chillers, and power supplies for the spectrometers run hard and constant. Control lights blink red, green, or yellow on various instruments around the room. The large window of the fume hood looms like a large TV picture of reactions, beakers, and bottles. Waves of heat reach out from the furnaces. Everywhere there are the sights, smells, and symbols of chemistry – the cabinets on the wall are stacked with chemicals and glassware, reflections come from bright surfaces of glass and chrome, vials and sinks, test tubes, computers, microscopes, and balances. Bits of bone, tooth, and pottery lie about on black lab benches next to sample bags labeled in numbered codes and strange names of exotic places from around the world. Storage boxes of completed samples fill the empty spaces. Posters, tables, and charts cover the open spaces on the walls. This is a place where people do interesting work.

The Laboratory for Archaeological Chemistry occupies several rooms in the Department of Anthropology in Madison. There are two large rooms for research: a wet lab for sample preparation and an analytical lab housing instrumentation. The sample preparation area is dedicated to processing samples and includes a fume hood, furnaces, a system for deionized water, balances for delicate weighing, drills and grinding equipment, and necessary tools, glassware and chemical supplies. Here samples are cleaned in ultrasonic baths, dried in ovens, washed with acid, roasted in furnaces, and scoured with coarse buffers and prepared for analysis (Fig. 1.10).

The two major instruments in the lab are inductively coupled plasma spectrometers. The older instrument is an atomic emission spectrometer (ICP-OES) capable of quantitatively analyzing more than 70 different elements at parts-per-million levels. Since beginning operation in 1988, more than 30,000 archaeological samples have been analyzed on this equipment. The newer instrument is a high-resolution, magnetic sector, ICP-mass spectrometer (ICP-MS) for elemental and isotopic analysis of liquid samples to the parts-per-billion level. Prepared samples of pottery, bone, soil, and other materials are put into solution and sprayed into the plasma chamber of the instrument to be split by temperatures approaching 8,000°C into charged atoms. The process generates energy in the form of light and electrical charges that are used to measure the quantities of the different elements that make up the archaeological materials in part per million or billion.

Fig. 1.10 Kelly Knudson preparing samples in the Laboratory for Archaeological Chemistry

The laboratory has two full-time staff members and employs several graduate and undergraduate students as laboratory assistants. The Lab Director is Doug Price, a professor of archaeology in the Department of Anthropology. The Associate Director is Jim Burton, a Ph.D. in geochemistry. The combination of archaeology and geochemistry works well together in solving questions about the past. Students go hands-on with the instrumentation, learning both sample preparation and analysis. Students are constantly in and out of the lab as their own research often involves the facilities and expertise of the staff.

The laboratory is also a center of training in archaeometric research. The staff regularly offers a lecture and lab course on archaeological chemistry. Students and professionals from universities around the world spend weeks and months in the lab learning theory and methods. Visitors from Denmark, Germany, India, Norway, Pakistan, China, Spain, Switzerland and elsewhere have learned principles and procedures of archaeological chemistry in the lab.

Research in the laboratory usually involves the study of the composition and source of different kinds of materials to answer archaeological questions about past human behavior. The lab methods involve the trace element and isotopic analyses of bones, stone, ceramics, and sediments and have expanded to include organic residues, lithics, pigments, and other materials. Research questions include past diet, human migration, raw material sources, interaction and trade, and the identification of activity areas on prehistoric sites.

The Laboratory for Archaeological Chemistry has active research projects on five continents. Collaborative projects have included the investigation of bone assemblages from Ireland, ores and gemstones from South Asia, ceramics from Arizona, soils from Alaska, reindeer teeth from Germany, and other studies in Australia, the Czech Republic, Denmark, Ecuador, Greenland, Hungary, Iceland, India, Mexico, Norway, Pakistan, Peru, Romania, Scotland, Senegal, Serbia, Spain, Sweden, and Turkey.

1.5 Summary

This chapter is intended to provide an overview of what archaeological chemistry is and definitions of important concepts and terms. Archaeological chemistry is a subfield of archaeology that involves the investigation of the inorganic and organic composition – elements and isotopes, molecules and compounds – of archaeological materials. Archaeological chemistry focuses on questions concerning the identification of unknown materials, the authentication of the antiquity of artifacts, the origin of raw materials and finished objects, and questions about past environments and human diet and other activities. Understanding the terms of archaeological chemistry is critical to such research. Much of this chapter is devoted to the definition of important concepts about matter, energy, organic material, measurement, samples, and laboratory protocols.

A brief history of archaeological chemistry is provided in order to give a sense of the development of the field. Archaeological chemistry began almost simultaneously with archaeology itself and has grown dramatically in the last 50 years as the instruments and procedures of chemical analysis become more readily available to scientists outside of chemistry. Simple chemical tests for specific elements, used in the early part of the last century have been replaced by multielement studies of archaeological materials. Isotopic investigations have grown enormously as mass spectrometers have become more widely available. Organic chemistry and the study of the residual compounds that survived from the past have also grown exponentially in the last two decades.

In order to provide a sense of how archaeological chemistry works, we discuss the kinds of laboratories and equipment that are involved in such investigations. There are laboratories all over the world conducting studies of the remains of the past. Finally, we describe our own Laboratory for Archaeological Chemistry to provide an idea about how labs are set up and operate.

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Chapter 2
What Archaeologists Want To Know

Contents

This chapter focuses on the research questions that lie at the heart of archaeology and archaeological chemistry. The questions we ask – what we want to know – determine where and how we look for answers. Archaeologists want to know about people in the past – what our ancestors were like, how they lived, what they ate, what sort of environment they inhabited, what kinds of things they did, their relationships with other people, religious beliefs and ceremonies, and more. These are really just who, what, where, when, and why questions about the past.

There are only a few huge questions in archaeology that concern the origins of humans, the beginnings of agriculture, the rise of social inequality, and large, complex state societies. Then there are bigger questions and smaller questions. The bigger questions are about how society works, what people believed, how changes in society happen, what the environment was like, if ancient societies practiced conservation, and the like. The smaller questions are usually about what things are, how they were used, where they were found, how old they are, and the like. Most studies have to answer lots of smaller questions before they can begin to consider the bigger ones. This chapter is about the bigger questions that drive archaeological research.

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The critical thing to remember is that archaeologists are trying to understand individuals and societies that lived in the past using the few, fragmentary items from that time that have survived to the present. Archaeology tries to understand the past from what remains today. We use the term *archaeological record* for the objects and information that still survives. Archaeologists try to connect the dots between the static nature of material objects (the archaeological record) and the dynamics of past human society, the lives and events of long-dead peoples. How do we understand the lives of peoples in the past from the bits and pieces of tools and trash, the ruins and mounds that still survive? This is a big problem for archaeology. In order to help solve this problem, archaeologists use a structured way to investigate our ancestors and their ancient societies. This framework of enquiry involves archaeological cultures, time, and space.

2.1 Archaeological Cultures

Culture is an obtuse term that has two important, but very different, meanings. On the one hand, all humans have culture – an ability to learn different behaviors and adapt to changes using intelligence and choice. *Culture* distinguishes us from the other animals and involves language, learning, and tool use. Culture is being human. The second meaning involves the concept of archaeological cultures. *Archaeological cultures* are the units we study in the past. They are more or less equivalent to past societies, groups of people who are related to one another in some distinctive way. In today's world, groups of people are often identified by shared nationality, ethnicity, language, or religion. There are Americans, Germans, Kurds, Baptists, Catholics, Muslims, Chinese, ad infinitum. In the past world, archaeological cultures are identified by artifacts such as stone or metal tools, or pottery, or distinctive building styles, or a combination of such features.

Archaeologists, for example, talk about the Bell Beaker Culture found in Central and Western Europe during the third millennium BC. These people used a distinctive shape of pottery vessel known as a Bell Beaker, introduced the first bronze and gold in the region, and practiced a particular form of human burial. These shared, common material artifacts and practice serve to identify the Bell Beaker Culture and distinguish it from other groups in Europe at that period of time. An example from the New World is the Old Copper Culture belonging to the Archaic period around 2,500 BC, found in the present state of Wisconsin. The Old Copper Culture was distinguished by the elaborate use of native copper, shaped into a variety of knives, spear points, and awls by hammering, long before agriculture arrived in this region. Such archaeological cultures do not necessarily equate with tribal, ethnic, or national groups, but rather reflect shared technology, raw materials, or beliefs. An archaeological culture shares space, time, and material culture.

Thus, archaeologists recognize archaeological cultures in the past and tend to equate them with distinct societies. In fact, we often cannot identify specific societies in the past because of the fragmentary nature of the archaeological record that survives and the problems of defining the time and space boundaries of such groups. Thus, archaeological cultures provide a proxy, or substitute, for that reality in many situations.

2.2 Time and Space

At this point in our discussion, then, we recognize the existence of archaeological cultures. Now it is necessary to define these cultures in terms of their place in time and geographic location. This aspect of archaeology is known as culture history, determining the chronology and distribution of past cultural groups.

Woody Allen once described time as nature's way of making sure everything didn't happen at once. Time is a special component of an archaeologist's perspective. It is essential to know the age of the materials we study in order to be sure we are dealing with contemporary events or that we are able to examine change over time. Archaeologists have spent a great deal of effort learning about the passage of time and finding ways to measure it. There are different ways of determining the antiquity of archaeological materials. Relative chronology can provide the approximate age of past things. More useful is absolute chronology that measures the age of materials in calendar years before the present.

Absolute chronology is laboratory science that involves sophisticated instrumentation and chemistry. The most common methods for measuring time in calendar years use annual events recorded in nature (e.g., tree rings, annual layers in ice or sediment) or radioactive decay. Dendrochronology is a method for using tree rings to date wood found at archaeological sites. Radiocarbon dating employs the radioactive decay of carbon to determine the time of death of organic materials.

Space refers to the geographical location and distribution of the archaeological materials of interest. Where in the world are these materials found? How widespread do they occur? For how long a period of time do they occur? Mapping the geographic location of archaeological items is a common practice made much more sophisticated by the recent addition of GIS (Geographic information Systems) to the archaeologist's tool kit. GIS offers computer mapping of landscape and its features in conjunction with archaeological objects and sites. The combination of time and space information provides two essential coordinates for locating archaeological materials and archaeological cultures. At this point, we know the age and location of materials of interest. Now we can ask more interesting questions about past cultures.

After determining the time and space parameters of archaeological cultures, our questions turn to describing the characteristics of these groups? What questions do we ask? What do we want to know about a "culture" in the past? At this point, our framework of enquiry expands to include a structured way of looking at society. In fact, there are a number of different ways of viewing human society, but there seem to be certain common components that provide a useful perspective for understanding how they operate. One can see this structure in the organization of the basic academic disciplines at universities that look at modern society: engineering, economics, sociology, political science, and religion.

Along similar lines archaeologists regard societies and archaeological cultures as made up of interacting components. These components include technology, economy, social organization, and ideology. Such societies operate in natural and social environments that can have significant impacts on its various components. Climate shifts, natural disasters, and invasion are some of the many such impacts that require societies to adjust and adapt to new conditions. Demography is an important characteristic of society and concerns human population – numbers, density, birth and death rate, and the like.

From this perspective then, questions about past archaeological cultures focus on features of society such as technology, economy, social organization, ideology, and demography. These are the big questions about the past. With some understanding of these features, we can begin to understand these past societies. Some of these features are easier to see in the archaeological record than others. Information on technology and economy are generally more accessible in material culture, than social organization and ideology. In the following paragraphs, we describe some of the basic aspects of each of these features and focus on those aspects that are of special interest in archaeological chemistry.

2.3 Environment

There are two important components of the environment in which societies exist. The physical environment (topography, climate, water, vegetation, soil, rocks, and minerals) provides the necessary resources and conditions for human society. The cultural environment refers to the humanly created environment, as well as relationships with other human groups in the physical environment.

The physical environment in which people live affects their lives in many ways. In colder regions, for example, adequate clothing and shelter is essential to survive the elements. In arid areas, the availability of water is a critical consideration. The physical environment can provide or lack important mineral, water, or other resources. Different environments make different demands and require different responses from society. Archaeologists investigate the environmental context of ancient societies in detail.

An important point to remember is that environments change over time. It is essential to determine the nature of the environment during the time of an archaeological culture. As an example, the Sahara Desert today is one of the drier areas on earth, but 8,000 years ago this area had rivers and extensive vegetation and supported numerous villages of herders and farmers. Satellite photographs using hitech scanning methods have revealed the location of these rivers and even some of the archaeological sites that lay along them (Fig. 2.1).

The cultural environment is a result of human activity. Today much of world around us is in fact a cultural environment. Very little of our landscape is unmodified by human activity. Cities for example are almost completely built up and

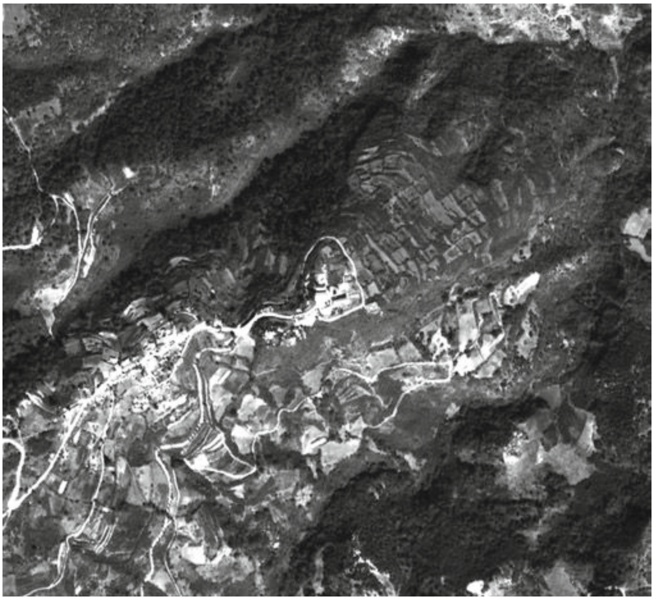

Fig. 2.1 Satellite view of the village of San Pedro Nexicho, Mexico, and the archaeological site on the terraces to the north and in the fields around the village

artificial. Many of the rural areas of the world have also been modified by agriculture, forestry, or other forms of human alteration. The cultural landscape also includes a social component. Other humans and other human groups in the surrounding world are part of that landscape and affect the decisions and behaviors of a society. Archaeology seeks to define and understand both types of environments in discussions of past human behavior.

2.4 Technology

Technology refers to the methods, materials, knowledge, and organization for making and using tools, equipment, facilities, and structures to control and adapt to the environment. The fragments of the tools and architecture that people used in the past, made of durable materials such as stone, ceramic, and metal, are the most common archaeological remains. Technology is a very human means for survival and success. Humans lack sharp teeth or claws; technology provides cutting edges on stone tools. Humans do not have fur or heavy body hair against the cold; technology provides fire, clothing, and shelter.

Technology takes many forms depending on the goal and the raw materials available. For example, a cutting edge can be made from bamboo, shell, sharp stone, bone, or metal. As technology becomes more complex and elaborate over time, more steps, more materials, more organization, and more knowledge are often required. The discovery of metals, for example, required advances in the technology of fire, of mining, and transport in order to provide finished metal products.

Function – the actual or intended use of tools, equipment, and facilities – is another important aspect of technology. But the use of artifacts and architecture in ancient societies is often unknown. What was a stone blade used for? Was this ancient pottery vessel used for cooking, storage, or another purpose? Was this fireplace for heat or cooking or firing pottery? Was this room used for residence or religious purposes? There are many such questions that arise in the finds from any excavation. These questions do not have easy answers, but archaeological chemistry can often help to provide some clues. Microscopic inspection of stone tools, organic residue analysis of pottery, trace element analysis of house floors are some of the methods used to determine function – how prehistoric people used the things they made.

2.5 Economy

Economy concerns the way in which people obtain, produce, and use the things they need to survive. Such things include food, shelter, raw material, and information. If technology refers to the methods, tools, and information for making equipment, facilities, and structures for survival and growth, economy is the way to obtain and produce these necessary things.

2.5.1 Food

Food is the most obvious need for human groups to survive and an assured source of sustenance is essential for long-term success. *Subsistence* is the term commonly used in archaeology for the foods we eat and subsistence pattern is used for different ways of obtaining food. There are several major patterns of obtaining food observed during the course of human prehistory: gathering, scavenging, hunting, and farming. Our earliest ancestors were largely vegetarians, like our nearest relatives the chimpanzees. These early ancestors collected and gathered leaves, seeds, roots, and other vegetable food as part of their daily fare. The importance of meat in early human diets is unclear. There is increasing evidence that chimps occasionally hunt and eat small animals. At the same time, the bones of large game are sometimes found at early archaeological sites. Archaeologists debate about importance of hunting vs. scavenging as a way of obtaining meat in our early prehistory. Did our ancestors take bits and pieces left from the kills of larger carnivores or did they hunt successfully on their own? This argument is unsettled and in all likelihood both methods were employed.

The term hunting and gathering is used to describe the pattern of subsistence practiced by human groups in many places before the advent of farming. Hunting and gathering also includes hunting large and small and the use of marine and aquatic resources as well. Hunting and gathering involves the use of wild food resources; these groups lived off nature. The origin of agriculture, on the other hand, involves the domination of nature, the domestication of plants and animals for human use and consumption. Farmers began, first about 10,000 years ago, to control the wild and to tame the earth. The first farmers cultivated and herded on a limited scale. Fields of crops and herds of animals were small. Hunting and gathering continued to provide some of the food that these groups were eating. As human societies grew in size and complexity over time, however, farming became more intensive and technologies more sophisticated in order to increase crop yields. Irrigation, terracing, raised fields, manuring, and other techniques were invented to enhance food production.

Archaeologists who study animal bones and plant remains can provide essential evidence about past human diets and can often distinguish between hunting and gathering and farming. Archaeological chemists also play an important role in such investigations. Various kinds of isotopic and organic analyses can help with the determination of past subsistence patterns and the importance of different kinds of foods. Examples of such studies are discussed in Chap. 6.

2.5.2 Shelter

In many environments, humans need or prefer some form of shelter from the elements, protection from cold and damp, and from predators and other humans. Shelter takes many forms from caves to fallen trees to purposefully built huts and houses and palaces. Archaeological science assists in the study of the places where people lived and the kinds of activities that took place there. Specifically the discovery and investigation of human settlements is an important component of archaeological chemistry. The search for ancient places involves many techniques including air photography, georadar, magnetometry, and many others. One method of searching involves the chemical composition of soil samples, focusing primarily on the element phosphorus. This technique has a long history and it is described in more detail in Chapter 6 archaeological chemistry also can provide information on the use of space within settlements and specifically within the places where people lived. The analysis of the chemical composition of the floors of houses and other areas within human settlements also can tell us about the activities that were taking place, the function of space. The chemical analysis of activity areas is also described in more detail in Chap. 8, Case Studies.

2.5.3 Raw Material and Production

All societies depend on raw materials for the food, shelter, tools, facilities, and structures and infrastructure. Most of these needed materials can usually be found in the local environment. Food, stone, clay, and wood are basic materials for many prehistoric cultures and are often ubiquitous in the environment. On the other hand, many societies want or need raw materials that are not found locally and must be obtained by trade or conquest. These foreign, or exotic, materials are often items of value and usually very visible archaeologically.

An extreme example of raw material utilization and acquisition comes from the ancient Near East. The earliest civilizations in the world arose in Mesopotamia, between the Tigress and Euphrates Rivers in the modern country of Iraq more than 5,000 years ago. This region was and is a huge basin filled by the sands and clays carried into and across the region by the rivers. There is no stone, mineral, timber, or other useful raw materials for hundreds of kilometers. There is only rich irrigated farmland and mud for bricks. Yet here were the first civilizations on earth and they grew and became powerful in part because of the need for raw materials and the large networks for exchange that they established to bring in these materials.

2.5.4 Exchange

Exchange is an important aspect of economy. One way to study interaction within and between societies is to look at the distribution of items of exchange. Individuals and groups exchange materials and ideas. When artifacts such as stone axes, obsidian knives, metal spear points, or certain kinds of food pass from person to person, or group-to-group, archaeologists speak of "exchange."

Three kinds of exchange can be distinguished: reciprocity, redistribution, and trade. *Reciprocity* involves the exchange of items of roughly equal value. Barter is a form of reciprocal exchange. Reciprocity or reciprocal exchange sometimes takes the form of gift giving, where objects of value are given to build alliances and friendship or to create debts. *Redistribution* involves the movement of goods to a central place from where they are rationed or portioned out to select members of society. Such a system of redistribution might be used to support relatives, an army, or priests, or craftsmen or the pyramid builders of ancient Egypt, for example. The Social Security system in the USA. is an example of redistribution in the economy today. Money from active workers is used to pay the pension of retirees, at least in theory.

Economic transactions known as *trade* involve bartering, buying, or selling goods (Fig. 2.2). Trade usually takes place in some sort of market economy, and perhaps using a monetary standard. A market is a place where trade and exchange take place using barter or a common currency. Trade is common in our own economic system today when objects are bought and sold for the purpose of making a profit. This level of exchange often involves a complex society with professional artisans, regular supplies of raw material, extensive transportation systems, protection of markets and traders against pirates, and enough customers to make the business worthwhile.

Archaeologists usually focus on "exotic materials" in the study of exchange and trade. The presence of objects and materials that are not available or locally produced in an area provides immediate evidence of interaction and external connections.

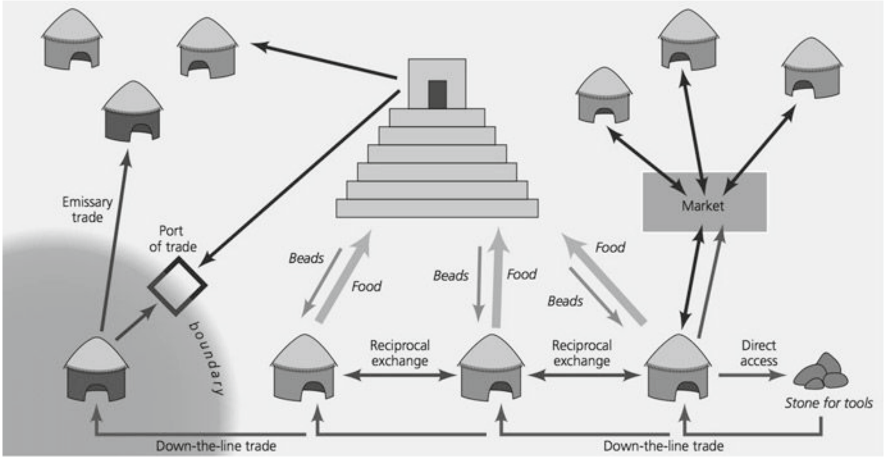

Fig. 2.2 A schematic depiction of different types of exchange and trade within society. The diagram shows several households and a palace. Distinctions among reciprocity and redistribution are indicated by the width of lines showing exchange. Down the line exchange is a process that moves specific goods further from their source in a sequence of trades. Redistribution involves the movement of food or goods to a central place from which these materials are rationed or provided to part of the population. The green houses represent another society. Trade involves the movement of goods in exchange for value. Societies trade with one another directly, through ports of trade (a common ground) or emissary trade (traveling merchants or foreign residence). A market is a place where trade and exchange take place involving barter or a common currency

Of great use in such investigations are artifacts or materials that come from a known location. It is in this area that archaeological chemistry has made an enormous contribution. There are many cases of such movement in exotic materials, often in the form of rare stones or minerals. There were no natural sources of turquoise in ancient Mexico, for example, but this beautiful blue-green stone was imported from the present state of New Mexico and used in the costumes and jewelry of the elite in Aztec Mexico. Archaeological chemistry had documented the sources of turquoise in the southwestern and found objects from Mexico that clearly came from those quarries. This example is discussed in more detail in Chap. 8, Case Studies.

The economic activities of prehistoric peoples were organized in different ways. A fundamental mechanism for the efficient organization of tasks is a *division of labor*. Individuals, separate groups, or segments of society perform different activities as part of an efficient organization of the economic process. A basic example is seen in many groups of hunter–gatherers where the division of labor is often by sex and production is at the level of the individual. Males are primarily hunters and females are primarily gatherers. Both groups contribute food to the subsistence of the society. In agricultural societies, households are an important unit of production for food and other essential materials. Economies become more specialized through time with larger groups or entire communities involved in the production of specific items. The emergence of specialist groups of producers – such as potters, metal smiths, or bead makers – marks more advanced agricultural societies. The organization of production can assume more formal arrangements such as guilds or unions in more complex civilizations.

2.6 Organization

Archaeologists usually combine social and political organization to discuss the how past peoples related to one another, both those nearby and those distant. *Social organization* refers to the structure of relationships within a particular society, ordered by kinship, marriage, and status. *Political organization* refers to the use and distribution of status, power, and authority within a society. *Settlement pattern* is the term used to describe how human groups are organized geographically in a region. Settlement patterns reflect the social and political organization of society as well as the use of the landscape. These three concepts are discussed in more detail in the following paragraphs.

2.6.1 Social Organization

All human societies structure the relationships among their individual members to promote harmony and survival. Most human societies establish relationships among individual members by rules of kinship and marriage. All human societies have families as a basic building block of larger social units. Families are normally male and female joined in marriage. Offspring are related by kinship to their parents and siblings. Families can be joined together into larger units by kinship connections through marriage or descent. Other genealogical ties can be established by adoption or choice.

Some of the larger units of human society are extended families, lineages, clans, and moieties. Extended families include several living generations of related families – grandparents, parents, children – in groups that might number 20 or more. Extended families are contemporaneous units, present at a moment in time. Lineages are families extended over many generations from long dead to living. A lineage is a family history, a genealogy, of a group of people related by blood and marriage. Descent can be calculated through male or female relatives. Lineages can often be recalled for many generations and are sometimes believed to have a mythical creature – animal or human – as their founder or original ancestor.

2.6.2 Political Organization

Social units within a society are also structured by political relationships. Political relationships are based on the distribution of power and status within and between individuals and social units. The distribution of power can be equal or unequal. Power in a family, for example, is usually distributed unequally, with parents having more authority and decision-making power. Nobles have more power than commoners; kings and queens have ultimate power. The distribution of status in society is one of the hallmarks of political structure. Societies with an even distribution of status are referred to as egalitarian and are usually small in size. Most groups of hunter–gatherers, for example, are egalitarian in terms of their political organization.

Societies with an unequal distribution of status are described as hierarchical. Inequality is common in most human societies today. Inequality is defined by status differentiation. Status means access to resources, information, and authority. Higher status individuals have more access; lower status individuals have less. Hierarchical organizations are usually those in which resources move up and decisions move down. King and queens collect taxes and tribute and tell others what to do.

One of the major changes in human society was the shift from egalitarian to hierarchical organization. A critical change took place in how status was obtained. In egalitarian societies, status is achieved and ephemeral. That is to say, an individual's status in society is determined by their accomplishments during their lifetime. For example, a successful hunter would be recognized for his abilities and his judgment would be respected; a woman known as a healer would obtain respect and status for her knowledge and skills. Their status in their society, however, exists only during their lifetime and is therefore ephemeral. Ascribed status, on the other hand, is passed from generation to generation and long-lived; children inherit the status of their parents in societies with status differentiation. In this manner, more powerful, elite individuals maintain their position in society.

Hierarchical societies are normally either ranked or stratified. Ranked societies are those in which birth order determines one's position in society. Within families, the first-born inherits the property; the seventh son inherits nothing. Rank determines status. Generational lines are also ranked so that lineages have status with regard to one another. Such systems are generally referred to as ranked societies, or chiefdoms.

Class stratification marks another level of hierarchical organization and involves the use of status, rather than kinship, to determine an individual's position in society. Stratified societies have fixed classes or levels of social organization, ranging in many cases from slaves at the bottom to kings and queens at the top. Social classes – something like the caste system that existed in South Asia – define your place in life and death, where you can live, your occupation, your potential marriage partner, and where you are buried. Status in a stratified society is determined by the class into which you are born.

Mechanisms of social organization such as ranking and class stratification insure a rigid hierarchy in society and make it difficult for most people to attain wealth or power. Such mechanisms provide benefit in that they operate so that there is efficient decision-making and rapid material flow in society. At the same time this form of organization also means that power, authority, and wealth are often concentrated in the hands of a few and that many are often exploited for their labor.

There are a number of ways to categorize political organizations. All such classifications are somewhat artificial; some have many categories and others have only a few. One useful classification that has been around for a long time describes political units as bands, tribes, chiefdoms, and states. The characteristics of these units include subsistence, social, and political attributes.

Bands are small, mobile societies of hunter–gatherers. Foods come from the wild resources of nature. Because such resources are often seasonally available, bands move frequently from place to place in small numbers to harvest these resources. Social organization is usually egalitarian and status is ephemeral. Band societies normally include tens of persons.

Tribes are commonly small-scale village farming societies where relationships are egalitarian and political organization is largely based on achieved status. Tribes are usually larger than bands and smaller than chiefdoms. Tribal societies number in the hundreds of individuals.

Chiefdoms are larger farming societies in which status differentiation by ranking operates to create powerful chiefs who direct many of the activities of the society. Chiefdoms incorporate thousands of individuals and often witness substantial trade and exchange in both raw and rare materials. Chiefdoms may include larger settlements, or towns, where chiefs are in residence and many different activities take place.

States are even larger organizations and are often associated with characteristics such as writing systems, taxation, monumental architecture, long-distance trade, and exchange. Settlement patterns include cities, towns, and villages. Intensive agriculture is practiced to increase food production. Class stratification defines social organization and powerful rulers stand atop these classes and direct nobles, warriors, merchants, commoners, and perhaps other classes. States number in the tens of thousands of individuals. Even larger states, called empires, are known from antiquity and include examples like Rome, the Inka, and Aztec.

2.6.3 Settlement Pattern

The concept of settlement pattern refers to the geographic distribution of human population on the landscape and is closely related to social and political organization. There are again a number of different classifications of settlement types, but one useful set arranged by increasing size, includes households, camps, villages, towns, and cities (Fig. 2.3). Settlement pattern combines aspects of social and political organization as the spatial manifestation of society's use of the landscape.

One important concept, particularly for smaller sizes of settlements, involves mobile vs. sedentary. Most hunter–gatherers, as already discussed, are mobile groups, changing settlement location regularly in response to resource availability. In addition, herders of domesticated animals are often mobile in residence, sometimes moving twice a year to better pasture, sometimes more.

Households are a particularly useful unit of study in archaeology as they represent the residence, or settlement, of families or extended families. Households provide a great deal of information about subsistence, consumption, and production at the level of the family unit. The household is the residence of the family unit and the place where many essential activities take place including food preparation,

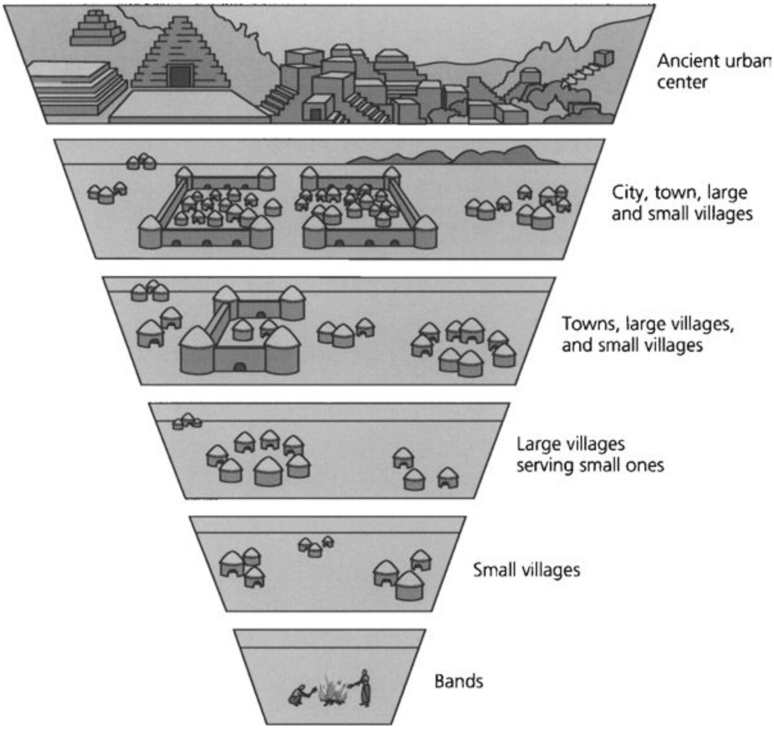

Fig. 2.3 A schematic depiction of different types of settlement and social group size and organization. Smaller groups on the bottom; larger and more complex settlements toward the top

eating, sleeping, storage, manufacture and repair of equipment, and small-scale craft production. In addition, in many societies it is the focus of many important events and ceremonies in the family like birth, death, marriage, and other rites of passage. Archaeologically, some information on these various activities is retained within the physical structure of the house.

A very useful distinction has been made in archaeology between compounds and villages as a settlement type. A compound is a specific kind of camp, a settlement of round huts, often in a circular arrangement, commonly constructed by mobile groups of hunter–gatherers or herders as a short-term residence. Villages are groups of square houses, usually in a more rectilinear arrangement, and associated with sedentary communities. The shift from round houses to square houses is associated with the shift from hunting to farming. Reasons for this change in house type may be related to the fact that square houses can be packed into limited space and new houses added more efficiently. Villages usually are rather homogeneous with houses of similar size, shape, and architecture. Villages may contain distinctive public structures associated with religious beliefs or burial practices.

State societies often have a range of settlement types, including cities, towns, and villages. Towns and cities are larger settlement units, both physically and in terms of population, and more varied in architecture and the use of space. These characteristics are more pronounced in cities than in towns. Towns and cities usually exhibit some degree of planning and distinctive areas of activities within their boundaries. Such activity areas might include religious complexes, craft production zones, markets, parks and public places, and the like. Towns are larger than villages and exhibit some internal differentiation in the size and location of structures. Towns usually contain one or more public buildings. Population numbers in the hundreds to a few thousand. Monumental architecture in the form of temples, walls, palaces, baths, harbors, aqueducts are most common in cities. Cities are very large with populations of 10,000 or more inhabitants. Cities have substantial internal differentiation and distinct civic or ceremonial areas within their boundaries. Cities may be defined by boundaries of walls or fortifications.

2.7 Ideology

Ideology refers to the set of doctrines, beliefs, and norms that guide the beliefs and practices of human societies. Ideology is society's model of how the world works. Ideology helps society to justify specific rules, practices, and behaviors. Ideology, often in the form of religion, helps to explain the unknown and provides answers to existential questions. Ideology encompasses the norms, values, and beliefs held by a society. This viewpoint affects much of what people do. Ideology is reflected in the clothes we wear, the food we eat, and the places in which we live.

Ideology is commonly expressed in material form in aspects of ceremony (especially burial), public monuments, symbolic objects, and writing systems. Today, the Christian cross, the Jewish star, and the crescent of Islam are vivid symbols of ideology. The material expression of ideology is often used by those in power to reinforce their authority and dominion as a symbol of social power. Political propaganda is commonly rife with symbols of ideology.

Ritual is ubiquitous in human society and a manifestation of ideology. Ritual usually involves symbolic, prescribed, and structured behaviors that are often repetitive in nature. Aspects of ritual behavior include animism, dance, divination, magic, music, mythology, rites of passage, sorcery and witchcraft, shamans and priests, taboos and totems. Ceremony and ritual usually involve information, artifacts, and architecture. Artifacts associated with various aspects of ritual behavior sometimes show up in the archaeological record. The term ritual is sometimes used to describe material remains that are not readily understood in terms of technology, organization, or economy.

In the study of the past, however, it is difficult to distinguish the ideological from the pragmatic. Because the material correlates of ancient beliefs, cosmologies, and ideologies are usually unknown, it is difficult in archaeology to identify which objects and architecture are ideological and which serve more practical and immediate purposes.

2.8 Summary

The preceding paragraphs describe a frame of enquiry for examining past human societies, a model of how archaeological cultures operate, and a perspective on some of the differences and changes that are present in the archaeological record. This frame reveals some of the information we would like to know about the past and some of the questions we can ask. For the most part, the questions raised in this chapter are the "big" questions about the nature of past human societies, about different kinds of economies that operated in the past, about different levels of social and political organization, and the role of the environment in human life.

Most archaeological research is aimed at answering these bigger questions, but the answers usually come from resolving many smaller issues. These are basic questions – what did people eat, how did they get their food, what kind of houses did they live in, how did people bury their dead? These issues are answered by even more specific questions about the details – how well is bone preserved, what kinds of animals were found at the site, what was this stone tool used for, what were the contents of this pot, how big were their houses? There are as many questions as archaeologists and, in fact, many more. Some of these questions fortunately can be answered by archaeological chemistry. The remainder of this book focuses on archaeological chemistry with a consideration in Chap. 3 of archaeological materials.

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Chapter 3
Archaeological Materials

Contents

3.1 Introduction

3.2 Archaeological Materials

The range of raw materials that humans use for food, construction, valuables, transportation, and other purposes is enormous. Many materials are found at archaeological sites. The Black Earth site in southern Illinois, a settlement of hunters dating from 4000 to 3000 BC provides an example. It is an enormous site, more than a city block in size, and the cultural layer is up to 1.5 m (5 ft) deep. The concentration of ash, excrement, and other organic matter in the sediments changed the chemistry of the soil, resulting in more alkaline conditions, favorable for the preservation of bone and other materials.

Preserved plant and animal remains document the diet of the inhabitants. The Indian occupants of the site used the river, lakes, and swamps in the area for aquatic resources and exploited the uplands for deer and nuts. Hickory nutshells are very common in the middens; acorn shells also occur throughout the occupation area, along with the remains of hazelnuts and walnuts. These nuts are available in

T.D. Price and J.H. Burton, *An Introduction to Archaeological Chemistry*,
DOI 10.1007/978-1-4419-6376-5_3,

Table 3.1 Grave goods buried with individuals at the Black Earth site

Mussel shell	Bone pin
Bone awl	Anculosa shell bead
Worked antler	Plummet
Unworked deer bone	Bar gorget
Chert projectile point	Crinoid-stem bead
Chert core	Elk antler cup
Chert drill	Red ochre
Chert Scraper	Fossil
Chert flake	Worked shale
Stone axe fragment	Worked stone
Bone needle	Hematite
Chert scraper	Water-worn pebble
Shell pendant	Banded slate
Miniature grooved axe	Fluorspar crystal
Worked turtle shell	

autumn and could easily be stored and used throughout the winter for food. Seeds from hackberry, wild grape, persimmon, bedstraw, and wild bean are also common. These plants ripen and are harvested during late summer and fall.

In addition to the residential area, there was a cemetery at the Black Earth site. At least 154 burials were found, sometimes buried with artifacts and other materials. A number of exotic items were found in addition to the local raw materials. One perforated disk of marine shell, probably from the Atlantic Ocean or the Gulf of Mexico, was found around the neck of a buried infant. A copper wedge from the Great Lakes area had been placed at the top of the neck of the skeleton, perhaps as a substitute for the missing skull of this particular individual. These materials had come from hundreds of miles distant to be buried at the Black Earth site.

Table 3.1 lists the grave goods placed with the dead. There are many different kinds of stone, bone, antler, shell, and minerals. Yet this is a rather early site, prior to the rise of agriculture and before more intensive trade and manufacturing. The range of raw materials here is actually small and mostly local. The variety of materials in use in more recent periods is enormous.

In order to understand chemically analyze the materials found at archaeological sites; it is essential to understand something about their context – sources, technology, use, and disposal. In this chapter, we examine some of the more common raw materials at archaeological sites – rock, pottery, bone, sediments, metals, and other things like shell, pigments, charcoal, and plant remains (Fig. 3.1). There are many other materials, generally less common, that we do not consider here.

3.3 Rock

Stone artifacts made by our human ancestors date back earlier than two million years, and are often the only remaining evidence at early archaeological sites. While our ancient ancestors undoubtedly had technologies that included materials

Fig. 3.1 Archaeological finds from the excavations of an historical site at Jamestown, Virginia. The items include from lower left a toothbrush, a pendant, a broach, a coin, a thimble, a whistle, a pipe, a glass stopper, and a potsherd (Photo by Kevin Fleming)

of animal and vegetable origins, stone is vastly more durable and more likely to remain after other materials have perished. Indeed, "Palaeolithic" – the Old Stone Age – is the name given to deepest antiquity. When the Mesolithic and Neolithic are included, the Stone Age comprises a period from roughly 2.6 million years ago to approximately 4,000–5,000 years ago, or 99.8% of our history! During this time stone artifacts evolved from the earliest Oldowan scrapers, choppers, and hammerstones into a highly diverse array of tools and other items including the use of stone for ornaments, pigments, ritual objects, construction materials, grinding and polishing, projectile points, and many other purposes. Many of these artifacts were made by percussion flaking, hitting one stone with another to remove flakes (Fig. 3.2). Either the flakes were removed to shape the object, or the sharp flakes themselves were used as cutting tools.

While archaeologists commonly describe stone tools functionally in terms of their use (e.g., flake, projectile point, borer, lithic debitage, groundstone, etc.), archaeological chemists focus upon the compositional characterization of these materials. This begins with the geological identification of the stone, i.e., what type of rock, and might proceed to an analysis of the minerals composing the rock to further analysis of the major, minor, and trace elemental composition and even to an isotopic characterization, depending upon the specific research questions.

Functional characterization often takes place in the field, and an archaeologist familiar with the materials can usually further distinguish items geologically in terms of different kinds of rocks, e.g., as greenstone, chert, obsidian, or marble. The type of rock chosen for a task normally has a close connection to the planned

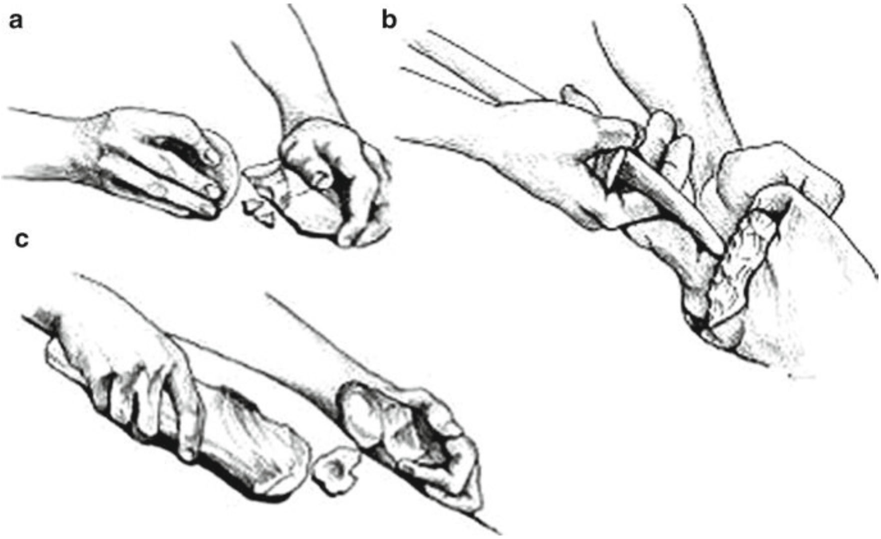

Fig. 3.2 Methods of flaking stone tools. A. direct percussion with a hard hammerstone, B. direct percussion with a soft antler or bone hammer, C. pressure flaking with an antler tool

functional use – you can make a finely knapped bifacial point from obsidian and a grinding stone from granite, but not vice versa.

Rock types can be identified at a relatively basic level without extensive geological training by recognizing a few textural attributes such as grain size and alignment and the homogeneity or heterogeneity of the texture, along with an ability to recognize about a dozen common rock-forming minerals (Table 3.2). Although there are many thousands of minerals, less than a few dozen minerals comprise the major components of almost all rocks. Recognition of these most common rock-forming minerals likewise is possible by recognition of their characteristic attributes and does not require extensive training.

Common rock-forming minerals and their distinctive attributes are listed in Table 3.3. Minerals have, by definition, not only a well-specified chemical formula (e.g., $CaCO_3$ for calcite and SiO_2 for quartz), but also a specific structure. Two minerals can have an identical chemical composition, but different structures, and thus be quite distinct minerals, with different properties. Probably the most commonly given example of this is graphite and diamond. Graphite is pure carbon with the carbon atoms bound to each other in sheets but the sheets do not share electron bonds between them. The sheets can slide easily over one another, without breaking chemical bonds, causing graphite to be among the softest of all minerals. Diamond is also pure carbon but each carbon atom is bonded to four other carbons in a three-dimensional array and is the hardest known substance.

Table 3.2 Types of rock and their important characteristics

Rock	Type	Appearance	Major minerals
Basalt	Igneous	Fine-grained, homogeneousDark, Brown, blue-grey, black	Feldspar, pyroxene, olivine
Andesite	Igneous	Fine-grained, homogeneous. with inclusions, usually medium brown or blue-grey tones	Feldspar, amphibole
Rhyolite	Igneous	Fine-grained, homogeneous, with inclusions	Feldspar, mica, quartz
Obsidian	Igneous	Fine-grained, homogeneous, green to gray to black	Quartz
Gabbro	Igneous	Dark, Coarse-grained, not banded	Feldspar, pyroxene, olivine
Diorite	Igneous	Coarse-grained, light and dark minerals, not banded	Feldspar, amphibole
Granite	Igneous	Light or pink, Coarse-grained, heterogeneous	Feldspar, mica, quartz
Shale	Sedimentary	Usually dark, Soft, Fine-grained, homogeneous	Clay
Sandstone	Sedimentary	Sand-sized grained	Quartz, feldspar
Limestone	Sedimentary	Usually fine-grained, light-colored, soft	Calcite
Slate & phyllite	Metamorphic	Usually dark, fine-grained homogeneous and may be shiny (from shale)	Clay, mica
Quartzite	Metamorphic	Hard, glassy, sand-sized grains(from sandstone)	Quartz
Marble	Metamorphic	Usually light-colored or white, softer than steel (from limestone)	Calcite
Gneiss	Metamorphic	Coarse-grained, homogeneous (from granite and others)	Feldspar, amphibole, mica, quartz

Table 3.3 Common rock-forming minerals and their distinctive attributes

Mineral	Color	Fracture	Hardness	Abundant in
Quartz	Light, clear	Irregular fracture	Harder than glass or steel	Sandstone, granite
Muscovite mica	Light, white/ yellow	Flaky	Much softer than glass or steel	Granite, gneiss
Feldspar	Light, white or pink	Blocky	Hardness same as glass and steel	Most igneous and metamorphic rocks, sandstone
Calcite	Light	Rhombohedral fracture	Much softer than glass or steel	Limestone
Olivine	Dark, green	Irregular fracture	Harder than glass or steel	Dark igneous rocks (basalt and gabbro)
Garnet	Dark, red	Irregular fracture	Harder than glass or steel	Some metamorphic rocks
Biotite mica	Dark brown or black	Flaky	Much softer than glass or steel	Granite, gneiss
Amphibole	Dark	Acute 60° and 120° angle cleavage	Hardness same as glass and steel	Many metamorphic rocks, andesite
Pyroxene	Dark	Right angle cleavage	Hardness same as glass and steel	Dark igneous rocks (basalt and gabbro)

Calcite and aragonite are another similar mineral pair. They are both calcium carbonate, $CaCO_3$, but have different structures. Shell, for example, commonly contains layers of both these minerals, which can be distinguished in the microscope by their optical properties. Thus, while chemical methods can be often be used to suggest a particular mineral, the definitive identification requires recognition either of distinct physical properties – most commonly by observation of unique optical properties in the petrographic microscope – or by direct determination of its crystal structure through X-ray diffraction (XRD). One should recognize this distinction between X-ray diffraction, which reveals structure but does not provide direct compositional data, and X-ray fluorescence (XRF), which is a spectral technique revealing composition, but not structure.

Knowing the type of rock also places strong constraints upon the geographic source of the material. Obsidian can be found, for example, only in young volcanic fields and in nearby deposits derived from them. Many can further visually identify stone materials from specific sources such as the green Pachuca obsidian found at sites in the Valley of Mexico or Hixton quartzite from west central Wisconsin, found at sites in the upper Midwestern USA. However, for most stone materials, distinction of the source of the raw material requires more sophisticated laboratory analyses.

Indeed, one of the major foci of archaeological chemistry has been to establish unique geochemical “fingerprints” by which sources of some of the more important rocks, especially obsidian can be determined. Analysts, ideally, elementally analyze rocks from all possible sources, find elements that differ among the sources, and then compare analyses of artifacts against the source data to determine geographic origins. It cannot be emphasized too strongly that a “match” between an artifact and a source does not necessarily mean the artifact can be attributed to that source, merely that the two cannot be distinguished. That the artifact chemically differs from other sources does, however, rule them out as possibilities and when all other possible sources can be so distinguished, any remaining source is the likely origin.

There are also a large number of geological materials such as native metals, precious stones and gems, and pigments that are not among the common rocks and minerals but the importance of which significantly outweighs their scarcity in the archaeological record. Because such materials are scarce, with sparsely distributed sources, and highly valued, their presence in an archaeological context can imply exploitation of distant resources and possibly imply exchange or other interaction with distant societies. In addition to obsidian, other geological materials that have received considerable interest from both archaeologists and archaeometrists include jade, turquoise, marble, metal ores, native metals, and chert.

Analyses of such geological materials sometime require basic identification studies of fine-grained pigments and stones that cannot be identified by eye or microscopically. For the identification of such fine-grained materials, X-ray diffraction (XRD) and Raman infrared spectroscopy are commonly employed, as will be illustrated in the case studies. XRD is more commonly applied to powders, but can be difficult to interpret on complex assemblages of more than a few minerals. Raman IR has an advantage in the case of solid stones of being nondestructive.

Bulk (meaning "total") elemental analyses of such are commonly done to try to identify specific sources.

Other studies on stones beyond identification and provenience studies include microscopic studies of use-wear and analysis of possible residues for DNA or other, biologically distinctive organic molecules, which will be separately discussed in a later section.

3.4 Pottery

While stone tools have been used for millions of years, fired clay figurines don't appear in the archaeological record until approximately 25,000 years ago and utilitarian pottery first is made only about 16,000 years ago. Made from relatively perishable clay, but strengthened by firing at high temperature (>700 °F), ceramic materials are much harder and more durable than the original raw clay. Potsherds, broken fragments of ancient ceramic vessels, persist in the archaeological record; even for sites several millennia old ceramic fragments often comprise the major portion of the present material record.

Because ceramic raw materials are plastic and may be shaped into virtually any form imaginable, their morphological and functional diversity is enormous, making them among the most studied of all archaeological materials (Fig. 3.3). Many volumes have been written on the general analysis (e.g., function, style, decoration, methods of manufacture, etc.) and the subject is far too extensive to discuss in detail here.

The most basic level of analysis, identification of ceramic material, is readily made in the field. The next level of analysis, the raw materials that were used, is usually done to ascertain the geographic source of the pottery. This usually includes morphological and stylistic information that assigns the ceramic to a culture area

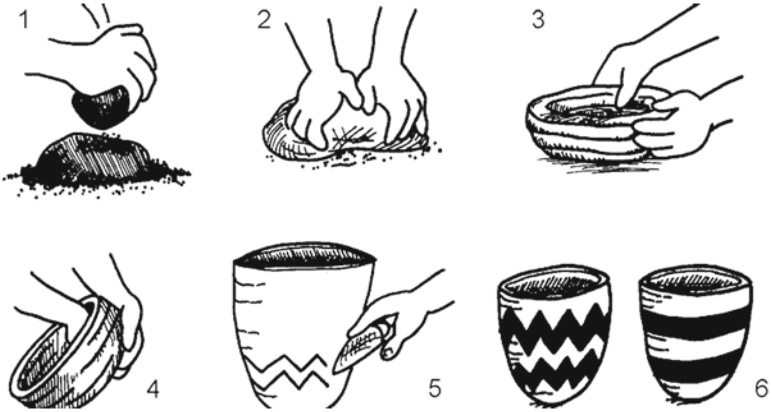

Fig. 3.3 Some of the basic steps in making pottery: 1, 2 – preparing the paste; 3, 4 – building the vessel; 5 – decorating the pot; 6 – finished vessels

and time period, but might also involve compositional analysis, either mineralogical or elemental to ascertain more specifically where the pottery was made.

Although all ceramic materials are necessarily made from clays, firing alters the structure of clay minerals such that their original mineral structure is destroyed and difficult or impossible to ascertain, either microscopically or by X-ray diffraction. Virtually all archaeological ceramics also contain other materials, added as *temper* to improve the firing characteristics or other properties of the basic clay component. Often potters add mineral sands ("grit") to temper ceramics; the identification of the minerals in the temper determine the original type of rock and in turn constrain the likely place of manufacture to the proximity of such rock types. If the mineral analysis cannot be done by eye or by inspection with a hand lens, then a thin-section may be made from a ceramic sherd. This is a small piece of pottery mounted on a glass slide and ground to a specific thickness of 0.030 mm, at which thickness most minerals become transparent and display diagnostic features when examined in a petrographic microscope, which is specially designed to use transmitted, polarized light and a rotating stage to observe these features.

When other materials such as shell or bone or crushed pottery ("grog") are used as temper, they don't so tightly constrain the geographic origin as rock temper but do sometimes inform us about the ceramic recipe and by inference the culture and geographic region that produced the ceramic.

Chemical analyses are frequently attempted to determine the geographic origins of pots, arguably being among the most common of all archaeometric studies. Often an important question is whether a certain pots with a distinct style that resembles the style of vessels made at some distance were imported from that region or represent a locally produced emulation of that style. A comparison of the compositions of locally obtained potsherds, both with and without the exotic style, to the compositions of sherds from the distant region can provide evidence to directly resolve such a question. If they differ from the distant pots but resemble the local ones suggests local emulation; if they resemble the distant pots and differ from the local ones, then importation is implied. If they resemble neither set, then a new hypothesis, and possible line of inquiry, is needed.

Because such chemical studies of pots are so numerous, there now exist quite large databases of ceramic analyses against which new multi-element analyses can be compared, providing that the chosen elements and the precision and accuracy of their measurements are comparable. Some analysts, particularly those at the Missouri University Research Reactor (MURR), have decomposed some of these databases into regional groups known as "compositional paste reference units" (CPU) against which new data can be compared.

Unlike chemical provenience studies of geological materials, the compositions of which normally remain unchanged by human choices, the composition of ceramics are the result of human choice, making the interpretation of such chemical data much more problematic. Potters at a given location can and do choose different recipes for different pots with different functions or styles. For example, water jars from Veracruz can give a different mix of clays and tempers for the base of the jar, for the filter, and for the funnel at the top, giving three different compositions for the same vessel.

Potters in northern Arizona have been known to individually exploit personal clay resources from either the marine Mancos shale or the volcanic Chinle formation, resulting in different compositions for pots made in the same village, while potters in New Mexico can likewise exploit the same widespread Mancos and Chinle clays. Thus pots made in Arizona could chemically resemble pots made in New Mexico more than they resemble other local pots.

Potters at the village of Paquime, in northern Mexico, mix as many as seven different clays for the paste of a single vessel; thus there could be huge compositional variation depending upon the personal choices of individual potters. Thus the Provenience Postulate, i.e., that compositional variation within a production location will be less than that among different locations, could be false and should actually be tested for its validity.

Another significant factor that can substantially affect the composition of ceramics after their manufacture is the addition or subtraction of elements during their burial in an archaeological context, i.e., diagenesis. Unlike stone tools that might weather on the surface, ceramics ordinarily have a highly porous microstructure and extremely small particle sizes that thus have enormous surface area and accordingly high chemical reactivity. This porosity and reactivity pervades the ceramic fabric. Soluble elements such as sodium and potassium in the pottery can be leached by groundwater solutions and conversely elements in groundwater can be deposited in the microscopic pore spaces of the ceramics. The change in chemistry will be reflected in any subsequent elemental analysis.

In addition to diagenetic alteration, treatments after excavation such as acid-washing or impregnation with stabilizers can also affect composition. Thus one should keep in mind that a ceramic analysis reflects the composition today, which might not be the same as when it was manufactured.

It should also always be kept in mind that ceramics are the products of diverse human technologies, not geological materials, and their compositions reflect human choices rather than simply that of a geographic provenience.

3.5 Bone

Bone is found occasionally on archaeological sites when conditions of preservation permit. Bone most often occurs at the inedible waste of meals or the remains of human burial. In addition, bone and other skeletal tissue from animals (teeth, antler, shell, horn) was often used to make certain kinds of tools and equipment. Archaeozoologists are trained to identify the genus and species of animal from small pieces of bone, as well as to determine the age and sex of the animals, how bone was fragmented, and how many individual animals are represented in a set of bones. Bone can answer questions about whether animals were scavenged, hunted, or herded, their age and sex, about how animals were butchered, about how important meat was to the diet, when animals died, and the process of domestication.

Similar kinds of information are present in human remains. The human skeleton is much more than a structural framework for supporting our bodies. Tooth enamel is the hardest part of our skeleton and is composed largely of the mineral apatite with virtually no organic component. Tooth enamel often preserves even under harsh burial conditions. Bone, a combination of mineral and organic matter, is more susceptible to decomposition and contamination. The distinction between cortical and trabecular bone tissue is an important one in understanding the survival of skeletal parts (Fig. 3.4). Most bones contain both kinds of tissue. The proportion of cortical and trabecular bone varies in the different bones of the skeleton. Cortical bone is the hard, dense bone that provides support and strength in the skeleton, and is more common in the limbs. Trabecular bone is the spongy bone tissue that makes up the interior of ribs, vertebrae, the pelvis, and other bones. Trabecular bone provides less structural support in the skeleton, but has an important role in metabolism. Because of the more porous and softer nature of trabecular tissue, it is usually the first type of bone to decompose during burial.

An enormous amount of information about both deceased individual is stored in human bones. Information on age and sex is recorded in the skeleton. The length and thickness of long bones provide an indication of an individual's size and strength. Evidence of disease or illness is often embedded in bone. It is often possible to determine age at death, cause of death, sex, history of disease or accident,

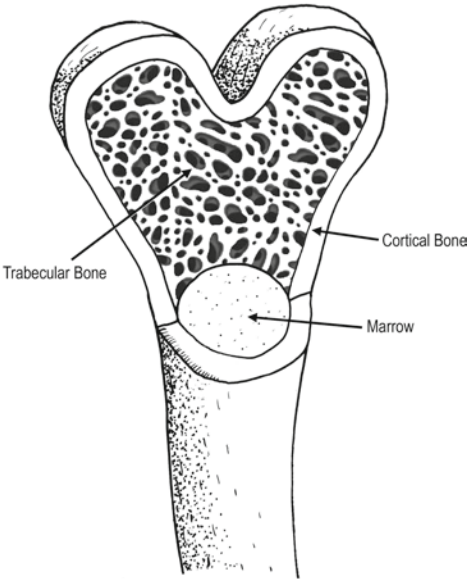

Fig. 3.4 Major characteristics of bone. Cortical bone is the dense heavy tissue that supports the skeleton; trabecular bone is lighter and more open and has several important functions in the body

occupation, movement, and nutritional status from the analysis of prehistoric human bone. Because bone is organic, it sometimes holds ancient DNA that can tell us many things about past activities and genealogical relationships.

Bone itself is a dynamic, cellular tissue with both structural and physiological functions. Bone makes up the skeletal frame that supports our body and provides the connections for movement. Bone also plays an important role in the metabolic and hematological functions – e.g., bone marrow produces white blood cells. These activities and functions require a complex substance.

Bone is in fact a remarkable "space-age" material, a composite of organic molecules and mineral crystals. Bone tissue is essentially a network of mineralized fibers, composed of a matrix of organic collagen filled with inorganic calcium phosphate (apatite) crystals. Bone has three major components: a mineral fraction (apatite), an organic matrix (collagen), and water. By dry weight, the organic materials constitute about 30% and minerals about 70% of bone. Bones and teeth are created by adding mineral crystals to collagen. In addition to the major components – calcium, phosphate, and water – a number of minor and trace elements are incorporated during the manufacture of bone tissue. Hydroxyapatite $(Ca, Sr, Ba)_5(PO_4)_3(OH,F)$ is the major mineral component of bone and enamel and provides the hardness to these tissues.

Collagen is a major structural protein, forming molecular cables that strengthen the tendons and vast, resilient sheets that support the skin and internal organs. Collagen contains one-quarter of the all of the protein in your body. Collagen comprises 90% of the organic portion of dry, fat-free bone. In spite of its essential nature, collagen is a relatively simple protein. Its major components include acetic acid, proline, and 4-hydroxylproline (e.g., $21(C_5H_9NO_3)$).

Bone tissue is created from the minerals and organic molecules that entered the body through drinking water and food and the chemistry of human bone holds information on the diet and life history of the deceased individual. Both the elemental and the isotopic composition of bone are important in studies concerned with dietary reconstruction. Elemental analyses focus on the mineral portion of bone, while isotopic studies are usually aimed at the organic part. Isotopic analyses are also used to study place of origin and past climate as recorded in tooth and bone. The role of archaeological chemistry in the study of prehistoric bones is discussed in further detail in Chap. 4 on Methods, and several examples are provided in Chap. 7, Environment and Diet.

3.6 Sediment and Soil

Sediment is an important term in geoarchaeology. Sediment is any particulate matter (clay, sand, silt, gravel, leaves, shell, and other materials) that can be transported by water or other fluids. Sediments are eventually deposited as a layer of solid particles. Sediments make up all of the earth's surface that is not water or rock. Virtually all buried archaeological materials are found in sedimentary deposits.

Rocks take a long time to form and most archaeological materials are simply too young to end up in a layer of rock. Volcanic eruptions can bury prehistoric artifacts in lava, but that is an exceptional case.

Soil is a special kind of sedimentary deposit produced in situ by the weathering of the earth's surface. Weathering refers to the chemical and biological processes that operate to breakdown and change the surface of the earth, altering its color, texture, or composition. These processes include rainfall, frost, and plant and animal activity as major forces of change. Soils are not only found on the surface of the ground. Old soils can be buried by later deposits. Buried soils provide a useful marker of the location of former land surfaces.

Soils form on the surface of sediments and usually exhibit zones of weathering that reflect changes in the physical and chemical nature of the deposit. There are many different kinds of soils depending on the type of parent material and the conditions of weathering. Soils also vary with temperature, rainfall, and the type of vegetation present. Most soils, however, share common features related to the process of weathering and the solubility of the material.

Most soils exhibit several strata or horizons that form during their development. The top of the soil is the organic or O horizon and contains dust, leaf litter, and other organic materials that accumulate on the surface. This horizon is normally dark in color from the decomposition of organic matter. The A-horizon (aka as topsoil) is also dark with organic matter and is a zone of generally loose and crumbly sediment. Rainwater from the surface leaching through the topsoil dissolves various minerals and nutrients and moves them down through the ground into the B-horizon or subsoil. Most of the leached materials stop and accumulate in this zone. Subsoil is usually lighter in color, lower in organic material, and more densely packed. The C-horizon is the transition zone where the breakdown of the parent material is initiated. Beneath the C-horizon is the unaltered parent material (bedrock or sediments). Soil chemistry and a variety of physical processes, along with plant and animal activities, dissolve and break down the parent material, changing rock into sediment and sediment into soil.

Size is the most important characteristic of the particles that make up a body of sediment. Gravel, sand, silt, and clay are the major categories of sediments (Fig. 3.5). The standard size ranges for these different kinds of sediment are provided in Table 3.4. Gravel, sand, silt, and clay particles are defined primarily by their size. Gravel is larger and very coarse ranging from pebble to boulder size. Sand is gritty to the touch and the individual grains can be seen with the naked eye. Silt is finer and the individual particles can only be seen with a microscope. Silt is smooth and slippery to the touch. Clay is extremely small and particles can only be seen with the very high magnification of an electron microscope. Clay is sticky and plastic when wet.

Soil scientists use the percentage of three components – sand, silt, and clay – to define the texture of soils. The diagram below (Fig. 3.6), the soil triangle, shows the various terms, for example, sandy silt, clayey sand, that are used to describe sediments. The three sides of the diagram show the percent of the three components of sediments – sand, silt, and clay. For a particular sediment, the percentage of these

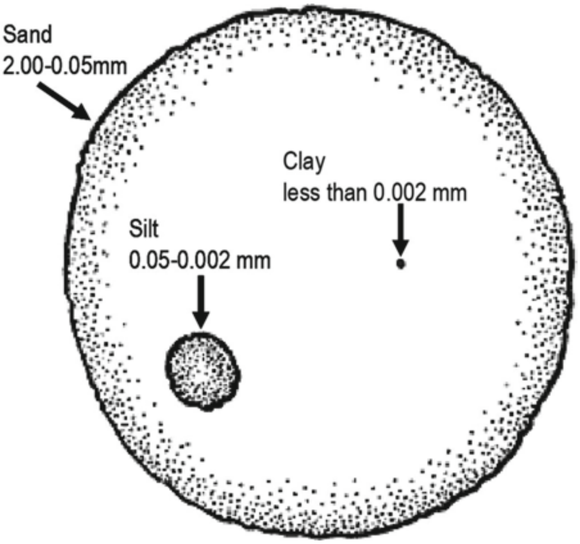

Fig. 3.5 Relative sizes of sand, silt, and clay, the particles that make up the mineral portion of sediments and soils

Table 3.4 Categories of sediments and size criteria

Gravel	>2.0 mm
Boulders	>256 mm
Cobbles	64–256 mm (baseball size)
Pebbles	2–64 mm (US quarter)
Sand	0.10–2.0 mm
Very coarse sand	2.0–1.0 mm
Coarse sand	1.0–0.5 mm
Medium sand	0.5–0.25 mm
Fine sand	0.25–0.10 mm
Very fine sand	0.10–0.05 mm
Silt	0.05–0.002 mm
Clay	<0.002 mm

three components is measured and plotted on the graph. The position of that point on the graph determines the designation of the sediment. For example, 30% sand, 10% clay, and 60% silt would be a sandy silt.

In addition to these different kinds of gravel, sand, silt, and clay, particles in sediments, there are many other materials that accumulate in surface deposits. Organic materials, volcanic ash, and a variety of plant products such as pollen, phytoliths, and starch grains are present. Organic material in soil, or humus, may be of plant, animal, or microbial origin and be relatively fresh or highly decomposed. Living organisms also inhabit the soil. The organic portion of sediment is reported as a percentage and determined by weighing a sample before and after burning, which removes the organic component.

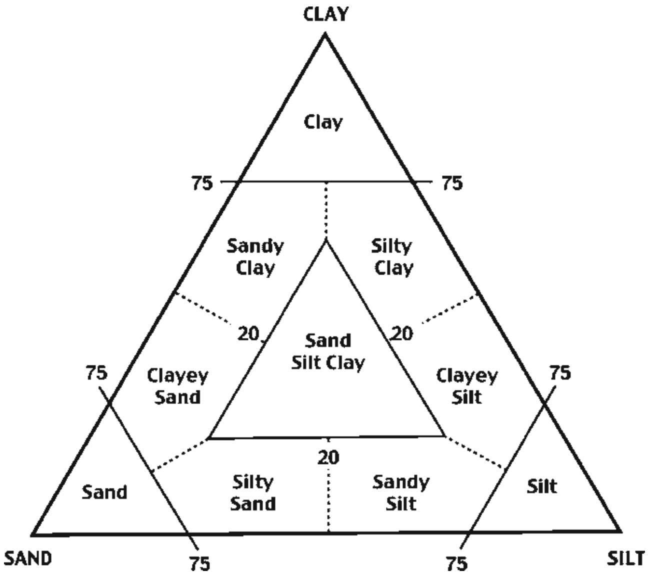

Fig. 3.6 The sediment triangle. This chart is used to find the best description for sediments, depending on the percent of sand, silt, and clay in the material found. For example, a sediment with 60% silt and 40% sand would be called a sandy silt

Sediments can provide answers to archaeological questions concerning the use of natural resources, environment and climate, settlement activity, technology, and construction. Sediments play a number of different roles in archaeological contexts: (1) as raw materials for pottery and building materials, (2) as a surface for the living places of past peoples, and (3) minor uses such as a binder for pigments, or for medicinal or cosmetic purposes.

Clay was commonly used for making pottery in prehistory. Silts are sometimes used in ceramics and are a basic component in building materials such as mud daub, mud bricks, adobe, and fired brick. Sods, soil, and other sediments were used in the construction of earthworks by prehistoric peoples for walls, tombs, and other monuments. For example, the early civilizations of China used rammed earth to build house foundations and enormous city walls. Silt was packed down in wood frames using heavy wooden rammers and layer after layer built up. Parts of the Great Wall of China were built using rammed earth more than 2,000 years ago and remain standing today.

The soils and sediments that make up the earth's surface were the focus of human activities in the past as they are today. Human settlement is almost always found on sedimentary deposits. Humans dig and build and move these sediments around. They also leave physical and chemical traces of their activities in the ground. The physical traces are the visible remains of pits and posts, earthworks and foundations that remain. The chemical traces are the invisible deposits of elements and molecules left behind by various kinds of activities. Manuring, for example, leaves a distinctive organic residue in agriculture fields that can be recovered in laboratory analysis. Phosphate often marks places of human residence from the concentration of bone, excrement, and other materials that accumulate. Human activities of various kinds leave distinctive chemical traces that can be analyzed to determine what took place.

The archaeological chemistry of soils and sediments is an important area of study because of the variety of information that these materials contain. Soils from prehistoric occupations may contain information on site extent, boundaries, activities, chronology, resource availability, or past environments. Although the chemistry of soil is remarkably complex, useful data have been obtained from a number of different elements. Arrhenius in 1929 first documented a correlation between soil phosphate and human activity and used that information to determine site location and study former beach lines.

