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**Cotsen Institute of Archaeology Press**

**Title**

An Archaeologist's Guide to Chert and Flint

**Permalink**

<https://escholarship.org/uc/item/7j8387sj>

**ISBN**

0-917956-75-3

**Author**

Luedtke, Barbara E.

**Publication Date**

1992

Peer reviewed

# **An Archaeologist's Guide to Chert and Flint**

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Archaeological Research Tools 7  
Institute of Archaeology  
University of California, Los Angeles  
1992

UCLA Institute of Archaeology Editorial Board

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Library of Congress Cataloging-in-Publication Data

Luedtke, Barbara E.

Archaeologist's guide to chert and flint / Barbara E. Luedtke.

p. cm. -- (Archaeological research tools ; 7)

Includes bibliographical references (p. ) and index.

ISBN 0-917956-75-3

1. Mineralogy in archaeology. 2. Chert. 3. Flint. 4. Stone implements.

I. University of California, Los Angeles. Institute of Archaeology. II. Title.

III. Series: Archaeological research tools ; v. 7.

CC79.M55L84 1991

549'.68--dc20

91-46805

CIP

Cover illustration: Scanning electron micrograph of fracture surface of light gray  
Arkansas novaculite from Magnet Cove, Arkansas.

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2nd printing, March, 1994

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## Acknowledgments

First, it is a pleasure to thank Kenneth Pisciotto, Barbara Purdy, Rip Rapp, Are Tsirk, and several anonymous archaeologists who each reviewed portions of this book. They made many constructive comments and saved me from committing several embarrassing mistakes. However, they should not be held accountable for any remaining errors.

Most of the trace element data that proved so useful throughout this book were obtained as a result of National Science Foundation grants GS-1196, GS-2242, and GS-3214 to the University of Michigan Museum of Anthropology. I received additional funding from the American Council of Learned Societies and the University of Massachusetts/Boston Faculty Development Grant program. Tom Meyers, Ed Wilmsen, and James B. Griffin all made vital contributions to this aspect of my research, and they have my heartfelt thanks. Mary Smith of the University of Massachusetts/Boston Biology Department helped me with the SEM micrographs, and Suzanne Lawson produced the rest of the fine illustrations.

Finally, I owe a special debt of gratitude to the faculty, guest speakers, staff, and students of the Center for Materials Research in Archaeology and Ethnology, which is based at the Massachusetts Institute of Technology and directed by Heather Lechtman. Participation in this Boston-area interuniversity consortium convinced me of the fruitfulness of a multidisciplinary approach to archaeological materials and stimulated me to begin this book.

*Barbara E. Luedtke*

# 1

## Introduction

**I**n a world dominated by things made of metal, glass, concrete, plastics, and a host of other synthetic materials, it is easy to forget that stone was once the most important raw material used by humans for technological purposes. For at least 2.5 million years humans have been using tools, and until just a few thousand years ago their most important tools were made of stone for cutting, piercing, scraping, and shaping wood, bone, shell, leather, fiber, and reed.

While human creativity found uses for all kinds of stone, the single most important and widely used stone in nearly every part of the world was chert (or flint, as it is often called). Its value was based on its general availability; ease of workmanship; sharp, durable edge; and interesting variety of colors and patterns.

Prehistoric peoples must have been intensely interested in chert sources and the relative properties of the different types of chert, but this interest faded when metals replaced stone for most tools. Although chert continued to be used until recent times in a few parts of the world for such minor purposes as flints in flintlock guns, ballast, blades in threshing machines, ceramics, and construction, it was no longer technologically significant.

Of that select portion of humanity still interested in chert, archaeologists must surely predominate, with geologists, gemologists, a few engineers, and miscellaneous others making up the balance. Chert is vital to many archaeologists' efforts to understand past cultures. Owing to their durability, artifacts made of chert are often the primary, and sometimes the only, surviving source of information about prehistoric cultures.

By studying the attributes of stone tools and chipping debris we can learn exactly how these tools were made. For researchers

interested in the early hominids, this knowledge provides insight into the evolution of human motor development and technological capabilities. Other researchers dealing with later cultures can identify manufacturing methods and traditions that help them define cultural entities, trace relationships among such entities, or chart the development of craft specialization. Use-wear studies help us determine how stone tools were used, thus providing insight into past technologies and economies, and very precise information about what activities took place at a particular site. Also, by determining the sources of particular kinds of chert, we can define social territories and trace trade networks.

Although archaeologists know a great deal about how chert was worked and used, we know far less about it as a raw material. Archaeologists are quite aware that different cherts can vary in appearance, in the way they break under specific applications of force, and in chemical composition. Source analysts use the variation in these properties to determine an artifact's source, and those persons studying manufacturing patterns and use-wear must consider variation when comparing artifacts made of different cherts. Yet despite our awareness of the variability in chert, we rarely ask what causes it or seek to connect the variability in one property with that in another.

We could better understand how past peoples used chert if we better understood chert itself. For example, we often assume that prehistoric people went to the trouble of obtaining a certain chert from a distant source because it was "better" than local cherts. We could be far more convincing if we could demonstrate how it was better—for example, that its strength or elasticity is superior to that of the local cherts. It would be equally informative

to demonstrate that the imported material was not mechanically superior to local cherts, thus implying that chert preferences were instead determined by ideological, social, or political factors. Ideally, we could achieve these goals without tediously measuring each mechanical property and instead could make one simple measurement of a property that is known to be correlated with the relevant mechanical property.

## Scope and Goals of the Book

The scope and intent of this book can be clarified by a brief explanation of why I decided to write it. Like most archaeologists, I first became interested in chert as a means toward a specific archaeological goal. I was a graduate student in the Department of Anthropology at the University of Michigan during a time when the Museum of Anthropology was involved in a long-term effort to explore the ways in which chemical analyses could be useful in archaeology. Considerable success had recently been achieved using neutron activation analysis to characterize obsidian on the basis of its trace element composition (for example, Griffin, Gordus, and Wright 1969), and the members of the Michigan project now sought to extend this technique to cherts. I wanted to use this method to assign artifacts objectively to different chert types. I could then study trade and interaction patterns by examining the distributions of different types of chert at sites of the Late Woodland period in Michigan (Luedtke 1976).

People who study the chemical composition of cherts quickly find themselves grappling with the issue of variability. Chert is far less homogeneous than obsidian, and any attempt to match an artifact to its source can be successful only if the differences among sources are greater than the variability within each source. My cherts varied a great deal, and I became interested in the variability itself. I wondered why some cherts varied so much in their chemistry while others were relatively homogeneous. There also appeared to be patterns of variability among elements; some were highly correlated and others were not (Luedtke 1978).

While continuing to use chemical data to determine the sources of chert artifacts (Luedtke 1979; Luedtke and Meyers 1984), I realized I must answer for myself why chert varies chemically before I could feel confident in drawing archaeological inferences.

By this time, I had other questions as well. Use-wear experiments left me curious about why cherts vary so much in their mechanical properties, and anyone who has handled chert must wonder why it varies so much visually. It seemed likely that many of these properties were interrelated and that they originated in the ways cherts form and are altered over time. It also seemed likely that other researchers had already found answers to some of the questions over which I agonized.

The goal of this book, then, was to draw together as much information as possible about chert and its properties. I wanted

to synthesize what was already known in order to determine what was not yet known and to define the areas where further research might be especially fruitful. I also wanted to create a basic reference book, a compilation of the many kinds of specific information that archaeologists need when they embark on technical studies of chert. Finally, I wanted to present this information in a form accessible to archaeologists, with our particular needs and concerns in mind.

Because this book is intended for archaeologists, I take a certain level of archaeological background for granted. Thus, I assume the reader knows what knapping means, how percussion flaking is done, and what a biface looks like. Such purely archaeological terms, as well as words like sediment and stratigraphy which are normally known by all archaeologists, are not defined here.

On the other hand, all the mathematical formulas and much of the technical terminology of the non-archaeological disciplines have been avoided in the interests of clarity. Another reason for keeping technical terminology to a minimum is that not all researchers use the same terms in exactly the same way. With chert being studied by researchers from various disciplines and subdisciplines, including archaeology, ethnography, art history, geochemistry, rock mechanics, petrology, crystallography, and mineralogy, there is no single "correct" definition for some of the crucial terms used here. Therefore, I have chosen definitions that appear to be most useful and widely held, and then tried to apply them carefully and consistently.

Because the literature concerning chert is vast, I adopted limits to keep this book manageable. Thus, this work is not a thorough literature review or a critique of research in each area. Only those references cited in the text are included in the bibliography. Citation has also been minimized and no attempt has been made to acknowledge all the researchers who have contributed to our knowledge of chert.

Further, this book is not a source of information about specific chert types, and it does not cover all types of cherts equally. Although a variety of cherts from various parts of the world are used as examples in each section, many are from my own midcontinental and northeastern North America research area. I found it easier to interpret specific findings for chert types I already know well and for which I have additional information. Thus, specific chert types are used here only to test hypotheses or exemplify broader conclusions.

Nor is this book a how-to manual of technical procedures. Beyond what is necessary to make a particular argument or conclusion clear, I do not describe specific analytical techniques. In general, a technique is mentioned only in order to discuss the kinds of information that can be learned using that procedure. References are given which describe these techniques in more detail.

Finally, archaeological applications of the data in this book

are only mentioned and not explored in depth. Its focus is always on chert as a raw material, not on how archaeologists use chert to study human behavior.

## Organization of the Book

This book is organized around the different properties of chert. These properties are not independent or randomly associated, and they exhibit relationships that are meaningful and at least somewhat predictable. Consequently, the chapters are interlocked in complicated ways, making a certain amount of redundancy unavoidable.

Chapter 2 defines chert, as a word, as a type of rock, and finally as a material with a particular composition and internal structure. It also introduces the many different levels on which chert can be studied, from the outcrop down to subatomic particles.

Chapter 3 deals with the origin of chert, a vastly controversial and complicated topic, but one in which much progress has been made lately. It concludes that chert can form under widely varying circumstances and through more than one pathway. It is exactly this heterogeneity that causes much of the variability in properties with which I deal in later chapters.

Chapter 4 discusses the chemical properties of chert. Chert is made up largely of silicon and oxygen, along with organic and inorganic impurities. Chemical variability results from the specific chemical and geological circumstances under which

each chert forms, and it dramatically affects some of chert's other properties.

Chapter 5 explores the visible properties of chert, those observable with the unaided eye and those visible only through the microscope. Color, luster, and texture, the most easily determined visible attributes, are strongly influenced by impurities.

Chapter 6 examines the mechanical properties of chert, especially strength, hardness, and elasticity, the most important attributes for toolmaking. Since stone tools are made primarily through controlled fracture, a good tool material must break in controllable and predictable ways, must perform the tasks for which it was intended, and must not wear or break too easily during use. The mechanical properties are essentially those of quartz, the predominant mineral in chert, as modified by impurities and the internal structure of the rock.

Chapter 7 describes the changes that occur in chert as a result of heat treating and natural processes such as weathering and patination. These processes produce interrelated changes in most properties.

Chapter 8 summarizes the causes of variation in chert and points out where additional research is needed.

Two appendixes, a glossary, and a bibliography complete the book. The first appendix outlines procedures for chert source analysis projects and suggests a type of database that would simplify such projects. The second appendix provides basic information about the chert types used as examples.





# 2

## The Nature of Chert

**T**he question “What is chert?” may be answered by considering the differing definitions of the word itself, outlining the relationship between chert and similar kinds of geological materials, and examining the physical structure of chert at different scales.

The first approach is essentially linguistic. Initially, I define the word *chert* as it is used in this work and then examine the relationship between it and other terms that are frequently used to refer to the same kinds of rocks, such as *flint*, *jasper*, and *chalcedony*.

The second approach examines the taxonomic relationships between chert and other geological materials. Some of these related materials also play important roles in the formation of chert.

In the third approach, chert’s internal structure is examined on scales ranging from the macroscopic to the submicroscopic. Several physical and chemical characteristics of chert, which are important for later chapters, are also introduced.

### The Word Chert

In this book, *chert* is used as the general term for all sedimentary rocks composed primarily of microcrystalline quartz, including flint, chalcedony, agate, jasper, hornstone, novaculite, and several varieties of semiprecious gems. This broad definition results in the grouping of materials whose properties vary considerably. Furthermore, the outer boundaries of the chert domain are fuzzy in places. For example there is a gradation between siliceous shales and shaley cherts and some cherts may form partly through hydrothermal action, thus bordering on the metamorphic. How-

ever, this situation is not unique to chert: “...rock types grade into each other, and a rock name is a convenient pigeonhole rather than a species of fixed composition” (Mason and Moore 1982:95). I believe there is a need for a general term that includes all the protean varieties of sedimentary fine-grained siliceous rocks since they have many important properties in common vis à vis other rock types.

The only other term with a serious claim for use in this general sense is *flint*. There has long been confusion concerning the exact relationship between the words *chert* and *flint*. The latter is apparently the older word. The Oxford English Dictionary states that the first printed reference to flint appeared about AD 700. The word *chert* is not documented in print until AD 1679. Some geologists and archaeologists have used these two words interchangeably (for example, Spielbauer 1976:152), while others have argued that they refer to two different materials (for example, Shepherd 1972:35). A few have defined chert as a variety of flint (for example, Wray 1948:25), whereas others consider flint to be a variety of chert (for example, Blatt et al. 1972:531). One geologist even suggested that flint be used to refer to artifacts and chert to the raw material from which they were made (Pettijohn 1975:394).

The major division in usage is geographic. Although most American geologists consider flint to be a variety of chert, British archaeologists and geologists generally consider them to be two different materials. Flint is traditionally used in a rather restricted sense in Great Britain to refer to the dark, high-quality nodular material found in the Cretaceous chalk formations that outcrop across much of southern England. Chert refers to the lighter-

colored, impure, lesser-quality materials found elsewhere as nodules in limestones or in beds among shales. This distinction is useful for British geology, but it quickly breaks down elsewhere in the world. In many places, dark materials are not necessarily of higher quality than light materials, and both light and dark materials may occur in either bedded or nodular form.

Therefore, I have adopted the American usage of chert and consider all the other terms, such as flint and jasper, to be varieties of chert. In fact, many terms can be considered archaeological “folk categories,” because they are based largely on color and are not precisely defined geologically. The color of cherts may indeed be important in some cultural contexts; for example, bright orange carnelian is more valuable than brownish sard to a dealer in semiprecious gems. Color is not, however, a reliable guide to most attributes of geological significance. For example, archaeologists generally call all red-, brown-, and mustard-colored cherts *jasper*, whereas geologists use the term to refer to cherts with a high iron content. However, some cherts with a high iron content are green or black, and not all red or gold cherts have a high iron content. Furthermore, geologists do not agree as to how much iron must be present before a chert can be called a jasper. Since the potential for misunderstanding is so high, I avoid using these folk categories unless they are parts of common names. Names such as Arkansas novaculite, Pennsylvania jasper, and Knife River flint have long traditions in the archaeological literature; no point would be served by calling them something else.

A somewhat different case concerns *chalcedony*, the only variety of chert that can be distinguished by microscopic form and other attributes. Unfortunately, the word *chalcedony* is used differently by archaeologists, petrologists, and mineralogists, with devastating effects on the comprehensibility of geological and archaeological literature. First, many archaeologists use *chalcedony* to refer to all translucent cherts. We frequently differentiate between raw material types on the basis of easily observable properties, and thus are prone to develop classifications based only on such properties. Second, petrologists generally use *chalcedony* to refer to quartz in its fibrous form (for example, Blatt 1982:386). These fibers, which cannot be seen with the naked eye, are obvious in thin section under a microscope. Furthermore, fibrous quartz apparently forms under somewhat different circumstances than the other more granular varieties of quartz. Because microscopic properties and origin are important criteria to petrologists, they consider *chalcedony* to be distinct from granular quartz. Mineralogists take a different view because the fibrous and granular forms of quartz have the same chemical composition and give the same X-ray diffraction pattern. They are therefore mineralogically identical; consequently, some mineralogists use *chalcedony* to refer to both fibrous and granular microcrystalline quartz (for example, Deer et al. 1963:209).

Although these three definitions of *chalcedony* overlap, they are not completely congruent. Most, if not all, cherts made up

largely of *chalcedony* are indeed translucent, but not all translucent cherts have a *chalcedonic*—that is, fibrous—microstructure. Knife River flint is a good example: it is translucent but is made of granular rather than fibrous quartz (Clayton et al. 1970). Thus, it is not *chalcedony* in the petrologic sense (nor is it flint in the British sense). Therefore, throughout this book, *chalcedony* is used in the petrological sense to mean fibrous quartz because cherts with this structure differ from granular cherts in a number of the properties of interest to us.

Two other terms, *chert type* and *chert source*, are also defined here. A *chert type* refers to chert that occurs in a discrete geological deposit and exhibits a restricted range of variation in at least some properties. Normally, such chert comes from a single geological formation, although sometimes different members within a formation may contain cherts distinct enough to be considered different types. This definition also conforms to common archaeological usage; thus, Flint Ridge chert is that type found in the Vanport formation, and Onondaga chert is from the Onondaga formation.

A *chert source* is a location where a particular type of chert can be obtained. Often, this will be a primary source, such as a quarry or an outcrop, where chert is found in situ where it originally formed in the bedrock. Chert also may be available from secondary sources, such as streambeds, beaches, or glacial deposits, to which it has been transported. Residual cherts, left behind when the surrounding bedrock weathered away, are considered secondary sources.

## Chert as a Rock Type

Returning to the original definition of chert as a sedimentary rock made up primarily of microcrystalline quartz, we must now define these crucial words: rock, sedimentary, quartz, and microcrystalline. Although archaeologists tend to use *rock* loosely as a synonym for *lithic* or *stone*, geologists use a more precise definition that makes more sense if we first define elements and minerals. Chemical elements are the basic building blocks of all rocks; they cannot be separated into different substances by ordinary chemical methods. Figure 2.1 shows the periodic table of elements. Minerals are combinations of elements; a mineral is defined as “a naturally occurring solid, generally formed by inorganic processes, with an ordered internal arrangement of atoms and a chemical composition and physical properties that either are fixed or that vary within some definite range” (Berry, Mason, and Dietrich 1983:3). Quartz (made of silicon and oxygen), pyrite (made of iron and sulphur), and diamond (made up solely of carbon) are examples of minerals. Rocks are aggregates of minerals, such as granite (made up of quartz and orthoclase feldspar, plus mica, amphibole, and pyroxene) and shale (made up primarily of various clay minerals). Chert, then, is a rock made up primarily of grains of the mineral quartz.

Group	IA	IIA	Transition Metals										IIIA	IVA	VA	VIA	VIIA	0
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1																	He 2
2	Li 3	Be 4																Ne 10
3	Na 11	Mg 12																Ar 18
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	(Tc) 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	* 57-71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	(At) 85	Rn 86
7	(Fr) 87	Ra 88	** 89															

Group	IIA	IIIA	IVB	VB	VIB	VIIIB	IB	IIB							
7	La 57	Ce 58	Pr 59	Nd 60	(Pm) 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
8	Ac 89	Th 90	Pa 91	U 92	(Np) 93	(Pu) 94	(Am) 95	(Cm) 96	(Bk) 97	(Cf) 98	(E) 99	(Fm) 100	(Md) 101	(No) 102	(Lw) 103

\*Rare Earth Metals

\*\*Actinide Metals

Figure 2.1  
Periodic table of elements.

Rocks are subdivided by mode of origin into igneous, metamorphic, and sedimentary. Igneous rocks form at very high temperatures from molten rock, metamorphic rocks form when existing rocks are altered as a result of being subjected to intermediate temperatures and pressures, and sedimentary rocks form at the low temperatures and pressures typical at or near the earth's surface. Sedimentary rocks can form either through the accumulation of fragments of other rocks, as with sandstone or shale, or by chemical precipitation, as with chert and some limestones. Figure 2.2 shows these relationships schematically.

Chert is also defined by its composition: it is composed predominantly of quartz. Quartz is one of a family of important minerals known as silicates (fig. 2.3), all of which are various combinations of silicon and oxygen, sometimes in combination with other elements. Silicon and oxygen are the two most abundant elements on earth (table 2.1); thus it is not surprising that 40% of the common minerals, and nearly all the igneous rock-forming minerals, are silicates (Klein and Hurlbut 1985:366). Quartz belongs to the silica family, which includes all those minerals with the chemical composition  $\text{SiO}_2$ . Thus all silica minerals have two oxygen molecules for every silicon molecule (usually linked to form a tetrahedron), with each silicon connected to four oxygens and each oxygen to two silicons. There are a few other rare silica minerals (not shown on figure 2.3), such as lechatelierite and melanophlogite, but these appear to have little or no relevance to chert and so are not discussed further.

Although all silica minerals have the same chemical composition,  $\text{SiO}_2$ , their crystal structures differ. Often X-ray diffraction is necessary to tell different silica minerals apart. This is accomplished by bombarding the substance with X rays, which are diffracted by the various planes of the atoms, forming a distinct pattern for each crystal structure.

Several *mineraloids*, substances that have considerable water content and poorly defined crystal structures, are closely related to silica minerals. Generally referred to as opals, they are subdivided into several varieties (Jones and Segnit 1971), the most important of which, for our purposes, are opal-A, opal-CT, and opal-C. Opal-A is amorphous, like glass; it produces a very diffuse diffraction pattern because it is made up of a random network of tetrahedrons (Calvert 1983:147). Both cristobalite and tridymite structures are present in opal-CT, and opal-C has a slightly disordered cristobalite structure.

Temperature and pressure determine which of the silica minerals will form (fig. 2.4). Only one of these minerals,  $\alpha$  quartz, is completely stable at surface temperatures and pressures, and this is the silica mineral that normally forms under these conditions. (When I use the word *quartz* unmodified in this volume, I am always referring to  $\alpha$  quartz.) The high-temperature silica minerals ( $\beta$  quartz, tridymite, and cristobalite), and the high-pressure forms (coesite and stishovite) are unstable at surface conditions and eventually become transformed into  $\alpha$  quartz. The

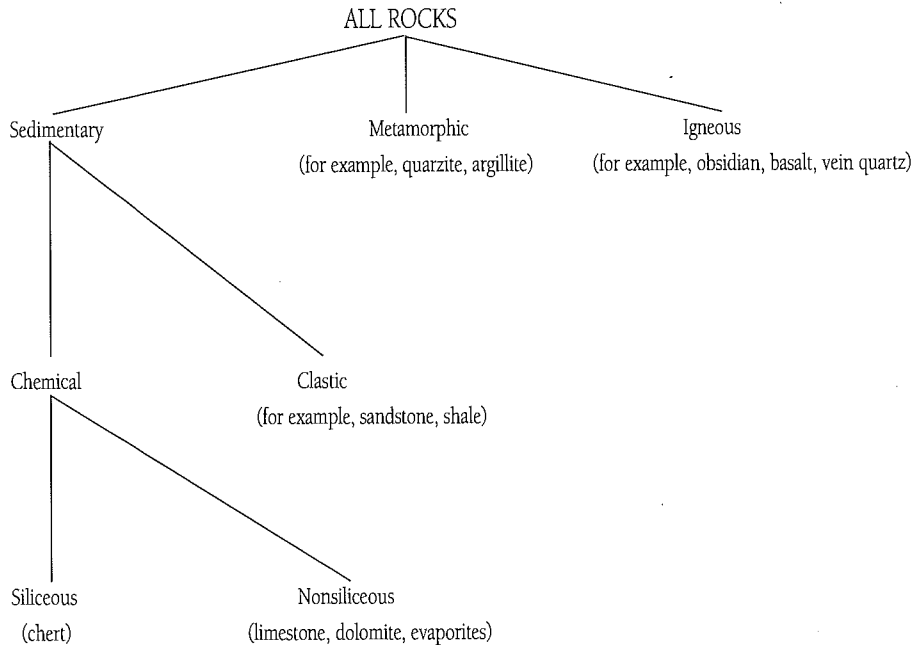
crystal structures of the high-temperature/pressure forms of silica are more symmetrical but less compact than  $\alpha$  quartz.