3.7 Metals

Metals are substances that have electrons freely distributed throughout the material, in contrast to other materials that have local chemical bonds in which electrons are shared only with adjacent atoms. In addition to the unique property of conducting electricity (because the electrons are free to move within the material), this lack of localized electrons is responsible for other properties such as the characteristically shiny "metallic" luster and ductility. Other substances with strong chemical bonds between adjacent atoms require that these chemical bonds be broken before the atoms can move relative to one another. In a metal atoms can move past one another without breaking bonds; thus pieces of most metals can be easily bent and shaped without fracturing. Both this ductility and metallic appearance are undoubtedly key attributes that attracted early human interest.

Most elements, in their pure "elemental" form are metals. But almost all elements are also quite chemically reactive and thus not found naturally in their elemental form. Metals that do occur naturally as pure elements include the "noble" metals, so-called because they are not chemically reactive, i.e., gold, silver, platinum, and rare "platinum-group" metals such as osmium and iridium, and copper. Copper is more reactive and more common and thus sometimes called a "base" metal.

In Europe and the Middle East, the appearance of copper artifacts in the archaeological record is significant enough that the term "Chalcolithic" – or "Copper Age" – was added to the tripartite stone–bronze–iron age system. Other regions such as the upper peninsula of Michigan, which has an abundance of native copper, also recognize ancient "Copper" cultures (Fig. 3.7). Copper must have been an attractive and useful material to prehistoric peoples. The earliest examples of copper are in the form of pendants and jewelry.

Several other elements, including tin, lead, and zinc, occur in nature in elemental form, as do natural alloys of some metals such as osmiridium (osmium + iridium) and awaruite (nickel + iron). However, such occurrences are extraordinarily rare,

Fig. 3.7 A native copper spearpoint cold-hammered from nodules of native copper, from the "Old Copper Culture" of Wisconsin and Upper Michigan, ca. 1500 BC

found only in unusual geological contexts, and are normally in quantities too small to be noticed, much less exploited.

Native copper is commonly associated with other copper minerals: the bright blue azurite and bright green malachite, both of which are copper carbonates, and various sulfides and arsenate compounds that are the primary ores of copper today. Heating these minerals in an oxygen-starved atmosphere (e.g., with excess charcoal) reduces them to metallic copper. More importantly, the inclusion of arsenic-containing copper sulfide yields copper in which some arsenic is dissolved. When arsenic mixes with copper, the resulting alloy has a lower-melting point than copper, flows better at high temperature, is easier to work, and produces a harder, less brittle metal, i.e., arsenical bronze. This discovery is of no small importance, and marks the transition from the Stone Age to the Bronze Age.

Although the earliest known bronzes are arsenical bronzes from the Levant and Mesopotamia, most archaeological bronze is tin bronze. There are copper-tin sulfide ores that might have been accidentally, then intentionally, used, but most tin is available in cassiterite or tin oxide, which is not usually associated with copper deposits and would have to be deliberately sought for its utility for making bronze.

Trying to decipher the technological, and geographic, history of bronze is an active area of archaeometric research. Much of the current interest in metals focuses upon lead isotopes. Although lead is not an essential component of bronze, it commonly contains several tenths of a percent of lead, probably through the accidental inclusion of lead-bearing copper ores. Lead has four abundant isotopes:

204, 206, 207, and 208, the ratios of which vary geographically. Because bronze is a technological product of materials that can come from different sources and because bronze itself was recycled and could represent mixing of bronzes originally from different sources, such studies can be problematic.

Once metal technology developed to the point that high temperatures could be attained in an atmosphere deficient in oxygen (and thus strips the oxygen as well as sulfur from metal compounds), other metals such as zinc, tin, lead, and iron could be produced. The Iron Age, the sequel to the Bronze Age (and which actually overlaps the Bronze Age by a millennium) began sometime in the late second millennium BC in the Middle East. Although there is a simplistic tendency to believe that this necessarily reflects some kind of linear progress for mankind, early iron was actually inferior to bronze. The first iron required higher temperatures than bronze for production and had low carbon content, and thus was brittle. Some speculate that a shortage of copper or tin resulted in a shortage of bronze and the inferior iron was produced as a substitute. Technology quickly advanced, however, to the point that high carbon steels could be produced. Steel is superior to bronze, especially for weapons and armor and began to replace bronze for this purpose.

Iron was actually known and used before the Iron Age. Many ancient cultures from the Sumerians to the early Inuit made artifacts of iron, though never in significant amounts. Most of these have been shown to be of extraterrestrial origin, i.e., from meteorites – and several ancient Mesopotamian words for iron mean "from heaven." There are also unusual geologic conditions that yield native, or "telluric," iron. Approximately 60 million years ago, off the west coast of central Greenland, an iron-rich magma erupted into coal-bearing sediments. The coal reacted with the lava, reducing its iron oxide into native iron and iron carbide, which collapsed into large globules, sometimes a meter across. The hardened lava now forms the basaltic cliffs of Disko Island, which are weathering away leaving large, erosion-resistant boulders of iron on the beaches. While this might be both an exotic and remote circumstance, at least 11 artifacts in the museums of Europe have been matched to this source.

Because metals in ordinary petrographic thin-sections are opaque, they are studied by using direct, reflected light instead of transmitting light through the sample. The metallographic microscope is similar to the transmitted light, petrographic scope except the illuminator is placed above a polished sample, rather than below it, and polarized light shines directly down on the sample. By observing characteristic textures and subtle changes in color and brightness when the sample is rotated in polarized light, an experienced petrographer can identify native metals, metal ores such as oxides and sulfides, and alloys.

Chemical analyses can be used, but for most metals one needs only to know the major elements such as copper and tin. Chemical identification of metals does not require either high precision or trace sensitivity. X-ray fluorescence has often been used in metal identification and has recently been developed into portable, nondestructive devices for field and museum use. X-ray diffraction can identify metals structurally, but this can be complicated by more than one compound in complex alloys such as steel.

3.8 Other Materials

Glass, Pigments and Dyes, Mortars and Cement, Shell

The list above includes only some of the kinds of raw materials and finished products that can be found on an archaeological site in addition to the more common stone, ceramic, bone sediments, and metal and we have already discussed. All of the kinds of things that people originally used and made may be present either physically or chemically.

The vagaries of decomposition often remove the most fragile materials. Organic remains such as plant materials, vegetable food, skin, and leather items are often the first things to go. Sites with excellent preservation, usually either extremely dry or extremely wet, may contain quantities of wood used for construction, fuel, and tools. In some cases of extreme cold, wet, or dryness biological tissue and other products may be preserved, examples include the Iceman, the frozen sacrificial victims in the Andes, and many others. In very dry caves human footprints and excrement are often found. Recent discoveries of coprolites (preserved feces) in a dry cave in Oregon have provided evidence of the earliest humans in the Americas ca. 14,250 years ago. Figure 3.8 provides some indication of both the varieties of materials present on archaeological sites and the effects of decomposition on different materials. Table 3.5 provides information on the approximate longevity of different materials in the ground and the favorable and detrimental conditions for preservation.

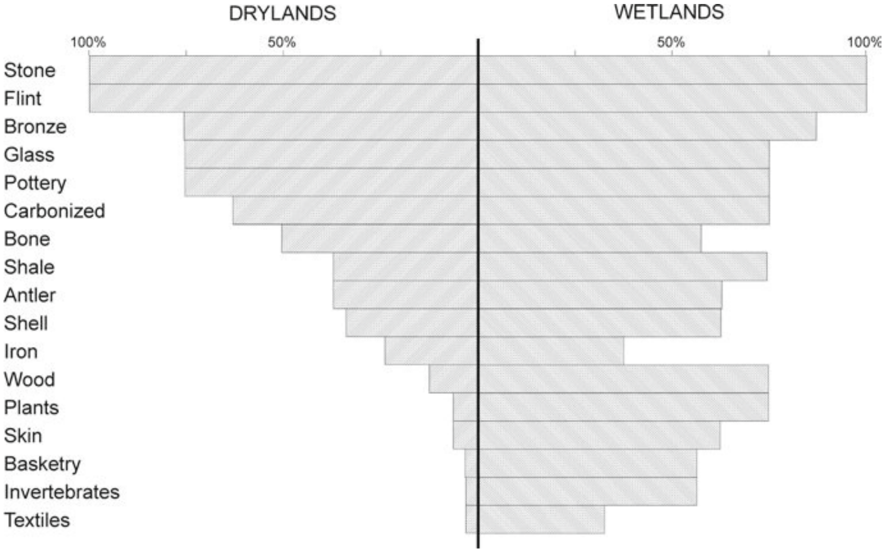

Fig. 3.8 Estimated percentage of survival of different materials in dry and wet conditions (After Coles 1979)

Table 3.5 Conditions of preservation and survival for various classes of archaeological remains (Based on Sutton and Yohe 2003: 103)

Material	Normal survival time	Conditions for preservation	Conditions against preservation
Stone	Millions of years	Most	Exposure in erosional environments
Copper/bronze	Millions of years	Most	Moisture, oxygen
Gold	Millions of years	Most	Few
Glass	Millions of years	Most	Plowing, acidic soils
Ceramics	Thousands of years	Most	Freeze–thaw, plowing, acidic soils
Iron	Hundreds of years	Few, no oxygen	Moisture, oxygen
Bone	Months to years	Rapid burial, wet, burning, alkaline soils, fossilization	Surface exposure, wet–dry conditions, acidic soils
Plants	Weeks to years	Dry, cold, wet	Moisture, warm temperatures, acidic soils
Flesh	Days to weeks	Dry, cold, wet	Moisture, warm temperatures, acidic soils

In this chapter, we have focused only on the most common archaeological materials. In this last section we describe a few more. There are still many things we don't cover because they are less common and we have limited space. Such materials might include wood, charcoal, plant remains, feathers, textiles, and many more. In the paragraphs below we focus on glass, pigments and dyes, mortars and cements, and shell as objects of interest in archaeological chemistry. Pigments and dyes were used for painting, decoration, and clothing; glass was originally made into beads, jewelry and containers, eventually used for windows; mortar and cement hold architecture together and includes plaster for floors and other construction; mollusk shells from various species – both fresh and saltwater varieties – were deposited as waste from food consumption, used in construction, or for the manufacture of jewelry or other items.

3.8.1 Glass

A glass is a material that is solid but resembles a liquid in that its molecules are randomly oriented, without any crystalline structure. This comes about by cooling a liquid so quickly that the molecules lose their energy to move around before they have time to link together into any regular arrangement. Although other substances can be chilled to produce solids without crystalline structure, here we use the term glass in the common parlance to mean glass made predominantly of silica (SiO_2), whether natural or man-made. Because glass molecules are randomly oriented, without an extensive network of chemical bonds, they do not interact strongly with light – and thus are translucent or transparent.

Pure silica melts at approximately 1,700°C, a temperature not possible prehistorically or in nature. The presence of other elements, especially the alkali elements – those in the first column of the periodic table – markedly reduce this melting point. Elements in the second column – known as the alkaline-earth elements – tend to raise the viscosity of molten glass, reducing the mobility of the atoms and making it harder for crystallization to occur. These elements tend to stabilize the glass during crystallization. Rocks that contain a lot of alkali elements such as sodium and potassium melt at temperatures less than 900°C. Even a trace of water in the mix can lower the melting point by another 100°C. If such a rock erupts at the surface of the earth and looses this water, its melting point rapidly rises and the rock can solidify into a natural glass like obsidian. Thus most obsidians have a composition of 70–75% silica, with 7–12% alkali oxides (Na_2O and K_2O) and 10–15% Al_2O_3.

Such mixtures of silica and other minerals would have made it possible to produce glass in antiquity by lowering the required melting temperatures. The earliest known glass comes from Egypt and the Near East from approximately 2500 BC when pyrotechnology had developed to the point that bronze could be smelted at temperatures well above 1,000°C. This was not coincidental; to achieve temperatures necessary for glass, one likewise needs to understand materials that can be used for high-temperature kilns as well as have the knowledge of fuels and ventilation techniques needed to sustain those high temperatures. The first glass objects were beads, perhaps initially produced as by-products of metal-working slag or during the manufacture of faience, a pre-glass vitreous material made by a process similar to glazing. *Faience*, or Egyptian faience, is a non-clay-based ceramic, made from sand, salt (natron), calcite lime, and mineral coloring, displaying surface vitrification which results a bright luster in various colors.

The first glasses were made by mixing silica-rich sand with alkali-rich plant ashes or naturally occurring alkali-rich minerals, along with some lime, either as natural material in the sand or as deliberately added limestone. Thus a lot of early glass has compositions a lot like that of obsidian, i.e., about 70% silica, 15% $Na_2O + K_2O$, and 10% $CaO + MgO$. Most glass produced today still has this basic "soda-lime" composition.

Early glass artifacts were solid and used as jewelry because of their beauty and value. The oldest fragments of glass vases (hollow glass objects) date back to around 1500 century BC and came from Mesopotamia. Once the basic recipe for making glass was established, additional components were added to refine its properties, especially color. Early raw materials for glass often included small amounts of iron, which imparted an unwanted brown or green appearance. Other minerals could be added to produce richer colors. For example, cobalt produces a deep blue while uranium develops a bright yellow color. More compounds could be added to change the luster and opacity.

Glassblowing began only at the end of the first century BC. Blowing glass inside molds sped up the production process and greatly increased the variety of shapes and designs that were produced. The Romans expanded the glass industry substantially and their cups, bottles, pitchers, and vases of glass were found across Europe and around the Mediterranean.

With their conquest of Egyptian glass production centers in Alexandria, Egypt, and Sidon, Syria, the Romans took glassmaking to an art form not rivaled until modern times. One of the most famous pieces of Roman glass is the Lycurgus Cup, an example of *dichroic* (two-color) glass. The appearance of this glass in reflected light is pale green, but when light shines through it, the cup appears dark, ruby red (Fig. 3.9). It was not until the twentieth century that archaeometric investigations revealed that the dichroic properties are due to the inclusion of extremely small amounts of gold and silver, which precipitated in the glass as submicroscopic particles, too small to see but just the right size to scatter light of the right color and impart the two-color appearance.

A parallel glass making tradition developed in China, again following the discovery of the pyrotechnology associated with bronze production. In China, however, lead oxide was used instead of alkali elements as the flux and barium, instead of calcium and magnesium, was used to stabilize glass.

The addition of lead oxide in glass production was further refined in the eighteenth century in Europe. Adding lead oxide softens the glass, making it easy to cut, and increases the density and index of refraction of glass, making it appear more brilliant, and giving rise to the leaded cut-glass or "crystal" industry.

Unlike obsidian, man-made glass is a technological product involving mixing of multiple components. While major element compositions are constrained by the requirements of making glass and its desired attributes, both the major and the trace elements in the mixture come from multiple ingredients. Their concentrations vary greatly depending upon the selection and quantities of particular materials. As a result, compositional studies of glass, in sharp contrast to those of obsidian, do not represent a specific geologic source, but reflect differences in regional recipes and

Fig. 3.9 The Lycurgus Cup, a fourth-century AD Roman glass masterpiece, currently housed in the British Museum. The two views show the piece in natural light and with the bicolor or "dichroic" effect caused by the two types of glass used and a background light source

technology. Thus compositional studies have some value in identifying the regional production centers for glass artifacts that find themselves a long ways from home. For example, during the European colonization of North America, glass beads from Europe were commonly brought in abundance to trade with natives.

3.8.2 Pigments and Dyes

Natural colorants can be conveniently divided into two categories: *pigments*, which are insoluble solids commonly of mineral origin, and *dyes*, which are normally used in liquid form and are commonly of organic origin. Pigments are used as paints and to create colored surface treatments, e.g., to paint murals and to decorate pottery; dyes are mainly used to color animal and plant fibers.

Pigments and dyes are compounds that reflect light of specific wavelengths (colors) and are suitable for coloring other materials (McLaren 1986). These colorants can be either natural or synthetic (artificially made), soluble or insoluble, and organic or mineral in composition. Colorants that are insoluble in water and usually inorganic are pigments. Organic colorants soluble in water are known as dyes.

Most pigments of archaeological interest are minerals, although other materials such as charcoal and burned bone can also be pigments. Table 3.6 provides a summary of some common minerals used for pigments along with their chemical formula and other information. Oxides of iron are among the most abundant and thus widely used pigments. Hematite, Fe_2O_3, the earthy red mineral responsible for the red color of red ochre is the oxide of iron in its "oxidized" +3 state. Coarsely crystalline hematite is a shiny, black mineral but when crushed to particles of microscopic size, they're red. Hematite naturally occurs in many clays in this microscopic and can impart a red color when present at levels as low as 1%. These hematite-bearing clays are the material commonly used as red ochre.

The hydrated form of iron oxide, FeO(OH), limonite or goethite, can similarly be shiny black as a coarsely crystalline material but is brownish yellow when finely powdered and is responsible for the color of yellow ochre as a pure material or in a clay matrix.

Magnetite, $Fe^{+2}Fe_2^{+3}O_4$, is a black oxide of iron that occurs in nature but is more likely produced by firing hematite-bearing pigments in an oxygen-starved environment, known as a "reducing" environment because it reduces the valence of some of the iron from +3 to +2. Conversely, firing a magnetite-bearing pigment in an oxygen-rich environment oxidizes the magnetite to hematite. This oxidation and reduction of iron, along with burning out carbon-rich organic matter, is responsible for the colors of many ceramic pastes, which normally contain several percent iron oxide.

Copper is another common element that has many brightly colored blue and green minerals used as pigments. These are mostly hydrated minerals or carbonates, which decompose upon heating to temperatures required by ceramics and

Table 3.6 Common minerals used for preparation of colorants and dyes, color, chemical composition, and additional information

Mineral	Color	Composition	Note
Hematite	Red	Fe_2O_3	The pigment responsible for the color of red ochre. Very widely used as a ceramic pigment
Magnetite	Black	Fe_3O_4	Common ceramic pigment. Can be made by firing hematite in oxygen-starved (reducing) conditions
Goethite Limonite	Yellow/brown	FeO(OH)	The pigment responsible for the color of yellow ochre
Cinnabar	Vermillion red	HgS	Unstable upon heating
Azurite	Deep blue	$CuCO_3$	Unstable upon heating
Malachite	Bright green	$CuCO_3$	Unstable upon heating
Sulfur	Yellow	S	Unstable upon heating
Orpiment	Orange-yellow	As_2S_3	Unstable upon heating Often with realgar and cinnabar
Realgar	Orange-red	As_4S_4	Often with orpiment and cinnabar Unstable upon heating
Chrysocolla	Turquoise blue	$(Cu,Al)_2H_2Si_2O_5(OH)_4 \cdot n(H_2O)$	
Lazurite	Ultramarine	$(Na,Ca)_8(AlSiO_4)_6(SO_4,S,Cl)_2$	Rare and highly valued in lapis lazuli
Calcite	White	$CaCO_3$	
Gypsum	White	$CaSO_4 \cdot 2H_2O$	
Kaolin	White	$Al_2Si_2O_5(OH)_4$	
Anhydrite	White	$CaSO_4$	May be natural or formed by heating gypsum
Charcoal	Black	C	

thus, if applied to pottery, must be applied after firing. Other metals such as nickel and chromium are more rare but have similarly brightly colored blue and green minerals that can be used as pigments.

Most pigments are strongly colored, fine mineral powders prepare by grinding solid raw materials. A few insoluble pigments of vegetable or animal origin are also known, from a certain kinds of tree bark, nut shells, and animal horn. Because pigments are insoluble, to apply them to the surface of a material, they are usually mixed with an adhesive binder, which could be a plant gum or resin, egg albumin, or other animal-derived adhesives.

One of the earliest uses of pigment can be seen in the cave paintings of the Upper Paleolithic in France and Spain, the oldest of which are dated to more 30,000 years ago. These pigments were likely mixed with a variety of binders such as egg white, mineralized water, blood before being applied to the surface of the cave or rock.

The use of portable Raman spectroscopy is greatly increasing the number of analytical studies of prehistoric art (Fig. 3.10). This technique is nondestructive, can be done in situ, and provides a reliable indication of the pigments and binders that are used in the paintings. A Raman spectrograph from a prehistoric cave painting in Spain is shown in Fig. 3.11. Raman spectroscopy at the famous painted cave at Altamira in Spain has been done on red, yellow, white, black, and brown pigments on the walls. No heat alteration of the pigments was observed suggesting that they had not been burned as part of the preparation process.

Dyes are normally organic, water-soluble and applied to organic materials such as textiles and fibers of animal or vegetable origin such as wool or cotton. Pigments and dyes are produced from a wide range of natural materials including plants, insects, and shellfish. The solubility trait of dye is essential for the color to be fixed to the fibers of the textile and be resistant to repeated washing. There are two general methods for dyeing cloth and fibers. Vat dyeing refers to the process of dissolving the dye in water and soaking the cloth. When the material dries, the color reconstitutes itself on the fabric. This method is often used with indigo dyes, which are largely insoluble without chemical reduction, usually fermentation in an alkaline solution. Mordant dyeing requires soaking fabric in a salt of iron or aluminum, prior to immersion in a dye suspension. A mordant is a substance used to set the color on fabrics by forming an insoluble compound with the dye. Mordant dyes are usually based on plants and the colors of red, yellow, and purple are common. Both types of dyes can survive for several thousand years under favorable conditions.

Thin layer chromatography (TLC) or high performance liquid chromatography (HPLC) are often used to try and identify visible natural dyestuffs. Ancient Peruvian

Fig. 3.10 Portable X-ray fluorescence instrument measuring composition of pigment in mural painting

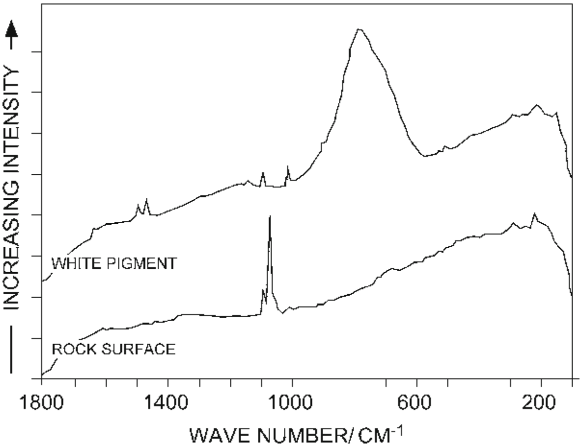

Fig. 3.11 Raman spectrography from a white portion of an Upper Paleolithic painting in La Candelaria Cave in Spain. Whewellinte, a white mineral, is seen in the upper spectrum along with hydrated lime; the lower spectrum is taken from an unaltered rock surface in the cave for comparison (From Edwards et al. 1999)

textiles are commonly investigated for information on dyes and colors used in their production. Textiles were an important aspect of life in the pre-Columbian Andes and both wool from llama and alpaca were used, as well as the fibers of cotton. Jan Wouters and his colleague Noemi Rosario-Chirinos have used HPLC, in combination with diode-array detection in the ultraviolet and visible region (UV–VIS) to study samples that belong to different pre-Columbian cultures, dating from 300 BC to AD 1532, along with a series of present-day Peruvian natural dyes. These techniques provide separation, relative quantification, and spectral characterization of all dye components that are detected.

Sources of dyes can be classified by source and color and are described briefly here. Animal Red: Cochineal comes from an insect that feeds on cactus in Central and South America. The principle component of dye is carminic acid which may be up to 20% of the insect by weight. This acid produces a range of beautiful shades of red. Vegetal Red: These red dyes are found in the roots and beneath the outer skin of the various members of the Rubiaceae plant family. Vegetal Yellow: There are more than 15 species of plants in South America that produce sources for yellow dye. The primary flavonoid components of these plants are luteolin and apigenin. Flavonoids, a class of plant secondary metabolites, are widely distributed in plants and fulfill many functions including producing yellow or red/blue pigmentation in flowers. Luteolin and apigenin are most often found in leaves and flowers of plants.

Vegetal Blue: The blue or purple color indigo is commonly derived from a plant known as Isatis tictoria or various Indigofera species. This was obtained from the plant leaves which were soaked in water and fermented to convert the glycoside indican in the plant to the blue dye idigotin. The precipitate from the fermented leaf solution was mixed with a strong base such as lye, pressed into cakes, dried, and powdered. The powder could be mixed with various other substances to produce different shades of blue and purple. The color indigo, now produced synthetically, is used in the production of denim cloth for blue jeans. Tannins: from many species of plants, found in the vacuoles or surface wax of the plants. Tannins were used to produce brown to dark brown colors. Tannins are astringent, bitter plant polyphenols that either bind and precipitate or shrink proteins. Tannins are also an important ingredient in the process of tanning leather.

The dyes in Peru were mixed with mordants and other additives to improve the process and extend the life of the color. The mordants and additives used in the dyeing process included several kinds of aluminum salts, derivatives of iron (e.g., black alcaparossa, a mineral), plant ash, tannins, lime, urine, and vinegar.

Organic dyes, however, generally tend to fade and degrade rather quickly in prehistoric materials, making analysis and identification more difficult. Complex chemical degradation of dyes and fibers takes place during both burial and museum storage contexts. When a fabric has completely lost its original color, the analysis is more complicated. For badly faded textiles, a different analytical path is involved, searching not for the dyes themselves but their detectible degradation products.

3.8.3 Concretes, Mortars, and Plasters

Concretes, mortars, and plasters are composites used primarily as building materials. Concretes are used to create an artificial, shaped stone. Concrete is a composite made up of cement, a fine aggregate such as sand, a coarse aggregate such as gravel, and water. Cement is a binding agent, usually including finely powdered burnt lime. There are two types of cements, non-hydraulic cements which set in air, and more durable, hydraulic cements which can set under water and are largely insoluble. Mortars are used to fill the gaps between blocks and bind them together in construction. Mortars generally contain other aggregates smaller than 5 mm in diameter; concrete has larger inclusions as part of its composition. Plasters are another composite material used to cover and protect exposed surfaces. Plasters are generally fine grained materials than can be used to create a smooth finished surface.

Lime ($CaCO_3$) is a common material used for making a hard and water-resistant cement. It is found in many parts of the earth as a component of limestone. It can be chemically altered by heating to produce stronger binding agents and it can be rather easily ground to a fine powder. Lime burned at 900°C turns into quicklime ($CaCO_3$), which can be combined with water in the absence of carbon dioxide to produce slaked lime ($Ca(OH)_2$). This wet mass sets slowly with the loss of water to produce interwoven crystals of $Ca(OH)_2$ and then combines with carbon dioxide in the air to produce lime (Fig. 3.12).

Barba and colleagues have reported a fascinating study of the sources of lime for construction in the ancient city of Teotihuacán in modern Mexico. This enormous city had a population of perhaps 125,000 people around AD 100 and covered some 26 km^2. There are a number of distinctive areas in the planned city, including pyramids,

Fig. 3.12 The stages of manufacture of lime binders and cement

$$\overset{\text{limestone}}{CaCO_3} + \text{heat at } 900^\circ C \rightarrow \overset{\text{quicklime}}{CaO} + CO_2$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \ \text{slaked lime}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

palaces, ceremonial precincts, major avenues, administrative areas, residential compounds, craft workshops, exchange areas, avenues, tunnels, two canalized rivers, and ceremonial caves. (Teotihuacán is also discussed in a case study in Chap. 8, Provenience.)

Much of this 2,000-year-old city is constructed, built up, and covered in plaster. The best guess for the amount of area covered with plaster is on the order of 12,000,000 m^2, an unimaginable amount. What is even more amazing is that the raw material for making this plaster is found nowhere near the ancient city itself. The Valley of Mexico in which Teotihuacán is located is a huge volcanic basin, made up of young metamorphic rocks. Lime plaster is made from limestone rock. The three closest outcrops of limestone are found to the south, the northwest, and to the east and lie between 60 and 150 km distant from the city. The production, transport, and use of this material must have played an important role in the economy of the city and for this reason understanding its place of origin is important.

Barba and his colleagues sampled the three outcrops of limestone to determine their distinctive signatures. This information was compared to lumps of calcium carbonate found in the finished plaster in the city. The group of scientists used several different techniques to examine the samples. The major element composition of the geological samples was determined by XRF. The major element composition of the lumps was determined by SEM-EDS. Trace element composition was determined by LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry) to measure the elemental composition of the plaster and the limestone. This methodology is well suited for analyses of very small lumps with microscopic spot sizes. The LA-ICP-MS method is able to analyze a large number of trace and rare earth elements with speed, precision, and high resolution, especially in cases where the major chemical composition does not appear to be particularly distinctive. The instrument worked extremely well for the characterization and determination of the provenance of the lime plaster source material.

Comparison of the ancient plasters with the limestone outcrops revealed that the lime must have been produced and transported from the closest source to the northwest in the state of Hildago, 60 km away. The geochemical results, for both the major elements and the trace elements, show that Hildalgo was the source for the Teotihuacán lime plasters (Fig. 3.13). The enormous labor costs involved in the quarrying, production, and transport of the lime imply extensive planning and the control of a great amount of human energy by the complex hierarchical organization that was present in the state-level society at Teotihuacan.

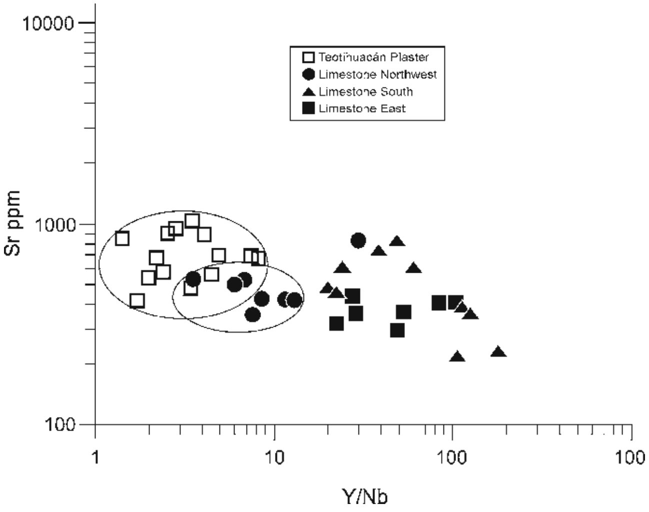

Fig. 3.13 A log–log scatterplot of strontium ppm vs. the ratio of Y to Nb in the samples of plaster and limestone document the close correspondence between the source of limestone rock in Hildago and the plaster used for covering parts of the ancient city of Teotihuacán. *Open squares* are plaster samples; *filled circles* are lime quarries to the northwest in Hildago; *filled triangles* are quarries to the south in Morelos; *filled circles* are quarries to the east in Puebla. The two ellipses are intended to show the close correspondence between the Tula limestone and the Teotihuacán plaster (From Barba et al. 2009)

3.8.4 Shell

Shells are occasionally found in archaeological sites, both naturally and as a by-product of human activity. Shellfish – such as oysters, clams, mussels, scallops, limpets, and many others – are an important category of foods eaten both today and in the past. Evidence for the consumption of shellfish dates back several hundred thousand years in human prehistory. Shellfish are a plentiful and easily collected source of protein and essential trace elements such as iron, copper, and magnesium. Shells from both fresh and saltwater species appear in archaeological sites.

Shellfish belong to the biological group of species known as mollusks, animals with a shell and a foot. Univalve mollusks have one shell and include many species of snails, conchs, and others. Bivalve mollusks have two shells and include clams, scallops, and oysters. There are many species of mollusks and both freshwater and salt water varieties. In addition to their use as food, shells were often used to make beads, fishhooks and other objects. Crushed shells have been used as a source of lime, for pottery temper, and as construction material. In some areas such as the South Pacific, shells of species like the cowrie have been traded as valued items over long distances and even used as money.

Large heaps of shells, known as shell middens, representing the accumulated refuse from thousands of meals can be found on coasts and river banks in various parts of the world. These shell middens can be enormous, hundreds of meters long, tens of meters wide, and up to 15 m high. The Emeryville shell mound in San Francisco Bay was 100×300 m in size (the area of six football fields) and more than 10 m high (equivalent to a three-story building).

Site seasonality can be assessed using the shells from certain mollusks which produce growth rings. The time of year that the shell was harvested can be determined from these rings, documenting the presence of human occupants. For example, many mollusks add an annual layer of shell. Figure 3.14 shows an oyster with several annual rings or layers of shell growth. Careful preparation and study of these shells can help determine how old the creatures were when they were harvested.

In addition to information about diet and seasonality, shells at archaeological sites provide information about the local habitat and climate change. Different species of shellfish live in different depths of water, and prefer different temperatures, salinity, and amounts of current. Shells are composed of calcium carbonate ($CaCO_3$) which is a molecule composed of calcium, carbon, and oxygen. The exact ratio of oxygen isotopes in shell depends on the temperature of the water in which the shell formed. Determination of that ratio in the shell can provide information on changes in water temperature (correlated with air temperature) over time. That information can be used to estimate where along a coast the shell is coming from.

An example of the investigation of oxygen isotopes in shell comes from prehistoric California where the species *Olivella biplicata* was used to make beads that were traded over long distance. The study by Eerkens and others measured oxygen isotope ratios in both modern and prehistoric shell from the Pacific Coast of California (Fig. 3.15).

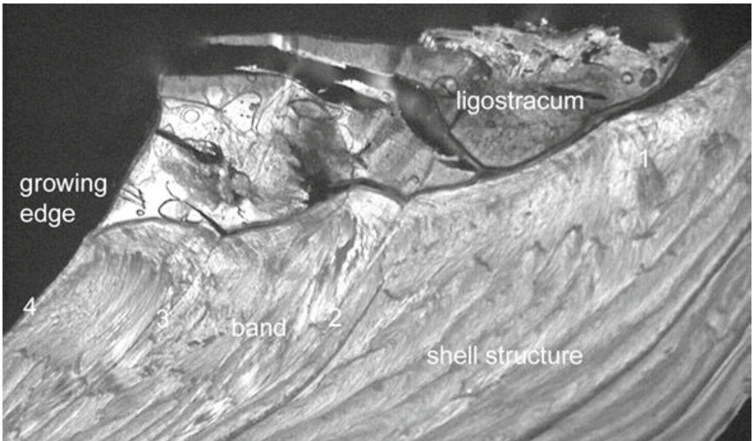

Fig. 3.14 Annual growth rings on a mollusk shell

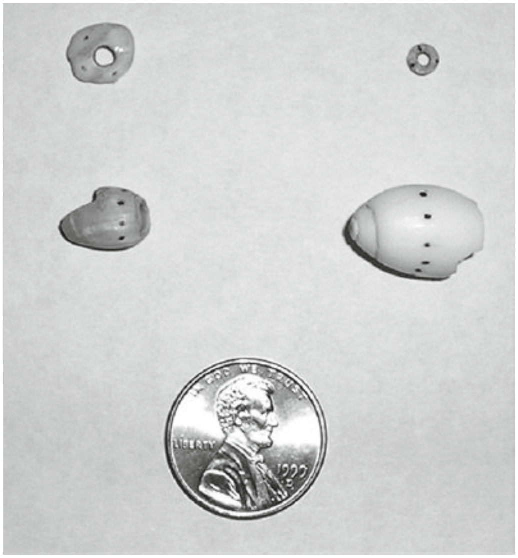

Fig. 3.15 Three archaeological beads of *Olivella biplicata* and one intact modern shell (white). The *black dots* mark sampling locations on the shell

The oxygen isotopic ratios of modern *Olivella biplicata* shells reflected local sea temperature and conditions. Figure 3.16 shows the oxygen isotope ratio for sequential samples from the same modern shell from Santa Barbara taken at 0.5 mm intervals. The samples record a complete year in the formation of the shell and isotope ratios reflect the changes in water temperature across the seasons.

Two different portions of the California coast could be distinguished on the basis of the isotopes. Basically it was possible to determine if shells came from the northern two-thirds, or the southern third of the state's coast. Analyses of a small sample of six prehistoric beads are from the Owens Valley in southeastern California and four from interior northern California, at distances up to several hundred kilometers from the sea, indicated that all ten were made in southern California.

Trace-element analysis has also been used to try to distinguish shells with limited success. Katherine Miller in 1980 showed that some elements, especially magnesium, strontium, and barium, which substitute for calcium in the calcium carbonate of shell, have some ability to regionally distinguish shells. Cheryl Claassen, taking advantage of the high magnesium content of the highly saline rivers that flow into the Gulf of Mexico in contrast to those that flow into the Atlantic, was able to distinguish Gulf vs. Atlantic sources for shells in archaeological contexts in the Southeastern US Problems with *diagenesis* (contamination), as well as burning of the shell, can alter the biogenic composition and confound elemental analyses.

3.9 Summary

This chapter concerns the major categories of material that archaeologists encounter in their research. These include rock for tools and construction, ceramics for containers and figurines, bone as a by-product of animal consumption also used

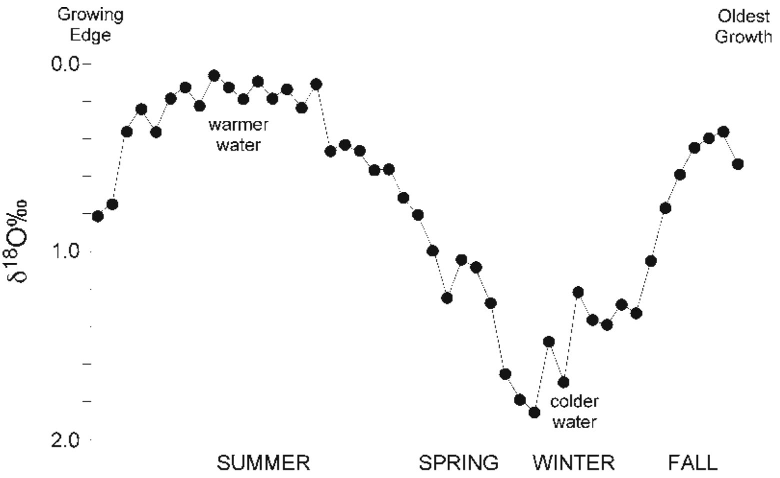

Fig. 3.16 Oxygen isotope ratios in sequential samples from the same modern shell over a 1-year period. Each circle represents one sample; samples taken at 0.5 mm intervals. The reverse order of the seasons is based on the growth of the shell from *left* to *right*

for tools and many other purposes, sediments and soils which provide raw material for construction as well as the surface on which people normally live, and metals used largely for tools and ornamental purposes until the Industrial Era when they became a major component of our lives.

Each of these different kinds of material involves distinctive physical and chemical composition and requires specific kinds of investigation. The questions asked, the procedures used, and the instrumentation employed are determined by the kinds of materials under study. For example, rocks usually involve geologically related questions about function and source. Their composition is largely inorganic and element and isotopic analyses are normally undertaken. Because of the importance of different kinds of material, this chapter has provided some information on their important characteristics. The following chapters will discuss in more detail how we study these materials. There are of course all varieties of material – mineral and vegetable, solid and liquid – at archaeological sites that we have not discussed. Identification of these materials is one of the goals of archaeological chemistry.

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Chapter 4
Methods of Analysis

Contents

In this chapter, we look at archaeological chemistry from another angle, specifically in terms of the kinds of analyzes that are common in the field and the kinds of tools – the instruments – that are normally used. We discuss specific kinds of analyses that are done involving magnification, elemental analysis, isotopic analysis, organic analysis, and mineral/compound analysis. This chapter is intended to document the general categories of investigation that go on in laboratories of archaeological chemistry.

Archaeologists use many different kinds of tools, from shovels, trowels, and brushes to mass spectrometers and atomic reactors. Laboratory archaeologists employ a wide range of equipment and instruments. They also use a lot of abbreviations. Five common types of instruments in laboratories of archaeological chemistry are

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DOI 10.1007/978-1-4419-6376-5_4,

described in this chapter, each based on different principles: (1) microscopes, including a scanning electron microscope (SEM), (2) spectroscopic and spectrometric methods, including inductively coupled plasma/mass spectrometry (ICP-MS), (3) neutron activation analysis (NAA) using a nuclear reactor, (4) X-ray diffraction (XRD), and (5) molecular analysis using gas chromatography (GC) and mass spectrometry (MS). These instruments can determine the composition of many kinds of archaeological materials. Each has advantages and disadvantages and each provides specific kinds of information about the material that is analyzed.

Instrumentation for chemical analysis can be conveniently divided into (1) methods for elemental and isotopic analysis that measure amounts of individual atomic components such as phosphorus and iron and their relatives, and (2) methods for the molecular analysis of organic materials that identify compounds such as dyes and animal fats. This distinction reflects the long-standing division between inorganic and organic analysis in the field of chemistry.

Instruments known as spectroscopes or spectrometers are generally used for elemental analyses. Spectroscopic methods examine the interaction between atoms and light and are defined primarily by the portion of the electromagnetic spectrum that they use. Instead of the spectrum, more powerful mass spectrometers use electromagnetic fields to sort atoms according to their weight. Specific atomic weights, or masses, correspond to specific elements and isotopes.

For the molecular analyses of organic compounds, differences in the physical properties of molecules are helpful in identifying them. These “chromatographic” methods are defined by specific properties, such as volatility and solubility, which are used to separate individual compounds. Such separation methods are commonly used in combination with mass spectrometers to sort and identify molecules by their weight.

Inorganic mineral compounds – for example, jadeite, turquoise, and many others – are defined by their crystal structure as well as by their elemental composition. Analysts use the petrographic microscope and XRD to reveal crystalline structure and infrared (IR) spectroscopic techniques to revealing the kinds of chemical bonds in the crystal. From this information individual minerals can be identified.

Each section of this chapter is organized in a similar way. The method of analysis is first described, followed by a consideration of the instruments that are used. There are brief examples provided with some of the methods; more case studies appear in Chaps. 5–9. We provide some information on how to interpret the results of analyses as well. The chapter concludes with a brief summary of the methods of analysis and capabilities of these instruments and how to choose the most appropriate equipment.

4.1 Magnification

Large, sophisticated, and expensive analytical laboratory instruments, and what they can do, are remarkable. But the most powerful tool for material characterization – and the one most often used by archaeologists – is undoubtedly the microscope, and specifically the binocular microscope. It may seem unusual to include microscopes in the instruments of archaeological chemistry, but there are several reasons for this. The optical microscope is one of the less expensive and complicated tools in the archaeometry lab. Little training is required for use and operational costs are minimal. It is much easier to maintain, at much lower expense. Usually an entire artifact can be examined, and the process is totally nondestructive. Moreover, many microscopes are portable.

Plant pollen, seeds, pottery, stone tools, bone, textiles, metalwork, and many other materials can be studied under a microscope. Microscopes are used for the detailed examination of the surfaces of archaeological objects and provide visual information through magnification. The microscope is commonly used to identify small particles such as bits of charcoal and shell. Important authentication studies have depended on microscopic observations of tool marks, pottery provenience through the recognition of ceramic tempers, and many other kinds of evidence. Microdebitage (tiny debris produced by human activity and deposited in archaeological contexts) provides data about technology and function; observations of seeds, pollen, phytoliths, and bone debris can inform us about diet. Experienced microscopists can easily identify many substances and provide important new information.

Two general kinds of microscopes are employed in archaeological studies, optical microscopes and electron microscopes, and described below. More sophisticated electronic microscopes, including the SEM, the scanning tunneling microscope (STM), and the atomic force microscope (AFM) can be used for measurement of the elemental composition of materials under analysis, thus combining visual and chemical capabilities in a single instrument.

4.1.1 Optical Microscopes

An optical microscope uses lenses at the ends of a hollow tube to magnify an object (Fig. 4.1). The same principle is found in a telescope. Optical microscopes are often used in the range of 5–100×, but sophisticated models can magnify image up to 1,000×. A light source is used to illuminate the object of study on a platform

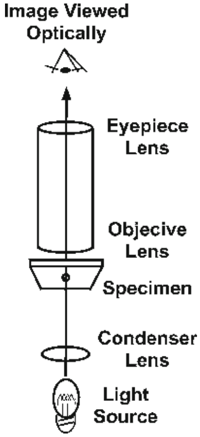


Fig. 4.1 Basic components of a simple optical microscope

beneath the microscope tube. The light source is commonly above the object. A standard, single-tube optical microscope has no depth in the field of view. A binocular microscope, with two independent tubes focused on the same object, magnifies in three dimensions. The large, bright stereoscopic field of the binocular microscope is ideal for examining a variety of archaeological materials including plant remains, small artifacts, usewear, and cutmarks.

There are more sophisticated tools for visualization and magnification than the simple binocular microscope. At the next level of sophistication are the petrographic (transmitted light) microscope and the closely related metallographic (reflected light) microscope. In contrast to the binocular microscope, which is commonly used in the range of 10–40×, both the petrographic and metallographic microscopes are used in the range of 40–1,000×, i.e., for viewing objects from a few millimeters to a few microns (1 μm = 1/1,000 mm). These types of microscopes are discussed in Sect. 4.5.1 below.

4.1.2 Scanning Electron Microscope

At a much higher level of sophistication is the SEM. Although the SEM is an awesome instrument (Fig. 4.2) capable of extremely high magnification (25,000× compared to 1,000× for optical microscopes), its utility for the archaeologist

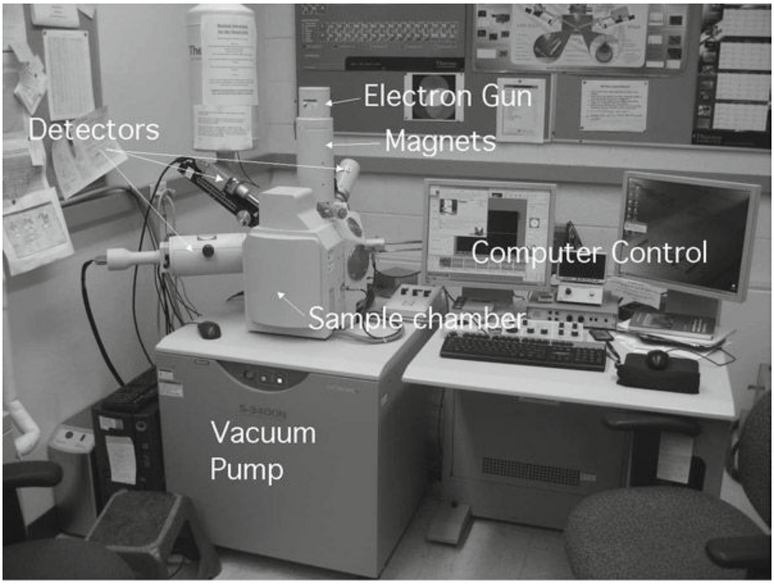


Fig. 4.2 An scanning electron microscope (SEM). Major components include the sample vacuum chamber, the electron source, the magnets that focus the electron beam, the detector, and the computer monitors where images are displayed

does not rely on this high magnification, but on its depth of field. Optical microscopes have a flat focal plane; any object or part of an object extending above or below this plane is out of focus and the thickness of this plane diminishes rapidly with increasing magnification. The SEM in contrast provides a sharp image with pronounced shadows, producing a distinctly three-dimensional aspect (although the actual image is flat). This makes the SEM superior to optical microscopy for identifying microscopic grains such as seeds, spores, and pollen and for studying in high detail microscopic features such as the grooves made by tools and animal teeth.

The SEM is widely used in archaeology to obtain high-resolution images of artifacts and other materials. An SEM can reveal features of materials like plant remains (Fig. 4.3) or stone tools that are otherwise invisible. Magnifications available on an SEM have an enormous range, commonly from about 25 to 250,000×. The SEM creates magnified images using high-energy electrons, instead of light waves. Such electrons behave like light waves except they have much shorter wavelengths and can be used to examine smaller objects than can be seen with an optical microscope. A sample is placed inside the vacuum chamber of the instrument and the air is removed. An electron gun fires a beam of electrons at the sample. This beam passes through a series of magnetic lenses that focus the electrons on a very small spot. As the electron beam hits the sample, secondary electrons are knocked loose from its surface. A detector counts and amplifies these signals for the computer and that provides the three-dimensional image of the object surface on a monitor.

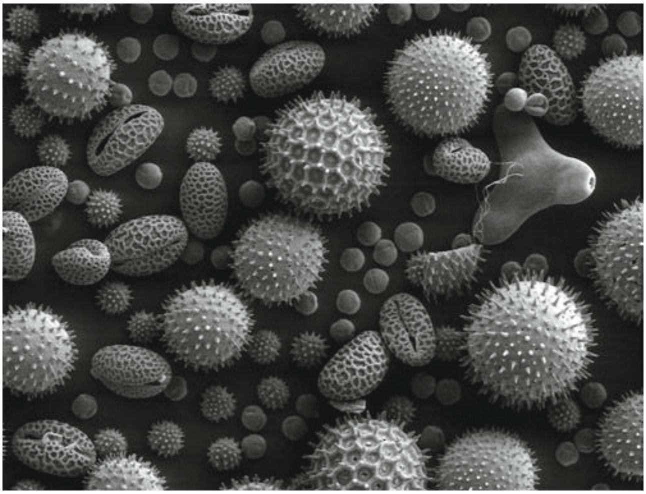


Fig. 4.3 Pollen grains viewed in a SEM. Notice the great depth of field, or three-dimensional appearance of the photograph. The pollen is from a variety of common plants: sunflower (*Helianthus annuus*), morning glory (*Ipomoea purpurea*), hollyhock (*Sildalcea malviflora*), lily (*Lilium auratum*), primrose (*Oenothera fruticosa*), and castor bean (*Ricinus communis*). The image is magnified some ×500; the bean-shaped grain in the bottom left corner is about 50 μm long. Image courtesy of Dartmouth Electron Microscope Facility

An SEM can also provide high-resolution compositional information by examining prepared flat surfaces on an object. If a sample such as a potsherd is ground and polished to a shiny, flat surface, then the number of electrons reflected, or "backscattered," from the surface can be recorded. This backscatter is proportional to the atomic density of the mineral being examined. Quartz (SiO_2), for example, has a lower atomic density than magnetite (Fe_3O_4) and appears much darker in a BSE ("backscatter electron") image (Fig. 8.4). In this way, an SEM can be used to determine the mineral content of some materials, as well as providing greatly magnified imagery.

Another aspect of the SEM of great utility to archaeologists is its capability to perform multielement analysis of a microscopic portion of a sample, a technique called "microbeam" analysis. For this analysis, one prepares a flat, polished surface, free of surface topography. The sample, a centimeter or two in diameter, is first cut with a saw to obtain a flat surface. This is then placed in a small cup with epoxy or another resin to make a resin plug with the flat surface exposed. The surface is then ground with relatively coarse abrasive to remove surface imperfections. Progressively finer abrasives are used to remove the scratches left by the previous abrasive until a nearly mirror-like finish is obtained. The surface is then coated very thinly with a conductive material such as gold or carbon, usually by electro-vapor deposition. Samples are placed in a vacuum chamber along with the conductive material that is heated until glowing hot. The conductive materials evaporated and condense as a thin layer on the sample surface. The plug is then ready to be placed in the SEM.

Because the incident electron beam can generate X-rays that are diagnostic of the material under the electron beam, one can obtain a quantitative analysis of the major elements, and minor elements as well if present with a precision of a few tenths of a percent or more. It is not highly sensitive for trace element work below hundreds of parts per million, however. The analyst should also be aware that, while the electron beam might be focused on a spot less than a micron across, X-rays can be generated from a much bigger volume several microns deep, so that the analysis might be sampling a bigger region than is visually apparent. This can be a factor in ceramic analysis – analyses of mineral grains that are hundreds of microns across might be accurate, but a clay paste with submicron particles typically has high and, on a micron scale, variable porosity. Clays can even be mineralogically heterogeneous on such a scale, so that microbeam analyses must be carefully checked for consistency. Other detectors, such as for cathodoluminescence, can be mounted in the SEM that can reveal additional compositional information.

4.2 Elemental Analysis

Elemental analysis involves measuring the composition of materials to determine the presence and amount of various elements and is a fundamental aspect of almost all chemistry. It is a predominant part of archaeological chemistry and has widespread applications. Elemental analysis has been employed in archaeological studies for more than a century. Virtually all kinds of archaeological materials have been studied in some way or another using elemental analysis.

Elemental analysis can perhaps be best understood in terms of the history of its development. Understanding the make up of the world around us seems to have been a long-term human endeavor. Fire was probably one of the more mysterious and fascinating parts of the world. Fire was a mystical force that changed water to steam, wood to ash, meat to steak, and produced heat and light. Aristotle assumed all substances to be mixtures of four elements: earth, water, air, and fire, and most early civilizations seemed to have identified these as the primary elements of nature. The Greeks and Romans took the next step in identifying atoms as an invisible part of matter, but their existence was not proven for a very long time afterwards.

The foundations of the modern science and the systematic investigation of the elements began in the Arabic world where experiments with scientific questions were well underway in the ninth-century AD. Jabir ibn Hayyan, one of the founding fathers of chemistry, was born in Persia and a prolific scholar. He emphasized experimentation and invented a wide variety of laboratory equipment, as well as a number of fundamental processes such as distillation and crystallization. He discovered and described many basic chemical substances – including hydrochloric and nitric acid, and the elements arsenic, antimony and bismuth – that are the basis of chemistry today. He was the first to purify and isolate sulfur and mercury as pure elements. He began to systematically describe the basic elements and provided the framework for the periodic table by distinguishing metals and nonmetals in his classification.

The periodic table is the contribution of a Russian scientist, Dmitri Mendeleev, who organized a long list of known chemical elements into a systematic framework in 1869 with 66 known elements. Mendeleev arranged the elements by mass and other properties and predicted the existence of new elements in his table based on the repetitive patterns he observed (the periodic behavior of the elements). This table of elements has now grown to more than 100 and new discoveries continue to be made, although only 90 are naturally occurring and of potential archaeological interest.

Of these 90 natural elements, hydrogen is the most abundant in the cosmos, the other elements being formed in nuclear processes within stars and during supernova explosions when a star dies. Within stars, hydrogen undergoes nuclear fusion to create helium, helium can then undergo fusion to generate elements with higher atomic numbers, which can themselves fuse to form still heavier elements up to a mass of 56, i.e., iron. Once a star begins to produce carbon, then additional neutrons become available to create yet heavier nuclei (e.g., ^{57}Fe and ^{62}Ni). When a star dies and catastrophically explodes, these elements are dispersed outward into space. Supernova eruptions that accompany the death of stars also eject subatomic particles in dense shockwaves that can interact with the elements formed earlier by stellar fusion to create elements of greater mass, i.e., most of the periodic table above iron.

These stellar processes are responsible for the relative abundances of the various elements, with lighter elements such as carbon, oxygen, nitrogen, sodium, aluminum, and silicon being more abundant by orders of magnitude than those produced in supernova (e.g., gold, platinum, uranium). The abundant, lighter elements generally comprise the major components of most archaeological materials. Carbon, hydrogen, oxygen, and nitrogen are the major elements for a virtually infinite variety of organic molecules while compounds of silicon, oxygen, and aluminum along with lesser amounts of other light elements such as sodium, potassium, calcium, magnesium, and iron comprise most geological materials. The amounts of these elements define the identity of many materials and, conversely, the analysis of these elements is useful in identifying such materials.

It is almost a truism to say that the heavier, rarer elements are not usually the major constituents of common archaeological materials (but sometimes can be the major component of rare materials, e.g., gold). These rarer elements more commonly occur only at "trace" levels of less than a fraction of a percent, sometimes many orders of magnitude less. Their abundances within various materials can sometimes vary greatly without substantially affecting the nature of the material. Thus they might not useful in basic identification but can be enormously useful in finding subtle distinctions among different samples of the same material. For example, native copper can be distinguished from modern, electrolytically refined copper because of the relative greater amounts of elements such as silver. These elements are quite important to archaeological chemists for fingerprinting materials from different regions, e.g., for provenience studies but geography is not the only cause of trace element variation, e.g., strontium and barium vary in bone due to dietary reasons while uranium and rare earths can be measures of contamination in the burial environment.

Prior to the middle of the twentieth century, elemental analysis was done mainly through various wet chemical methods and colorimetric and spectrographic techniques that were fairly time-consuming and tedious, restricting analyses mainly to major elements (at levels >1%) and to basic applications such as identification of materials. During the mid-twentieth century spectroscopic methods became more efficient and more sensitive, especially with the development of emission spectrographic techniques allowing nearly simultaneous measurements of many elements. Cold War financing of nuclear and space programs created both a need and funding for precise multielement analyses, especially NAA capable of analyzing many dozens of elements.

These multielement analyses opened the door to provenience studies, the number of elements increasing the likelihood of finding a distinguishing attribute among multiple sources. By the latter half of the twentieth century, the numbers of elements that could be measured, as well as the ability to measure extremely low levels into the parts per billion range along with greatly reduced sample requirements into the milligram range, allowed elemental analysis to become a routine part of archaeological investigations, especially for provenience studies of geological materials and ceramics. Today scientific equipment has progressed to the level that instruments measure not only elemental abundances, but also their isotopic ratios, providing entirely new dimensions of inquiry.

4.2.1 Spectroscopy

More common methods for elemental analysis – to determine the elemental contents of a sample – include spectroscopy and spectrometry. Spectroscopy measures changes in atoms that cause a specific light photon to be either absorbed (absorption spectroscopy) or emitted (emission spectroscopy). This light has a precise wavelength or energy, characteristic of a specific element in the periodic table. The simplest (and oldest) form of elemental analysis was not spectroscopic, in fact, but colorimetric. This method was based on the reaction of a strongly colored chemical in a solution. The appearance of a specific color in the solution revealed the identity of the element of interest. If the color intensity is proportional to the amount of that element present, the method can also be used to estimate the amount of the element present.

One colorimetric technique still in use in archaeology is a field test for soil phosphate. Phosphate in soils and sediments is an indicator of past human activity. Phosphate testing of soil samples is used to look for such indications (Fig. 4.4). A small sample of soil is mixed with hydrochloric and ascorbic acid to release soluble phosphates. The reaction produces a distinctive blue color in the presence of phosphate and the intensity of the color reflects its concentration. Results can be determined by eye or with the use of an instrument.

Colorimetric tests are not possible for many elements, however, and in some cases several elements can produce the same reaction. More sophisticated methods have replaced colorimetric techniques, using other parts of the electromagnetic spectrum. Even the spectroscopic techniques, however, rely upon the same principle, that a particular part of the spectrum can be used to measure the amount of a specific element in a sample.

Fig. 4.4 Visual phosphate tests involve comparison of sample color with color intensity in a series of test vials. In this example, ten different vials of increasingly darker blue solutions are used. The darker the color, the higher the concentration of phosphate. This test kit is produced by the company CHEMetrics

A simple colorimetric spectrometer provides a good example for the operation of more sophisticated techniques. The instrument employs a lamp, a monochrometer (a device, either a prism or a diffraction grating, to disperse light from the lamp into a spectrum), a slit through which a particular color can be selected, a sample through which the light of a specific color passes, and a photosensitive detector that measures how much light passes through the sample (Fig. 4.5). Hundred percent of the light is transmitted through the instrument if the sample solution is clear; none is absorbed. With increasing intensity of a color in the solution, less light is transmitted, more is absorbed, and the amount absorbed can be measured.

The amount of an element in a sample is determined by comparison to a known reference material. The intensity of the radiation being absorbed or emitted is measured for a set of samples of the reference with known concentrations of the element of interest. A graph, or "working curve," of the relationship between the measured radiation and the concentration in the reference sample allows us to calculate the concentration in an unknown sample (Fig. 4.6).

More complex instruments, used for atomic absorption spectroscopy, are similar to the simple spectrometer but they measure absorption from the behavior of atoms, not color intensity (Fig. 4.7). Atomic absorption is often called "flame AAS." The sample is normally in a solution that is sprayed into a flame that atomizes the sample (i.e., it breaks the sample down into individual atoms). The atoms are introduced into the flame in their low-energy state and can be excited to a higher energy state by absorbing a photon of a specific wavelength, ordinarily in the visual part of the spectrum. This photon is provided by a lamp in the instrument that emits precisely the required wavelength. To measure calcium, for instance, a lamp with a calcium filament, with the exact wavelength needed for calcium, shines through the flame with the sample. A detector records how much calcium light is absorbed by the sample, which is proportional to the amount of calcium in the solution. Other elements can be measured in the same way using the appropriate elemental light sources.

Newer instruments, however, utilize "emission" methods. They use different techniques for exciting atoms into a higher energy state and then measure the photons emitted by the excited atoms, rather than requiring a variety of lamps and measuring absorbed light. Both optical emission and absorption methods are best

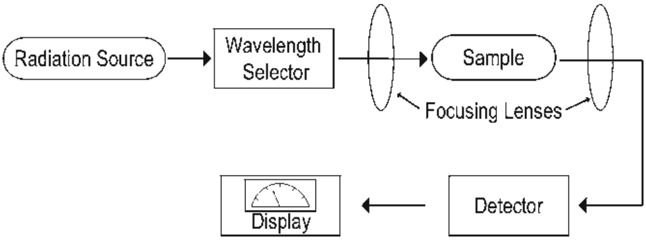


Fig. 4.5 Schematic drawing of a simple absorption spectrometer. A light source shines on a prism or grating to generate a spectrum, a portion of which is focused through the sample onto a detector that measures how much of a specific color is absorbed by the sample

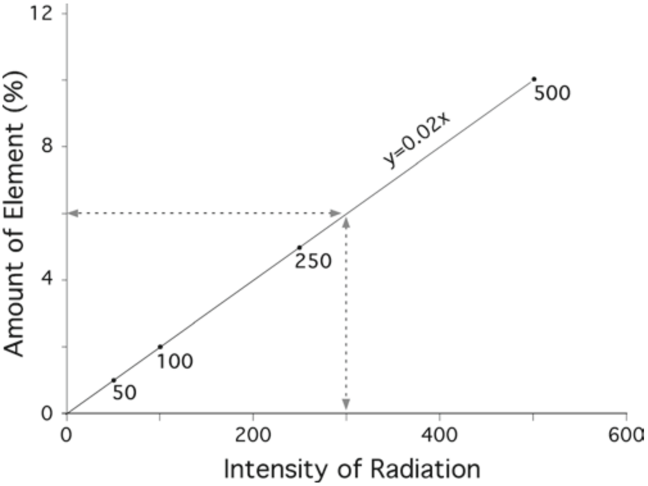


Fig. 4.6 Example of a "working curve" in which the relationship is determined between the amount of measured radiation and the actual amount of an element present in a reference sample. For example, solutions with known levels (0, 1, 2, 5, and 10%) of an element produce results of 0, 50, 100, 250, and 500, respectively. Using a graph of these results, measurement of a new, unknown sample with a radiation of 300 indicates a 6% concentration of the element in the sample

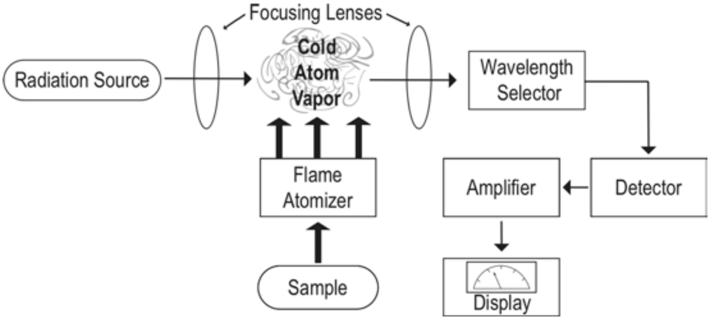


Fig. 4.7 Schematic drawing of an atomic absorption spectrometer: Light of a particular wavelength, absorbed by a specific element, is focused upon an atomized sample and the amount of that light that is absorbed is measured by the detector. The amount of light missing is proportional to the amount of a specific element in the atomized sample

suited for elements that are easily atomized and have a spectrum in the visible range, i.e., those elements in the first and second columns of the periodic table and the transition metals. By including the ultraviolet portion of the spectrum, a few additional elements can be added – phosphorous, for example, is an important one for archaeological studies of soils.

The results from most types of elemental analysis today are values for the elements selected for measurement in parts per million or parts per billion depending

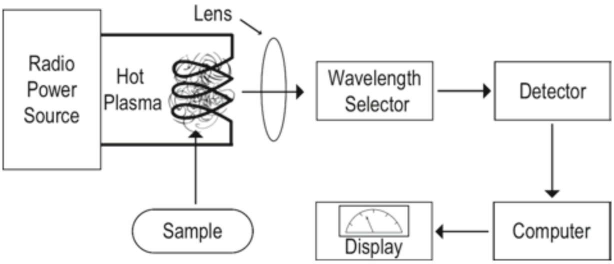


Fig. 4.8 Schematic drawing of an ICP emission spectrometer. Instead of shining a light of an appropriate color through the sample, the sample is heated in an electrical plasma until the elements glow, each with specific wavelengths. The amount of each color is measured and the intensity of that color is proportional to the amount of the emitting element in the hot gas

on the resolution of the instrument in use. Figure 4.8 shows typical output from a modern spectrometer. The *X*-axis shows time and the *Y*-axis shows absorbance. The height of the curve on the graph indicates the amount of the element in the sample. In this case the instrument is measuring chromium in an aqueous solution.

4.2.2 Inductively Coupled Plasma-Optical Emission Spectrometer

The most common type of emission spectrometer in use today (inductively coupled plasma-optical emission spectroscopy, or ICP-OES) atomizes a sample by passing an electric current into a gas plasma that contains the sample. In these optical emission methods, the sample is heated to high temperature. At this temperature the individual elements glow with their representative colors, e.g., red for potassium, yellow for sodium. The light from the sample is focused on a monochrometer to select a wavelength appropriate for the element of interest. That light at the correct wavelength is focused on a detector that measures its intensity (Fig. 4.8).

Emission spectroscopy is used to measure concentrations of a wide range of elements. Complex mixtures of elements heated to high temperature display characteristic emission spectra composed of multiple monochromatic lines – the sum of the spectra of the individual elements. When the light is separated into individual spectral lines by the spectrometer, each element is represented by several lines and the pattern of these lines is unique to that element. The intensity of the light indicates the amount of an element present in the mixture. This principle provides for the quantitative recording of elemental abundance.

Ideally, an emission source should atomize a sample completely and provide a stable signal over a wide range of concentrations. Argon plasma comes close to this ideal. Argon plasma is a hot, gaseous fountain of atoms, ions, and electrons, held in place by a magnetic field produced by a radio frequency induction coil.

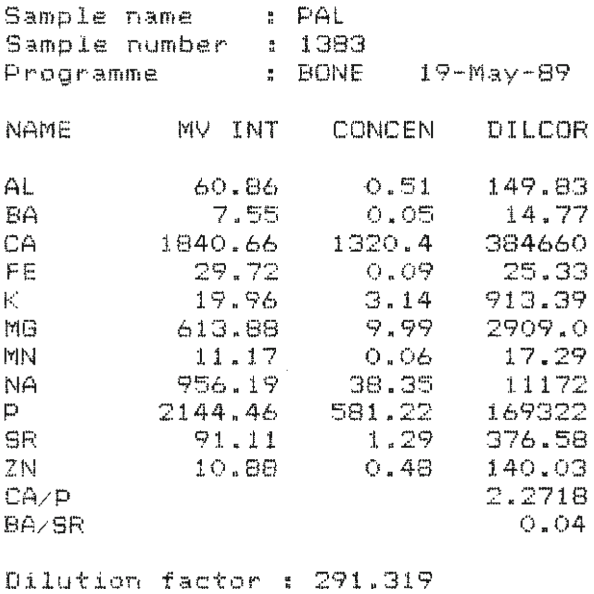
Radio frequency energy is inductively coupled with the plasma, creating an immense number of argon ions and electrons along with intense heating. The resulting discharge reaches temperatures of 8–10,000 K, the temperature of the surface of the sun, which will atomize and excite even the most difficult refractory samples.

Traditional excitation sources included combustion flames, arcs, and sparks. Flames are limited by relatively low temperatures so that it is difficult to analyze refractory elements or elements with high excitation energies, particularly at low concentrations. In addition, combustion products and flame gases cause both chemical and spectral interferences. Arcs and sparks are capable of higher temperatures, but are strongly affected by the nature of the sample. Minor variations in sample composition can cause variation in the excitation conditions, requiring a close matching of samples and standards or the use of an internal standard.

Argon plasma offers a number of advantages as a source for emission spectroscopy. Argon is an inert gas and will not react with the sample so chemical interference is greatly reduced. At plasma temperatures, atomization is complete and elemental spectra do not reflect molecular components. Detection limits are high for most elements. Accuracy and precision are excellent. In addition, ICP/OES requires less sample preparation and less sample amount than other techniques.

ICP/OES can be conducted either simultaneously or sequentially. Simultaneous instruments rely on a polychromator or direct-reading spectrometer to read up to 60 elements from the same sample excitation. Sequential analyses use a computer-controlled, scanning monochromator system. The light emitted by the sample in the plasma source is focused on the entrance slit of the monochromator and the spectrum is scanned through the region of interest. Typically, it is possible to determine several elements per minute in the sample in a sequential spectrometer.

The results from most types of elemental analysis today are values for the elements selected for measurement in parts per million or parts per billion depending on the resolution of the instrument in use. Figure 4.9 shows typical output from a modern spectrometer for an analysis of bone ash. The first several lines give information about the identity of the sample, the analytical program used to analyze the sample, and the date of the analysis. The four columns present, in order from left to right, the element being analyzed (NAME), the brightness of the spectral line measured by a phototube in millivolts (MV INT), the concentration of the element in the analytical solution measured in micrograms per milliliter of solution (ppm) (CONC), and the amount of the element in the actual sample (DILCOR), calculated by multiplying the solution concentration by a dilution factor, which adjusts for the amount of sample used for a given volume of solution. Most instruments' outputs are easy to customize to present any desired information; here, the measured concentrations are followed by calculated values for the calcium to phosphorous ratio and the barium to strontium ratio. The dilution factor used to calculate the sample concentration is presented in the last line of the figure.



```
Sample name     : PAL
Sample number   : 1383
Programme       : BONE    19-May-89

NAME         MV INT    CONCEN    DILCOR

AL            60.86      0.51    149.83
BA             7.55      0.05     14.77
CA          1840.66    1320.4    384660
FE            29.72      0.09     25.33
K             19.96      3.14    913.39
MG           613.88      9.99    2909.0
MN            11.17      0.06     17.29
NA           956.19     38.35     11172
P           2144.46    581.22    169322
SR            91.11      1.29    376.58
ZN            10.88      0.48    140.03
CA/P                             2.2718
BA/SR                              0.04

Dilution factor : 291.319
```

Fig. 4.9 Typical output from an ICP emission spectrometer. The major variables are element name (Name), the intensity of the spectral line in millivolts (MV Int), the concentration of the element in the analytical solution (Concen), and the measured amount of the element in the sample in ppm (Dilcor)

4.2.3 X-Ray Fluorescence Spectroscopy

The history of elemental analysis has seen a gradual shift from the use of visible light to the invisible parts of the spectrum. X-ray fluorescence spectroscopy (XRF) is similar to optical emission spectroscopy, but X-rays rather than electric currents are used to excite atoms. Unlike absorption methods, in which the incoming photon must have a precise wavelength, XRF is an emission method; the incident photons are used to excite the atom to fluoresce. This technique is similar to using an ultraviolet light (higher incident energy) to cause materials to glow (fluoresce) in the visual spectrum (lower emitted energy). In XRD, distinctive "secondary" (or fluorescent) X-rays are emitted from a sample that has been excited by bombarding it with high-energy X-rays or gamma-rays (Fig. 4.10). There is a characteristic X-ray diagnostic for each element. The intensity of emitted X-rays of a particular energy can then be measured to determine the abundance of that particular element (Fig. 4.11).

In contrast to most spectroscopic techniques, which generally require the sample to be in solution, XRF can be used on solid samples, normally as a powder. XRF is useful for archaeological materials such as ceramics and stones. XRF can sometimes be used in a nondestructive way, and today there are portable XRF instruments that can be carried into the field (Fig. 4.12).

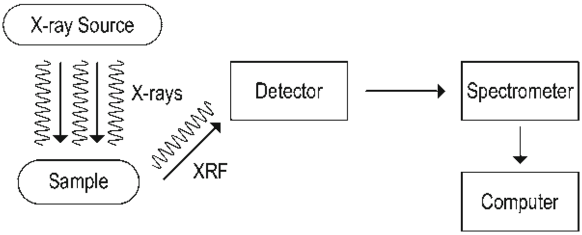


Fig. 4.10 Schematic drawing of an X-ray emission spectrometer. The sample is excited ("heated") by an X-ray beam and the wavelengths in the X-ray spectrum that are emitted by the elements in the sample are then measured by an X-ray detector. The intensity at each X-ray wavelength is proportional to the amount of the element present in the sample

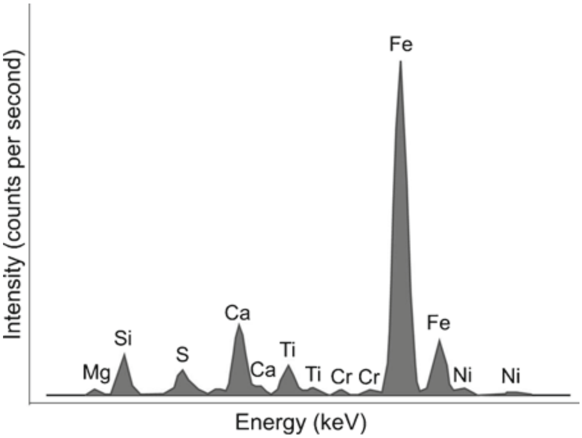


Fig. 4.11 Typical output from XRF analyses. Intensity at each X-ray wavelength indicates the relative amount of an element present

Fig. 4.12 Archaeological chemistry student Brianna Norton using the Bruker "Tracer III" portable XRF unit (foreground) to nondestructively analyze a human tooth for lead in the Laboratory for Archaeological Chemistry, Madison

X-ray spectroscopy is also a useful tool when used in combination with a SEM. The SEM uses very short-wavelength, high-energy electrons, commonly exceeding 15,000 v, to stimulate X-ray emission much as an incident X-ray beam would. When an X-ray detector is coupled to an electron microscope, a compositional analysis of very small areas, only a few microns wide, is possible. One application is the identification of the mineral grains that are found in complex materials such as prehistoric pottery, which is particularly useful for identifying small mineral grains in complex matrices such as tempered pottery.

4.2.4 CN Analyzer

There are several instruments for elemental analysis that run on principles other than spectroscopy and that are designed for one or a few specific elements. One such instrument sometimes used in archaeological chemistry is a CN (carbon and nitrogen) Analyzer (aka a Carlo-Erba analyzer) and more advanced versions that measure CHN or CHNS or CHNSO (carbon, hydrogen, nitrogen, sulfur, and oxygen). These instruments are designed for the simultaneous determination of total carbon and nitrogen (and the other elements – hydrogen, sulfur, and oxygen) in wide range of sample types, both organic and inorganic. The discussion below focuses on the principles of the CN analyzer (Fig. 4.13).

The sample is weighed into a tin container and moved to the combustion chamber at 1,020°C. Combustion of the tin container causes a powerful reaction in an atmosphere of enriched oxygen, completely oxidizing the sample. The combustion products (CO_2,

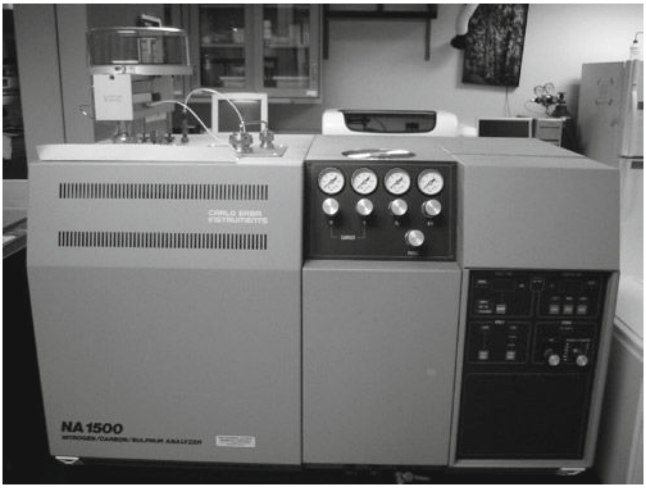


Fig. 4.13 The Carlo-Erba NA 1,500 CNS analyzer for the determination of total carbon, nitrogen, and sulfur

N_2, NO_x, and water) first go through an oxidation catalyst in the combustion chamber and then pass through a reduction reactor which contains metallic copper heated to 650°C. Excess oxygen is removed and the nitrogen oxides are reduced to elemental nitrogen. The nitrogen, CO_2, and water then move to a magnesium perchlorate tube that removes the water. Nitrogen and carbon are separated by a chromatographic column and moved to a thermal conductivity detector that measures the concentrations of the two elements. The repetitive analysis of known standards under the same conditions is used to calibrate the instrument and quantify the amount of nitrogen and carbon.

The ratio of carbon to nitrogen in a sample is used as a measure of the quality of preservation in bone and a means to determine if samples are reliable for the analysis of collagen for radiocarbon dating and dietary analysis using light isotopes. The ratio of C:N in living bone is 3.2; a ratio between 2.8 and 3.5 has been suggested as indicative of fossil bone sufficiently well preserved for analysis.

4.2.5 Neutron Activation Analysis

One of the more widely used techniques of the last 50 years has been NAA, sometimes defined as instrumental neutron activation analysis (INAA). NAA uses gamma-rays, the highest energy end of the spectrum, to measure a wide variety of elements to parts-per-million concentrations. At the same time, NAA requires a nuclear reactor – not readily available to many researchers.

NAA is gamma ray spectroscopy that uses the slow "thermal" neutrons from a nuclear reactor to excite the nucleus of an atom. When an atom absorbs a thermal neutron, its atomic mass increases by one and the nucleus becomes unstable. One or more nuclear reactions then take place that release gamma-rays with energies characteristic of the particular nuclear decay reactions, along with other radiation (Fig. 4.14). While

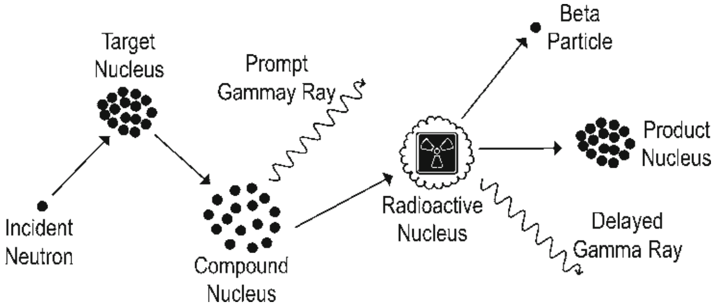


Fig. 4.14 The reaction involved in neutron activation. The neutron strikes the nucleus of an element in the sample (target nucleus), making the atom unstable and radioactive. This nucleus then decays, through various processes including emission of gamma-rays. The number of gamma-ray emissions of a particular energy or wavelength are measured to determine the concentration of the element originally present in the sample

the gamma-ray wavelengths are characteristic of particular elements, the intensities of these characteristic gamma-rays are proportional to the number of atoms undergoing the decay process. Typically, gamma-ray intensities are measured shortly after irradiation (after a few days) for short-lived decay processes and again after a few weeks to measure decay processes with longer half-lives. A large range of elements can be measured with good precision. NAA requires a powdered sample and is useful for materials such as pottery, the major archaeological application of NAA, and obsidian.

4.3 Isotopic Analyses

The Scottish chemist Frederick Soddy first used the term isotope to describe his observation than atoms with different atomic masses have the same chemical properties and occupy the same position in the periodic table. Today we understand that the number of protons in the atomic nucleus defines the chemical properties and the identity of an element, but there can be different numbers of neutrons associated with the same number of protons, resulting in the same element having several possible masses, or isotopes.

Isotopes are involved today in virtually all areas of chemistry. The use of isotopes in archaeological chemistry is widespread and rapidly growing, with many different applications. Different isotopes are used with many different kinds of materials to answer a variety of questions. Some of these isotope ratios are listed in Table 4.1 along with additional information on their abundance in nature, the kinds of materials sampled, and the kinds of information obtained in archaeological applications. Isotopes of oxygen, carbon, nitrogen, and strontium isotopes are more commonly used in archaeological applications and are discussed in more detail in this chapter.

Table 4.1 Important isotopes in archaeological investigations and information on natural abundance, the isotope ratio of importance, the kinds of materials analyzed, and applications

Element	Isotope ratio	Natural abundance (%)	Material analyzed	Applications
Hydrogen	$^{2}H/^{1}H$	$^{1}H=99.985$, $^{2}H=0.015$	Water, bone	Climate, environment, origin
Carbon	$^{13}C/^{12}C$	$^{12}C=98.89$, $^{13}C=1.11$	Bone, soils	Diet, environment, source
Nitrogen	$^{15}N/^{14}N$	$^{14}N=99.63$, $^{15}N=0.37$	Bone, soils	Diet, environment
Oxygen	$^{18}O/^{16}O$	$^{16}O=99.76$, $^{18}O=0.204$	Bone, sediment	Climate, origin
Sulfur	$^{34}S/^{32}S$	$^{32}S=95.00$, $^{34}S=4.22$	Bone	Diet, origin
Strontium	$^{87}Sr/^{86}Sr$	$^{86}Sr=9.86$, $^{87}Sr=7.02$	Bone, pottery	Origin
Lead	$^{208}Pb/^{206}Pb$ $^{207}Pb/^{206}Pb$ $^{206}Pb/^{204}Pb$	$^{206}Pb=24.1$, $^{208}Pb=52.4$ $^{207}Pb=22.1$, $^{204}Pb=1.4$	Bone, pottery, metals	Origin, source

4.3.1 Oxygen Isotopes

Oxygen isotopes are used in archaeology primarily to study ancient environments and to examine past human mobility. Isotope measurements are always reported as a ratio of one isotope to another, lighter and more common cousin. Ratios are used in order to standardize the value that is reported, regardless of the amount of material measured or the concentration of the element present.

The ratio of oxygen isotope 18 to oxygen isotope 16 is often used to measure past climate because it is directly related to atmospheric temperature. Oxygen isotopes are used as a proxy for temperature in studies of marine sediments, ice cores, faunal remains, and other materials. The abundance of the two isotopes depends on temperature-related fractionation processes such as evaporation, condensation, and transpiration.

During evaporation at the ocean's surface, the lighter isotope, ^{16}O, is preferentially released into the atmosphere because of its higher vapor pressure (Fig. 4.15). As moisture-laden clouds move inland, the heavier isotope (^{18}O) precipitates preferentially and rain clouds become progressively depleted in ^{18}O as they move inland. Polar and inland rain is lighter than tropical and coastal rain; summer precipitation is less depleted than winter precipitation. Since condensation is also dependent on temperature, further depletion of ^{18}O occurs at higher elevations and latitudes. Evaporation of

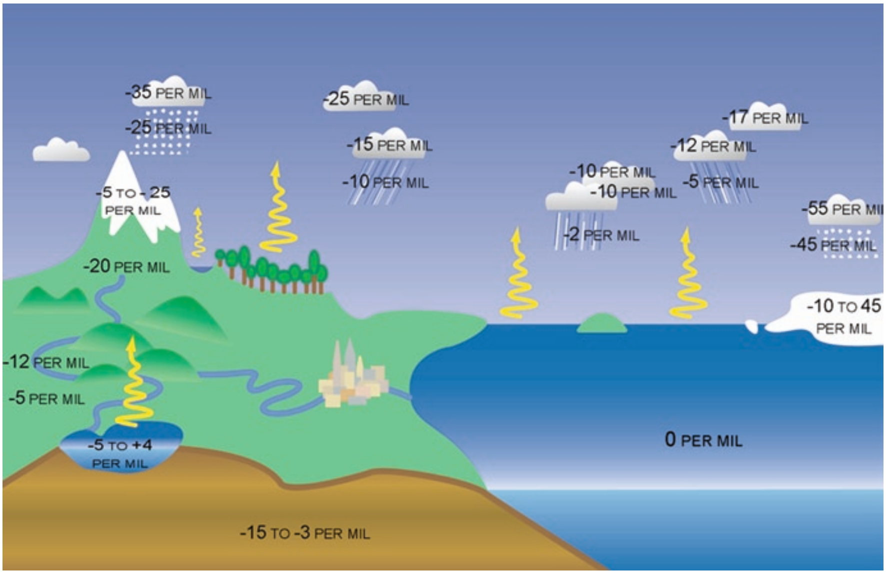


Fig. 4.15 The oxygen isotope ratio measured by δ^{18}O varies with temperature, latitude, and elevation. Depending on atmospheric temperature, ^{16}O evaporates faster than ^{18}O from the ocean's surface. As rain clouds move inland or toward cooler areas, the heavier isotope (^{18}O) precipitates preferentially and rain clouds become progressively depleted in ^{18}O as they move inland. δ^{18}O provides a proxy for atmospheric temperature

inland surface water and evapotranspiration of water by plants releases more of the lighter isotope (^{16}O) into the atmosphere and concentrates the heavier isotope in surface water and plants. Because of higher rates of evaporation, surface water and plants in arid regions exhibit more enriched $\delta^{18}O$ values than moister regions.

$\delta^{18}O$ values of precipitation are passed on to plants and animals living in that environment. Oxygen isotopes in humans come primarily from drinking water. Water from food and atmospheric oxygen are minor, secondary sources. Meteoric water (rain) is the primary source of drinking water.

Oxygen isotopes in ancient human skeletal remains are found in both bone and tooth enamel. Samples for the analysis of human skeletal remains are normally taken from dental enamel due to conditions of preservation and resistance to diagenesis. The hydroxyapatite mineral, a primary component of enamel, contains oxygen, in both phosphate groups (PO_4) and carbonates (CO_3). Phosphate and carbonate produce comparable results for oxygen isotope ratios, but less sample is needed for carbonate, preparation is less demanding, and results between laboratories are more comparable.

Oxygen isotope measurements are reported as a ratio of ^{18}O to ^{16}O. This ratio ($\delta^{18}O$) is reported relative to a standard, and expressed in parts per thousand (per mil, ‰). The standard used is commonly VSMOV (Vienna Standard Mean Ocean Water) for phosphate, or PDB (PeeDeeBee dolomite) for carbonate oxygen. The results from the use of these standards differ but can be calibrated. Values using the VSMOW standard are generally negative and range from approximately $0‰_{(PDB)}$ to $-90‰_{(PDB)}$, or $+20‰_{(SMOW)}$ to $-70‰_{(SMOW)}$, in continental waters.

4.3.2 Carbon and Nitrogen Isotopes

Carbon and nitrogen isotopes in archaeology are used primarily in the study of past diet, but there are also important applications that concern past environments and human activity. Carbon and oxygen isotopes have been used in proveniencing to determine the source of marble and other forms of carbonate rocks. Carbon isotopes have been used as survey tool to locate the boundaries of ancient soils and determine the extent of certain types of vegetation. The discussion below focuses on human bone and questions about past diets, the primary application of these two isotopic systems. These principles are also involved in the study of other questions.

The isotopes of carbon ($^{13}C/^{12}C$) and nitrogen ($^{15}N/^{14}N$) are measured in bone collagen using a mass spectrometer. While the level of these elements in bone is under strict metabolic control, the ratio of the stable isotopes reflects the ratio in the diet. Values for $d^{13}C$ in human bone collagen range between approximately −5‰ and −25‰. There are two primary sources of variation in ^{13}C in human diet and bone collagen – different ratios in the kinds of plants we eat and different ratios between terrestrial and marine foods. ^{13}C is more abundant in certain kinds of tropical plants, such as corn, and in the oceans. Carbon isotopes can tell us about the types of plants we eat and the importance of seafood in the diet. Thus, less negative values for collagen in bone mean either marine foods or C_4 plants in the diet, or both.

Figure 4.16 shows the different sources of carbon isotopes in C_3 and C_4 plants and these ratios might appear in human bone.

Nitrogen isotopes are used in much the same way as carbon isotopes, but they provide different information about diet. The ratio of ^{15}N (0.37% of all nitrogen in nature) to ^{14}N (99.63% in nature) is used in paleodiet studies. Nitrogen is reported as $\delta^{15}N$ and values in human bone range from approximately −5‰ to +10‰. This nitrogen ratio is measured in bone collagen using a mass spectrometer. Nitrogen isotopes can tell us about the importance of meat in the diet, the role of freshwater fish, and the trophic level of human diets. Thus, a more positive nitrogen isotope

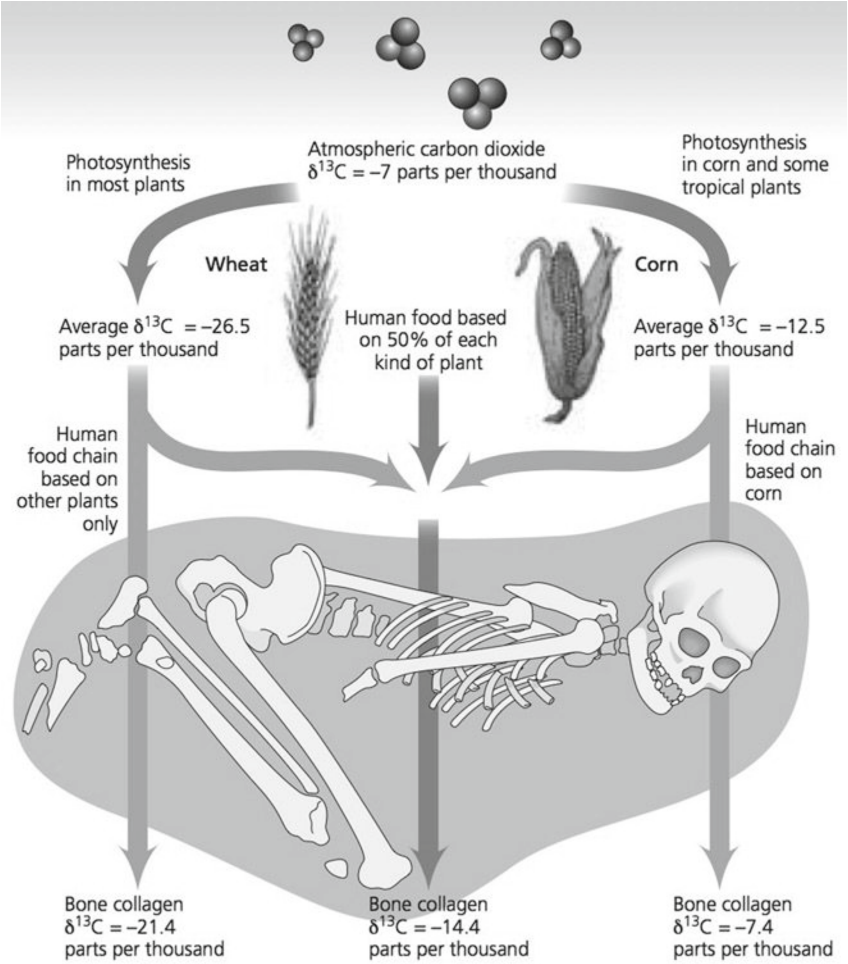


Fig. 4.16 Carbon isotope ratios differ substantially between C_3 and C_4 plants. In this illustration, corn (C_4) and wheat (C_3) are consumed separately or as a mixed diet. Each diet results in a different carbon isotope ratio in the bone of the individual consuming that diet. The mixed diet of C_3 and C_4 plants results in an intermediate value for $\delta^{13}C$ in human bone

ratio reflects a higher trophic level. Further details on isotopic studies of past diets using carbon and nitrogen are described in Chap. 7 on Environment and Diet.

A simple example comes from Eastern North America. Almost all of the Native American groups in the Eastern US were eating corn at the time that Columbus arrived in AD 1492. Corn was domesticated in southern Mexico more than 5,000 years ago and must have spread north over time. Corn is a rich and productive source of food. An important question concerns when corn arrived in the Eastern US as it may have had a big impact on the Indian societies that added it to their diets. Because corn is a tropical plant, a special kind of grass, it has a different ratio of carbon isotopes ($^{13}C/^{12}C$) than the other plants that people in the Eastern US were eating. For this reason, measurements of the carbon isotope ratio in human bone can indicate if people were eating corn. Analysis of human bones from various time periods in the prehistory of the Eastern US reveals when corn became important in the diet (Fig. 4.17). The graph shows carbon isotope ratios in human bone from the last 5,000 years in the region. Significant change in the values after AD 750 reflects the introduction and rapid spread of corn and its increasing importance in the diet.

4.3.3 *Strontium Isotopes*

Strontium isotopes, reported as the ratio $^{87}Sr/^{86}Sr$, have been used primarily in the study of human movement in the past. There are, however, a number of other potential applications usually involving the sourcing or proveniencing of other kinds of objects and materials such as pottery, stone, textiles, or animals.

The analysis proceeds through the sampling of tooth enamel to obtain the isotopic signal of the place of birth. The local isotopic signal can be determined in several ways: in human bone from the individuals whose teeth are analyzed, from the bones of humans or archaeological fauna at the site, or from modern fauna in the vicinity. The local geological isotope signals of strontium have been constant over the last several 1,000 years. These isotope ratios have been reported for the rocks,

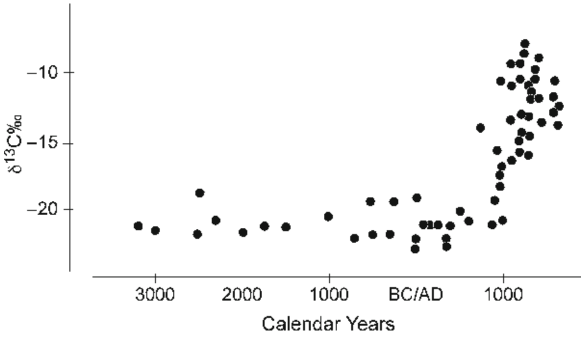


Fig. 4.17 Carbon isotope ratios from human bone in Eastern USA over the last 5,000 years. The dramatic increase in these values after AD 750 reflects the rapidly increasing importance of corn in the diet of the prehistoric Native American inhabitants

soils, and waters of the region of human and faunal remains from archaeological contexts throughout the region. Figure 4.18 shows the estimated values for strontium isotope ratios in bedrock for the USA.

Dental enamel, especially in teeth less than a few millennia old, is relatively robust against diagenetic alteration. The permanent first molar is preferred both for consistency and the fact that the enamel of this tooth forms during gestation and very early childhood. Preparation involves lightly abrading the surface of a single cusp of a molar using a dental drill to remove surficial dirt and calculus and also the outermost enamel due to the possibility of contamination by diffusion (Fig. 4.19). This cusp is

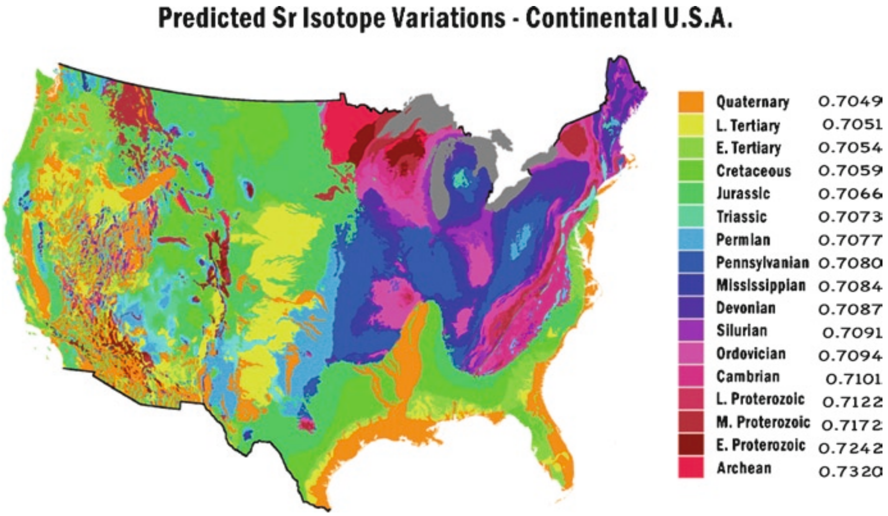


Fig. 4.18 Estimated strontium isotope ratio values calculated by age variation in basement rocks in the USA (after Beard and Johnson 2000)

Fig. 4.19 Sampling tooth enamel. The first step is to lightly grind the surface of the enamel to remove contamination

then cut from the tooth with a crosscut blade and any remaining dentine removed with a drill. If a clean cusp is not available, a small chip is removed from the side of the molar or 5–10 mg of powder is drilled from the enamel.

Samples weighing 2–5 mg are then dissolved in 5-molar nitric acid. The strontium fraction is purified using ion-specific resin and eluted with nitric acid followed by water. This solution is loaded onto a titanium filament for placement in the instrument (Fig. 4.20). Isotopic compositions are obtained on the strontium fraction thermal ionization mass spectrometer (TIMS). This is a single focusing, magnetic sector instrument equipped with multiple Faraday collectors. Strontium is placed on a thin filament and measured. $^{87}Sr/^{86}Sr$ ratios are corrected for mass fractionation using an exponential mass fractionation law. $^{87}Sr/^{86}Sr$ ratios are reported relative to a value of 0.710250 for the NIST 987 standard (e.g., if the $^{87}Sr/^{86}Sr$ ratios for the standards analyzed with the samples average 0.710260, a value of 0.000010 is subtracted from the ratio for each sample).

Strontium isotopes have also been used in the investigation of wood and maize (corn) at the ancient site of Pueblo Bonito in Chaco Canyon by geologists in Arizona and Colorado. This ancient, multistory apartment complex housed approximately 1,000 people from AD 850–1200. The pine, fir, and spruce trees that pro-

Fig. 4.20 Loading sample strontium solution on a filament for measurement in the thermal ionization mass spectrometer (TIMS)

duced the large timber beams used in construction at sites like Pueblo Bonito did not grow in Chaco Canyon. These timbers were averaged 5 m (16′) in length, 22 cm (9″) in diameter, and they weighed about 275 kg (565 pound). An estimated 200,000 beams were used in the construction of the 12 major pueblos in the canyon. One of the interesting questions about the archaeology of this area is where did the inhabitants get their wood for construction?

Conditions were too dry in Chaco Canyon for trees to grow to any size. Today pine, fir, and spruce grow only at higher elevation in the mountains around the site (Fig. 4.21). Comparison of strontium isotopes in the soils from the mountain area to the south and west of Pueblo Bonito with the timber at the site provided a good match (Fig. 4.22). These areas (Chuska and San Mateo), more than 80 km (50 miles) to the west, were the source of the wood beams at Chaco Canyon (Fig. 4.21).

A similar study was done with ancient corncobs from Chaco Canyon. It has been argued that the canyon itself did not have sufficient water or cultivable areas to provide maize for the several thousand people that lived there 1,000 years ago. Agriculture on the canyon floor today is very marginal. The study of past climate

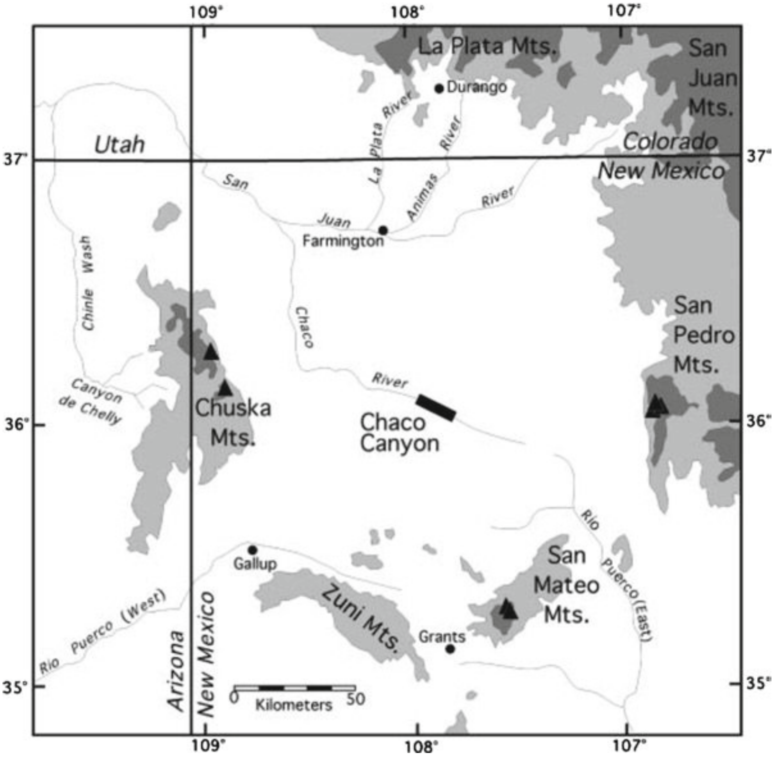


Fig. 4.21 A map of the four corners region of the Southwestern USA and the location of Chaco Canyon. The mountain areas around the canyon were all potential sources for the pine and fir timbers that were brought to Pueblo Bonito. The *light gray* areas show where pine grows today; *dark gray* shows the areas where fir trees grow; *triangles* are sampling sites for the study

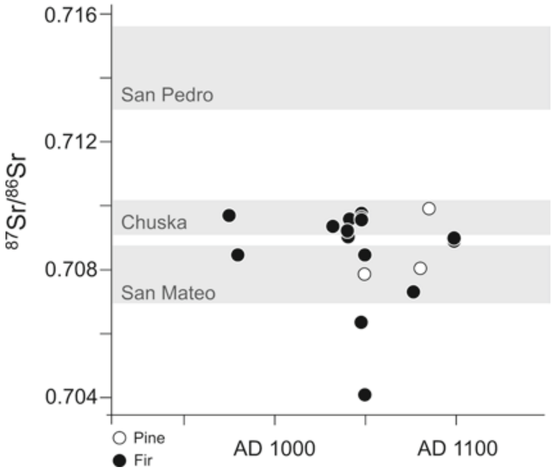


Fig. 4.22 $^{87}Sr/^{86}Sr$ ratios of timbers from Pueblo Bonito. The age of the timbers was determined by dendrochronology. The strontium isotope ratios indicate that the timbers, which could not grow in Chaco Canyon, came from the Chuska and San Mateo Mountains to the west and south of the site. The *light gray bands* show the range of strontium isotope values from soils and modern trees in three mountain ranges around Chaco Canyon (see Fig. 4.21)

in the area suggests that this would also have been the case at the time of the prehistoric occupation. Again comparison of the corn cobs with soils from different regions around Chaco indicates that some corn was likely imported from fields some 80 km to the north of the canyon.

The place of origin of prehistoric people can also be determined. The isotopic proveniencing of human remains, using ratios of strontium isotopes, has been employed in archaeology for approximately 20 years. Strontium isotope analyses have been used successfully in a number of studies. The basic principle involves comparison of isotope ratios in human tooth enamel with local levels in bone or other materials. Because isotopic ratios vary geographically, values in human teeth (marking place of birth) that differ from the local ratio (place of death) indicate migration. This method of analysis is described in more detail in Chap. 8, Provenience and Provenance.

4.3.4 Mass Spectrometers

Because mass spectrometers can resolve atomic weights that differ by less than one atomic mass unit (AMU), they are able to measure isotope ratios for a specific element. Many elements have atoms of more than one atomic weight. Although they are chemically identical, isotopes of the same element have a different number of neutrons – which change the weight but not the chemical properties – in the atomic nucleus. For example, all strontium atoms have 37 protons, which define strontium as a chemical element. Stable strontium atoms can have 47, 49, 50, or 51 neutrons yielding atomic weights (neutrons plus protons) of 84, 86, 87, and 88, respectively. Importantly, one of these, ^{87}Sr, is radiogenic, created by the decay of ^{87}Rb, which has a half-life on the order of 50 billion years. The ratio of ^{87}Sr (7% in nature) to ^{86}Sr (10% in nature) varies and has significant archaeological applications that will be discussed in a subsequent chapter.

Mass spectrometers (aka, mass specs) do not use visible light or other wavelengths in the electromagnetic spectrum. These instruments do, however, separate atoms and molecules into a "mass spectrum" according to their weight. They then count the number of particles at a known weight that corresponds to a specific element or molecule. Mass specs sort particles according to their weight by putting an electric charge on the particle and accelerating the particle through an electric or magnetic field (or both).

There are several different types of mass spectrometers. One common type is the quadrupole mass spectrometer in which atoms with an electric charge are accelerated inside of four metal rods to which alternating voltages are applied (Fig. 4.23). If the frequency of the voltage change is just right, then an atom of the desired weight is attracted from one rod to the next as it passes among the rods toward the detector. A lighter atom will be more quickly drawn to one of the electrified rods and expelled; a heavier atom will be too sluggish to respond to the alternating voltage changes. Thus, at a particular voltage and frequency of change, only atoms of a specific mass can successfully traverse the quadrupole device toward the detector; heavier and lighter atoms are thrown out.

Quadrupole mass spectrometers have relatively low resolution and have some problems with interferences. Two elements with the same atomic weight, e.g., CaO^{+1} and Fe^{+1}, both with a mass of 56, cannot be distinguished. Quadrupole mass specs have advantages, however, of being relatively simple and small: these instruments, for example, can be placed on board spacecraft or combined with other analytical instruments such as chromatographs for the identification of molecules, discussed below.

Better resolution of masses and alleviation of the problems with interference can be obtained by using a strong magnet. "Magnetic sector" mass specs accelerate ions into a strong magnetic field, which applies a force pushing the atoms in a direction perpendicular to the line of their movement. The magnetic field pushes lower weight

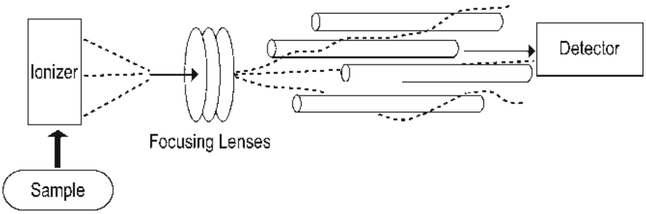


Fig. 4.23 Scheme of a quadrupole mass spectrometer, a beam of atoms of various weights is ionized and focused through four rods to which various voltages are applied. By selecting appropriate DC and high frequency voltages, ions of a specific mass are focused onto the detector, while others masses are rejected

particles to the side more easily than heavy ones, so that the lighter particles are deflected more from their original path. A simple analogy for this mechanism would be a fan blowing perpendicular to a moving stream of golf balls and ping-pong balls. The ping-pong balls will be deflected further from their course than the golf balls. By adjusting the magnetic field, like adjusting the speed of the fan, the deflection can be precisely calibrated so that a particular mass arrives at the detector, while others of a different weight are deflected short or wide of the detector and not counted.

Thus by putting a particle detector at an angle to the original flight path of the atoms, one can focus a particular mass range on the detector by choosing an appropriate magnetic field strength (Fig. 4.24). The strength of the magnetic push is proportional to the speed of the particle, so that varying the electric field that accelerates the particles adds a further degree of control over mass selection. These instruments are generally much larger (and more complicated and costly) than quadrupole instruments. At the same time, magnetic sector mass specs can resolve differences in mass much less than one AMU and can eliminate much of the interference between molecules and atoms with the same weight.

Magnetic sector instruments are further distinguished by their method of sample introduction – how the sample is put into the electromagnetic field. Many instruments today use a plasma, identical to that in optical ICP spectroscopy (ICP-MS). In the mass spec, the plasma is used to ionize the atoms. Although the plasma emits the characteristic spectra used in ICP-OES, this visible light output is not used by the mass spectrometer. Figure 4.25 shows the ICP-MS in the Laboratory for Archaeological Chemistry at the University of Wisconsin–Madison.

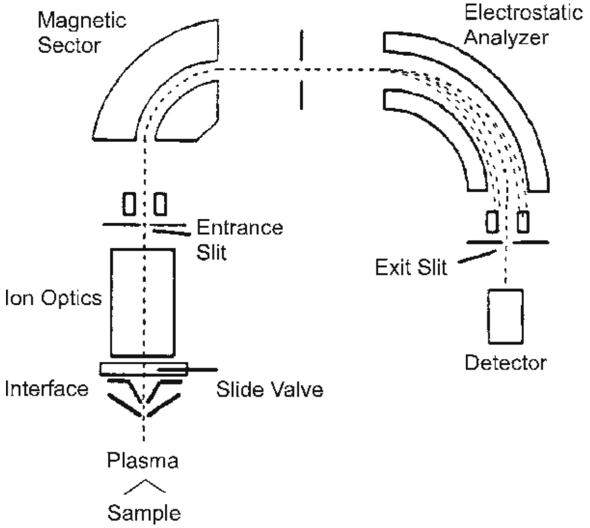


Fig. 4.24 Basic components of ICP-MS. Samples are ionized in the plasma and moved through entrance slit and toward the detector by a magnetic field that separates the atoms by weight. The detector counts the atoms of different weights that arrive

Fig. 4.25 James Burton and Doug Price with the Element ICP-MS in the Laboratory for Archaeological Chemistry at the University of Wisconsin–Madison

Neither quadrupole nor magnetic sector machines with just a single ion detector, known as a “collector,” have adequate precision (better than 0.01%) for most isotope ratio studies. For isotope ratios, multiple collectors are used so that measurements of the different isotopes can be done at the same time. Multiple collectors are commonly employed with the ICP-MS discussed above (“MC-ICP-MS”) and on thermal ionization magnetic sector mass spectrometers (TIMS). TIMS uses a wire filament on which the purified element of interest is heated to ionize the sample (“thermal ionization”), instead of using plasma.

ICP instruments are designed for input of aqueous solutions, but many archaeological samples such as lithics and ceramics are not easily put into solution. Thus a laser is sometimes used on the front-end of the ICP-MS (“laser ablation,” or LA-ICP-MS). The laser is focused upon a small spot on the sample and ablates a small part of the material into a gas stream that flows into the plasma.

Mass spectrometers usually measure two or more isotopes at one time and calculate their ratio. Standards are measured at the same time in order to confirm the precision of the instrument and allow corrections to be made if needed. The results of the analysis provide the ratio measurements along with several other kinds of information. Table 4.2 shows some typical results from a mass spectrometer, in this case a list of calculated strontium isotope ratios on human tooth enamel measured on TIMS. The first column in the table gives the sequential lab number for each individual sample. The site is the place from where the sample comes. The corrected $^{87}\text{Sr}/^{86}\text{Sr}$ is the isotope ratio for strontium in the sample, corrected on the

Table 4.2 Typical data from mass spectrometer measurement of strontium isotope ratios in human tooth enamel

Lab number	Site	Corrected $^{87}Sr/^{86}Sr$	% Std err	Ratios	Date run	Raw 87/86	Av of stds	No. stds
F5025	Xcambo	0.709006	0.0007	88/100	3/23/09	0.709020	0.710264	10
F5026	Xcambo	0.708865	0.0007	89/100	3/23/09	0.708879	0.710264	10
F5027	Xcambo	0.708983	0.0008	86/100	3/23/09	0.708997	0.710264	10
F5028	Xcambo	0.709043	0.0008	87/100	3/23/09	0.709057	0.710264	10
F5029	Xcambo	0.708123	0.0007	87/100	3/23/09	0.708137	0.710264	10

The first three columns provide sample number, site name, and corrected strontium isotope ratio. The remaining columns provide details of the instrument analysis

basis of standard reference data collected repeatedly in the instrument. The percent standard error is an estimate of error in the isotope ratio. Ratios indicate the number of successful counting episode in 100 tries. Date run tells us when the sample was analyzed. The information on raw 87/86, average of standards, and number of standards is used to correct the final $^{87}Sr/^{86}Sr$ value.

4.4 Organic Analysis

The foods and many of the raw materials that humans use are organic – meat, fish, fowl, vegetables, fruits, wood, hide, bone, antler, thatch, fur, and more – and come from living things. These materials were once abundant at the living places of prehistoric people. The bad news is that in most cases this "biological" component of the past is very susceptible to decomposition and degradation and normally does not survive to the present. Fungi and bacteria feed on carbon-based materials and eventually consume them. The good news, however, is that those biological materials sometimes leave traces in and on artifacts and sediments that can survive for thousands of years.

A variety of archaeological materials may contain trace organic compounds, including ceramics, stone tools, grinding stones, cooking slabs, plaster, fecal material, soil, and sediments. The best preservation seems to be in artifacts such as pottery that have absorbed trace organic compounds into their structural matrix, reducing the accumulation of "contaminants" from diagenesis, handling, and post-depositional treatments, as well as the oxygen-induced degradation that can interfere with the identification of the original parent material. These organic molecules appear to bond to clay and to cling tightly to that bond over long periods of time. Organic compounds from the interior of ancient potsherds, for example, have been dated to more than 6,000 years before present.Trace organic compounds are distinguished from visible organic residues such as charred food on pottery or other macroscopic organic remains. Analysis of trace organic compounds, which have adhered to or been absorbed into the structural matrix of archaeological materials, can provide information about past artifact function, diet, and other aspects of

Table 4.3 Organic residues in archaeological chemistry

Basic component	Complex molecule	Contexts	Applications
Lipid (fatty acids, glycerols, sterols)	Fat	Vessel residues, soils	Diet, activity areas
Amino acid	Protein	Soils, tools	Activity areas
Nucleic acid	DNA, RNA	Animal and plant remains	Identity of materials
Simple sugars	Polysaccharides, starches	Vessel residues, soils	Diet
Terpenes	Pitches and resins	Gums, resins binders	Identification and origin of materials
Hydrocarbons	Tars and waxes	Tars and waxes	Identification and origin of materials

Some of the important categories of materials that can be preserved along with their archaeological context, and some recent studies

prehistoric societies. This branch of archaeometry is sometimes referred to as molecular or "biomolecular" archaeology.

Common organic residues in archaeology include lipids, amino acids, nucleic acids, simple sugars, terpenes, and hydrocarbons. The type of molecule, contexts where these residues are found and the kinds of archaeological information they may provide are listed in Table 4.3.

Lipids are a major component of such organic residues and the component most studied by archaeological chemists. Lipids are a generic category of compounds that originate as constituents of living tissues defined by (1) their insolubility in water (hydrophobic), (2) solubility in organic solvents such as chloroform, methanol, or ether, and (3) they contain long-chain hydrocarbon groups in their molecules. Lipids are the most efficient energy storage molecules in cells.

Although the term *lipid* is sometimes used as a synonym for fats, fats are a subgroup of lipids. There are many different forms of lipids, including alcohols, aldehydes, fatty acids, waxes, bile acids, and sterols. Of these, the most relevant in archaeological studies are the fatty acids and sterols. Their identification in archaeological contexts provides a means of distinguishing the biological materials that were originally present.

Fatty acids, the building blocks of storage fats, are long-chain hydrocarbons with a terminal carboxylic acid group (–COOH). Fatty acids in which all the other carbon atoms are bonded by single bonds to four other atoms of carbon or hydrogen are known as "saturated" fatty acids because they have the maximum amount of hydrogen. Many important fatty acids have carbons that are doubly bonded to each other, reducing the total amount of hydrogen by two atoms for each double-bond. These are thus known as unsaturated fatty acids. Those with just one carbon double-bond are known as monounsaturated and those with more than one are known as polyunsaturated fatty acids.

Fatty acids are identified in a shorthand notation by the number of carbon atoms in the hydrocarbon chain followed by the number of double bonds. For example, the saturated 18-carbon octadecanoic acid (also known as stearic acid) is C18:0; the 20 carbon arachidonic acid with four double bonds is C20:4 (Fig. 4.26).

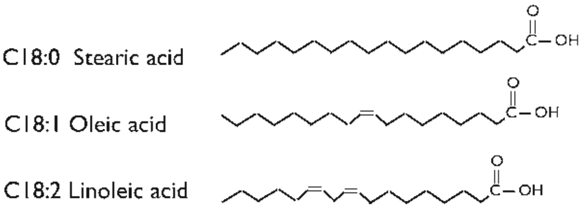


Fig. 4.26 18-carbon fatty acids: Saturated stearic acid with no double bonds, monounsaturated oleic acid with one, and polyunsaturated linoleic acid with two. Each kink is a carbon atom

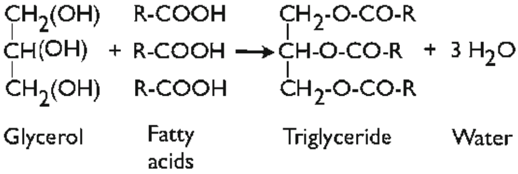


Fig. 4.27 Reaction between glycerol and three fatty acids to produce a triglyceride (fat) plus water

Fatty acids are found in free form only in small quantities; in most cells they are combined with the alcohol glycerol to form glycerides (Fig. 4.27). Glycerol can combine with one, two, or three fatty acids to create monoglycerols, diclycerols, and triglycerols, respectively.

Lipids tend to survive better than other organic compounds in archaeological contexts and are amenable to sensitive methods of analysis such as gas chromatography/mass spectrometry (GC/MS). Their insolubility in water increases their chances for survival. Lipids have been recovered from sediments that are millions of years old and have been identified in materials where no cellular structure remains. Lipids are also important because of their specificity. Certain kinds of lipids differ greatly not only between plants and animals, but among the various families and genera of plants and animals.

Also, because fatty acids in animals tend to be mostly saturated fatty acids and polyunsaturated fatty acids are known mainly in vegetable oils, there is an enormous difference between plants and animals in the ratio of polyunsaturated to saturated fatty acids (Table 4.4). Thus, an analysis of this ratio can give some indication of vessel use.

Diagnostic fatty acids tend to be unsaturated, i.e., with one or more carbon double bonds, which are also those most susceptible to decomposition. In as little as 6 months, unsaturated fatty acids can degrade to the point that no diagnostic markers remain and the ratio of unsaturated acids (suggesting plants or fish) to saturated acids (suggesting other animal fats) changes too significantly to use simple unsaturated to saturated fatty acid ratios as reliable dietary indicators.

Although the major emphasis in archaeological research has been on fatty acids, sterols may also be useful because of their potential to further resolve the identification

Table 4.4 Ratio of polyunsaturated to saturated fatty acids by weight

Source	Ratio
Lard	0.23
Butter	0.05
Corn oil	4.55
Sunflower oil	5.29
Safflower oil	7.06

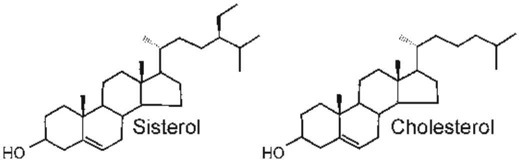


Fig. 4.28 Structures of sitosterol, found in plants, and cholesterol, found in animals

of organic traces. There are substantial differences among the plants and animals. Sterols are widely distributed in animals (zoosterols) and plants (phytosterols) and they can strongly discriminate different plant and animal classes, possibly to species levels (Fig. 4.28).

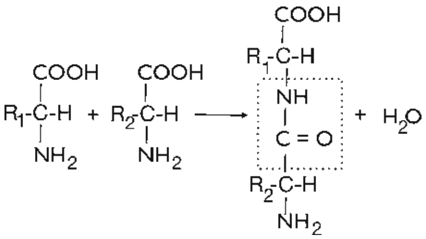
There are no major, and extremely few minor, sterols that are present in both plants and animals. This means that if several parent materials were stored in a vessel or processed by an artifact, division of the residues into plant and animal groups should be straight forward, and the chemical signature of the sample can be more readily identified as to its parent material(s).

There are a number of lipid compounds specific to fecal material, including sterols, bile, and some others that can be found either in soils or coprolites. A by-product of these sterols is a compound known as 5β-stanol, produced in the gut of animals from cholesterol. 5β-stanol is a distinctive marker in animal feces. The presence of this compound in prehistoric agricultural fields has been used as evidence of intentional fertilization.

Investigations of sterols in archaeological contexts have generally been limited to the study of coprolites or preserved human tissue although some applications to ceramics and sediments have been reported.

Although most of the organic residues have involved lipids, some have studied protein residues and others have looked for remains of sugars and complex carbohydrates. Proteins are complex, sometimes immensely complex, molecules made of long chains of amino acids connected through a series of peptide bonds. An amino acid is an organic molecule that has a carbon characterized by bonds to four distinct functional groups (see Table 1.1 of Functional Groups): a carbonic acid group, an amino group, hydrogen, and the remainder of the organic group “R” by which the amino acid is identified. A peptide bond forms when the amino group of one amino

Fig. 4.29 Reaction of two amino acids to form a peptide bond plus water



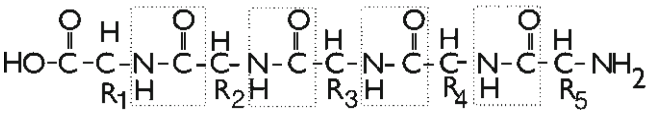


Fig 4.30 A five-chain peptide with peptide bonds selected for emphasis. Proteins normally have long chain peptides with many thousands of peptide bonds

acid reacts with the carbonic acid group of another, with the release of water (Fig. 4.29). Proteins normally have long chains of peptides with thousands and thousands of peptide bonds (Fig. 4.30).

Even though proteins have problems of degradation and preservation and have not received the attention that lipids have, there is a great deal of current excitement about protein analysis because of the tremendous potential for proteins being highly source specific. Moreover, not only do they vary by species, but humans and other animals have highly evolved immunological responses by which species-specific proteins are recognized. These immunological responses are now being employed in the laboratory with similar specificity to identify small traces of proteins from individual species. For example, trace blood residues on a stone tool can be tested specifically for immune or “anti-antibody” responses for trout, deer, bear, and other individual species. Nonetheless even the analysts themselves caution that the research is relatively new and must be critically evaluated.

Most of the effort, and success, in the organic analysis of archaeological residues has been in characterizing specific organic molecules and relative abundances of fatty acids retained in potsherds. Unglazed pottery absorbs food residues as can been seen in the dark stains that accumulate in new pottery. These residues can be extracted from their ceramic matrices with common organic solvents and identified by their diagnostic spectra with the use of liquid chromatography or gas chromatography coupled with mass spectrometry (LC–MS and GC–MS, respectively).

Initial investigations of lipids in archaeological materials relied on thin-layer chromatography (TLC) or IR spectroscopy. These techniques provided only broad classifications of the organic compounds under investigation and were not well suited for the analysis of degraded substances. The use of a GC/MS instrument has become standard practice in the analysis of organic compounds. GC/MS not only separates different organic compounds but also measures their mass spectra, which make possible both a positive identification of each component and a sensitive way to determine minor variations between similar components. These variations include differences in the carbon chain structure, changes in the position of double or triple bonds, and alterations in the direction of branch chains, all of which can be diagnostic of parent material.

Scientists have, for example, analyzed the contents of pottery to identify the presence of olive oil and have also discovered milk, fat, beef suet, oil of Cruciferae, and other food residues. A ceramic vessel from the southwestern Cape of South Africa yielded marine animal lipids, suggesting that perhaps seal meat had been cooked in this pot. Cocoa was identified in ceramic vessels from the Maya Site of Rio Azul and more recent studies, described in Chap. 5, have identified chocolate residues in pottery found in New Mexico.

A wide range of lipid compounds have been identified in ceramics and it is possible to see differential distribution of lipids within the same vessel. Oudemanns and Boon, for example, examined residues on the inside of an Iron Age vessel from the Netherlands. They found molecules like pyrrole and toluene, which are markers for proteins, and others like furan, which is a marker for sugars (aka carbohydrates), and organic acids that come from fats, waxes, and oils. This range of molecules indicates a variety of uses for this pot.

Lipid quantity and type and location on the vessel have also been used to distinguish function of pots. This technique helped to distinguish storage from cooking vessels and to discover that cooking materials concentrated around the rim where they tended to boil over. Characterization of lipid contents reveals the kinds of materials associated with the pottery.

The ratio of saturated to unsaturated fats in pottery residues has been used to distinguish animal-derived residues from those of plants. Fish, in particular, have highly diagnostic unsaturated fatty acids with multiple, double (unsaturated) bonds. Cholesterol and the plant analog, sitosterol, likewise differentiate animal from vegetable products. Dairy products contain acyl lipids and large amounts of cholesterol. A distinctive mix of an alcohol, a ketone, and an alkane, all with the same number of carbon atoms, identified the leaves of vegetables such as cabbage.

Specific residues from fruits, milk, wine, olive oil, tar, and cedar wood oil have been identified in various studies. Other potentially diagnostic compounds recovered from potsherds include proteins, some of which are diagnostic of certain animal foods. No doubt as scientific instrumentation becomes more sensitive to the identification of ancient compounds and as these instruments become more accessible to archaeology, studies of trace organic compounds with become a more important aspect of archaeometry.

Although the analysis of trace organic compounds has a great potential in archaeological research, a number of problems remain, largely due to postdepositional changes in the molecules either through contamination – the addition of new materials to the matrix – or the breakdown of the original molecules into small, unidentifiable components. Another factor complicating the identification of parent materials is the processing or storage of multiple parent materials within the same ceramic vessel. Since different plants and animals have different kinds and percentages of lipids, the mixing of several different species will alter the "signature" pattern making it difficult to distinguish the individual parent materials responsible for the residues.

Basic procedures for the analysis of organic residues involve extraction of the molecules by (1) Powdering the archaeological material, (2) Ultrasonicating the powder in a mixture of chloroform and methanol, (3) Centrifuging and decanting the total lipid extract (TLE), (4) Decant dried in a stream of nitrogen. (5) TLE is then reacted with a compound to produce a more volatile set of derivative compounds. These volatile derivatives are then introduced into a Gas Chromatograph/Mass Spectrometer (GC/MS). The GC/MS separates of the different molecules by passage through a long column containing a solid that slows some of the gas molecules more than others by physical and chemical interactions. As the column is heated the most volatile compounds pass more quickly through the column with the least volatile appearing last. The molecules exit from the tube sequentially, in order of decreasing volatility, and pass over a detector (e.g., a flame) that registers a peak for each type of molecule. These molecular components are individually fragmented in the detector and injected into a mass spectrometer that sorts the fragments by their mass. Because different molecules break down in characteristic ways, analysis of these mass fragments provides additional information about the identity of the original molecule. These mass spectra are then compared with the spectra from known molecules in order to make identifications.

Technology has now advanced to the point that one can obtain stable $\delta^{13}C$ and $\delta^{18}O$ ratios of individual fatty acids. Because different species isotopically fractionate fatty acids in different ways and to different degrees, these ratios can be used to identify further the fats from different sources (Fig. 4.31). One such study examined

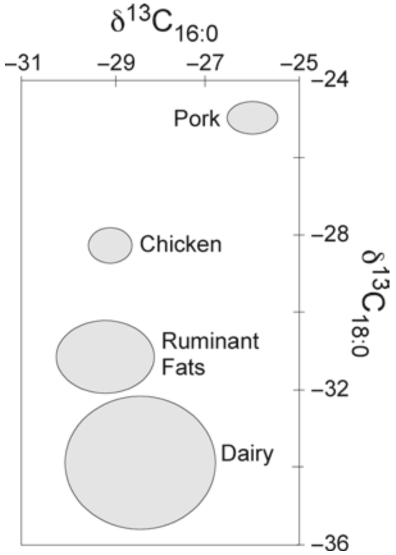


Fig. 4.31 Graph of $\delta^{13}C$ ratios of palmitic (C16:0) and stearic (C18:0) acids from a variety of animal sources. Data from Dudd and Evershed (1998)

the use of ceramic containers as oil lamps and characterized the type of oil used on the basis of fatty acids from pigs, cattle, and sheep. Dairy products have been identified in Neolithic ceramics through the same methods.

4.4.1 Methods of Organic Analysis

Two general approaches have been taken in the analysis of organic materials. The first involves the separation of the complex mix of organic molecules by chromatography; each component is then identified by MS. Often this involves the search for a few, highly diagnostic molecules. The second approach, less frequently employed, involves the bulk analysis of organic compounds by Nuclear Magnetic Resonance (NMR) or IR spectroscopy that measures the atoms and bonds involved in the molecules. The spectra of residues can provide a fingerprint of the remaining material, depending on conditions of preservation and the extent of contamination.

Initial investigations of lipids in archaeological materials relied on TLC or IR spectroscopy. These techniques provided only broad classifications of the organic compounds under investigation and were not well suited for the analysis of degraded substances. The use of a GC/MS instrument has become standard practice in the analysis of organic compounds. GC/MS not only separates different organic compounds but also measures their mass spectra, which make possible both a positive identification of each component and a sensitive way to determine minor variations between similar components. These variations include differences in the carbon chain structure, changes in the position of double or triple bonds, and alterations in the direction of branch chains, all of which can be very diagnostic of parent material.

Basic procedures for the analysis of organic residues involve extraction of the molecules by (1) Powdering the archaeological material, (2) Ultrasonicating the powder in a mixture of chloroform and methanol, (3) Centrifuging and decanting the TLE, (4) Which is then dried in a stream of nitrogen, and (5) The TLE is then introduced into a GC/MS. The GC/MS separates the hundred of molecules by passage through a long column containing a solid that slows some of the gas molecules more than others by physical and chemical interactions. The molecules then exit from the tube sequentially and pass over a detector that registers a peak for each type of molecule. The GC/MS produces a chromatograph, a spectrum of the weight and amount of the various molecules present in the extract (Figs. 4.32 and 4.35). These spectra are compared with known materials in order to make identifications.

4.4.2 Gas/Liquid Chromatography–Mass Spectrometry

In the laboratory, the most common instrument for the study of organic remains combines the techniques of chromatography and MS to separate different molecules and identify them, respectively.

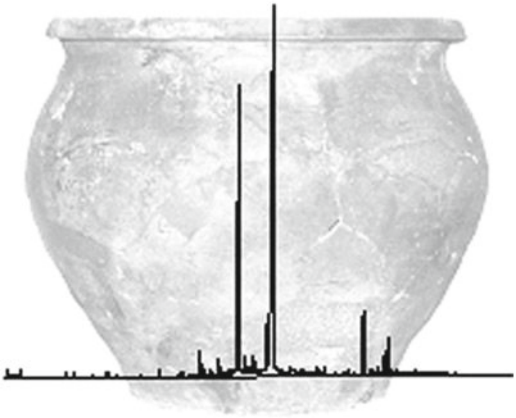


Fig. 4.32 GC/MS mass spectrometer output for the organic residue in a ceramic vessel

The normal techniques used to separate mixtures of different organic substances for identification are called "chromatographic" methods. Chromatograph literally means "color writing" and early methods produced a colored graph showing the separation of components in a sample. The basic principle underlying these methods can easily be demonstrated by creating an ink spot on a piece of absorbent paper and then adding a few drops of alcohol. As the alcohol spreads across the paper, different components in the ink will move outward from the spot at different speeds depending upon their solubilities in alcohol. The result will be a set of approximately concentric rings (Fig. 4.33); each ring holds a different component of the ink (commonly a different color). Chromatographic methods involve a "stationary phase," in this case the paper, and a "mobile phase," in this case the solvent used to separate various components of a sample. The separation of the sample compound is based on a physical property that effects among the separate components

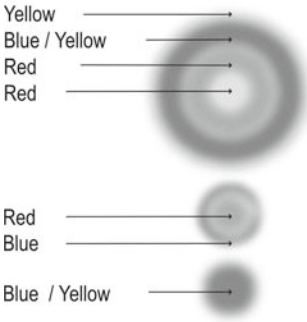


Fig. 4.33 Simple paper chromatography where alcohol is used as a solvent to separate the colors in an ink

of the compound differently. In our ink example, solubility is the property that separated the components.

Paper chromatography is in fact one of the early methods for the analysis of organic compounds. This technique uses paper as the stationary phase and a solvent such as alcohol as the mobile phase. Usually the samples are arranged along the bottom edge of a sheet of absorbent paper, which is placed in a tray with a shallow layer of the solvent. More commonly, the sheet of paper is replaced by a sheet of glass coated with a thin layer of an absorbent material such as silica gel. In this method, known as "TLC," the various components move various distances up the glass sheet depending on their relative solubilities in the solvent. The sample components are rarely as colorful as in the ink example. However, the sheet can be sprayed with a reagent that will react with specific components to produce a colored band, or the components, which are usually organic, can be chemically or physically burned to produce a charred stain where an otherwise invisible component is located. Fluorescent gels can be used in conjunction with a UV lamp to reveal the locations of many components without using chemical reagents or charring.

While chromatographic methods separate chemical compounds, they do not identify them as specific compounds. For this purpose one needs a good knowledge of what is most likely to be in the mixture. Known "control" substances can be analyzed along side the unknown samples. Discrete bands of the various components can then be identified against the known material that travels the same distance on the paper or glass sheet (Fig. 4.34).

TLC and paper chromatography, while quite simple and inexpensive, are limited in their application to relatively simple mixtures. More sophisticated instrumental methods have been developed that allow smaller samples to be analyzed with much better resolution of different compounds. These methods also use the same principal of using stationary and mobile phases based upon a specific physical property that isolates the components of the mixture (Fig. 4.35). The most widely used methods

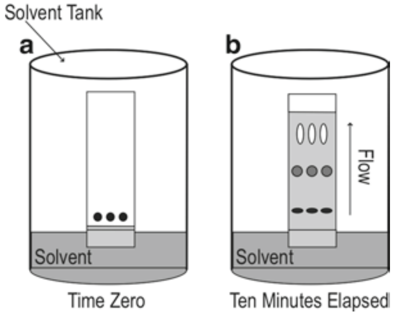


Fig. 4.34 Chromatograph of three samples placed near the bottom of the sheet, the bottom tip of which was placed in solvent (**a**). As the solvent was wicked upward across the sheet, various compounds with different solubilities moved upward and more soluble compounds moving farther than less soluble ones (**b**)

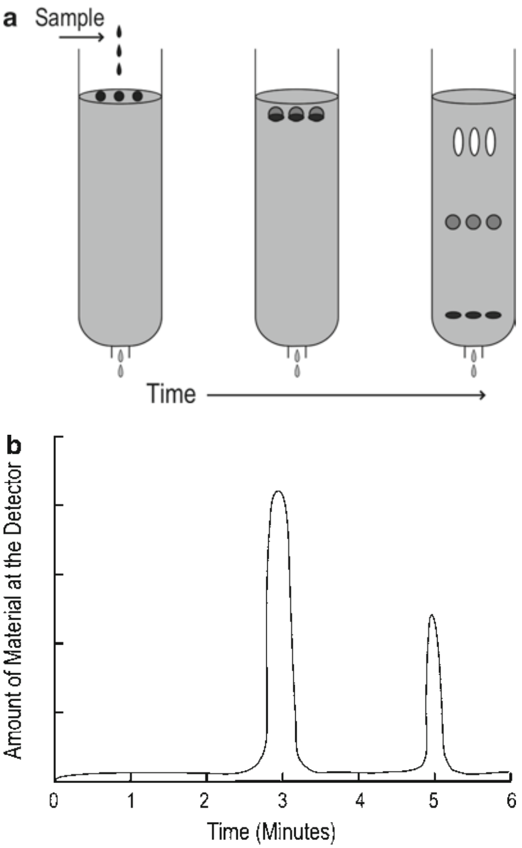


Fig. 4.35 A schematic drawing of liquid chromatography (LC). The drawing (**a**) shows the events in the column over time. The sample is added at the top of the column (*left*) and gradually moves down the column. Heavier molecules move more quickly through the column and out the valve at the bottom. The graph (**b**) shows how these materials separate over time, i.e., what comes out of the valve when

are distinguished by the mobile phase, whether a liquid solvent (LC) to separate materials by solubility or a heated gas (GC) to separate materials by their volatilities. Other chromatographic methods use sophisticated stationary phases, such as microscopically porous materials that act like filters. These filters allow tiny molecules to pass, but larger molecules cannot. These methods are generally used to separate mixtures of quite large organic molecules such as fatty acids, oils, and waxes.

Instrumental methods differ from paper and TLC in that the sample components are separated by time, rather than distance. Instead of measuring the distance that substances move along a plate, the time at which the materials move past a specified point in space is recorded. For example, a detector at the end of the instrument records when components arrive (Fig. 4.36). More mobile (e.g., more soluble or

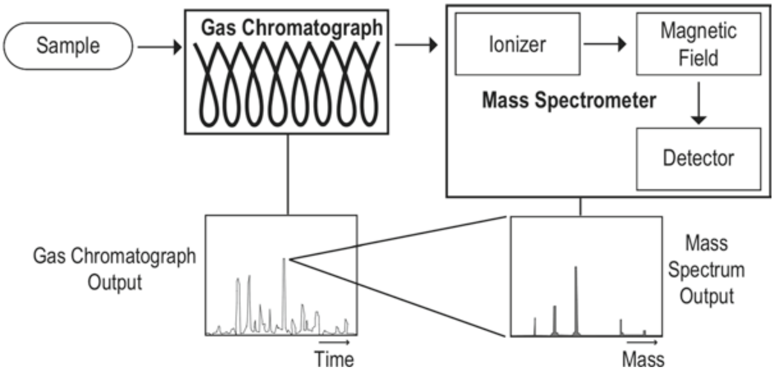


Fig. 4.36 Schematic drawing of a gas chromatograph/mass spectrometer (GC/MS): basic components and output. Sample is converted to gas and introduced into gas chromatograph that separates molecules by weight. Different molecules are ionized, fragmented and sent through magnetic field in the mass spectrometer that separates the submolecular fragments by weight. The pattern of these fragments is often diagnostic of the original large molecule. Output graphs below show the separate results of the GC and the MS

volatile) substances arrive earlier. The relative abundance of each component can usually be determined as well.

These instrumental methods also have limitations in that they do not provide a specific identification of the components they record. For relatively common mixtures with known components, reference substances can be run through the instrument and results compared to the unknowns. Because archaeological materials are old and organic components have decomposed over time, there is a need to identify a broad array of complex mixtures and their often-incomplete contents.

In order to get more detailed information, instrumental chromatographs are connected to mass spectrometers. The compounds separated by chromatography are sent into the mass spec as they arrive, so that the output of the chromatograph is the input of the mass spectrometer (thus the synonyms "GC–MS" and "LC–MS") (Fig. 4.37). The mass spectrometer calculates the mass and abundance of the unidentified component and this information can be used to identify the material. In addition, molecules of a sample commonly break apart in characteristic ways at the chromatograph/mass spectrometer interface. The mass spec measures the masses and relative abundances of these distinctive submolecular fragments as well. A knowledgeable analysis of these fragmentation patterns, along with computerized comparison to large databases of such fragmentation patterns, helps to identify unique molecular compounds.

GC/MS analysis of residues from ceramic vessels in the Southwestern United States revealed the presence of theobromine, a compound distinctive for chocolate (Fig. 4.37a). The output from the GC analysis (Fig. 4.37b) clearly revealed the presence of this molecule and its daughter products from the fragmentation of the original theobromine. The MS analysis confirmed the molecular weight of the theobromine and its derivatives in the sample (Fig. 4.37c).