Quartz is one of the most common minerals on earth. It occurs in a variety of forms, including the large free-standing crystals often found lining cavities, the veins of milky quartz that cut through other rocks, and the tiny irregularly shaped grains that are components of many rocks, including chert. Although all these kinds of quartz have the same chemical composition and internal crystalline structure, the outer shapes of the crystals vary, depending on the conditions under which they formed. The familiar quartz crystal, shaped like a six-sided needle topped with a pyramid, is the largest and most perfect form (fig. 2.5). It is often described as *euhedral*, referring to its well-formed crystal faces, but it is simply called *macrocrystalline quartz* here.

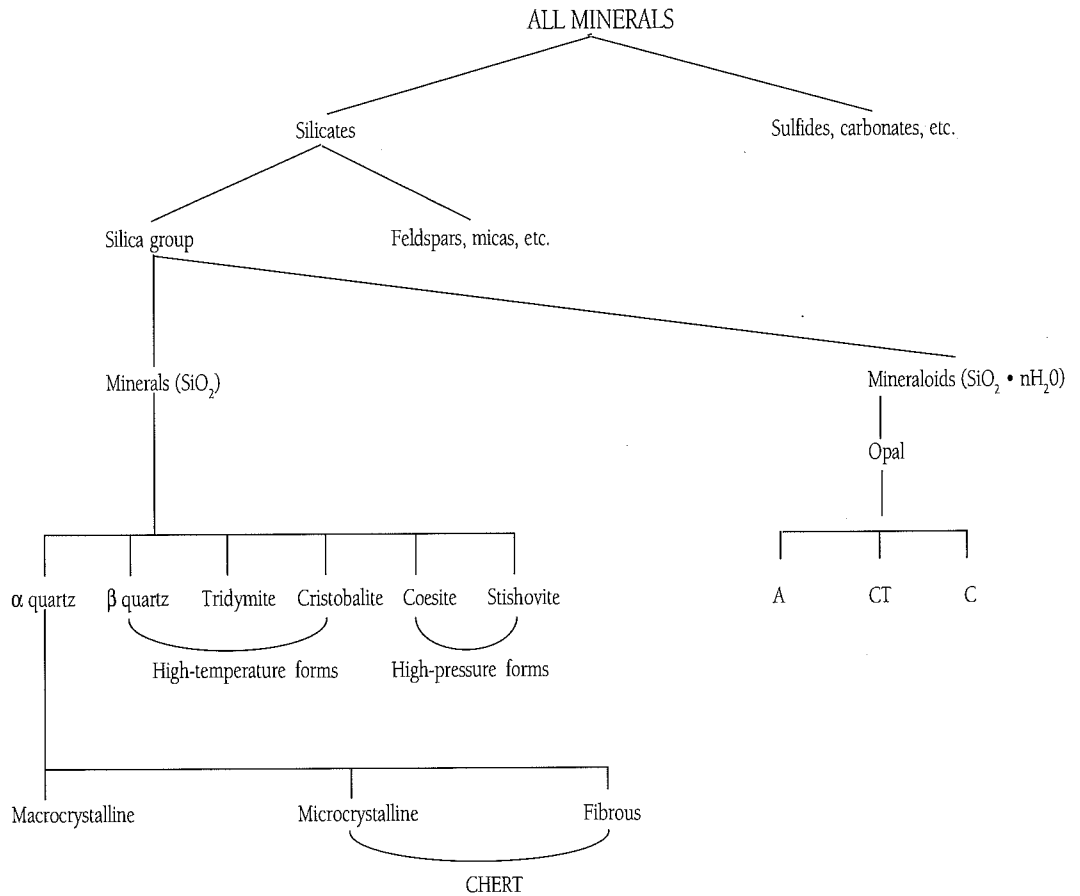
Chert may occasionally contain macrocrystalline quartz crystals, but it is composed mostly of microcrystalline quartz, whose grains are too small to be seen with the naked eye. Though these tiny grains have the same internal structure as the quartz in large quartz crystals, they lack the flat, shiny crystal faces seen in the macrocrystalline crystals because the grains impinged on one another as they grew. For the same reason, they do not have the typical quartz-crystal proportions, with length being considerably greater than width. The quartz grains in chert are roughly the same diameter in all directions or are only slightly elongated. Some definitions of chert also refer to cryptocrystalline quartz; technically, grains that range from 2 to 50  $\mu$  in diameter are called microcrystalline, while grains less than 1 or 2  $\mu$  in diameter are cryptocrystalline (Ozol 1963:72). The grains making chert can be in either size range, but since most chert grains range from 5 to 20  $\mu$  in diameter (Blatt 1982:380) I use the term microcrystalline.

Quartz can take yet another shape, the fibrous form typical of chalcedony. These fibers are not simply long, skinny quartz crystals; the internal arrangement of silica tetrahedrons is oriented differently than in macrocrystalline quartz crystals, and the fibers are often bundled and twisted around each other. These fibers can range from 20 to 1000  $\mu$  in length, but average about 100  $\mu$  (Folk 1974:80). Fibrous quartz is sometimes subdivided into different varieties, such as quartzine, lutecite, or zebraic chalcedony, each of which has a slightly different internal structure.

Again, although the macrocrystalline, microcrystalline granular, and fibrous forms of quartz may look very different, they all have the same chemistry and their X-ray diffraction patterns have peaks in the same places. These peaks can vary in shape, however, depending on the regularity and orderliness of the internal crystal structure. Quartz varieties with tight, well-ordered, and continuous crystal structures produce narrower and more sharply pointed X-ray diffraction peaks than those varieties with less orderly internal structures (Murata and Norman 1976). Thus, although all these forms of quartz are crystalline, it is legitimate to say that



**Figure 2.2**  
Relationship of chert to other rocks.



**Figure 2.3**  
Relationships between the silicate minerals.

**Table 2.1 Average Amounts of the Elements in Rocks of the Earth's Crust (ppm)**

Symbol	Element	Crustal average	Symbol	Element	Crustal average
O	Oxygen	466,000	Sm	Samarium	6.0
Si	Silicon	277,200	Gd	Gadolinium	5.4
Al	Aluminum	81,300	Yb	Ytterbium	3.4
Fe	Iron	50,000	Hf	Hafnium	3.0
Ca	Calcium	36,300	Dy	Dysprosium	3.0
Na	Sodium	28,300	Cs	Cesium	3.0
K	Potassium	25,900	Be	Beryllium	2.8
Mg	Magnesium	20,900	Er	Erbium	2.8
Ti	Titanium	4,400	Br	Bromine	2.5
H	Hydrogen	1,400	Ta	Tantalum	2.0
P	Phosphorus	1,050	Sn	Tin	2.0
Mn	Manganese	950	As	Arsenic	1.8
F	Fluorine	625	U	Uranium	1.8
Ba	Barium	425	Ge	Germanium	1.5
Sr	Strontium	375	Mo	Molybdenum	1.5
S	Sulfur	260	W	Tungsten	1.5
C	Carbon	200	Eu	Europium	1.2
Zr	Zirconium	165	Ho	Holmium	1.2
V	Vanadium	135	Tb	Terbium	0.9
Cl	Chlorine	130	Tm	Thulium	0.5
Cr	Chromium	100	Lu	Lutetium	0.5
Rb	Rubidium	90	Tl	Thallium	0.5
Ni	Nickel	75	I	Iodine	0.5
Zn	Zinc	70	Bi	Bismuth	0.2
Ce	Cerium	60	Sb	Antimony	0.2
Cu	Copper	55	Cd	Cadmium	0.2
Y	Yttrium	33	In	Indium	0.1
La	Lanthanum	30	Hg	Mercury	0.08
Nd	Neodymium	28	Ag	Silver	0.07
Co	Cobalt	25	Se	Selenium	0.05
Sc	Scandium	22	Ru	Ruthenium	0.01
Li	Lithium	20	Pd	Palladium	0.01
N	Nitrogen	20	Te	Tellurium	0.01
Nb	Niobium	20	Pt	Platinum	0.01
Ga	Gallium	15	Rh	Rhodium	0.005
Pb	Lead	13	Os	Osmium	0.005
B	Boron	10	Au	Gold	0.004
Pr	Praseodymium	8.2	Ir	Iridium	0.001
Th	Thorium	7.2	Re	Rhenium	0.001

Note: Rare gases and short-lived radioactive elements are omitted. Adapted from Mason and Moore (1982:46–47).

macrocrystalline quartz is more crystalline than chalcedony. Although these different varieties of quartz can grade into one another to some extent, they are usually quite distinct (Folk 1974:80).

Chert can be thought of as a material whose basic properties are those of quartz, modified by such common impurities as water, clay minerals, carbonate minerals, iron minerals and organic compounds, and by its own internal structure.

## The Structure of Chert

The structure of chert is different at different scales of measurement. One way to clarify the relations among these scales is to examine a hypothetical chert nodule at different magnifications, from the macroscopic level at which archaeologists are most accustomed to dealing with chert down to the molecular level. In doing this, we will be forced to use unfamiliar, exceedingly small units of measurement. Some of these units have more than one name and abbreviation, as indicated in table 2.2. For simplicity's sake, most measurements below a millimeter will be expressed in terms of microns ( $\mu$ ).

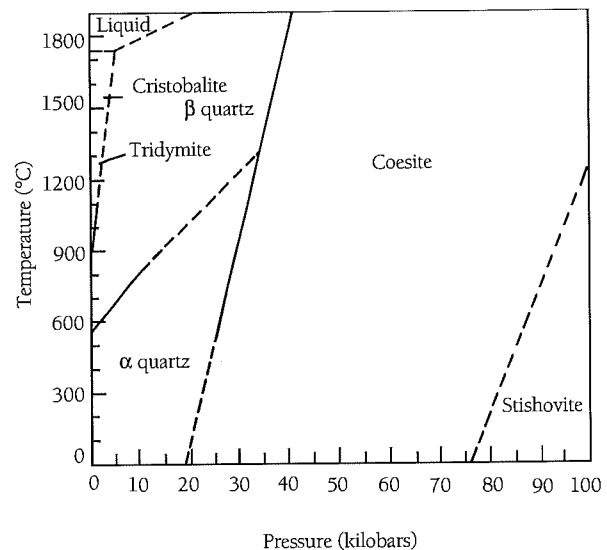
A relatively small chert nodule, about 10 cm in diameter, is shown actual size in figure 2.6. This sample is a composite of several types of chert whose characteristics were chosen to exemplify certain phenomena. At the first few levels of magnification, this hypothetical nodule is fairly homogeneous in color, with the exception of the lighter cortex area. Several small veins cut through the body of the nodule, and a few fossils show as faint light spots.

The same chert is shown in figure 2.7 at a magnification of 10x; the width of the frame is now 1 cm. One of the veins is quite prominent, appearing slightly shinier and somewhat more translucent than the rest of the nodule. A large cavity marks the location where a calcareous crinoid fragment has dissolved.

At 100x, figure 2.8 shows essentially what would be visible in thin section. The body of the chert appears as a mass of gray dots that represent the quartz grains. Impurities are visible, including a dolomite rhomb at the upper left and a scattering of iron oxide dust to the right. Across the bottom is the vein, which can now be seen to be filled with fibrous chalcedony. Fibers this long are often described as flamboyant; note that they are oriented perpendicular to the walls of the vein.

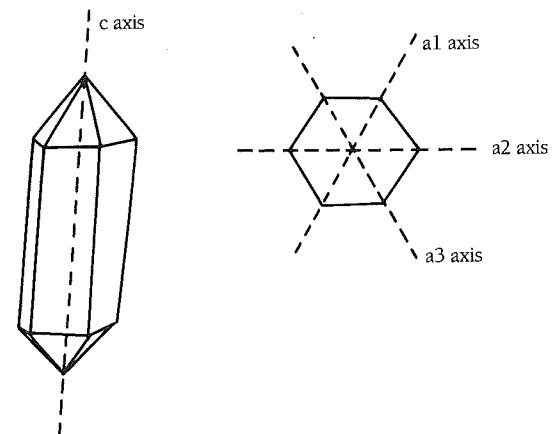
Figure 2.9 shows the chert at a magnification of 1000x, the range usually viewed with a scanning electron microscope. The limit for most light microscopes is about 500x (Blatt 1982:61). Note that we are now examining a fracture surface, not a ground and polished surface as in the thin section (fig. 2.8). At this scale, the chert exhibits an irregular "platey" or lumpy structure, where the fracture has passed around the more resistant clumps of quartz grains. Again, little solution cavities indicate where calcareous materials used to be.

In figure 2.10, individual grains, or microcrystals, of quartz show clearly. The grains in most cherts range from 5 to 20  $\mu$  in diameter. There are theoretical reasons why they should not be much smaller than 0.2  $\mu$  (Blatt et al. 1972:532), and they would be considered macrocrystalline if they were larger than 50  $\mu$ . The grains, around which the fracture has passed, are roughly the same diameter in all directions and are polygonal. Their surfaces are slightly curved rather than flat because they represent interfaces among two masses, much like the films among soap bubbles (Folk



**Figure 2.4**

Relationship of the varieties of silica to temperature and pressure (after Klein and Hurlbut 1985:440).



**Figure 2.5**

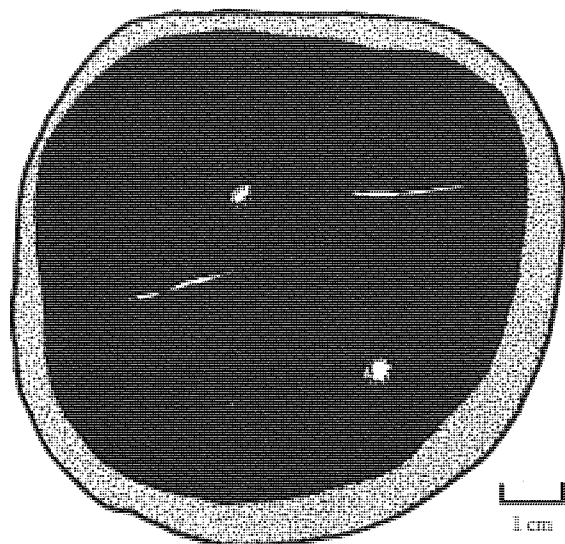
Quartz crystals, side view and top view.

and Weaver 1952:506). These surfaces are not true crystal faces like those visible on large quartz crystals.

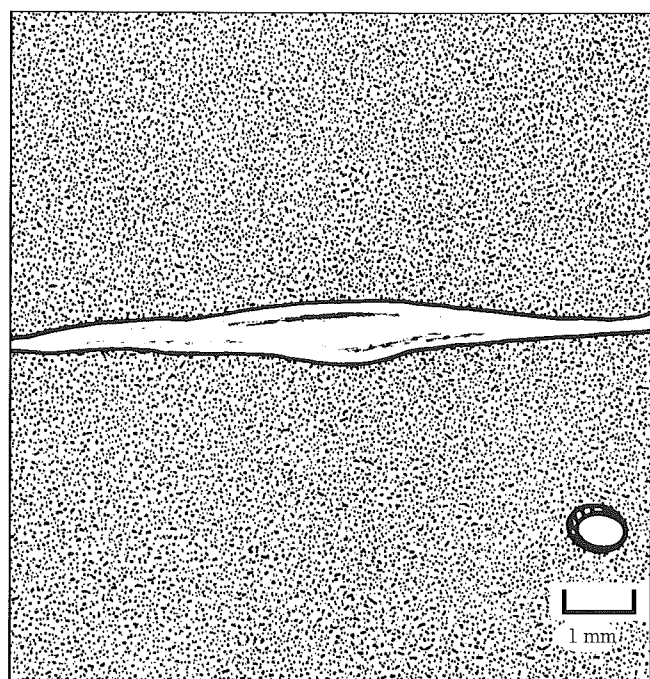
Part of the surface of one grain is shown in figure 2.11 at 100,000x. The large blob is a vacuole, or bubble, filled with water; such fluid inclusions are quite common in chert, and water can also be found in the cavities or cracks between grains. This water, sometimes referred to as "free" water, can be removed from chert fairly easily by heating. At 100,000x, we have reached the upper limit of resolution for most scanning electron microscopes; in fact, clearest resolution is usually below 50,000x (Blatt 1982:61).

New developments in microscopy have greatly increased our ability to observe very small phenomena, but, to the best of my knowledge, such extremely high-power methods have not yet





**Figure 2.6**  
Idealized chert nodule, life size.



**Figure 2.7**  
Chert nodule at magnification of 10x.

been used on cherts. Thus figures 2.12 through 2.15 show structural features that have been deduced through physical testing but not actually observed. Based on various lines of evidence, Micheelsen (1966:360) suggested that chert grains were themselves made up of stacks of flat plates of quartz from 0.03 to 0.1  $\mu$  thick and as long and wide as the grains. Furthermore, he argued that these plates are made up of smaller, more homogeneous quartz units he called subgrains, which ranged from 0.2 to 3  $\mu$  in size and which had slightly different orientations (Micheelsen 1966:322). While Micheelsen pointed out that scanning electron

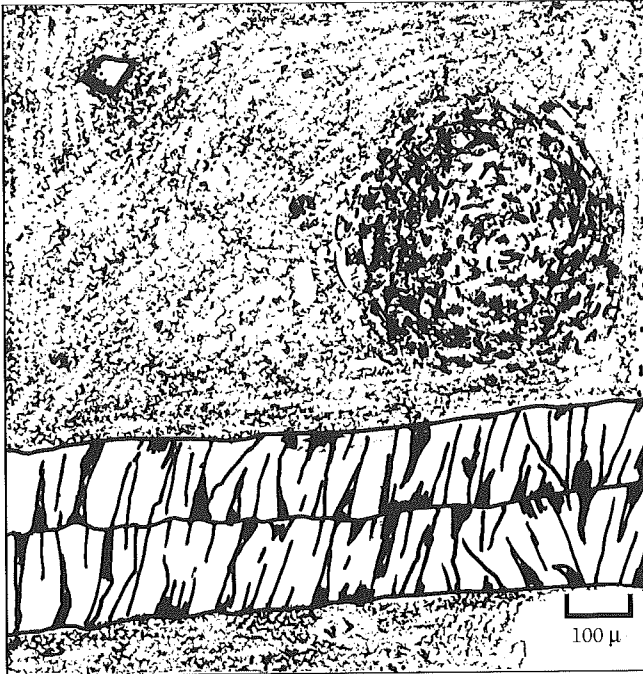
**Table 2.2 Measurements**

Unit	Abbreviation	Proportion of a meter
Meter	m	1
Decimeter	-	0.1 (one tenth of a meter)
Centimeter	cm	0.01 (one hundredth of a meter)
Millimeter	mm	0.001 (one thousandth of a meter)
-	-	0.0001 (one ten thousandth of a meter)
-	-	0.00001 (one hundred thousandth of a meter)
Micron	$\mu$	
or micrometer	$\mu$ m	0.000001 (one millionth of a meter)
-	-	0.0000001 (one ten millionth of a meter)
-	-	0.00000001 (one hundred millionth of a meter)
Millimicron	m $\mu$	
or nanometer	nm	0.000000001 (one billionth of a meter)
Ångstrom	Å	0.0000000001 (one ten billionth of a meter)

microscope pictures of fractures through chert grains tended to show a platy structure, thus supporting his deductions, the plates and subgrains shown schematically in figure 2.12 must still be considered hypothetical. Micheelsen also deduced that the silicons on the surfaces of the quartz plates were bonded to hydroxyl molecules and that a single layer of water molecules lay between each plate. Unlike free water, this water, sometimes referred to as "bound" water, is chemically bonded to the quartz; it can only be driven off by heating the chert to very high temperatures.

A schematic representation of the crystal structure of quartz is shown in figure 2.13. The long axis of a quartz crystal is called the *c* axis, and the three axes perpendicular to it are called *a* axes (fig. 2.5). The *a* and *c* axes meet at a 90° angle, and the angle between the *a* axes is 60°. Structurally, the SiO<sub>2</sub> tetrahedra are "grouped around the vertical [*c*] axis like the steps on a spiral staircase" (Berry, Mason, and Dietrich 1983:82). One implication of such a structure is that the silica tetrahedra are packed a little closer together along the *c* axis than along the *a* axes; the structure is "looser" in one direction than in the other. Thus, quartz is slightly anisotropic, meaning that its properties are measurably different depending on whether they are measured parallel or perpendicular to the *c* axis. The quartz grains making up chert have the same internal structure as quartz crystals so each grain also has one *c* and three *a* axes and is anisotropic. However, the grains themselves are assumed to be randomly oriented in chert, thus canceling out one another's anisotropy and making chert an isotropic material. This issue is discussed further when we examine the mechanical properties of chert.

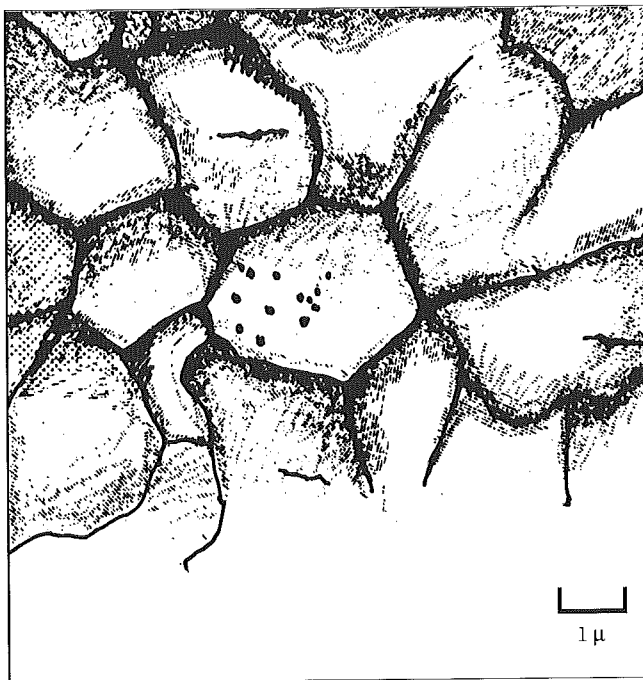
A silica tetrahedron, the basic building block of quartz and most other silicates, is shown in figure 2.14. Each tiny silicon is surrounded by four larger oxygens, each oxygen is attached to two silicons, and imaginary lines connecting the centers of each atom form a figure with four triangular faces. Atoms are bonded to one another by attractions between their positively and negatively charged particles. Four different kinds of bonds have been distin-



**Figure 2.8**  
Chert nodule at magnification of 100x.

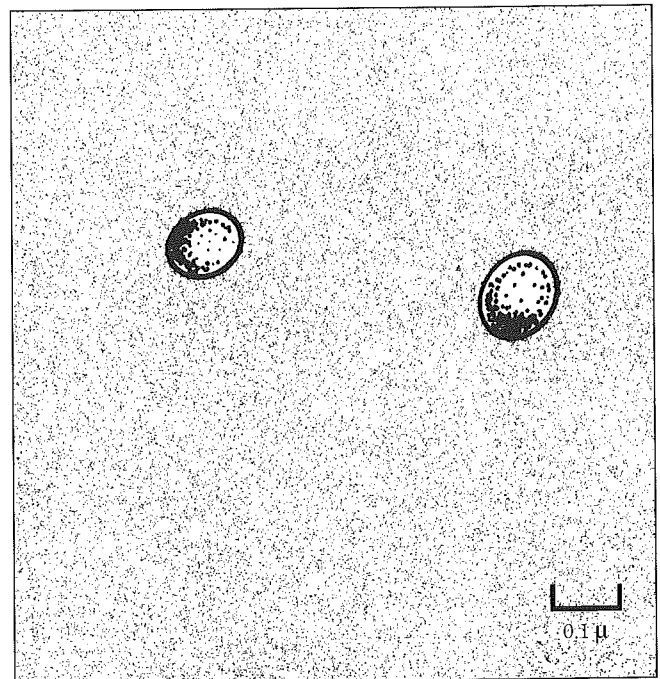


**Figure 2.9**  
Chert nodule at magnification of 1000x.



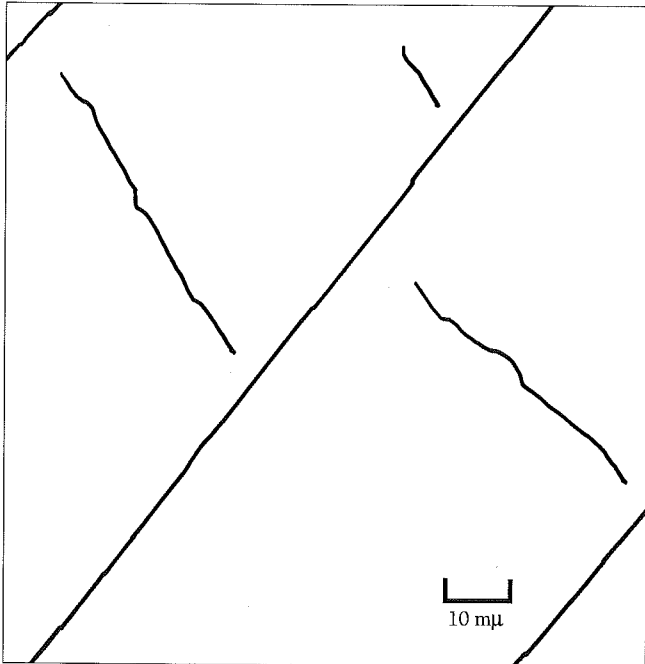
**Figure 2.10**  
Chert nodule at magnification of 10,000x.

guished and they have important effects on the physical properties of the resulting materials. These bonds are not mutually exclusive, and many minerals have intermediate forms of bonding. The rule of thumb is that a material's properties are determined by its weakest bond.