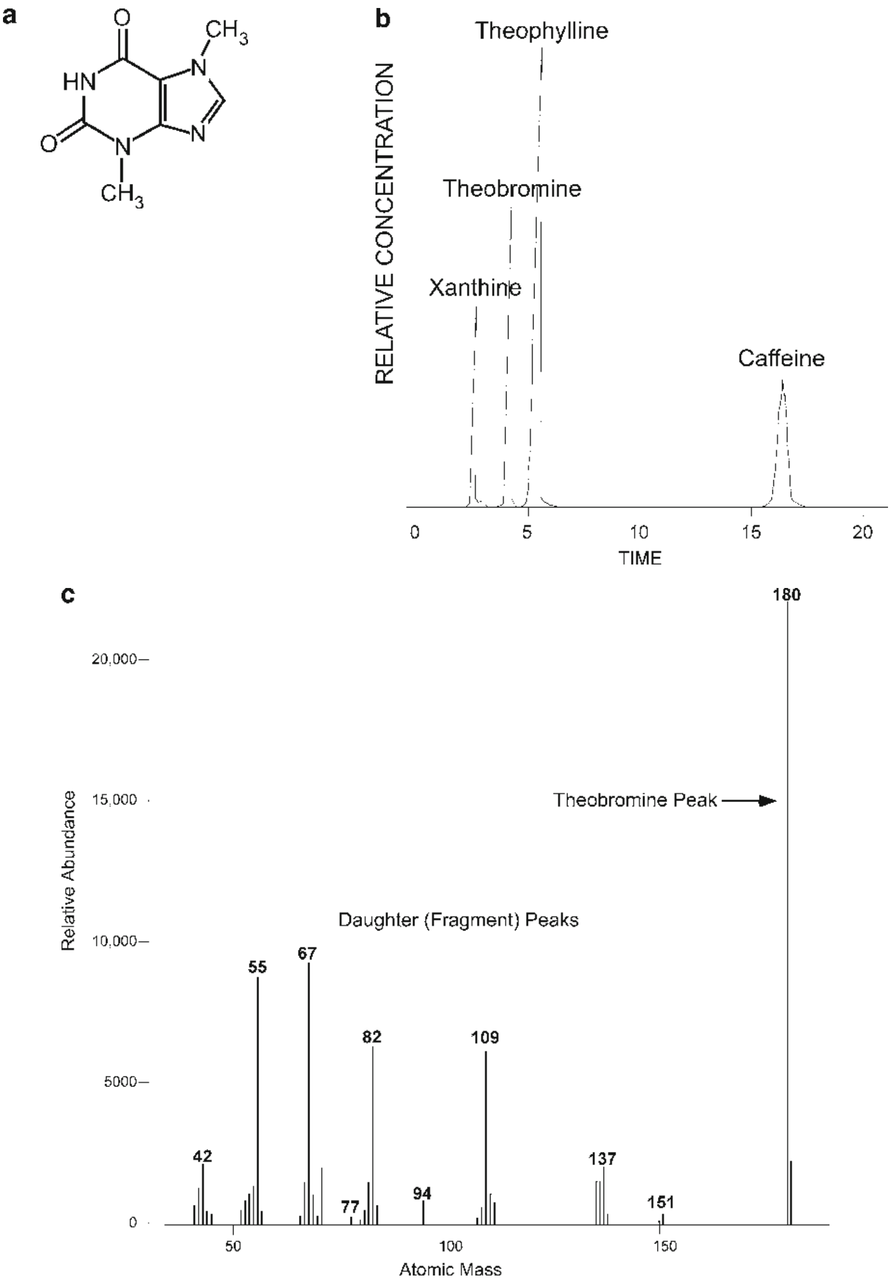


Fig. 4.37 (**a**) The molecular structure of theobromine. (**b**) Chromatograph output from a 6 μl sample of a mixture of closely related chemicals found in coffee and chocolate. The peaks appear from *left* to *right* in order of decreasing solubility. Each peak represents a different compound; the height of the peak is proportional to the amount present. (**c**) Mass fragmentation pattern of theobromine, which appeared in (**b**) after 4 min (peak #2) at mass of 180. The large peak on the *right*

4.5 Mineral and Inorganic Compounds

Minerals are inorganic compounds that are found in nature and have both a well-defined composition and crystalline arrangement of atoms. Coal and petroleum hydrocarbons are organic and thus not minerals. Obsidian is not a mineral because it has neither crystalline structure nor a specific composition. Stones such as chert and flint, which are mainly silica, SiO_2, have a relatively precise composition but lack crystalline structure, so are not minerals. While copper is a mineral, brass and bronze do not occur in nature and do not have a fixed elemental composition, so they are not minerals. A synthetic material can be a mineral, however, as long as it is also found in nature. Hematite can be produced artificially by firing ceramics in an oxidizing environment, but it is still considered mineral because hematite can be found in nature. A synthetic ruby is likewise a mineral because rubies do occur in nature, but modern cubic zirconia is not.

Because minerals are defined both by composition and structure, minerals can have the same composition but different structures and thus are distinctly different minerals. Diamond and graphite are both pure carbon but have different atomic arrangements and thus are different materials, with quite different properties. Likewise calcium carbonate, $CaCO_3$, has a definite composition but this is not a mineral name because calcium carbonate can occur as aragonite or as calcite, each with a unique arrangement of atoms.

Because this structural arrangement of atoms is essential to the identity of an element, methods used to study minerals differ from those used to assess elemental composition. The major tools include microscopy, X-ray methods, and molecular spectroscopy. These directly examine the molecular structure and the kinds of bonds between atoms rather than elemental abundances.

Because rocks are composed of one or more minerals, if these cannot be determined visually in a hand-sample, they are examined with the petrographic microscope or, in the case of opaque oxides, ore minerals, and metals, with the metallographic microscope. Because rocks are identified compositionally, it's sometimes necessary to assess the percentages of the different minerals, which can be done by using a grid in the field of view of the microscope and counting the number of grains of each mineral at the cross-sections of the grid. For example, a 10 × 10 grid has a hundred intersections. If 40 of these intersections fall on a quartz grain, then approximately 40% of the rock is quartz. By taking several such counts of the grains, one can accurately assess the mineral components and identify the rock. Because minerals have well-defined elemental compositions, one can assess the

Fig. 4.37 (continued) is the "base" peak for the theobromine molecule. The smaller peaks on the *left* are the masses of the characteristic submolecular fragments of theobromine (put following credit in photo credits). Image from technical note: A rapid extraction and GC/MS methodology for the identification of Psilocybn in mushroom/chocolate concoctions: Mohammad Sarwar and John L. McDonald, courtesy of the USA. Department of Justice major elemental composition of a rock from this quantitative measurement of mineral abundances.

Just as major elements are used to identify materials, while trace elements are used to "fingerprint" the origins of materials, the determination of major minerals is mainly used to identify rocks and minerals, e.g., fine-grained pyroxene, plagioclase, and olivine imply that the rock is basalt, while rare trace-minerals can be used to "fingerprint" the origins of geological materials.

Tools such as XRD and IR spectroscopy are useful when the rock contains only one or two minerals, but both IR and XRD spectra become too complex, with multiple overlapping peaks, when there are more than a few minerals. Thus these tools are mainly used for identifying the major mineral components.

When there are more than a few minerals, e.g., for most rocks, the petrographic microscope is the most useful too, The SEM using backscattered electron imaging coupled to an X-ray detector is also a powerful tool in identifying the compositions of individual minerals in a rock section, although it is more difficult with the SEM to quantitatively determine the percentage of each mineral because of the limited field of view at such high magnification. It is invaluable, however, in being able to determine the identity of minerals smaller than 10 or 20 μm, which can in turn be valuable for provenience studies of geological materials including ceramics.

4.5.1 Petrography

Optical mineralogy employs the use of polarized light, which is light waves in which all the waves are oriented in the same direction, to probe the structure of inorganic materials. For materials that are homogenous without crystalline structure such as obsidian, there is no preferred orientation that would preferentially affect light polarized in any particular direction. Likewise, for highly symmetric minerals such as halite, the mineral name for sodium chloride, and diamond, which have cubic crystals, there is no preferred orientation within the crystal and no effect on polarized light. Most minerals, however, lack such symmetry and refract light differently in different directions. By using the directional properties of polarized light and orienting the minerals in different directions with respect to the direction of polarization, one can determine the nature of the crystal symmetry of a mineral. This information along with other optically observable features such as color and cleavage – the way in which a crystal breaks – usually suffices to uniquely identify a mineral.

A petrographic microscope (Fig. 4.38) is a special kind of binocular microscope, designed for the study of thin sections – slices of rock, pottery, or other materials – ground and polished to a thickness of only 0.3 mm. This slice, or section, is so thin that light from beneath can pass through the material. Two kinds of light are used for viewing thin sections, normal and polarized light. Normal light is the standard source from the microscope. Polarized light is constrained to a single plane, in the same way that polarized sunglasses reduce glare. Many minerals change color and

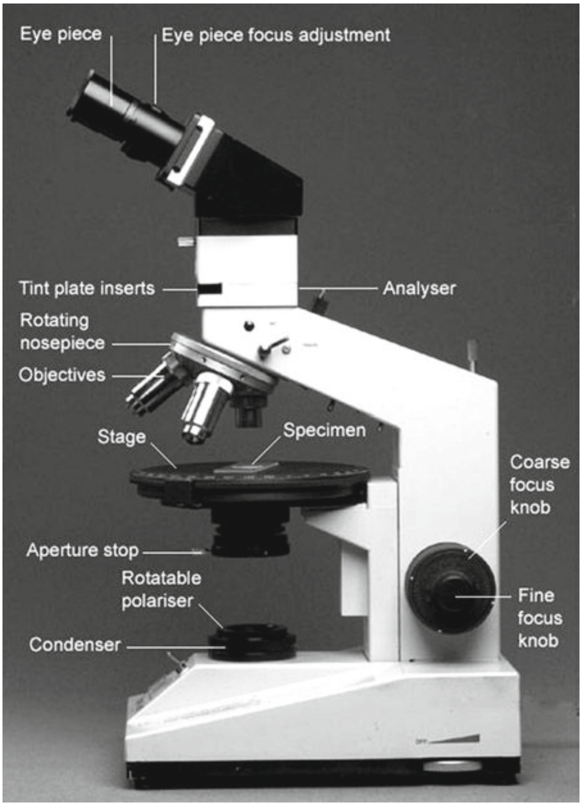


Fig. 4.38 A petrographic microscope with component parts labeled. Image courtesy of the University of Cambridge DoITPoMS Micrograph Library

brightness when polarized light passes through them. These changes are a useful way to identify specific minerals in a thin section. While the petrographic microscope was designed by geologists to examine the minerals within rocks, archaeologists mainly use instrument this to identify the mineral grains in sand-tempered pottery, as well as to record grain-size and textural attributes that can be useful in determining the provenience of the pottery.

Closely related to the petrographic microscope is the metallographic microscope (Fig. 4.39). It uses similar optics and polarized light to study metals and metal ores, except these are opaque when viewed in a thin section, so the metallographic microscope uses reflected light rather than light transmitted through the sample as in the petrographic scope. Because samples are not transparent, they don’t need to be sliced to the precise 0.03 mm required by thin sections. Instead samples are usually embedded in a small resin plug with a flat surface that is then highly polished, ideally removing surface imperfections down to approximately a micron. This allows one to see the grain structure of metals, which can be highly informative about technology. The metallographic microscope is used primarily for studying

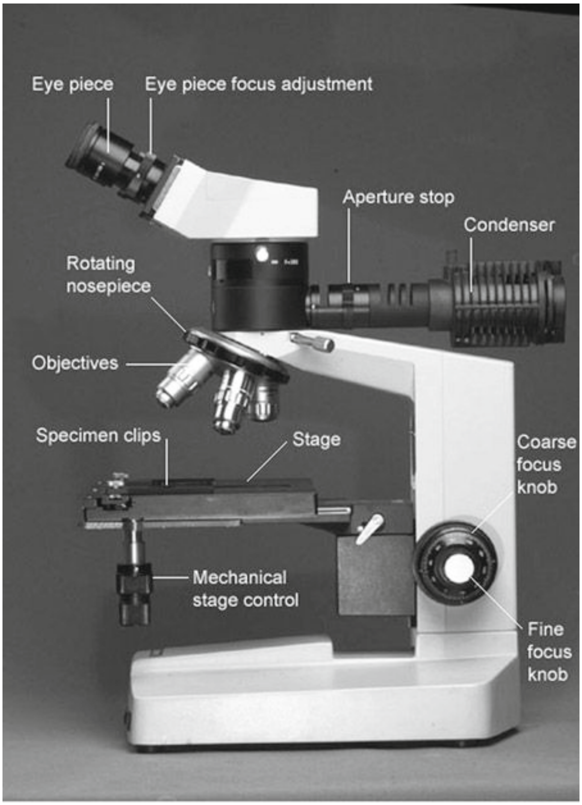


Fig. 4.39 Metallographic or reflected-light microscope with parts labeled. Image courtesy of the University of Cambridge DoITPoMS Micrograph Library

technological evolution from the use of native metals through the development of bronze and iron to recent historical metallurgy.

When copper is shaped by hammering at low temperatures, processes known as "work-hardening," the copper grains become flattened, long, and thin. While copper atoms move easily within individual grains, they are blocked by the boundaries of grains and can't move easily or far within the thin grains of work-hardened copper. Thus work-hardened copper cannot be as easily deformed or shaped as copper that has not been worked. This makes it stronger and harder but also more brittle. One can, however, restore ductility to copper by heating it, which allows the grains to recrystallize into much larger, more equidimensional grains, in a process known as "annealing." Figure 4.40 shows images in a metallographic microscope of (a) work-hardened copper and (b) the same copper after heating to 800°C. Such microscopic observations can thus provide direct information about prehistoric metallurgical technology.

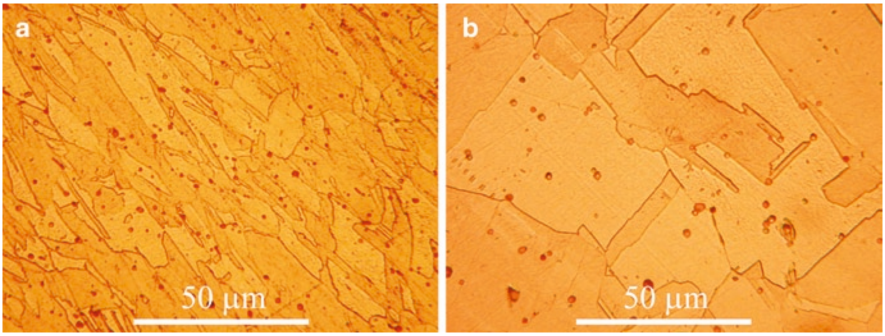


Fig. 4.40 Metallographic, reflected-light sections of (**a**) work-hardened copper and (**b**) the same copper heated to 800°C, annealing the grains. Notice the directionality of the work-hardened copper and the lack of directionality in the annealed copper, as well as the increased grain-size. Scale bar represents 50 µm (0.05 mm). Image courtesy of the University of Cambridge DoITPoMS Micrograph Library

4.5.2 X-Ray Diffraction

In 1913, shortly after the discovery of X-rays at the turn of the century, William Henry Bragg and his son, William Lawrence Bragg examined patterns made by X-rays as they passed through various types of crystals such as halite. They not only correctly surmised that the patterns were a response to the regular arrangements of atoms within the crystals, but also developed the rigorous mathematics from which one could determine the arrangements of atoms from the X-ray patterns. For this they were awarded the Noble Prize, making William Lawrence Bragg at age 25 the youngest recipient ever.

XRD works a bit like that irritating flash of sunlight from the flat face of your wristwatch that aligns perfectly to hit you in the eye. In XRD a beam of X-rays is projected onto a mineral and the angle at which the beam is reflected onto a detector is recorded (Fig. 4.41). X-rays will reflect from a layer of atoms in a crystal but X-rays penetrating deeper into the crystal travel a farther distance, on both entrance and exit, than X-rays coming off a more shallow crystal surface. These deeper X-rays travel farther and thus lag behind the more shallow X-rays.

For the general case, the wave height of the deeper X-ray will shift behind that of the shallower X-ray and their waves will interfere with one another such that X-rays will not be observed at the detector. However, when the distance between the crystal layers and the angle of the incident is such that the extra distance traveled is exactly equal to an integral multiple of the wavelength of the X-ray, the wave heights will then coincide; constructive interference occurs, and an X-ray reflection is observed at the detector. Specifically, when the wavelength, l, is equal to an integral multiple, n, of twice the crystal spacing, d, times the sine of the incident angle, θ, one observes an X-ray at the detector. This is the famous equation discovered by the Braggs:

$$nl = 2d\sin(\theta)$$

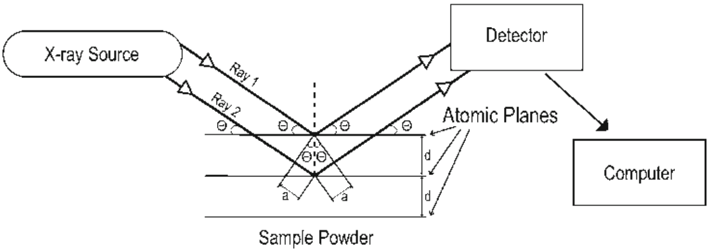


Fig. 4.41 The X-ray diffractometer beam path and detector

The wavelength *l*, chosen in advance, is constant and known, so that one only needs to know the angles θ at which X-rays are diffracted to calculate the crystal lattice distances, *d*, from which the identity of the unknown mineral can be determined.

In practice, for essentially all known minerals, the angles at which they diffract X-rays are known and tabulated in searchable databases. Modern diffractometers commonly use such databases to match the pattern obtained from an unknown sample to specific minerals, removing the need for calculating the crystal dimensions.

In an actual application, a small sample, 5–10 mg or more, would be taken from an artifact and crushed to a powder and mounted in the middle of the diffractometer. As the detector, as shown in Fig. 4.41, rotates around the sample, the computer counts the intensity of the X-rays at each angle and reports them in a graph as shown in Fig. 4.42. The angles at which the sample diffracts X-rays are then listed, along with their relative intensities, and compared to those in the searchable database. The computer then presents the closest matches to know minerals. In the example here, the material from an archaeological stone bowl is identified as the mineral chlinochlore.

4.5.3 IR Spectroscopy

Extending beyond the visible region into the longer, lower energy wavelengths of the electromagnetic spectrum, we enter the IR and microwave regions. These wavelengths, on the order of fractions of a millimeter up to centimeters, are too large to interact with individual atoms. This scale is appropriate, however, for groups of atoms such as molecules. IR spectroscopy works by inducing vibrations within a molecule. Specific IR wavelengths correspond to particular modes of vibrations among particular atoms (Fig. 4.43). For example, molecules of carbon dioxide (CO_2) can absorb photons with a specific energy by transforming this energy into vibrations that stretch the carbon–oxygen distance; photons of a different energy cause vibrations in a mode that bends the molecule along its oxygen–carbon–oxygen axis. Water has similar vibrational modes, but the specific atoms are different so the wavelengths at which it absorbs light are different from those of CO_2, even though the types of vibrations are similar.

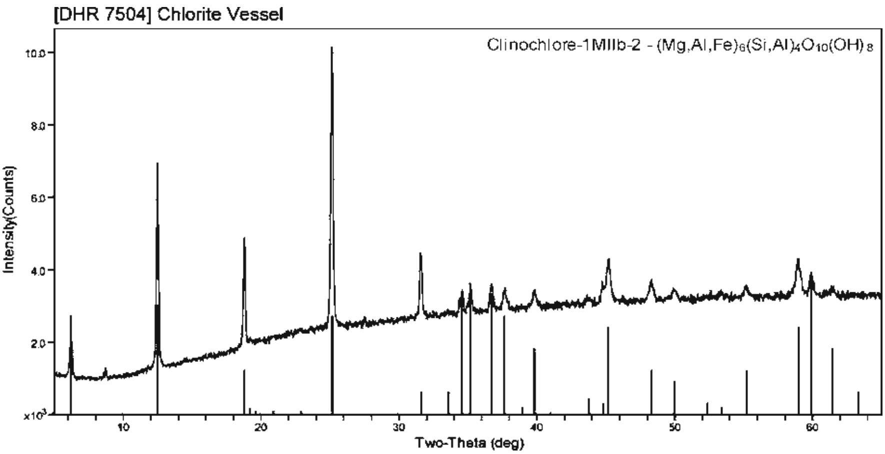


Fig. 4.42 Typical output of an X-ray diffractometer. The horizontal axis is the angle between the X-ray source and the detector, increasing from *left* to *right*. At specific angles, diagnostic of a particular mineral, intense X-rays are received by the detector. The continuous line from *left* to *right* is the XRD pattern for a powdered sample from a stone bowl. The vertical lines along the *bottom* are those from the XRD mineral reference database for the mineral clinochlore, matching the angles at which peaks appear in the XRD pattern, thus identifying the material from which the bowl was carved as clinochlore, a variety of chlorite

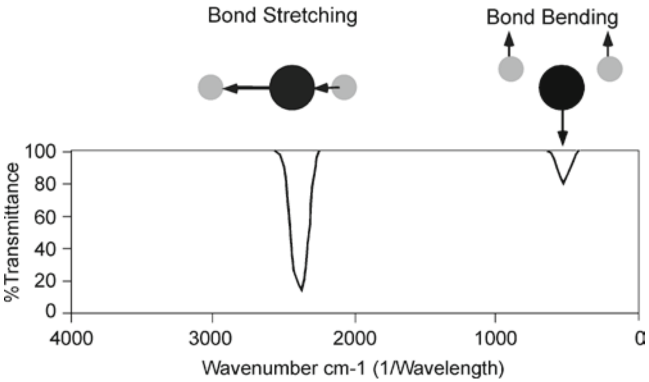


Fig. 4.43 Infrared spectrum of a carbon dioxide molecule showing the absorption of infrared light at two different wavelengths (measured as “cm^{-1}”), each corresponding to a way in which the molecule may vibrate. The wavelength is diagnostic of specific molecular vibrations, from which the identity of the molecule can be deduced

In the most basic form, IR spectroscopy is similar to colorimetry and absorption spectroscopy. The spectrometer projects IR light through a transparent film of the unknown sample and the amount of light absorbed by the sample is recorded over the relevant wavelengths. Many modern instruments, however, use “Raman scattering,” which is similar to a fluorescent or emission technique. In Raman-IR, a particular wavelength is projected onto a sample and the wavelengths of the light scattered at a high angle are recorded.

Rotations of the molecules as well as vibrations can absorb energy from the incident light so that the scattered light will be missing this energy. Because decreasing energy corresponds to increasing wavelength, the wavelength of this scattered light will increase by a precise amount corresponding to the energy loss of the vibrations. Changes induced by the incident light can also produce vibrational and rotational modes with less energy, and the scattered light can thus also be shifted to lower wavelengths of correspondingly higher energy. The resulting spectra are often more characteristic of materials than are simple IR spectra. The Raman method can be applied to a much wider array of materials than standard IR spectroscopy. Because it only examines light reflecting off the surface of an object, the method is nondestructive. Portable instruments for Raman IR spectroscopy are available that allow the method to be used in the field and in museums.

4.6 Summary

This chapter is intended to provide an overview of the different kinds of analyses that are being done in archaeological chemistry. The major categories we describe here include magnification, elemental analysis, isotopic analysis, organic analysis, and mineral and compound analysis. We discuss these methods separately from instruments because different instruments can do different kinds of analyses.

Magnification involves observation and is the most subjective of the analyses discussed here. At the same time it is also one of the most powerful. A variety of instruments are available for enlarging and observing archaeological materials. A major difference exists between optical microscopes and electron microscopes. Optical microscopes use visible light and a system of lenses to enlarge images up to ca. 500×. Electron microscopes in their more elaborate forms as AFMs or tunneling microscopes operate at a nanoscale and can discern a carbon atom, a magnification of 5,000,000×. In addition to the qualitative aspects of observation, some electron microscopes have capabilities for quantitative chemical analysis.

Elemental analysis, determination of the chemical composition of material, is the most common type of analysis in archaeological chemistry. A variety of instruments can be used for such analyses including SEM microprobes, ICP spectrometers, mass spectrometers, CN analyzers, NAA analysis, and many others. The instruments chosen for elemental analysis depend on several factors including availability, elements of interest, the nature and size of sample, cost, turn-around time, and others. A variety of materials have been investigated with elemental analysis, almost any kind of archaeological material that exists.

Isotopic analysis has become an important part of archaeological chemistry in the last 25 years, used for provenience and diet studies primarily. One of the early uses of isotopes in archaeology involves locating the sources of marble and metals.

The Getty Kouros, described in Chap. 6, documents the use of light isotopes (carbon and oxygen) in the identification of quarries for this stone. Lead isotopes have been utilized in the study of metal sources, particularly with regard to iron and copper. Today strontium, oxygen, and lead isotopes are being used to investigate the place of origin of human remains as well and prehistoric plants and animals. There is a great potential for isotopes in archaeological research and every reason to predict their growing role in the investigation of the past.

Organic materials are the last frontier in archaeological chemistry. Organic molecules and compounds do survive in a range of conditions from the past and contain information about the plants and animals that our ancestors ate and used. Some of this information is stored within the walls of broken pottery vessels, some of this information may be stored on stone tools, or house floors, or storage pits, or grinding stones, or a variety of other tools, equipment, and facilities that were used in the past. Organic analysis is difficult because of the breakdown of these products over time and the fragmentary nature of the molecules and compounds today. The process of creating a reference library of ancient organic residues is a long and slow journey.

Some of the different instruments discussed in this chapter are listed in Table 4.5 and information about their use is provided. The information in the table includes the isotope ratio(s) of interest, the abundance of the isotopes in nature, the kinds of materials studied in archaeology, and the kinds of information that can be learned.

Fortunately, there are many different kinds of instruments available. Each instrument has different capabilities and produces somewhat different results. There are many decisions to be made when selecting an instrument to use for the analysis of archaeological materials. Foremost considerations include the type of material to be studied and the questions that are being asked. Based on the material and question, a decision as to the kind of information that is needed can be made (elemental concentrations, isotopic ratios, molecular identification?) and an instrument selected. At the same time, different instrumentation can provide similar data. For example, elemental concentrations can be obtained using XRF, NAA, or ICP/OES. Further decisions are sometimes required involving the precision and quality of the data that are needed.

Atomic absorption and emission spectroscopy (mainly inductively coupled plasma spectroscopy) are best for easily ionized atoms that absorb light in the visible wavelengths, i.e., those in the first columns of the periodic table, including some of major interest: Ca, Sr, and Ba, but they have lower sensitivity, being more suited for parts-per-million (e.g., for Sr, Ba and Zn) than parts-per-billion measurements (e.g., not for uranium and rare-earth elements). Inductively coupled plasma source mass spectrometry (ICP-MS), at present one of the most popular tools for elemental analysis, has much higher sensitivity in the parts per trillion range, but suffers from molecular interferences, particularly in the low mass ranges (which include calcium and phosphorus). NAA likewise is best at the bottom of the periodic table for large atoms that are easy to "activate" by hitting them with neutrons (e.g., uranium and REE). A particular research issue might require an instrument with unusual sensitivity for particular elements.

Sensitivity and accuracy are, of course, important factors in the selection of an instrument for the analysis of archaeological materials. Table 4.6 provides a summary

Table 4.5 Instruments for archaeological chemistry: principles, units of analysis, sample state, data, cost, and applications

Instrument	Principle	Unit of analysis	Sample state	Data	Cost of analysis	Applications
Optical microscope	Magnification of light	Objects 2×–1,000×	Natural	Photos	$1s	Most archaeological materials
SEM	Electron magnification	Objects 25×–100,000×	Microscopic objects, polished sections	Photos	$10s	Most archaeological materials
ICP-OES	Light spectrometry	Elements	Liquid	Elemental abundance ppm	$10s	Stone, pottery, soils, bone, metals
ICP-MS	Mass spectrometry	Elements/isotopes	Liquid/solid	Elemental abundance ppb/Isotopes	$10s	Stone, pottery, soils, bone, metals
IR	Infrared spectrometry	Minerals, organic molecules	Powders, thin films, natural materials	Molecular identification	$10s	Rocks, organic molecules
TIMS	Thermal ionization mass spectrometry	Isotopes	Purified element	Isotope ratios	$100s	Pottery, bone, metals
XRD	Diffraction of X-rays	Crystals	Powder, single crystals	Mineral identification	$10s	Minerals, pigments
XRF	Fluorescence of X-rays	Elements	Powder/natural	Elemental abundance ppm	$10s	Stone, pottery, soils
NAA	Gamma radiation	Elements	Powder	Elemental abundance ppm	$10–$100s	Stone, pottery
GC–MS	Volatility/molecular weights	Large organic molecules	Dissolved in solvent	Molecular identification, %	$10s	Foodstuffs, dyes, resins
LC–MS	Solubility/molecular weights	Large organic molecules	Dissolved in solvent	Molecular identification, %	$10s	Foodstuffs, dyes, resins

Data from Holland et al. (1991)

Table 4.6 Sensitivity and accuracy of spectroscopic methods of elemental analysis

Technique	Sensitivity	Accuracy (%)
AAS – flame	1–10 ppm	1–5
AAS – graphite furnace	1–10 ppb	1–5
OES/AES	100 ppm	7–10
ICP-AES	0.5–100 ppb	3–5
ICP-MS	50–1,000 ppt	0.1–1.0
LA-ICP-MS	1–100 ppm	5–10

From Pollard et al. (2007)

of sensitivity and accuracy for various spectroscopic methods of elemental analysis. The various instrument abbreviations in the table include atomic absorption spectrometry (AAS), Optical emission spectrometry/atomic emission spectrometry (OES/AES), ICP-AES, ICP-MS, and LA-ICP-MS. Sensitivities are described in parts per million (ppm), billion (ppb), or trillion (ppt). Accuracy is described in terms of percentage variation.

In practice, however, the choice of the instrument for analysis often depends less on data quality and more on the pragmatic issues of availability and cost. Key factors in choosing a particular instrument tend to be the accessibility of the instrument, the "turn-around" time required for the analyses, and the costs of analyses. Obviously any one of these could be, and often is, prohibitive. If, for example, one can choose between an inexpensive, but rarely available, research instrument at a university and an expensive, but immediately available, commercial service, funding and deadlines will be determining factors in the decision.

There is considerable variation among instrumental techniques in their ability to measure specific elements. But ideally any instrument designed for elemental analysis, with adequate sensitivity, precision, accuracy, and proper calibration can be used. Important concerns in instrumental analysis also include the demands of sample preparation – whether a technique is destructive – and the size and quality of the sample needed. Many types of instruments require a powder or liquid sample that involves destructive preparation. Archaeological materials are turned into powders for NAA and XRD, liquids or solids for ICP-MS, and gas for GC–MS. But rare, significant, or unusual specimens cannot be destroyed for analysis. A few instruments with larger sample chambers can perform nondestructive analyses. There are also new techniques, such as LA, that cause very little damage to the sample.

The sample size needed for analysis is also an important consideration. The pragmatic issue of sample size may not matter when several grams of samples are readily available for destructive analyses. On the other hand, extremely rare, valuable, or small materials such as the teeth of early hominids require instruments that are either nondestructive or can analyze very small quantities. Each laboratory will likely have its own preparation protocols depending upon the particular requirements of each type of instrument and the kinds of samples that they normally analyze.

Suggested Readings

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Chapter 5
Identification and Authentication

Contents

5.1 What Archaeological Chemistry Can Do

A previous chapter (Chap. 2) focused on some of the more important and general questions that archaeologists ask about the past – what our ancestors were like, how they lived, what they ate, what sort of environment they inhabited, what kinds of things did they do, their relationships with other people, religious beliefs and ceremonies, and many others. There are many ways that archaeologists try to answer those questions – many perspectives, many ideas, many methods, and many subdisciplines. Fieldwork provides the basic information in the form of artifacts and a variety of other materials that humans buried, abandoned, or lost. Specialists in archaeozoology, archaeobotany, bioarchaeology, geoarchaeology, ceramic and lithic analysis, architecture, and more work to describe and understand the materials that are recovered in excavation and other types of fieldwork. The bones studied by archaeozoologists can tell us about the animals that were hunted or herded and what humans ate. The human bones studied by bioarchaeologists can tell us much about the life history of their owners – age, sex, disease and trauma, cause of death, and much more.

T.D. Price and J.H. Burton, *An Introduction to Archaeological Chemistry*,
DOI 10.1007/978-1-4419-6376-5_5,

Archaeological chemistry can help answer a number of these questions about the past. Archaeological chemistry can be used to investigate a variety of different materials – stones, ceramics, bones, metals, sediments, and more – as discussed in Chap. 3. Archaeological chemistry is most useful for the identification of unknown materials, the authentication of objects of questionable antiquity, the function of artifacts and architecture, the characteristics of the environment, the place of origin or provenience of archaeological remains, the reconstruction of diet, and other past human activities. Each of these topics is considered in more detail in the following chapters along with a series of case studies. The remainder of this chapter deals with identification and authentication.

5.2 Identification and Authentication

Two fundamental tasks in archaeological chemistry are the identification and authentication of unknown artifacts and materials. This has been an important part of research in the field for many years. Identification involves the determination of the material from which an object is made. Authentication deals with determination of the genuine nature of the object. In archaeology and art history, this generally involves verifying the antiquity of a piece. Authentication can sometimes be done using archaeological dating methods such as radiocarbon. In many cases, however, more detailed methods are employed to examine the materials and techniques of manufacture to be sure that these are appropriate for the age of the artifact.

A variety of methods are used for identification and authentication, ranging from microscopes to the most complex and sophisticated scientific instruments available. In the examples provided in this chapter, we consider the microscopic identification of species-specific starch grains from South America to identify early traces of plant domestication. An SEM is used to identify plant remains from the Pacific and the very early spread of sweet potatoes from South America westward. A petrographic microscope is used to characterize the micromorphology and identify the contents of house floors in a prehistoric site in British Columbia. Finally GC/MS instrumentation is used to identify the chocolate contents of distinctive ceramic jars found in Chaco Canyon, New Mexico.

Several examples of authentication in archaeology and art history are also discussed in this chapter. A very famous Greek statue – the Getty Kouros – remains unauthenticated to this day in spite of elaborate investigations of its composition and place of origin. The Vinland Map is another mysterious artifact, purported to portray the New World before the time of Columbus. Its validity also remains in question. Human skulls carved from a single piece of crystal are purported to come from the Maya Civilization of Central America, but careful analysis of these objects has indicated that they were forgeries. Finally, one of the most famous religious relics of all time – the Shroud of Turin – has been examined using radiocarbon dating by three different laboratories and shown to come from the thirteenth-century AD, long after the death of Christ.

5.3 Identification

The identification of many archaeological objects happens in the field or shortly thereafter when recovered items are cataloged. The catalog of finds includes the location and context of an item, as well as a detailed description. This description includes both identification as to type of object (for example, arrowhead, grinding stone, awl, potsherd, and so forth) and material (for example, obsidian, sandstone, bone, ceramic, respectively). Nonetheless, some objects cannot be readily identified.

There are many mysteries in an archaeological excavation. Often there are objects or materials that are completely unknown. Or an item might be recognized as to type – for example, as a hammerstone, as a pigment, or as a hafting resin – but the type of raw material is unknown. There are objects such as stones with microscopic grain sizes, powdered pigments, building mortars, and many organic materials such pitch or resin and other plant remains that cannot be so easily identified. This is where archaeological chemistry can help.

For inorganic materials, such as fine-grained rocks and minerals, the initial level of analysis often involves a microscope. A binocular microscope might suffice to identify sand-sized ceramic inclusions in a piece of pottery. This is a first and simple evaluation with minimal destruction of the artifact beyond superficial cleaning. A more sophisticated examination of mineral grains in pottery could be done using a petrographic microscope. Petrographic studies involve more knowledge and experience involving experts in the field and also require some destruction of the potsherd which must be cut and a slice removed to make a transparent "thin-section."

Another, relatively new approach to mineral identification in pottery and stone is the use of Raman infrared spectroscopy, discussed in Sect. 4.5, which has the advantages of being both nondestructive and portable. Raman spectroscopy provides information about molecular vibrations that can be used for sample identification and quantification. IR spectroscopy provides compositional information about specific compounds, rather than elemental concentrations. IR spectroscopy works by inducing vibrations within a molecule. Specific infrared wavelengths correspond to particular modes of vibrations among particular atoms.

An example of such study involves stone tools from the Bronze Age in China. Z.C. Jing used a portable Raman Infrared spectrometer to nondestructively analyze these objects. The artifact was placed on a transparent window on the IR spectrometer, which accumulates spectra as shown on Fig. 5.1 for both reference minerals (left-hand side) and artifacts (right hand side). The infrared energy is displayed along the bottom axis and the shape of each line shows at what energy the mineral absorbs infrared light. The lower the dip in the line, the greater the absorbance. The energy at which absorbance is strong identifies the type of chemical bond. For example, calcite ($CaCO_3$), the lowest line on the left half of the chart, shows several absorptions due to CO_3 vibrations. Artifact M49:7, the spectrum of which is the lowest line on the right hand side, matches the spectrum of calcite, thus identifying the material as marble, the rock name for coarsely crystalline calcite. In order from bottom to top, other artifacts could be nondestructively identified as being made from dickite, chlorite, antigorite, tremolite nephrite, and actinolite nephrite, respectively.

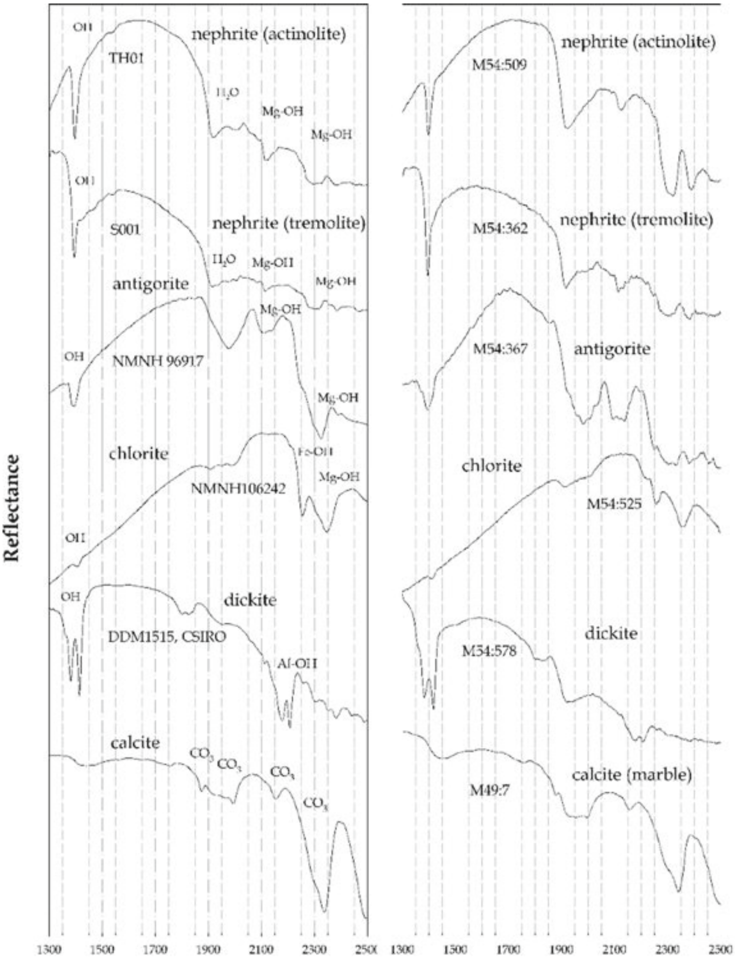

Fig. 5.1 IR spectra of mineral standards (*left*) and artifacts (*right*). Because each mineral has an IR spectrum determined by its own chemical bonds, the mineral spectra have different shapes. Thus they can be distinguished and the minerals composing artifacts can be identified by matching the spectra to those of the mineral standards (spectra courtesy of Z.C. Jing)

Some geological materials, specifically clays, ochres, and finely powdered mineral pigments have particle sizes too small to be studied by petrography, but can be analyzed by either Raman IR spectroscopy or by X-ray diffraction. The interpretation of data from both methods, however, is difficult if more than a few minerals are present.

For organic compounds, quite different methods of study are required. Usually a small quantity of the material in question is dissolved in an organic solvent. The individual organic compounds in the substance are separated by a chromatographic method and mass spectrometry to identify these compounds. The composition of the original material can often be determined from the kinds of compounds present.

Infrared spectroscopy may also provide data useful in identifying relative pure organic compounds.

Microscopes play a big role in the examples of identification we discuss below –starch grains from South America from early domesticates plants, the introduction of the sweet potato, an important crop, to the islands of the Pacific, and the fine details of floor sediments in prehistoric British Columbia. Finally, a GC/MS identifies chocolate as the contents of ceramic cups found in ancient New Mexico.

5.3.1 Starch Grains and Early Agriculture

Material: Starch Grains
Instrumentation: SEM
Application: Identification
Place: Ecuador
Time Period: Archaic, 9000 BP
Question: Can starch grains be used to identify domesticated plants in tropical America? What plants were people eating in the tropics?

Key References

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It is remarkable that any materials survive from the past. In most cases, only the hardest materials remain as an indication of former human presence. Organic materials like food, skin, wood, fur, and the like rarely last long in the ground. The evidence for our early human ancestors is almost exclusively in the form of stone tools that they discarded. In tropical environments, preservation is very poor. Warm temperatures, heavy precipitation, dense vegetation, and acidic soils often destroy most traces of past human activity. We know relatively little about human diet and behavior in the American tropics, for example.

Some things do survive in such conditions, however. One of those is starch, in the form of microscopic grains. Most species of plants contain starch, concentrated in fruits, seeds, rhizomes, and tubers. Starch is produced during photosynthesis as a way to store glucose for energy. Starch granules are made primarily of glucose molecules with a quasi-crystalline structure. Grains range in size from 1 to 100 μm and have shapes from spherical to elliptical. Starch grains are often identifiable as to their species. Because it is designed by nature to be stored, starch is a long-lasting molecule. For these reasons, starch grains are a useful material for archaeological investigations of plants and past human diets.

Starch grains have been found in dry caves as well as tropical forests. Starch grains can be found on the stone tools, in pottery vessels, or in the soil at archaeological sites. Starch grains can be separated from artifacts and sediments by a series of mechanical or chemical scrubbing and ultrasonic washings. A binocular microscope or SEM is normally used to examine and identify the species of starch. Starch grains have been used to identify the uses of stone tools, to obtain information on past vegetation and climate in a region, and to examine ancient human diets. Seeds, roots, and tubers are the main sources of dietary starch for humans.

A recent study of starch grains removed from stone tools used for cutting and grinding from early archaeological sites in western Panama documents the utility of this method. This area of rainforest receives more than 3 m of rainfall per year and preservation of prehistoric remains is poor. In spite of the absence of intact organic remains at these sites, residues were visible in microcrevices in the artifacts and removed in an ultrasonic bath. Starch grains were isolated from the residue using heavy liquid flotation that brought the starch to the surface of the bath for extraction. Grains were then rinsed, concentrated, and examined at 400× with an optical microscope. Identification of the grains was made using a large, comparative collection of known starch grains.

Several species were identified among the starch grains present (Fig. 5.2). Maize (corn), manioc, and arrowroot starch grains were found on the artifacts, along with several local plants that were also eaten such as yam. Maize, manioc, and arrowroot were originally domesticated elsewhere and spread to the crossroads of continents that is Panama and Central America. Maize is a major food staple in the Americas, originally domesticated in the highland river valleys along the southern, Pacific coast of Mexico around 9,000 years before present. Maize starch is found in Panama ca. 7,800 bp, spreading south from southern Mexico Manioc and arrowroot are starchy root crops that probably originated in South America. Manioc was likely domesticated in southwestern Brazil where its wild ancestor is known. Manioc in Panama by 7,000 years ago indicates that this domesticated plant was moving north about the same time maize was moving into South America. Arrowroot was likely also coming from South America and reaches Panama some 7,500 years ago.

5.3.2 Pacific Plant Identification

Material: Charcoal (burned plant remains)
Instrumentation: SEM
Application: Identification
Place: Pacific Ocean
Time Period: 1000–1500 AD
Question: What plants are present at archaeological sites in the Pacific?

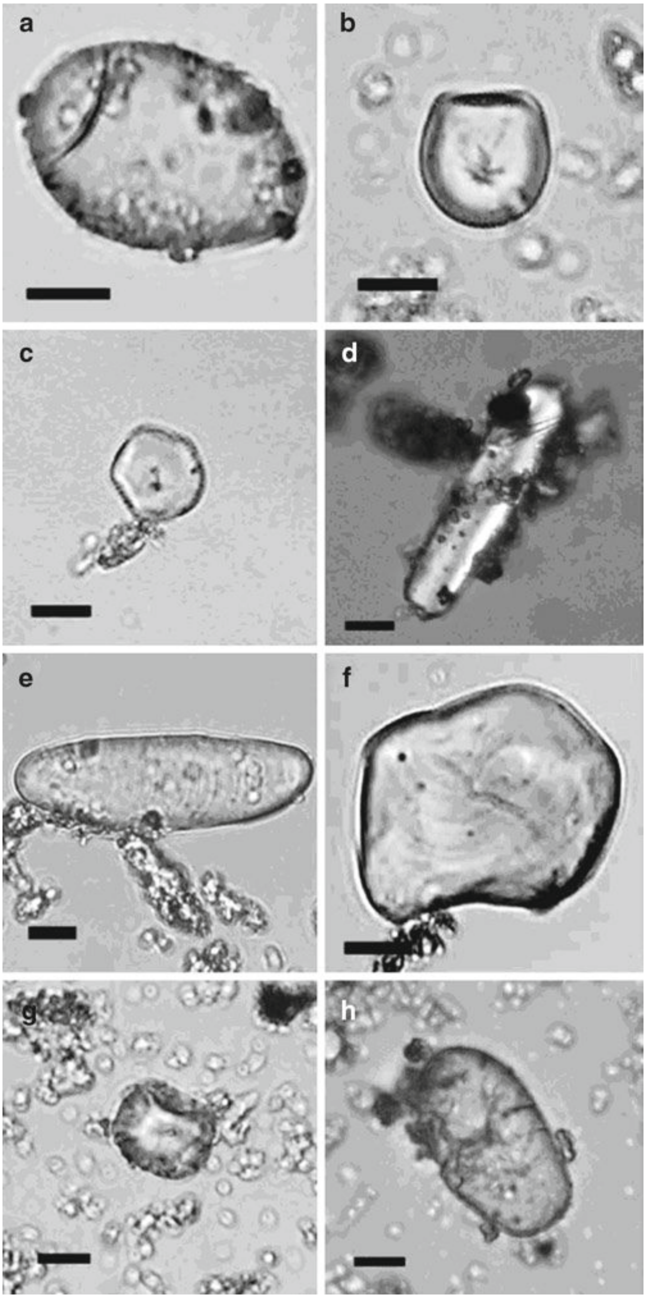

Fig. 5.2 Starch grains seen under high magnification. (**a**) arrowroot, (**b**) manioc, (**c**) maize, (**d**) Dioscorea sp., (**e**) Calathea sp., (**f**) Zamia sp., (**g**) maize, (**h**) Dioscorea sp. The scale is 10 μm

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Charcoal is the term used for the heavily burned fragments of wood and other plant tissues found at archaeological sites. Charcoal is technically an inorganic material – impure carbon produced by heating wood or other organic matter in the absence of air. Because it is largely inorganic, it will preserve when other organic materials disappear. On the other hand it is fragile and disturbances of the ground like animal activity or freeze–thaw cycles will often turn charcoal to powder in the soil.

Charcoal is useful for several reasons. Charcoal often retains the original structure of the plant tissue and can be identified as to species. It is thus possible to determine the kinds of woods that were intentionally or accidentally burned at archaeological sites. This information is useful for reconstructing environments and learning about cultural differences in the selection of wood for various purposes. A case study in wood charcoal identification from the island of Thera in the Aegean is discussed below.

Because the anatomy of the wood is retained in charcoal, identification at the genus or even species level is possible. In those unusual cases where the wood itself is preserved, the same procedures are used for identification. Because the diagnostic structures in the wood are very small, a microscope is used at magnifications between 40 to 400× to examine specific characteristics.

In addition to the identification of seeds, nuts, fruits, and tree species, the investigation of charred plant remains has recently advanced to the other tissue. In particular, SEM [Scanning Electron Microscope] studies have been able to identify charred parenchymous tissues. Parenchyma is the most common plant tissue and makes up the bulk of the primary plant body, including the leaves, flowers, roots, the pulp of fruits, and the pith of stems in woody plants. The thin-walled parenchyma cells have large empty spaces and distinctive intercellular areas (Fig. 5.3).

Parenchyma is a relatively unspecialized tissue commonly found in roots and tubers. Roots and tubers were often a source of carbohydrates for prehistoric groups, but because of problems with the identification of these plant organs, they have been almost invisible in the charred plant remains recovered from archaeological sites. Now with the development of SEM analysis, compendiums of reference material, and keys for parenchymous tissue identification, new plant foods are being added to descriptions of past diets.

Fig. 5.3 Scanning electron microscope (SEM) photo of parenchyma tissue (thin-walled cells with large empty spaces) in modern *Sambucus* (Elderberry) stem

In much of the Pacific, for example, root crops such as *taro*, *cassava*, and the *sweet potato* are rarely found in archaeological excavations. Taro (*Coloscia esculenta*) is sometimes called the potato of the tropics and a staple for many people across the Pacific Ocean. Taro is slightly toxic and must be cooked to be eaten. The root of the plant is a large starchy bulb that is boiled, baked, or roasted or ground into flour. Cassava (*Manihot esculenta*) is a woody shrub with an edible root, growing in tropical and subtropical areas of the world. Also known as manioc, the starchy roots can be stored for up to 2 years in the ground and powdered, boiled, or eaten raw.

Sweet potatoes are well known. The sweet potato (*Ipomoea batatas*) is of particular interest archaeologically because of questions about its antiquity and its spread across the Pacific. The sweet potato is an important crop in eastern Polynesia (Hawaii, Easter Island, and New Zealand) and the highlands of New Guinea. Yet the original home of the sweet potato is in South America.

The sweet potato spread to the Pacific prior to the arrival of European explorers who collected herbarium specimens of the plant when they first visited New Zealand and other islands. But direct archaeological evidence of this early spread has been lacking. In 1989, however, excavations at a deep rockshelter in the Cook Islands, smack in the middle of the South Pacific, recovered charred plant remains dating to AD 1000, long before the European voyages of discovery. Several diagnostic features observed with the scanning electron microscope confirm a number of these specimens as sweet potato.

Another recent bit of evidence regarding contact across the Pacific comes from a chicken bone found in Chile and dating between AD 1000 and 1500. Chickens were domesticated in China and carried by the colonists across the Pacific. The fact

Fig. 5.4 A South American chicken and the early chicken bone, made into an awl or spatula, from Ecuador. The chicken bone predates the arrival of Columbus in the New World

that a chicken was present in South America before the arrival of the Spanish (Fig. 5.4). The remaining question then is who was responsible for these plants and animals turning up unexpectedly – Pacific explorers or by South American voyagers? Did the Polynesians sail to the coast of South America? Or vice versa?

5.3.3 Keatley Creek House Floors

Material: House floor sediment
Instrumentation:
Application: Identification
Place: British Columbia, Canada
Time Period: 400 bc – ad *1000*
Question: How did the house floors form and what do they contain?

Key References

Hayden, Brian. 2000. *The Pithouses of Keatley Creek.* New York: Harcourt.

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Micromorphology is a rapidly growing area of archaeological science involving the study of *anthropogenic* sediments at the microscopic level. These sediments usually come from past living surfaces where the almost invisible trash and dust of everyday life accumulates. Standard soil analysis techniques generally do not work well with anthropogenic sediments because of the inclusion of a variety of organic and artifactual material. Identification of the contents of ancient living surfaces and how they formed using micromorphology provides greater insight on past behavior.

Undisturbed blocks of sediment are removed from a site and taken to a laboratory. The block is embedded with polyester resin to harden it and then a thin slice is cut and polished so it can be examined at 20–200 magnification under a petrographic microscope.

Under the microscope, important observations include *composition* (the mineral and organic contents), *texture* (size and sorting of sediments), and especially the *fabric* – the geometric relationships – of the constituents. At the early Neolithic site of Catalhöyük in Turkey, for example, micromorphology revealed that some of the house floors had been plastered with a thin coat of clay at least 50 times. These thin layers of plaster incorporated many small finds of plant remains and other evidence.

At Keatley Creek, a prehistoric site in British Columbia, micromorphological examination of samples from the house floors revealed the compaction of the living surface and a variety of microartifacts. The site is visible today as a concentration of more than 100 large depressions or pits that mark the location of the houses of the former inhabitants (Fig 5.5). There were a total of 120 houses at the site. The largest of these house depressions are 18–21 m (around 60′) in diameter, almost the size of a tennis court in area. These great structures were among the largest buildings in prehistoric North America. The site was initially occupied around 2800 BC but the most intensive occupation was from 400 BC to AD 1000.

The living floors of these houses provided substantial information on both contents and context (Fig. 5.6). Several techniques were used to study the house floors. Paul Goldberg of Boston University did the micromorphology study. Figure 5.7

Fig. 5.5 The site of Keatley Creek in interior British Columbia, Canada

Fig. 5.6 Excavated floor of the larger house pit at Keatley Creek

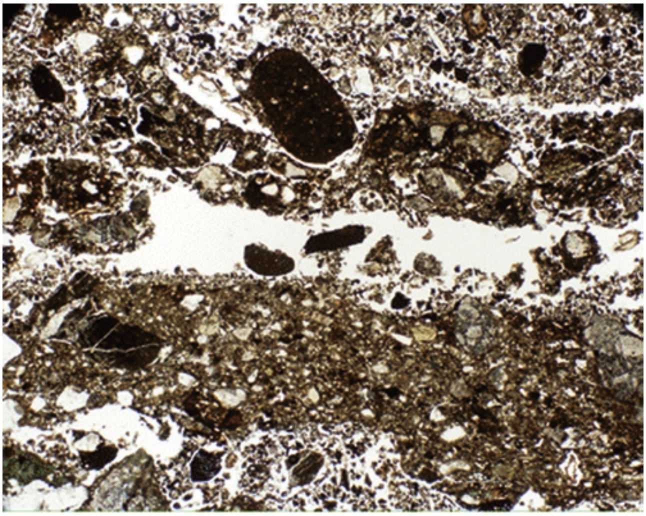

Fig. 5.7 Micromorphology slide of the house floor from Keatley Creek. The *lower half* of the photo shows the house floor as compact fine sediments covered by Polarized Light; width of the photo is about 3.5 mm

shows a slide from his investigations. Samples for thin sections were taken from different contexts at the site including roof and floor deposits, hearths and ash layers, and the fill of pits. Sample thin sections were examined under a petrographic microscope using different kinds of light and magnification and revealed the house floor as a dense, compact sandy silt in the lower part of the photo. Deposits associated with floors or occupation surfaces were generally richer in fine mineral matter, which produces the slightly lighter color of these layers. The amount of anthropogenic material – bone, ash, burned stones, or fine charcoal – in the thin sections of the house floors was surprisingly low. There was however usually a 1–2 mm thick deposit of salmon bones directly on top of the living surface of the floor.

In addition, in this sample (Fig. 5.7) there is a gap or crack between the house floor and the upper deposits, likely left by the decay of vegetation, perhaps mats on the floor. During excavation the upper deposits peeled away easily from the more compact house floor. Micromorphological studies revealed the nature of this house floor and the deposits that accumulated on it, both during and after use.

5.3.4 Chaco Coco

Material: Organic residues in ceramics
Instrumentation: chromatography, mass spectroscopy (LC–MS, GC–MS)
Application: Identification/Function
Place: Pueblo Bonito, Chaco Canyon, southwestern US
Time Period: Anasazi, AD *850–1250*
Questions: What was the purpose of the unusual cylinder jars at Chaco Canyon? How far did trade items come to Chaco Canyon?

Key References

Crown, Patricia L., and W. Jeffrey Hurst. 2009. Evidence of cacao use in the Prehispanic American Southwest. *Proceedings of the National Academy of Sciences 106: 2085–2086.*

Henderson, John S., Rosemary A. Joyce, Gretchen R. Hall, W. Jeffrey Hurst, and Patrick E. McGovern. 2007. Chemical and archaeological evidence for the earliest cacao beverages. *Proceedings of the National Academy of Sciences 104: 18937–18940.*

Chaco Canyon is a region of archaeological sites in northwestern New Mexico that was a major cultural center of ancient Puebloan people at the end of the first millennium AD (ca. AD 850–1250). One of the most extraordinary aspects of these sites is that they had unusual networks for procurement, over substantial distances, of everything from raw materials to finished goods. Ceramics imported from distant sources is not unusual, but Chacoans also imported building materials such as large timbers, some weighing many hundreds of pounds, from distances exceeding a hundred kilometers. There is some evidence that food was brought from considerable distances and finished goods such as copper bells from Mesoamerica came from distances exceeding 1,000 km (Fig. 5.8).

The importation of exotic items such as the copper bells and also Scarlet Macaws from Mesoamerica led archaeologist Patricia Crown to wonder if there might be another Mesoamerican connection: unusual cylinder jars, found in a room at, Pueblo Bonito, the largest site in Chaco Canyon (Fig. 5.9). These cylinder jars

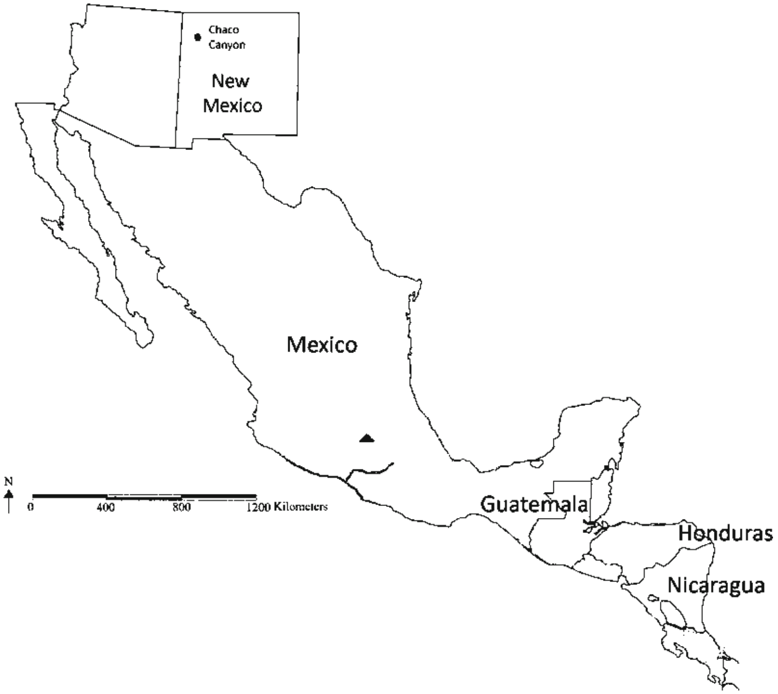

Fig. 5.8 The location of Chaco Canyon in New Mexico and some of the countries of Central America, including Mexico and Guatemala, potential sources of the chocolate imported to Chaco Canyon

Fig. 5.9 Cylinder jars from Chaco Canyon used for chocolate drink containers (Image courtesy of University of New Mexico, http://www.sciencedaily.com/releases/2009/02/090203173331.htm

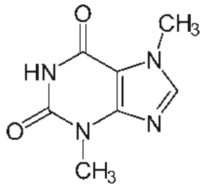

Fig. 5.10 The chemical structure of theobromine (3,7-dimethylxanthine)

are in a Puebloan black-on-white style but the form is quite atypical of Puebloan pottery. Cylinder jars are known from Mesoamerica, however. Some of the Mesoamerican vessels have inscriptions and drawings indicating that they were used for the consumption of chocolate, a beverage now known to have been used by the early Mesoamerican cultures, since approximately 1500 BC. Crown wondered if the Puebloan vessels could have had a similar function.

Theobroma cacao ("theobroma" means "food of the gods") is the scientific name for the cacao plant that produces the bean that is used to make chocolate. Cacoa is a tropical plant, a small evergreen tree that grows in the jungles of Central America and the Amazon and produces large pods full of cacao beans. Recent evidence suggests that this plant was first domesticated in South America and then spread through Central America. The beans were so important in Mesoamerica that they were used as currency in some areas.

The early use of chocolate in Mesoamerican had been recently established through an study of ancient pots that stylistically resemble modern Mexican chocolate pots. Archaeologists John Henderson and Rosemary Joyce in collaboration with archaeometrist Patrick McGovern and Jeffrey Hurst, a chocolate chemist for the Hershey Chocolate corporation, analyzed organic residues from these early vessels.

Liquid chromatography–mass Spectrometry (LC–MS) and GC–MS were used to analyze the residues from sherds of presumed ancient chocolate vessels from Honduras. Only the residues that had been absorbed into the pottery were extracted and analyzed. Residues were collected by heating sherds in distilled water, methane/methanol, or chloroform/methanol and filtering. The liquids and precipitates that accumulate inside pottery can be preserved because they are bound up in the clay matrix and less susceptible to contamination.

The organic analyses contained traces of theobromine, or 3, 7-dimethylxanthine (Fig. 5.10), a caffeine-like chemical abundant in the cacao bean, but not produced in abundance by other plants. Theobromine is a "smoking-gun" indicator for cacao and chocolate. Henderson and others were able to find theobromine traces in pots from northern Honduras, as old as 1000 to 1400 BC.

Crown contacted Hurst, who then analyzed residues from midden sherds from Pueblo Bonito that appeared to be from cylinder jars. In many of these Hurst found the diagnostic theobromine traces, connecting Pueblo Bonito to the cacao fields of the Maya, several thousand kilometers away.

5.4 Authentication

Archaeologists and art historians are sometimes called upon to determine if an artifact, object, statue, or painting is old and authentic. Authentication, the verification of the identity or history of an object, is actually a bit of a misnomer; all an archaeometric study can actually do is to try to deauthenticate a claim, that is, to prove the claim to be false. As a questionable item fails tests to prove that it is a forgery, confidence that it is genuine is enhanced. It is rarely, if ever, possible to actually verify an item as completely genuine.

Tests to prove an item is a forgery generally involve either to dating materials or workmanship to show that they are anachronistic (not from the period or age that is expected) or that there are otherwise inappropriate materials or techniques that would not have been available to the object's maker. While items that clearly fail these tests are forgeries, items that pass these tests still might be the product of a careful forger who could have cleverly selected appropriate ancient materials and techniques to fool the investigator. For examples, the cloth of the Shroud of Turin, originally believed to be the 2,000-year old burial shroud of Jesus, was radiocarbon dated to the thirteenth-century AD, invalidating its claim to authenticity. The parchment of the Vinland Map, purported to be a pre-Columbian fifteenth-century map showing a portion of North America was dated to the early fifteenth century. However, the use of old parchment did not prove its authenticity because a forger, with knowledge of modern dating methods, could have selected an unused piece of parchment from a manuscript known to be of this age – as some have proposed. Further details on the Vinland Map and the Shroud of Turin are provided further on in this chapter.

Archaeometric authentication is often complimented by other lines of evidence such as paleography, i.e. the study of the vocabulary and writing styles of ancient documents – even the types of abbreviations and errors that might be found in them. The "Archaic Mark" was thought to be a copy of the Gospel of Mark, possibly dating to the thirteenth or fourteenth century. An archaeometric study by Mary Orna of blue pigment from one of its illustrations identified the pigment as Prussian Blue, which was invented in 1704, suggesting the manuscript is a forgery. However, a genuine manuscript could have been retouched using this pigment after the seventeenth century to restore its appearance. The text is recognized as an early Greek style that closely follows the Codex Vaticanus, one of the oldest existing copies of the Greek Bible, dating to the fourth century AD. In 2006 the University of Chicago made available digitized images of the Archaic Mark for further study. Stephen Carlson noticed that the Archaic Mark contains errors matching those made by Philipp Buttman in his 1860 copy of the New Testament, convincing many scholars that the Archaic Mark is indeed a forgery.

Another important aspect of authentication is documentation of the chain of custody of an artifact. An artifact that has a clearly documented history that goes back to the artifact's discovery in a carefully excavated or recorded context lends much more credibility to authenticity than does an artifact recently marketed by an anonymous collector. For example, the Archaic Mark first appeared at the University of Chicago in 1937 and the known provenience of the Shroud of Turin can only be traced back to 1357.

Authentication can also be a somewhat controversial application of archaeometric research. While its value to research and museum collections is undisputed, authentication of artifacts for sale from private collections, sometimes illegally looted from archaeological contexts, can immensely increase the value of these items and contribute in a major way to encourage further looting and destruction of the archaeological record. Archaeologists are discouraged by professional organizations not to provide evaluations or market appraisals of antiquities.

5.4.1 The Getty Museum Kouros

Material: Stone – Marble
Instrumentation: NAA elemental analysis
Application: Authentication/Provenience
Place: Greece and Los Angeles
Time Period: Classic Greece, 600–300 BC
Questions: Is this Greek statue authentic? Where did the marble come from? Where was the statue made?

Key Reference

Bianchi, Robert. 1994. Saga of The Getty Kouros. *Archaeology* 47:3.22–24.

A *kouros* (Greek: youth) is a stone statue of a nude, muscular young man carved during the classic period of Greek civilization between the sixth and third century BC. The statues have several distinctive features (Fig. 5.11). The hands are balled into fists and are placed along the body. The hair is arranged in a systematic grid of vertical and horizontal lines. The feet are placed with the left foot forward. The faces of the statues are very distinctive and appear to depict individuals in life-like portraits, not generic human faces. The eyes are open wide and the mouth formed in a serene, closed-lip smile. The kouroi statues have been variously identified as gods, warriors, or victorious athletes. There are only a dozen examples of such figures in good condition in existence. When the opportunity to obtain such a piece came to the J. Paul Getty Museum in Los Angeles in the late 1980s, excitement was high.

The statue was accompanied by documents that indicated its origin and authenticity. The Museum checked with the governments of Greece and Italy to be sure that the statue had been legally removed. Art historians, conservators, archaeologists, and archeometrists studied the piece. Opinions regarding its authenticity were divided. Why was it in such good condition, and so white? The techniques for depicting the hair and feet were different. Would an ancient sculptor have combined several styles in a single piece? Because ancient marble statues are so valuable, there have been forgeries and fakes almost as long as the statues have been made. The Getty wanted to be sure they had an authentic piece.

Because of the questions that were raised, a detailed scientific study of the statue was commissioned. An exceptional group of more than 20 scientists from around the

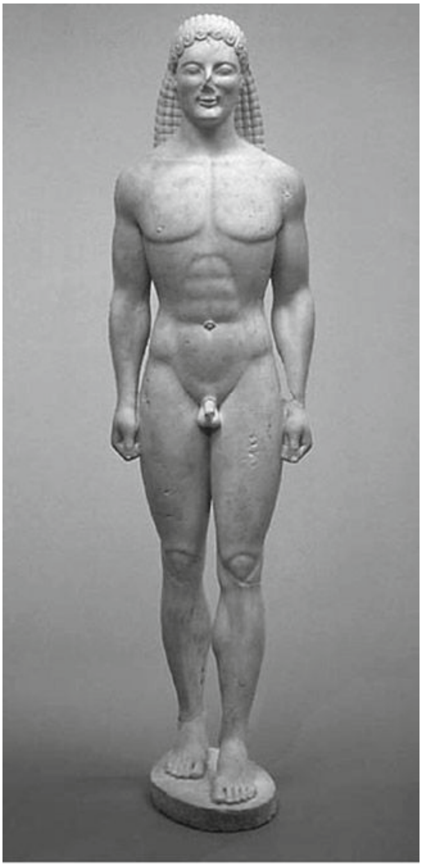

Fig. 5.11 The Getty kouros

world was assembled. A huge range of archaeometric techniques were employed to study the kouros including cathodoluminesence, ultraviolet microscopy, strontium isotope analysis, FTIR analysis, AMS dating, stable isotope analysis, neutron activation analysis, carbonate geochemistry, dedolomitization acceleration, laser microanalysis, quantitative X-ray diffraction, and transmission electron microscopy.

A geologist, Stanley Margolis, studied the source of the marble and the surface finish. Margolis was given permission to remove small samples of the marble by drilling is less visible places. Samples were examined with SEM, electron microprobe, X-ray diffraction, X-ray fluorescence, and mass spectrometry.

Marble is a metamorphic rock, created from limestone or dolomite by high temperature and pressure in the earth's crust. X-ray diffraction revealed that the kouros marble was almost pure dolomite, more durable and resistant to weathering than calcite marbles. This type of marble should preserve better than others. Marble is a carbonate mineral, composed of substantial amounts of both carbon and oxygen. The analysis of carbon and oxygen isotopes in such minerals can provide information on both their geographic origin and the nature of surface changes in the object

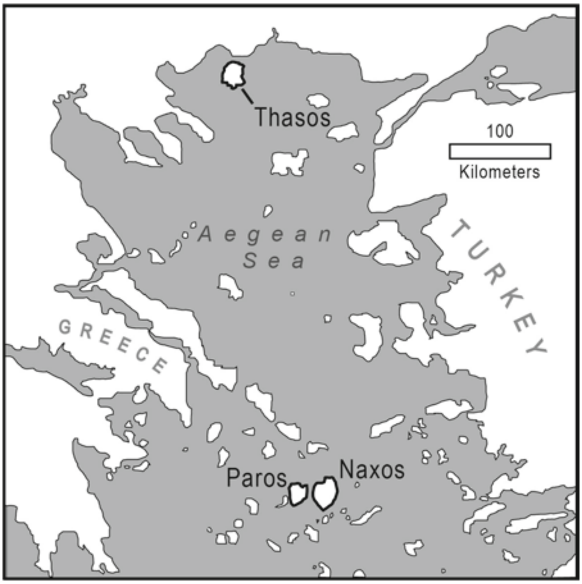

Fig. 5.12 The Aegean region and the "marble" islands of Paros, Naxos, and Thasos where much of the marble for Greek and later Roman statuary was quarried

of interest. Norman Herz, another geologist, measured these isotope ratios in the kouros and compared the values with known ratios for other quarries in the Aegean region (Fig. 5.12). These studies pointed to the island of Thasos, an ancient quarry site, as the source of the marble. Quarries for dolomitic marble were active during the period when the kouros should have been carved and similar statues are known from the island.