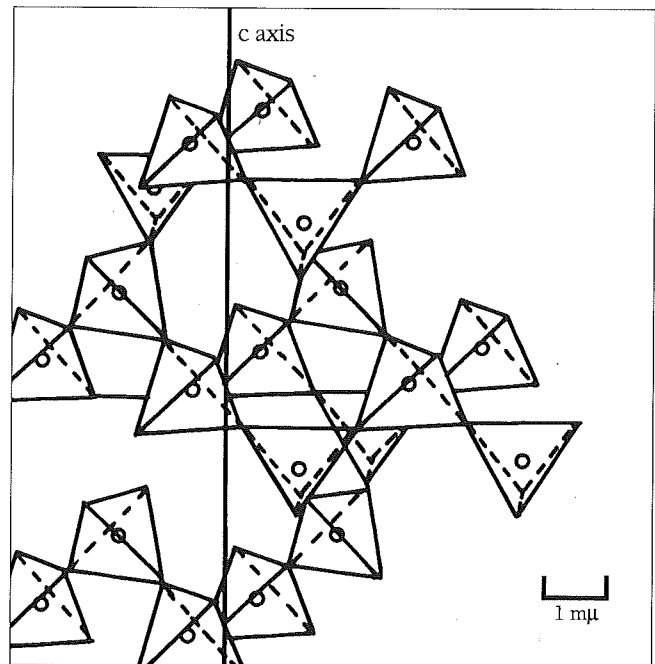


**Figure 2.11**  
Chert nodule at magnification of 100,000x.

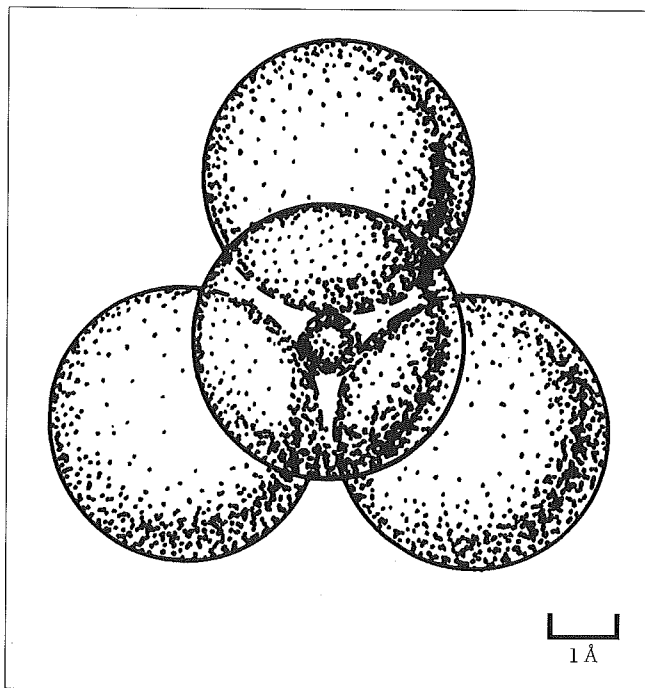
One of the strongest bonds is covalent bonding, in which atoms share electrons in such a way that the outer shells of the atoms are filled, resulting in an extremely stable configuration. Diamond is an example of a mineral with covalent bonding. This type of bonding is common in organic compounds but is rare in



**Figure 2.12**  
Chert nodule at magnification of 1,000,000x.

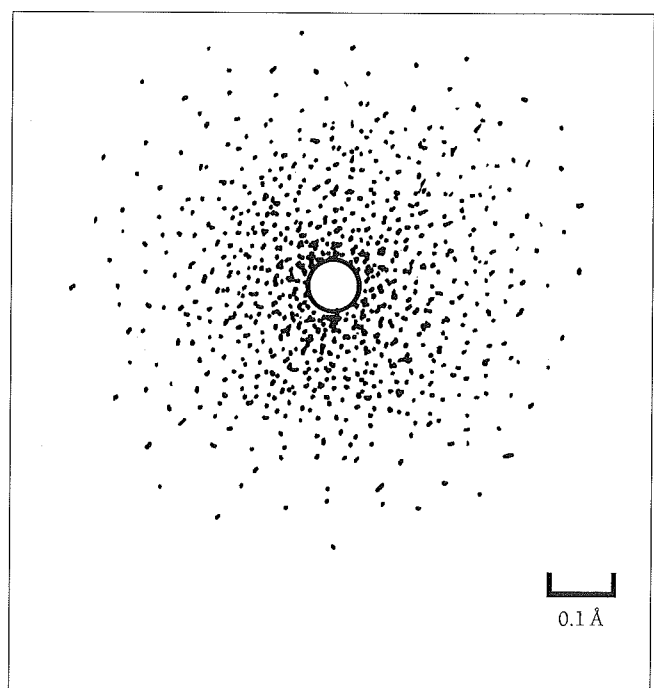


**Figure 2.13**  
Chert nodule at magnification of 10,000,000x.



**Figure 2.14**  
Chert nodule at magnification of 100,000,000x.

minerals. Most minerals are characterized by ionic bonding, in which the outer shell of an atom gains or loses enough electrons to achieve a stable configuration. This is accomplished by one atom joining with another atom and exchanging electrons. Elements classed as metals readily lose their outer electron; so,



**Figure 2.15**  
Chert nodule at magnification of 1,000,000,000x.

electrons are easily shared and move around freely. This metallic bonding is responsible for the excellent electrical and thermal conductivity of metals.

The weakest bonding is Van der Waals bonding, in which there is a weak attraction between atoms whose outer electron

shells are filled. An example is the mineral graphite, in which carbon atoms are covalently bonded into sheets that are linked only by van der Waals bonding, and so they slip easily across one another. A combination of both ionic and covalent bonding links the atoms in quartz, resulting in a very strong bond. In fact, it has been said that “the powerful bond that unites oxygen and silicon atoms is the cement that holds the earth’s crust together” (Klein and Hurlbut 1985:366).

Figure 2.15 shows a silicon atom. Like all elements, silicon is composed primarily of electrically neutral neutrons, positively charged protons, and negatively charged electrons. In this case, 14 protons and 14 neutrons are grouped in the nucleus at the center of the silicon atom, while 14 electrons circle the nucleus in five shells, or energy levels. Research has shown that not all electrons follow spherical orbits around nuclei, and that some follow orbits that resemble dumbbells or clover leaves. Thus atoms are no longer drawn like miniature solar systems, but rather like a planet surrounded by clouds at different elevations. When electrons are added to or subtracted from an atom, the result is an ion, or charged particle.

A silicon atom is smaller than an oxygen atom to begin with, but when they become bonded together the disparity is even greater. This is because the silicon has given up four electrons to the oxygens, leaving it with a net positive charge and causing the protons in the nucleus to pull the remaining electrons in tightly.

On the other hand, the oxygen has gained two electrons, giving it a net negative charge and causing it to expand because the protons are no longer able to hold the electrons so tightly. Thus the oxygens in their ionic form are more than three times larger in diameter than silicon ions, and this size differential means that silicons are always nestled in the middle of oxygens, with little excess space to spare in the tetrahedron. Also, any structure formed of such tetrahedra will always have oxygens on the outside, and those oxygens right at the surface will be attached to only one silicon and thus not fully bonded. As a result, under most conditions particles of quartz have a negatively charged “skin” that tends to repel other negatively charged particles.

It might seem that we have strayed a long way from the chert artifacts that concern us as archaeologists. However, it is important to realize that chert is not a homogeneous solid mass, as it often appears, but is actually made up of particles, which are in turn made of smaller particles, which are made of even smaller particles, and that the nature of the bonds between these different-sized particles varies. Certainly any discussion of how chert breaks must start with a clear understanding of the material’s microstructure. In fact, each of the concepts introduced above will reappear later and will lead to a better understanding of chert as a raw material. Even the last point above is relevant to the next chapter, which deals with the processes through which chert is formed.



# 3

## Origins of Chert

**C**hert comprises less than 1% of the total volume of sedimentary rocks (Blatt 1982:381), an infinitesimal proportion of all the rocks on earth. Nevertheless, it occurs in a wide range of geological contexts and is found in almost all regions, which partially explains its importance as a material for stone tools. Chert has been forming throughout earth's history, from as early as 3.5 billion years ago (Schopf and Packer 1987) to as recently as the Pleistocene (Surdam et al. 1972). It forms in sedimentary, metamorphic, and even volcanic rocks, in deep or shallow seas, in lakes or on land. It occurs as nearly spherical nodules, irregular shapes that resemble abstract sculpture, thin tapering lenses, or thick beds. Chert can form anywhere silica, in solution at low temperatures, can precipitate, and this apparently happens often. It is not a simple unilinear process, however. The diversity of contexts in which it is found shows the complexity of its formation.

Although I will not discuss the history of research for subsequent sections of this book, a very brief summary is necessary here because of the unusually tangled history of the research into the origins of chert. Research questions, methods, and interpretations have changed greatly over time, and it is important to put the voluminous literature into context. This summary is followed by a discussion of the important processes involved in the formation of chert, and then by several case studies, to illustrate the ways in which these processes have interacted during the formation of specific chert types.

### History of Research

The origin of chert has long been one of the more intractable

problems in geology. First, until relatively recently chert was not known to be forming naturally anywhere on earth, so geologists could not observe this process directly. Second, most of the physical and chemical processes involved in chert formation proceed exceedingly slowly at normal temperatures and pressures, on the order of thousands and even millions of years; thus, chert cannot be created easily in the laboratory. Third, much chert appears to have formed through a multistage process in which each new stage destroys vital evidence of the previous stage. Thus it is difficult to reconstruct the formation process from the end product alone. Finally, it is increasingly obvious that chert can form through more than one pathway, thus frustrating attempts to devise a simple overall model for how chert forms.

For convenience, I have divided the history of geological research into three periods, each with different methods and questions. In the earliest period, until roughly 1945, geologists usually studied chert in the field or with relatively simple methods in the laboratory. They focused on questions that could be addressed by observing the geological contexts within which chert was found, as well as the shapes of nodules, crack fillings, fossil replacement, and so forth. A major question was whether chert formed while the surrounding sediments were being deposited (the syngenic theory), after slight consolidation had occurred (the penecontemporaneous theory), or through replacement of the surrounding sediments after they solidified into rock (the epigenetic theory). Many geologists favored the syngenic theory and believed that chert formed from large blobs or layers of silica gel that had been deposited directly on the ocean floor (for example, Tarr 1917). There was also considerable debate as to the

source of the silica in chert, with some researchers arguing that it came primarily from siliceous organisms, while others argued in favor of volcanic origins.

While many of these questions continue to be of interest to geologists, other questions were being asked during the second period, from roughly 1945 to 1970. A hallmark of this period was increased emphasis on laboratory research, coinciding with an upsurge of interest in quartz in general. Quartz was first synthesized in the laboratory in 1845 (Deer et al. 1963:194), but research into this material was not a major priority until World War II. The war stimulated an intense demand for quartz crystals, which were essential for radios and other electronic devices, at a time when both Europe and the United States were cut off from easy access to Brazil and other important sources of natural crystals.

Quartz synthesis made great strides during and after the war, and large-scale commercial production began in the late 1950s (Arem 1973). One result of this work was heightened interest in defining the conditions under which quartz dissolves and precipitates (for example, Krauskopf 1956; Siever 1962). In addition, new technology and procedures, such as electron microscopy and oxygen isotope analysis, brought about important changes in our understanding of the origin and nature of chert. For example, Folk and Weaver (1952) used the electron microscope to investigate differences between the fracture surfaces of microcrystalline quartz and chalcedony. All this research tended to shift geological consensus away from the concept of direct precipitation of silica as gel and toward the idea that much chert formed through replacement of preexisting sediments.

The third period in chert research began about 1970 when the first results of the Deep Sea Drilling Project (DSDP) began to appear in print. Several years earlier, a number of oceanographic institutions had joined in a major effort to sample ocean floor sediments. Previously, only dredge hauls or short cores 10 m or so in length had been obtained, and we knew only about the very surface of ocean sediments. A new research vessel, the *Glomar Challenger*, drilled in water up to 7,000 m deep and cored as deeply as 1,700 m into the ocean floor (Blatt 1982:393). To many people's surprise, the DSDP encountered chert forming deep in the sediments of most major ocean basins. DSDP data have altered the course of chert research by demonstrating the actual conditions under which some chert is forming today and have spurred considerable laboratory experimentation and research. Increased realization of cristobalite's significant role during chert formation is another contribution of this period.

Thanks to these studies, many aspects of chert formation are now far better understood, but there are still many unresolved questions and a continuing discontinuity between the conditions under which chert can be observed forming today and the conditions under which many ancient cherts must have formed. For example, while siliceous organisms played a crucial role in the formation of most of the cherts encountered by the DSDP, the

massive Precambrian iron-rich cherts of the Lake Superior region appear to have formed without any significant organic involvement. In general, the problem is no longer one of origin but rather of origins; clearly chert can form in more than one way.

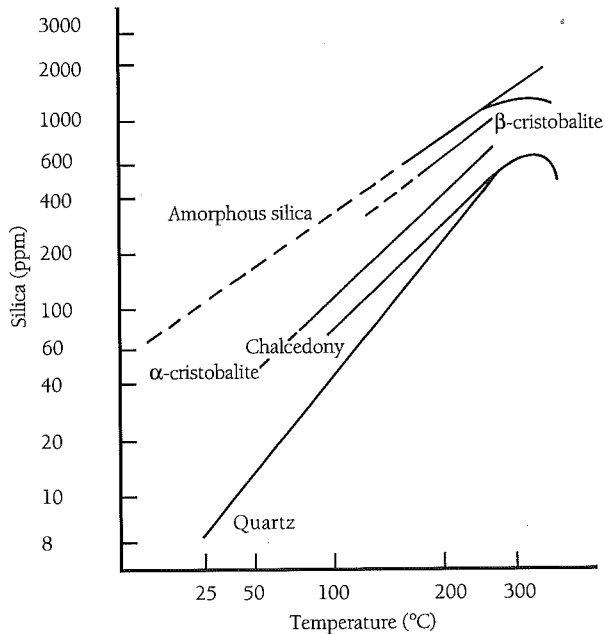
## Silica Solubility

Unlike sedimentary rocks such as sandstone, which form by the accumulation of rock fragments, chert is a chemical sediment; that is, silica must go into solution in water and then be precipitated out again for chert to form. Solution may occur in bulk or along a thin film (Maliva and Siever 1988a), but it must occur. In fact, there is good evidence that both solution and precipitation occur at more than one point in the formation of many cherts, and therefore, an understanding of these two processes is crucial.

Solubility is defined as the amount of a substance that can be dissolved in a given solvent under specified conditions. For example, the solubility of pure crystalline quartz in pure water at 25° C is 6 ppm (Blatt 1982:206). This means that quartz will continue to dissolve until the concentration of silica in the water reaches 6 parts silica per each million parts water, at which point the solution will be in equilibrium and quartz will stop dissolving. A solution at this equilibrium point is said to be saturated; if the solution had only 2 ppm silica it would be undersaturated, and if it had 300 ppm it would be supersaturated with regard to quartz. As implied by the words "under specified conditions," the solubility of a material is not an absolute property, but one that is affected by many variables. Factors controlling the solubility of silica include (1) the type of silica, (2) temperature, (3) pressure, (4) pH, (5) particle size and surface area, (6) presence of a disturbed surface layer, and (7) impurities. The influence of each factor has been experimentally investigated, but many interrelate in rather complicated ways. It can be difficult to disentangle their various effects.

As discussed in chapter 2, there is more than one silica mineral, and these different types of silica vary in many properties, including solubility. Quartz crystals, which have the best developed and tightest crystal structure, are the least soluble at 6 ppm (at surface pressures and room temperature, usually standardized to 25° C). Amorphous silica, which has no detectable crystal structure, is far more soluble (at around 120 ppm) under the same conditions. The solubilities of other types of silica, especially opal-CT, chalcedony, and microcrystalline quartz, lie between these extremes, but their solubilities have proved difficult to determine because the other variables can rarely be held constant (Iler 1979:33). Most values appear to be closer to crystal quartz than to amorphous silica, however. For example, the solubility of cristobalite is about 27 ppm at 25° C (Iler 1979:33). Thus, the unstable and more loosely crystalline types of silica are more easily dissolved than the stable, tightly crystalline types.

Temperature has a well-determined effect on silica solubility,

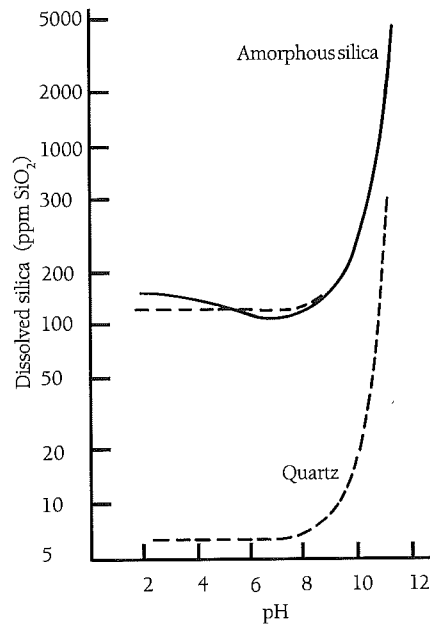


**Figure 3.1**

Effect of temperature on silica solubility (after Kastner et al. 1977:1042).

and some researchers argue that it is the most important factor under natural conditions (Blatt 1982:206). As figure 3.1 shows, the solubility of all types of silica increases greatly with temperature. Pressure, on the other hand, is a relatively unimportant determinant of silica solubility, especially in the low ranges (between 1 and 608 bars) typical of the conditions under which most cherts form (Hurd 1983:190). In one test, the solubility of amorphous silica increased from 30.5 to 44 ppm when pressure was increased from 1 to 1236 bars (Willey 1974). Such pressure changes would be roughly equivalent to going from the earth's surface to a depth of about 3708 m. A rule of thumb in geology is that temperature increases by 1° C for every 30 m of depth (Strahler 1981:66). According to this approximation, the temperature at 3708 m is about 124° C, at which point silica solubility increases to about 400 ppm. In other words, outside the laboratory, changes in pressure are always accompanied by changes in temperature, and temperature has a much greater effect on silica solubility than does pressure.

Silica solubility is little affected by variations in pH below about 9, contrary to the older literature (Krauskopf 1979:133). Above this point, solubility of all types of silica increases rapidly (fig. 3.2). It may also rise slightly at very low pH, below 2 (Brady and Walther 1990). Most natural environments are not highly alkaline, and so this variable generally has little effect on silica solubility. For example, Krauskopf (1979:28) reports that only playa lakes normally produce pH values of 9 or higher. In contrast, the ocean gives values of 8.1 to 8.3, while values of 7 to 8 are typical for streams in arid regions, and 5 to 6.5 for streams in humid areas.



**Figure 3.2**

Effect of pH on silica solubility (after Krauskopf 1979:133).

Water in the vicinity of decaying vegetation produces pH values of around 4, and pH values of 0 or less were recorded in the vicinity of oxidizing pyrite.

Decreased size and/or increased surface area of silica fragments increase silica solubility owing to the free energy on the surface of silica. When the ratio of surface area to volume is large, that free energy (which results from incompletely bonded ions) can alter chemical behavior, especially solubility (Williams et al. 1985:304). Thus, tiny fragments of silica, or fragments with complicated porous surfaces, are more soluble than larger, more solid fragments. Solubility can also be increased by grinding the mineral's surface, creating a layer of disturbed silica (Iler 1979:30). Presumably, the crystal lattices at the surface become mechanically distorted and behave like one of the more disordered forms of silica.

The presence of certain impurities profoundly affects silica solubility. Most salts have little effect, although they may decrease silica solubility slightly at high concentrations (Spencer 1983:112). However, several other common impurities, especially certain metals, readily form insoluble compounds on the surface of the silica fragments and block further solution (Iler 1979:57-58). While most of these compounds require specific pH ranges to form, aluminum, in particular, dramatically decreases solubility in even tiny quantities and at most pHs (Iler 1979:56).

Organic compounds can either increase or decrease solubility. Some are adsorbed on the surface of the silica and form a barrier to further solution (Iler 1979:58); others actually increase silica solubility by acting as chelating agents that capture ions



within a ring structure. Silicon ions are especially susceptible to chelating agents because of their high ionic charge and small size (Blatt 1982:34).

Recent research has shown that only certain organic compounds increase the solubility of quartz and that they do so both by weakening the bonds between silicon and oxygen and by "hiding" the silicon and oxygen ions so that the water does not become saturated and continues to dissolve silica (Bennett et al. 1988). "Chelating agents can extract ions from otherwise insoluble solids and enable the transport of ions in chemical environments where they normally would be precipitated" (Blatt 1982:34).

The rate at which solution occurs is conceptually different from solubility, but it is affected by most of the same variables as solubility. Amorphous silica, which has the highest solubility, dissolves about 13 times faster than quartz at 25° C and pH of 8.5 (Williams et al. 1985:304). All other forms of silica dissolve very slowly (Yariv and Cross 1979:268). The rate of solution rises with increases in temperature, pH, surface area, and surface disturbance, and in the presence of salts and certain organic acids (Iler 1979:65–75; Bennett et al. 1988). On the other hand, the rate of solution is decreased by the presence of aluminum (Iler 1979:56) and by certain other organic and inorganic compounds at specific pHs (Iler 1979:75).