The scientists then looked more closely at the isotopic signatures of the marble quarries on the island of Thasos (Fig. 5.13). The ratios of carbon and oxygen isotopes were compared among the values for different quarries and three different sculptures, the Getty kouros, a torso from a known kouros forgery, and a marble head from a statue of Zeus, thought to be original. The isotope ratios in the head matched a specific quarry known to have been used in ancient times. The values from the fake torso match both ancient and modern quarries on the island. For the Getty kouros the ratios resemble several ancient quarries but generally do not fit the pattern for Thasian quarries in the south of the island. Perhaps the Getty kouros came from unknown quarry elsewhere on the island.

The geologists also took a careful look at the surface of the kouros. Patina refers to the distinctive changes that take place on the surface of many types of stone exposed to weathering and the elements for long periods of time. The Getty kouros has a tan/red patina on much of the surface and on the old breaks in the status as well. An optical microscope revealed that this patina was composed of iron oxide and soil and clay minerals. Both electron microprobe and X-ray diffraction determined that this patina was a continuous layer of calcite 10–15 μm in thickness.

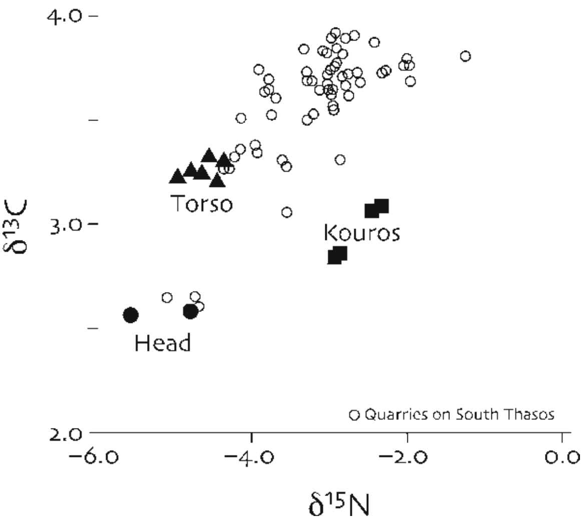

Fig. 5.13 Carbon and nitrogen isotope ratios in marble sources and statues from Greece. The information indicates that the torso and head of the known forgery come from two different quarries

Calcite forms on the surface of dolomite as calcium replaces the magnesium in the rock by weathering. The scientists argued that calcite crust that could have only developed over a long period of time.

Finally, the scientists compared both carbon and oxygen isotopes in both the calcite surface and the dolomite interior. These ratios were similar and also resembled the ratios measured in dolomite in nature. Thus, Margolis and his collaborators argued that the scientific evidence suggests that the marble of the status was dolomite from Thasos which would preserve very well, that the surface alteration of the statue (the patina) was compatible with what was known about weathering in dolomite, and that the formation of this patina must have taken a long time. The scientific investigation of the kouros produced a wealth of data, none of which indicated that the statue was a forgery. The Getty then purchased the *kouros* for a huge sum and it was put on display.

Then in the early 1990s evidence arose that the authenticating documents were forgeries. In addition, a fake marble torso very similar to the Getty *kouros* was found. New tests were done on the museum piece as well as the forged torso and the debate regarding the statue was invigorated. The torso was shown to have been treated in an acid bath to simulate aging. New analyses revealed that the surface of the Getty *kouros* was much more complex, not a simple calcite, but calcium oxalate monohydrate rather than calcium carbonate) with certain characteristics that could not be duplicated in the laboratory at that time. Furthermore, the Getty *kouros* and the torso had different surfaces. The new studies were not conclusive.

The story of the Getty *kouros* is a classic example of an archeometry in action, where art and science meet. There is no doubt that the Getty statue is a *kouros*. To most visitors, it is beautiful, it is art. The question is whether it is ancient art or a fake. While most art historians and archeologists believe the status is a forgery, the scientists involved believe it to be authentic. The status of the Getty *kouros* remains a mystery. The information sign with the statue at the museum today reads "Greek, 530 BC or modern forgery".

5.4.2 Vinland Map

Material: Parchment
Instrumentation: Radiocarbon dating, microscopy, micro-X-ray diffraction *(XRD), and scanning electron microscopy (SEM)/energy-dispersive X-ray analysis (EDX), Transmission electron microscopy (TEM),Particle-induced X-ray Emission Spectroscopy (PIXE), Raman microprobe spectroscopy*
Question: Is the map genuine or a clever fake?
Place: The map belongs to Yale University in Connecticut USA
Time Period: ad *1400–1500?*

Key Reference

J. Huston McCulloch. 2005. The Vinland Map – Some "Finer Points" of the Debate. http://www.econ.ohiostate.edu/jhm/arch/vinland/vinland.htm

The Vinland Map is purported to be a fifteenth-century document, drafted from even older maps of European origin, that shows land west of Greenland, i.e. the Americas, and includes a text claiming discovery by the Norse (Fig. 5.14). If genuine, the map proves that Europeans were aware of America before Columbus. The map, bound with a fifteenth-century document, called the Tartar Relation (TR), appeared in1957 when an anonymous library offered it for sale to the British Museum. Because it was of uncertain provenience and was mounted in a modern binding, the offer was declined. Shortly afterwards, however, another document, the Speculum Historiale (SH), was discovered, dating to 1440, of which the Vinland Map apparently had been a part. The SH has paper identical to that of the Vinland Map, matching watermarks, and even holes made by bookworms that are perfectly aligned with those in the Vinland Map.

The map was discovered in 1957 and, after years of covert authentication by the British Museum, it was purchased and announced to the world on Columbus Day, 1965.

A Viking village at L'Anse aux Meadows in Newfoundland, Canada, had been discovered in 1960. The village dated to approximately AD 1000, and proved that the Vikings were aware of lands west of Greenland 500 years before Columbus. But the Vinland Map could nonetheless still be forgery.

A microscopic analysis of the map's ink was made by a forensic specialist, who reported the presence of anatase, a modern pigment, on the maps lines and thus declared the map to be fake. Others noted, however, that other ancient artifacts contain anatase and that this pigment could have been generated by chemi-

Fig 5.14 The Vinland Map which appears to show the east coast of North America and which was purportedly drawn before the discovery by Columbus

cal processes not involving modern pigment production. A second study using particle-induced X-Ray emission (PIXIE), failed to find significant anatase in the ink. Another study by Raman infrared microprobe spectroscopy concluded there was significant anatase and that the particle-size characteristics are that of the modern pigment. The evidence regarding the anatase is not conclusive.

Another test of the map's authenticity involved radiocarbon dating of the parchment itself, using accelerator mass spectrometry (AMS). The development of AMS dating techniques in the 1980s made much smaller sample sizes possible – in this case about 50 mg. The AMS study provided a date of AD 1423–1445, along with evidence for some unknown surface treatment to the map at a later date, possibly in the 1950s. Critics pointed out that a modern forger could have used, or even reused, parchment from a fifteenth-century source, possibly blank pages from the manuscript that accompanied the map and thus the date of the parchment is not necessarily the same as the date when the map was drawn.

Although quite a number of the map's details have been debated as evidence both for authenticity and forgery, the presence of modern anatase pigment is recognized as the "smoking-gun" argument for forgery. Nonetheless, there are still many scholars who find the evidence on both sides to be equivocal.

5.4.3 Maya Crystal Skulls

Material: Mineral – Quartz
Instrumentation: Scanning electron microscopy, X-ray diffraction, Raman spectroscopy
Application: Authentication
Place: Mexico
Time Period: ad *1200–1500 ?*
Question: Are the large crystal skulls in the Smithsonian and British Museum of authentic Maya origin or are they forgeries?

Key Reference

Sax, M., J.M. Walsh, I.C. Freestone, A.H. Rankin, and N.D. Meeks. 2008. The origins of two purportedly pre-Columbian Mexican crystal skulls. *Journal of Archaeological Science* 35: 2751–2760.

At the end of the nineteenth century, George Frederick Kunz, Vice-President of Tiffanys, approached the British museum with an offer to purchase an extraordinary, approximately life-sized skull carved from a crystal of pure quartz (Fig. 5.15). Kunz argued that the skull was believed to be from Mexico and of ancient origin. However, the lack of a source for such crystals in Mexico led to suspicions of a more modern origin. In the 1940s a geologist, Ernest Brown, opinioned that the large, clear crystal of quartz from which the skull was made probably came from eastern Brazil, where such large crystals are common, although there are no known

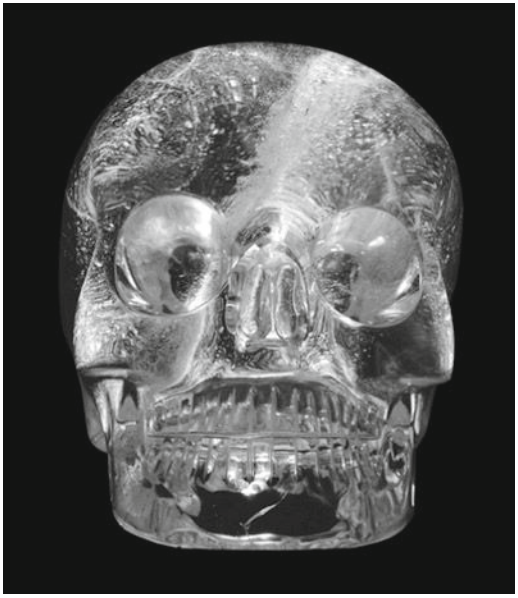

Fig. 5.15 One of the carved crystal skulls that was claimed to be from ancient Mexico

connections between the peoples of ancient Mexico and Brazil. In 1960, the museum undertook a study with an optical microscope and thought they could see evidence of cuts from a rotary disc blade, a tool not known in ancient Mexico. In 1990, the museum published evidence for and against the authenticity of the skull and concluded that it remained an open question.

Since that time several other similar skulls have made their way into other famous museums, including Paris’s Musée du Quai Branly and the Smithsonian. Although they were likewise attributed to origins in ancient Mexico, this was anecdotal; none were from documented archaeological contexts. At least four of these skulls, however, were traced to the same dealer of Mexican antiquities, Eugéne Boban. Considering that no Mesoamerican archaeological investigations over the past century have ever documented discovery of such a skull from any archaeological context, questions arose anew of whether they should be displayed as ancient artifacts. The museums decided it was important to answer the question of authenticity and began a more comprehensive analysis of the skulls in the British Museum and the Smithsonian.

To address the issue of whether or not rotary discs were used to cut the skulls, museum scientists decided to use scanning electron microscopy to provide much higher resolution of the grooves in the crystal. Because the skulls are far too large to place in the SEM and cutting sections from the skulls would be too destructive to be considered, another approach was necessary. They had recently developed a technique, now commonly employed by those studying ancient bead technology, in which a flexible silicone mold is made of the cut surface. The molding material accurately preserves, in relief and at a microscopic scale, the groves and other surface markings. The material is also flexible enough that it can be removed from holes in the artifact and placed in the SEM.

They also examined a large number of authentic cut crystal and hard-stone artifacts from documented Olmec, Maya, Aztec, and Mixtec contexts for comparative purposes. The SEM results showed for the British Museum skull unambiguous evidence of high-speed rotary disc cutting and the use of extremely hard abrasives. Although diamond and corundum are two naturally occurring abrasives of adequate hardness, they were not in use in ancient Mesoamerica and the authentic artifacts showed no such SEM evidence.

Examination of the Smithsonian skull similarly showed marks produced by high-speed rotary cutting and also retained trace amounts of the abrasive material. Although only traces were found, this was nonetheless enough to perform an X-ray diffraction analysis and identify it as silicon carbide, a synthetic abrasive invented at the end of the nineteenth century.

Although these studies suffice to demonstrate the both skulls are modern forgeries, museum researchers also noticed microscopic mineral inclusions in the clear British Museum skull. They analyzed these inclusions microscopically, then with Raman infrared spectroscopy, to determine they are chlorite. Chlorite is a micaceous mineral indicative of a specific "greenschist" grade of metamorphism that is consistent with a Brazilian origin of the quartz, but not consistent with a Mexican origin.

The research team also accessed the archives of the Smithsonian, the British Museum, the Bibliotheque National and the Musée de l'Homme in Paris and the Hispanic Society of America, New York, in which they could document that the Museo Nacional de Mexico had rejected as a fake the skull later acquired by the British Museum and Boban left Mexico after being denounced by Leopoldo Batres, the official Mexican protector of prehispanic monuments. The Smithsonian Institution had likewise been warned about Boban by a mineralogist, Wilson Blake, who said Boban bought the skull in Europe.

5.4.4 The Shroud of Turin

Material: Linen Cloth
Instrumentation: AMS – Accelerator Mass Spectrometry Radiocarbon Dating
Application: Authentication
Place: Italy
Time Period: ad *0?*
Question: Does the Shroud of Turin date from the approximate time of the death of Jesus Christ?

Key References

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Van Biema, David. Science and the Shroud. *Time Magazine*, April 20, 1998.

The Shroud of Turin is a religious relic that many people believe was used to wrap the body of Christ. The linen shroud bears detailed front and back images of a bearded man who appears to have suffered whipping and crucifixion (Fig. 5.16). It was first displayed in France in the fourteenth century AD and eventually came to Turin where it was housed in the Cathedral there in 1694. Every 20 years or so the shroud is put on display. At the last showing in 1998, some three million people viewed the linen cloth.

The shroud has been examined for authenticity on a number of occasions. Traditional radiocarbon dating could not be used because a large sample of the cloth would have been destroyed. With the advent of AMS dating, however, three laboratories at Arizona, Oxford, and Zurich were invited in 1987 by the Archbishop of Turin to date samples of the shroud. A small strip of cloth was removed from one side and divided into three postage stamp-size pieces. One piece of the shroud, along with three control samples of different dates, was given to each lab. At two of the laboratories the scientists did not know which of the four carbon samples came from the shroud itself.

The control samples were pieces of ancient cloth of known date to be used to validate the results from the different labs. One of the control samples was a piece of linen from a tomb in Nubia. Islamic embroidery and Christian inscriptions on the cloth suggested a date in the eleventh or twelfth century AD. A second control sample was taken from the linen wrappings of the mummy of Cleopatra in the British Museum. This cloth had been dated using tradition radiocarbon methods between 110 BC and AD 75, around the time of the birth of Christ. The third control

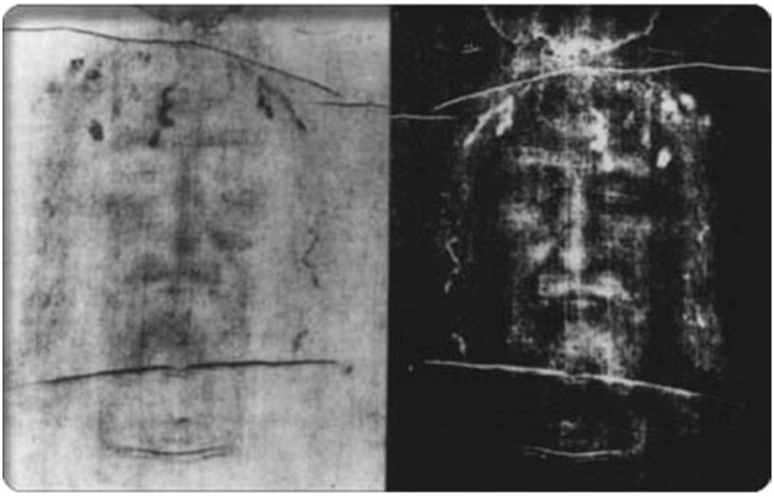

Fig. 5.16 The face from the Shroud of Turin. The linen cloth of the shroud is believed by some to have recorded an image of the body of Jesus. The head region is thought to show bloodstains resulting from a crown of thorns

sample consisted of threads removed from a cloak of a French saint who lived during the reign of King Phillipe IV, AD 1290–1310.

At the three laboratories, samples were cleaned and treated following standard procedures to remove contaminants. The cloth samples were then combusted to gas and their radiocarbon content was measured in an Accelerator Mass Spectrometer. The almost identical AMS measurements at the three laboratories provided a calendar age range of AD 1260–1390 with at least 95% confidence (Fig. 5.17). The results from the three control samples agree with previous radiocarbon measurements and/or historical dates. The AMS dating provides conclusive evidence that the linen of the Shroud of Turin is medieval.

Of course whenever science and religion meet, there are controversies. That is certainly the case with the Shroud. A heated debate continues today. One of the scientists, perhaps in exasperation, declared that anyone who believed the shroud was genuine was a "flat-earther." The shroud supporters raised hundreds of questions about the validity of the AMS results, claiming that burned cloth was dated, that there was varnish on the cloth, that the samples came from later repairs to the shroud, that mold growing on the cloth produced a younger date, among many others. Scientists pointed out that any contaminants would have had to be present in amounts three times the weight of the sample to cause such an error.

The AMS dating of the shroud appears reliable, but at the same time that it is clear that no matter what evidence is brought to bear, true believers will continue to venerate this cloth and not question its authenticity. Questions and debate continue for now because the church has recalled all samples and no additional tests are planned.

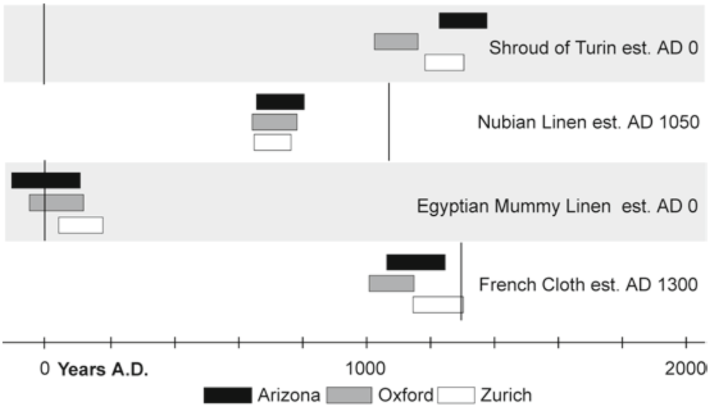

Fig. 5.17 Average radiocarbon dates with ±1 standard deviation for the Shroud of Turin and three control samples. The vertical lines mark the estimated ages of the samples. The age of the shroud is AD 1260–1390, with at least 95% confidence

Suggested Readings

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Courty, Marie-Agnes Paul Goldberg, and Richard Macphail. 1990. *Soils and Micromorphology in Archaeology.* Cambridge University Press.

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Chapter 6
Technology, Function, and Human Activity

Contents

This chapter combines three major areas of investigation in archaeological chemistry – technology, function, and human activity. Technology refers to the means that humans use to obtain resources and modify the world around them. Function, related to technology, refers to how tools, equipment, and facilities were used by humans in the past. Human activity is a generic term for the study of the function and use of space. What did humans do in the places they lived, gathered food, and worked? What was the function of the spaces that humans utilized in the past? These three related areas of investigation are discussed individually in more detail in the following pages of this chapter.

A series of case studies are used to illustrate the study of technology, function, and past human activity. These studies include a variety of microscopic and instrumental methods to look at a number of different kinds of material. The discovery of the early use of fire has involved both archaeological chemistry and distribution studies of specific artifact types to try and document that humans used and controlled fire more than 500,000 years ago.

T.D. Price and J.H. Burton, *An Introduction to Archaeological Chemistry*,
DOI 10.1007/978-1-4419-6376-5_6, © Springer Science+Business Media, LLC 2011

6.1 Technology

Technology is the interface between humans and the environment. Technology includes the tools, facilities, and knowledge used to obtain or create the resources needed for human existence. It is also the aspect of past culture that is most readily observed in archaeological data. Many of the artifacts that survive in the ground are related to technology. The fragments of the tools and architecture that people used in the past, made of durable materials such as stone, ceramic, and metal, are the most common archaeological remains. Technology also involves aspects of making, using, and recycling materials.

In archaeological chemistry, the study of technology takes several directions. The investigation of technology itself, how things were created or manufactured, is an important area. Information on the materials that were used, the temperatures, conditions, and methods of production can tell us about the capabilities of society and the evolution of technology.

Ceramics provide a good example of the application of archaeological chemistry to the study of technology. In its simplest form, pottery is made of clay. The type of clay used determines the quality of the ceramic that is produced. Types of clay can be identified using techniques like X-ray diffraction described in Chap. 6, Instruments. Temper is often mixed with raw clay to produce an improved material for firing. The material used for temper (sand, fine gravel, shell, bone, or other materials) can be identified using a binocular microscope.

Using fire to harden, or vitrify, pottery clay requires high temperature. The specific temperature depends on the type of clay being used. In general, better quality pottery requires higher firing temperatures. Moreover, different clays require different firing temperatures. Firing temperatures are determined by types of fuel and the conditions of the fire or kiln. The temperature required to fire different kinds of prehistoric pottery can be determined in the laboratory.

Typical prehistoric pottery, called earthenware, requires temperatures between 900 and 1,200°C (1,650–2,200°F) to vitrify. Fine porcelain pottery made from kaolin clay is fired at 1,280–1,350°C (2,300–2,400°F); it is white and often translucent. A modern kitchen stove will produce temperatures ca. 260°C (500°F). An open wood fire produces temperatures in the range of 800–900°C (1,450–1,650°F). Closed kilns, a kind of oven, can reach temperatures of 1,000°C (1,830°F) or more. Table 6.1 provides some information on firing temperatures, kiln conditions, and the type of ceramic produced. The conditions of firing determine the color of the pottery that is produced.

Pottery in a closed kiln is fired in a reducing atmosphere, lacking oxygen. Vessels fired in an open-air hearth are oxidized. Oxidizing atmospheres produce pottery with dark, black cores, while reducing atmospheres produce ceramics with lighter, reddish interiors.

Table 6.1 What happens as clays and glazes are fired

Temp. (°C)	Color in Kiln	Events
100		Water boils
100–200		Typical kitchen oven baking temperature
374		"Critical" temperature of water. Chemically combined water leaves clay
500	Red	
573		"Quartz inversion" A relatively sudden change in the clay causes quick expansion. Slow, Careful Firing Until 600°C
800		All organic matter in clay burns out by this temperature
800–1,000	Orange	Low-fire earthenwares and low-fire lead glazes mature. Normal firing temperature for red bricks, flower pots
1,000–1,160	Yellow	High-fire earthenwares mature. Feldspars begin to melt
1,170–1,190	Bright yellow-white	Mid-range clays and low-fire stonewares mature. High iron-content clays begin to melt
1,250–1,285	White	Stoneware clays vitrify, feldspathic glazes mature
1,285–1,350		High-fire stonewares, porcelains vitrify
		Most studio pottery is fired at 1350° or lower

6.1.1 The Discovery of Fire

Material: Clay lumps, stone tools, wood, and seeds
Instrumentation: SEM, magnetometer
Analysis: Technology
Place: Africa, Israel
Time Period: Lower Paleolithic, ca. 800,000 years ago
Questions: What is the earliest evidence for the intentional use of fire?

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Gowlett, J.A.J., J.W.K. Harris, D. Walton, and B.A. Wood. 1981. Early archaeological sites, hominid remains and traces of fire from Chesowanja, Kenya. *Nature* 294: 125–129.

Fire is an essential ingredient in many human endeavors. Fire provides heat, light, protection against predators, and a means for cooking. Cooking provides a number of advantages in addition to making food more tender and palatable. Cooking improves the digestibility of many foods and destroys harmful toxins and microorganisms. Boiling removes juices and fats from plants and animals that are otherwise inedible. For our early human ancestors, cooking probably made it possible to add many new foods to the diet. The controlled maintenance and use of fire also represents a sophisticated achievement by early human groups.

Fire was used for many technological advances in the course of human prehistory to produce pottery, metals, and many other kinds of materials and equipment. Fire is a basic part of being human. For these reasons, the origin of fire is one of those fundamental questions in archaeology and, like many fundamental questions, it is a difficult one. Identifying the earliest use of fire is a major scientific challenge. Fires frequently occur by accident in nature and demonstrating that humans controlled and used fire in the very distant past is complex. There are obvious fireplaces and even clay ovens from the Upper Paleolithic after 40,000 years ago. As well there are deep beds of ash and charcoal from the Middle Paleolithic, dating back to perhaps 250,000 years ago. But before that date, during the Lower Paleolithic, the evidence for the use of fire is scanty and vague.

A number of sites have been proposed as candidates for the evidence for the earliest use of fire, but there are problems with many of them. In the early 1980s evidence of fire from the site of Chesowanja in Kenya was proposed an early association of hominins and fire, ca. 1.4 million years ago. Along with an early human skull fragment and stone tools were found a number of small lumps of burned clay that exhibited a distinctive magnetism that was likely produced by heating. Although these lumps were not found outside the area of the site, there is still the strong possibility that they were produced by bush fires, lightening strikes, or even volcanic activity rather than human causes. This evidence has generally been disregarded.

A second example comes from South Africa. The cave of Swartkrans has layers with the remains of our human ancestors and many other animals going back two million years or more. C.K. Brain and Andrew Sillen examined almost 60,000 fragments of bone from the cave deposits and found some 270 burned pieces. These burned bones came largely from a layer dating to approximately one million years before the present. The primary evidence for burning came from measurement of the percent of carbon, hydrogen, and nitrogen in the burned bones. These elements are measured in a CHN Analyzer which uses a combustion process to determine the percentages of each element. The *C/N* ratio (carbon to nitrogen) was elevated in the burned bones, similar to modern examples experimentally reproduced in campfires. While the evidence from Swartkrans is intriguing, it impossible to demonstrate that natural fires did not burn through the accumulated brush and debris that must have filled these cave openings at various times in the past.

More convincing evidence comes from Gesher Benot Ya'Aqov in Israel where several lines of evidence point to the intentional use of fire beginning around 800,000 years ago. This open-air site lies in a geologically active zone where folding and faulting of ancient geological layers are common events. The horizontal surfaces on which the ancient people of Gesher Benot Ya'Aqov lived have since been tilted to an angle of almost 45° (Fig. 6.1). The deposits at the site are waterlogged so there

Fig. 6.1 The deposits at Gesher Benot Ya'Aqov in Israel have been folded by geological forces and today lie at an almost 45° angle from the horizontal. Here excavations are in progress exposing the living surfaces at this 800,000-year-old site

is some preservation of botanical materials, including wood and bark. The evidence for burning comes from both archaeological and botanical remains.

The archaeological evidence is in the form of burned pieces of flint, the raw material for making stone tools. Pieces large and small exhibit characteristics of burning including changes in color and breakage induced by temperatures of around 350–500°C. The burned flint was found concentrated in several small areas of the site, suggesting the presence of distinct fire areas (Fig. 6.2). Such a pattern would not be expected if the burning was natural.

Seeds of fruits and small pieces of wood were found throughout the excavated area and a small proportion, about 5%, had been burned. SEM observations documented the species and burning of these specimens. Several types of wood were burned there, including willow, poplar, ash, and wild olive. The excavators of the site make a convincing argument that the clustered distribution of the burned flint and the presence of burned wood and seeds argue for the presence of several fireplaces at Gesher Benot Ya'Aqov.

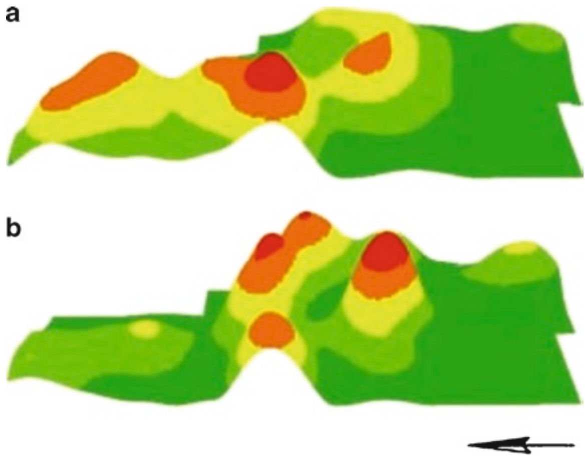

Fig. 6.2 A raised isobar map of one of the occupation layers at Gesher Benot Ya'Aqov. (**a**) Shows the distribution of all flint in the layer; (**b**) shows the distribution of burned flint in the layer. The differential distribution of the burned flint in small concentrations argues for the presence of fireplaces at the site

6.1.2 Maya Blue

Material: Pigment
Instrumentation: GC/MS
Application: Identification/Technology
Place: Yucatan, Mexico
Time Period: Maya, AD *300–1500*
Question: How did the ancient Maya produce the pigment known as Maya Blue?

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The Maya of Central America achieved a remarkable civilization beginning around 2,000 years ago. The heartland of this society lay in what is today an enormous and almost unexplored rainforest covering the northern half of Guatemala, Belize, and the southern Yucatan peninsula of Mexico. Sophisticated architecture, engineering, mathematics, astronomy, calendars, writing, trade, art, and statecraft were among their many achievements of the Maya. A comparable level of technology was required to make these achievements possible.

Among many technological marvels from that era is a pigment known as Maya Blue. This startling, turquoise-like color was used extensively by the Maya for many purposes (Fig. 6.3). The Maya used the pigment for paint that was applied to sculpture, wall murals and pottery, among other objects. They also used the pigment to color the bodies of sacrificial victims before they were thrown into sacred wells or had their hearts cut out at temple altars.

The pigment is a mixture of organic and inorganic compounds bonded by hydrogen that, in addition to its spectacular color, has an exceptional durability. The color still remains on a variety of Maya artifacts and architecture. It is resistant to natural acids, alkalis, solvents, heat, and vegetation. Maya blue is resistant to color loss after centuries in the tropical rainforest of the Maya heartland.

Maya Blue is the result of a combination the organic material indigo and clay mineral palygorskite. Indigo is present in many plant species, but concentrated in relatively few. In Central America, the two species *Indigofera suffructicosa* and *Indigofera arrecta* are the most important native dye bearing plants of the genus. The indigo is taken from the leaves of a flowering tropical shrub known as *añil (Indigofera suffructicosa)*. Palygorskite is an unusual clay with long interior channels. One of the principal constituents of kaopectate, this clay mineral was also used by the Maya as a curative for certain illnesses. A source for palygor-

Fig. 6.3 Maya mural painting depicting a ball player against a background of Maya Blue

skite in the Maya region was unknown until the 1960s, when two *sinkholes* were identified as quarries near the town of Ticul, south of the modern city of Merida in the northwest quarter of the Yucatán Peninsula. But only in the last few years has the secret of its production come to light, a combination of good luck, science, and observation.

Experimental work trying to reproduce this pigment has demonstrated that sustained low heat (ca. 150°C) is necessary to create the pigment, fix the color, and create its stability and durability. These experiments have also shown that very little indigo is necessary to make Maya Blue, less than 2%. A third element in the creation of Maya Blue appears to be copal, a hardened sap or resin from certain trees in the tropical rainforest. Copal was used in the past, and continues to be used today, as incense in Maya ceremonies and religious activities. Copal is burned to give off copious amounts of smoke and a distinctive aroma. It is likely that Maya Blue was produced by burning copal, indigo, and palygorskite together. The question remained, however, about how this production took place, on a large scale at regional manufacturing centers or more locally and small scale.

Dean E. Arnold has been pursuing the mystery of Maya Blue since he was a graduate student almost 40 years ago. In 2007, he was in the bowels of the Field Museum of Natural History in Chicago. The storerooms here hold treasures from the past including the finds from the archaeological dredging of the sacred cenote of the Maya site of Chichen Itza (Fig. 6.4). The Maya believed that these sinkholes were gateways to the underworld and sacrificed food, pottery, jewelry, and people to their gods by tossing them into the waters of the cenote. Many of these objects must have been covered in Maya Blue. In fact, the archaeologists working described more than 4 m of deposits at the bottom of the well with a distinctive blue color.

Archaeologists, recognizing these places as treasure houses of ancient objects and information, began excavating the contents more than 100 years ago. Divers and dredging equipment were used to bring up the sediments from the bottom of the cenote. These deposits contained an enormous number of offerings made at the sacred well, including copal incense, pottery, wood, gold rubber, jade, and leather, in addition to human sacrifices. In the storerooms of the Field Museum, Arnold came across a three-footed bowl from the cenote deposits (Fig. 6.5). The contents of the bowl were still intact, a melted mass of copal with white flecks of the clay mineral still visible on the bottom of the mass. Such pottery containers with a mass of blue color and copal incense were common in the deposits of the cenote.

Detailed study of the contents of the vessel provided new insight on the manufacture of Maya Blue. An SEM revealed the presence of both indigo and palygorskite, the two main ingredients of Maya Blue. Secondary electron and backscattered electron images of white, needle-like particles in the material resembling the structure of palygorskite. Energy-dispersive X-ray analysis of the indigo component indicated its organic origin, in with indigo. The ancient Maya must have burned a mixture of the resin of copal, indigo, and palygorskite clay to produce the distinctive Maya blue.

Fig. 6.4 The limestone sinkhole, or cenote, at the Maya site of Chichen Itza where thick layers of Maya Blue pigment were found in the bottom. The pyramid known as El Castillo and the center of the site can be seen in the background

Fig. 6.5 A Maya pottery vessel with resin heated to high temperature to produce the Maya Blue pigment

6.2 Function

Function is another important area of study in archaeology and archaeological chemistry. Function refers to how tools, equipment, and facilities were used. In order to understand what people did in the past, it is essential to understand the purpose of their tools, facilities, and architecture. That can be a tall order when so much time has passed. There are no modern analogs for many of the tools and technologies of the past. In many cases it is necessary to investigate ancient artifacts and structures in order to determine how they were used. It's not an easy job.

The dictionary definition of function refers to the action for which a thing is specially fitted or used or for which a thing exists. Function is the purpose for which an artifact or facility is intended. Determination of ancient and unknown objects is problematic, if not impossible in some cases. It is often difficult to know the function of many objects in our modern society. The artifact utensil in Fig. 6.6 has a very specific purpose. Do you know what it is? (Answer at the end of this section.) Now imagine that it has decomposed and survives only as a small fragment.

An example from the Upper Paleolithic in France illustrates the difficulty of identifying function for many prehistoric objects. This so-called baton de commandant (Fig. 6.7) is approximately 25,000 years old, 25 cm long, and its intended use is completely unknown.

Case studies of functional investigations in archaeological chemistry described here include two of the most common classes of archaeological remains – the microscopic analysis of early stone tools and the application of organic chemistry to determine what pottery was used for by hunter-gatherers in prehistoric Denmark. There are many other studies, not discussed here, regarding the use of prehistoric artifacts and structures to be found in the archaeological literature.

The modern artifact shown in Fig. 6.6 is a pepper grinder.

Fig. 6.6 A modern steel and plastic artifact

Fig. 6.7 A baton de commandant: of reindeer antler from the Upper Paleolithic period in France

6.2.1 Microwear Analysis

Material: Stone Tools
Instrumentation: Binocular Microscope
Analysis: Function
Place: East Africa
Time Period: 1.5 million years ago
Questions: How were Paleolithic stone tools used? What materials were they applied to? How important were plants to these early human ancestors?

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One of the primary questions about prehistoric stone tools concerns how they were used in the past. Archaeologists tend to name the things they find and many types of stone tools have been given names that imply a certain kind of function: handaxes, scrapers, arrowheads. But in fact the actual uses of most stone implements are unknown. The term handaxe comes from a French word implying that it was an axe held in the hand, but this hallmark of the Paleolithic was likely used for many purposes, a kind of Stone Age Swiss army. The point could be used for digging or gouging, the edges for cutting, the heavy butt end for chopping or hammering. Scrapers are usually somewhat heavy tools with a thick curved edge. The name implies that they were used for scraping; their use for cleaning animal hides is often assumed. In fact, however, these tools may have been used for a range of purposes in addition to scraping. Arrowhead is a generic name for pointed lithic artifacts but in fact many so-called arrowheads in North America were more likely mounted at the working end of darts and spears or used as knives. The bow and arrow arrive late in most of North America, sometime after the birth of Christ.

Because of these problems in understanding the function of stone tools, researchers have developed new methods for learning about how these implements were used. *Microwear analysis* involves the use of high-powered microscopes to study the magnified edges of stone tools (Fig. 6.8). The breakthrough in microwear studies

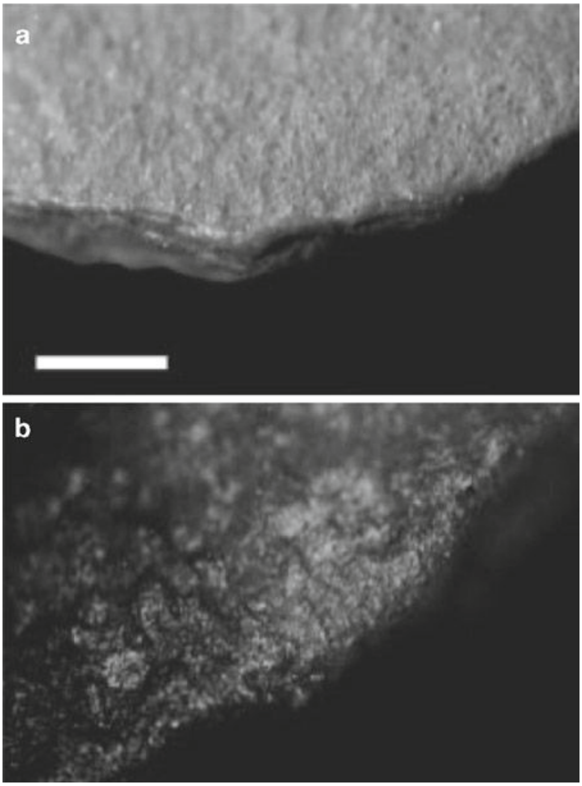

Fig. 6.8 Microwear analysis and curated tools from an Upper Paleolithic site in Austria. (**a**) Clear edge rounding under low magnification (30×). (**b**) Same location on edge at 200× showing rough polish and striations

came with the recognition of distinctive polishes on the edge of tools. Modern experimental studies, using stone tools on known materials like dry hide, meat, wood, and plant fibers, allowed researchers to characterize polishes specific to certain kinds of materials and activities.

"Blind" tests have been an important part of this research. The identification of polishes is difficult and learning to distinguish different varieties is time-consuming. Microwear analysts have followed a protocol in which they identify polishes on a series of samples they have not seen before. The origin of each polish is known to the person handling the samples, but not to the analyst. Researchers who can identify these polishes "blindly" demonstrate their knowledge and skill.

Microwear studies have provided important clues about the use of stone tools. Lawrence Keeley, of the University of Illinois-Chicago, used a high-powered microscope to examine the edges of stone artifacts from the 1.5-million-year-old site of Koobi Fora in East Africa. His experimental work had demonstrated that different materials left different kinds of traces in the form of polish on the edges of tools. At a magnification of 400×, Keeley observed microscopic polish and wear, indicating the cutting of meat, the slicing of soft plant material, and the scraping and sawing of wood, on about 10% of the flakes. Two of the flakes with evidence of meat butchering were found within 1 m (3 ft) of a large herbivore bone exhibiting cutmarks. Such an association supports the use of these stone artifacts as butchering tools. The evidence for woodworking suggests that wooden tools were also being made, perhaps crude digging sticks for finding roots and tubers. This indirect information is the only evidence that exists for the use or consumption of plant materials at this early time.

More recent investigations of microwear are incorporating sophisticated instrumentation including SEM and a variety of techniques for quantitatively identifying polish and wear on tool edges. Some specialists are working to identify the elemental chemistry of microwear in order to define the material being worked. Others are using new kinds of microscopes to quantify wear and polishes on tool edges in order to develop more systematic descriptions of wear.

Larry Kimball is employing an Atomic Force Microscope to study polish and wear on stone tools. The AFM uses the atomic forces between the scanning tip of the microscope and the microwear polish on the stone tool to produce a three-dimensional map of the surface of the polish (Fig. 6.9). This map is digital and can be quantified in terms of the roughness of the surface. Kimball calculated the roughness for both the peaks of the polish topography and the valleys and compared these results for different kinds of experimentally produced, known polishes (Fig. 6.10). As can be seen from the graph, roughness clearly varies between the peaks and the valleys with the valleys exhibiting less polish (more roughness). In this graph, the fresh flint surface is not measured but experimentally produced polishes from working antler, wood, dry hide, and meat are reported. Antler produces the most polish and wear on both the peaks and valley of the flint surface, while meat produces the least. Measuring roughness of polishes clearly provides a quantitative means to compare use wear on stone tools and other materials.

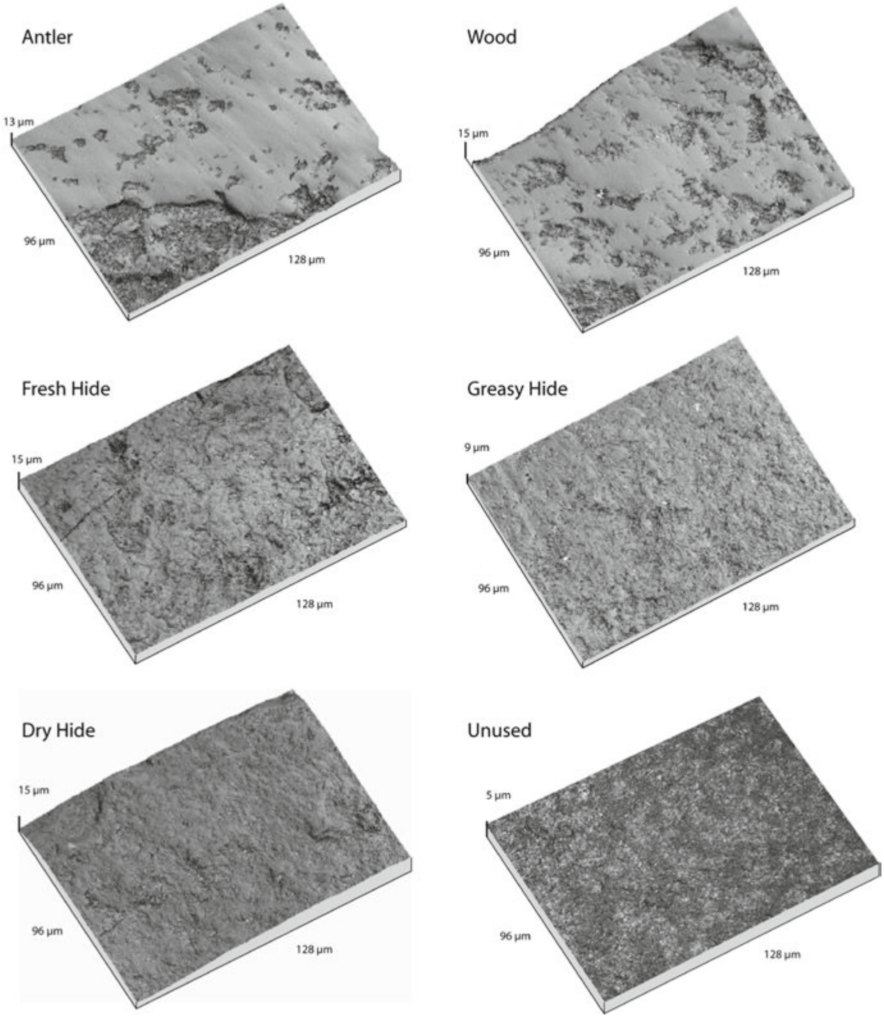

Fig. 6.9 AFM micrographs (100×) of five wear types and the fresh, unused surface of flint

6.2.2 Danish Pottery

Material: Ceramics
Instrumentation: GC/MS
Application: Function
Place: Denmark
Time Period: Mesolithic, 4500 BC
Question: How was this early Danish pottery used? What were the contents?

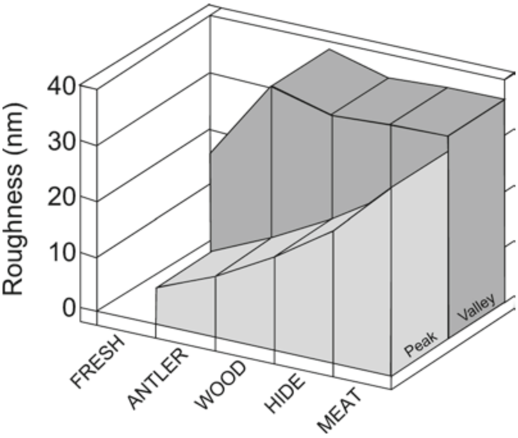

Fig. 6.10 A graph of the roughness of stone tool edges following use with antler, wood, dry hide, and meat. Roughness was measured in both the peaks and valleys of the surface. This roughness (less wear) is highest for meat use and lowest for antler

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Ceramics again provide a good example of how archaeological chemistry can help to determine the use of artifacts. Pottery was made and used in northern Europe more than 6,000 years ago before farming arrived in this area. One of the intriguing questions about these pottery vessels concerns their use and contents.

Tybrind Vig is a remarkable underwater archaeological site in Denmark, dating from the Stone Age, approximately 6,500 years ago. Although the inhabitants of this site were hunter-gatherers, they also made and used distinctive pointed-base pottery vessels for cooking and storage. Because of the quality of preservation at this underwater site, traces and residues from heating and cooking have been preserved on some of the pots. Soot or burn marks on the outside of a vessel are one indication of use for cooking. Other residues, known as food crusts, are the result of the burning and charring of food in and on the vessel. Figure 6.11 shows a synthesis of where traces of cooking appear on these vessels from Tybrind Vig, both on the inside and outside.

The heaviest traces are on the outer lip and neck, likely from boiling over during cooking. A second area of concentrated food residues is found on the inside bottom of the pot, where heavy charred remains can be observed (Fig. 6.12). In this food

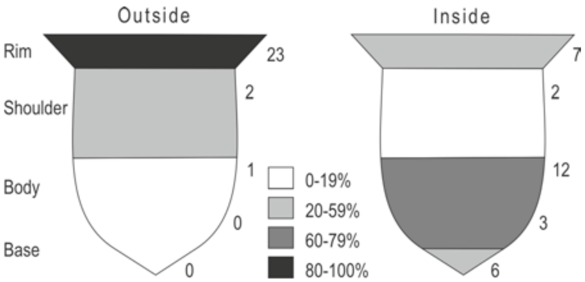

Fig. 6.11 Cooking traces and residues on the inside and outside of Mesolithic pottery from the site of Tybrind Vig, Denmark. The shaded areas show the concentration of food crusts inside and out

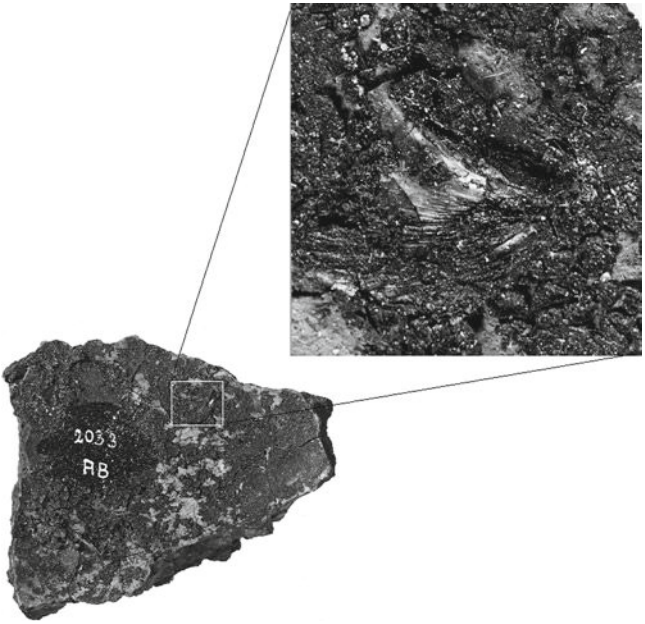

Fig. 6.12 A potsherd from the Mesolithic site of Tybrind Vig, Denmark, showing fish scales and seed impressions in the food crusts on the bottom of the pot. The enlargement shows a bone from cod embedded in the food crust. The potsherd is approximately 7 cm (3″) in diameter

crust on some of the vessels, there are visible traces of fish scales and small fish bones. Under a microscope thin, grass-like stalks of plants can also be seen.

Several radiocarbon (^{14}C) dates were made from the carbon in the food crusts in these vessels to obtain an age for the pottery of around 4500 BC. The radiocarbon laboratory also measured the stable carbon ($^{13}C/^{12}C$) and nitrogen ($^{15}N/^{14}N$) isotope ratios in the samples. These data (Fig. 6.13) suggested to the researchers that the charred contents of the vessels were largely from terrestrial, rather than marine, foods. This information contradicts the evidence from the cod bone and indicates

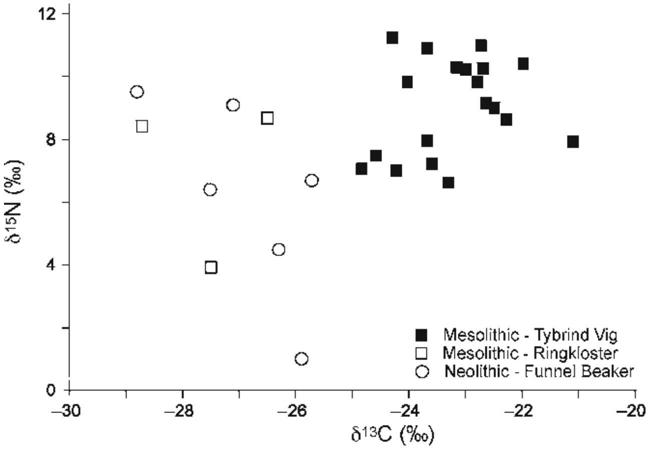

Fig. 6.13 Plot of carbon and nitrogen isotopes in pottery from Mesolithic (Tybrind Vig and Ringkloster) and Neolithic sites (Funnel Beaker). A distinct separation of these two groups is seen reflecting the more terrestrial diet of the Neolithic farmers. This pattern is also seen in the carbon and nitrogen isotope ratios in human bone collagen from the Mesolithic and Neolithic in this region

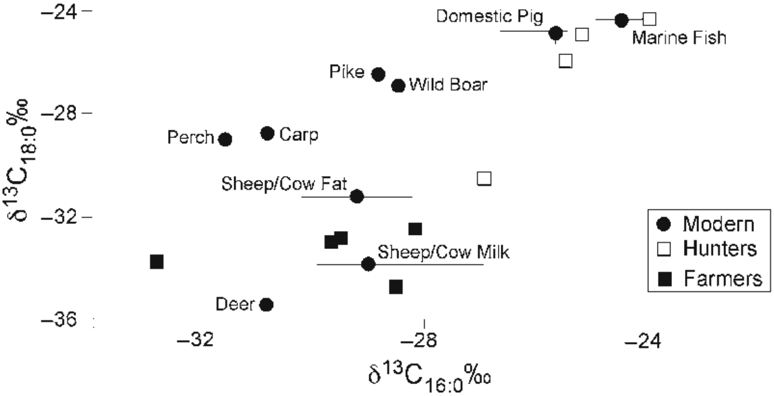

Fig. 6.14 A plot of $\delta^{13}C$ isotope ratios for two fatty acids (C16:0, C18:0) that are different for marine and most terrestrial animals. The *circles* are values from modern animals; the vertical and horizontal lines show the range of variation in the values. The *open squares* are potsherds from places where hunters lived 6,500 years ago; the black squares are potsherds from places where farmers lived 5,500 years ago in northern Europe. The hunters' pottery had more marine contents; the farmers' pottery had more terrestrial contents, perhaps including milk

that the pots were more for vegetables than fish. Nitrogen isotopes were also measured in the cooking residues and suggest somewhat more animal protein in the diet, compared to inland groups and early farmers in the area (Fig. 6.13).

More detailed study of the organic contents of the crusts and residues on these sherds has been done. Carbon isotopes were measured in specific fatty acid residues in the crusts to determine the origin of the foods. Figure 6.14 shows a plot of

$d^{13}C$ isotope ratios for two specific fatty acids (C16:0, C18:0) that are different in marine and most terrestrial animals. The black circles are values from modern animals; the vertical and horizontal lines show the range of variation in the values. The open squares are potsherds from places where hunters lived 6,500 years ago; the black squares are potsherds from places where farmers lived 5,500 years ago in northern Europe. In this study, the hunters' pottery shows more marine contents; the farmers' pottery has more terrestrial contents, perhaps including milk.

A few charred sherds provide a great deal of information on the use of prehistoric pottery. Examination of the pot contents at Tybrind Vig is continuing. A recent study of the cooking residues using GC/MS focused on the soluble lipids. Oliver Craig and his colleagues identified specific chemical markers among the lipids for marine and freshwater fish that can survive for long periods of time in charred residues. In addition, they remeasured the carbon and nitrogen isotope ratios in the food residue samples (Fig. 6.15). They argue that the combination of the biomarker lipids for aquatic species and the isotope data indicates that the pots at Tybrind Vig must have been used for cooking fish among other foods.

In regard to the Tybrind Vig pottery analysis, different studies appear to produce contradictory results. The radiocarbon investigations pointed to a terrestrial source for the carbon in the pottery; the organic chemistry indicates a marine and freshwater origin for the carbon. The physical evidence in the visible residues on the pottery itself contains both fish bone and terrestrial plant remains suggesting that foods from both land and water were cooked in the pots. It is also very important to remember that these ceramic vessels have a life of months or years and likely have many different things cooked or stored in them during that period.

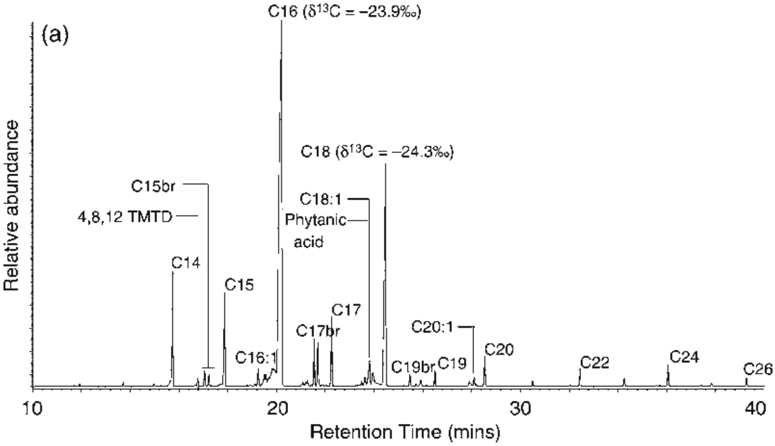

Fig. 6.15 Chromatogram of organic residue extraction from Tybrind Vig pottery. After about 20-min palmitic acid (C16) reaches the detector and is introduced to the isotope-ratio mass spectrometer, which measures a $\delta^{13}C$ of −23.9‰. Likewise, after 24 min, stearic acid (C18) reaches the detector, with a $\delta^{13}C$ of −24.3‰. By comparison to the data on Fig. 6.14, one can see this matches the $\delta^{13}C$ data for marine fish

6.3 Human Activity

The analysis of sediments is potentially one of the most informative aspects of archaeological chemistry. Soils may contain information on site extent, boundaries, activities, chronology, resource availability, agricultural fields, or past environments. One of the first applications of this kind involved the analysis of phosphate in soils. The Swede Olaf Arrhenius in 1929 first documented a correlation between soil phosphate and human activity and used that information to find buried prehistoric sites. Since that time, archaeologists and soil scientists have tried to find new ways to look into the earth with chemical analysis.

One relatively recent archaeometric application is the use of multielement and organic chemistry to determine past human activities. The focus is on living floors where people carried out various activities. Chemical analyses are being applied to dirt house floors, plazas, and floors of ceremonial buildings to determine what happened in the past at particular locations, to determine the uses of particular rooms and other spaces. While this might require a long and sometimes tenuous chain of inferences, archaeologists are actively studying both ancient and modern ethnographic contexts to develop rigorous methods of inference.

Samples from house floors are useful, for example, because they are typically carefully prepared prior to habitation and represent a more or less homogeneous baseline, or "tabla rasa," against which chemical variations due to human activity stand out. Organic and elemental residues in the activity area accumulate in the microscopic pores spaces in the floor and adsorbed onto submicron soil particles, while other areas remain chemically unaltered by the activity. Some chemical patterns are fairly easy to interpret – for example, a midden in which bone debris accumulates will be high in calcium and phosphorous in contrast to regular soil elements such as iron and aluminum. An area of shell working would likewise have the high calcium but not the high phosphorous. Wood ash leaves high levels of potassium (originally derived from "pot ash"), which reveals the presence of long-extinct hearths. Organic chemical analyses reveal accumulations of waxes, fats, oils, and even ancient fecal matter that would otherwise be invisible in the archaeological record. For example, an abundance of certain stanols, a class of organic chemicals produced in the guts of animals, has been used to delineate animal pens.

William Middleton, while working in the Laboratory for Archaeological Chemistry, developed a method that excludes insoluble silicates while being more responsive to anthropogenic inputs of relatively soluble elements. This has been applied to sediments from contexts in the USA, Guatemala, Mexico, Turkey, and elsewhere. These studies include ethnographic studies of modern house floors and blind test against complementary data from chemistry and micromorphology (e.g., pH, carbonate, microdebitage) as well as archaeological contexts. For example, Middleton worked at Building Five at Çatalhöyük, a Neolithic (ca. 7500–6500 BC) residential structure that had been deliberately abandoned, and consequently had little in the way of artifactual information for the organization and use of space. Multielement analyses of floor samples reveal distinct compositional patterns than can be linked to compositional, ethnographic studies of modern house floors to identify specific activity areas. In Building Five, five kinds of activity areas were identified (Fig. 6.16); a general occupation area, a very low activity zone, an area characterized by food residues (emphasized by high sodium, shown here, reflecting both food spillage and storage), an ash scatter zone characteristic of domestic hearths, and finally a plastered surface. Building Five at Çatalhöyük therefore appears to be simply a domestic structure.

Trace-element analyses, while relatively inexpensive at tens of dollars per sample, quickly become prohibitively expensive when analyzing soil grids: a basic 10 × 10-m space produces more than a hundred samples if samples are taken on a 1-m grid. The number of samples and the costs expand exponentially as the space is increased or the sample unit is decreased. Half-meter sampling of the same 10 × 10-m grid would produce more than 400 samples! And organic analyses by GC/MS or LC/MS could be more expensive than the elemental analyses.

Luis Barba has recently proposed that inexpensive spot tests, which can be done in the field, can be used as an efficient proxy for the elemental and organic analyses. He demonstrated that patterns revealed by spot test measurements of pH, carbonate, phosphate, and organic materials correspond closely to those revealed by the more sophisticated analyses. Although the data from spot tests are difficult to interpret in terms of specific activities, they are quite helpful in selecting much smaller subsets of the original samples that can then by analyzed for elements and organic molecules.

To illustrate the investigation of past human activity, three examples are provided below: the discovery of a major Iron Age town in Sweden using phosphate analysis, the investigation of activities inside an Aztec temple discovered in the center of modern Mexico City, and the experimental study of elemental and organic chemistry of an earthen living floor in an experimental Iron Age house in modern Denmark.

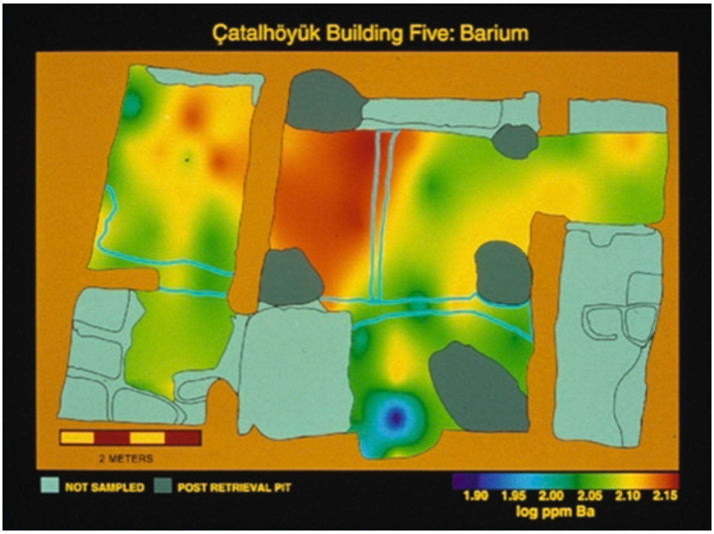

Fig. 6.16 Barium distribution in a Catalhoyuk house floor which reflects deposition of food remains (Middleton and Price 2002; Middleton et al. 2005)

6.3.1 Phosphate and Uppåkra

Material: Soil Samples
Instrumentation: Field Tests
Application: Phosphate Analysis
Place: Sweden
Time Period: Late Iron Age, AD *200–1000*
Question: Where are the highest concentrations of phosphate in the landscape of southwestern Sweden?

Key Reference

Hårdh, B. & Larsson, L. Uppåkra – Lund före Lund. 2007. Föreningen Gamla Lund.

The modern city of Lund, Sweden, is a thriving university town today, with a population of around 100,000 inhabitants, of whom more than 25,000 are students. The university was founded in 1666.The town itself is older and has been an important center for many years as the religious seat of the bishop and home of the regional cathedral. Lund was founded around 990 by the Danish King Canute I as a royal town complete with a royal compound and a mint. The bishopric was founded in 1060 and cathedral was built in Lund sometime before 1085. That's a long, deep history. But archaeologists want to know what was here before the town of Lund. Were their earlier towns or only villages? Has this area been important for a longer period of time? What was the region like in earlier times?

Archaeological interest in a place called Uppåkra began in the 1930s with two important events. Construction of a farm building at the site uncovered skeletons, pottery, and 2 m of archaeological deposits, dating to around AD 400 during the Iron Age. In that same decade, the local sugar beet industry made maps of the phosphate content of the soils across much of southern Sweden to find the best agricultural fields. The phosphate tests were done using a simple colorimetric chemical reaction. Darker blue colors in the reaction indicated higher amounts of phosphate in the soil. Olaf Arrhenius was employed in this soil survey. More than 500,000 soil samples from 500,000 hectares of land were tested. When the results were plotted on maps, Arrhenius observed that high concentrations of phosphate corresponded to areas of human settlement. Urine and plant and animal tissues, especially bone, contain large amounts of phosphate and enrich the soils at places where people have lived. It was even possible to trace old paths.

The area around Uppåkra had the highest levels of phosphate in the entire province (Fig. 6.17). Clearly this was a place of archaeological significance and roadways using this technique.

Further work was planned to investigate the significance of the high phosphate concentrations. It was not until 1996, however, that sufficient interest, energy, and money was available to begin investigations at Uppåkra. Soil boring, phosphate testing, and metal detectors were used to investigate the site before excavations were begun (Fig. 6.18). More than 20,000 metal artifacts have been found, far exceeding any known Iron Age site.

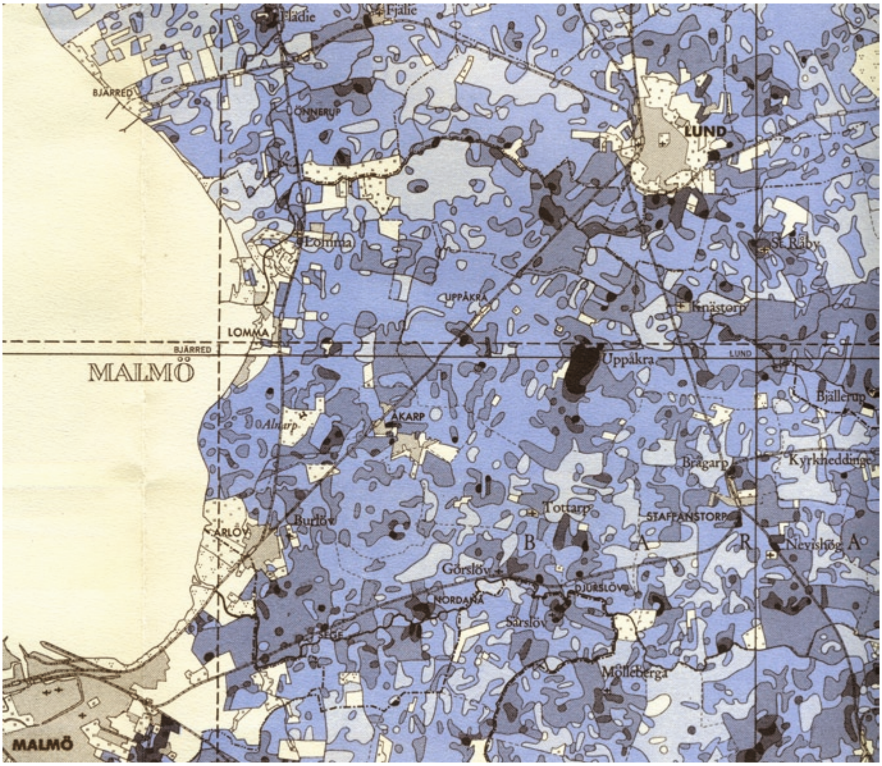

Fig. 6.17 A map of the location of Lund and Uppåkra in southwest Sweden showing the regional distribution of phosphate. The darker the color, the more phosphate is present in the soil. The site of Uppåkra shows up very distinctly in the center of the map. The map covers an area of approximately 15 km^2

Excavations were conducted near the center of the site, the area where the rulers were thought to have lived. Several buildings of various sizes were founds and included houses and larger halls (Fig. 6.19). The most interesting structure was one of the smallest, only 13×6.5 m. The construction used for this building was very massive with huge posts at the corners and down the center. The best explanation is that this was a tall building, perhaps several stories high. It would have been visible from long distance in the relatively flat landscape of southwestern Sweden. This structure was constructed in AD 200 rebuilt several times, and finally razed during the Viking Age, probably in the ninth century AD, shortly before the founding of Lund. Because of the construction and the unusual finds in and around this building it has been described as a cult house, or pagan shrine, used for special purposes at Uppåkra.

Uppåkra was clearly a major focus of population and power prior in the first millennium AD. The first traces of settlement date to the first century BC and only a few centuries later, Uppåkra was southern Sweden's largest community. By AD 400, it was an urban settlement with up to 1,000 inhabitants. The settlement contained

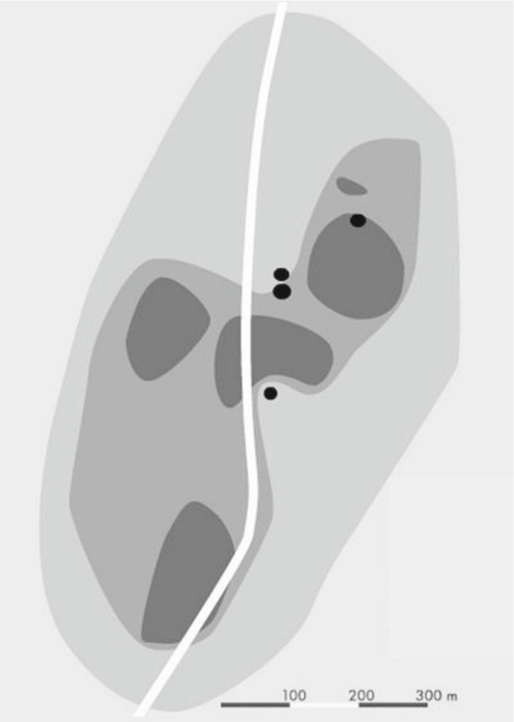

Fig. 6.18 The site of Uppåkra, 1,100 × 600 m. The white line through the center of the site marks a prehistoric road. The small dark circles are burial mounds. The site itself is shown by the shading; darker areas have higher concentrations of phosphate and artifacts and mark denser human occupation

30–40 farmsteads of various sizes, with dwellings, workshops, storage buildings and barns, in addition to the royal compound. Christianity arrived in Scandinavia after AD 1000 and Canute ignored the pagan center and cult house at Uppåkra when he founded Lund and placed the cathedral there.

6.3.2 Ritual Activities in the Templo Mayor (Mexico)

Material: Soil
Instrumentation: ICP spectroscopy, GC–MS, spot tests
Application: Human Activity
Place: House of the Eagle Warriors/Templo Mayor (Mexico City)
Time Period: Aztec, AD 1200–1500
Questions: Is it possible to identify chemical enrichment patterns on floor surfaces that reveal the function of archaeological spaces? Can the ritual activities depicted in the ancient codices be identified?

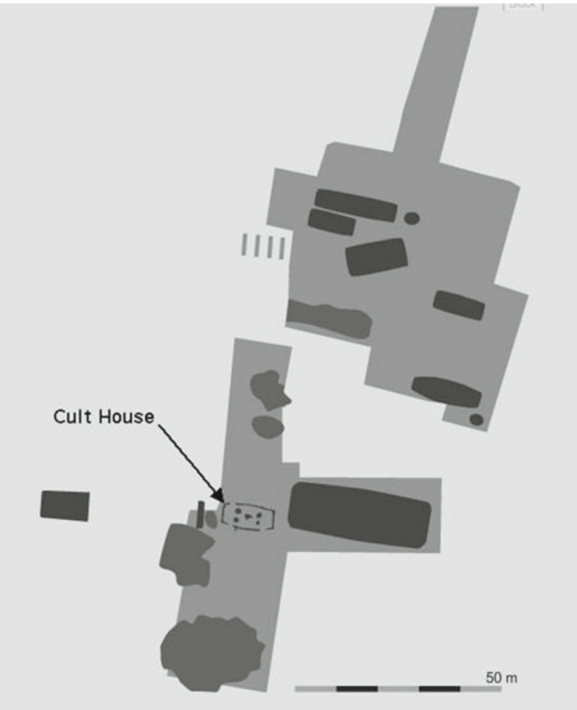

Fig. 6.19 Archaeological excavations in the eastern central portion of the site of Uppåkra. The darker rectangles mark prehistoric houses and halls; the dark gray areas are pavements and weapons sacrifices; the lighter gray rectilinear areas mark the boundaries of excavation. The location of the cult house is shown

Key References

Middleton, William D., Luis Barba, Alessandra Pecci, James H. Burton, Agustin Ortiz, LauraSalvini, Roberto Rodriguez Suárez. 2010. The Study of Archaeological Floors: Methodological proposal for the Analysis of Anthropogenic Residues by Spot Tests, ICP-OES and GC–MS. *Journal of Archaeological Method and Theory* 17:183–208.

Barba, Luis A., A. Ortiz, K.F. Link, L. López Lujan, and L. Lazos. 1996. The Chemical Analysis of Residues in Floors and the Reconstruction of Ritual Activities at the Templo Mayor, Mexico. In Archaeological Chemistry: Organic, Inorganic and Biochemical Analysis. Mary Virginia Orna (Editor). Washington DC: American Chemical Society. pp. 139–156.

The House of the Eagle Warriors, part of the fifteenth century Templo Mayor in Mexico City, comprises five main areas, the floors of the which were made of a lime plaster mixture of hydrated lime and ground volcanic rock. Ancient books from the Aztec period suggest activities that might have occurred in this structure included self-mutilation in front of a statue of a deity and burning a resin incense called *copal* in the braziers (Fig. 6.20).

Fig. 6.20 Aztec ritual blood-letting with sting-ray spines and burning copal in front of deities as shown in an illustration from the Tudela Codex

All samples were analyzed at the Archaeometry Laboratory at the Universidad Nacional Autónoma de México with spot tests for pH, carbonate, phosphorus, and organics including lipids and proteins. Based on the results of the spot tests and the distribution maps of the resulting patterns, 20 samples were selected for subsequent analysis by GC/MS.

The results of the spot tests show that one of the outstanding areas of activity was in front of the main altar (Fig. 6.21). Here high contents of lipids were probably related to the burning of resins in front of the main altar and in the braziers. Other areas in which spot tests have high values are the entrances, where clay figures representing Eagle Warriors and *Mictlantecuhtli* were found. In other rooms, the highest values are also directly associated with the location of the braziers and altars. In some of these areas, the presence of fatty acids is strongly related to the distribution of other organic residues, such as carbohydrates and proteins, possibly due to blood offerings.

Subsequent GC–MS analyses of a subset of samples selected for their high lipid content in the spot tests found differences between fatty acids found in the main altar and those found at secondary altars, suggesting that different materials were involved in specific rituals. The samples taken from the large lipid concentration close to the main altar were characterized by their high molecular weight and were identified by Barba and colleagues as *copal* residues, confirming the ritual aspects proposed for the space.

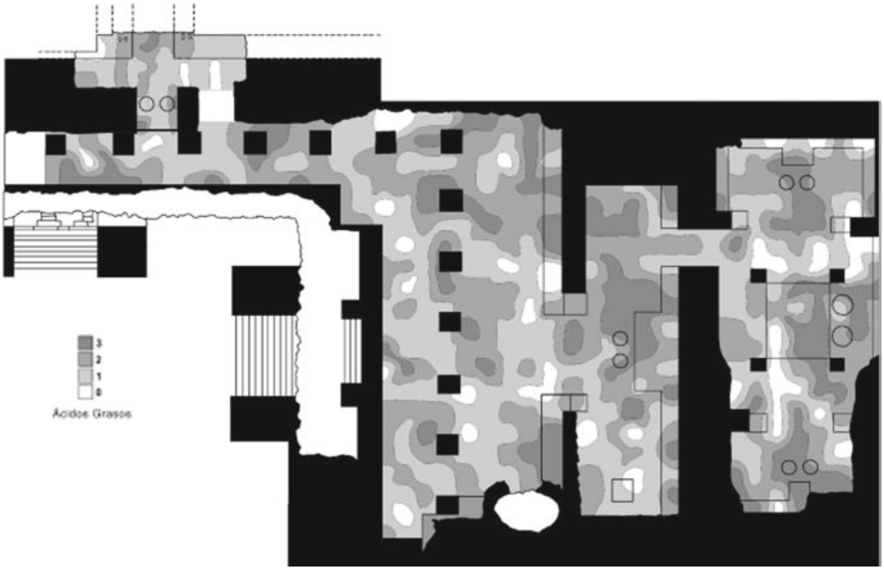

Fig. 6.21 Map of fatty acid distributions in the floor of the House of the Eagle Warriors. Darker areas represent higher lipid content. Notice the enriched areas adjacent to the altars (*circle pairs*)

6.3.3 Lejre House Floor

Material: Sediment
Instrumentation: GC/MS
Application: Human Activity
Place: Denmark
Time Period: Modern
Question: Can different human activities be distinguished in the chemistry of house floors?

Key Reference

Hjulstrom, B., & S. Isaksson. 2009. Identification of activity area signatures in a reconstructed Iron Age house by combining element and lipid analyses of sediments. Journal of Archaeological Science 36: 174–183.

The potential for soil chemistry to tell us about past human activities is enormous, but also very difficult. Clear patterns can usually be found in chemical studies of house floors and other activity areas but interpretation of their meaning is complex. One of the best ways to learn more about chemical patterns is to study known situations, where activities can be observed or reconstructed from other information. Contemporary households where earthen floors are in use have provided a context for this kind of study in several instances. The inhabitants of the house could be observed or interviewed regarding the use of space and activities that had taken place.

Fig. 6.22 The experimental Iron Age village at Lejre and a large reconstructed house similar to the one used in the study described here

Another situation with potential information comes from experimental archaeology and the construction and use of "prehistoric" houses by modern people. Lejre is an Experimental Archaeology Research Center in Denmark where a variety of different experiments are conducted to reproduce the technology, architecture, and activities of the past. Lejre is also home to a number of wattle and daub, thatched-roof houses that replicate Iron Age structures (Fig. 6.22). In the summer months, interested individuals and families occupy these houses for weeks at a time, attempting to reproduce the daily lives of the prehistoric inhabitants. The earthen floors of these structures absorb and retain the residues of their activities.

Two Swedish scientists interested in the chemistry of ancient house floors, Björn Hjulstrom and Sven Isaksson, took samples from one of these experimental houses at Lejre, along with the floor of a separate smithy in order to compare known activities to patterns in the chemical residues. The small smithy structure was located about 100 m from the house. The two scientists investigated both organic and inorganic residues, providing a more complete look at the chemistry of the floors. Figure 6.23 shows the house, the smithy, fireplaces, control samples on the natural soil, the location of sediment samples taken for this study, and the activities that took place on the floors of these two structures. It is a fairly large house, 14 × 5 m (44 × 16 ft), 70 m^2 in area. The roof is supported by two rows of posts down the middle of the floor. Activities in the house were varied and include cooking and sleeping areas as well as animal stalls in the eastern third of the structure. An entrance area with a stone pavement was also present near the center of the house.

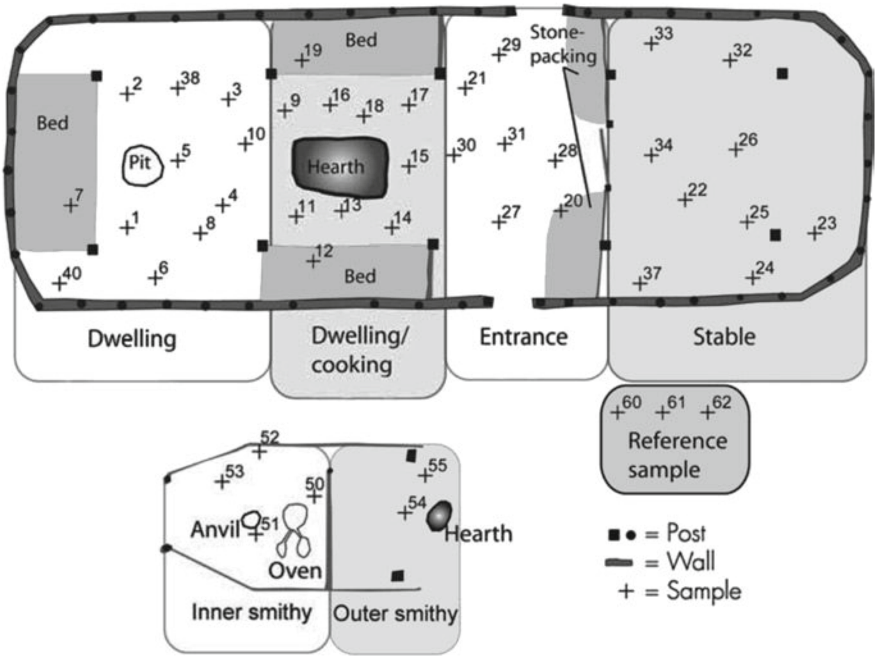

Fig. 6.23 Floor plan of the house and smithy at Lejre showing the major activity areas, hearths, and sample locations

The smithy was a much smaller structure with two rooms and contained a hearth, oven, and anvil as permanent features.

Multielement analysis of the sediment samples was done using an Atomic Absorption Spectrophotometer. Concentrations of calcium (Ca), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), lead (Pb), and zinc (Zn) were measured in each sample and recorded for analysis.

Plots of these elements on the house floor (Fig. 6.24) show clear differences and patterns. The results of the elemental analysis demonstrate different areas in the two structures. The smithy has low Ca, Cu, Fe, and K, while values for Mg, Mn, and Pb are above average. The two rooms in the smithy also show differences. In the residential structure, the stable areas are generally average for most of the elements, although Fe, K, Mn, and Zn are slightly higher in some of the samples. Zones of movement in the structures, doorways and entrance area, have lower concentrations of residues in the sediment, due to the erosion of the surface from movement.

A statistical technique known as principle components analysis was used to define the groups or sets of elements that behaved similarly in the house floor samples (Fig. 6.25). Two factors or groups of elements defined more than 60% of the variation in the samples, a very good resolution of the patterning. Factor 1 include high positive readings of Mg and Fe and high negative loadings of K and

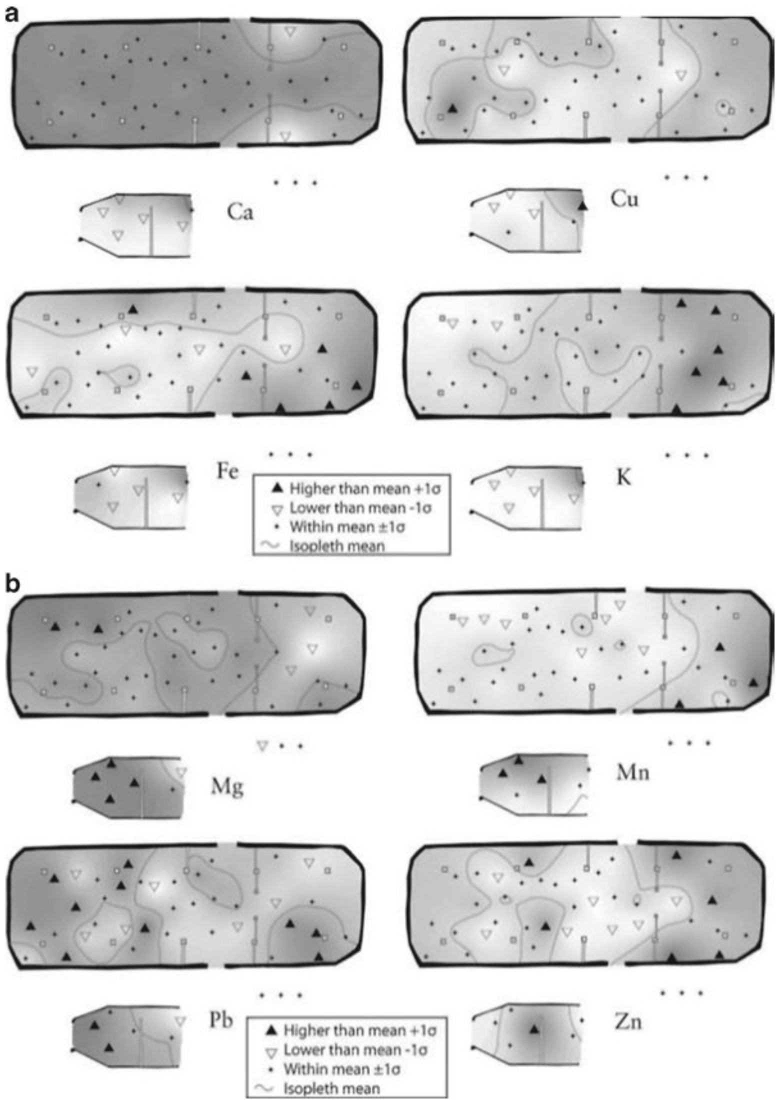

Fig. 6.24 Variations in Ca, Cu, Fe, K, Mg, Mn, Pb, and Zn contents across the floor of the house and smithy. The contours show the absolute values. Cross = sample value falling between mean ±1 s; upward triangle = higher than the mean ± 1 s, and downward triangle = below the mean ±1 s. The lines are based on the standardization of the samples. Solid lines denote the mean, broken lines the mean ±1 s, decreasing by 1 s for each broken line, and thin lines the mean ± 1 s, increasing by 1 s for each line

Cu. That means that this group was where Mg and Fe were found together and K and Cu were generally absent. Factor 2 was defined by high positive values of Mn (0.79) and Zn (0.84). A plot of Factor 1 vs. Factor 2 with individual samples identified as to activity shows good correspondence with the known activity in several

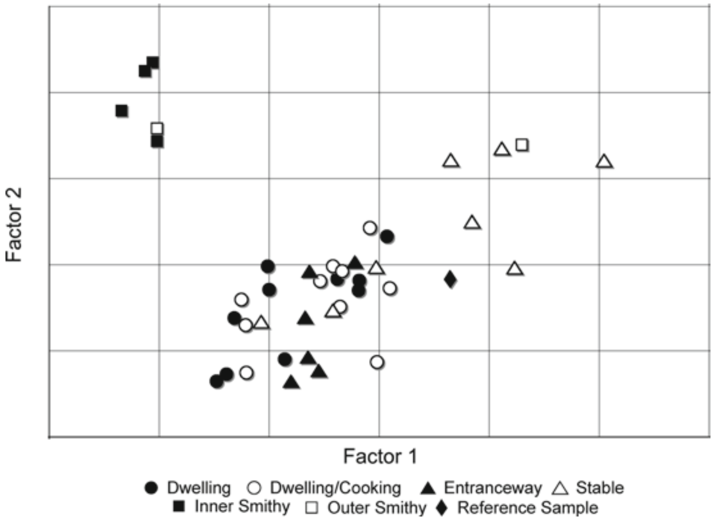

Fig. 6.25 A scatterplot of Factor 1 vs. Factor 2 of the groups of element concentrations found in the house floor at Lejre. The analysis reveals a clear separation of the inner smithy and the stable from the rest of the house

cases. The principle components analysis and plot clearly distinguish the smithy and the stable area from the rest of the house. Activity areas within the house, however, are not isolated by the elemental data from the house floor.

Analysis of the organic compounds in the house and smith floor focused on lipids. Organics were extracted from the sediment samples with a mixture of chloroform and methanol and analyzed in a GC/MS. Lipids include a variety of organic compounds oils, acids, and sterols (see Chap. 1). These compounds come from both plants and animals, as products of deposition and decomposition of the organisms themselves or various materials that are produced by plants and animals such as excrement. The primary source of lipids in soil is vegetation. Human activity will affect the soil composition both directly, by adding substances, and indirectly, by changing the vegetation. One of the best-known applications of organic chemistry in soil analysis involves the identification of coprostanol to identify the practice of manuring in ancient agricultural fields. Coprostanol (5b-cholestan-3b-ol) is a product of the microbial reduction of cholesterol that is formed by microbial action in the gut of humans and other mammals.

The organic chemistry of this study focused on some of the most common sterols in soils, i.e., cholesterol, 24-ethylcoprostanol, stigmasterol, campesterol, and b-sitosterol. 24-Ethylcoprostanol has been used as biomarker for (nonhuman) herbivore fecal matter. Results of the BC/MS analysis of one of the sediment samples is shown in Fig. 6.26 and the presence of these sterols clearly identified. This sample is taken from the stable area and clearly shows the presence of coprostanol and 24-ethylcoprostanol indicating enrichment by fecal material from herbivores.

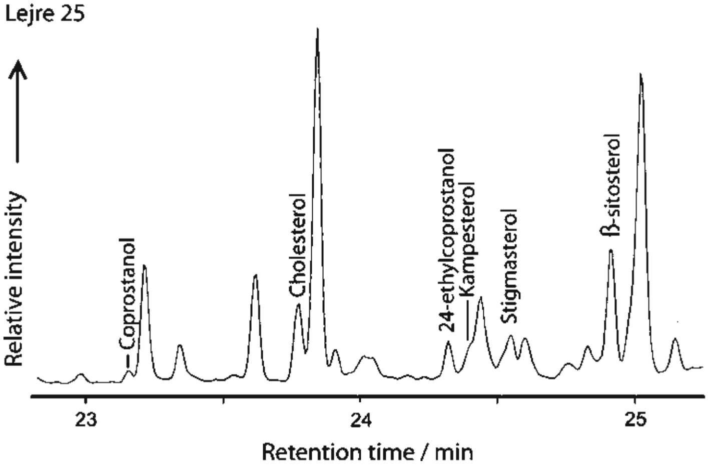

Fig. 6.26 GC/MC total ion chromatogram of the sterol fraction in sample 25 from the stable area of the house. The presence of coprostanol and 24-ethylcoprostanol confirms the presence of herbivore excrement

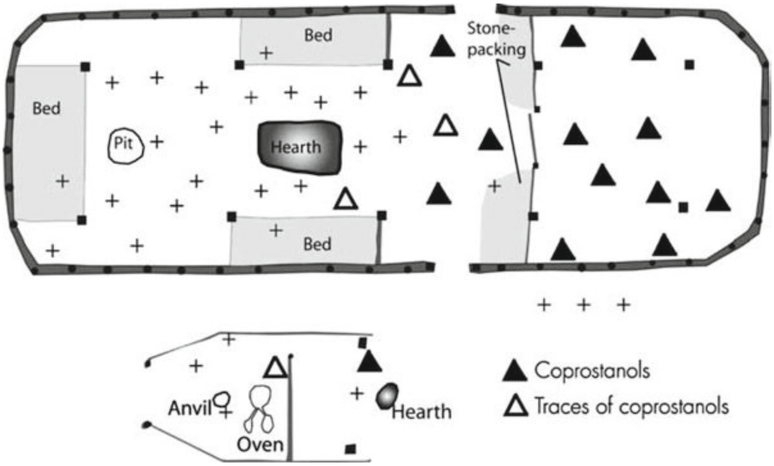

Fig. 6.27 The distribution of coprostanol and 24-ethylcoprostanol on the house floors at Lejre showing the close correlation with the stable area and entranceway of the house

The plan of the house floor (Fig. 6.27) with indications of the presence of coprostanol and 24-ethylcoprostanol clearly shows the concentration in the stable and entranceway area of the house, along with some presence in the smithy.

This study of the floor sediments at Lejre involved a context where modern humans had carried out known activities including daily living, sleeping, cooking, preparing food, making and repairing tools and equipment, stabling animals, and working metal. Several areas were distinguished on the basis of known activities, including dwelling, dwelling/cooking, entranceway, stable, and smithy. Both inorganic and organic chemistry were used to characterize samples of the floor from the two structures. Elemental analysis distinguished three areas in the structures the smithy, the stable, and the rest of the house. The lipid analysis basically revealed the same three areas based on the organic residues present. The biomarker 24-ethylcoprostanol was particularly useful for the identification of the stable. The sterol ratio was successful in identifying and characterizing the dwelling area as distinct from the rest of the house. However, differences between the dwelling space and the dwelling/cooking space could not be observed. In sum, the chemical analysis of the house floors provided very useful information on the possibilities and the limitations of such studies.

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Chapter 7
Environment and Diet

Contents

This chapter deals with two important and related topics in archaeological investigations: the environment in which people lived, and the foods that they ate. The environment plays a major role in the diet that is available to human groups. This relationship is seen both in terms of the specific kinds of plants and animals that are available and in terms of changes in climate and resources over time that impact the human population.

Examples of environmental studies discussed in this chapter include two extreme locations, cold, treeless Greenland and the hot and humid rainforest of Central America. Greenland was discovered and settled by the Vikings around AD 1000, during a period of good climatic conditions. Greenland was abandoned by Europeans a few hundred years later as the climate deteriorated. The Maya area of southern Mexico, Guatemala, Belize, and parts of Honduras was also largely abandoned around AD 800–900 for still unknown reasons. One possible cause, considered in the discussion below, may have been a major drought. In two very different places, with two different environmental catastrophes, human societies are forced to leave formerly productive areas. Climate and environment remain a major force in our lives as the current concern with global warming dramatically demonstrates.

Diet refers to the food and water that we consume to survive. In today's world, where a variety of foods are available at the nearest supermarket, we are a bit removed from the necessity of finding foods in the wild through hunting and gathering, or cultivating and herding domesticated plants and animals by farming the land. In order to understand past human behavior it is essential that we know what our ancestors ate

T.D. Price and J.H. Burton, *An Introduction to Archaeological Chemistry*,
DOI 10.1007/978-1-4419-6376-5_7,

and where and how they obtained their food. Archaeological chemistry provides an important avenue of research on diet, based in part on the premise that you are what you eat. The foods that we consume are used to construct the tissues that comprise our bodies and skeletons. The chemistry of the human skeletons that survive from the past contains information on the diet of these individuals and isotopes are particularly useful. Detailed discussion of the application of carbon and nitrogen isotopes for investigating past diets are discussed at the beginning of this section of the chapter.

Three examples of paleodiet studies in archaeological chemistry are provided in this chapter. Antigen–antibody analysis of human coprolites from the Southwestern USA provide strong evidence that cannibalism was practiced on occasion in this region in the past. Isotope ratios of carbon and nitrogen were used to investigate past human diet in ancient hunters and early farmers in Denmark and document a dramatic shift in diet from marine to terrestrial foods. In South Africa, isotopes of carbon and nitrogen were used to identify the diet and place of origin of a series of burials found along the coast.

7.1 Environment

The investigation of past environments is an important part of archaeology and the natural sciences in general. Today, global warming and its impact on human society is a great concern. In order to understand our world today, it is essential to know what the earth was like in earlier periods of time. It is particularly important to know the conditions in which previous people lived to better understand their behavior and how they responded to those conditions. Questions about past environments concern not only climate, but also vegetation cover, animal life, natural resources, sea level change, topography, and more.

There are a number of methods in archaeology and other natural sciences such as geology, botany, zoology, and geography for learning about past environments. Most archaeological research has concentrated on flora and fauna, identifying the animals and plants that were present in the past as indicators of the environment and climate at that time. For example, during the Ice Age (Pleistocene epoch) a species of cold-adapted elephant called a woolly mammoth lived in Europe and North America. As temperatures increased at the end of this epoch, these creatures became extinct, unable to tolerate the warming climate.

Archaeologists and other natural sciences use a variety of plant and animal species as climatic indicators. Tree rings are one of the most obvious and best known indicators of past climate conditions. Tree rings, which mark each year of a tree's life history, vary in thickness depending on various climatic factors such as rainfall and temperature. Measurement of tree ring width can thus provide a long-term and well-dated record of climatic changes in a region. Figure 7.1 shows the relationship between precipitation and tree ring widths for wet and dry seasons in New Mexico for more than 100 years. There is a very close correspondence between cool-season rainfall and tree ring width.

What is important for such climate studies it that the material under study have a record of annual or at least regular deposits that can be used to estimate time. Tree

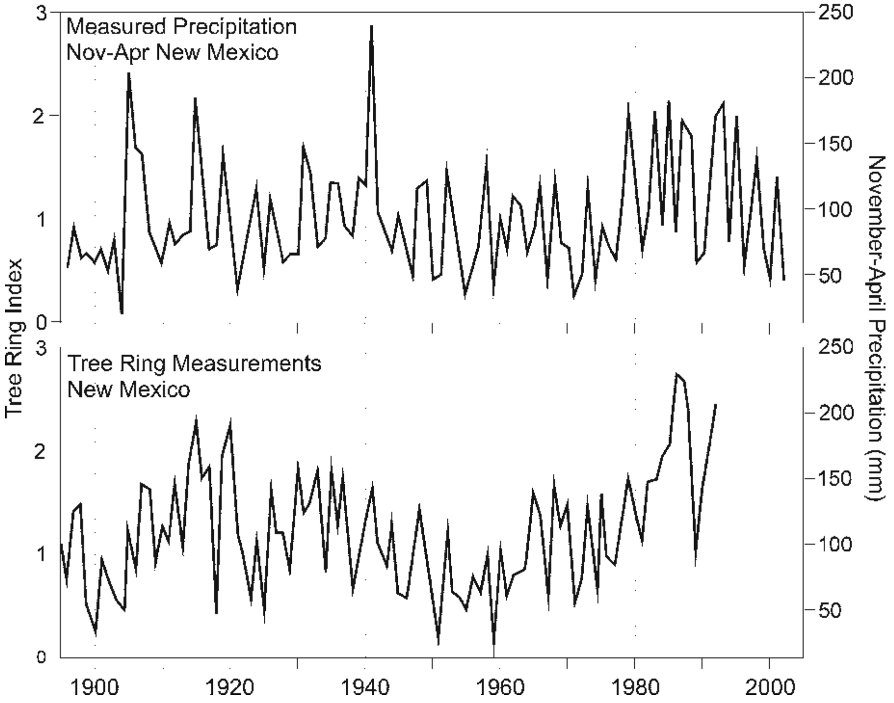
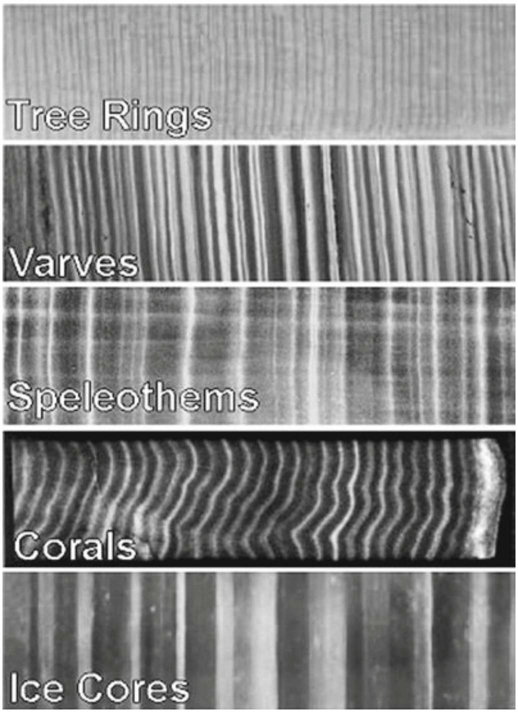


Fig. 7.1 The relationship between tree growth and cool-season precipitation. The lower graph shows the tree-ring growth index for El Malpais National Monument, New Mexico and the upper graph depicts precipitation recorded by rain gauges in New Mexico. Notice that while the tree rings do a good job of matching dry winters, they do not quite match the wet years. Above a certain threshold, precipitation is no longer limiting on tree growth. Also note the very dry conditions during the 1950s and the post-1976 wet period

rings and other proxies of climate such as lake sediments, speleothems, coral, and ice layers other deposits, can be enhanced by isotopic investigations (Fig. 7.2). Carbon and oxygen isotopes are particularly useful in such studies.

Chemistry provides a number of tools for the investigation of past physical environments. Oxygen isotopes, for example, can be used to estimate past temperatures. The ratio of ^{16}O to ^{18}O varies depending on temperature. This ratio can be measured in a variety of materials, including shell, bone, and water. A remarkable project in Greenland, described in the next section, provides a good example of how oxygen isotopes can tell us about past climate using dated layers of ice. In recent years, studies of the stalagmites and stalactites (known collectively as speleothems) in limestone caves have provided detailed climate records. These cave features form similar to trees with an annual rings of calcite (Fig. 7.3) deposited on the speleothems as water drips into and through the cave. Also similar to tree rings, the width of these calcite rings varies with rainfall and temperature, and other factors (King et al. 2004). In periods of drought, rings may not form at all or be very narrow. Calcite is a carbonate mineral ($CaCO_3$), made up of calcium, carbon and oxygen. Isotopes of carbon and oxygen can be measured in the calcite of these

Fig. 7.2 Deposits with annual layers that provide material for isotopic investigations include tree rings, lake sediments (varves), speleothems (cave deposits), corals, and ice cores



speleothem growth rings to provide a quantitative estimate of past climatic conditions. Oxygen isotopes reflect the temperature of the rainwater that fell above ground. Carbon isotopes reflect in part the kind of vegetation present on the ground surface above the cave. Thus these rings can provide well-dated, yearly indicators of past climate.

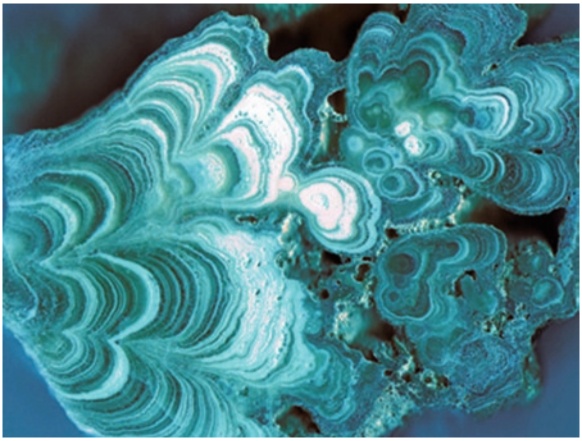


Fig. 7.3 Cross-section through a speleothem showing annual deposits of varying size

7.1.1 Greenland Vikings

Material: Bone
Instrumentation: Light Isotope Mass Spectrometer
Application: Diet and Environment
Place: Greenland
Time Period: Viking period, AD *1000–1450*
Question: Did climate change force the Vikings to leave Greenland?

Key References

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Columbus arrived in the Caribbean islands in 1492 as we learn in elementary school. But the first Europeans to set foot in the Americas came almost 500 years earlier and they were not Italian but Scandinavian – the Vikings.

Their daring journey across the North Atlantic was made in a series of shorter trips from Norway, Sweden, and Denmark to the Western Isles (Britain and Ireland) and then to the Faeroe Islands, Iceland, Greenland, and eventually to Newfoundland in eastern Canada (Fig. 7.4). The Vikings took over parts of Britain and Ireland by AD 800 and occupied many of the island groups in the northern British Isles, including the Shetlands, Orkneys, and Hebrides. As explorers and colonists, they were the first people to settle on the Faeroe Islands, Iceland, and Greenland (AD 874). In North America, the Eskimos and American Indians had been present for thousands of years.

The story of the Viking exploration of the North Atlantic is an incredible saga of many tales. One chapter concerns the colonies on Greenland, their success and their failure in the light of major climate change. A group of Icelandic farmers led by Erik the Red founded the Eastern Settlement in southwest Greenland around AD 985. Another group from Iceland went further north along the west coast of Greenland and colonized the Western Settlement. These Viking groups took domesticated cereals and animals with them and successfully cultivated these crops and fed their herds. North Atlantic climate began a particularly good around AD 900, known as the Medieval Warm Period. Temperatures were 1–2°C warmer than today on average and the growing season was longer. The Viking population of Greenland soon expanded to between 4,000 and 5,000 people. However, after AD 1300 those numbers began to decline and by the middle of the fifteenth century Greenland was completely abandoned by the Norse.

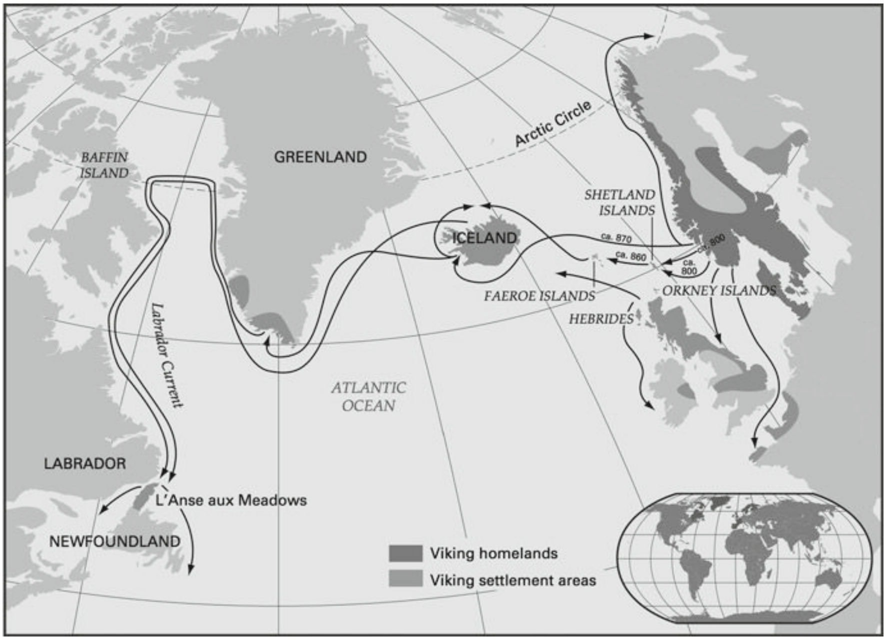

Fig. 7.4 The homelands, settlements, and routes of the Vikings in the North Atlantic

The present icecap on Greenland provides remarkably detailed evidence as to what happened to the climate. The Greenland ice sheet is more than 2 km thick, made up of layer upon layer of ice and frozen snow in a stratigraphy of the last several hundred thousand years. Borings deep into this ice provide information on past climate and show a steady decline in maximum temperature during the 500 years of the Viking occupation of Greenland.

Ice coring projects in Greenland have been ongoing for several decades and are providing extraordinary paleoclimatic information for thousands of years into the past. The ice sheet that covers Greenland today is more than 3 km thick in places. This ice holds a long series of annual layers of the accumulation of snow and ice that created the glacier in the first place (Fig. 7.5). By carefully drilling through the ice and removing the cores from the drills, the scientists can obtain a long-term climatic record for more than 200,000 years. By measuring the ratio of ^{18}O to ^{16}O in the water of the ice cores and comparing these values to modern values from Greenland, it is possible to obtain an estimate of temperature at known dates in the past. An example of the temperature estimates from the ice core data is shown in Fig. 7.6. We can see that temperature changed dramatically over time, reflecting the sequence of warmer and colder periods that the earth experienced over the last 200,000 years or more.

More detail on climate during the Viking period is also available from the ice cores (Fig. 7.7). Two major episodes, one cold and one warm, dominate this period. The Medieval Warm Period between AD 800 and 1,300 witnessed the expansion of the Vikings across the North Atlantic during a time of warmer temperatures and

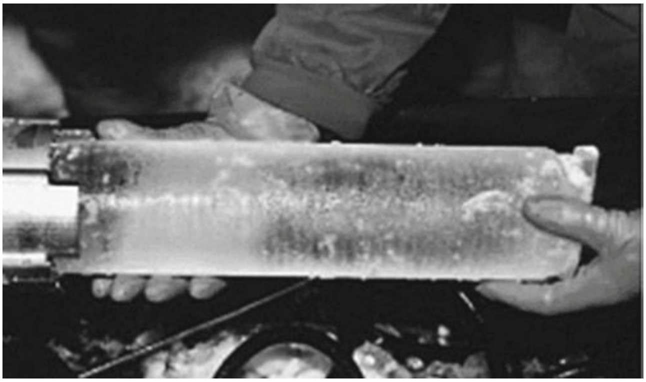

Fig. 7.5 Section of a Greenland ice core with visible annual layers

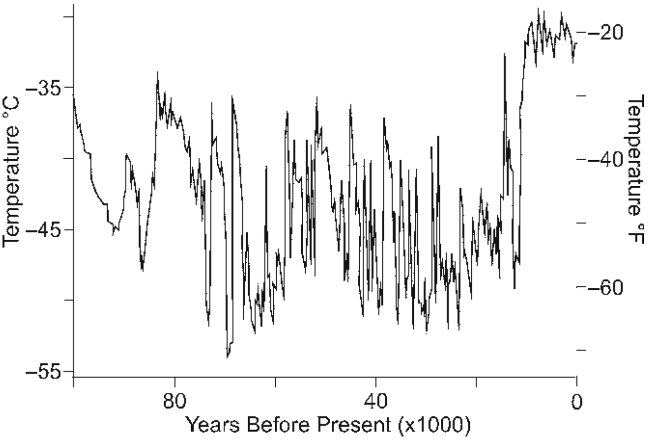

Fig. 7.6 The estimated temperature record from a Greenland ice core based on oxygen isotope ratios. δ^{18}O in the layers of ice is a proxy for air temperature over Greenland. The data indicate the abrupt nature of climatic change over the last 100,000 years. The sharp increase in temperature that began ca. 10,000 years ago marks the onset of the current climatic episode known as the Holocene

longer growing seasons. The cold period that followed between AD 1300 and 1850 has been designated as the Little Ice Age. This cold episode brought colder winters to portions of Europe and North America and glaciers in mountain areas expanded. Its effects were dramatic in the North Atlantic – pack ice expanded, the growing season shortened considerably, and the population of Iceland declined by 50%. The effects on Greenland were devastating.

Isotopic studies of the tooth enamel from Viking burials from Greenland document these changes in climate (Fig. 7.7). Oxygen isotopes in tooth enamel show a

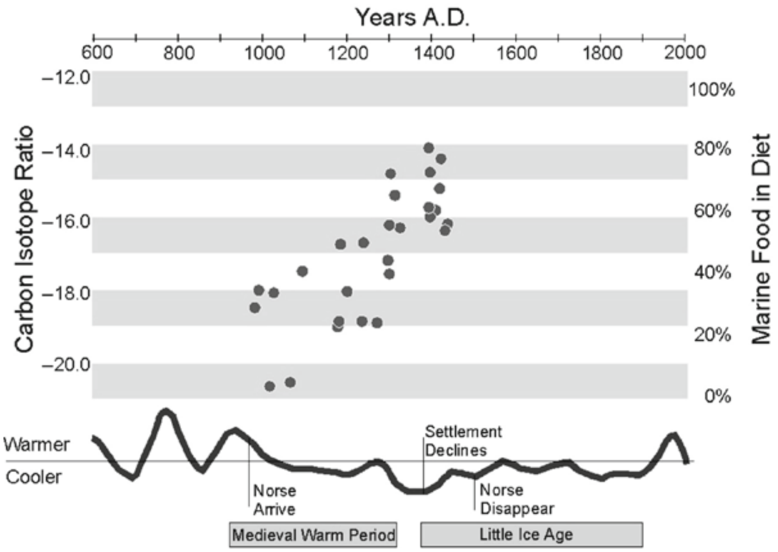

Fig. 7.7 Climatic changes over the last 1,400 years revealed in Greenland ice cores document periods of warmer and colder conditions than today. The Medieval Warm Period witnessed the expansion of the Vikings across the North Atlantic while the Little Ice Age documents a time of cooler conditions and declining harvests. The carbon isotope evidence from human tooth enamel shows a shift from terrestrial to marine diet during this period (data from Dansgaard et al. 1975; Arneborg et al. 1999)

clear decline in atmospheric temperature during the period of settlement. Carbon isotopes in the enamel indicate a marked increase in the proportion of marine foods in the diet over time, from approximately 20% when the Vikings arrived to something like 80% at the end of their time on Greenland (Fig. 7.7). It appears from the evidence that as temperatures and growing season declined, the Viking people of Greenland ate more seals and fish. A longer summer was necessary to grow hay to store and feed their cows and sheep through the spring, when the Norse could hunt seals on the ice. If the cattle and sheep died before the seals arrived, the Norse would starve.

Archaeological evidence collaborates this scenario. Excavations at Norse houses from the later period of the settlement have revealed the skeletons of cattle that died in their stalls during the winter. Other bioarchaeological information suggests a clear decline in nutrition. There are indications of a decline in stature in the Greenland Vikings over time and a number of the later skeletons exhibit evidence of disease and malnutrition.

Changes in climate played a major role in course of Viking history. The Medieval Warm Period provided better growing conditions in Scandinavia and supported expanding population that may have forced exploration for new land. Five hundred years later, as the Little Ice Age took hold the growing season declined, and the Viking way of life collapsed. Greenland was abandoned by the Vikings. At the same time, colder conditions on Greenland increased the herds of seal and reindeer and the Greenland Eskimo hunters further to the north flourished.

7.1.2 The Maya Collapse

Material: Sediment and shell
Instrumentation: Light Isotope Mass Spectrometer, ICP-MS
Application: Environment
Place: Caribbean
Time Period: Classic Maya Period, AD *300–900*
Question: Did climate cause the collapse of Maya civilization?

Key References

Hodell, David A., Mark Brenner and Jason H. Curtis. 2005. Terminal Classic drought in the northern Maya lowlands inferred from multiple sediment cores in Lake Chichancanab (Mexico). Quaternary Science Reviews 24: 1413–1427.

Yaeger, J., & D. Hodell. 2007 The Collapse of Maya Civilization: Assessing the Interaction of Culture, Climate, and Environment. In El Niño, Catastrophism, and Culture Change in Ancient America, ed. by D.H. Sandweiss & J. Quilter, pp. 197–251. Washington, D.C.: Dumbarton Oaks.

Ancient civilizations rose and collapsed in a pattern that continues to the present. One of the most fascinating cases comes from the Maya region, which lies for the most part in the eastern one/quarter of Mexico, Belize, and Guatemala. Much of the central part of this region today is covered by dense, uninhabited tropical jungle. Yet beneath that forest canopy lie the ruins of the cities, villages, farms, and fields of the Classic Maya. This literate culture spanned the centuries between AD 300 and AD 900. Yet, by the time the first Spanish conquistadores entered the area in AD 1525 there was almost no one living there. Their disappearance, along with eerie images of abandoned temples overgrown by rain forest, has fostered the mystery of the Maya.

The Maya achieved many of the hallmarks of advanced society. Their culture was characterized by monumental stone architecture; great pyramidal temples; magnificent palaces and tombs; cities, roads, and reservoirs; long distance trade; accurate calendrical and numerical systems; a written hieroglyphic language used for recording number; dates; and important events, astronomical observations, extraordinary art, endemic warfare, and a stratified social system dominated by powerful kings and priests. The population of the Maya region at its height must have been counted in the hundreds of thousands, or millions, of people. Subsistence was based on agriculture; corn, beans, and squash would have been the primary staples.

Several pieces of evidence, however, point to a rapid decline for the Maya. The Maya erected many dated monuments during their heyday, but around AD 800 the number declines (Fig. 7.8). At the same time, royal dynasties disappear from view and many major centers were abandoned without evidence of violence or destruction. Another indication can be seen in the radiocarbon dates from the area, showing a precipitous decrease after AD 800. However, the dates show a decrease, not a disappearance, indicating that some human presence continued in the area.

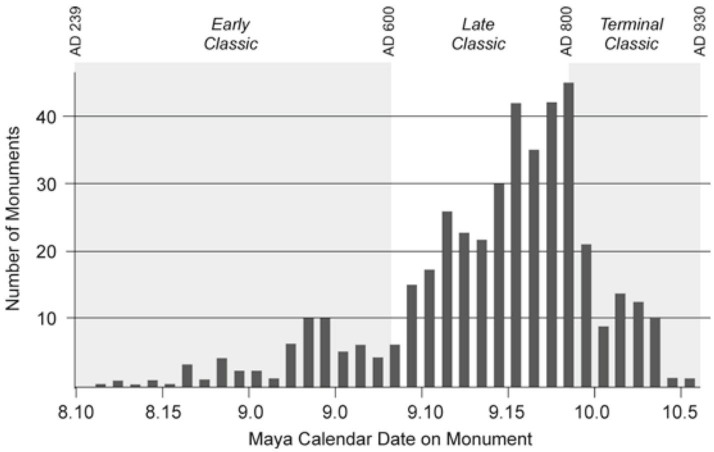

Fig. 7.8 The number of monuments erected over time in the Maya region. The monuments are inscribed with a date in the Maya calendar. It is clear that the monument production stopped gradually rather than abruptly after AD 800

The question of what happened to the Maya – why their civilization and its inhabitants had largely disappeared by the time of the Spanish arrival – has intrigued scholars for decades. Many theories have been put forth concerned with either the demise of just the elite class or the collapse of the entire social system (Table 7.1). In the elite scenario, common folk continue to live in the region for some time, but eventually die out. Theories for the collapse of the entire society involve either short-term catastrophic events or long-term changes to explain the abandonment of the Maya region.

Table 7.1 Some explanations of the Maya collapse

Elite collapse
1. Peasant revolts
2. Internal warfare
3. Foreign invasion
4. Disruption of trade
Society collapse
1. Demise of trade networks
2. Ideological overkill
3. Earthquakes, hurricanes, or volcanic eruptions
4. Climatic change (drought)
5. Epidemic human disease
6. Exhaustion of agricultural lands

There are many ideas about the Maya collapse and relatively few hard facts. Drought is suggested by some to have forced the abandonment of the Maya region. Drought is one of the major issues today in debates regarding the collapse, perhaps in part because of concerns with global warming. While much of the Maya region was rain forest, this is an area of limestone and, for the most part, there is little surface water on this porous rock landscape. There were large lakes in some places and the Maya created reservoirs and farmed wetlands, but drought would have created substantial problems for this civilization.

Major questions concern the extent and duration of droughts in this region during the Classic Maya period. Several studies have been undertaken to examine the nature of rainfall and aridity in this area. These investigations have involved a variety of chemical measures including elemental concentrations, isotopic ratios, and salinity proxies.

Curtis and his colleagues in 1995 reported a long-term sequence of climatic change on the Yucatan Peninsula, based on measurement of oxygen isotopes in shells found in sediment cores from lakes in the region. Accelerator mass spectrometry (AMS) was used to date the sequence of sediments and oxygen isotope ratios were measured using a light isotope mass spectrometer. This sequence from beginning roughly 3,500 years ago showed three major episodes of climate. There was a long episode of relatively wet conditions from ca. 1500 BC to AD 250. The period between AD 250 and 1100 was persistently dry with major droughts at AD 862, 986, and 1051. After AD 1100 there was a return to wetter conditions similar to the present. The drier period marked by the major droughts coincides with the time of the Classic Maya and perhaps helps to explain their demise.

Haug and colleagues criticized the model of Curtis and others and pointed to problems from disturbances in the lake cores and with the chronology associated with the Maya collapse. The dates that Curtis proposed were younger than the Classic Maya collapse. Haug and colleagues studied undisturbed annually laminated sea sediments off the coast of Venezeula to obtain a chronologically controlled data set for the period of the Maya collapse (AD 750–900). Although the core was in northern South America, they argue that it lies within the same weather pattern as the Maya region.

AMS was used to determine the age and rate of accumulation of the core. They measured bulk titanium content in the layers of marine sediment using a micro X-ray fluorescence system with very high precision, able to measure titanium content 50 mm resolution. The amount of titanium in such sediments increases during periods of increased rainfall, and decreases during dry periods. The evidence from the Venezuelan seafloor core shows several multiyear episodes of intense drought at approximately AD 760, 810, 860, and 910 (Fig. 7.9). They conclude, based on the correlation between the timing of drought and collapse, that these episodes put a general strain on resources in the Maya region contributing to the social stresses that led to the collapse.

More recently, information has been collected from Lake Chichancanab in north-central Yucatan. Deposits here have yielded a sensitive paleoclimatic record because of the effectively closed hydrology of the lake, the near saturation of the

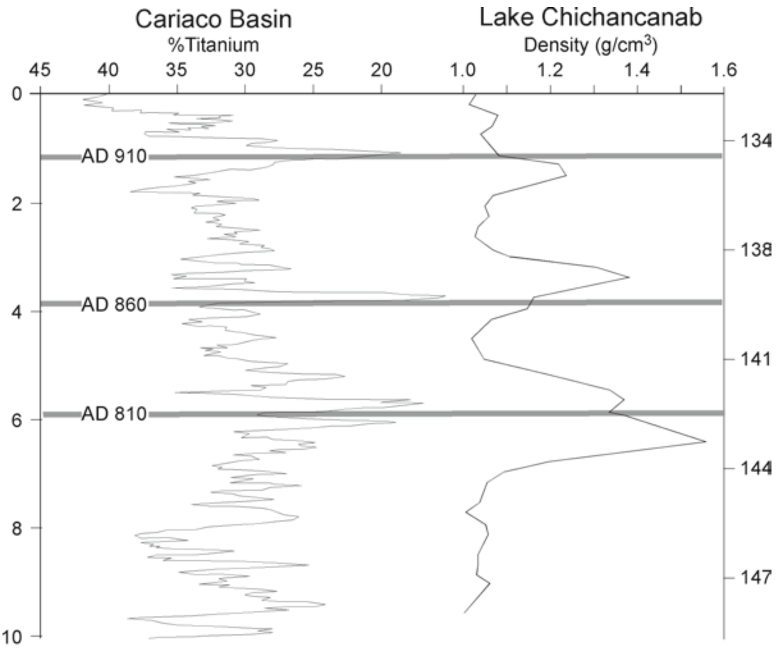

Fig. 7.9 Titanium concentrations in the ocean deposits of the Cariaco Basin, Venezuela, annually laminated marine sediments (*left*) and gypsum concentration in the sediments from Lake Chichancanab in the Northern Yucatan (*right*). Higher amounts of titanium and increased gypsum concentrations reflect decreased rainfall. The time period is from approximately AD 730–930. Three major episodes of drought are observed at AD 810, 860, and 910

mineral gypsum ($CaSO_4$), and low density of human occupation in its watershed. Sediment cores from the bottom of this lake have been investigated by Hodell and colleagues and reveal a record very similar to the Venezuelan data. Hodell and his colleagues found three very high-density bands of gypsum in the Chichancanab core, corresponding closely to the droughts reported by Haug and others (Fig. 7.9). A period of generally reduced precipitation was punctuated by distinct multiyear drought events with a 40- to 50-year periodicity (ca. AD 760, 810, 860, and 910). The drought at AD 810 appears to have been the most severe for several thousand years. There is also evidence from the lake bottoms in the Maya area for environmental degradation, showing that decreasing forests, increased erosion, and more runoff into the lakes are associated with growing Maya population.

Clearly climate change needs to be considered in debates about the collapse of the Maya. Clearly as well climate change is not the only possible cause. And, of course, the question still remains as to whether there were significant droughts during the period that the Classic Maya flourished and before the collapse. If drought was a periodic phenomenon in this region, it would not help explain the collapse. The reasons for the disappearance of the Maya civilization are still not understood.

7.2 Diet

Air, water, and food are the minimum essentials for immediate human survival. Air and water are generally available in most places on earth. The quest for food often dominates human behavior and directly affects many aspects of human society, including group size and social organization, residence patterns, technology, and transportation. Many fundamental questions in archeology revolve around the nature of human diet and sources of food.

Our way of life in the past was often defined by how we obtained our food, for example, were we scavengers, hunters, or farmers? Did we live from the sea or the land? Questions about the kinds of food that our ancestors consumed, the importance of meat, the role of seafood in diet, when farming began, status and gender differences in food consumption are significant issues in archaeology. Information on past diet has traditionally come from a number of lines of analysis: the study of preserved animal bones and plant remains, fecal matter, tooth wear and disease, and the physical characteristics of the human skeleton.

Archaeological chemistry can also provide substantial information about past human diet. The basic principle in these studies is a fundamental one – you are what you eat. The foods we consume and the water we drink provide the elements and molecules needed to create and maintain our bodies. Because the hard tissue of the skeleton is sometimes preserved from the ancient past, research has concentrated on these remains. Both elements and isotopes have been used in the study of past human diet.

The most successful work has focused on carbon and nitrogen isotopes in human bone. These isotopes get into our bodies through the food we eat and are deposited in significant amounts in the skeleton. Carbon and nitrogen are also elements of biological interest with two or more stable isotopes. In each case the lightest isotope is present in much greater abundance than the others. Carbon-14 is radioactive and decays with a known half-life, a principle used in the radiocarbon dating method.

Carbon 12 = 98.89%   Carbon 13 = 1.1%   Carbon 14 = 0.000001%
Nitrogen 14 = 99.63%   Nitrogen 15 = 0.37%

7.2.1 *Carbon Isotopes*

Studies involving stable isotopes at or near natural abundance levels are usually reported as a ratio or delta, a value given in parts per thousand or per mil ("o/oo"). Delta values are not absolute isotope abundances, but the difference between sample reading and a standard reference material. The standard reference material for nitrogen is air and for carbon it is a mineral deposit known as PeeDee Belemnite (PDB). Carbon is reported as $\delta^{13}C‰$ and nitrogen as $\delta^{15}N‰$. Naturally occurring $\delta^{13}C$ numbers for biologically interesting carbon compounds are negative in value and range from roughly 0 to −25‰. The numbers are negative because observed ratios are lower than the standard.

$$\delta^{13}\mathrm{C} = \frac{{}^{13}\mathrm{C}/{}^{12}\mathrm{C}_{\mathrm{sample}} - {}^{13}\mathrm{C}/{}^{12}\mathrm{C}_{\mathrm{standard}}}{{}^{13}\mathrm{C}/{}^{12}\mathrm{C}_{\mathrm{standard}}} \times 1{,}000$$

$$\delta^{15}\mathrm{N} = \frac{{}^{15}\mathrm{N}/{}^{14}\mathrm{N}_{\mathrm{sample}} - {}^{15}\mathrm{N}/{}^{14}\mathrm{N}_{\mathrm{standard}}}{{}^{15}\mathrm{N}/{}^{14}\mathrm{N}_{\mathrm{standard}}} \times 1{,}000$$

There are two sources of heavier ^{13}C isotopes, the sea and C_4 plants. ^{13}C/^{12}C ratios in seawater bicarbonate are higher than in atmospheric carbon dioxide. These differences are observed between the plants from the land and sea, as well as in the bone collagen of the animals that feed on these species. Thus human diets that include marine foods, C_4 plants, or the animals that ingest C_4 plants can be distinguished using stable carbon isotope ratios. Carbon isotope ratios are reported in d^{13}C values that generally become more positive (less negative) along the continuum from plants, to herbivores, and to carnivores in marine and terrestrial regimes. Terrestrial C_3 diets appear as δ^{13}C‰ values in collagen around –20. Marine or largely C_4 diets exhibit δ^{13}C‰ values in human bone collagen around –10 (Fig. 7.11).

On land, two distinct photosynthetic pathways produce distinct carbon isotope ratios among plant species. Maize and many other tropical plants (designated as C_4 species) utilize a photosynthetic pathway that efficiently metabolizes carbon dioxide by initial conversion to a four-carbon compound that incorporates more available ^{13}C. The C_3 plants, which are more common in temperate areas, produce a three-carbon compound (Fig. 7.11). Woody, round-leafed species are 95% of all plants and utilize C_3 photosynthesis. C_4 is a more efficient pathway for photosynthesis and is found in plants, grasses, sedges, and grains in drier, warmer regions. The carbon isotope ratios in the bone collagen of animals feeding on 3- or 4-carbon plants reflect these differences.

For example, people who eat corn have higher ratios of carbon isotopes in their bones. Changes in this isotope ratio in prehistoric bone can indicate when corn becomes an important component of the diet. Such studies have been done both in Mexico to ascertain when corn was first domesticated and in North America to record when this important staple first arrived. Analysis of carbon isotopes from human bone collagen in Mexico indicates that a heavy dependence on corn began around 4500 BC.

Most of the paleodiet work using carbon isotopes has focused on the organic collagen in bone. Carbon also is found in the mineral, or carbonate, portion of bone and tooth enamel and contains information on diet. Although there are potential problems with contamination, this information can provide additional insight on questions regarding diet and place of origin of the individual from whom the sample was taken.

Differences in stable carbon isotope ratios between the apatite and collagen compartments of bone in the same individual were first reported by Krueger and Sullivan in the mid-1980s. They proposed that consumer collagen carbon was

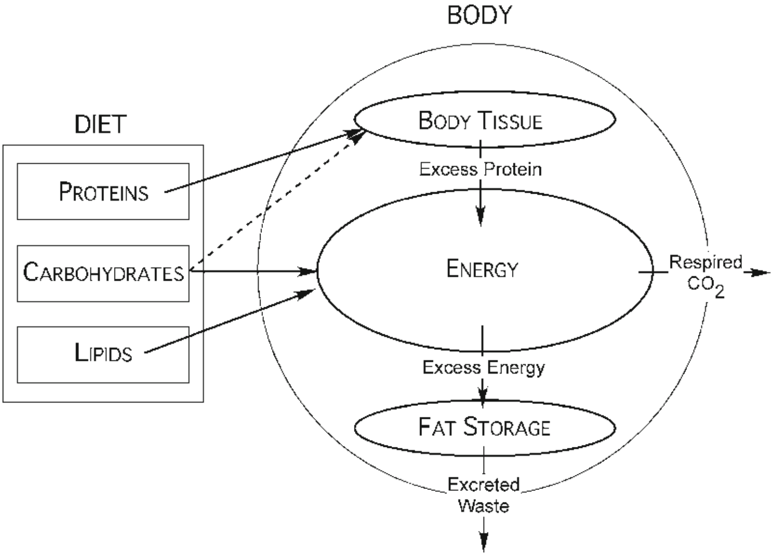

Fig. 7.10 A routing model for dietary carbon. Dietary protein carbon is normally used to build body tissues including collagen. Excess protein is burned as energy. Carbon in carbohydrates and lipids in the diet are used primarily for energy except when there is insufficient protein for maintaining body tissue. Carbohydrates and lipids are burned by the body to produce energy; waste products are CO_2 and H_2O. Excess energy is stored as fat. CO_2 is exhaled and wastes are excreted. Illustration courtesy of Tamsin O'Connell

derived from dietary protein and apatite from dietary energy sources (Fig. 7.10). They used this model to explain systematic differences in the isotopic composition of collagen and apatite of nonhuman herbivores vs. carnivores and omnivores, and marine vs. terrestrial human diets. In protein deficient diets, some of the carbon for collagen is taken from carbohydrates.

Later, controlled diet experiments with rodents confirmed their model, demonstrating that carbon isotopes in collagen reflected the protein portion of the diet, while apatite carbon reflected the isotopic composition of the total diet. These experiments showed that when the protein and bulk diet have the same $\delta^{13}C$ values, collagen is enriched by 5.0‰, and apatite is enriched by 9.4‰ relative to the total diet, and the apatite-collagen spacing is 4.4‰. In these experiments, the enrichment factor for apatite relative to the bulk diet was constant, regardless of the isotopic composition of the dietary components (proteins, fats, and carbohydrates). However, consumer collagen-diet $\delta^{13}C$ spacing values could be systematically varied by changing the $\delta^{13}C$ value of dietary protein relative to that of the bulk diet, because more than half the carbon in collagen was derived from dietary protein. They determined that the difference between whole diet and collagen $\delta^{13}C$ values is greater when the protein component of the diet is enriched in $\delta^{13}C$ compared to the bulk diet; diet to collagen spacing is less when the protein component is less enriched compared to the bulk diet.

The results of these experiments permit more detailed reconstruction of the isotopic composition of prehistoric human diets. The bulk diet δ^{13}C value can be reconstructed from the apatite δ^{13}C value minus 9.4‰, and that of dietary protein can be reconstructed from the apatite-collagen difference ($\delta^{13}C_{\text{ap-coll}}$). Specifically, a difference of 4.4‰ occurs when the protein and bulk diet have the same δ^{13}C value. A spacing of less than 4.4‰ indicates that dietary protein is isotopically enriched relative to whole diet. If the spacing is greater than 4.4‰, then dietary protein is isotopically lighter than whole diet.

Marine foods, being rich in protein, will contribute disproportionately to the amino acids in collagen compared to terrestrial plants. Moreover, being enriched in ^{13}C, marine proteins will disproportionately increase the collagen δ^{13}C values relative to the bulk diet, and relative to apatite δ^{13}C. In marine contexts with no C_4 plants, protein comes from mainly from ^{13}C-enriched marine animal resources, while carbohydrates and some proteins come from ^{13}C-depleted C_3 plants and C_3-feeding animals. Because the marine protein source is more enriched in the heavy carbon isotope, the diet to collagen spacing ($\Delta^{13}C_{\text{diet-coll}}$) should be greater than 5‰, and collagen to carbonate spacing ($\Delta^{13}C_{\text{diet-coll}}$) should be less than 4.4‰. Because the marine protein source is more enriched in ^{15}N, collagen δ^{15}N values should also be high. In a coastal environment lacking C_4 plants, a positive correlation should exist between collagen δ^{13}C and δ^{15}N, and a negative correlation should occur between δ^{15}N and $\Delta^{13}C_{\text{diet-coll}}$. In terrestrial high latitude diets, the entire foodweb is based on ^{13}C-depleted C_3 plants, so the bulk diet and dietary protein should have very similar δ^{13}C values. The diet-collagen spacing should be 5‰ and the apatite-collagen spacing at least 4.4‰.

7.2.2 *Nitrogen Isotopes*

Nitrogen isotope ratios are also of interest with regard to past diet. Natural δ^{15}N levels in biological materials typically range from –5‰ to +10‰ (Fig. 7.11). Variations in nitrogen isotope ratios are largely due to the role of *leguminous plants* in diet and the *trophic level* (position in the food chain) of the organism. Atmospheric nitrogen ($\delta^{15}N = 0$‰) is isotopically lighter than plant tissues; values in soil tend to be even higher. Non-nitrogen-fixing plants, which derive all of their nitrogen from soil nitrates, can thus be expected to be isotopically heavier than nitrogen-fixing plants, which derive some of their nitrogen directly from the atmosphere.

Grazing animals show δ^{15}N enrichment relative to the plants they consume; predators show further δ^{15}N enrichment relative to their prey species. Thus stable nitrogen isotopes tend to reflect trophic level in the food chain. In one sense, nitrogen isotopes reflect the proportion of animal protein in the diet. Non-nitrogen-fixing plants, which derive their nitrogen from the soil, are isotopically heavier than nitrogen-fixing plants, which derive some of their nitrogen directly from the atmosphere.

Consumers of terrestrial foods generally have bone collagen d^{15}N values of 10‰ or less, while people who eat a great deal of seafood may have values up to 20‰.

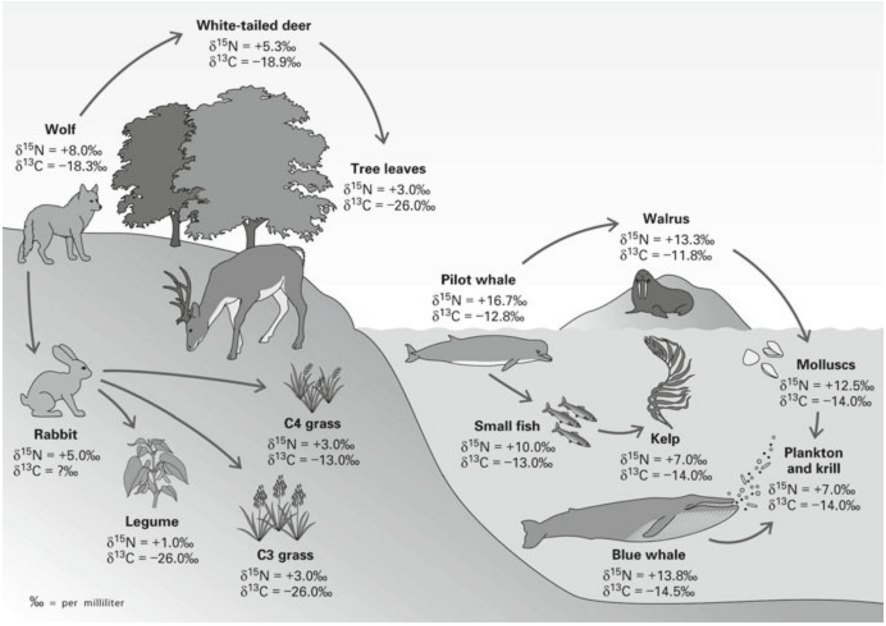

Fig. 7.11 Carbon and nitrogen isotopes in terrestrial and marine food chains. Note that ratios are generally higher in the marine system

In arid areas, where rainfall is less than about 400 mm per annum, terrestrial systems, too, may yield elevated d^{15}N.

Carbon and nitrogen isotope analyses today are a routine part of the study of human skeletal remains. They are usually calculated along with radiocarbon measurements at dating laboratories. There are other isotopes that may also be of interest in the study of diet such as hydrogen and sulfur, but these are less well understood.

There are other methods for investigating past diet as well and our first example discussed below illustrated one of them – the use of antigen–antibody reactions. This is a very special case where the preservation of unusual human remains makes possible the preservation of proteins that reveal evidence for cannibalism.

7.2.3 Arizona Cannibals

Material: Coprolites (human feces)
Instrumentation: GC/MS
Application: Diet
Place: Colorado
Time Period: Anasazi, AD *1100.*
Question: Was cannibalism practiced in the ancient Southwestern US?

Key Reference

Marlar, R.A., B.L. Leonard, B.R. Billman, P.M. Lambert, J.E. Marlar. 2000. Biochemical evidence of cannibalism at a prehistoric Puebloan site in southwestern Colorado. *Nature* 407: 25–26.

Cannibalism is an emotionally charged topic. Because of strict cultural taboos against cannibalism, many people do not want to believe it was practiced in the past in spite of the fact that there are a number of historically documented examples from various places around the globe.

There are also a number of examples, often controversial as well, in archaeology from the Paleolithic to the recent past. At the cave of Krapina in Yugoslavia, the bones of at least 13 human individuals were found mixed with those of various herbivores and other animals. The human bones had been burned, split to extract marrow, and treated just like the bones of the animals that provided the meals for the inhabitants of the site. Such practices may represent rituals of consecration of the dead or simply individuals from enemy groups that were added to the larder is unclear. On the other hand, it has also been argued that these bones may have been accidentally burned and broken by later inhabitants the sites. The Aztecs of ancient Mexico were reported by the Spanish conquistadores to have killed, butchered, and eaten thousands of their enemies and sacrificial victims (Fig. 7.12). These reports have been called into question as possibly exaggerated by the conquering Spanish, but the evidence is incontrovertible. Many fragments of small, broken, and weathered human bones have been found in temple precinct of the Aztec capital.

Fig. 7.12 Aztec illustration of the extraction of the heart of a sacrificial victim atop a pyramid. The Spanish reported that the bodies of these victims were then thrown down the steps of the pyramid to be butchered and distributed to the populace

Another example of this debate about cannibalism comes from the southwestern US. A recent book entitled Man Corn: *Cannibalism and Violence in the Prehistoric American Southwest* by Christy and Jacqueline Turner has stirred great controversy. The Turners examined the skeletal remains from 76 sites in the prehistoric southwest and find indications of cannibalism at more than 40. Many people refused to believe the vivid evidence that was presented, preferring instead a politically correct view of the Pueblo Indians as peaceful and ecological. In fact, a growing body of data suggests warfare and violence as rife in this region in the past.

An example of the evidence for cannibalism comes from an Anasazi pueblo ruin, designated as Mancos 5MTUMR-2346, in southwestern Colorado. Analysis of the skeletal remains by Tim White revealed that nearly thirty men, women, and children were butchered and cooked there around AD 1100. The remains of these individuals were scattered and discarded in various rooms of the pueblo. Comparison of the human remains with those of animals that were eaten indicates skinning, dismembering, cooking, and fracturing of the human bones.

In spite of the evidence, detractors have argued that there are other possible explanations for the appearance and location of the bones. Various arguments have been proposed from disturbance of earlier burials to the killing and dismemberment of witches in Pueblo society. The thorny question was whether these individuals had really been eaten or not.

The science of archaeology strikes once again. A group of investigators, lead by Brian Billman, searched for the answer to this question. At another site where the skeletal material indicated cannibalism had taken place, a human coprolite (preserved feces) was found in an old fireplace. The coprolite apparently resulted from a meal of just meat, as no plant remains were observed in the contents. A series of biomolecular tests were undertaken to identify the contents. A distinctive protein, human myoglobin, was found in the coprolite. Myoglobin is a protein found only in skeletal and cardiac muscles, where it carries oxygen to the energy-producing apparatus within each cell. The presence of the myoglobin proved that human tissue had been eaten.

Figure 7.13 shows the results of the analysis using ELIAS assay testing. Enzyme-linked immunosorbent assay (ELISA) is a biochemical technique used mainly in immunology to detect the presence of an antibody or an antigen in a sample. The ELISA has been used as a diagnostic tool in medicine and plant pathology, as well as archaeology. An unknown amount of antigen is affixed to a surface. A specific antibody is then washed over that surface to be able to bind to the antigen. This antibody is linked to an enzyme, and in the final step a substance is added that the enzyme can convert to some detectable signal. Dose–response curves demonstrate the reaction between sample and antibodies for animal myoglobin from a number of species in the area and human myglobin. The myoglobin samples were assayed by serial log-dilution. Each species of myoglobin was purified by ion-exchange chromatography after extraction from muscle tissue. The other species tested were bison, deer, elk, rabbit, turkey, rat, canine, feline, and pronghorn antelope. The human myoglobin in the feces from Mancos is very distinct from other species of animals.