In general, then, the less internally ordered varieties of silica are always more soluble than the more highly crystalline types, and all the silica minerals become more soluble as temperature, pressure, and pH rise; as surface area is increased; and in the presence of some organic compounds. Most other impurities decrease both solubility and the rate of solution. Crucial ranges exist for all these parameters, and if conditions shift outside these ranges silica precipitates out of solution.

## Silica in Solution

Silica is found in solution in all of the earth's rivers, lakes, and oceans. Some of it comes from quartz and other silica minerals, but there are also other sources of the silica in water. Large quantities of SiO<sub>2</sub> are released during the weathering of a wide range of silicate minerals, including feldspars, clays, and volcanic rock and ash (Wollast and Mackenzie 1983:43–48). Another source is the volcanic gas released around undersea hydrothermal vents, especially those along the midoceanic ridges. This latter source contributes only about 6% of the silica in the ocean today; however, some geologists believe that volcanic emissions may have been more important in past geological periods (Wollast and Mackenzie 1983:66).

Most natural waters are rather low in silica, although concentrations vary considerably. Oceans, which make up the majority of all surface waters and in which most modern chert is forming, are undersaturated with regard to silica. Concentrations vary,

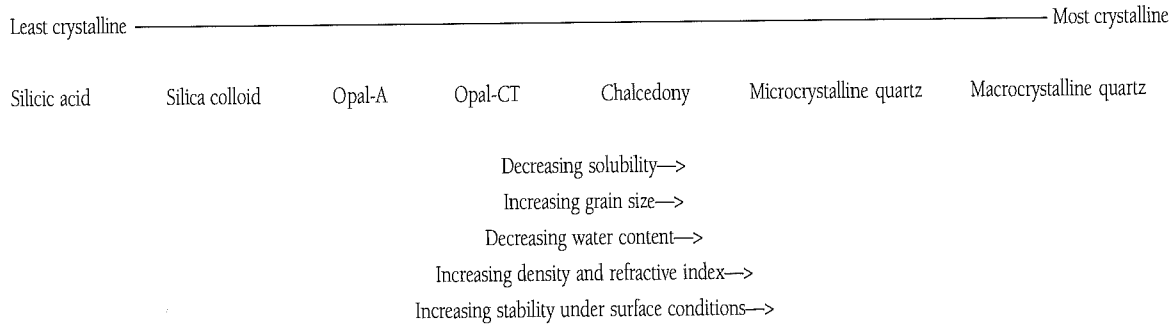
though, with surface waters generally at less than 1 ppm and concentrations in the deep sea reaching 6 ppm (Blatt 1982:388). Freshwater rivers and lakes have average concentrations ranging from 4 to 13 ppm (Aston 1983:83). Silica concentrations are somewhat higher in sediments; Siever et al. (1965:70) sampled interstitial waters from ocean sediments in many parts of the world and found concentrations ranging from 3 to 81 ppm, with most values being between 20 and 50 ppm. Water deep in terrestrial rock formations was found to have about 15 ppm (Siever et al. 1965:71). Siever (1962) also pointed out that silica concentrations could reach high levels where layers of clay act as semipermeable membranes, allowing water, but not larger molecules such as silicic acid, to pass through. Much higher concentrations have been found in hydrothermal waters, such as Opal Springs in Yellowstone National Park, which has registered 762 ppm silica (Dunbar and Rogers 1957:249). The highest concentrations, up to 2,700 ppm, come from desert playa lakes with high pH and high rates of evaporation (Jones, Rettig, and Eugster 1967). Even some unnatural waters contain appreciable silica; archaeologists will be interested to know that the beer they drink contains 60 to 100 ppm silica, dissolved from the malt husks (Iler 1979:744).

Most of the silica in solution is in the form of silicic acid, H<sub>4</sub>SiO<sub>4</sub>, a weak acid resulting from the combination of one SiO<sub>2</sub> and two water molecules (Krauskopf 1979:132). In highly alkaline waters of pH 9 or greater, some of the silica also exists as ions, or charged particles. When a solution is supersaturated, some of the silica is present as a colloid. In all these forms, silica can travel from the place where it first dissolved to any other location permeable to water, unless it encounters conditions that cause it to precipitate.

## Precipitation of Silica

One might wonder how silica can reach some of the saturations described above in low temperature, non-alkaline waters. Shouldn't quartz precipitate out of the solution as soon as the silica concentration gets above 6 ppm? As it happens, the different varieties of silica can usually dissolve more rapidly than they can precipitate, at least at low temperatures. Quartz in particular, though it requires the lowest concentrations of dissolved silica to precipitate, does not do so readily at low temperatures because it also requires a great deal of energy to form its tight, complex crystal structure (Blatt 1982: 288). Several of the other types of silica actually form more easily than quartz, though they are less stable in the long run.

For precipitation to occur, atoms of silicon and oxygen must form tetrahedrons, which then become attached to one another in specific configurations corresponding to the different forms of silica (see chap. 2, this vol.). The types most relevant to this discussion are shown below, arranged from the least to most crystalline. The boundaries between them are not necessarily clear



or abrupt, and they are not always easy to identify macroscopically or even microscopically. In fact, X-ray diffraction is usually necessary to identify opal-CT with certainty.

Precipitation is controlled by many of the same factors that control solubility, including temperature, pressure, pH, and impurities. In addition, the concentration of silica in the solution and the presence or absence of nuclei upon which crystallization can begin are important factors. In general, increases in temperature, pressure, and pH increase the rate of precipitation. Impurities may either retard or accelerate precipitation, depending on the type of impurity. Degree of saturation is a major determinant of the type of silica that will precipitate. A particular type cannot precipitate from a solution that is very much undersaturated and may also be unable to precipitate from a solution that is too highly saturated, for kinetic and chemical reasons. Finally, some types of silica require nuclei upon which to form (Iler 1979:78). Often, these nuclei are fragments of crystalline silica, but sometimes other ions serve as well.

The effects of these various factors can best be illustrated by examining the conditions under which various types of silica are believed to precipitate. These types are discussed in order from least to most crystalline and from most to least easily formed.

### Colloidal Silica

Most silica in undersaturated solutions exists in the form of single molecules of silicic acid,  $H_4SiO_4$ . Once concentrations approach the saturation point for amorphous silica, about 100 ppm, some of the molecules begin to join, forming tiny particles called *polymers* (Iler 1979:174). The silica is then in a colloidal state; that is, consisting of small particles (0.001 to 1  $\mu$ ) of one substance—dispersed in another substance, in this case, water (Krauskopf 1979:121). The shape of these polymers depends on the pH and impurities. The polymers form chains at pH values less than 7 or at higher pHs when salts are present. In salt-free solutions with a pH greater than 7, the polymers form tiny spheroids (Iler 1979). In both cases, the polymers tend to grow in size and decrease in number over time as the bigger particles grow at the expense of the smaller (and thus more soluble) particles. In a relatively pure solution, the polymer particles stay separate because their nega-

tively charged surfaces repel one another. High temperatures (for example, 80 to 100° C) can also keep polymers from aggregating because Brownian motion constantly moves them about. In the presence of ions with a positive charge, however, the silica polymers begin to attach to one another, forming first a viscous fluid and eventually either a true gel or a gelatinous substance.

True gels are rubbery, rigid masses consisting of a three-dimensional network of chained polymers surrounding a large amount of trapped water (Iler 1979:364–365). Like a gelatin dessert, a silica gel contains the same amount of water as the original solution. Silica gels are quite easy to make in the laboratory, either by cooling a supersaturated solution prepared at high temperature or by adding acid to a sodium silicate solution (Krauskopf 1979:133). Such gels are relatively stable at low pH even when salts are present, but above a pH of 6 they are only stable if the salt concentration is low (Iler 1979:233). No silica gel is stable indefinitely.

On the other hand, gelatinous precipitates form under alkaline conditions or where there are substantial quantities of salts or even small amounts of some metals and organic compounds (Iler 1979:233). Under these conditions, the silica polymers tend to coagulate and settle out of the water in a soft, squishy mass quite different from a true gel (Krauskopf 1979:134). This is far more likely to happen under natural conditions than is the formation of a true gel. Like gels, gelatinous substances are unstable and will eventually dehydrate and form one of the other types of silica. Although chemists consider gels and gelatinous precipitants to be distinct, geologists do not always discriminate between them.

Consequently, the term gel is often used to refer to either or both. Geologists have long been attracted to the notion that silica gel is a precursor to chert. Nodular cherts especially, with their fine textures, rounded surfaces, and occasional concentric banding, bear a tempting resemblance to “petrified gel balls.” However, the high concentrations of silica necessary to form gels are now known to be uncommon in natural waters. Also, gels cannot form if many impurities are present, especially aluminum, which is common in most natural settings. Wise and Weaver (1974) point out that silica gel was never found in any of the innumerable DSDP cores. Finally, when gels dehydrate they do not shrink and harden but

instead “disintegrate into flaky opaque material” (Krauskopf 1979:137). Thus, it is unlikely that silica gel plays a major role in chert formation, except perhaps on a very small scale or local level.

### Opal-A

Opal-A is amorphous silica, which has no definite crystal structure. It can only be precipitated from water with a very high concentration of silica, above about 120 ppm. Inorganic opal-A forms naturally around some geysers and hot springs, where hydrothermal waters rich in silica reach the surface, encounter a sudden drop in pressure and temperature, and deposit the silica (Williams and Crerar 1985:317). Opal-A can also be deposited at low temperatures, as in the case of precious opals, which are believed to form when an alkaline solution with few impurities slowly evaporates. The silica concentration gradually increases until polymers form as tiny spheres, about 0.03 to 0.04  $\mu$  in diameter. These small spheres gradually cluster into larger spheres consisting of concentric layers of the tiny spheres. When these clusters reach 0.1 to 0.3  $\mu$  in diameter, they begin to settle out of solution and into cavities in rocks (Darragh et al. 1976). The spheres become cemented together by more amorphous silica, forming solid rock in a process believed to take thousands of years. If all the spheres are uniform in size and if they settle into an orderly array, precious opal results, with striking color and optical effects. If the spheres are not all the same size and the array is irregular, common opal forms (Darragh et al. 1976).

Opal-A can also be produced by a variety of plants and animals. These organisms capture silica even from undersaturated solutions and secrete it to form rigid frameworks that support their soft tissues. Examples are the phytoliths that form in plants, the cell walls of diatoms (a form of algae), and the spicules formed by some sponges. The silica will not dissolve while these organisms are alive, even in undersaturated ocean waters, because the organisms' metabolic processes keep the silica in dynamic equilibrium with the surrounding water (Hurd 1983:191). The major aquatic silica-secreting organisms and their time ranges are presented in table 3.1.

Today, and probably for the last 70 million years, diatoms have been the most abundant of these silica-secreting organisms. They account for nearly 80% of the silica being secreted as opal-A (Blatt 1982:254), although other organisms are sometimes important locally. In fact, some researchers believe that diatoms are responsible for modern oceans being so undersaturated with regard to silica (for example, Krauskopf 1979:134). Under laboratory conditions, diatoms have been observed to reduce the silica concentration from initial values of 0.65 to 1.25 ppm to concentrations as low as 0.065 to 0.085 ppm. They also can live under a wide variety of conditions, including fresh water and muds. In the ocean, they require only water temperatures between 15 and 19° C, sufficient oxygen and sunlight for photosynthesis, and enough silica to form their cell walls. Thus, diatoms generally live in

surface waters. One study found them in greatest densities around the outside of the North Atlantic gyre (Calvert 1983:163). They are especially abundant around the mouths of rivers and near volcanoes where great amounts of silica enter the ocean (Stein 1977:20).

Silica secreting organisms do not form chert directly, but they play an important role in removing silica from solution, concentrating it, and depositing it in sediments where chert forms. As discussed previously, opal-A is highly soluble, especially in the irregular porous shapes secreted by these organisms. Therefore, it would be expected to dissolve in sea water as soon as the individual plant or animal died. Large amounts of opal-A are carried to the ocean bottom, however, in the fecal pellets of many larger organisms that feed on diatoms and other plankton (Stein 1977:2).

Opal-A is not stable indefinitely and is rarely found in deposits older than the Eocene. However, some DSDP-derived sediments containing opal-A are as old as the Cretaceous (Greenwood 1973:706).

### Opal-CT

Cristobalite and tridymite normally form above 1,470 and 870° C, respectively. Disordered silica that produces an X-ray diffraction pattern indicating the presence of both cristobalite and tridymite structures can form, however, at much lower temperatures. This variety of silica, named opal-CT (and often used almost interchangeably with cristobalite), is stable over millions of years, though it has not been found in rocks or sediments older than the Cretaceous (Williams et al. 1985:303). It precipitates from solutions that are not highly alkaline and which have between 30 and 100 ppm of silica. Williams and Crerar (1985:317) pointed out the basic similarity between the orientation of the silicon and oxygen ions in silica polymer chains and in the relatively loose crystal structure of cristobalite. They suggested that this may explain why opal-CT frequently forms so far below the “normal” temperature range for cristobalite. Also, because its structure is comparatively open, cristobalite tolerates considerable quantities of impurities; in fact, these impurities may buffer or reinforce the structure, keeping it stable.

Under the microscope, opal-CT can look like isotropic glass or like a felted mass of microfibers (Greenwood 1973). Where there is sufficient space available, opal-CT often takes the characteristic form of lepispheres (fig. 3.3), little balls composed of numerous intersecting crystalline blades of cristobalite about 0.05 $\mu$  thick (Oehler 1975:255). Most lepispheres range from 1 to 20  $\mu$  in diameter, although some are larger, and they do tend to become bigger and lumpier over time (Williams et al. 1985:306). They are often found lining hollows in cherts.

Opal-CT has been created under laboratory conditions by Kastner, Keene, and Gieskes (1977), who put clean siliceous shells of diatoms and radiolaria into water and let them sit for 1 to 6

**Table 3.1 Major Aquatic Silica-Secreting Organisms**

Name	Type of organism*	Habitat	Time range	Siliceous portion of organism
Radiolarians	Single-celled organisms (K = protocista, P = radiolariata)	Ocean	Precambrian to recent	Skeleton
Sponges	Multi-celled animals (K = animalia, P = porifera)	Ocean	Early Cambrian to recent	Spicules
Diatoms	Algae (K = protocista, P = bacillariophyta)	Ocean  Freshwater	Cretaceous to recent  Tertiary to recent	Outer cell wall
Silicoflagellates	Single-celled organisms (K = protocista, P = chrysophyta)	Ocean	Late Cretaceous to recent	Skeleton

\* Kingdom (K) and phylum (P) designations after Lowenstam (1981).

months. Gradually, the shells dissolved and opal-CT lepispheres formed. These researchers argue that both magnesium and a source of hydroxyl (OH) ions are crucial to the precipitation of opal-CT, at least in carbonate sediments, because these ions form the nuclei around which precipitation occurs. Once these nuclei are used up, new lepispheres cannot form, but the existing ones can grow still larger. Hydroxyls of aluminum, iron, and manganese also serve as nuclei, but they are usually less abundant in seawater. If clay is present, it adsorbs the magnesium and other ions, retarding the precipitation of opal-CT. Opal-CT precipitated in the presence of clay has, however, a slightly tighter crystal lattice than opal-CT precipitated under other conditions, and it is more easily transformed into quartz (Isaacs 1982). Many organic impurities appear to affect opal-CT precipitation in a similar manner (Hinman 1990).

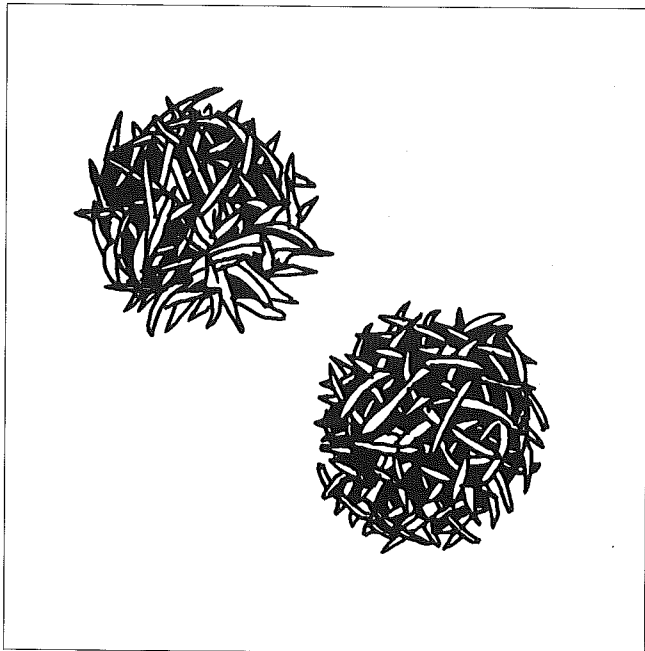
### Chalcedony

Chalcedony is made of quartz, but its crystals, instead of forming grains, grow as radiating fibers in bundles. The resulting structure is more porous than that of microcrystalline quartz. There has been considerable controversy as to exactly how chalcedony forms. Iler (1979:79) states that the required silica concentrations are lower than those of amorphous silica, and presumably of opal-CT, but higher than the saturation point for quartz, which would mean concentrations between 6 and 30 ppm. Several characteristics of chalcedony, most notably its radiating fibers and common external "botryoidal" shape resembling bunches of grapes, tend to suggest, however, that it formed from a relatively viscous solution of somewhat higher concentration (Berry, Mason, and Dietrich

1983:134). Oehler (1976:1146–1147) describes a mechanism by which such radiating fibers might form. As crystals grow in a viscous solution they remove pure silica from the liquid and reject any impurities. These impurities accumulate in a layer around the growing crystals because they cannot easily diffuse owing to the viscosity. If this layer is thin, the tips of the crystals continue to grow, extending above the impurity layer; they cannot grow laterally because the impurities block normal crystal growth. These impurities also cause the growing crystals to branch at low angles. The result will be radiating fibers.

Oehler implies that a thick layer of impurities would block crystal growth altogether, and empirical observation suggests that the solutions from which chalcedony forms cannot be highly impure. Although the open structure of chalcedony could easily contain many impurities, chemical analyses show that chalcedonies which have not been subjected to secondary staining are considerably lower in trace elements than most other cherts (see chap. 4, this vol.). The fact that most chalcedony is translucent and pale further supports the idea that it does not form in the presence of large quantities of clay or metal minerals which would cause it to be darker and opaque (see chap. 5, this vol.). Certain impurities, especially sulfates, may actually be necessary for chalcedony to form (Kastner 1980).

Thus it seems likely that chalcedony precipitates from relatively clean solutions having higher than expected silica concentrations; alternatively, it may form by alteration from an initial colloidal or amorphous silica. In support of the latter possibility, White and Corwin (1961) synthesized chalcedony in the laboratory under hydrothermal conditions and found that it formed in



**Figure 3.3**

Opal-CT lepispheres, each about 10  $\mu$  in diameter.

a glass rod, which is fundamentally amorphous silica. They also found that chalcedony did not precipitate directly onto the walls of the autoclave or onto quartz "seeds," although microcrystalline quartz and cristobalite did. Oehler (1976) found that chalcedony was the predominant crystalline variety that formed when he subjected silica gel to hydrothermal conditions and, in fact, it is likely that higher temperatures encourage chalcedony to form (Kastner 1980). Oxygen isotope data indicate that some chalcedony agates formed at temperatures as high as 250° C (Graetsch et al. 1985), although others formed at a relatively cool 50° (Fallick et al. 1985).

To further complicate the problem, there are actually several different kinds of chalcedony. The major distinction is between "length-fast" and "length-slow" chalcedony, so named because of differences in the rate at which light traverses the length of the fibers. In length-fast chalcedony, the most common variety, the individual quartz crystals that comprise the fibers are oriented with their *c* axes perpendicular to the fiber length. If these fibers are helically twisted around the axis of elongation they show a distinctive zebra-striped pattern in thin section; this subvariety is known as zebraic chalcedony (Keene 1983). Much less common is length-slow chalcedony (also called quartzine) in which the crystals are aligned with their *c* axes parallel to the fiber length. In another uncommon variety, lutcite, the crystals are oriented at a 30° angle to the fiber length.

Presumably, each of these varieties forms under different conditions. Folk and Pittman (1971) pointed out that length-slow chalcedony is often associated with evaporite and sulfate deposits and suggested that this variety of chalcedony might be a good

indicator of shallow evaporite environments. However, Keene (1983) found length-slow chalcedony in cherts from a variety of deep-water environments, and Kastner (1980) determined experimentally that the chemistry of the solution is the crucial factor. Length-slow chalcedony forms where both magnesium and sulfate ions are present, whereas length-fast chalcedony forms where sodium, instead of magnesium, is present. However, Oehler found both varieties of chalcedony forming from a silica gel in close proximity to each other. He argued that the length-slow chalcedony formed in the early stages of crystallization and/or around organic materials and that length-fast chalcedony formed in later stages, perhaps from a less viscous solution (Oehler 1976). Karhu and Epstein (1986:1750) add to the debate by pointing out that some length-fast chalcedonies produce unusually low oxygen isotope values, suggesting that they have formed either at high temperatures or in the presence of fresh water. The origins of lutcite and zebraic chalcedony are even less well understood. Obviously, the formation of chalcedony requires a great deal more research.

### Microcrystalline Quartz

Microcrystalline quartz is composed of small interlocking grains rather than fibers. Theoretically, this variety of quartz precipitates from solutions with relatively low silica concentrations, around 6 ppm, probably in the presence of numerous centers of nucleation. Again, chemical analyses indicate that microcrystalline quartz usually has more impurities than chalcedony, and it seems reasonable to assume that some or all of these impurities may have acted as nuclei upon which the silica precipitated, resulting in numerous grains of quartz abutting one another. Such impurities would greatly slow down precipitation, however, and may explain why microcrystalline quartz has not been duplicated on any large scale in the laboratory.

The size of the quartz grains has considerable effect on fracture properties of chert (see chap. 6, this vol.). Thus archaeologists should be especially interested to know what causes this variation in grain size. While this issue is rarely addressed explicitly in the geological literature, three factors are mentioned most often as being important delimiters: density of nucleation sites, rate of crystal growth, and temperature. These variables are not always independent of one another, and it is often difficult to determine which is most important.

When Oehler embedded algae in silica gel and subjected the samples to hydrothermal conditions, he noted that smaller quartz grains formed near the organic materials, which apparently functioned as nucleation sites. He pointed out that naturally formed cherts also often show smaller grain size in the vicinity of fossils, presumably for the same reason (Oehler 1976:1145). Rate of crystal growth is also a well-known control on crystal size, with smaller crystals forming where growth is fastest. Silica saturation is a second factor likely determining the rate of growth (Folk and

Pittman 1971:1054); grains should be smaller in microcrystalline quartz that formed from more saturated solutions. Temperature may be a third factor. Kolodny and Epstein (1976) found that relatively coarse-grained (that is, 10  $\mu$  in diameter) cherts encountered by the DSDP had lower oxygen isotope values than fine-grained cherts, implying that the coarser cherts formed under higher temperatures. These findings are supported by the research of Hein and Yeh (1981).

I therefore offer the as-yet-untested hypotheses that coarser-grained cherts form where there are not many impurities of the types suitable to act as nucleation sites, or from lower silica concentrations, or in the presence of higher temperatures (as would be the case if sediments were deeply buried or if hydrothermal waters were involved). Fine-grained cherts form in the presence of many nucleation sites, from higher silica concentrations, and/or at cooler temperatures. Maliva and Siever (1988c) have recently suggested an alternative, and not necessarily contradictory, hypothesis based on their research: microcrystalline quartz forming from an opal-CT precursor cannot, for kinetic reasons, form grains larger than 10  $\mu$ . They therefore suggest that fine-grained cherts would generally form from opal-CT precursors, whereas cherts that formed by direct precipitation of quartz would tend to have larger grains.