The question still remains as to why cannibalism was practiced. Several suggestions have been made. Cannibalism might have been intended to terrorize enemies,

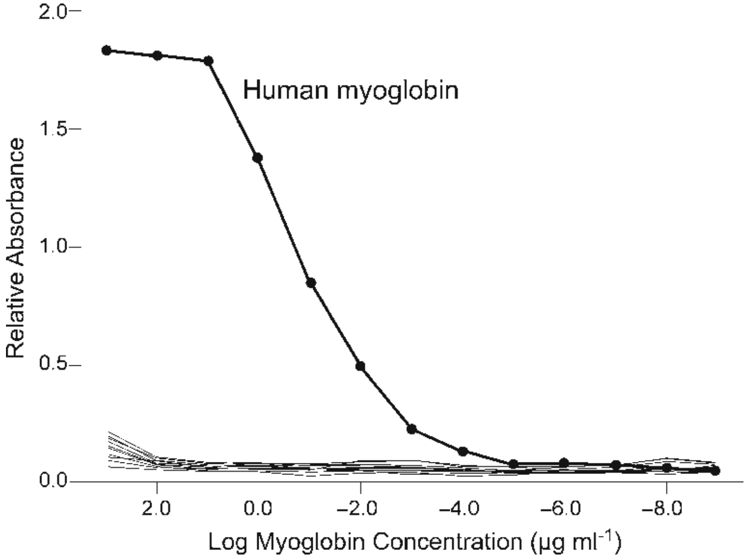

Fig. 7.13 Myoglobin concentration in various modern species, indicating the much higher ratio present in humans. The cluster of lines at the bottom of the graph come from eight modern species: bison, deer, elk, rabbit, turkey, rat, canine, feline, and pronghorn antelope

or perhaps was borrowed as a ritual practice from Mexico. Another idea suggests hunger brought on by periods of starvation during from a long drought. An invasion by violent outsiders might also explain the practice. The investigators, however, proposed that cannibalism was associated with violent conflict between Anasazi communities in the mid-1100s, concomitant with a period of drought. They note a sharp increase in evidence of cannibalism between 1130 and 1150, followed in each case by site abandonment of the site, then a decrease in the practice during the 1200s as rainfall increased.

There are in fact four kinds of cannibalism recorded in archaeological remains. These include survival cannibalism in cases of extreme starvation, ritualized, sacrifice-related cannibalism such as associated with the Aztec, reverential funerary cannibalism, and warfare-driven cannibalism, such as that seen among the Anasazi Indians. There is in fact evidence for cannibalism in almost every society and time period in prehistory.

7.2.4 Last Danish Hunters

Material: Bone
Instrumentation: Mass Spectrometer
Application: Diet
Place: Denmark
Time Period: Late Mesolithic – Early Neolithic 4000 BC

Question: How important was seafood in the diet of the Mesolithic hunter–gatherers of Denmark 6,000 years ago? Did diet change with the introduction of agriculture?

Key Reference

Tauber, H. 1981. δ^{13}C for dietary habits of prehistoric man in Denmark. Nature 292: 332–333.

Thirty years ago, descriptions of the hunting groups in southern Scandinavia around 5000 BC focused on the hunting of large animals as the primary means of obtaining food. Archaeological sites contained many bones from large terrestrial animals like elk and wild boar. These groups were thought to have been fairly small and mobile hunters. The fact that the larger sites were located on the coastlines and that fish bones were common at such sites was almost ignored. The discovery of burial grounds from this period, however, along with other evidence led to suggestions that these groups were more sedentary. Isotopic studies of the human bones in those graves led to other new insights and completely changed the understanding of how these "hunters" survived.

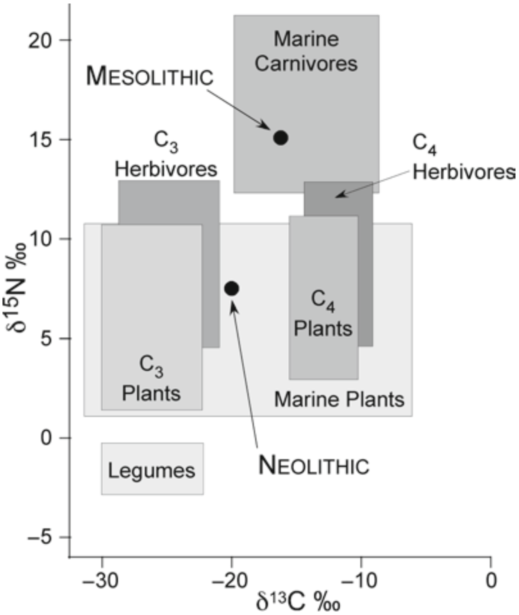

Fig. 7.14 A scatterplot of carbon and nitrogen isotopes. The boxes show expected values for different plant and animal species in nature. Species higher in the food chain are generally toward the top of the diagram; marine species are generally to the right in the diagram. Isotope ratios in the collagen of human bone from the Mesolithic and Neolithic of Denmark indicate that Neolithic farmers ate a much more terrestrial diet than the hunters of the Mesolithic

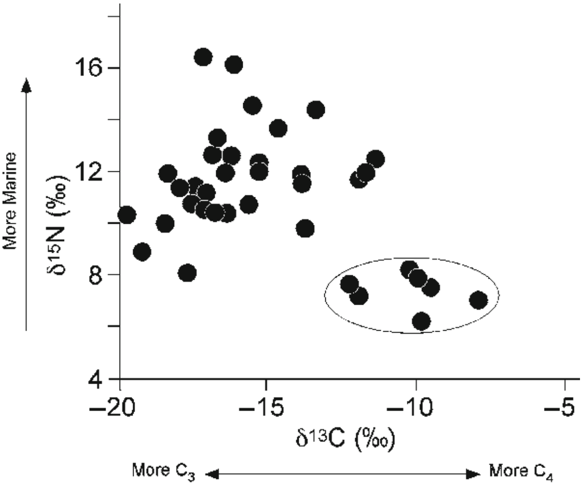

Fig. 7.15 Carbon and nitrogen isotope ratios on the burials from Cape Town, South Africa, the circled group appears to have a very different diet from the rest of the individuals

Measurement of carbon and nitrogen isotopes in the bone collagen of these burials provides substantial new information about diet. As we have noted earlier, marine animals exhibit carbon isotope ratio values ranging between –10 and –18 δ^{13}C. Human values less negative than –20‰ indicate marine foods in the diet, while more negative values are more closely related to the consumption of terrestrial plants and animals. There are no C4 plants available in northern Europe at this time. Terrestrial foods generally produce bone collagen δ^{15}N values of 10‰ or less, while people who eat a great deal of seafood may have ratios up to 20‰. Samples in which both δ^{13}C and δ^{15}N are more positive reflect marine foods in the diet.

Henrik Tauber of the National Museum of Denmark measured the carbon isotope ratio in the bones of skeletons from Vedbæk, along with a number of other burials from Scandinavia and Greenland (Fig. 7.14). The ratios from Vedbæk range from –13.4 to –15.3 δ^{13}C and are close to values for historical Eskimo skeletal material. Greenland Eskimo consumed marine foods extensively, perhaps as much as 70–90% of their diet, and a similar proportion of seafoods may have characterized the diet of the later Mesolithic. Saltwater fish, seals, porpoise, whales, and molluscs contributed a major part of the diet at Vedbæk. Measurement of a dog bone from the Vedbæk area gave a reading of –14.7 δ^{13}C, within the human range, suggesting a very similar diet for the canine. Neolithic burials in Denmark show a sharp decline in carbon isotope ratios, indicative of a decrease in the importance of seafood among the early agriculturalists.

7.2.5 Cape Town Slaves

Material: Human Tooth and Bone
Instrumentation: Light Isotope Mass Spectrometer

Application: Diet and Provenience
Place: Cape Town, South Africa
Time Period: Between 1750 and 1827
Questions: Were the individuals buried in the unknown graveyard in Cape Town slaves? Where did they come from?

Key Reference

Cox, Glenda, Judith Sealy, Carmel Schrire, and Alan Morris 2001 Stable carbon and nitrogen isotopic analyses of the underclass at the colonial Cape of Good Hope in the eighteenth and nineteenth centuries. World Archaeology 33(1):73–97.

Europeans from the Netherlands first settled at the Cape of Good Hope on the southern tip of Africa in 1652 to establish rest and repair station for ships sailing between northern Europe and the Far East. More than 60,000 slaves were brought to Cape Town, until a ban on the slave trade in 1808. Slaves were brought into the colony shortly after the initial settlement because more workers were needed for food production. The slaves were equally from Africa and Asia. Africans were brought from Madagascar and East Africa, and Asians from India, Sri Lanka and the Indonesian archipelago. African slaves usually worked as laborers; Indians, Indonesians and free blacks were craftsmen, artisans, builders, coachmen, and hawkers. Women worked as laundresses, wet nurses, and household servants.

In 1994, construction activities in the modern city of Cape Town exposed an old graveyard at Cobern Street with 63 graves and the skeletal remains from 121 individuals. The burial ground was largely in use between 1750 and 1827 and appears to have been informally used, as graves were irregularly placed and frequently disturbed by later burials in the cemetery. The informal treatment of the dead and the general lack of burial goods suggests that Cobern Street was the burial place of the slaves and free blacks in Cape Town society. Analysis of the upper arm strength of both males and females in the cemetery using the cross-section of the humerus indicated these individuals were manual laborers.

Carbon and nitrogen isotope analysis was carried out on the human remains from Cobern Street to learn about diet and ethnic affiliation. As discussed in Chap. 4, these methods can tell us about the consumption of marine vs. terrestrial foods, about the kind of plants being eaten, and about the importance of meat and fish in the diet. Fifty-three individuals were selected for study based on the completeness of the skeleton. The scientists wanted to sample the teeth, long bones, and ribs of each individual they studied. They argued that tooth dentine would represent the diets of these individuals during their youth. The spongy bone of the ribs was more recent and should reflect a diet consumed later in life. The hard, cortical bone of the femur takes longer to form and would represent an average value for the diet over the last 15–20 years of the individual's life. Comparison of the dentine from childhood with the bone from later life should provide information on changes in diet during the lifetime of these individuals.

A plot of nitrogen and carbon isotopes in the tooth dentine reveals two distinct groups (Fig. 7.15). Seven individuals separate as a group in the lower right of the

Fig. 7.16 The individuals with a different diet also exhibited a distinctive form of tooth modification characteristic of individuals from Mozambique. In this example the upper front incisors have been filed diagonally

cluster of points. The less negative values for $\delta^{13}C$ indicate a diet that included tropical plants such as maize, sorghum, and millet. These are C_4 plants. Photosynthesis in these plants produces more ^{13}C than C_3 plants which are temperate area species such as wheat, oats, or rice. Samples in which both $\delta^{13}C$ and $\delta^{15}N$ are more positive reflect marine foods in the childhood diet. Terrestrial foods generally produce bone collagen $\delta^{15}N$ values of 10‰ or less, while people who eat a great deal of seafood may have values up to 20‰.

The seven individuals in the small cluster have more positive $\delta^{13}C$ values and relatively low $\delta^{15}N$ ratios. This group was eating largely terrestrial, C_4 foods in childhood. Moreover, all seven of these individuals had similarly modified front teeth, flaked and filed to produce a pointed appearance (Fig. 7.17). This cultural practice is well known from Africa and was thought to enhance one's physical attractiveness. This pattern of modification is known to have been practiced in Mozambique. These seven distinctive individuals were very likely born in Mozambique and brought to Cape Town as slaves. On the other hand, four out of five of the Type C burials have very negative $\delta^{13}C$ values, and appear as outliers on the left-hand side of the graph. Their diets were based on C_3 plants from temperate environments.

The isotope data also make it possible to look at changes in diet during the lifetime of these individuals. Three groups can be distinguished. Fifteen individuals showed a substantial change in isotope ratios between childhood and death, including five of the seven individuals in the small cluster described above. These individuals clearly switched to a diet based on C_3 food sources after childhood. A second group of 26 burials showed no changes in diet over time. These individuals are likely locally born in the area and exhibit no significant changes in life history. A third group was distinct in several ways. These individuals had been buried on their right side in a shroud, without a coffin or any grave goods. All of the individuals buried in this manner were placed in the grave so that they were facing a local landmark known as Signal Hill. This hill was an important place for the Muslim population of Cape Town. Finally these individuals exhibit isotope ratios in the childhood dentine that indicate they grew up in a temperate environment with a C_3-based diet (such as rice) and small quantities of some C_4 foods. These characteristics – simple burial, orientation toward an Islamic landmark, and the isotope ratios – suggest that these individuals were Muslims when they died and that they may well have come from South Asia or Indonesia.

Even more can be learned from a combination of the isotope data and the archaeological context of the burials. The authors of the original study (Cox et al. 2001) nicely describe these conclusions. "Burial 3, probably a locally born felon, still carries a shackle on his leg; Burial 61, a young woman, has two valuable silver objects such as were unlikely to have been legally owned by a poor person. Another woman (Burial 52) was born in tropical Africa according to her isotopic profile and modified teeth. She died after a short while at the Cape, and was buried in a hand-me-down British military jacket. And, finally, there is the little family in Burial 20, of two newly landed African slaves and a child, who may have died on board ship or shortly after arrival."

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Chapter 8
Provenience and Provenance

Contents

8.1 Provenience and Provenance

An essential term in archaeology is provenience. Provenience has two meanings: the place of discovery and the place of origin. The provenience of an artifact can be the place where it was found in excavations – that is a very important piece of information. Artifacts and other archaeological objects with an unknown provenience provide very little information for learning about the past. Provenience of discovery implies context, meaning that there is additional information available about the object of interest. Provenience also means the place of origin, or source, the place from where an artifact, object, or person came; the term might refer to the place of manufacture. Thus, one should be clear about the precise usage.

The terms *provenience* and *provenance* are largely synonymous, but with different contexts of use. Both spellings mean the place of origin, or source, the place from where an artifact, object, or person came. Your own provenience, for example, would be the place where you were born. Knowing the place of origin of items is important information for understanding exchange and interaction among past human groups. The term provenance is used in Britain and much of the Old World to mean the place of origin of archaeological materials. The word is also commonly used in the fields of art history and classical archaeology everywhere, again meaning source or origin and history. One way to think about the terms comes from an anonymous comment on the internet: “provenience is an artifact’s birthplace; provenance is an artifact’s resume.

T.D. Price and J.H. Burton, *An Introduction to Archaeological Chemistry*,
DOI 10.1007/978-1-4419-6376-5_8,

The term provenience is used in the Americas by most archaeologists and archaeological chemists. The term provenience is used by archaeological chemists, and in this book, to refer to the place of origin for artifacts and other archaeological materials, including human and animal remains. The provenience of a piece of obsidian would be its volcanic source, not just the archaeological context from which it was recovered. Knowing the place of origin of items is important information for understanding exchange and interaction among past human groups, as well as for establishing the authenticity of an object.

An important part of studying the origin of archaeological materials involves the application of the *provenience postulate* – a rule that states that chemical differences within a single source of material must be less than the differences between two or more sources of the material, if they are to be distinguished. In principle, this means that if a source is chemically distinct, pieces removed some distance from their source share that same chemistry and can be identified. That is to say, the provenience or place of origin of the piece can be determined. That sounds rather simplistic, and perhaps it is. However, the strength of this rule is that we can use chemical differences among geological sources to isolate these different places. This principle has been applied to a variety of archaeological materials including pottery, turquoise, tin, and many others.

The validity of the provenience postulate must be established on a case-by-case basis. Hypothetical examples of the provenience postulate may help to illustrate this (Fig. 8.1a–d).

Because the provenience postulate can, and normally does, fail using measurements of individual elements – which are usually abundances such as percent iron or parts-per-million (ppm) niobium – archaeometrists often employ multielement analytical techniques such as neutron activation analyses (NAA), which can provide sensitive measurements for most elements. NAA studies of archaeological samples commonly measure more than two-dozen elements, providing enhanced ability to distinguish materials that likely would not be distinguished by single element analyses. Archaeometrists also employ a variety of multivariate statistical methods to reveal distinguishing combinations of elements that might otherwise be unnoticed. Frequently, after such statistical analyses, the data can be "reduced" such that much of the difference between groups can be revealed by examining just a few elements, although exactly which specific elements might have been unknown prior to analysis.

An ideal provenience study would involve a natural material, the composition of which remains unaltered after extraction, only a small number of possible sources, an adequate number of samples from each source to adequately assess their compositional variation, and one or more combinations of elements or compounds that adequately distinguish the sources. Just as there is no proverbial "spherical cow," such ideal materials are almost as rare.

Obsidian comes as close as any material can to this situation. It is restricted to relatively few areas of young volcanic rocks. Humans do not alter obsidian artifacts compositionally. And many known obsidian sources in different parts of the world have been chemically distinguished (Fig. 8.2). Moreover, we now have large databases for obsidian sources against which artifact data can be compared, without requiring further source characterization, and portable, nondestructive methods have been developed so that rapid characterization can be made of artifacts in museum collections.

For most other raw materials, the number of sources cannot be so easily constrained. Even for obsidian, new sources are frequently being discovered that were

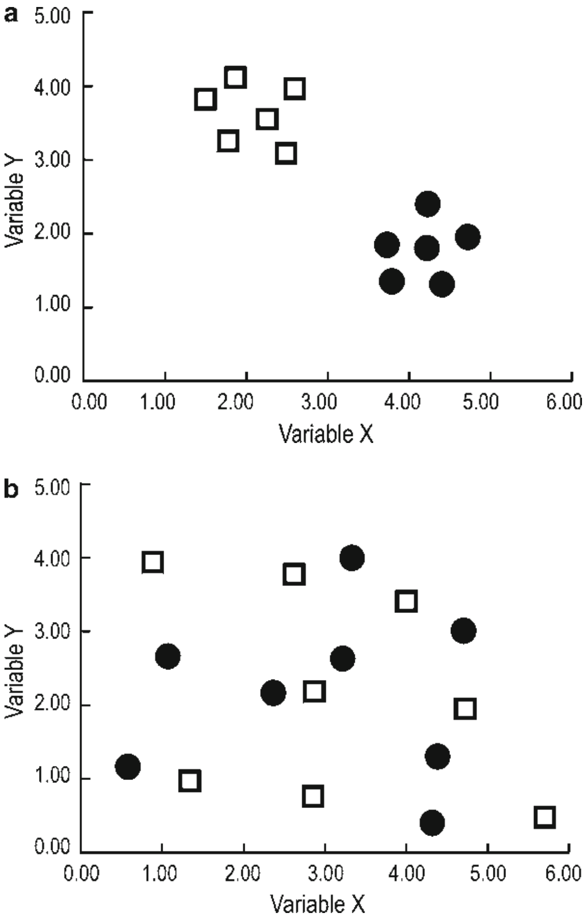

Fig. 8.1 (**a**) Provenience postulate is true for both variable x (*horizontal axis*) and for variable y (*vertical axis*). The variations, or range, within group A (*open squares*) and group B (*filled circles*) are small compared with the differences in the variables between the two groups. Thus, the two groups appear distinct. An unknown sample belonging to either group could thus be safely assigned to one or the other. (**b**) Provenience postulate is false for both variable x (*horizontal axis*) and for variable y (*vertical axis*). The variations, or range, within group A (*open squares*) and group B (*filled circles*) are both greater than the differences in the variables between the two groups. Thus the two groups are not distinct and an unknown sample could not be safely assigned to either.

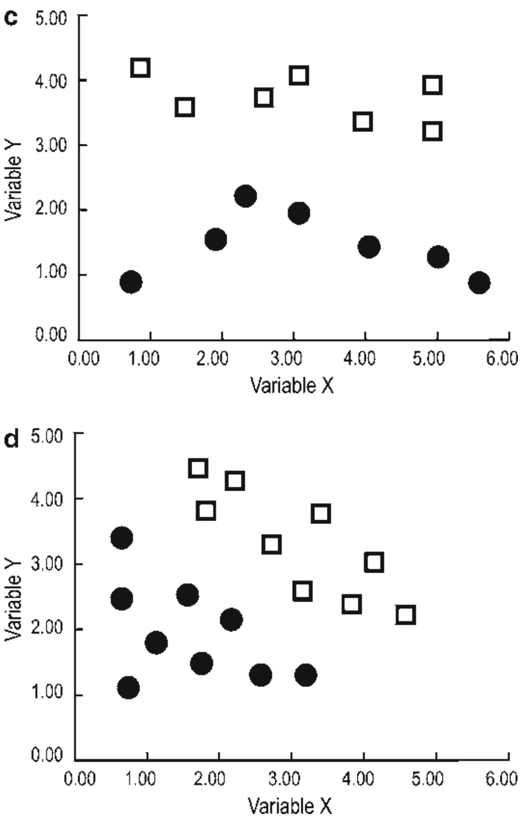

Fig. 8.1 (continued) (**c**) Provenience postulate is false for variable *x* (*horizontal axis*) but true for variable *y* (*vertical axis*) – and thus true overall. The variations in variable *x* for each group are large compared with the difference between the groups along the *x*-axis, but variations in variable *y* are small compared with the difference between groups along the *y*-axis. Thus, the two groups are distinguishable; an unknown sample could be safely assigned. (**d**) Provenience postulate is true, even though it fails for each variable taken independently. Groups overlap in their values for both *x* and *y*, but can be distinguished when *x* and *y* are examined together. Thus, for a given value for *y*, group A (*open squares*) will have a distinctly higher value for *x* than group B (*filled circles*). Likewise, for a given value for *x*, group A will also have a distinctly higher value for *y*

unknown a decade ago. For common materials, such as chert, granite, basalt, and sandstone, potential sources are far too numerous to characterize. For these materials, an absolute provenience determination to a discrete location usually cannot be made. If we can constrain artifact origins to a small subset of possible sources, then we can possibly distinguish an artifact from some of these sources, but we must keep in mind that a "match," a failure to distinguish an artifact from a particular source, leaves open the possibility of attribution to a source that remains unknown or at least uncharacterized. Other lines of evidence (e.g., the discovery of a quarry or distribution maps of artifact abundances) might be needed to constrain the provenience more precisely.

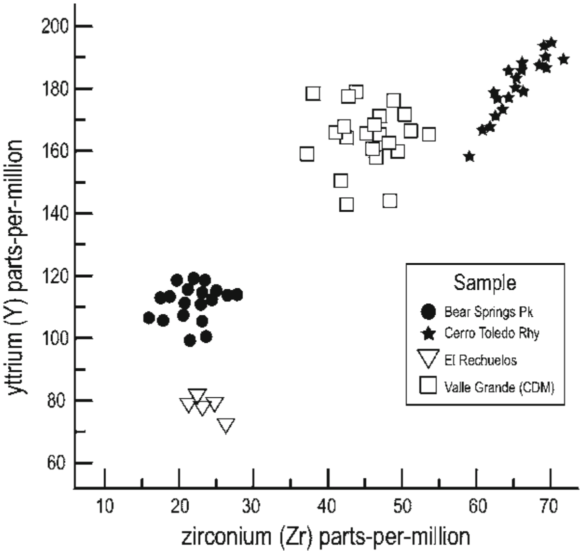

Fig. 8.2 Bivariate plot of zirconium (Zr) in parts-per-million on the *Y*-axis and yttrium (Y) in parts per million on the *x*-axis, showing that the two elements neatly resolve four obsidian sources in New Mexico

Ceramics are a major class of such materials that certainly do not have only a small number of discrete sources, yet archaeologists pursue provenience studies of ceramics through elemental analyses with great vigor. Ceramics are made from geological materials, clay being an essential component, and clay is ubiquitously abundant. Archaeological ceramics are most frequently mixtures of clay and tempering materials, which can themselves be compositionally heterogeneous. Clay/temper ratios, as well as the selection of what clays and tempers, may vary at the choice of individual potters, who are ultimately the “sources” of pots. Potters can also use different mixtures for parts of the same vessel, according to desired performance attributes and may even mix multiple clays (e.g., potters in Paquime, Mexico sometimes use as many as seven clays in the same vessel). Thus ceramics should not be approached as a geological material, but as a cultural product, the composition of which might vary geographically, but this is not the only compositional factor.

Thus ceramic studies tend to have a regional focus in the hopes that differences can be found between the ceramics made by different people. Although some labs include regional clay samples in their analyses for comparison, most ceramic studies necessarily take an empirical approach in ceramic samples, as sets, sometimes with known provenience, are compared with other sets to see if they can be distinguished.

Elemental analyses have been applied to an enormous variety of materials, including other cultural products such as glass and metals and biological materials such as maize cobs and human teeth. Although sometimes regional differences can be found, elemental variation in other technological products and biological tissues can be produced in many ways other than just geography, tending to produce highly variable data that challenge validation of the provenience postulate. For these cases, archaeometrists are currently exploring isotopic approaches with more success.

In comparison to multielement studies, heavy isotope ratio studies for provenience studies have a disadvantage in that there are not normally many elements with useful isotope systems, and they do not have many variables that can be used (e.g., $^{87}Sr/^{86}Sr$ for strontium and $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ for lead). They have a big advantage for some materials; however, neither biological processes nor technological processes significantly affect them except for mixing of components from different sources. For example, $^{87}Sr/^{86}Sr$ is abundant in biological tissues and does not change on going from the soil through the diet into calcified tissues. Lead isotope ratios likewise reflect the ratio of ores used to make bronze, although mixing or recycling of materials from more than one source can complicate the analysis.

Light isotope ratios (i.e., $^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{15}N/^{14}N$) also have geographic variation that is being used in provenience studies – for example, strongly elevated ^{13}C in animal tissues implies the availability of certain grasses in the diet, which in turn might imply a specific ecological zone.

Because animal teeth incorporate carbon and oxygen isotopes over a period of many months, multiple samples taken along the long axis of a tooth reflect different times and thus provide a record of animal mobility, although they might not indicate a specific provenience. In general, there are many causes of variation in stable isotopes; separating geographic variation from others is currently an active area of research.

There are a number of case studies in this chapter because we believe that provenience is one of the more interesting and important questions in archaeological research. The examples deal with a range of provenience issues and a variety of materials. Jim Burton details his early experiences in archaeology, searching for the source of an unusual ceramic temper in Ecuador. A second example comes from the Laboratory for Archaeological Chemistry in Madison, Wisconsin, and the work of a graduate student investigating the origin of lead glazes on Mexican ceramics. Elemental composition is used in another study to distinguish the sources of copper at early historical sites. Metal in the form of copper is known from before European contact in North America, making it harder to distinguish the introduction of European copper.

Stone in the form of obsidian is the focus of the next case study. Obsidian, a dark volcanic glass, is a rare and prized material for making tools in prehistory. Obsidian was traded over long distances, and determination of the sources of these pieces helps us to understand the nature of exchange and interaction in the ancient Near East. Ceramics are also the target of NAA and provenience studies. An example from Pinson Mounds in Tennessee provides a cautionary tale about interpreting the results of such analyses and the role of other methods of investigation in better understanding the evidence.

Finally, two examples from Mexico document the investigation of place of origin in prehistoric humans. The first from the site of Teotihuacán, outside modern Mexico City, documents a high rate of migration into this ancient city as well as evidence for the nonlocal origin of many sacrificial victims. The second example comes from the Maya area and the site of Copan, where the remains of an early ruler were studied in depth to help identify this individual and his place of birth.

8.1.1 Ecuadorian Pottery

Material: Pottery
Instrumentation: Petrographic microscope, electron microscope
Application: Provenience
Question: Where is the pottery come from? With whom did the Andean people have contact?
Place: Ecuador
Time period: 1000–0 BC

Key Reference

Bruhns, Karen O., James H. Burton, and George R. Miller. 1990. Excavations at Pirincay in the Paute Valley of Southern Ecuador, 1985–1988. *Antiquity* 64: 221–233.

Among the influences that led me, Jim Burton, to enter archaeometry as a profession was my study as a student of pottery from the Andes Mountains of southern Ecuador. Archaeologists working at a highland site called Cerro Narrío had found early pottery from the first millennium BC that was very different from all the known local Andean ceramics. Some of the differences in the so-called "Group X" were red designs offset by deep grooves from a buff background (Fig. 8.3). The clay of this pottery fires to a buff color and tempered with fine black sand has a "peppered" appearance. Karen Bruhns, an archaeologist working in the region, asked me for help with Group X. I was working at that time on how mixtures of sand and mud change under heat and pressure and had the tools and expertise to examine the sherds. I used petrographic "thin sections" at a thickness of 0.03 mm. Minerals in the thin section become transparent and can be identified by their optical properties under a microscope.

The petrographic microscope examination revealed that the black sand temper in the clay was not volcanic ash, but a glass, possibly obsidian particles. Because obsidian sources are relatively few, geographically restricted to the vicinity of modern

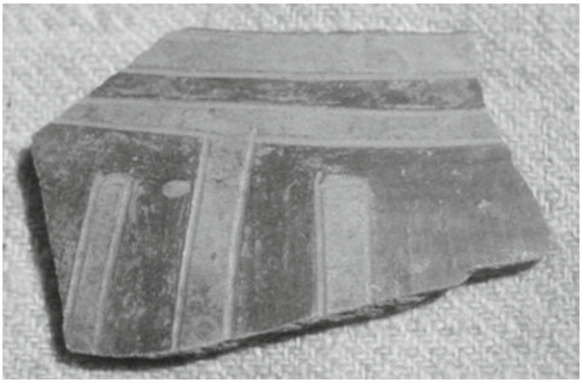

Fig. 8.3 Red-Banded Incised sherd from highland Ecuador

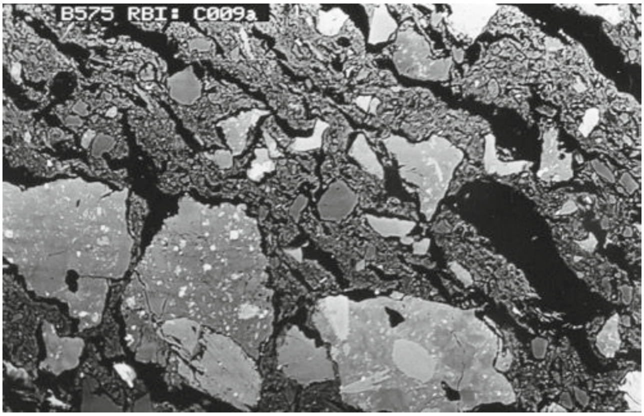

Fig. 8.4 Back-scattered electron (BSE) image of volcanic rock temper in a clay matrix in Andean RBI pottery. Each *shade* of *grey* is a different mineral

volcanoes, and often chemically distinguishable (see Sect. 8.1.4), it might be possible to determine the place of origin of the glass. But for this kind of analysis, a more sophisticated instrument, the electron microscope was needed.

With the greater magnification of the electron microscope (Fig. 8.4), I could see that the black glassy particles were not true obsidian but basaltic glass with abundant inclusions of the minerals pyroxene and olivine, not found in obsidian. Basaltic glass is more unusual. It might be easier to locate the source. Basaltic glass only lasts for a few million years in the ground, which suggested that the source might be an active volcano. Basalt is created at much higher temperatures than obsidian, which in the Andes suggests a deeper, more eastward origin than the obsidian sources.

The electron microscope also revealed microscopic particles of chloritoid in the clay, a metamorphic mineral characteristic of a particular "greenschist" grade of metamorphism. The temper in the pottery is undoubtedly of igneous origin, while the paste was derived from a metamorphic terrain. Because the temper and clay for pottery are normally collected close to where ceramics were made, the source of the pottery was likely near a young volcano erupting through a metamorphic terrain. There is one such place with basaltic lavas in a metamorphic terrain, called Sangay, a majestic 5,200 m (17,000′) volcanic cone in the upper Amazonian jungle (Fig. 8.5). Sangay is the most active volcano in Ecuador and the closest to the site of Cerro Narrio, about 90 km away (55 miles).

Some pieces of pottery similar to those from the site of Cerro Narrío had been found in the vicinity of Sangay, so I analyzed these sherds as well and found the same temper and paste. Bruhns and I then traveled to the eastern slopes of Sangay, which was actively erupting at the time. There we found identical RBI pottery as well as the glassy igneous rock used for the temper – indicating that this region was probably the source of the pottery found at Cerro Narrío.

Archaeological investigations at Cerro Narrío had revealed marine shell ornaments that documented a connection to the west between the Andean highland sites and the

Fig. 8.5 Map showing the location of Cerro Narrío and Sangay in Ecuador, and the likely river route connecting the two places

Pacific coast, some 90 km (60 miles) away, during the early first millennium B.C. (Fig. 8.5). Our pottery study demonstrated that these highland sites were also at that time in contact with groups to the east. More than 2,000 years ago, people in the Andes Mountains of Ecuador were in contact with people in the Upper Amazon drainage.

8.1.2 Lead Glaze on Mexican Ceramics

Material: Pottery
Instrumentation: Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
Application: Provenience: Where did the pottery come from?
Question: Can a common chelating agent, EDTA, be used to develop a non-destructive method of artifact characterization?
Place: Mexico/Spain
Time period: Sixteenth to eighteenth century AD

Key Reference

Reslewic, Susan, and James H. Burton. 2002. Measuring Lead Isotope Ratios in Majolica from New Spain Using a Nondestructive Technique. In *Archaeological Chemistry: Materials, Methods, and Meaning*, Kathryn A. Jakes (ed.), pp. 36–47. Washington, DC: American Chemical Society.

At the University of Wisconsin-Madison, in the archaeological chemistry class, students undertake a short analytical project, usually lasting for 3 of 4 weeks, involving relatively few samples, which can investigate some question of archaeological interest. An example of such a project was the study done by Susan Reslewic to look for a simple, nondestructive method for determining artifact provenience.

Burton recalled warnings about using Mexican lead-glazed pottery for storage of fruit juice due to potential lead poisoning. He suggested that Reslewic find out if ethylenediaminetetraacetic acid (EDTA), a chemical in fruit juice that has a powerful tendency to combine with lead and other metals, could be used to extract enough lead from such pottery to perform a lead isotope analysis. EDTA is a long, flexible molecule that has two pairs of oxygen atoms on each end and two nitrogen atoms in the middle, providing high potential for chemical bonding (Fig. 8.6). Because of this property, it is commonly sold as a detoxification aid, to aid against heart disease, and especially in cases of acute lead or mercury poisoning.

The use of tin and lead glazes on ceramics was probably discovered in the Middle Ages, somewhere around the western Mediterranean Sea. These ceramics were produced during the Renaissance and are characterized by an opaque, white glaze containing lead oxide, and were usually painted in several colors. Lead added to the glaze added color and luster to the finish of the ceramics, which are sometimes known as lusterware. The tin or lead glaze provides a brilliant white, opaque surface for painting. After the Spanish conquest of Mexico in AD 1521, the first lead

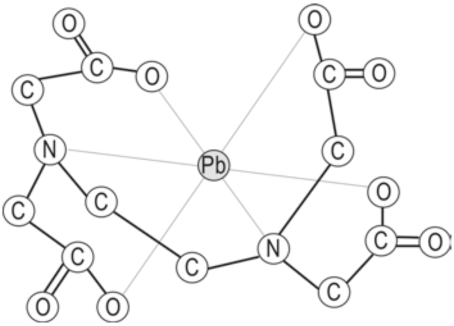

Fig. 8.6 EDTA, $(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$, is a long, flexible molecule that has two pairs of oxygen atoms on each end and two nitrogen atoms in the middle that gives it the ability to act like two hands with four fingers (O) and a thumb (N) on each, which it can use to grab lead and similar metal atoms. Because of this, it is commonly sold as a detoxification aid, to aid against heart disease and especially in cases of acute lead or mercury poisoning

glazed ceramics were brought to the New World on the ships from Spain, along with many other items. The generic term for such pottery is majolica ware.

By AD 1540, however, these pottery vessels were being produced in Mexico using locally available materials. Lead from the famous mines around San Luis Potosoi may have been one of the major ingredients. This pottery was then distributed through the region of the Spanish Conquest, including the American Southwest. In this region, the provenience of the majolica pottery is an important question regarding the age of the first settlements of the Spanish, known as presidios. A presidio was a fortified base established by the Spanish during the sixteenth century to protect against attacks of the local Native Americans. The earlier presidio settlements contain more of the European majolica ware than the later ones.

To investigate the question of lead glazes in the New World and the usefulness of ETDA for extracting lead samples from pottery, Reslewic and Burton obtained approximately six-dozen sherds of lead-glazed majolica from presidios along the northern borderlands of New Spain (northern Mexico and the Southwestern US) (Fig. 8.7). Where these sherds (fragments) pieces of pottery imported from Spain or were they copies of such pots manufactured in colonial Mexico?

Fig 8.7 Map of Northern New Spain and the Six Presidios from which sherds were sampled for the lead glaze study

Reslewic soaked the sherds overnight in an EDTA solution, which was prepared by adding powdered EDTA to ultrapure water, letting it saturate for several days, then diluting it 50% with more ultrapure water to give a solution of approximately 250 ppm EDTA, nearly pure water! Reslewic found that this solution easily extracted enough lead from the sherds to perform an accurate lead isotope ratio analysis, using the laboratory's ICP-MS. Moreover, after removing the sherds from the EDTA solution, they were rinsed with deionized water and showed no visible alteration whatsoever – the method was essentially nondestructive! Because the method is not destructive, it is much easier to gain permissions for artifact analyses, and sherds can be returned essentially unaltered after study. Isotope ratios from the presidio sherds compared well with the published lead isotope data for central Mexico, but not those for Spanish ore sources, indicating that most, if not all, of these pots were made on the New World, not the Old.

After the successful ceramic trial, for her project in the archaeological chemistry course, Janelle Scharon tested the EDTA method as well as DTPA, a similar chelating agent, on other materials including bronze, brass, and lead crystal glass. Chelating agents are used in chemistry to form multiple bonds with a single metal ion and can be used to mobilize metals such as in this example, removing lead from other metals and glass. Janelle likewise found that EDTA extracted sufficient material for lead isotope ratio measurements on these samples. Randall Law, another student in our department, then used the method on silver artifacts from the Indus Valley as part of his dissertation research. The nondestructive aspect of the method was essential for permissions for the chemical analysis of these valuable artifacts.

8.1.3 European Copper in North America

Material: Copper
Instrumentation: SLOWPOKE NAA Research Reactor
Application: Provenience
Question: Can one identify European trade copper at Native American sites?
Place: Great Lakes, US and Canada
Time period: Early colonial, 1600–1700 AD

Key References

Hancock, R.G.V., L.A. Pavlish, R.M. Farquhar, R. Salloum, W.A. Fox and G.C. Wilson. 1991. *Archaeometry* 33: 69–86.

Hancock, R.G.V., L.A. Pavlish, R.M. Farquhar and W.D. Finlayson. 1995. Analysis of copper-based metals from archaeological sites at Crawford Lake, south-central Ontario, Canada. In *Trade and Discovery: The Scientific Study of Artefacts from Post-medieval Europe and Beyond*, edited by Duncan R. Hook and David R.M. Gaimster British Museum Occasional Paper 109. pp. 283–297

Mauk, J.L., and R.G.V. Hancock. 1998. Trace element geochemistry of native copper from the White Pine Mine, Michigan (USA): Implications for sourcing artefacts. *Archaeometry* 40: 97–107.

Copper has been a valuable material in the New World since early human occupation nearly ten millennia ago. In addition to being an unusually bright and shiny material, it is malleable and could be easily shaped and cut into a variety of items from tools to animal effigies to body ornaments. By Hopewell times, 2,000 years ago, copper was widely distributed more than a thousand kilometers from known sources.

This extraordinarily long-distance trade coupled with the discovery in the 1840s of prehistoric copper mines around Lake Superior created an interest among archaeologists in trying to determine its geographic origins. Thus copper became one of the earliest materials examined by archaeological chemists for provenience studies.

However, it turns out that native copper is extraordinarily variable in composition even within single sources. Native copper normally contains a variable amount of other, nonmetallic minerals including copper sulfides, oxides, and silicates. These other minerals are not ductile but break upon cold-working the copper, which decreases the amounts of these minerals in varying amounts and thus alters the composition. Other elements that are soluble in an alloy solution with copper increase in abundance simply because the ratio of metal to nonmetal changes.

Although these variations can be estimated to some extent (e.g., by examining correlations among elements that increase or decrease together), copper is also problematic because not all sources are in bedrock. Most of the native copper in North America, indeed in the world, is from the region around Lake Superior, where it occurs in metamorphosed basalts but also as deposits left by glaciers, which can mix copper from multiple sources as well as transport it considerable distances from its bedrock origin.

To attempt to sort out some of these issues with sourcing native copper, Ron Hancock and colleagues at the SLOWPOKE nuclear reactor facility at the University of Toronto decided to use the multielement capability of neutron-activation analysis. They started with 43 samples from 19 collections of native copper and 23 samples of copper from archaeological contexts but which were believed to be reworked metal of European origin. Five other samples of copper from artifacts from known contexts but of unknown source were also included. To maximize the possibility that the provenience postulate would be true, they included 27 elements in their analytical procedure and got useful data for 22 of them. They also analyzed 14 subsamples from the same specimen to assess within sample variation and three modern copper samples for comparison.

They found, as others had, a huge variation in the native copper in most elements, some by orders of magnitude. Some samples were grouped into a “dirty” group with high levels of iron or arsenic, while others were “clean” with low levels, but these were not diagnostic enough to define a specific source. European copper was taken from American archaeological contexts and thus from unknown sources to begin with. European copper as a set, however, was conspicuously higher in several elements that can alloy with it: arsenic, antimony, silver, nickel, and especially gold. Gold values were so high in the European copper such that measurements had to be made in ppm instead of parts-per-billion, three orders of magnitude higher. Native American copper ranged from ten to a hundred parts-per-billion; European coppers ranged from about 10,000–100,000 parts per billion, making it possible to unambiguously identify European copper recovered from contact-period archaeological sites in North America.

As a follow up application to this study, Hancock and colleagues began analyzing copper from archaeological sites in southern Ontario. They used NAA to measure the chemical composition of 111 pieces from Iroquois sites dated approximately to AD 1250–1650, focusing on whether or not pre-European contact sites could be distinguished from contact sites. Although the absence of European metal does not necessarily imply the absence of contact, the presence of such indicates a post-contact date. Their analyses revealed the following: 12 of the pieces were native, 27 were European copper, 71 were European brass, and one was European zinc (Fig. 8.8). The European metals were found in seven of the sites, unambiguously assigning them to the "Protohistoric" period (AD 1500–1651).

They also noticed that many of the European metal pieces were chemically identical, leading to the idea that chemical groups, rather than individual metal pieces, could be used to assess the minimum number of metal trade vessels. The metal in European trade items was often more valuable as the metal itself instead of as an item such as a kettle. They surmised that as few as two to four copper pots and three brass kettles could have provided all the 39 pieces of European copper and brass.

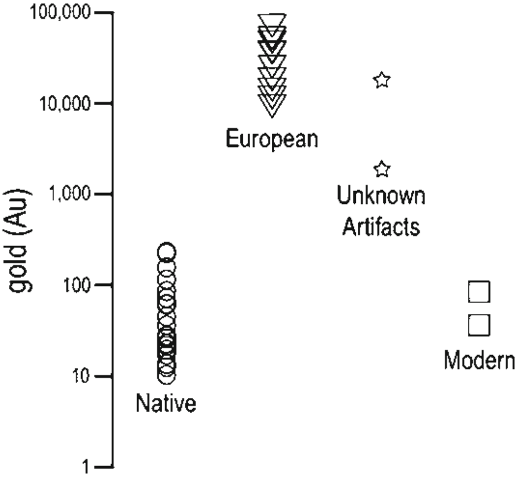

Fig. 8.8 Gold measurements in parts-per-billion plotted on a logarithmic scale for native American copper, modern copper, European copper, and pieces originally of unknown origin that appear to be European. The individual data points are shown as *open symbols*. Notice that European copper has nearly 10,000 times as much gold as American copper. Artifacts resemble European copper but not native American copper

8.1.4 Turkish Obsidian

Material: Stone – Obsidian
Instrumentation: NAA elemental analysis
Application: Provenience
Place: Turkey
Time period: Neolithic period, 10,000–6,000 BC
Questions: Where does the obsidian at archaeological sites in the ancient Near East come from? What does the provenience of obsidian tell us about trade and interaction in the ancient Near East?

Key Reference

Renfrew, Colin, and John Dixon. 1976. Obsidian in Western Asia: A Review. In Problems in *Economic and Social Archaeology*, edited by G. de G. Sieveking, I. H. Longworth and K. E. Wilson, pp. 137–150. Gerald Duckworth & Co., London, England.

Obsidian is a translucent, hard, black glass, produced by volcanoes. Molten silica sometimes flows out of a volcanic core and hardens into this stone, highly sought after by prehistoric makers of stone tools. Obsidian, as glass and flint, fractures easily and regularly, creating very sharp edges. Obsidian scalpels have been used in modern surgery because of their sharpness. Because of the demand for high quality obsidian in the past, it was often traded or exchanged over long distances, hundreds of kilometers or more.

Obsidian is also interesting because it is available from only a few places, limited by proximity to volcanic mountains and the chance of formation of a silica flow. Most sources for obsidian are known because of their small number and the unusual nature of this material. It is also possible to fingerprint different flows of obsidian through minor differences in the chemical composition of the material. This chemical signature is specific to one source and allows pieces found elsewhere to be traced to the places where they originated. The sources of obsidian in the Near East, the Aegean area, North America, Mexico, and elsewhere, have been studied using these methods.

Most of the obsidian in Near East comes from sources either in the mountains of Turkey (Anatolia) or in northern Iran (Armenia), both outside the Fertile Crescent. Information on the sources of obsidian found at early Neolithic sites provides data on both the direction and intensity of trade. Sites in the Levant generally obtained obsidian from Anatolia, while sites in the Zagros used Armenian material. The percentage of obsidian in the total flaked stone assemblage at these sites indicates that sites closest to the sources use a great deal of obsidian, while those furthest away have only a small amount available. At Jericho, for example, 700 km from the Anatolian sources, only about 1% of the stone tools are made from obsidian; a similar situation holds at Ali Kosh, 800 km distant from the Armenian sources.

Obsidian is a translucent, hard, black or dark green glass, produced during volcanic eruptions. Molten silica sometimes flows out of a volcanic core and hardens into this stone, which was highly sought by prehistoric makers of stone tools. Obsidian, like glass and flint, fractures easily and regularly, creating very sharp edges (Fig. 8.9).

Fig. 8.9 An obsidian core and two blades. This glass-like stone produces very sharp edges and was a highly desired raw material in prehistory

In the past, obsidian was often traded or exchanged over long distances, hundreds of kilometers or more. It is available from only a few sources, limited by proximity to volcanic terrain and the chance of formation of a silica flow. Most volcanic sources for obsidian are known because they are rare and the material is unusual.

It is possible to fingerprint different flows of obsidian through minor differences in the chemical composition of the material, allowing pieces found elsewhere to be traced to the places where they originated. This procedure relies on what is known as the Provenience Postulate in archaeology. In principle, this means that if a source is chemically distinct, pieces removed some distance from their source share that same chemistry and can be identified, and the provenience or place of origin of the piece can be determined. This principle has been applied to a variety of archaeological materials including pottery, turquoise, tin, and many others.

NAA is commonly used in studies of obsidian. The sources of obsidian in Southwest Asia, the Mediterranean, North America, Mexico, and elsewhere have been examined using NAA. Most of the obsidian in Southwest Asia comes from sources either in the mountains of Turkey or in northern Iran, both outside the Fertile Crescent. The graph below shows the results of the NAA measurement of the elements iron (Fe) and scandium (Sc) in obsidian in Southwest Asia (Fig. 8.10). Samples were also taken from the original sources. There are clear differences among most of the sources.

The identity of the sources of obsidian found at early Neolithic sites provides information on both the direction and intensity of trade (Fig. 8.11). Sites along Mediterranean coast generally obtained obsidian from Anatolia, while sites in the eastern part of the region used the Armenian material. The percentage of obsidian in the total flaked stone assemblage at these sites indicates that places closest to the sources used a great deal of obsidian, while those farthest away had only a small amount available. At Jericho, for example, 700 km (400 miles) from the Turkish sources, only about 1% of the stone tools were made from obsidian.

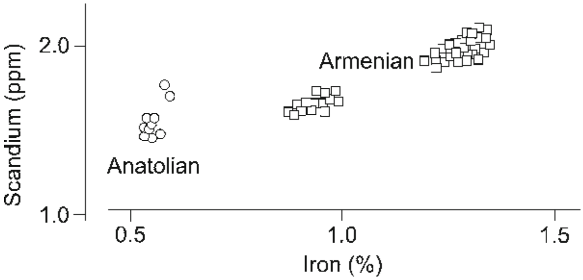

Fig. 8.10 Elemental characterization of obsidian sources in Armenia and Anatolia, Turkey. The graph plots the percent of iron vs. the parts per million (ppm) of scandium to show how the amounts of these two elements distinguish the sources of obsidian

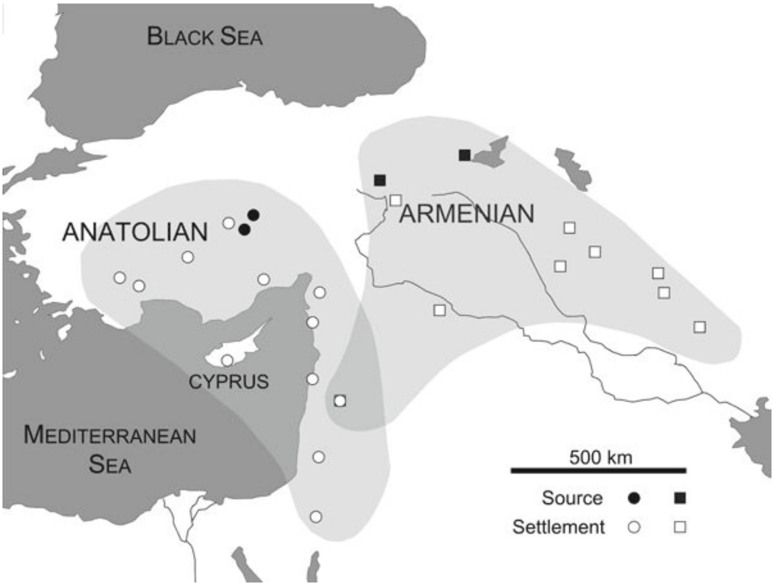

Fig. 8.11 The location of obsidian sources and samples in the early Neolithic of Southwest Asia. Major rivers shown on the map are the Nile, Tigris, and Euphrates. Two major sources are shown in Anatolia and two in Armenia. The distribution of obsidian from these sources is seen at settlements across the area. The distributions are largely separate with the exception of one site where obsidian from both source areas is found

8.1.5 Pinson Mounds Pottery

Material: Pottery
Instrumentation: Research reactor, petrographic microscope
Application: Provenience
Question: Where does the pottery come from?
Place: Southwestern Tennessee
Time period: Middle Woodland, 200 BC–AD *400*

Key References

Mainfort, R.C., Jr., Cogswell, J.W., O'Brien, M.J., Neff, H. & Glascock, M.D. 1997. Neutron-activation analysis of pottery from Pinson Mounds and nearby sites in western Tennessee: Local production vs. long-distance importation. *Midcontinent Journal of Archaeology* 22: 43–68.

Stoltman, J.B. & Mainfort, R.C., Jr. 2002. Minerals and elements: Using petrography to reconsider the findings of neutron activation in the compositional analysis of ceramics from Pinson Mounds, Tennessee. *Midcontinent Journal of Archaeology* 27: 1–33.

Pinson Mounds is a large Middle Woodland site in southwestern Tennessee dating to approximately AD 100–350, and the largest site from this time period in the south-eastern USA. The site covers 1.6 km² (400 acres) and contains 17 large earthen mounds (Fig. 8.12), a large, circular earthen enclosure more than 350 m in diameter, and habitation areas. Pinson Mounds belongs to the Hopewell Interaction Sphere that covers much of the Midwestern and Southeastern US in this time period. One of the characteristics of Hopewell is the movement of a variety of exotic materials including obsidian from the western US, copper from the Great Lakes region, galena from the Missouri, mica from western North Carolina, and shell from the Gulf of Mexico. All of these nonlocal materials and more are found at Pinson Mounds as well, documenting participation in the Hopewell exchange network.

Tens of thousands of ceramic sherds have been excavated at the site, documenting the extensive use of pottery for cooking, storage, and transport of materials. Some of the ceramics also have a distinctively nonlocal character seen in the decoration of the pottery and in the temper used in the ceramic paste. Grit, bone, and limestone are used as temper in the ceramics with exotic decoration, and not in the clearly local

Fig. 8.12 Sauls' Mound at the site of Pinson Mounds, Tennessee, is the second highest prehistoric mound in the United States with a height of 22 m (72 ft)

pottery. The nearest limestone to Pinson Mounds is more than 100 km (60 miles) to the east. One of the interesting questions concerning sites such as Pinson is whether the pottery with nonlocal decoration and temper is imported or produced locally as a copy of known exotic types.

NAA study of approximately 170 sherds from the site was undertaken to answer this question. This totally included 117 sherds and three fired clay samples from Pinson Mounds, 39 sherds from nearby contemporary sites, five samples of clay sources in the area, and six sherds from a Hopewell site in Georgia. Nineteen of the sherds from Pinson appeared to be nonlocal in style and temper. The research reactor at the University of Missouri was used to irradiate the samples and instruments measured the abundance of 33 elements in ppm in the pottery. Statistical analysis of the data from the NAA study was then undertaken. The authors of this study, Mainfort and colleagues, removed a number of samples with unusually high or low data values (known as outliers) from their study, arguing that these outliers can cause samples to appear more similar.

A scatterplot of the results, with outliers, removed, showed three groups of pottery based on their elemental composition (Fig. 8.13). The values used on the *X*- and *Y*-axes of the scatterplot are based on principle components, a technique to create summary statistics that combine the results from all of the elements used in the study. Each data point on the graph represents a sherd sample from Pinson Mounds. Thus, the *X*- and *Y*-axes use most of the results of the NAA measurements. The authors of the study then drew ovals around clusters of data points in the graph to distinguish three compositional groups. These ovals should encompass 90% of the data points in the group. These compositional groups should represent pottery

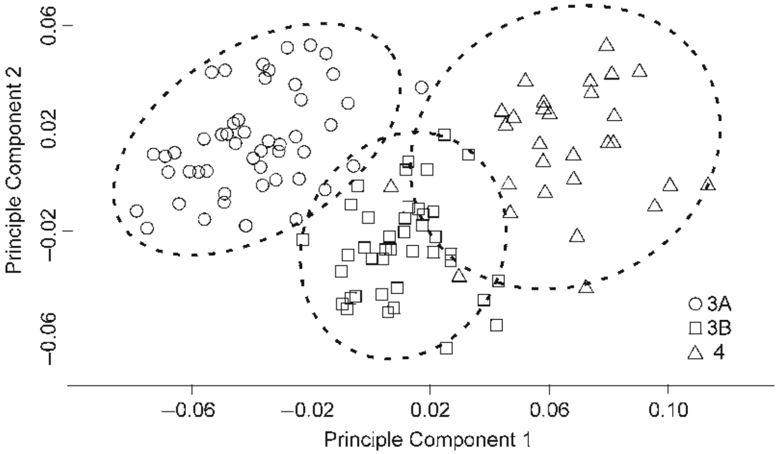

Fig. 8.13 Principle components scatterplot of sherds in the NAA study of Pinson Mounds. Three large clusters of sherds were identified (3A, AB, and 4), which are said to be all local in origin. These samples included pottery that had distinctively nonlocal decoration and temper

with somewhat different chemical composition. It should also be noted that there are still some data points outside the ovals on the graph.

The authors of the study did not so much attempt to determine the composition of exotic pottery from different places for comparison in their study, but rather relied on the provenience postulate. The provenience postulate states that chemical differences within a single source of material must be less than the differences between two or more sources of the material, if they are to be distinguished. Thus, Mainfort and colleagues in this study argue that chemical differences within the pottery from Pinson Mounds are large, and thus all of the pottery studied in their sample was produced locally. They found no chemical evidence for the long-distance importation of pottery.

A few years after the NAA study, Mainfort worked with James Stoltman using another technique to reexamine the question of pottery import at Pinson Mounds. Stoltman used ceramic petrography to study the physical composition of the sherds. Ceramic petrography involves the identification of minerals in the temper of the pottery and the measurement of the matrix of the sherd in terms of particle size. The percentages of silt-size inclusions plus the type, size, and percentage of mineral inclusions of sand size and larger were determined to characterize each sherd. This is very different information from the chemical composition recorded in NAA studies. The two approaches characterize ceramic compositions in distinctly different ways – one in terms of chemical elements, the other in terms of minerals and rocks – and are generally believed to provide complementary information.

Stoltman and Mainfort examined 39 specimens from Pinson (including four soil samples) and 13 other "local" sherds (most were also measured in the NAA study) using petrographic analysis (Fig. 8.14). The goal of this new study was to assess the difference of the two analytical techniques to discriminate locally produced from imported ceramic vessels at prehistoric sites.

The petrographic analysis resulted in the recognition of 25 sherds of local manufacture. The remaining 23 sherds were then divided into two groups: sherds with temper other than sand (11) and sherds with "non-local" decoration (12). Four of the 11 non-sand temper sherds were argued to be nonlocal because of exotic temper, either metamorphic rock or limestone. Neither type of stone is found within 50 km of Pinson Mounds. The remaining seven non-sand sherds have grog, bone, or organic tempers, which are not typical of ceramics from the region. Two sherds also have nonlocal decoration and unusual physical composition and are argued to be nonlocal. Another vessel in this group has a red surface finish that is very rare at Pinson Mounds. The remaining four of the non-sand temper sherds may be local as the evidence is uncertain. The 12 sherds with sand temper but nonlocal decoration have styles of decoration known from areas to the east, west, and south. Four of these sherds have nonlocal body composition and four contain locally available ingredients.

In summary, petrographic observations of the 48 Pinson-area sherds suggest that at least nine likely were nonlocal products (Fig. 8.15). The conclusion of the NAA study that "none of the analyzed sherds with nonlocal surface treatments was manufactured from nonlocal clays" was strongly contradicted, calling into question the effectiveness of NAA to address reliably issues of ceramic production and exchange.

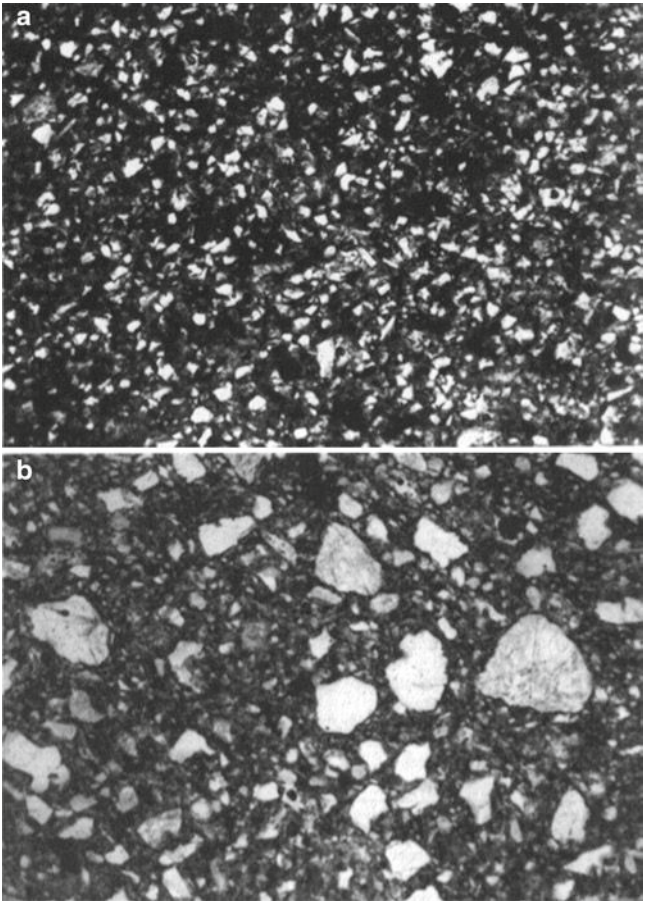

Fig. 8.14 Petrographic microscope 10× photographs of pottery thin sections from Pinson Mounds. (**a**) The typical local pottery known as Furrs Cordmarked. (**b**) A presumably exotic sherd found at Pinson Mounds with large quartz grains not seen in local ceramics

Stoltman and Mainfort discussed some of the problems with NAA and most chemical composition studies of pottery. Neutron activation does not identify the minerals in the pottery; it identifies only the chemical elements, and those elements that can occur in many different types of parent rock. Pottery is a human artifact whose chemicals derive from at least five sources: (1) the clay; (2) any added material such as temper; (3) the water used to moisten the clay, which may contain such soluble elements as sodium, potassium, calcium, magnesium, or iron; (4) any substance stored, cooked, or transported in the pot; and (5) diagenesis, the absorption of chemicals from the soil in which the sherds have lain buried for millennia. Because it identifies minerals, ceramic petrography can link the sherd to the bedrock geology from which the temper came; NAA, by contrast, cannot distinguish among the five sources that contributed the elements recorded.

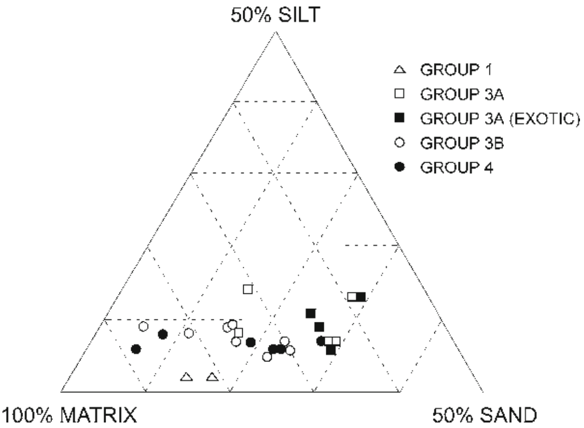

Fig. 8.15 A triangular diagram of the Neutron Activation Analysis groups of ceramics at Pinson Mounds. The diagram indicates the proportions of sand, silt, and matrix (largely clay) in 25 sherd examined by petrographic analysis and indicates that the NAA groups in fact do not separate the exotic examples

Such studies comparing different methods of analysis often reach conflicting results and point to the need for multiple lines of evidence for the arguments we seek to make in archaeology. NAA and ceramic petrography can complement one another when used judiciously, along with archaeological logic and an awareness of context and variation in the archaeological record.

8.1.6 Mexican Pyramid

Material: Tooth enamel
Instrumentation: Mass spectrometer
Application: Provenience
Place: Mexico
Time period: Classic Teotihuacan, 150 BC–*600* AD
Question: Where did the inhabitants of the ancient city of Teotihuacan in Mexico come from? Where did they get the victims who were sacrificed in their temples?

Key References

Price, T. D., L. Manzanilla, and W.D. Middleton. 2000. Immigration and the Ancient City of Teotihuacan in Mexico: A study using strontium isotopes ratios in human bone and teeth. *Journal of Archaeological Science* 27:903–913.

Price, T.D., J. Burton, L.E. Wright, C.D. White, and F. Longstaffe. 2007. Victims of Sacrifice: Isotopic Evidence for Place of Origin. In *New Perspectives on Human Sacrifice and Ritual Body*

Treatments in Ancient Maya Society, V. Tiesler & A. Cucina (eds), pp. 263–292. London: Springer Publishers.

White, C.D., T.D. Price, and F.J. Longstaffe. 2007. Residential histories of the human *sacrifices at the Moon Pyramid: evidence from oxygen and strontium isotopes. Ancient Mesoamerica* 18:159–172.

The ancient city of Teotihuacan is located in the Central Highlands of Mexico, approximately 50 km northeast of modern Mexico City. Teotihuacán – the spectacular "city of the gods" – was named to the UNESCO list of World Heritage Sites in 1987 and is protected in Mexico by presidential decree. The original city was about approximately 10 sq. miles in area, but the center of the protected archaeological zone today covers about 1 sq. mile today and includes more than 5,000 structures.

Teotihuacan was one of the most complex, urban developments in the prehispanic New World. During the First Intermediate Period (150 BC–0 AD), a major population center began to develop here. The city grew very quickly in the centuries after 0 BC, and this rapid increase must have involved immigration into the city. At its maximum, population numbers are estimated at more than 125,000 people. There are a number of distinctive areas in the planned city, including pyramids, palaces, ceremonial precincts, major avenues, administrative areas, residential compounds, craft workshops, exchange areas, avenues, tunnels, two canalized rivers, and ceremonial caves (Fig. 8.16).

Our previous studies of strontium isotopes at Teotihuacan in the Central Highlands of Mexico compared burials from several different areas in the ancient city (Fig. 8.17), including the Barrio de los Comerciantes, the Oaxaca Barrio, Oztoyahualco, and Cuevas de las Varillas and del Pirul. The Barrio de los Comerciantes,

Fig. 8.16 The Pyramid of the Moon at the site of Teotihuacán in Mexico

or the Merchant's Compound, is an area of the city with architecture and artifacts characteristic of the Gulf Coast region. Individuals buried in the Oaxaca compound are thought to represent migrants from the Monte Albán area in Oaxaca. Oztoyahualco is an early residential compound in the city thought to contain local inhabitants. The Cuevas de las Varillas and del Pirul are located beneath the ceremonial center of the city. Individuals buried in these caves are later inhabitants of the city from the period after collapse. These individuals may have come to the city from outside areas such as Tula to the north or they may be local inhabitants who remained after the collapse of Teotihuacán.

Results of strontium isotope analyses at the site (Fig. 8.17) show substantial variation in enamel $^{87}Sr/^{86}Sr$ ratios. The local ratio at Teotihuacan is estimated from the nine rabbit bones shown at the left in the diagram. Interpretation of these values suggests that many of the individuals were migrants. Comparison of several individuals in the Oaxaca barrio at Teotihuacan shows a strong similarity of some individuals with samples from Monte Alban itself.

A separate study at Teotihuacán focused on the victims sacrificed during the construction of the Pyramid of the Moon, one of the largest structures at the site. The pyramid was built in a series of stages, with each new building covering the previous. Tunnels excavated into the structure have exposed seven superimposed building stages dating between AD 200 and AD 400. The first structure was square

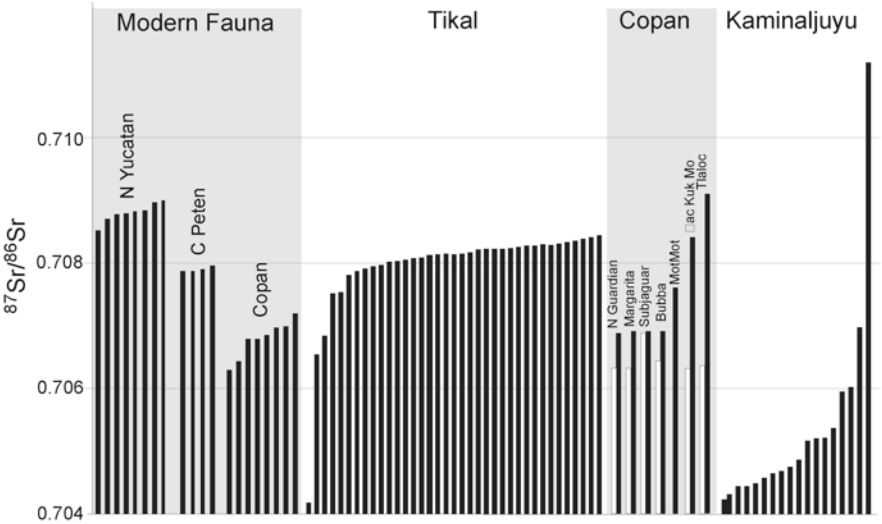

Fig. 8.17 Bone vs. Tooth $^{87}Sr/^{86}Sr$ ratios in the individuals from Teotihuacan. *Black bars* are tooth enamel; *open bars* are bone. Paired bone and tooth bars are from the same individual. Values grouped by location of burials. Local average shows mean for nine rabbit bones from Teotihuacan

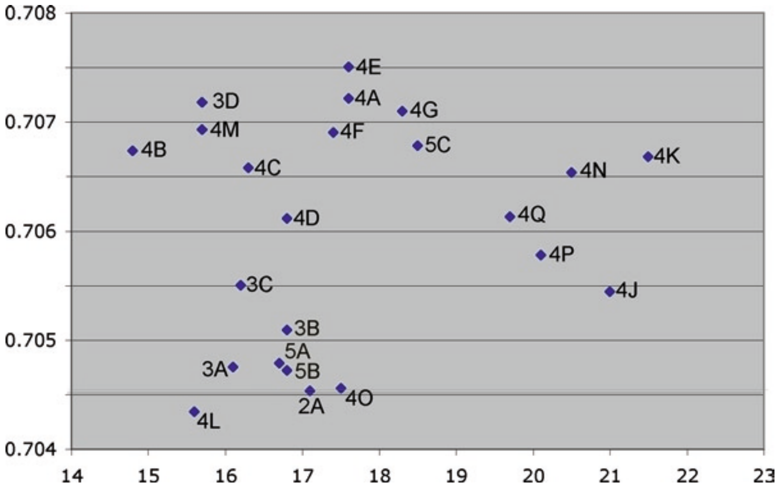

Fig. 8.18 $^{87}Sr/^{86}Sr$ and $\delta^{18}O_p$ values in the individuals from the Moon pyramid at Teotihuacan. Three (or four) possible clusters (places or origin) can be seen in this plot. The labels indicate the designation of the individual sacrificial victims

and they gradually increased in size until the fourth stage, when it was enlarged considerably to the north, probably during a crucial time in the political organization of the city. The tunnel excavations also exposed a series of distinctive sacrificial interments of almost 40 individuals marking various phases of construction. There were six separate burial groups uncovered during the excavations.