Grain size can also vary within a single nodule, and several archaeologists have noted that chert found near the outer cortex of a nodule is often finer grained than that in the interior (for example, Crabtree 1967:14). In this case, temperature is unlikely to have varied substantially, and silica concentration would be expected to be lower, if anything, in the later stages of nodule formation. Therefore, it is possible that the decrease in grain size is caused by an increase in nucleation sites. It is assumed that the nodule grows from the inside out; thus, its surface area increases as it grows larger, providing the preferred nucleation sites for quartz crystal growth. Alternatively, one could argue that impurities are pushed outward as the nodule forms, thus increasing the availability of nucleation sites. Yet another alternative explanation, that the center of the nodule has undergone recrystallization, is discussed below.

### Macrocrystalline Quartz

Quartz crystals, the most stable and highly crystalline form of silica, do not form easily at low temperatures. Much of the quartz in nature, and almost all synthetic quartz, forms between 350 and 400° C. The solubility of quartz is much higher at these temperatures, enabling precipitation from more concentrated solutions (Yariv and Cross 1979:272). At low temperatures precipitation requirements for macrocrystalline quartz are rather restrictive. First, very low silica concentrations are necessary. In one of the few studies to synthesize quartz crystals at room temperature, Mackenzie and Gees (1971:534) found that crystals precipitated from solutions of only 4 to 6 ppm silica. Apparently, if concentrations are much

higher, silicic acid tends to become adsorbed on the crystal surfaces in disordered form, thus impairing crystal growth (Iler 1979:79). True quartz crystals also require a clean solution. Mackenzie and Gees, who grew their crystals in filtered salt water, cautioned that the presence of organic materials, clay, or iron oxides would probably prevent crystals from forming.

At either low or high temperatures, macrocrystalline quartz needs nuclei upon which to form. Commercial quartz is grown upon "seeds" of quartz crystals, and Mackenzie and Gees found their crystals grew only on other fragments of quartz. They suggest that the lack of such nuclei makes it nearly impossible for quartz to precipitate easily from supposedly saturated solutions. Space is another factor; quartz crystals can form only where there is room for them to grow without impinging on one another. For this reason, quartz crystals are most often found lining cavities in chert. Finally, stable conditions and a great deal of time are necessary for quartz crystals to form. After three years under optimal conditions, MacKenzie and Gees' crystals grew only 3 to 5  $\mu$  long.

### Summary

The discussion above suggests some preliminary conclusions regarding the conditions under which each variety of silica forms. Specifically, at low temperatures silica concentration and the quantity and kinds of impurities appear to be the most important determinants of the type of silica which will precipitate. When solutions are highly saturated with silica, colloidal gels and/or opal-A form. When the silica concentration drops below 100 ppm, opal-CT is most likely to form, especially in the presence of impurities. Chalcedony may precipitate from pure but viscous solutions, and microcrystalline quartz is most likely to form where silica concentrations are low and impurities are abundant. In very pure solutions with silica concentrations below about 7 ppm, true quartz crystals can precipitate. The more crystalline the silica, the longer it takes to form.

### Diagenesis

From the discussion above, one might assume that the formation of chert is straightforward, involving simply precipitation from the proper solution. On the contrary, current evidence suggests that chert rarely, if ever, forms in a single step. Rather, it forms through a long process that usually involves more than one variety of silica. In other words, it undergoes diagenesis: "low temperature/low pressure changes that frequently take place in sediments prior to, and often contributing to their lithification [that is, their conversion into rock]" (Berry, Mason, and Dietrich 1983:181). The main diagenetic processes are compaction, cementation, chemical alteration, replacement, and recrystallization, and all are probably involved in creating the different cherts.

In many cases, chert seems to form through the sequence of opal-A → opal-CT → quartz. Williams and Crerar (1985) point out several reasons why this pathway is so common. Most cherts form in the oceans, where waters are so low in silica that even quartz is not likely to precipitate directly. Only silica-secreting organisms can remove silica from such undersaturated waters and deposit it, in the form of opal-A, on the ocean floor. Stein (1977:2) points out that algae are among the earliest forms of life known. Since the major silica secretors today are algae, it is possible that organic processes played a role even in the formation of some Precambrian cherts. Radiolarians and siliceous sponges were well established by the end of the Cambrian, and diatoms had evolved at least by the Cretaceous. So most cherts formed in the last 600 million years are assumed to have formed partly through the action of these silica-secreting organisms. Some geologists have argued persuasively, however, that silica released from volcanoes or from the underwater weathering of volcanic deposits has also played a major role in the formation of certain cherts (Paris et al. 1985; Pollock 1987).

Once a silica-secreting organism dies and settles into ocean sediments, its protective organic coating begins to decay. The highly soluble opal-A of its skeleton is exposed to the undersaturated waters of the ocean, which dissolve it. The rate at which this process occurs is partly a function of the organism itself. For example, diatoms are small and have greater surface areas than the larger, more robust radiolarians which thus dissolve slower. Some of this dissolved silica will be lost to the water column by diffusion out of the sediments, but much of it will accumulate in the sediments. In fact, the rather high values of dissolved silica found in ocean sediments are believed to result primarily from the dissolution of diatoms (Siever et al. 1965). In this way, the water in ocean sediments can become so saturated with silica that opal-CT will precipitate.

Some older references state that opal-A can also change to opal-CT through a solid-to-solid transformation, as a result of maturation over time, simply because opal-CT is inherently more stable than opal-A. However, much data supports the current belief that opal-A dissolves and reprecipitates as opal-CT. First, sediments containing opal-CT often show only casts or ghosts of diatoms or other siliceous organisms, indicating that the original opal-A has dissolved (Williams et al. 1985). Also, oxygen isotope values have been found to be different for opal-A and opal-CT existing in the same geological formation (Murata et al. 1977). The values of oxygen isotopes (discussed more fully in chapter 4) reflect the temperature and salinity of the water in which the silica forms. A solid-to-solid transformation would not result in a change in oxygen isotope values because the silicon and oxygen atoms are only being rearranged. If, however, the opal-A dissolves and reprecipitates as opal-CT, the latter incorporates oxygen from the water in which it precipitated, which is unlikely to be identical in temperature or salinity to the water in which the initial opal-A

formed.

As opal-A dissolves in sediments on the ocean floor, the interstitial waters quickly become supersaturated because opal-A can dissolve much faster than any of the other forms of silica can precipitate. While the silica concentration levels are thus generally too high for quartz to precipitate, they are ideal for opal-CT. Opal-CT precipitates more rapidly in carbonate sediments because abundant magnesium and hydroxyl ions are present, apparently forming a compound that serves as a nucleus (Kastner and Gieskes 1983). Opal-CT precipitates slower in clay-rich sediments because of the lack of appropriate nucleation sites and the presence of aluminum minerals that retard precipitation (Isaacs 1982). The presence of dissolved organic matter also retards opal-CT precipitation, although the opal-CT that does form is more highly ordered (Hinman 1990). Once opal-CT is precipitated, it undergoes a small amount of recrystallization, presumably as a result of time. This recrystallization is detectable by X-ray diffraction as a decrease in the spacing of the crystal lattice, and it does not involve solution and reprecipitation. Murata et al. (1977) found no difference in the oxygen isotope values for less-crystalline and more-crystalline opal-CT in the same formation.

Opal-CT is an inherently unstable form of silica that must eventually change to quartz, the more stable form. Again, some geologists have argued that this is a solid-to-solid transformation (for example, Ernst and Calvert 1969), but more recent research indicates that the change from opal-CT to quartz also involves solution and reprecipitation. Stein and Kirkpatrick (1976) reexamined Ernst and Calvert's data and showed that their findings actually supported the latter model rather than a solid-to-solid transformation. In addition, oxygen isotope values were again found to be different for opal-CT and quartz in the same formation, supporting the solution and reprecipitation model (Murata et al. 1977). Sediments containing opal-CT are generally quite porous and have a great deal of water, so solution is likely to occur. Opal-CT is far less soluble than opal-A, though, and thus the resulting silica concentrations in the water are low and appropriate for precipitation of quartz. Murata et al. (1977) observed tiny quartz nuclei forming within a mass of opal-CT and suggested that impurities and water were being pushed outward as the quartz grew. Again, the rate of this transformation from opal-CT to quartz is slower in the presence of clay (von Rad et al. 1978).

Thus, the opal-A → opal-CT → quartz sequence is a logical one, and there is considerable evidence, in the form of relic lepispheres, for the existence of an opal-CT stage somewhere in the background of many cherts (for example, Clayton 1986; Maliva and Siever 1988c). However, some marine cherts, especially those forming in pure carbonate sediments, are argued to have formed without an opal-CT stage (Greenwood 1973; Lancelot 1973), and no evidence of a cristobalite stage has been found in certain nonmarine cherts (Eugster 1967). Williams and Crerar (1985) also suggest that quartz could be precipitated directly from

dissolved opal-A if the silica concentration of the water was lowered considerably by the adsorption of silica onto clays. Also, even those who argue strongly for the opal-A → opal-CT → quartz sequence agree that quartz can be precipitated directly on a small scale, as when fossils are replaced or veins are filled (Heath and Moberly 1971).

Williams et al. (1985) argue that the differences in silica solubility and precipitation relationships drive the whole chert diagenesis system and that temperature only affects the rate at which the reactions occur. Other geologists believe that temperature plays a more determinative role. For example, Murata et al. (1977) argued that diagenesis occurred when Monterey-formation sediments reached certain temperatures because of deep burial. They found that the opal-A in these sediments formed at temperatures around 15° C, reflecting ocean temperature. Opal-CT from these sediments generally indicated a formative temperature around 48° C, with quartz at about 79° C. Hein and Yeh (1981) also argue that temperature is a major cause of diagenesis, especially in shallow marine deposits. Kastner and Siever (1983) demonstrated that high temperatures resulting from the intrusion of basalt sills have had a dramatic effect on siliceous sediments forming recently in the Gulf of California. Temperatures in the hydrothermal range, about 150 to 200° C, caused opal-A to transform directly to quartz without passing through an opal-CT stage, and greatly increased the rate of quartz nucleation and growth.

All agree that chert forms very slowly, though, even under optimal conditions. Von Rad et al. (1978) studied DSDP data concerning cherts forming in the deep ocean basins, close to the water/sediment interface and at low temperatures. They estimated that cherts require 30 to 60 million years to form in clay-rich sediments, whereas cherts in carbonates require only 5 to 20 million years to form. Kolodny (1986) points out that cherts forming in shallower seas or on land are subjected to warmer temperatures and therefore may form considerably faster, but still on the order of millions of years. Even the fastest growing cherts appear to require at least a few thousand years to form (Kastner and Siever 1983). It should thus be clear why chert has never been synthesized under low-temperature conditions in the laboratory.

Chert formation can also involve more than one episode of silicification, thousands or millions of years apart. In some cases, calcite or aragonite fossils appear to have been replaced by silica well before the rest of the chert formed (Heath and Moberly 1971; Maliva and Siever 1988b). At the other end of the formation process, cherts commonly contain small cracks or cavities that were filled with chalcedony or macrocrystalline quartz crystals long after the bulk of the chert formed. Some concentrically banded nodules may also have formed in several stages of silicification, and some cherts show evidence of silica cementation on a very fine scale (Astin 1987). Perhaps the most obvious example of this phenomenon is chert breccias, which can occur when chert

forms in sediments that are still soft (Dapples 1979:125). When pressure from overlying sediments or local folding deforms the softer matrix, the rigid chert is broken into fragments, which are then cemented together by more silica (Kolodny and Epstein 1976). Chert can even be dissolved and replaced by carbonates (Walker 1962), although this is unlikely to affect more than the surface because most cherts are dense and not especially porous.

A final issue relevant to chert diagenesis is whether chert can recrystallize after it forms, either altering from chalcedony to microcrystalline quartz or from fine-grained to coarse-grained microcrystalline quartz. It is often assumed that this transformation can happen (for example, Pettijohn 1975:395), usually as a result of a process known as Ostwald ripening (Morse and Casey 1988). Such recrystallization is assumed to be a solid-to-solid transformation (Williams and Crerar 1985:318). Murata and Norman's data on comparative chert crystallinity are often cited in support of this belief (Murata and Norman 1976). They found that older cherts tended to be more crystalline than younger ones; however, the fact that some of their Precambrian cherts were less crystalline than Cretaceous cherts indicates that time alone is not sufficient to explain the differences in chert crystallinity. As discussed previously, conditions during chert formation can affect grain size: thus, the initial grain size must be known before we can determine the effects of time. In fact, it could be argued that the major role time plays is to increase the probability that a given chert will have been subjected to metamorphism, which definitely can cause recrystallization. Again, the causes of differences in chert crystallinity need further investigation.

## Metamorphism

As a result of deep burial or of regional events such as vulcanism or mountain building, some cherts have been subjected to temperatures and pressures in the metamorphic range, involving temperatures from roughly 150 to 650° C and/or pressures ranging from several hundred to 10,000 bars (Krauskopf 1979:433–434). Under these conditions cherts often recrystallize and coarsen and may appear foliated or sugary. In some cases, microcracks may be healed (Brantley et al. 1990). In thin section, grains appear deformed and welded together, and the scanning electron microscope shows that the grains have assumed a distinctive three-point or polygonal texture (see chap. 5, this vol.) (Ehlers and Blatt 1982:567). Metamorphosed chert grades into fine-grained metaquartzites (Folk 1974:81). The actual mechanisms of metamorphic change in chert have been little studied, although Karhu and Epstein (1986) have pointed out that recrystallization and grain coarsening in chert are often associated with changes in oxygen isotope values, suggesting that solution and reprecipitation may sometimes be involved. In addition, Keller et al. (1985) state that the presence of organic matter or clay retards metamorphic recrystallization.



## Contexts of Chert Deposition

Much work must be done to bridge the gap between the studies of the chemistry involved in chert formations and empirical observations of the geological contexts within which chert is found. Although recent work is filling this gap (for example, Siever 1983; Hein and Parrish 1987; Maliva and Siever 1989), many textbooks still note simply that chert is most often found either in nodular form in carbonates or in bedded form in shales.

Nodular cherts are said to occur most often as spheres or lumpy ovals in limestone or dolomite formations, to comprise a relatively small proportion of such formations, and to be areally limited (Dapples 1979:100). The association of chert with carbonates is a common one for several reasons. First, the water and temperature conditions preferred by the carbonate-secreting organisms that form limestone are also suitable for many silica secretors. In addition, low pH waters encourage carbonates to dissolve and silica to precipitate, thus suggesting a means by which silica can be mobilized and then deposited in the spaces left by dissolving carbonates. Finally, the presence of carbonates accelerates the formation of opal-CT. Most such deposits appear to have formed in quiet, shallow seas, and evidence indicates that chert formed relatively early in diagenesis when the carbonates were somewhat compacted but not yet solidified (Maliva and Siever 1989). For example, some fossils that are fragmentary in the carbonates are whole in the chert, suggesting that they were silicified before they were crushed by the weight of overlying sediments (Pettijohn 1975:404). Beds of carbonates sometimes are found bent around chert nodules (Blatt 1982:381). Maliva and Siever (1989) add that chertification appears to begin when overburden reaches depths of 30 to 1,000 m. Knauth suggests that many cherts may have formed where fresh and salt waters mix at continental margins, an ideal condition for carbonate solution and silica deposition (Knauth 1979).

In contrast, the stereotypical bedded cherts occur as layers or massive beds that are areally extensive and make up a large proportion of the volume of their formation (Pettijohn 1975:401). They are interbedded with shales, turbidities, and volcanic deposits and often appear to have formed in deep water near the edges of converging margins of continental plates (Ehlers and Blatt 1982:484). The common association of bedded cherts with volcanic sediments suggests to some geologists that much of the silica making up such cherts came directly from these sediments, without the involvement of silica-secreting organisms (for example, Calvert 1983:176). Others point out that volcanically active areas attract silica-secretors whose remains are often found in such deposits (for example, Blatt et al. 1972:540). These cherts appear to have formed early in diagenesis, before sediments had become compacted and solid; folding and slump structures are common (Pettijohn 1975:405; Dapples 1979:122).

However, there are numerous exceptions to these two ideal-

ized models; chert in some formations grades laterally from nodular to bedded form while other cherts form in tapering lenses that could be considered transitional between nodules and beds (Dunbar and Rogers 1957:248). Some massive bedded cherts appear to have formed in shallow waters, while some deep sea cherts have formed as nodules in carbonates (Dapples 1979:124). Other cherts do not conform to these two models in any way. Therefore, rather than attempting to summarize all the ways in which chert forms, it seemed more useful and interesting to examine a series of case studies that illustrate the range of variation in chert formation processes.

## Case Studies

These are not necessarily "typical" cherts but rather were chosen primarily because they are cherts for which considerable information exists.

### English Chalk flint

Perhaps the single most famous, and best studied, chert in the world is English Chalk flint. Nodules of this distinctive black, fine-grained material are found in a wide band across southeastern England, and although it is certainly not the only type of chert in England, it is usually the type chosen for experiments by archaeologists and geologists. Despite this status as a prototype, the Chalk flint, along with other European Cretaceous flints, formed under rather unusual conditions compared to most other cherts of the world. The English Chalk was deposited during the Late Cretaceous, with maximum flint development occurring in beds deposited around 85 million years ago (Jenkyne 1986:393). At that time, sea levels were especially high all over the world, and many low-lying continental areas, including much of England and adjacent parts of continental Europe, were flooded by shallow seas approximately 150 to 200 m deep (Jenkyne 1986:389). Very little sediment from the land was washed into these seas; so, deposits on the continental shelves consist almost entirely of the calcareous shells of foraminifera and ostracods, plus fragments of coccoliths, bivalves, echinoderms, bryozoa, sponges, corals, brachiopods, belemnites, and ammonites. Rates of deposition were as high as 15 cm/1000 years (Jenkyne 1986:391), resulting in great thicknesses of chalk such as those exposed in the famous white cliffs of Dover. The total accumulation of chalk measured 482 m (Shepherd 1972:64). The sea level and rate of deposition were not constant throughout this period, however, and rhythmic cycles of varying lengths, presumably caused by climatic fluctuations, are recognized. Felder (1986) describes cycles in which sediments gradually became finer, the rate of deposition decreased, and there is evidence of lower levels of water energy, presumably all reflecting increasing depth. Flint is most often found in the middle of this cycle. Above the flint, the sediments show a gradual increase in grain size, sedimentation rate, and water energy. Changes in fauna

parallel the inferred changes in bottom conditions.

The generally well-oxygenated floor of this Late Cretaceous sea was home to a variety of organisms that thoroughly churned the soft, limey muds. Especially significant for our purposes are the *Thalassinoides* burrows made by tiny lobster-like crustaceans. These burrows, only 1 to 5 cm in diameter, form great branching, largely horizontal, systems. They were excavated 0.5 to 1.5 m deep into semi-consolidated chalk (Håkansson et al. 1974). Because they were dug into the chalk at a time when it was relatively well consolidated, the burrow interiors held their shape, gradually filling with soft, porous sediments and attracting algae, fungi, worms, and other organisms (Bromley 1967). Chert formation often started in these burrows.

Spicules from siliceous sponges are the primary source of the silica for this flint. Shepherd points out that there is an inverse relationship between the amount of soluble silica in the chalk, especially in sponge spicules, and the amount of flint (Shepherd 1972:80). Pore-water-carrying silica dissolved from these scattered spicules must have migrated through the chalk, following zones of greater porosity, such as bedding planes, burrow systems, and fractures and cracks.

Clayton argues that this silica began to precipitate rather early in diagenesis, only 5 to 10 m below the sediment surface (Clayton 1986:42). According to his scenario, organic matter deeper in the chalk was being degraded by anaerobic bacteria in a process that released hydrogen sulfide ( $H_2S$ ) into the pore water. This pore water migrated upward until it reached a zone where aerobic bacteria were able to oxidize the  $H_2S$ , releasing hydrogen ions as a by-product and thereby lowering the pH of the pore water. At times when this boundary between reducing and oxidizing conditions was relatively stable (that is, when deposition rates were low), the calcium carbonate of the chalk dissolved and silica precipitated. Silica deposition usually began in the relatively porous zones, such as burrows, and the presence of organic matter in such places may also have played a role. Silica first replaced the calcite in calcareous fossils; then lepispheres of opal-CT, about 5 to 20  $\mu$  in diameter, began to form. Later, the opal-CT was transformed to quartz, but the lepispheric structures, which make up 60 to 95% of the flint, are evident when flint specimens are etched with acid (Bradley and Clayton 1987). The transformation of opal-CT to quartz must have occurred about the same time that a chalcedony cement filled the remaining spaces between lepispheres, as both microcrystalline quartz and chalcedony have similar oxygen isotope ratios. After the flint formed, the chalk was compacted and uplifted.

The flint resulting from this process varies a great deal in size and shape (Shepherd 1972:20–29). Its size ranges from small, isolated fingerlike nodules to great boulders 1 m across. It can be tabular along bedding planes or cracks that cut across bedding planes, or it can form symmetrical nodules. Most often, it fills burrows, often making interconnected networks, but it may also

extend beyond burrows and sometimes has replaced the bodies of sponges or echinoids. Nodules on any given bed are often rather similar, and such beds have been correlated across great distances (Bromley and Ekdale 1986). Despite all this variety of outward form, the flint itself is generally black with a few gray to white blobby areas and a cottony white cortex. The gray areas are said by some to be “ghosts” of smaller burrows (Håkansson et al. 1974:227), while others consider them to be areas where the quartz has recrystallized and water has been redistributed (Bradley and Clayton 1987).

Chalk flint has been used by the inhabitants of southern England from the Lower Paleolithic to the present. Even after metals replaced stone for tools, flint nodules continued to be used as cobblestones and in walls of buildings. Flint was also crushed and put in concrete, pottery, and glass, and it was being knapped into gunflints as recently as 1950 (Shepherd 1972:188). Natural exposures exist in many places, such as the beaches at Brighton and Dover, and the flint was also quarried. Grimes Graves, in Norfolk, is an especially impressive quarry system in which over a thousand pits and shafts were dug by Late Neolithic people, who used deer antlers as their primary tool to reach the particular flint horizons they considered most desirable for stone axes and knives (Skertchly 1984). These excavations, with vertical shafts up to 14 m deep and horizontal galleries extending out along the flint beds, are oddly reminiscent of the *Thalassinoides* burrows where much of the flint formed.

### Monterey formation

In the Monterey formation of California, chert is caught virtually in the act of forming. This classic geological case study is one of the few situations in which many aspects of chert formation are evident from field relations alone (Bramlette 1946). A widespread formation, it outcrops throughout the Coast Ranges from north of San Francisco to south of Los Angeles, attaining thicknesses up to 1,600 m (Norris and Webb 1976:195). It contains an enormous quantity of silica, consisting primarily of diatomite (compressed but relatively unconsolidated diatom shells), porcellanite (somewhat more compacted and lithified diatomite), and chert, with minor amounts of shale, mudstone, cherty shale, sandstone, volcanic ash, carbonates, phosphates, basaltic lava, coal, and petroleum deposits. This extremely variable formation, with rock types grading into one another, is usually easily recognized by its thin to very thin beds and its pale buff to white color (Norris and Webb 1976:258).

The Monterey formation began to form about 17 million years ago during the middle Miocene (Hurst 1986) in a series of relatively deep ocean basins near the coast. These basins are similar to those in which diatoms are accumulating today in the Gulf of California. Conditions off the coast of California appear to have been ideal for diatoms. Water temperatures were favorable, and volcanic activity on land supplied plenty of silica to the sea.

At the same time, relatively little terrestrial sediment was being washed into the basins, either because the basins were far from land or perhaps because volcanic activity and faulting disrupted drainage patterns on land (Bramlette 1946:12). The bedding is thin and often rhythmic, suggesting that repetitive processes of deposition took place (Bramlette 1946:34). Diatoms flourished in this environment; foraminifera, sponge spicules, and fish remains are also abundant, though mollusk remains are rare. When these organisms died, their bodies settled into the basins, which were below the wave base, protected from currents and apparently stagnant enough to have low oxygen content, but which were not so deep or cold that hard parts dissolved.

As early sediments were buried under the weight of later sediments, temperatures increased. The opal-A in the diatom shells dissolved and reprecipitated as opal-CT, the primary component of porcellanite. Porcellanite is much harder than diatomite, is much less porous, and has a matte or dull luster. Molds of diatom shells form some of the pores, which are often lined with opal-CT lepispheres (Oehler 1975). This transformation from diatomite to porcellanite tended to occur somewhat abruptly at about 48° C (Murata et al. 1977). It was not strictly a function of depth or temperature, though, as beds of porcellanite are found interbedded with diatomite, and the different rocks grade laterally into one another. Local conditions, and especially the proportion of clay and other impurities, played an important role in determining which specific beds were transformed into porcellanite and which remained as diatomite (Isaacs 1982).

Opal-CT then underwent reordering, involving a tightening of the crystal lattice and probably expulsion of impurities, either as a function of time or depth of burial. When the opal-CT was sufficiently ordered, it dissolved and reprecipitated as microcrystalline quartz. Murata et al. (1977) found that this transformation occurred in suitably ordered opal-CT at temperatures around 79° C, though, again, the process is influenced by impurities. The resulting chert is most often found as thin beds or lenses up to several centimeters thick. It often shows fine laminations, some of which are continuous from the surrounding matrix, reflecting the fine bedding in the original sediments. The chert is generally lustrous and ranges in color from white to black, while the surrounding matrix is usually light. This suggests either that silica was more likely to precipitate in the presence of abundant organic matter or that crystalline silica trapped the organics which later were leached from the more porous matrix. In a few horizons, usually where the original diatomite was massive and unbedded, the chert formed as ellipsoidal nodules, some of which show both horizontal and concentric banding (Bramlette 1946:16).

Sediments continued to fill the basins throughout the late Miocene, but deposition was ended by widespread uplift during the Pliocene, which created the Coast Ranges (Norris and Webb 197:196). Some or all of the chert must have formed by this time, since pebbles of Monterey chert are found in Pliocene conglomer-

ates (Bramlette 1946:50). The Monterey formation was uplifted, however, before chert formation was complete. There is a lot of chert in the lower beds, porcellanite predominates in the middle beds, and diatomite is predominant in the upper beds. The result is a textbook example of how some cherts form.

### **Pennsylvania jasper**

For 10,000 years, Native Americans excavated hundreds of open-pit mines in the ridges stretching across southeastern Pennsylvania. These ridges are known to geologists as the Reading Prong. These quarry pits, which range from 3 to 30 m in diameter and from 3 to 11 m deep (Miller 1982:119), are evidence of the value Native Americans placed on the iron-rich chert that archaeologists call Pennsylvania jasper (Hatch and Miller 1985). This chert is glossy, fine grained, and usually yellow-brown to reddish brown, but it can also be dark red, yellow-gray, and a variety of other colors (Lavin 1983:49). It formed in quite a different way from the Chalk flint or the cherts of the Monterey formation—through replacement as a result of high temperatures and pressures generated by the metamorphism that affected the region.

Pennsylvania jasper is found in the Hardyston formation of lower Cambrian age. This formation was deposited on top of eroded Precambrian metamorphosed sedimentary and volcanic rocks nearly 600 million years ago, probably first by rivers and later in the sea, which was slowly inundating the land (Aaron 1969:31). The lower levels of this formation have coarse, angular sediments that show little weathering, while later beds have finer sediments and show more reworking. The source of these sediments was probably the Precambrian highlands to the west and north, since the types and forms of minerals are very much the same (Aaron 1969:32). The Hardyston is primarily a light gray sandstone made predominantly of quartz but with a great deal of feldspar. In many places, the sandstone has been cemented by secondary silica to form an orthoquartzite, or nonmetamorphosed quartzite, and there are beds of quartz pebble conglomerate and shale. Trilobites and possible worm trails are the only fossils (Aaron 1969:30). The Hardyston formation is over 200 m thick at the southwest end of its outcrop area but thins to about 30 m in the east (Aaron 1969).

The rocks of this region have a complex history, with alteration and deformation beginning as early as the Cambrian when pegmatites were injected into the Hardyston formation (Drake 1969:95). The Reading Prong area was also folded and faulted by the Taconic, Acadian, and Appalachian episodes of mountain building, and the rocks show many signs of low-grade regional metamorphism (Drake 1969). The jasper formed during one or more of these episodes.

Pennsylvania jasper does not occur predictably in any one part of the Hardyston formation, and the exact context of the highly localized occurrences is often difficult to determine be-

cause of overburden. This jasper is often found in association with limonite ore, and five of the seven occurrences studied by Miller (1982:112) were adjacent to faults. Pennsylvania jasper formed when warm fluid saturated with silica and iron flowed through the formation and altered the quartzite to chert, probably through a process of solution and reprecipitation. The quartzite apparently began to alter in patches, which gradually grew and became pervasive. In some samples, the quartzite remains as small patches or streaks (Lavin 1983:140).

The source of the silica could well have been the Hardyston formation itself, which could have provided silica from the quartz and also from the decomposition of feldspar. Much of the quartz is strained (Aaron 1969:24) and is therefore more soluble than unstrained quartz. Much of the iron may have been brought in from outside the formation. Although magnetite and limonite are the most common heavy minerals in the Hardyston, they are still not very abundant and occur in much larger quantities elsewhere in the Reading Prong (Drake 1969:53). The jasper consists mostly of microcrystalline quartz, but grains of chalcedony are also scattered throughout. The iron occurs as very fine grains of both hematite and limonite (Prothero 1983:351).

Thin sections reveal many signs of Pennsylvania jasper's replacement origin. Traces of the original bedding are sometimes visible, as are isolated quartz grains, ghosts of quartz grains outlined with iron minerals, and quartz that has assumed the outward form of the plagioclase feldspar crystals it replaced. Irregular sutures resulting from pressure and solution outline some quartz grains and form boundaries between the chert and the unaltered quartzite (Prothero 1983:353).

Was the microcrystalline quartz precipitated directly from solution or was the silica deposited first as a viscous colloid that later altered to microcrystalline quartz? The fact that the fine particles of iron oxide are often described as forming "clouds" or "clots" or "streaks" (Prothero 1983:351-356) would seem to support the latter interpretation. Miller (1982:108) reports the existence of tiny manganese and iron oxide dendrites which she believes must have formed in a gel. More studies of the relationship of the jasper to its host rock are necessary before this question can be answered with certainty.

Pennsylvania jasper frequently shows small quartz-lined cavities and tiny veins, the latter ranging from 0.05 to 0.3 mm wide. Although Miller (1982:108) has interpreted these as shrinkage cracks, they most likely formed after the jasper hardened, since they have sharp intrusive boundaries that cut across the jasper at different angles and sometimes cross-cut one another. They are filled with macroscopic quartz crystals and chalcedony, and rarely with hematite. These secondary cavities and veins may have resulted from later metamorphism that affected the Hardyston, along with the rest of the Reading Prong, as this part of the northeastern US slowly took its present shape.

## Agates

Agates are a variety of translucent chert characterized by alternating bands or stripes of color, or sometimes by clouds and mosslike inclusions. They can be any color, though they are usually pale, and they commonly form in small cavities of other rocks. They are perhaps best known to most of us as semiprecious gems in jewelry, but they have also been used for stone tools (Crabtree 1967:12). They can form in cavities in any kind of rock and are often found in limestone or dolomite (Pettijohn 1975:474). However, some of the most spectacular agates occur in extrusive volcanic rocks, especially those formed from basaltic lava, which tend to have numerous gas bubbles because they are less viscous than siliceous lava. Such is the case in Rio Grande do Sul, southern Brazil, where many beautiful agates have been found in massive lava flows.

Near the end of the Jurassic period, the great supercontinent of Gondwanaland began to break apart as the continental plates shifted. This major reorganization of the earth's crust was accompanied by extensive volcanic activity in many parts of the world (Bowen 1966). Starting about 120 million years ago, the pattern of rather placid sedimentary deposition that had been typical of the Paleozoic in southern Brazil was interrupted as vast amounts of basaltic lava spilled out of cracks in the earth, eventually forming the thickest and most extensive plateau basalts known on any continent (Piccirillo et al. 1988). This is the Serra Geral formation, over 1,700 m thick in some areas and made up of many individual lava flows interbedded with shales and sandstones (Bowen 1966). The basalts stand as dramatic headlands along the coast of southern Brazil and as inland hills resistant to erosion.

There are numerous holes in the lava, some the size of caves and others quite small. Many of these holes have been filled by secondary minerals, including crystal quartz, amethyst, chalcedony, calcite, zeolites, native copper, copper minerals, green iron silicates, and especially agates (Baker 1923:73; Bank 1970).

Flörke et al. (1982) studied a number of these agates in some detail to determine how they formed. All the samples were bluish gray, with thin concentric bands of chalcedony ringing the walls of the cavity, horizontal bands of microcrystalline quartz and chalcedony inside this rim, and often macroscopic quartz crystals in the center. Both the wall-lining and horizontal deposits often alternate between translucent, relatively porous layers and dense, milky layers, thus creating the distinctive banding so characteristic of agates.

While most chert nodules grow from the center out, agates grow from the outside in. Flörke et al. (1982) imply that agate growth may have begun before the enclosing lava hardened, when extremely hot fluids from the molten rock, supersaturated with silica, entered cavities and experienced a sudden drop in pressure and temperature. These fluids rapidly deposited a thin layer of short-fibered and highly stressed chalcedony around the outside of the cavity, following its contours exactly. Then more hot fluid

entered the cavity and deposited layers of less-stressed chalcedony, with longer fibers, around the walls of the cavity, forming concentric bands. Some agates are composed entirely of such concentric bands, but many of the Serra Geral agates show horizontal banding as well.

Flörke et al. attribute horizontal banding to a different form of deposition. They believe that these bands were deposited under the control of gravity from cooler, more viscous, and less saturated liquids. They state that either microcrystalline quartz or opal-CT may have been deposited, sometimes in alternation, but that the latter then altered to chalcedony. (They do not explain why they believe the chalcedony did not precipitate directly.) They found more impurities in the horizontal layers than in the wall-lining bands, with the impurities concentrated at boundaries between layers. Sometimes deposition of the horizontal layers was interrupted by another pulse of volcanic activity that injected fluid into the cracks and fissures. Deposition of more wall deposits, followed by additional horizontal deposits, resulted. Finally, when volcanic activity ended and liquid with a low concentration of silica had cooled to room temperature, quartz crystals often grew in any open spaces remaining in the agates.

Differences between the wall-lining and the horizontal deposits are thus attributed largely to temperature. Temperature also appears to have played a role in determining whether a particular layer was translucent or opaque and milky. Impurities do not vary systematically between these two kinds of layers (Flörke et al. 1982), but oxygen isotope values do differ and suggest that the milky bands formed at a higher temperature than the translucent bands (Graetsch et al. 1985).

Wang and Merino (1990) suggest a different interpretation of Serra Geral agates. They argue that the repetitive textures and alternating bands in these agates can best be explained by assuming a self-organizational process of crystallization that started in lumps of silica gel or amorphous silica within the lava, controlled primarily by the proportion of aluminum present in the system. Many aspects of this model remain to be tested.

Most agates are naturally pale in color, but they are easily stained because they are comprised largely of chalcedony, which has a relatively open, porous structure. Circulating groundwater may penetrate some agates and deposit iron or other minerals in the more porous layers, resulting in spectacular high-contrast banding. Gem dealers sometimes stain agates to enhance their beauty.

### **Silicified wood**

During the middle Triassic period, about 210 million years ago, northern Arizona was a basin flanked by the ancestral Rockies to the east and southeast and by an arc of intermittently erupting volcanoes to the west and southwest (Ash 1987). The area around present-day Holbrook, Arizona, was a broad channeled floodplain with ponds and marshes where insects, fish, reptiles, and amphib-

ians lived. Ferns and cycads grew in the lowlands, and tall pine-like trees grew along the rivers and on the flanks of the hills. When the volcanoes erupted explosively, many of these conifers were blasted down, leaving landscapes reminiscent of those created by the eruption of Mount St. Helen in 1980. These trees, up to 62 m tall and 30 to 70 cm in diameter, were rafted down rivers to accumulate in great logjams on the floodplain (Ash 1987). The trunks of the trees, minus most branches, roots, and bark, were quickly covered by volcanic ash and by mud washed down from the newly denuded slopes. Within these sediments, the logs became silicified, that is, impregnated with silica. Younger sandstones, limestones, and shales were deposited on top. Much later the whole Colorado plateau was uplifted and dissected, exposing over 280 m of the colorful shales of the Chinle formation, which forms much of the Painted Desert and contains many fine examples of silicified wood. The major concentrations are located in what is now the Petrified Forest National Park.

The source of the silica also in this case is probably volcanic ash, which is made largely of tiny bubbles of highly soluble silica glass (Chronic 1983). Another source of silica exists; each of the four major silicified wood deposits at the Petrified Forest is apparently either in or just above or below a bed of sandstone (Ash 1987:406). These sandstones may have supplied some of the silica or may simply have facilitated the water's gaining access to the logs so silicification could occur.

Sigleo (1979) argues, on geochemical grounds, that silicification occurred in a watery environment without much oxygen and with intermediate to slightly acidic pH, such as would be found in the bottom muds of a swamp or stagnant pond. This implies that silicification began not long after the logs were buried in mud. Silica in the water penetrated the wood as silicic acid or a thin colloid. The rate at which such a solution can move through wood depends partly on the kind of wood and its condition; cracks and decaying areas would allow the silica solution easier access. The solution would move rapidly longitudinally, but more slowly transversely, through the ray cells, penetrating the cell walls through micropores (Scurfield and Segnit 1984:163). Silica appears to have been deposited in the cell walls first, probably because it readily forms hydrogen bonds with the lignin and cellulose in those walls (Sigleo 1978; Stein 1982). Because the wood served as a template for silica deposition, its structure was reproduced in detail. Later, silica filled the cells and canals in the wood as well. In addition, as some of the remaining organic material decayed and was removed by percolating water, more silica was deposited in the resulting voids.

Silica is often deposited first in wood as opal-A. Stein (1982:1280) shows a microphotograph of a specimen from Yellowstone National Park in which tiny microspheres of opal-A, about 0.1  $\mu$  in diameter, are lined up along cellulose fibers. Scurfield and Segnit (1984) report what appear to be dehydration cracks in some cell fillings of their specimens of silicified wood

from Australia, suggesting that the original precipitate was either a gel or a form of silica with high water content, such as opal-A. In all but the youngest silicified wood, opal-A has altered to opal-CT, chalcedony, or microcrystalline quartz. Scurfield and Segnit (1984) found all of these silica varieties in the 75 specimens they examined, usually one variety per specimen. Sometimes, however, two varieties of silica were found together. Stein (1982:1280) states that both microcrystalline quartz and chalcedony are commonly found together in petrified wood. Some of this heterogeneity may result from minor differences in the microenvironment of deposition, while some may represent separate episodes of silicification (Scurfield and Segnit 1984). Recrystallization may also occur over time. Stein (1982) found a general increase in the degree of crystallinity of her samples with age, which she attributes to the same process of maturation that alters silica in ocean sediments. Some of these changes may also be related to depth of burial; Sigleo (1978) reports that the organic material still present in the Petrified Forest specimen she examined had been subjected to temperatures ranging from 50 to 130° C, presumably as a result of burial under other sediments. Such temperatures would also encourage silica recrystallization.

The degree of mineralization varies a great deal for silicified wood. Some logs have been completely replaced, cell for cell, while in others extra silica was deposited only in pore spaces. In general, the more crystalline the quartz, the less wood microstructure is preserved, although the gross morphology is usually still present. Sigleo (1978) found that silicification could vary within a single specimen. For example, the interior portion of a 4 cm diameter branch from the Petrified Forest was black, significant quantities of the original organic material were present, and the wood textures were excellently preserved. The outer layers, on the other hand, were reddish and beige, and the wood structure was less well preserved in these more thoroughly mineralized zones.

Decomposed volcanic ash also releases clays, iron oxides, and manganese oxides, which give petrified wood its colors. Sigleo (1979) found that some of these minerals were deposited along with the silica, while others migrated into the silicified wood after the silica had been deposited. Each of the four geographically and stratigraphically isolated concentrations of silicified wood in the Petrified Forest seems to have been affected by slightly different conditions. The so-called Rainbow Forest, in the southern part of the park, is the oldest and has the widest variety of coloring agents. The Jasper and Crystal Forests are younger; the former is primarily colored by iron oxides, and the logs of the latter have many cavities lined with well-formed quartz crystals. The Black Forest, located in the northern part of the park and deposited most recently, is stained with a black mineral, perhaps some form of manganese (Ash 1987:406).

Crabtree points out that palm roots, aquatic plants, algae, bog material, shell, and bone can also become silicified and then used to make stone tools (Crabtree 1967:13). Heinrich (1988) reported

that the several different kinds of silicified wood found in archaeological assemblages from Texas were most often used to make larger tools with durable cutting edges. More homogeneous cherts were usually preferred for tools with delicate cutting edges, such as projectile points. This suggests that the fracture properties of some silicified woods are impaired by the remnant woody structure.

### **Magadi-type chert**

Some of the oldest hominid bones on earth are found in the Pleistocene deposits at Olduvai Gorge in northern Tanzania, along with tools made from some of the youngest chert on earth (Stiles et al. 1974). These cherts formed some 1.6 million years ago when the area that is now Olduvai Gorge was a broad, shallow basin bordered on the east and south by active volcanoes of the Eastern Rift Valley. Streams draining the slopes of the volcanoes flowed into the basin, forming a lake that probably lacked an outlet (Hay 1971). The climate of the area was hot and dry, the rate of evaporation was high, and the lake became strongly saline and alkaline. It also became supersaturated with silica, perhaps as high as 1,450 ppm (Eugster 1967) as a result of the weathering of volcanic ash deposits and rocks.

Occasional influxes of fresh water into this lake may have caused the precipitation of sodium-silicate minerals, especially magadiite,  $\text{NaSi}_7\text{O}_{13}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$  (Eugster 1967). Under the right conditions, including the absence of significant amounts of aluminum (Iler 1979:159), magadiite is deposited as tiny spheres in fine laminae only 1 mm thick, perhaps representing annual increments (Eugster 1967). These laminae can form beds up to 60 cm thick. The magadiite is white, crystalline, and plastic, with the consistency of soft putty (Surdam et al. 1972). Eugster argued that magadiite remains stable as long as the water around it is alkaline, but if it is exposed to more acid conditions the sodium is removed and the magadiite is altered to quartz, perhaps through an intermediate stage of kenyaite, a closely related mineral (Eugster 1967). More recent research suggests that magadiite can also transform to chert spontaneously in the presence of alkali brines, though later stages in the development of the chert nodules may require fresh water (Schubel and Simonson 1990). Formation of magadi-type chert apparently does not include a cristobalite phase (Surdam et al. 1972). In the case of Olduvai Gorge, the lake in which the magadiite was deposited fluctuated in size. When the magadiite was exposed to air and rainwater, it was altered to chert. This alteration appears to have happened extremely rapidly by geological standards, perhaps within 10,000 years (Stiles et al. 1974). Thus, the formation of magadi-type chert is different in many ways from that of most other cherts.

Magadi-type chert also looks different from most other cherts. Magadiite is soft and easily deformed, and when it is transformed to chert, it loses 25% of its volume. The resulting nodules sometimes look as if they had been squeezed from a giant

tube. Many are twisted and irregular in overall shape, with spikes and lobe-shaped protrusions. The surfaces of the nodules usually have desiccation polygons, which give them a distinctive reticulated or net-like pattern, and there are often casts of mud cracks and crystals of evaporite minerals such as natron (Surdam et al. 1972). Nodules from a single horizon are often similarly shaped (Hay 1968), suggesting that shape is partly a response to local conditions. Magadi-type chert has been identified, primarily on the basis of surface features, from several locations in the western United States (Surdam et al. 1972) and elsewhere in the world.

The chert at Olduvai Gorge, which is found in a matrix of clays in the sandy conglomerate member of Bed II, forms irregularly shaped nodules from 5 to 20 cm long (Stiles et al. 1974:288). The nodules have an opaque white cortex and a reticulate pattern on their surfaces, but the chert within is primarily homogeneous, translucent, and milky white to pale yellow. It can also be opaque white, brown, or pale red, and some nodules show concentric

color zoning. It appears to have been used by the inhabitants of the area almost as soon as it formed.

The cherts chosen for these case studies are not archetypes but simply examples of the many ways cherts can form. Most nodular cherts do not form in chalk, and there are bedded cherts that differ greatly from those of the Monterey formation, such as the Arkansas novaculite with its meters-thick beds and lack of evidence of silica-secreting organisms. The vast deposits of bedded jaspers in the Lake Superior region could not form in the same way as Pennsylvania jasper, and agates in dolomite must surely have formed through a different mechanism than those in lava beds. Chert is more variable in its origin than most of us realize. Its formation often involves several steps, and it continues to be subject to alteration after it has formed, both while it is encased in bedrock and when it is exposed on the ground surface. To a considerable extent, this variation in mode of origin causes the variation in properties discussed in the following chapters.

# 4

## Chemical Properties

**T**hough cherts may form through a variety of pathways, they all form in close association with other rocks, sediments, or organic remains. Thus, no chert is composed of pure silica. All cherts have impurities, and these impurities are the primary focus of this chapter. The impurities in chert are a major cause of its visible characteristics, they may affect some mechanical properties, and they surely influence the ways in which different cherts respond to weathering and heat treating. In addition, the chemical properties of chert have a direct archaeological application: they are one way of determining the original geographic point of origin of archaeological artifacts. Uses of, and procedures for, source determinations are discussed in appendix A.

Chemical data concerning the impurities in cherts are most often available in one of three forms: descriptions of thin sections, proportions of major element oxides, or elemental abundances. Each of these forms has advantages and disadvantages. Thin section analysis (discussed further in chapter 5) is the microscopic examination of very thin slices of rock. The major minerals in the rock are identified by their color and optical properties, and their abundance and distribution are described. Since minerals have fairly well-determined chemical compositions, by definition, the chemical composition of the impurities can be estimated indirectly from thin sections. Most thin section analyses are qualitative rather than quantitative, however; a few provide estimates of the proportions of the minerals present, but more often a given impurity is described only as being absent, present, or abundant. Also, "trace elements" (those present in very small proportions) and elements not present as separate minerals cannot be detected with this method.

Major elements are often determined through classic chemi-

cal analysis in which a sample of rock is crushed, ground to a powder, and subjected to wet chemical tests using acids, organic solvents, and heat to dissolve and/or precipitate the major chemical constituents. The results are traditionally presented as oxides of the elements in percent by weight. This method, which gives quantitative data, must be done with care; contamination is a problem at all stages of the process, especially with a very hard rock such as chert. Errors made at one step of the analysis can affect results for other elements (Jeffery and Hutchison 1981:15). In addition, the oxides do not usually represent the actual minerals present, and this method is not sensitive enough to deal with trace elements.