Burial group 2 contained a single high status male (2A), 40- to 50-years old. Burial group 3 contained four individuals, who may have been sacrificed as dedications. Individual 3D in this group was unique with special symbols of authority placed at his head and feet, respectively. Burial group 4 contains 17 skulls, possibly of low status individuals as there were no associated offerings. However, different geographic origins are suggested by the diversity of cranial and dental modification styles they exhibit. Burial group 5 contains three individuals with jade from Maya region suggesting that they may be from Guatemala.

The strontium isotope data (Fig. 8.17) for the Moon Pyramid sacrifices shows that most of the individuals were not born at Teotihuacan. Only three of the victims (5B, 3A, 5A) have strontium isotope ratios directly comparable to the local signature for Teotihuacán. Most of the remaining values are higher and the distribution of these values suggests that several different areas provided the sacrificial victims. A scatterplot of the combined oxygen and strontium isotope values for these samples is shown in Fig. 8.18. These results give a slightly different perspective on place of origin. The combination of isotopic measurements would therefore suggest that the Moon Pyramid sacrifices are dominated by people who were not from Teotihuacan.

Fig. 8.19 A computer reconstruction of the central acropolis at Copan, Honduras

8.1.7 A Maya King

Material: Tooth enamel
Instrumentation: Mass spectrometers
Application: Place of birth
Place: Honduras
Time period: Classic Maya, AD *300–900*
Question: Where did the first king of Copan come from? Was he born in Teotihuacan and sent to rule Copan?

Key References

Buikstra, J.E., T.D. Price, L.E. Wright, & J.H. Burton. 2003. Tombs from the Copán Acropolis: A Life History Approach. In *Understanding Early Classic Copan*, E. Bell, M.A. Canuto, & R.J. Sharer (eds), pp. 185–205. Philadelphia: University of Pennsylvania Museum.

Price, T.D., J. Burton, L.E. Wright, C.D. White, & F. Longstaffe. 2007. Victims of Sacrifice: Isotopic Evidence for Place of Origin. In *New Perspectives on Human Sacrifice and Ritual Body Treatments in Ancient Maya Society*, V. Tiesler & A. Cucina (eds), pp. 263–292. London: Springer Publishers.

The ancient Maya city of Copán is located in western Honduras not far from the Guatemalan border. The ruins of the site cover approximately 15 ha, centered on

Fig. 8.20 The primary burial under the acropolis at Copan, Honduras, probably the tomb of Yax Kuk M'o

the great acropolis that is composed of five plazas, major pyramids, temples, and other structures (Fig. 8.19). The major occupation of the site took place during the Classic period from AD 300 to AD 900. Recent tunnel excavations into the great acropolis that has been the discovery have revealed a series of temples and major tombs that appear to represent the burial place of Copán's earliest rulers.

These tombs vary from the elaborate crypts of rulers to the simple interment of a sentinel at the entrance to a passageway leading into one of the structures. One elaborate tomb was found to the west of the major group. This grave (designated as SubJaguar) is possibly associated with Ruler 7 at Copán, who died in AD 544. Another tomb, designated as Motmot, included a primary interment of a young adult female and several peripheral skulls, possibly sacrifices. A single male burial (called Bubba), 18–25 years of age, was found to the north of the royal tombs at the base of an Acropolis façade, dating to ca. AD 480.

The so-called Tlaloc Warrior tomb, dating to ca. AD 450, contained an individual buried with cut shell "goggles," and other artifacts that explicitly link him to central Mexico. The Tlaloc remains are those of a robust male, apparently over 40 years of age. Interred at approximately the same time, the Northern Guardian was a large, robust male at least 30–40 years of age, found near the outer entrance to the Margarita Tomb, perhaps also a guardian. The Margarita tomb was an elaborate structure containing the single skeleton of a female more than 50 years of age. The nearby Hunal tomb contained the partially disarticulated remains of an older adult male. The tomb's architectural and artifactual associations suggest that he was Yax K'uk Mo (Fig. 8.20). Epigraphic information states that Yax K'uk Mo was a warrior, who came from the north, and the founder of the Copán dynasty. The interment in the Margarita tomb is thought to have been his wife. However, the identification of Yax K'uk Mo is inferential. There are several lines of evidence, including isotopic proveniencing, that support this contention.

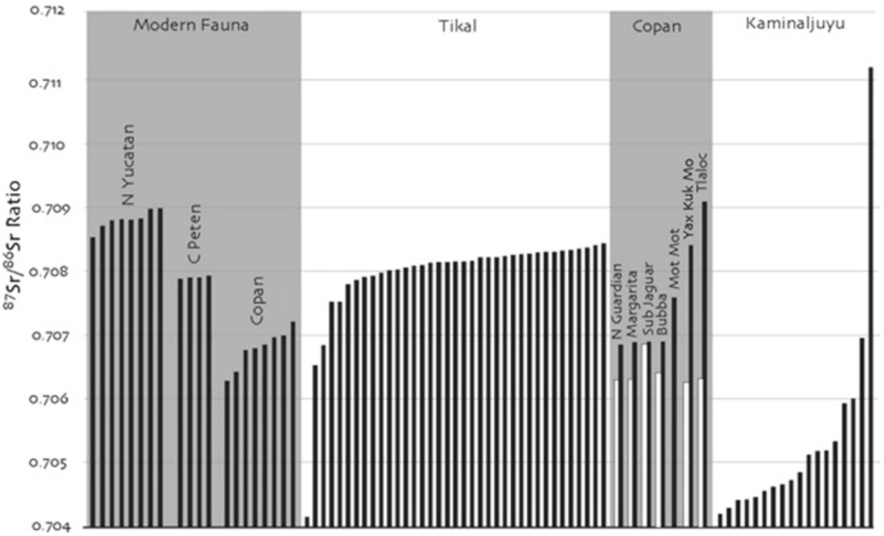

Fig. 8.21 Bone and Tooth $^{87}Sr/^{86}Sr$ ratios in fauna and humans from the Yucatan, Tikal, Copan, and Kaminaljuyu. *Black bars* are tooth enamel; *open bars* are bone. Paired bone and tooth bars are from the same individual. Values grouped by location of burials

Strontium isotopes have been measured in the individuals buried under the great acropolis as well as from other graves at Copán and in local fauna. The strontium isotope analysis of these burials and of comparative human remains from Tikal and Kaminaljuyu, and fauna from the Northern Yucatan and the Central Peten, shed some light on the place of origin of Copán individuals (Fig. 8.21). Strontium isotope ratios in modern fauna from Copán are variable, ranging between 0.7062 and 0.7072. Modern fauna from the Central Peten average almost 0.7080; fauna from the northern Yucatan have ratios between 0.7085 and 0.7090. Human samples from Tikal exhibit an average $^{87}Sr/^{86}Sr$ value of 0.7080, while individuals from the highland Maya site of Kaminaljuyu average 0.7050.

In this context, the seven burials from the underground tombs at Copán are particularly interesting. Four of the individuals exhibit bone and enamel values within the range of local fauna at the site. These individuals (Northern Guardian, Margarita, SubJaguar, and Bubba) are likely indigenous inhabitants of the site. Three individuals appear to have come to Copán from elsewhere. The origins of these individuals, as reflected in the strontium isotope ratio for enamel, are geographically separate and impossible to determine precisely as yet. The ratio for the enamel from Motmot suggests an area in the lowlands of Guatemala. The Tlaloc individual may have come from a highland area with older lithological units, but at the same time we cannot rule out a coastal region. The strontium isotope ratio for Yax K'uk Mo is consistent with an origin in the Central Peten, a place that corresponds closely with epigraphic records for this individual and helps to identify him as the first ruler of Copan.

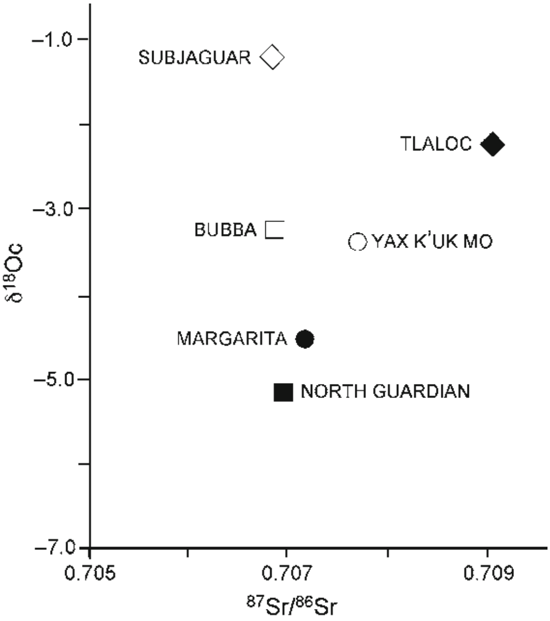

Fig. 8.22 First molar enamel values for $^{87}Sr/^{86}Sr$ ratios and $\delta^{18}O$ (carbonate) for six burials from the Copan acropolis

The measurement of carbonate oxygen isotopes on the burials from Copan did not improve the geographic discrimination among these individuals. Three of the four local individuals, based on strontium isotopes, fall fairly close together in terms of oxygen isotope ratios (Fig. 8.22). The fourth, SubJaguar, has a much less negative oxygen signature. The two "foreign" individuals for whom oxygen isotopes were measured, Yax K'uk Mo and Tlaloc, also have somewhat distinctive values. The significance of these differences in oxygen isotopes is unclear.

The individual in the central tomb was an older male, between 50 and 60 years of age, and his skeleton showed a number of old breaks and lesions that were probably the result of conflict and warfare. Certainly, the age of the individual, the wounds he had suffered, and the probable place of birth correspond with what we know of Yax Kuk Mo'. This is likely his tomb and his skeleton at the base of the Copan acropolis.

Suggested Readings

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Chapter 9
Conclusions

Contents

We have reached the last chapter of this book on archaeological chemistry, a large and complex subject. The path through these pages has been a long and demanding journey. To conclude we have chosen to do several different things. In one sense, this chapter ties up loose ends and provides a place to cover a few subjects that we only touched upon in the preceding pages. In addition, we want to flaunt some of the extraordinary kinds of results that are being achieved when several different methods are applied to an important archaeological discovery.

Several of the studies we have discussed in these pages have involved more than a single analysis or line of investigation. Often it is the case that multiple kinds of evidence from archaeological chemistry can provide greater insight or reveal more information about the object or material under study. An initial small example reiterates the importance of different lines of evidence and multiple means of analysis.

A fascinating recent study focused on an unusual, small ceramic jar (Fig. 9.1) from the site of Antinoe in Roman Egypt, dating to the fifth to seventh century AD. Ribechini and her colleagues conducted a multianalytical chemical study on the well-preserved contents of the jar. Scanning electron microscopy with an energy-dispersive X-ray spectrometer (SEM-EDX), Fourier transformed infrared spectroscopy (FTIR) and X-ray diffraction (XRD) were used to characterize the inorganic components of the contents. The organic substances were analyzed using FTIR, direct exposure mass spectrometry (DE-MS) and gas chromatography–mass spectrometry (GC–MS).

The inorganic component was largely halite (NaCl), sea salt. Among the NaCl crystals, small objects of apatite were identified as the scales of small fish (Fig. 9.2). The organic compounds were monocarboxylic acids, α,ω-dicarboxylic acids, and

T.D. Price and J.H. Burton, *An Introduction to Archaeological Chemistry*,
DOI 10.1007/978-1-4419-6376-5_9,

Fig. 9.1 The small ceramic jar and contents from Antoine, Egypt, AD 400–600

Fig. 9.2 Tiny fish scales among halite crystals found in the contents of the jar from Antoine

cholesterol, consistent with the presence of lipids of animal origin. Diterpenes likely from pine pitch were also identified. The sum of the evidence points to the contents of the jar as a residue of fish sauce, a prized condiment and an essential element in Roman cooking. The sauce was made by crushing and fermenting the intestines of various fishes such as mackerel, tuna, eel, and others in sunlight for several months and then rehydrating that mixture in a brine. That is probably enough information about fish sauce.

Another fascinating, many faceted investigation appears in the first section of this chapter, involving the Iceman, a frozen body from the Neolithic period, more than 6,000 years old, found high in the Italian Alps. Since his discovery in 1991, a series of investigations have taken place to learn as much as possible about his life and death. It is absolutely remarkable how much has been discovered in the two decades since the body was found.

The investigation of human bodies brings up a second important subject in our discussion of archaeological chemistry – ethical considerations. What are the responsibilities and ethical issues that archaeology, and archaeological chemistry in particular, face in the twenty-first century? We focus on matters of importance to archaeological chemistry – more generally the question of the destructive analysis of archaeological materials and in particular on the study of human remains – in the second segment in this chapter.

Finally, in a third and last segment, we take crystal ball in hand and look to the future. What will the next decade or two hold for archaeological chemistry? What new methods, instruments, and techniques may appear to help us understand our human past? Archaeologists have a hard time interpreting the past, and there is no reason that predicting the future of archaeological chemistry should be any easier. The chapter concludes with a few suggested readings.

9.1 Multiple Investigations

9.1.1 Italian Iceman

Material: Various
Instrumentation: XRD, Light Isotope Mass Spectrometer, TIMS, GC/MS, aDNA
Applications: Multiple
Place: Italian Alps
Time Period: Neolithic, 4300 BC
Question: Where did the Iceman come from? What can we learn about his life?

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Müller, W., H. Fricke, A.N. Halliday, M.T. McCulloch, J.A. Wartho. 2003. Origin and Migration of the Alpine Iceman. *Science* 302: 862–866.

Rollo, F., M. Ubaldi, L. Ermini, I. Marota. 2002. Ötzi's Last Meals: DNA Analysis of the Intestinal Content of the Neolithic Glacier Mummy from the Alps. *Proceedings of the National Academy of Sciences* 99: 12594–12599.

A classic example of the use of multiple lines of evidence in archaeological chemistry involves the 1991 discovery of the Iceman, the frozen body of a person from the Neolithic (Fig. 9.3), found in the Italian Alps (Fig. 9.4). The Iceman is one of the most studied archaeological finds of any period. Many of these investigations involved archaeological chemistry in one form or another, and involved the clothing and artifacts found with the Iceman, as well as the frozen remains of the man himself. Nicknamed Ötzi after a nearby valley, he is one of the most important archaeological finds of all time.

Fig. 9.3 The body of the Iceman as he was discovered, still partially frozen in ice on an Italian mountaintop

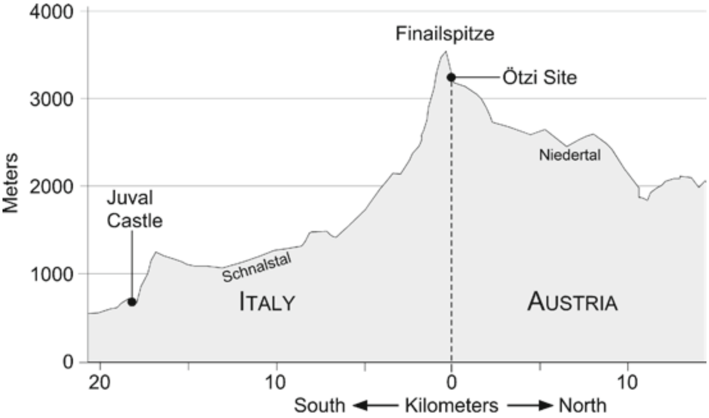

Fig. 9.4 The location of the Iceman's body, high in the Italian Alps, a few meters from the border with Austria. The elevation profile through the region also shows important landmarks, including the highest peak (Finailspitzer), major valleys (Niedertal, Schnalstal), and Juval Castle, the location of a contemporary Neolithic site that may have been home to the Iceman

The Iceman was carrying a substantial amount of gear with him, including seven articles of clothing and 20 items of equipment. These materials were found scattered up to 10 m from the body. The items included a bow and quiver of arrows, bow strings, bone points, a needle, a hafted copper axe (Fig. 9.5), a wooden rucksack frame, two birch bark containers, a hafted knife of flint and its sheath, several flint tools (including a scraper, an awl, a flake), a tool for flaking flint, a net (perhaps for catching birds), a piece of ibex horn, a marble pendant, and birch

Fig. 9.5 The Iceman's axe, found as part of the equipment of Ötzi, frozen in the ice with the preserved body of a man 5,300 years old. The copper axe was bound to the haft with sinew and a birch pitch

fungus (possibly used as medicine). He carried several items that were incomplete or in need of repair – most of his arrows were unfinished, for example.

His clothing included a large belt with a pouch, holding up a leather loincloth and skin leggings, a coat of deerskin, a cape of woven grass, a conical leather cap with fur on the inside and a chin strap, and shoes with bearskin soles filled with grass for warmth. No obvious food was found among his possessions, but a few small bone fragments and a few fruits were found nearby. The bones come from ibex, a mountain goat. The fruits are sloe, a small, bitter, plum-like fruit, and may have been carried as provisions.

More than 150 specialists have been studying all aspects of the Iceman and his equipment. Over 300 books and scientific articles have been published about the Iceman as of 2008. One of the more interesting investigations involves the axe; it is almost pure copper. When first discovered, the axe was assumed to be bronze because early copper axes were unknown in this part of Europe. The Iceman was thought to belong to the Bronze Age. Soon, however, radiocarbon dates from the body and the equipment the Iceman carried were obtained and indicated an age of around 4300 BC, in the Neolithic period, long before the Bronze Age.

The raw material of the axe was studied to learn about its composition. A non-destructive X-ray diffraction (XRD) analysis of the ax showed this material to be almost pure copper, not bronze at all. This new metal documents the widespread use of copper in Europe during the latter half of the Neolithic period. Copper was being mined and smelted in several areas of eastern Europe by this time and traded as far north as Scandinavia.

Analysis of the pitch used to haft the copper hatchet of Ötzi the Iceman provides a good example of the identification of unknown organic compounds. Sinew was used to lash the ax head to the wooden haft and an unknown adhesive material was used to bind or glue the sinew, wood, and copper together. Sauter and his colleagues used gas chromatography and mass spectrometry in their study to isolate and identify lupeol and betulin in the binder. These are kinds of oils known as terpenes, found in the resin of some tree species. Lupeol and betulin are always found in pitch made from birch bark, but never in abundance in those from ash, oak, or elm (Fig. 9.6).

In order to more accurately determine the source of the binder, the scientists prepared pitches from birch and several other tree species for comparison. Resins from modern alder, hazel, elder, and birch trees were heated and reduced to pitch. GC/MS

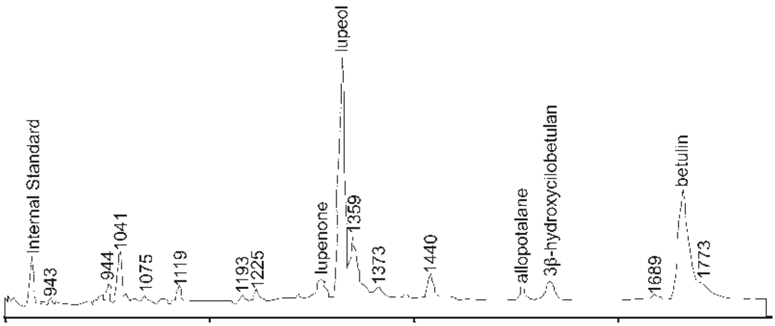

Fig. 9.6 GC/MS spectrum of pitch used to haft Ötzi's copper axe, showing peaks due to lupeol and betulin, diagnostic or birch

analysis of the modern pitches demonstrated that the residues from Ötzi's axe matched those of birch pitch, but not of the other species (Fig. 9.7). A statistical technique known as principle components analysis was used to group the different compounds in the pitches into classes, or components, that best defined the species.

The Iceman was approximately 45 years old at the time of his death. He was not a tall man, 159 cm (5′ 2.5″) in height. The more difficult questions about the Iceman include how he died and where he came from. The extent of preservation of his body is remarkable; most of the internal organs, as well as the eyeballs, are intact. Although the body was hairless from the effects of freezing and thawing, hair was found around the body. His lungs are black with the hearth smoke that filled early Neolithic houses. Tattoos were clearly visible on his back and right leg. X-rays

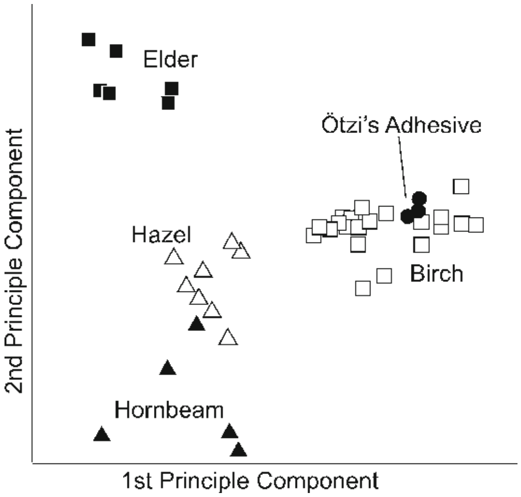

Fig. 9.7 Graph comparing chemical distributions in Ötzi's pitch to those made from birch and other trees. Ötzi's pitch matched that derived from birch and was distinguishable from all other tree species. The principle components are statistically defined groups of compounds that best describe the different species of trees

revealed several broken ribs and indicate that the Iceman suffered from arthritis in his neck, lower back, and right hip. Some of these injuries may have resulted post-mortem in the ice. An absence of stomach contents and the presence of material in the large intestine indicate that he had not eaten for 8 h. His last meal included unleavened bread, some greens, and meat. DNA analysis had identified the meat as coming from red deer (European elk) and ibex.

Until recently there were several theories about how the Iceman died in the high Alps, involving either an accident or some kind of escape. Some suggested he may have been a shepherd in the mountains, caught by an early fall blizzard. Autopsy of the body has revealed several wounds. Deep cuts to his hand and wrist suggest he was in an armed struggle and an arrowhead lodged in his back may well have been the cause of death if it cut an artery. In addition, recent CAT scans of the crania suggest that the Iceman also suffered severe trauma to his head at the time of death, either from a fall or a blow. It now seems that the Iceman died as a result of violent conflict. It also appears that he did not die on the exact spot where he was found but that his body floated to that spot during earlier thaws. That floating would also explain the dispersal of his clothing and equipment away from the body.

Analysis of pollen in the stomach contents indicates he died between March and June. His death was probably caused by an arrow wound in his back. Isotopes have played a large role in the investigations. Stable carbon and nitrogen isotope analysis of the hair of the Iceman was undertaken to obtain information on diet (Table 9.1). Hair provides very different information from bone collagen. Bone tissue contains a long-term record of human diet over many years; human hair on the other hand grows quickly and is cut or shed. The collagen in hair likely contains a record of diet for a few weeks or months. The δ^{13}C value from the hair was slightly more positive than both the goat fur and the grass-like plant. The similarity of these values reveals little about the diet of the Iceman. Nitrogen isotopes provide more insight on his diet. As discussed previously, δ^{15}N values in protein are enriched 2–3‰ from one trophic level to the next in the food chain. The δ^{15}N value for the Iceman's hair suggests a diet based primarily on plant foods. However, carbon and nitrogen isotope values from his bone collagen indicate a diet of approximately 30% meat.

One of the more difficult questions concerns from his place of origin. The high Alps are uninhabitable in winter; the Iceman's home must have been elsewhere at lower altitude. He probably came from valleys to the south in Italy, less than a day's walk away. He carried a small ember of charcoal, for use in starting fires, which came from the wood of trees that grow south of the Alps. A grain of wheat attached to his clothing and his last meal suggest connections with farming villages. Pollen found in his

Table 9.1 Stable carbon and nitrogen isotope ratios in human hair, goat fur, and grass-like plant from the Iceman discovery (Macko et al. 1999)

Sample	δ^{115}C (‰)	δ^{15}N (‰)
Ice man hair	−21.2	7.0
Goat fur	−22.5	6.9
Grass-like plant	−23.9	4.0

intestines came from the hornbeam tree, which grew only to the south of the Alps. In addition to the pollen, tiny fragments of moss from the species known as *Neckera complanata* were found in his intestines, perhaps used to cover and protect the food that he carried. This species of moss grows only on the southern slopes of the Alps (Fig. 9.8) and also points to that nearby region of Italy as the place from where he came.

In order to examine the question of his origin in more detail, Müller and colleagues undertook an isotopic study of the Iceman's tooth enamel, bone, and stomach contents to determine his birthplace, habitat, and range. Their study focused on strontium, lead, and oxygen isotopes to determine his movements.

Müller and colleagues identified four major rock units in the potential homelands of the Iceman on the basis of strontium and lead isotope ratios (Fig. 9.9). These include Eocene basalts (ca. 0.705–0.708), Mesozoic limestones (ca. 0.710–0.714), and Permian volcanics (ca. 0.717–0.719), and a mixed unit of phyllites and gneisses (ca. 0.720–0.724). These last two geological units overlap slightly in their isotope ratios. Strontium isotope ratios in the enamel of the Iceman averaged 0.721 and values in bone were approximately 0.718. These values are most congruent with the

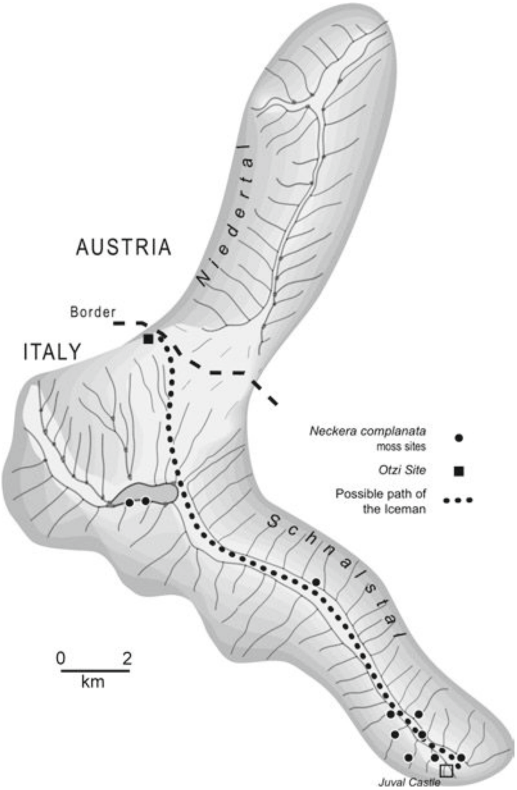

Fig. 9.8 The location of the discovery of the Iceman and relevant geographic places in the Alps Mountains and valleys. Several *lines* of evidence suggest he came from the south into the high Alps. Note the find locations of the *Neckera complanata* moss that grows on the south slopes of the mountains

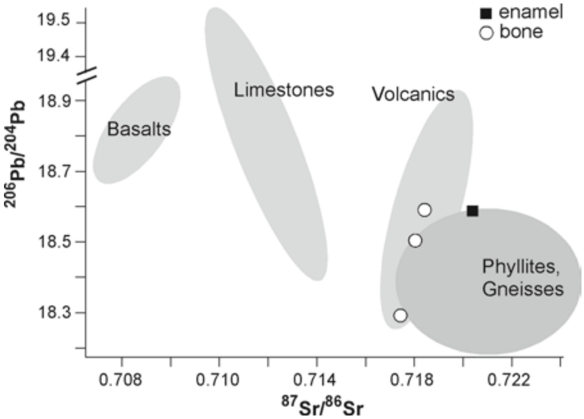

Fig. 9.9 Lead 206/204 and strontium 87/86 isotopes in soil from rock units in the larger region around the find location of the Iceman. Four distinct units can be identified with some overlap between the volcanics and phyllites/gneisses. Four samples from the enamel and bone of the Iceman are shown on the graph, indicating that the Iceman was born and lived on the volcanics and phyllites/gneisses that are found south of the find location in Italy. After Müller et al. 2003: p. 864, Fig. 2b

volcanics and phyllites/gneisses which are found largely to south of the find location in Italy and suggest to the researchers that the Iceman spent most of his life in this area no more than 60 km from where he was found.

Oxygen isotopes were measured in streams and springs in the region to establish baseline values. In general, lower $\delta^{18}O$ values were found north of the Iceman's find location (ca. −13.0 to −15.0‰) and less negative $\delta^{18}O$ values occurred to the south (ca. −11.5 to −14.0‰). The differences between the northern and southern streams were on the order of 1–2‰. These observations fit expectations based on the sources of rainfall for this area. Rainfall to the north comes from the cooler, more distant Atlantic Ocean; the rainfall to the south comes from the warmer and closer Mediterranean Sea. Oxygen isotope ratios in the skeletal tissue of the Iceman ($\delta^{18}O = 11$‰ for enamel carbonate and 11.5‰ for bone carbonate) better match the water values to the south of the find locality and support the inference based on strontium and lead. Müller et al. argue that their strontium isotope ratios indicate that the Iceman's place of origin was to the south in Italy, a direction which fits well with the information from the plant remains associated with the body.

The study of the Iceman's frozen corpse, clothing, and the artifacts that were found with his body has revealed an extraordinary picture of his life and death. The autopsy and archaeological chemistry that were done tell us that this 45-year-old man died in the spring of the year from a violent encounter that included an arrow in his back. The technological sophistication of his equipment is remarkable. The very early copper axe reveals long distance exchange networks across parts of Europe more than 6,000 years ago. Several lines of evidence point to the valleys south of the Alps as his place of birth. Mysteries of course remain – part of the allure of the past. For example, what was Ötzi doing high in the Alps at the time of his death? Some of these questions may never be answered.

9.2 Ethical Considerations

Archaeology is about the past but it is also about responsibility, about caring for the past and the future, about protecting our heritage, about sharing the remarkable items that have survived from antiquity and what we have learned. Archaeologists have a duty to themselves and to the public to protect and preserve the past and to share their knowledge of the past. Duty, responsibility, sharing – these are ethical issues and an important part of archaeology today.

Ethics *n.* The concept of human duty, of doing the right thing; the body of rules of duty; a particular system of principles and rules concerning duty; rules of practice in respect to a single class of human actions; as, political or social *ethics*.

Ethics is an important and growing concern in modern life. Ethics in archaeology is an increasingly complex subject, related to issues of heritage, native peoples, treatment of the dead, and the preservation of the past. One participant in discussion of the subject is the Society for American Archaeology (SAA). The major professional organization for archaeologists in the USA, the SAA was founded in 1934, and today the society's membership includes more than 6,500 professional archaeologists and students. The SAA is intended to stimulate interest and research in American archaeology, to advocate for and aid in the conservation of archaeological resources, to encourage public access to and appreciation of archaeology, to oppose the looting of sites and the purchase and sale of stolen archaeological materials, and to serve as a network for archaeologists in the Americas. The promotion of ethical behavior is an important aspect of the society's activities and to do that the SAA has adopted a set of principles of ethical practice (Table 9.2).

Table 9.2 Eight ethical principles of the Society for American Archaeology

1. *Stewardship*. The archaeological record is irreplaceable and it is the responsibility of all archaeologists to practice and promote stewardship of the archaeological record
2. *Accountability*. Responsible archaeological research requires a commitment to consult with affected group(s) to establish a working relationship that can be beneficial to all parties involved
3. *Commercialization*. The buying and selling of objects contributes to the destruction of the archaeological record on the American continents and around the world. Archaeologists should discourage and avoid activities that enhance the commercial value of archaeological objects
4. *Public education and outreach*. Archaeologists should work with the public to improve the preservation, protection, and interpretation of the record
5. *Intellectual property*. A researcher may have primary access to original materials and documents for a limited and reasonable time, after which these materials and documents must be made available to others
6. *Public reporting and publication*. The knowledge that archaeologists obtain in their investigations must be presented to the public
7. *Records and preservation*. Archaeologists should work actively for the preservation of archaeological collections, records, and reports
8. *Training and resources*. Archaeologists must ensure that they have adequate training, experience, facilities, and other support necessary to conduct a program of research

These principles encompass the major concerns of archaeology. Stewardship concerns the protection of our common archaeological and cultural heritage. Unless this heritage is protected it will disappear. This principle of protection and preservation also extends to the collections and records that archaeologists accumulate. Accountability concerns archaeology's interaction with the individuals or groups who are involved with particular archaeological sites or materials. These individuals and groups include the landowners where archaeological projects may take place and Native American groups whose beliefs incorporate ancient artifacts and human remains. A third ethical principle regards the commercialization of the past, and particularly the illegal trade in antiquities that remains a major force in the destruction of the past by looters and thieves. It is the responsibility of an archaeologist to discourage and avoid such activities. For example, an archaeologist should not provide estimates of the value of antiquities to collectors and retailers. As might be expected, these principles are guidelines and very general and largely nondirective in nature. These can be controversial matters and there is no consensus on the best solution to many of the problems addressed.

Beyond these issues of concern to all archaeologists, there are some specific topics particularly relevant to archaeometry and archaeological chemistry. We discuss two of these – destructive analysis and the study of human remains – in more detail below.

9.2.1 Destructive Analysis

One of the issues that archaeological chemists constantly confront is the problem of destructive analysis. Most of the methods in use today involve destroying a small portion of valuable artifacts, human skeletons, and other archaeological materials. These materials are often in the hands of curators who are responsible for protecting the contents of their museum against loss and damage. These individuals resist the destruction of the cultural properties under their control and occasionally refuse, or more often request lengthy justification for proposed studies involving instrumental analysis. Thus, the controversy over destructive analysis comes into play.

Museum curators often try to find a compromise and suggest waiting for new methods that do less damage. That appears to be a reasonable argument, but assumes several things: that new methods will appear in the foreseeable future, that time, money, and energy will be available when that technology arrives, and that artifacts and materials will always be curated. None of these are given. Theft, warfare, and natural catastrophes have demonstrated time and again that nothing can be protected forever. Everything eventually disappears. Moreover, science is a cumulative endeavor; what is learned is built on what is known. Study of materials today will provide new information and raise new questions to be answered in future research. Without those questions, new research may never be attempted.

Our position as archaeological scientists is that materials from the past are collected, excavated, and curated in order to increase knowledge and to be cared for as part of our common heritage. Destructive analysis is a question of weighing the potential knowledge to be gained against the damage to or loss of important cultural materials. From our perspective, more knowledge is usually the better option. As can be seen in Table 4.5, most of the common analytical techniques in use today require sample preparation and destruction. Samples are powdered or dissolved prior to introduction into the instrument. At the same time, only a small, usually a tiny, amount of material is needed.

The trend in both instrumentation and preparation methods is toward the use of minuscule samples and nondestructive means of analysis. For most kinds of investigations today sample sizes are in the milligram range. For strontium isotope studies of tooth enamel, we use a 3 mg sample, about the same weight as a small ant. This means that we can remove a tiny amount of enamel from a tooth and return the specimen largely intact to the museum curator. Figure 9.10 shows the sample sizes needed for radiocarbon dating using AMS techniques, and in most cases less than a milligram of sample is needed. For the most part, destructive techniques remove only a small amount of material from priceless museum objects.

It is also the case that some materials require a bit more material in order to obtain an accurate analysis. For homogeneous materials, a few milligrams will suffice, but for heterogeneous materials such as pottery and some rocks, one must take a sample that represents the whole, as an average. For coarsely tempered pottery, this might require a gram or more, regardless of the instrument used for analysis.

This issue of destructive analysis also involves the question of human remains, since small amounts of bone and other tissues are often destroyed when scientific analysis is undertaken. Human remains are the subject of the next section.

9.2.2 *The Study of Human Remains*

An even more sensitive and contentious issue involves the disposition of ancient human skeletal remains. North American archaeologists have been excavating burials along with other cultural materials for many years. The Smithsonian Institution in Washington, DC, for example, housed the remains of more than 16,000 Native Americans

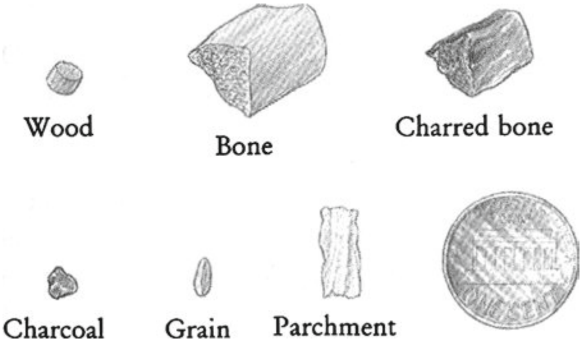

Fig. 9.10 Samples sizes of material needed for AMS radiocarbon dating, compared to a US penny (*lower right*)

collected over the years. By some estimates, more than 100,000 Native American graves have been excavated in the USA and the skeletons usually placed in museums. Because of growing concern about these materials and the desire of native peoples to reclaim these remains for reburial, the Congress passed the Native American Graves Protection and Repatriation Act (NAGPRA) in 1990.

NAGPRA provides a mechanism for museums and Federal agencies to return certain Native American cultural materials – human remains, funerary and sacred artifacts, and objects of cultural patrimony – to lineal descendants, culturally affiliated Indian tribes, and Native Hawaiian organizations. The major requirements of NAGPRA are listed in Table 9.3. Items requested for return must be repatriated to a lineal descendent or related group. Several different lines of evidence are required to determine cultural affiliation, including geographic, biological, archaeological, linguistic, and anthropological evidence. The law also forbids trafficking in Native American cultural or human material and establishes procedures for notification and consultation with tribes for planned excavation or accidental discovery of cultural materials on tribal property. Because of NAGPRA and similar legislation, the Smithsonian has repatriated more than 4,000 sets of human remains to native tribes for reburial since 1984.

The repatriation of human skeletal remains is not always a clear-cut issue, however, and this legislation has created several controversial situations. One of the best known involves the Kennewick Man from the state of Washington. This skeleton was discovered along the Columbia River in 1996. The radiocarbon date from the bone was approximately 7500 BC, making Kennewick one of the oldest human skeletons in North or South America. A most important discovery and one that might tell us a great deal about the first inhabitants of the New World. At the same time, Kennewick highlights the ethical dilemma that the discovery of human remains raises. Because of the NAGPRA legislation, the remains were supposed to be returned to native people in the state of Washington. The archaeologists, however, argued that the remains were of major importance and that they were not demonstrably related to Native American groups in the area, questioning the legality of the tribes claim. The debate lasted for years in the court system and was finally decided in 2004 in favor of the scientists.

The ongoing conflict between science and belief is highlighted in such issues. The public battle over burial rights and the pursuit of knowledge about the past has both underscored and brushed aside the importance of the Kennewick find. In all

Table 9.3 Major stipulations of the Native American Graves Protection and Repatriation Act (NAGPRA) of 1990

Federal agencies and museums must identify cultural items in their collections that are subject to NAGPRA, and prepare inventories and summaries of the items
Federal agencies and museums must consult with lineal descendants, Indian tribes, and Native Hawaiian organizations regarding the identification and cultural affiliation of the cultural items listed in their NAGPRA inventories and summaries
Federal agencies and museums must send notices to lineal descendants, Indian tribes, and Native Hawaiian organizations describing cultural items and lineal descendancy or cultural affiliation, and stating that the cultural items may be repatriated. The law requires the Secretary of the Interior to publish these notices in the Federal Register

the anger, argument, and hubbub about who should control these remains and how they should be handled, the importance of learning more about the past of all of us is lost. In fact a great deal has been lost in the last few decades because of NAGPRA and the return of collections of human skeletal remains.

It is of course essential to respect the rights, beliefs, and wishes of everyone involved in such issues. In cases where direct ancestry can be demonstrated, human remains should be returned to descendants for reburial. But in many cases, there are no direct lines of affiliation. Native American groups have been decimated and pushed from place to place across more recent American history. So much information is lost to science, to Native American peoples, and to all of us by the reburial and eventual destruction of these skeletal remains. We would know much more about the human past if such materials were available for study. We can only hope that legislation such as NAGPRA will be revisited and revised in light of a more realistic perspective on the importance of the past.

9.3 What Does the Future Hold?

Time is the most difficult dimension with which archaeologists have to contend. It's hard enough to understand what life was like at the beginning of the twentieth century AD, much less in the Bronze Age, or Neolithic, or Paleolithic. One hundred years ago few could have believed that humans would fly, that cities would be incinerated, that a man would walk on the moon, that computers would interconnect the planet, or that a cow would be cloned. Why should it be easier to predict the past?

In a 1989 issue of Archaeology magazine focused on the future of archaeology, Robert Dunnell forecast that "In 50 years, artifacts from two millimeters to ionic sizes will be the backbone of archaeological research." In fact, his prediction has already come true. Archaeometry and archaeological chemistry have grown dramatically in the last two decades. With this growth have come new and exciting developments that are simply revolutionizing the way we do archaeology. The range of material under investigation is enormous: metal, glass, pottery, stone, soil, fiber, dye, bone, DNA, organic residues, and many others. The acronyms for the instrumentation in use alone are mind-boggling: NAA, FTIR, GC/MS, EMPA, SEM, ESR, NMR, ICP-AES, LC/MS, PiXIE, and many more.

Archaeological chemistry is growing rapidly and the next 20 years will undoubtedly see many new developments. Several trends seem to be clear. Because of all the exciting new discoveries in genetics, this has been tagged as the century of biology. Indeed, universities and corporations are pouring huge amounts of money into research and development of genetic technology. Without a doubt, studies of both modern and ancient DNA are going to continue to revolutionize our understanding of ourselves and our past. aDNA studies of archaeological fauna are beginning to find genetic evidence of domestication and helping to document the origins of agriculture. aDNA will play a major role in the study of both organic (plants and animals) and human remains from archaeological sites.

New instrumentation and techniques will be coming online in the next years that will change how research is done. Miniaturization and portability will be a major theme in new instruments as will nondestructive analysis. Portable units for element analysis are available now. More powerful units are being developed and it is only a matter of time until isotopic and organic analyses are also available. These instruments will push the growth of studies of organic residues and living floors (and many other analyses) because of the increasing ease of use and decreasing cost.

The coming years should also see more instrumentation in more laboratories dedicated to archaeometry and archaeological chemistry. Major scientific instruments are very expensive and maintenance and repair is a constant cost. A trained technician or scientist needs to spend a great deal of time just keeping such instruments running. Because of the costs, today there are relatively few laboratories and very few high-end scientific instruments installed in archaeological facilities. That situation should improve as more academic departments add archaeological scientists to their staff and as instruments becomes smaller, cheaper, and more reliable.

It may be more of our wish than a fact, but universities will have to find the higher levels of funding needed to keep these laboratories operating. Until recently, archaeology has been a rather inexpensive branch of science. That is changing and money is needed to make it happen. In addition, students and professionals must be trained to understand and to carry out some of these analyses themselves. Archaeology is moving toward the harder sciences in terms of the focus of investigations.

9.4 In the End

As authors and archaeological chemists, we hope that you have enjoyed this book and that you have gained a greater appreciation of our chosen field of study. We believe that archaeological chemistry is quickly becoming a large and important part of archaeology. There is no doubt that the future for archaeological chemistry is very bright as new methods and ideas will emerge to improve our understanding of the human past. The future of the past is in the laboratory. We strongly encourage both students and professionals to become knowledgeable of the basic methods, instruments, and results of archaeological chemistry. Understanding the methods that are used is fundamental to understanding the results that are obtained. In addition, we urge students to consider archaeological chemistry as a specialty. It is a growing field and qualified candidates are sure to be in demand for jobs. There is also an unending fascination inherent in this field of study that can inspire lifelong interest. In the end, we would be happy to hear from you with suggestions, corrections, additions, and improvements for future editions of this book.

Suggested Readings

Fowler, Brenda. 2000. *Iceman: Uncovering the Life and Times of a Prehistoric Man Found in an Alpine Glacier*. New York: Random House.

Lambert, J. 1997. *Traces of the Past: Unraveling the Secrets of Archaeology Through Chemistry.* New York: Addison Wesley Longman.

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Macko, S., G. Lubec, M. Teschler-Nicola, V. Rusevich, and M. Engel. 1999. The Ice Man's diet as reflected by the stable nitrogen and carbon isotopic composition of his hair. *The Federation of American Societies for Experimental Biology (FASEB) Journal* 13: 559–562.

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Scarre, Chris, and Geoffrey Scarre (eds.). 2006. *The Ethics of Archaeology. Philosophical Perspectives on Archaeological Practice.* Cambridge: Cambridge University Press.

Spindler, Konrad. 1995. *The Man in the Ice: The Discovery of a 5,000-Year-Old Body Reveals the Secrets of the Stone Age*. New York: Three Rivers Press.

Zimmerman, Larry J., Karen D. Vitelli, and Julie Hollowell-Zimmer. 2003. *Ethical Issues in Archaeology*. Walnut Creek, CA: Altamira Press.

An Introduction to Archaeological Chemistry

Technical Information

This section is intended for technical things, information not appropriate in the body of the book, protocols, useful notes, tips, conversions, tables, and the like.

Journals, Books, Conferences

Information about archaeological chemistry is available from a number of different sources. This section lists journals, books, conferences and societies that focus on or include archaeological chemistry. There are two major, international associations (Archaeometry and the Society for Archaeological Science) that meet regularly (Archaeometry and the Society for Archaeological Science) and have associated journals (*Archaeometry* and the *Journal of Archaeological Science*).

Journals

Journal of Archaeological Science
Archaeometry
International Journal of Human Osteology
American Antiquity
Geoarchaeology
Journal of Field Archaeology

Books, Reports, Newsletters

Archaeological Chemistry, vols. 1–5 (American Chemical Society)

Ceramics and Civilization, vols. 1–4 (American Chemical Society, with various editors, beginning 1974)

Materials Issues in Art and Archaeology, vols. 1–7 (Materials Research Society)

MASCA Research Reports (Museum of the University of Pennsylvania)

SAS Bulletin (Society for Archaeological Sciences)

Scientific Conferences

Meetings, symposia, and conferences are important parts of a scientist's calendar. Archaeological chemists and archaeometrists hold regularly scheduled conferences to get together and present new methods and results and to socialize. Such conferences are important for the field so that information is quickly shared and so that the participants can meet each other. Such meetings often result in collaborative research and new ideas, as well as more personal relationships among the participants. An *Archaeometry* meeting takes place every 2 years in different parts of the world. The meeting lasts for 5 days and covers a wide range of topics through oral presentations and posters sessions. The *Society for Archaeological Sciences* meets every year at different venues and hosts symposiums. The *American Chemical Society* often holds a special session for archaeological chemistry at its annual meetings. In addition, many smaller, more specialized conferences on specific aspects of archaeological chemistry and archaeometry take place frequently. These are usually more intense discussions of a focus topic intended to exchange information and ideas and to work toward new approaches to problems. All these conferences share common goals of increasing information flow, research efficiency, and knowledge.

Weights and Measures

Most people when faced with very small, or large, numbers have little idea of the size involved. The following examples may help understand what these numbers mean.

If you wanted a very dry martini, you might make a recipe of five parts per million (5 PPM) vermouth in your favorite gin. What would it take to mix this drink? *PPM* parts per million, *PPB* parts per billion, *PPT* parts per trillion.

Dry martini recipes

5 PPM ⇒ 1 oz. vermouth + 1,562.5 Gallons of Gin
This is enough Gin to fill a party size hot tub 10 × 10 × 2 ft

5 PPB ⇒ 1 oz. vermouth + 1,562,500 Gallons of Gin
This is the equivalent of a very large swimming pool 100 × 200 × 10 ft

5 PPT ⇒ 1 oz. vermouth + 1,562,500,000 Gallons of Gin
This is the equivalent of the flow of the Mississippi River for about 6 h.

Equivalents for several important measures are given below.

Kilogram (kilo, kg) – kilo means 1,000, there are 1,000 g in a kilogram. A cube of water 10 cm on a side is 1 l (10 cm^3) and weighs 1 kg.

Gram (gm, g) – A gram is 1/1,000th of a kilogram and equal to the weight of water in a cube 1 cm on a side (1 cm^3).

Milligram (mg, mgs) – Milli means 1/1,000 and 1 mg is 0.001 g, or 1,000 mg = 1 g. A milliliter is 1/1,000th of a liter. A cubic centimeter of water is a milliliter (usually abbreviated as cc).

Microgram (μg, μgs) – Micro means 1,000,000th, so 1 μg = 0.001 mg, or 1,000 μg = 1 mg, or 1,000,000 μg = 1 g. A microliter is 1/1,000,000th of a liter.

Volume measure

10 milliliters (ml)=	1 centiliter (cl)	
10 centiliters=	1 deciliter (dl)	=100 milliliters
10 deciliters=	1 liter (l)	=1,000 milliliters
10 liters=	1 dekaliter (dal)	
10 dekaliters=	1 hectoliter (hl)	=100 liters
10 hectoliters=	1 kiloliter (kl)	=1,000 liters

Cubic measure

1,000 cubic milliliters (mm^3)=	1 cu centimeter (cm^3)
1,000 cubic centimeters=	1 cu decimeter (dm^3)
=	1,000,000 cu millimeters
1,000 cubic decimeters=	1 cu meter (m^3)
=	1 stere
=	1,000,000 cu centimeters
=	1,000,000,000 cu millimeters

Weight

10 milligrams (mg)=	1 centigram (cg)	
10 centigrams=	1 decigram (dg)	=100 milligrams
10 decigrams=	1 gram (g)	=1,000 milligrams
10 grams=	1 dekagram (dag)	
10 dekagrams=	1 hectogram (hg)	=100 grams
10 hectograms=	1 kilogram (kg)	=1,000 grams
1,000 kilograms=	1 metric ton (t)	

Glossary

Absolute dating Method of dating can provide an age in calendar years.

Accelerator mass spectrometer (AMS) A huge scientific instrument used for sorting and counting isotopes. AMS dating allows much smaller samples to be used in archaeology.

Accuracy The ability of an instrument to provide the correct answer.

Activity area Location of specific tasks or behaviors within a site.

Additive technique Manufacture of an object involves making a bigger item from smaller pieces; example pottery or house building.

Adobe A brick made of earth and straw and dried by the sun.

Agriculture Subsistence practice based on the cultivation of domesticated plants and/or the herding of domesticated animals.

Aliquot An equal, measurable part of a large whole.

Amino acid Simple organic compounds containing carbon, hydrogen, oxygen, nitrogen, and in certain cases sulfur. Twenty amino acids are the building blocks of proteins.

Analysis The search for information and pattern in archaeological materials.

Ancient DNA (aDNA) Genetic material preserved in archaeological or paleontological plant, animal, or human remains.

Anthropogenic Created or produced by human activity, e.g., anthropogenic soils are a result of human activity.

Anthropological archaeology Archaeological investigations that seek to answer the larger, fundamental questions about humans and human behavior taught in departments of anthropology.

Apatite The mineral part of bone and tooth enamel, $Ca_{10}(PO_4)_6(OH)_2$.

Appendicular skeleton The limbs (the clavicles, scapulae, bones of the pelvis, and the upper and lower limbs, including the hands and feet).

Arboreal pollen (AP) Pollen from trees.

Archaeobotany (aka paleobotany, paleoethnobotany) The study of archaeological plant remains.

Archaeological chemistry The investigation of inorganic and organic composition, elements and isotopes, molecules and compounds in archaeological materials.

Archaeological context The buried or surface context in which archaeological remains are found; what survives to the present.

Archaeological culture A group of related materials from a region that indicate a common or shared way of doing things.

Archaeological record The body of information about the past that has survived to the present.

Archaeological science A generic term that includes non-instrumental areas such as faunal analysis, paleoethnobotany, and human osteology.

Archaeology The study of our human past, combining the themes of time and change, using the material remains that have survived.

Archaeometry The measurement of the chemical or physical properties of an artifact in order to solve problems of chemical composition, technology, chronology, etc. Sometimes described as "instrumental" archaeology.

Archaeozoology The study of animal remains in archaeology.

Articular The portion of the bone that touches another bone, usually a surface at the end or edge of a bone.

Artifacts Any object or item created or modified by human action; the objects and materials that people have made and used.

Atomic mass The total number of protons and neutrons in a single atom, often expressed in unified atomic mass units (AMU).

Atomic number The number of protons in the nucleus of an atom, distinctive for each element.

Atomic weight The average atomic mass for the different isotopes of an element, weighted by the abundance of each isotope.

Attributes Detailed characteristics of archaeological materials and information.

Base The lower part of a ceramic vessel.

Bifacial A term describing a flaked stone tool in which both faces or sides are retouched to make a thinner tool. See also "Unifacial."

Bioarchaeology The study of human remains from archaeological contexts.

Biological anthropology The study of the biological nature of our nearest relatives and ourselves.

Body sherd Fragment of broken pottery that do not include the rim of the vessel.

Bronze A mixture of tin (or arsenic) and copper that produced a harder metal. Produced in both the Old and New Worlds.

Bundle burial A disarticulated group of bones buried in a group, probably tied in a bundle or wrapped in a skin or cloth.

Burial population The set of human remains found interred in a site or cemetery.

Calibration Correction of radiocarbon dates for the difference between calendar years and radiocarbon years.

Cementum annuli Annual deposits of cementum around the base of teeth.

Ceramic Fired clay.

Ceramic petrography Microscopic technique for study of the mineral composition of pottery.

Chelating agent Used in chemistry to form multiple bonds with a single metal ion and can be used to mobilize metals such as obtaining lead samples from ceramics, metals, and glass. Chelates are used in medicine to remove heavy metals, such as lead or mercury, from the bloodstream.

Chert A cryptocrystalline quartz with sub-microscopic crystal size and impurities that give it color and cloudiness.

Chromatograph A spectrum of the amount of the various molecules present in a sample.

Chronology A framework of time to show the order of events, a dated sequence of events in the past.

Civilization A generic term for state-level societies that refers to the presence of characteristics such as monumental architecture, writing, stratified social organization, and large population.

CN analyzer Instrument used in archaeology to measure carbon and nitrogen abundance in organic materials.

Collagen The protein that makes up the organic portion of bone.

Composition The mineral and organic contents in a petrographic thin section.

Compounds Combinations of elements in either organic or inorganic molecules.

Conservation Preservation and restoration of archaeological materials in the laboratory and museum.

Context Place and association among the archaeological materials and the situation in which they occur.

Correlation A measure of association between two sets of numbers.

Cortical bone Hard, dense bone tissue commonly found in limbs and supporting structure of the skeleton.

Crystalline Materials with atoms arranged in a regular geometric pattern, used in XRD analysis.

Culture (1) Learned human behavior; (2) human societies or ethnic groups.

Data Information collected in a study, including numbers, text and/or images; the observations and measurements of archaeological materials.

Deciduous teeth The first set of "baby" teeth that are lost when the permanent teeth erupt.

Dendrochronology A dating technique used in archaeology to date old pieces of wood, based on the principle of annual growth rings in trees.

Descriptive statistics Used to summarize information and for the comparison of numbers in different sets of data; mean, median, mode, range, variance, standard deviation are descriptive statistics.

Diachronic Dealing with change over time, comparing two or more time periods.

Diagenesis Post-depositional contamination of materials, chemical changes in artifacts.

Diatom Silicate shells of microscopic algae.

Dichroic (two-color) A translucent material of two colors depending on the direction of the light.

Diffraction Principle of X-rays being scattered when striking a crystal, used in X-ray diffraction analyses.

Diffusion The spread of new ideas or materials from one group to another.

Discriminant analysis Statistical technique for classifying a set of observations into predefined classes based on new measurement.

Division of labor Individuals, groups, or segments of society perform different activities.

Ecofacts Unmodified, natural items found in archaeological contexts, often plant or animal material.

Economy The means and methods that society uses to obtain food, water, and resources for maintenance and growth.

Electromagnetic spectrum The wavelength or energy range of all possible electromagnetic radiation.

Element Building blocks of matter, different atoms by atomic number.

Environment The natural and social milieu in which human societies operate.

Enzyme A protein that catalyzes a chemical reaction.

Epiphysis Joint ends of bones where growth occurs.

Ethnoarchaeology Study of living societies of information on the past.

Evolution Generally accepted explanation for the development of life on earth.

Excavation The exposure, recording, and recovery of buried materials from the past.

Exotic Foreign, unusual, in archaeology refers to artifacts and other materials from non-local sources.

Fabric The geometric relationship of the constituents in a petrographic thin section.

Faience Non-clay based ceramic, made from sand, salt (natron), calcite lime, and various mineral pigments, displaying surface vitrification which results a bright luster.

Fatty acid Organic compound in animal and vegetable fats and oils. A straight chain hydrocarbon with a carboxylic acid (–COOH) group at one end, which reacts with glycerol ($C_3H_5(OH)_3$) to make a fat.

Fauna Generic term for the archaeological remains of animals; the category of animals.

Faunal remains The animal ecofacts found in archaeological contexts, including bone, teeth, antler, ivory, shell, scales, and the like.

Features The permanent facilities and structures that people construct in or on the earth.

Fieldwork An important part of archaeological research involves survey for and excavation of archaeological materials, practices normally done outdoors (in the field) and collectively known as fieldwork.

Fill Geomorphological terms for deposition of sediments, also human filling.

Flake A type of stone artifact produced by removing a piece from a core by chipping or knapping. Flakes are made into a variety of different kinds of tools or used for their sharp edges (without further retouching).

Flint A hard siliceous stone that breaks in predictable ways to produce sharp flakes, common raw material for stone tools in prehistory.

Flora Generic term for the archaeological remains of plants; the category of plants.

Flotation A process to recover charred or burned plant materials by floating them in water.

Fluorine absorption An archaeometric test for relative dating based on the assumption that fluorine accumulates at a constant rate in buried bone.

Fossil The mineralized bone of an extinct animal. Most bones associated with humans in the Pliocene, Pleistocene, and Holocene are too young to have been mineralized, but the term *fossil skull* or *fossil bone* is often used generically in these cases as well.

Fossile directeur (French: indicator fossil) a single fossil species as a marker of a time horizon.

Fractionate Process through which the ratio of isotopes in a material can be changed by heat, photosynthesis, enzymes, or other natural mechanisms.

Fume hood A ventilation system for removal of toxic gas in a chemistry lab.

Function The use of an artifact; the action or activity for which it was made.

Gas chromatograph–mass spectrometer (GC–MS) Archaeometric technique for organic materials, samples in gas state separated in a column and exit sequentially to a detector that produces a spectrum of the weight and amount of the molecules.

Geiger counter A device for measuring radioactive emissions.

Geoarchaeology Archaeological research concerned with geology and the earth sciences.

Geographic information systems (GIS) A computer program(s) for the storage, display, and analysis of geographic and spatial data. The basic concept involves the use of overlaid maps of an area in combination with locational information and spatial analytical capabilities.

Geomorphology The branch of geology concerned with the study of the shape of the land, and involves classification, description, origin, and change of land forms.

Glaze A metallic or glass mixture used to change the surface of the pottery vessel for decorative purposes.

Glow curve In thermoluminescence, a graph of the amount of light emitted with temperature for a specific mineral.

Hieroglyph originally, the pictographic script of ancient Egypt; any depictive, art-related system of writing, such as that of Mesoamerica. also may refer to an individual symbol.

Histogram A graph of the number of measurements in interval form.

Horizon Usage includes a soil horizon or a cultural horizon (1) layer or assemblage associated with geological strata or archaeological contents, (2) the geographic extent of similar artifacts and design in space.

Hunter–gatherers People who obtain their food from wild plant and animals, not domesticated species. Also called foragers. Contrasts with farmers.

Hydrocarbon One of many organic compounds that contain only carbon and hydrogen.

Hydroxyapatite The mineral component of bone, $Ca_{10}(PO_4)_6(OH)_2$.

In situ (Latin) An object in its original position of discard or deposition, in place, primary context.

Inductively coupled plasma–mass spectrometry (ICP–MS) Archaeometry technique, samples introduced to plasma source are ionized and elemental mass and concentration are measured.

Inferential statistics Used for making decisions about data and relationships among variables; inferential statistics use probability and confidence limits for comparison and decisions. Chi-square, *t*-test, *f*-test are kinds of inferential statistics.

Ingot A casting of pure metal intended for transport and reuse, usually oblong or disk-shaped.

Inhumation Burial of all or part of the corpse, contrast with cremation.

Inorganic compounds Molecules that do not contain carbon.

Ion Electrically charged atoms that have lost or gained electrons.

Infrared (IR) spectroscopy Instrument that provides compositional information about specific compounds, by inducing vibrations within a molecule.

Isotopes Slightly different atoms of the same element with the same atomic number, but a different numbers of neutrons.

Kouros Ancient stone statue of a nude Greek youth.

Leguminous plants An erect or climbing nitrogen-fixing bean or pea plant.

Lipids A generic category of greasy compounds including fats, oils, waxes, sterols, and triglycerides, that are constituents of living tissues.

Lithic assemblage The complete set of stone artifacts found at an archaeological site.

Lithics A generic term used for stone artifacts in archaeology and more specifically for flaked stone artifacts.

Living floor The actual places where people lived and carried out their activities.

Macroscopic Visible to the naked eye.

Magnetometer (Aka gradiometer) measures the earth's magnetic field at an archaeological site to located buried walls and pits.

Mass spectrometer Any analytical instrument that records components of a spectrum by mass.

Material culture Tangible, surviving evidence of human activities.

Mean The average for ratio scale data calculated by dividing the sum by the number of numbers.

Median The exact middle number of the nominal or ordinal values.

Mesoamerica Geographic and anthropological term for the area of Mexico, Guatemala, Belize, and parts of Honduras and Salvador where several early civilizations including the Aztec and Maya emerged.

Metal detectors Instruments that emit an electromagnetic field that is disrupted by the presence of metal objects in the ground, used for finding buried metal objects.

Micromorphology The study of anthropogenic sediments at a microscopic level.

Microscopic Visible only with magnification.

Microwear analysis Microscopic studies of damage and polish on the edges of stone artifacts to reveal the materials that were worked.

Migration Movement of new people into an area.

Mitochondrial DNA (mtDNA) Modern genetic material taken from the mitochondria, inherited only through the maternal line.

Molecular archaeology Sometimes used to refer to the organic component of archaeological chemistry and particularly to the investigation of ancient DNA in plant and animal remains, including humans. Sometimes called biomolecular archaeology.

Molecule A combination of atoms held together by chemical bonds.

Myoglobin A protein found in human tissue, its presence in human feces is used as evidence for cannibalism.

Native American Graves Protection and Repatriation Act (NAGPRA) Federal legislation intended to protect and return certain archaeological human remains and culturally significant artifacts to native Americans.

Neutron Particle in the core of an atom with no electrical charge.

Neutron activation analysis (NAA) Archaeometry technique using a neutron bombardment to release detectable element-specific gamma rays in samples.

Non-arboreal pollen (NAP) Pollen from plants other than trees.

Normal curve The standard, or normal, shape of measured values plotted in a frequency diagram.

Nucleic acid Compounds found in all living cells and viruses, composed of purines, pyrimidines, carbohydrates, and phosphoric acid.

Observation Term used for each value recorded in a data set.

Obsidian A glassy rock produced in volcanic conditions, excellent material for stone tools.

Ochre A red, yellow, or brown iron mineral sometimes found in prehistoric graves.

Old World The term describes the world as known prior to the European discovery of the Americas (the New World) and included the continents of Europe, Asia, and Africa.

Ordinal scale of measurement Ranked information with an ordered relationship between numbers.

Organic compounds The molecules of living organisms with the element carbon as a base.

Paleobotany Study of fossil plants.

Paleoethnobotany The study of plant use by both living and prehistoric peoples.

Paleontology Study of fossil animals.

Palynology The study of pollen from plants for information on species, environment, and climate.

Parenchymous tissues Parenchyma is plant storage tissue, commonly found in roots, tubers, rhizomes and corms.

Parry fracture A distinctive break in the forearm resulting a blow to an arm raised in protection.

Paste Mix of clay and other materials used to make pottery.

PCR See "Polymerase Chain Reaction."

Periodic table Summary information for the known elements, organized by atomic weight and relationships among elements.

Petrographic microscope A specialized version of a binocular microscope designed for the study of thin sections of rock or pottery.

Phase A particular period in time and space where an assemblage occurs.

Plan view A bird's eye or top down view of a site or region. A kind of map of the features and characteristics of a place. A standard representation of archaeological sites and areas.

Plasma The gaseous state of hot ionized material consisting of ions and electrons used as a source for ions in spectrometry.

Political organization The use and distribution of status, power, and authority within a society.

Pollen Covering of the gametes of flowering plants released in sexual reproduction.

Polymerase chain reaction (PCR) Technique in genetic studies to increase quantities of DNA sample by rapid cloning.

Population (1) All of the people living at a place or in a region. An archaeological population generally refers to the people related through membership in the same group. (2) All of the items or units of interest in statistical sampling.

Pottery Ceramic container.

Precision The measure of how exactly an instrument can reproduce the same measurement.

Prehistory The time in the past before written history, often synonymous with archaeology.

Primary context An object in its original position of discard or deposition, in place (Latin: in situ).

Protein Complex organic macromolecule composed of more chains of amino acids containing carbon, hydrogen, oxygen, and nitrogen; fundamental components of all living cells and many substances such as enzymes, hormones, and antibodies.

Proton Particle in the core of an atom with a positive electrical charge.

Provenience The place of discovery or origin. Where an item was found or came from (aka provenance in classical archaeology).

Provenience postulate States that if differences within a source of material are less than differences with other sources, then it is possible to distinguish individual sources, or provenience.

Radiocarbon A radioactive isotope of carbon (^{14}C, carbon-14); an important dating technique in archaeology.

Radiopotassium, or potassium–argon, dating Dating technique for old samples that is based on half-life for decay of potassium into argon in new rock.

Raman infrared spectroscopy A particular wavelength from IR in the electromagnetic spectrum is projected onto a sample and the diagnostic wavelengths of the light scattered at a high angle are recorded.

Ratio scale of measurement Measurements with a true zero point made using an instrument.

Reciprocity The exchange of items of roughly equal value.

Redistribution The movement of goods to a central place from where they are rationed or portioned out to select members of society.

Relative dating Method of dating that determines whether an object or layer is older or younger than another.

Research design The overall strategy of intended methods, research area, and planned analysis for answering a question or questions about the past.

Residue Traces of physical and chemical remains on archaeological materials such as pottery, stone tools, and other artifacts.

Resistivity meter Used to measure electrical conductivity in soils that may be due to the presence of buried disturbances such as fireplaces, burials, or other structures.

Sample A sample means a portion of a whole as a noun and to take a part of a deposit, site, feature, or artifact for analysis as a verb. The term sampling is used to describe the process of taking a sample. This can be a one-time event, a series of actions, or a statistical process. Statistical sampling is a specific method for taking samples that allows probability estimates to be made about the population that is being sampled. Archaeologists almost always take samples, but only rarely is this done in a statistical fashion.

Sampling fraction The portion of the whole population or mass that is sampled.

Scale (1) Different levels of discovery, analysis, and interpretation in archaeology, or (2) the size of a map relative to the area it portrays.

Scale of measurement Measurements can be made using nominal, ordinal, or ratio scales of numbers.

Scanning electron microscope See "SEM."

Scatterplot A single graph combining two sets of numbers simultaneously.

Sediment Any particulate matter (clay, sand, silt, mud, gravel, leaves, shell, and other materials) that can be transported by water or other fluids, opposite = rock.

SEM Scanning electron microscope.

Sensitivity The measure of the smallest amount that can be reliably measured.

Settlement pattern The organization and distribution of human settlement across the landscape.

Sherd Broken piece of pottery.

Silica SiO_2, the major mineral component of sand.

Site Accumulation of artifacts and features, representing a place where people lived or carried out certain activities.

Social organization Structure of human society based on relationships among members and hierarchical arrangements.

Soil In situ weathered sediments on the earth's surface with specific physical and chemical characteristics.

Species Scientific classification of plants and animals uses a hierarchy of groups including class, family, and a number of others. Species is a very specific group of organisms that can mate and produce sexually viable offspring. Modern humans belong to the genus *Homo* and the species *sapiens*.

Specimen Any material collected for scientific analysis.

Speleothem Cave formation, a secondary mineral deposit in the form of stalagmites, stalactites, flowstone, and other features.

Standard deviation (s.d.) The square root of the variance, a single measure of spread.

Starch grains Microscopic grains of a complex carbohydrate found in certain species of plants.

Sterol Unsaturated solid alcohol, such as cholesterol and ergosterol, present in the fatty tissues of plants and animals.

Subsistence Food; refers to how humans obtain food, hunter–gatherers vs. farming.

Subtractive technique The continuous removal of material from a larger original piece in the manufacturing process; examples include stone working and wood carving.

Synchronic Dealing with a moment in time, a single time period.

Taphonomy The study of what happens to an organism after its death, including decomposition, post-mortem transport, burial, and the biological, physical, and chemical changes.

Technology The material, equipment, techniques, and knowledge that allows humans to convert natural resources into tools, food, clothing, shelter, and other products they need or want.

Temper A non-plastic substance intentionally added to clay in order to reduce breakage caused by shrinkage and firing.

Thermal ionization mass spectrometer (TIMS) A scientific instrument for measuring isotope ratios of heavier elements.

Thermoluminescence (TL) dating Technique for absolute dating based on the principle of the rate of accumulation of TL after heating, used with burned flint and clay.

Tool Any equipment, weapon, object intentionally modified by humans to change the environment around them.

Trabecular bone Spongy bone tissue found in the interior of bone.

Trade Economic transactions between individuals or groups involving bartering, buying, or selling.

Trophic level Position in the food chain, e.g., herbivore, carnivore, bottom-feeder.

Ultrasonic cleaner Lab equipment using ultrasound in liquid bath for cleaning.

Variance A single measure of spread or range in ratio data.

Wet lab A chemistry facility with lab tables, equipment, and running water.

X-ray diffraction (XRD) Method for measuring mineral components of inorganic solids using distinctive patterns of X-ray scattering.

X-ray fluorescence (XRF) Archaeometric method for measuring element abundances in inorganic materials; X-rays are used to excite atoms to fluoresce and emit a characteristic signal for each element.

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