Elemental analyses determine the proportion of each element present in a rock sample, and results are generally expressed in parts per million. A wide variety of analytical techniques is available for performing elemental analysis (for example, Nicol 1975; Reeves and Brooks 1978). Neutron activation analysis, X-ray fluorescence, and atomic absorption analysis are the techniques most often used on cherts. Each technique has different strengths and weaknesses, but all are quite accurate and can detect even minute amounts of trace elements. However, these methods do not indicate which minerals are present. For example, an elemental analysis will tell how much iron is present in a chert but not whether iron is present as hematite, limonite, or pyrite, or many other possibilities.

Ideally, one would prefer to know both the mineral and elemental compositions of cherts because these data are complementary. Unfortunately, both kinds of analysis are rarely performed on the same samples, although they may be available for different samples of the same type of chert. All three types of



chemical data are used in the following discussion of the impurities usually found in cherts, their location in the chert structure, how they got there, and how and why they vary between and within geological formations.

## Impurities

The major impurities in cherts are clays, carbonates, iron oxides, and organic matter. All are often seen in thin sections as patches of unreplaced matrix, scattered grains or crystals, or dust-size fragments that may appear as streaks, clouds, or sometimes haloes around fossils or other inclusions. Thin sections clearly indicate that most impurities are located outside the quartz grains.

Some impurities are also dissolved in the water that makes up about 1% of most cherts by weight. This water is located in pores and fissures in the chert and in the tiny vacuoles, or bubbles, about  $0.1 \mu$  in diameter, found on the surfaces of some grains (Folk 1974:80). Water also occurs in chert as a thin film between crystal layers (Micheelsen 1966) but as this layer is only one molecule thick there would seem to be little room for other ions.

A few impurities are actually inside the quartz grains that make up chert, either as substitutes for silicon in the silica tetrahedron, as ions tucked into empty spaces in the crystal structure, or along flaws and dislocations in the quartz crystal structure. In general, one element can substitute for another in a mineral if their ions are roughly the same size and if their electric charge is similar. While such substitutions are common for some elements, silicon has a very small ionic radius and a high charge (+4). These characteristics limit the number of elements that can substitute for it. Only aluminum and germanium are commonly believed to substitute for silicon in quartz, but germanium is not an abundant element and aluminum has the wrong electrical charge. Aluminum can substitute for silicon if other ions, most often lithium, sodium, or potassium, are present in the crystal interstices to balance the charge. Aluminum has been detected in natural quartz crystals in proportions ranging from 10 to 500 ppm (Smith and Steele 1984). The amount of aluminum in quartz decreases, however, as the temperature of formation decreases (Fronde1 1962:143). This suggests that little aluminum is likely to be substituting for silicon in cherts, which usually form at very low temperatures. In general, "The structure [of quartz] is such that there is very limited space for accommodating extra atoms, and silicon cannot be replaced readily by any other common quadrivalent cation" (Berry, Mason, and Dietrich 1983:397).

Impurities are also present in quartz along flaws or subgrain boundaries within the quartz grains. For example, Micheelsen (1966:305) indicates that finely divided carbon and calcite are present inside the quartz grains of Stevns chert. For most cherts, though, the proportion of contaminants inside the quartz grains is surely insignificant compared to the proportion located among quartz grains.

## Sources of Impurities

The majority of the impurities in most cherts are minerals that were present in the area of deposition and which simply became incorporated into the chert as it formed. Examples are clays or sand grains washed into the sea from adjacent landmasses, unreplaced fragments of calcium carbonate, and bits of organic matter. These residual impurities also probably account for most of the elements present in chert in proportions of a percent or more.

Other impurities were not initially present in the sediments but rather are minerals that precipitated from solution, often the same solution out of which the silica was precipitating, and then became incorporated into the chert as it formed. Examples are crystals of pyrite, hematite, dolomite, and certain clays that formed in place. Some of these minerals formed early in chert diagenesis, while others precipitated later into pores, cracks, and cavities in the chert. They are quantitatively less important than residual impurities for most cherts but may be important for some.

Finally, some impurities are not present as minerals in their own right but are associated with other minerals in various ways. For example, many metallic elements can substitute for one another in minerals, and some small ions can fit into the interstices of the crystal structures of other minerals. Other materials, especially clays and organic materials, easily adsorb stray ions on their surfaces (Blatt 1982:40, 97). Many trace elements are probably present in such forms.

Any single element may be present in more than one form. For example, iron could be present in a specific chert partly as hematite from weathered soils, partly as newly precipitated crystals of pyrite, and partly as ions adsorbed on the surface of clays. This mineralogical complexity is one of the reasons why elemental data and mineral data are both complementary and necessary.

The impurities present in a specific chert are a reflection of many factors, including the types of rock present on adjacent landmasses, the weathering processes affecting those rocks, the nature of the processes transporting sediments to bodies of water, the distance between the basin where chert is forming and the land, the presence of volcanoes in the region, and the nature and quantity of flora and fauna living in the waters where the chert is forming. The kinds and quantities of impurities are also strongly affected by chemical conditions in the basin of deposition, especially temperature, pH, and Eh, which will determine which minerals dissolve and which precipitate. Finally, the process of chert diagenesis itself affects impurities. As a further complication, not all these factors are independent of one another (Spencer et al. 1968:982). For example, an active volcano in a region may encourage diatoms to flourish by adding silica to the water while at the same time adding volcanic ash to the sediments and releasing gases that influence chemical conditions in adjacent waters.

Because of the complexity of this situation, it will be a long time before we can accurately predict a chert's chemistry by knowing the conditions under which it formed or vice versa. Some tentative conclusions are possible, however, based on geochemical principles derived from studies of other sedimentary rocks in conjunction with the chemical data available for cherts.

## Chert Geochemistry

Geochemistry is the study of the distribution of the various elements in rocks and minerals, along with the principles governing these distributions. While geochemistry is a well-established branch of geology, the geochemistry of chert must be considered an underdeveloped twig. An intrepid band of chert geochemists does exist, but chert is neither an abundant rock nor one of economic importance in the modern world; consequently it has not received as much study as many other rock types. Thus, many of the generalizations given below are derived from relatively limited studies or from geochemical studies of other sedimentary rocks. It must also be stressed that, when it comes to interpreting chemical data for a particular chert, the general principles discussed here cannot substitute for detailed knowledge of the history and characteristics of that chert.

There are 103 known elements, but 15 do not occur naturally. Table 4.1 shows the natural elements arranged by name, symbol, and atomic number. Of these natural elements, the four that are radioactive with very short half-lives and the six inert gases are irrelevant to chert geochemistry. This leaves 78 elements of potential relevance, including silicon and oxygen. A number of references summarize the data available regarding the behavior of each element in various geologic settings (for example, Goldschmidt 1958, Wedepohl 1969–1978). Many elements covary, and most are remarkably predictable on the basis of their chemical properties. Nevertheless, the geochemistry of the impurities in chert is complex and not easily summarized. Therefore, I discuss chert geochemistry in terms of major constituents rather than deal with each element separately.

Table 4.2 shows the 76 elements that can be considered contaminants in chert and the major types of impurities with which each is most likely to be associated. Silicon and oxygen are, of course, found primarily in quartz, so they are not listed. This table, which is based on a synthesis of data in Wedepohl 1969–1978 and numerous articles on chert geochemistry, must not be used dogmatically. It is intended only as a guide to where to look first when attempting to interpret chemical data from a specific chert source. It may also be helpful for selecting which elements to analyze, as prior knowledge of a chert's mode of origin should allow at least limited prediction of which elements are likely to covary or to occur in unusually high or low proportions.

Two sets of elements are grouped in table 4.2: rare earth elements, sometimes called the lanthanides (lanthanum, cerium,

praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium, plus yttrium), and the platinum metals (ruthenium, rhodium, palladium, osmium, iridium, and platinum). The elements in each group behave so similarly that they are rarely treated separately in geochemical treatises.

## Silicon and Oxygen

Silicon and oxygen, in the form of silica ( $\text{SiO}_2$ ), comprise the bulk of all cherts. Both are also present in other minerals; for example, the chemical composition of the clay kaolinite is  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . Such impurities contribute relatively little silicon and oxygen to cherts, however, compared with the amounts in quartz. The proportion of silica in most cherts is probably more than 90% and some are over 99% pure (Cressman 1962), but the proportion can be less. There is no well-defined cutoff, and a continuum exists with highly siliceous cherts at one end grading into shaley or chalky cherts, and then into siliceous shales or carbonates.

Although silicon and oxygen are taken for granted in chert and are generally considered far less fascinating than the elements present as impurities, one aspect of oxygen chemistry, the stable isotopes, is of considerable interest to chert geochemists. Isotopes are slightly different varieties of the same element. As discussed in chapter 2, atoms are made up primarily of neutrons, protons, and electrons. Although all atoms of a given element must have the same number of electrons and protons, they can differ in the number of neutrons present in the nucleus. If they do differ, then two atoms of the same element will have slightly different masses or atomic weights, and these different varieties of the same element, its isotopes, may have slightly different chemical properties. The great majority of elements have more than one isotope, and some have eight or more (Krauskopf 1979:488). Isotopes may be stable or radioactive; a familiar example for archaeologists is carbon, which has three isotopes,  $^{12}\text{C}$ ,  $^{13}\text{C}$  and  $^{14}\text{C}$ . Carbon 12 and  $^{13}\text{C}$  are stable isotopes; their relative proportions are fixed once they become incorporated into a mineral or organism. Carbon 14 is radioactive; its proportion relative to the stable isotopes of carbon decreases predictably over time and can therefore be used to date archaeological materials.

Oxygen has three stable isotopes, with atomic masses of 16, 17, and 18. Oxygen 17 is very rare, but  $^{16}\text{O}$  and  $^{18}\text{O}$  are abundant, and their relative proportions provide important clues as to the conditions under which cherts have formed. Basically, different isotopes have different chemical properties because the atoms of the lighter isotope vibrate at a higher frequency than those of the heavier isotope. They are thus less strongly bonded to other atoms (Krauskopf 1979:504). For some elements, including oxygen, this difference can lead to fractionation. For example, when water evaporates,  $^{16}\text{O}$ , the lighter isotope, evaporates more easily. As a result,  $^{18}\text{O}$ , the heavier isotope, is concentrated in the remaining water.

**Table 4.1 Naturally Occurring Elements**

By atomic number			By symbol			By element name		
1	H	Hydrogen	Ac	Actinium	89	Actinium	Ac	89
2	He	Helium	Ag	Silver	47	Aluminum	Al	13
3	Li	Lithium	Al	Aluminum	13	Antimony	Sb	51
4	Be	Beryllium	Ar	Argon	18	Argon	Ar	18
5	B	Boron	As	Arsenic	33	Arsenic	As	33
6	C	Carbon	Au	Gold	79	Barium	Ba	56
7	N	Nitrogen	B	Boron	5	Beryllium	Be	4
8	O	Oxygen	Ba	Barium	56	Bismuth	Bi	83
9	F	Fluorine	Be	Beryllium	4	Boron	B	5
10	Ne	Neon	Bi	Bismuth	83	Bromine	Br	35
11	Na	Sodium	Br	Bromine	35	Cadmium	Cd	48
12	Mg	Magnesium	C	Carbon	6	Calcium	Ca	20
13	Al	Aluminum	Ca	Calcium	20	Carbon	C	6
14	Si	Silicon	Cd	Cadmium	48	Cerium	Ce	58
15	P	Phosphorus	Ce	Cerium	58	Cesium	Cs	55
16	S	Sulfur	Cl	Chlorine	17	Chlorine	Cl	17
17	Cl	Chlorine	Co	Cobalt	27	Chromium	Cr	24
18	Ar	Argon	Cr	Chromium	24	Cobalt	Co	27
19	K	Potassium	Cs	Cesium	55	Copper	Cu	29
20	Ca	Calcium	Cu	Copper	29	Dysprosium	Dy	66
21	Sc	Scandium	Dy	Dysprosium	66	Erbium	Er	68
22	Ti	Titanium	Er	Erbium	68	Europium	Eu	63
23	V	Vanadium	Eu	Europium	63	Fluorine	F	9
24	Cr	Chromium	F	Fluorine	9	Gadolinium	Gd	64
25	Mn	Manganese	Fe	Iron	26	Gallium	Ga	31
26	Fe	Iron	Ga	Gallium	31	Germanium	Ge	32
27	Co	Cobalt	Gd	Gadolinium	64	Gold	Au	79
28	Ni	Nickel	Ge	Germanium	32	Hafnium	Hf	72
29	Cu	Copper	H	Hydrogen	1	Helium	He	2
30	Zn	Zinc	He	Helium	2	Holmium	Ho	67
31	Ga	Gadolinium	Hf	Hafnium	72	Hydrogen	H	1
32	Ge	Germanium	Hg	Mercury	80	Indium	In	49
33	As	Arsenic	Ho	Holmium	67	Iodine	I	53
34	Se	Selenium	I	Iodine	53	Iridium	Ir	77
35	Br	Bromine	In	Indium	49	Iron	Fe	26
36	Kr	Krypton	Ir	Iridium	77	Krypton	Kr	36
37	Rb	Rubidium	K	Potassium	19	Lanthanum	La	57
38	Sr	Strontium	Kr	Krypton	36	Lead	Pb	82
39	Y	Yttrium	La	Lanthanum	57	Lithium	Li	3
40	Zr	Zirconium	Li	Lithium	3	Lutetium	Lu	71
41	Nb	Niobium	Lu	Lutetium	71	Magnesium	Mg	12
42	Mo	Molybdenum	Mg	Magnesium	12	Manganese	Mn	25
44	Ru	Ruthenium	Mn	Manganese	25	Mercury	Hg	80

**Table 4.1 Naturally Occurring Elements (cont.)**

By atomic number			By symbol			By element name		
45	Rh	Rhodium	Mo	Molybdenum	42	Molybdenum	Mo	42
46	Pd	Palladium	N	Nitrogen	7	Neodymium	Nd	60
47	Ag	Silver	Na	Sodium	11	Neon	Ne	10
48	Cd	Cadmium	Nb	Niobium	41	Nickel	Ni	28
49	In	Indium	Nd	Neodymium	60	Niobium	Nb	41
50	Sn	Tin	Ne	Neon	10	Nitrogen	N	7
51	Sb	Antimony	Ni	Nickel	28	Osmium	Os	76
52	Te	Tellurium	O	Oxygen	8	Oxygen	O	8
53	I	Iodine	Os	Osmium	76	Palladium	Pd	46
54	Xe	Xenon	P	Phosphorus	15	Phosphorus	P	15
55	Cs	Cesium	Pa	Protactinium	91	Platinum	Pt	78
56	Ba	Barium	Pb	Lead	82	Polonium	Po	84
57	La	Lanthanum	Pd	Palladium	46	Potassium	K	19
58	Ce	Cerium	Po	Polonium	84	Praseodymium	Pr	59
59	Pr	Praseodymium	Pr	Praseodymium	59	Protactinium	Pa	91
60	Nd	Neodymium	Pt	Platinum	78	Radium	Ra	88
62	Sm	Samarium	Ra	Radium	88	Radon	Rn	86
63	Eu	Europium	Rb	Rubidium	37	Rhenium	Re	75
64	Gd	Gadolinium	Re	Rhenium	75	Rhodium	Rh	44
65	Tb	Terbium	Rh	Rhodium	44	Rubidium	Rb	37
66	Dy	Dysprosium	Rn	Radon	86	Ruthenium	Ru	44
67	Ho	Holmium	Ru	Ruthenium	44	Samarium	Sm	62
68	Er	Erbium	S	Sulfur	16	Scandium	Sc	21
69	Tm	Thulium	Sb	Antimony	51	Selenium	Se	34
70	Yb	Ytterbium	Sc	Scandium	21	Silicon	Si	14
71	Lu	Lutetium	Se	Selenium	34	Silver	Ag	47
72	Hf	Hafnium	Si	Silicon	14	Sodium	Na	11
73	Ta	Tantalum	Sm	Samarium	62	Strontium	Sr	38
74	W	Tungsten	Sn	Tin	50	Sulfur	S	16
75	Re	Rhenium	Sr	Strontium	38	Tantalum	Ta	73
76	Os	Osmium	Ta	Tantalum	73	Tellurium	Te	52
77	Ir	Iridium	Tb	Terbium	65	Terbium	Tb	65
78	Pt	Platinum	Te	Tellurium	52	Thallium	Tl	81
79	Au	Gold	Th	Thorium	90	Thorium	Th	90
80	Hg	Mercury	Ti	Titanium	22	Thullium	Tm	69
81	Tl	Thallium	Tl	Thallium	80	Tin	Sn	50
82	Pb	Lead	Tm	Thulium	69	Titanium	Ti	22
83	Bi	Bismuth	U	Uranium	92	Tungsten	W	74
84	Po	Polonium	V	Vanadium	23	Uranium	U	92
86	Rn	Radon	W	Tungsten	74	Vanadium	V	23
88	Ra	Radium	Xe	Xenon	54	Xenon	Xe	54
89	Ac	Actinium	Y	Yttrium	39	Ytterbium	Yb	70
90	Th	Thorium	Yb	Ytterbium	70	Yttrium	Y	39
91	Pa	Protactinium	Zn	Zinc	30	Zinc	Zn	30
92	U	Uranium	Zr	Zirconium	40	Zirconium	Zr	40

**Table 4.2 Contaminants and Associated Elements**

Element	Clays	Iron minerals	Carbonates	Organics	Other
H				1	Water, hydroxyl ion
Li	1				
Be	1	4		2	
B	1	4		2	Volcanic, hydrothermal
C			1	1	
N				1	
F	1		2		Hydrothermal, apatite
Na	2		3		Salts, volcanic, hydrothermal
Mg	2		1		
Al	1				
P	2	2		2	Apatite
S		2		1r	Volcanic, hydrothermal
Cl	3				Salts, volcanic, hydrothermal
K	1				Salts, feldspar
Ca	3		1		Feldspar, apatite
Sc	2	2			
Ti	1			4	Rutile
V	1			4	
Cr	1				
Mn	3	1	2		
Fe	3	1		4r	Volcanic, hydrothermal
Co		1		4r	
Ni	3	1		4r	
Cu	2	1		3	
Zn	2	1	4	3	
Ga	1				
Ge	1			3	
As	2	1		2	Volcanic, hydrothermal
Se	2	1		3r	
Br	4			2	Salts
Rb	1				
Sr			1		Apatite, feldspar
Zr	4	3			Zircon
Nb	1				
Mo		1		2	
Ag				2	Silver ores
Cd	1			3r	Hydrothermal
In		1			
Sn	1				Cassiterite
Sb	2	2		2r	Volcanic, hydrothermal
Te		1			Volcanic, hydrothermal
I	3			1	Volcanic, hydrothermal
Cs	1				
Ba	2	2	4	1	Barite
REE & Y	1	2	4	3	Feldspars, apatite
Hf	2				Zircon
Ta	1				
W	2	1		3	
Re		1		2	
Pt metals	2			3	Platinum ores
Au	3			4	Gold ores
Hg	1			3	Volcanic, hydrothermal
Tl	1			3r	Volcanic
Pb	1	3		3	
Bi		2		2	Volcanic, hydrothermal
Th	1				Monazite
U	3			1r	Uranium ores

1 = most often associated; 2 = frequently associated; 3 = sometimes associated; 4 = rarely associated;  
r = associated with reducing conditions

By convention, the proportions of the major oxygen isotopes are presented as a single value, " $\delta^{18}\text{O}$ ," which represents the difference between the ratio of  $^{18}\text{O}$  to  $^{16}\text{O}$  in a sample and the ratio of  $^{18}\text{O}$  to  $^{16}\text{O}$  in standard mean ocean water (SMOW). A high  $\delta^{18}\text{O}$  value means that the sample is enriched in the heavier isotope, while a low  $\delta^{18}\text{O}$  value means that the sample is depleted in the heavier isotope relative to SMOW. The most important cause of variation in the 18/16 ratio for cherts is temperature: the lower the temperature under which the quartz formed, the higher the  $\delta^{18}\text{O}$  value. In fact, cherts have some of the highest  $\delta^{18}\text{O}$  values of all rocks, ranging from 15 to 36, compared to a  $\delta^{18}\text{O}$  of 12 for igneous rock (Knauth and Epstein 1976). Thus, oxygen isotopes are being used more and more to determine the temperature conditions under which specific cherts formed.

Oxygen isotope data for cherts must be used with care, however. It is important to remember that the  $\delta^{18}\text{O}$  for chert will change at any stage in diagenesis at which solution and reprecipitation occur. Thus, chert isotope values represent the temperature of the last such diagenetic change, not the original ocean temperature (Hein and Yeh 1981). In fact, "Nearly all the processes which affect cherts during diagenesis lower their  $\delta^{18}\text{O}$  value" (Kolodny and Epstein 1976:1202). In addition, temperature is not the only variable affecting  $\delta^{18}\text{O}$ . Regardless of temperature,  $\delta^{18}\text{O}$  is higher if the chert formed under evaporitic conditions and lower if fresh water was involved in diagenesis. This is the case because these types of water have isotopic compositions that differ from SMOW (Knauth and Epstein 1976).  $\delta^{18}\text{O}$  will also be lower if significant proportions of detrital quartz or clay, both of which have low  $\delta^{18}\text{O}$  values, are present. Because of all these complications, cherts show more variability in  $\delta^{18}\text{O}$  than do most other rock types (Knauth and Epstein 1976). Jones and Knauth (1979) document a range in  $\delta^{18}\text{O}$  from 18 to 34 for a single widespread formation, Arkansas novaculite, which varies over its outcrop area in the quantity of impurities present and in the conditions of diagenesis.

Silicon also has several isotopes, but they appear to have little potential for shedding light on any of the issues of concern to us (Douthitt 1982). Isotopes of other elements that occur in cherts, especially hydrogen, carbon, and sulfur, have been useful in other contexts, but little research has been done on them regarding cherts. Strontium isotopes, however, have been used successfully to determine the geological age of cherts (Brueckner and Snyder 1985).

## Clays

The clays are a highly diverse family of minerals, all of which can be described chemically as hydrous aluminum silicates and most of which have a platy or sheetlike crystal structure. The bonds among the ions in this structure are rather weak and loose, permitting a great deal of substitution and making most clays quite variable in composition. Also, because of their platy structure,

clays have a large surface area and the ability to adsorb many other ions on their slightly charged surfaces (Krauskopf 1979:482). In fact, clays seem to pick up other ions as a shag carpet picks up lint. Thus, a chert that has a high clay content will usually have high proportions of many elements.

All clays contain aluminum, silicon, hydrogen, and oxygen. Montmorillonite also has magnesium and iron, and illite and the micas have potassium. Among the common substitutions are manganese and zirconium for the magnesium in montmorillonite and barium for potassium in illite. Most of the extraneous elements are present, however, as ions adsorbed on the surface of the clay (Krauskopf 1979:482). In interpreting elemental data for cherts, it is usually safe to assume that virtually all the aluminum is present in the form of clays, and that the potassium, titanium, vanadium, chromium, rubidium, and cesium are also associated almost exclusively with clays. As table 4.2 indicates, a wide variety of other elements also may sometimes covary with clays.

Clays are found in virtually all cherts, doubtless because they are ubiquitous in nature. The quantity of clay in a chert is determined by such factors as the distance of the basin of deposition from land, the extent and type of erosion and weathering occurring on adjacent landmasses, and the extent to which clay has been either mobilized and washed away or diluted by silica during diagenesis. The proportions of the different major clay elements are largely a function of the kinds of clay present, which is usually determined by the nature of the parent rock in combination with weathering conditions or hydrothermal processes (Krauskopf 1979:153). Proportions of various minor elements would primarily reflect those other types of rocks on land or under water which contributed to the sediments.

## Iron Minerals

Iron is the fourth most abundant element in the earth's crust (table 2.1) and is found in a great many minerals. Manganese, while not nearly so abundant, behaves similarly to and is often discussed together with iron. The iron minerals most commonly found in cherts are hematite ( $\text{Fe}_2\text{O}_3$ ), goethite ( $\text{HFeO}_2$ ) (called limonite when hydrated), pyrite ( $\text{FeS}_2$ ), and magnetite ( $\text{FeFe}_2\text{O}_4$ ). The most common manganese minerals in chert are probably pyrolusite ( $\text{MnO}_2$ ), which forms the dendrites common in some cherts, and manganite [ $\text{MnO}(\text{OH})$ ]. Many metallic elements can substitute for iron and manganese in these minerals, and iron and manganese oxides and hydroxides also adsorb other ions, similarly to clays. Among the more common elements that tend to covary with iron and manganese in cherts are cobalt, nickel, and copper.

Iron is concentrated by hydrothermal action and some weathering processes so that its proportion in cherts would presumably be controlled in part by these factors. In addition, iron and manganese geochemistry is strongly affected by oxidizing or reducing conditions. Under the oxidizing conditions common on the earth's surface, iron and manganese form highly insoluble

oxides that tend to accumulate in sediments. Iron and manganese will dissolve in reducing and acid waters, however, and do not always readily precipitate again when conditions change. Rather, they tend to form colloids that may be transported for long distances (Krauskopf 1979:213). Pyrite ( $\text{FeS}_2$ ) will precipitate in the presence of sulfur and reducing conditions.

In many cherts, iron and other metals are present primarily in association with clays, and there is often a close correlation between metals and clays both between and within formations (Cressman 1962). Jaspers are a major exception to this generalization; they are high in iron by definition, but many are not especially enriched in clays. Also, a few cherts form in close association with manganese deposits, and are unusually enriched in this element (Cressman 1962:3).

### Carbonates

Many cherts form by replacement of such carbonate rocks as chalk, limestone, and dolomite. Thus, carbonate minerals are common contaminants in chert. Unreplaced patches of these minerals are often visible under magnification, and sometimes even to the naked eye. In addition, "clouds" of dust-sized carbonate fragments are sometimes seen, and dolomite rhombs are common. Furthermore, many cherts contain fossils of carbonate secreting organisms, some of which have been replaced by silica but others of which still retain part of their original aragonite or calcite shells. Calcium, carbon, and oxygen are present in most of the carbonate minerals, and magnesium is an essential component of dolomite. Magnesium, manganese, iron, and strontium commonly substitute for the calcium in carbonates; sodium, barium, the rare earth elements, and several other elements may also covary with carbonates in some cherts. In general, calcium, magnesium, and strontium can be considered the best indicators of the carbonate content of cherts.

Ratios among the different carbonate-related elements are not constant and can be influenced by several factors. For example, the ratio of calcium to magnesium (Ca/Mg) is apparently affected by temperature; it decreases toward the equator in many calcium carbonate secreting organisms (Glover and Lee 1984). Different organisms secrete different forms of calcium carbonate, which affects the resulting chemistry. The structure of aragonite favors substitution by large ions, such as sodium, strontium, and barium, while the tighter structure of calcite favors the smaller ions, such as magnesium, manganese, iron, copper, zinc, and cadmium (Veizer 1983).

The proportion of carbonate-related elements in a chert is determined largely by its mode of origin, as well as the quantities and kinds of organisms in the basin of deposition. In general, carbonates would be expected to be removed during chert diagenesis because the chemical conditions favoring precipitation of silica also favor the solution of carbonates. The extent of carbonate removal would presumably be determined by local chemical

conditions in the basin of deposition and by the nature of the waters that participated in later diagenesis.

### Organic Matter

Cherts often form in close association with biological organisms including, but not limited to, the carbonates. Thus, organic matter affects some aspects of most cherts' geochemistry. In many cases, organisms are directly or indirectly responsible for the silica component of cherts. Silica-secreting organisms, such as diatoms, radiolarians, and sponges, directly concentrate and precipitate the silica from which many cherts form. In addition, organic matter can chelate silica, resulting in solutions that are highly supersaturated with silica and from which silica is easily precipitated by slight changes in the chemical environment. Silica precipitation also appears to be encouraged by organic matter in wood, coal beds, and animal burrows.

Organic compounds also comprise some of the impurities in cherts. Hydrogen, carbon, nitrogen, and oxygen are the basic elements present in organic matter, but most organisms also require other elements, such as silicon, calcium, sodium, iron, phosphorus, and sulfur. Many organisms concentrate certain elements in their soft tissues or hard parts, for reasons that are not well understood, and these elements may then become concentrated in cherts. For example, diatoms are often high in germanium, while radiolarians are generally low in that element (Maxwell 1963). Similarly, titanium is concentrated by some siliceous sponges and diatoms (Cressman 1962:13). Terrestrial plants are also known to concentrate a wide range of elements, which may then contribute to the chemistry of silicified wood and of cherts formed in association with coal beds (Given and Miller 1987).

Organic matter can affect the chemical composition of cherts in other ways. First, organic compounds can form complexes with some elements, thus transporting and concentrating them. Fragments of organic matter can also adsorb ions on their surfaces, just as clays and iron oxides do. Perhaps most significantly, the decay of organic matter causes reducing conditions that play an important role in determining which minerals precipitate and are incorporated into chert and which dissolve and are removed from the area in which chert is forming. For example, many metals form insoluble compounds with sulfur under reducing conditions, hence the frequent occurrence of pyrite in cherts. Uranium also appears to be concentrated by the decay of organic matter and then precipitated under reducing conditions; it is correlated with organic carbon content in some sedimentary rocks (Mason and Moore 1982:177).

### Other Geological Factors and Processes

While varying proportions of clays, iron oxides, carbonates, and organics can account for much of the chemical variability among cherts, other factors may play a role in specific cases. For example,

cherts forming in association with unusual rock types, such as sandstone, schist, or gabbro (for example, Lavin 1983:47–55), must surely be affected by the chemistry of the surrounding rock. In addition, detrital minerals that are not usually common in the environments where chert forms, such as zircon or feldspar, may sometimes find their way into a particular basin of deposition and influence the chemistry of the chert forming there.

Volcanoes may also affect the chemistry of some cherts. Geologists have long noted that many cherts occur in association with sediments of volcanic origin. Volcanic activity (either on land or under water) has been credited with encouraging chert formation either by releasing silicon into water, by spewing forth ash or lava that releases silica into sediments upon weathering, or by creating conditions especially favorable for silica-secreting organisms. Volcanic activity usually results in the release of large quantities of water vapor and gases, which enrich adjacent waters with sulfur, chlorine, and sometimes fluorine. These form compounds with other elements common in volcanic emanations, especially sodium, silicon, potassium, calcium, magnesium, aluminum, and iron. Volcanoes vary in composition; so a wide variety of other elements may also be present in specific cases (Krauskopf 1979:377). Cressman states that a predominance of sodium over potassium in a chert is evidence that volcanoes contributed to its chemistry (Cressman 1962:15).

Hydrothermal activity plays a role in the diagenesis of some cherts. Hydrothermal processes are those in which groundwater has been heated to temperatures between 50 and 500° C because of the nearby presence of hot magma (as at Yellowstone National Park) or metamorphism. Such heated fluids flow under pressure through rocks, dissolving and depositing as they go, and sometimes issuing forth as geysers or hot springs. Hydrothermal fluids may be directly responsible for the origin of some cherts, especially certain jaspers (Lovering 1972) and agates such as those found in the Serra Geral formation. Such waters carry large quantities of dissolved salts, especially those composed of sodium, chlorine, potassium, calcium, magnesium, and sulfur, plus such metals as iron, manganese, silver, arsenic, antimony, gold, mercury, and sometimes lead, zinc, and copper (Krauskopf 1979:393–396). Lovering states that silver, arsenic, bismuth, indium, and antimony are usually enriched in hydrothermal jaspers, while most other elements are depleted, especially sodium (Lovering 1972:35). High levels of barium can also be an indicator of hydrothermal activity (Hein et al. 1983).

Finally, virtually all cherts form in contact with salty waters, including seawater, hydrothermal brines, or alkaline lakewater. Even the water deep in rock formations is often enriched in sodium, chlorine, and calcium (Siever et al. 1965). It is thus reasonable to assume that soluble salts often become incorporated into the water in cherts, perhaps accounting for some of the sodium, magnesium, bromine, sulfur, potassium, chlorine, and

barium found there. Data from Roedder and Turner support this assumption; Roedder (1958:258) found appreciable amounts of sodium, chlorine, potassium, lithium, rubidium, cesium, and sulfur in fluid inclusions in a dark gray chert, and Turner (1988) reports the presence of sodium chloride and potassium chloride in fluid inclusions and healed fractures in chert.

### Rare Earth Elements

The rare earths are relatively uncommon elements that are often treated as a group because they have similar sizes, electrical charges, and chemical properties. They include all the elements between atomic number 57 (lanthanum) and 71 (lutetium), plus yttrium. The rare earths rarely form minerals of their own and are too large to substitute for most major elements, except calcium (Berry, Mason, and Dietrich 1983:180). Thus they occur most often adsorbed on other minerals, especially clays but also on iron and manganese oxides and on organic matter (Wang et al. 1986). They are considered good indicators of source rocks because they are transferred almost directly into sediments and are not strongly fractionated by most common sedimentary and metamorphic processes (McLennon et al. 1980).

The absolute quantity of rare earth elements in cherts is often correlated with the amount of clay and is thus relatively uninteresting, though it can sometimes be a key to determining the depositional environment (Murray et al. 1990). In addition, the relative proportions of the different rare earths themselves can sometimes be informative. Because these relative proportions are constant in many igneous rocks, it is traditional to normalize rare earth element data relative to the values typical of the chondritic meteorites, which are believed to represent the average composition of the earth in general (Krauskopf 1979:517). Such normalization should result in a fairly horizontal line if no fractionation has occurred, and any deviations from this line are then of interest. Aspects to examine include: (1) the proportions of the lighter rare earths (lanthanum through europium) versus the heavy rare earth elements (gadolinium through lutetium), (2) anomalous proportions of cerium relative to the other rare earth elements, and (3) anomalous proportions of europium relative to the other rare earth elements.

In the first case, oxides of the lighter rare earth elements dissolve more readily in acid waters and less readily in alkaline waters than the heavier rare earth elements (Sigleo 1979; DeBaar et al. 1985). Thus the lighter rare earth elements are often enriched in terrestrial sediments, while the heavier ones are often enriched in deep sea sediments. The proportions of cerium are often anomalous relative to the other rare earth elements because this element behaves somewhat differently from the rest under oxidizing conditions. Europium is often anomalous because it behaves differently from the other rare earth elements under strongly reducing and/or hydrothermal conditions.



## Summary

Cherts are composed primarily of silicon and oxygen, but virtually any other element can also be included, as a contaminant or impurity. Such impurities occur most often in association with clays, iron oxides, carbonates, or organic matter, usually located outside the grains of silica. The proportions of each major form of contamination are determined by specific conditions within and adjacent to the basin of chert deposition, and by such factors as the composition of hydrothermal waters which may also affect later stages of chert diagenesis.

While it is possible to generalize about the behavior of specific elements in chert, very few elements are associated with only one type of impurity, and some have appeared with monotonous regularity each time a new process or form of contamination has been introduced. Nevertheless, understanding the geochemistry of any particular chert is not an impossible goal. Mineralogical information from thin sections can be extremely helpful in interpreting elemental abundances of a specific chert. In addition, correlation coefficients often clearly indicate which elements covary in a particular chert, and inferences can be drawn from this information. Both of these approaches are used in the next section as we move from general principles to specific chemical data derived from cherts.

## Chemical Variability in Chert

The remainder of this chapter deals primarily with the issue of variability, both within and among chert types, and illustrates various aspects of variability with chemical data from a number of specific chert types. Data from a wide variety of publications, dissertations, and theses are used, but I have relied most heavily on data produced by the University of Michigan Museum of Anthropology neutron activation analysis project. This is partly because I have access to the raw data from this project, which is not always the case with data from other sources, and partly because I feel confident that the Michigan data are at least internally comparable. The Michigan data set is described further in appendix B, which also includes brief descriptions and descriptive statistics for each of the chert types discussed in this chapter.

### Chert compared with other rock types

Before dealing with variability within chert, it is useful to set the stage by examining the range of values actually found for the different elements in cherts and to consider how chert compares to other rock types. Chert is often referred to as a monomineralic rock because it is composed almost entirely of a single mineral, quartz. This implies that cherts, in general, should have lower quantities of all other elements than do most other multimineralic

rock types. Tables 4.3 and 4.4 demonstrate that this is generally true.

As with so many other tables in this book, tables 4.3 and 4.4 must not be overinterpreted because none of the columns are guaranteed to be representative of all rocks of each type worldwide. These values are simply best estimates based on available data. The granite column does accurately represent one particularly well-studied granite; however, granites in general vary considerably in mineral composition and therefore in elemental composition. The shale, sandstone, and carbonate columns are taken from Turekian and Wedepohl (1961), who compiled and published values for these and several other rock types. Both of these geochemists have long experience in the field and excellent judgment concerning the likelihood that these values are representative, but they admit the limitations of generalizations based on samples drawn from a relatively small number of sources. In fact, their caveat is equally appropriate for tables 4.3 and 4.4: "Any compilation is necessarily subject to great uncertainties in the reliability of the analytical work, the sampling, and the interpretations, both of the original investigator and the compiler. Hence the accompanying table should be accepted not so much as a doctrine but as a motion on the floor to be debated, and amended or rejected" (Turekian and Wedepohl 1961:175).

The chert values in table 4.3 are from the University of Michigan project. Means of element values were calculated for each chert type, and table 4.3 shows the range and median of these averages for twenty elements. The median was used rather than the mean of means because most of the chert type averages were distributed toward the lower end of the total range. Just a few types produced values considerably higher than the rest. The mean of means would thus have been misleadingly high for most elements, and the median is a better measure of central tendency. These data do represent a relatively wide range of chert types, but all are from North America and most are from the Great Lakes region. Thus, it is impossible to judge whether they are truly representative of cherts worldwide. When I compiled elemental values obtained by other analysts for chert types elsewhere in the world, however, nearly all their values fell within the ranges determined from the Michigan sample. (Where a value did fall substantially above or below the range obtained from the Michigan project cherts, I expanded the ranges on table 4.3.) It is thus likely that the ranges shown here will encompass most chert values, though the accuracy of the median is naturally open to question.

The chert columns in table 4.4 represent data from other researchers' analyses for the elements not determined in the University of Michigan project, and these data must be considered even more speculative than the chert columns in table 4.3. First, *N*, the number of analyzed sources is often lower, and sometimes very low, though I did exclude all elements for which analyses from fewer than five chert types were available. Second, several different methods of analysis were used to obtain these values,

**Table 4.3 Chert Compared to Other Rock Types** (UMMA sample; all data ppm)

Element	Granite (G-1) <sup>a</sup>	Shales <sup>b</sup>	Sandstones <sup>b</sup>	Carbonates <sup>b</sup>	Chert Md <sup>c</sup>	Chert R <sup>c</sup>	N
Na	24,600	9600	3300	400	334	11 – 6750	30
Sc	2.9	13	1	1	0.36	0.06 – 5.0	30
Cr	20	90	35	11	3.8	0.30 – 31	30
Fe	13,700	47,200	9800	3800	1300	14 – 120,771	30
Co	2.4	19	0.3	0.1	0.46	0.04 – 14	30
Zn	45	95	16	20	4.2	0.98 – 108	24
Br	0.4	4	1	6.2	1.5	0.03 – 11	28
Rb	220	140	60	3	4.2	0.39 – 51	27
Sb	0.31	1.5	X	0.2	0.05	0.01 – 1.5	30
Cs	1.5	5	X	X	0.15	0.004 – 1.0	30
Ba	1220	580	X	10	37.5	0.9 – 3452	31
La	101	24	16	6.3	1.0	0.08 – 16	30
Ce	170	50	30	10	2.4	0.36 – 28	30
Sm	8.3	5.8	3.7	1.4	0.21	0.03 – 1.4	30
Eu	1.3	1.1	0.8	0.3	0.05	0.01 – 0.4	30
Yb	1.1	2.2	1.2	0.7	0.09	0.02 – 0.5	29
Lu	0.19	0.6	0.4	0.2	0.014	0.003 – 0.1	30
Hf	5.2	2.8	3.9	0.3	0.18	0.02 – 0.7	30
Th	50	12	1.7	1.7	0.34	0.02 – 2	28
U	3.4	3.7	0.45	2.2	0.59	0.0 – 50	27

X = no data available. Sources: a = Mason and Moore 1982:46–47; b = Turekian and Wedepohl 1961:175; c = Appendix B (Amherstburg, Arkansas novaculite; Bayport, Bois Blanc, Brush Creek, Burlington, Cordell, Coxsackie, Delaware, Dover, Flint Ridge, Indiana hornstone; Kettle Point, Knife River flint; Lambrix, Limerock, Norwood, Onondaga, Plum Run, Put-in-Bay, St. Ignace, Stoney Creek, Tenmile Creek, Upper Mercer, Vera Cruz jasper; Zaleski). Minimum expanded: Florke et al. 1982 (Fe), Aspinall and Feather 1972 (Cs), Micheelsen 1966 (Ba), Ives 1984 (Ce). Maximum expanded: Matsumoto and Iijima 1983 (Na, Rb, U), Hein et al. 1983 (La, Sc, Ba), Pollock 1987 (Cr), Hatch and Miller 1985 (Fe), Jarvis 1988 (Br).

ranging from classical chemical analysis to atomic absorption, X-ray fluorescence, and neutron activation analysis. (For classical chemical analyses, oxide values were converted to elemental values using the conversion factors given in Glascock 1988:114.) Thus not all values may be completely comparable. Third, as with table 4.3, the extent to which these values are representative of cherts worldwide is unknown, although I did omit elements for which only values from unusual chert types, such as jaspers, were available.

Despite all these uncertainties, tables 4.3 and 4.4 can serve several useful functions. The chert ranges and medians provide “ballpark figures” for the elemental abundances researchers are most likely to find when they analyze cherts. They should also make it possible for researchers to spot any unusual elemental abundances for newly analyzed types. These values are crucial to the upcoming discussion of chemical variation among formations because they allow us to state that a specific chert type is relatively high or low for a given element compared to most other cherts. Finally, the tables illustrate important points regarding chert chemistry and the relationships between cherts and other rock types.

Specifically, the tables demonstrate that most cherts are quite

pure compared to the other rock types shown here. Those falling at the low end of the chert range are nearly pure quartz. For most elements, the chert median is below the mean of the sandstones, carbonates, and relatively pure monomineralic sedimentary rocks, and even further below the mean of the much “dirtier” shales and igneous rocks. At the upper end of the chert range, though, some cherts (including many that are of artifact quality) have considerably more of some elements than the average granite, shale, sandstone, or carbonate. The chert microstructure is capable of incorporating large quantities of impurities, to the point where cherts can grade imperceptibly into other rock types. Also, the wide range of conditions under which chert can form and undergo diagenesis results in considerable variability in impurity content.

### Chemical variation among chert types

It seems logical to assume that much of the chemical variation among chert types is owing to differences in their modes of origin and especially to the chemical composition of the adjacent rock. Thus, one might expect that a chert which formed by replacing limestone would be high in the carbonate-related elements, whereas one that formed between beds of shale would be rich in clay-related elements. Data from my own and other analyses can be

**Table 4.4 Chert Compared to Other Rock Types (non-UMMA sample; all data ppm)**

Element	Granite (G-1) <sup>a</sup>	Shales <sup>b</sup>	Sandstones <sup>b</sup>	Carbonates <sup>b</sup>	Chert Md <sup>c</sup>	Chert R <sup>c</sup>	N
Li	22	66	15	5	6	1.4 – 36	9
B	1.7	100	35	20	15	1.2 – 104	15
C	200	X	X	X	1546	200 – 18,900	12
Mg	2400	15,000	7000	47,000	302	1.2 – 5548	27
Al	74,300	80,000	25,000	4200	3651	16 – 25,450	21
P	390	700	170	400	141	15 – 645	20
K	45,100	26,600	10,700	2700	410	19 – 10,042	28
Ca	9900	22,100	39,100	302,300	1836	57 – 66,000	24
Ti	1500	4600	1500	400	170	12 – 1258	16
V	17	130	20	20	18	1 – 44	7
Mn	195	850	X	1100	101	0.02 – 1703	23
Ni	1	68	2	20	20	3 – 55	9
Cu	13	45	X	4	7	0.5 – 82	12
Ge	1.1	1.6	0.8	.2	0.5	0.2 – 3	5
As	0.5	13	1	1	1	0.2 – 30	13
Sr	250	300	20	610	14	1 – 95	12
Zr	210	160	220	19	8	1 – 62	8
Mo	6.5	2.6	0.2	.4	2	1 – 15	6
Ta	1.5	0.8	X	X	0.008	0.001 – 0.022	14

X = no data available. Sources: a = Mason and Moore 1982:46–47; b = Turekian and Wedepohl 1961:175; c = Aspinall and Feather 1972, Brueckner and Snyder 1985, Cressman 1962, Florke et al. 1982, Hatch and Miller 1985, Hein et al. 1981, Hein et al. 1983, Ives 1984, Jarvis 1988, Lovering 1972, Matsumoto and Iijima 1983, Maxwell 1963, Micheelsen 1966, Ozol 1963, Pollock 1987, Purdy 1974, Sieveking et al. 1972, Sigleo 1979, Truscott and Shaw 1984, Weis and Wasserburg 1987.

used to examine this assumption with regard to the cherts of different origin discussed in chapter 3. Although each type is represented by a slightly different set of elements, general patterns are usually clear. In all cases where a chert type is discussed in detail, the chemical data compared are given in appendix B.

#### CHALK FLINT

English Chalk outcrops found over quite a large area and flints from these different outcrops vary somewhat in their chemical composition (Sieveking et al. 1972; Aspinall and Feather 1972; Craddock et al. 1983). Thus, for purposes of this discussion, Chalk flint is represented by chemical data for the flint from Grimes Graves, the great Neolithic flint quarry in Norfolk. Thin section data for chalk flints in general indicate that the only visible contaminants are a few rhombohedral carbonate inclusions, scattered fine calcite dust, occasional grains of iron minerals, and granules of carbonaceous organic material (Weymouth and Williamson 1951; Shepherd 1972:23).

Chemical data support the conclusion that the chalk flints are relatively pure; none of the average values for analyzed elements in Grimes Graves flint are especially high. Compared to other cherts, Grimes Graves flint is quite low in clay and iron-related elements (aluminum, potassium, scandium, chromium, iron,

cesium, and thorium), reflecting the fact that the sediments in which these cherts formed received little clay or other terrigenous material. In addition, this flint is low in calcium and magnesium. Apparently, the carbonate elements were very thoroughly removed as the chalk dissolved and the flint precipitated. Grimes Graves values are near the median for sodium, phosphorus, uranium, lithium, and tantalum, perhaps reflecting the important role played by organic matter in the formation of many chalk flints (Clayton 1986).

Sieveking et al. (1972:156) state that the amounts of clay minerals, phosphate minerals, and organic matter vary both laterally and vertically in the chalk, with lateral variation being less significant than vertical variation, except toward the margins of the chalk. They assume that this same pattern should be evident in the cherts forming in these chalks. This may explain the relatively high values for such metals as iron, cobalt, and chromium in chalk flint from Grand Pressigny, France (Aspinall and Feather 1972). For most elements, though, the chalk flints appear at the low end of the range for cherts in general (for example, De Bruin et al. 1972; Micheelsen 1966).

#### OTHER CARBONATE CHERTS

While chalk flints are abundant in parts of Europe, chert formed

in less pure limestones and dolomites in most other parts of the world. Thus, the Onondaga chert of upstate New York may be more typical of carbonate cherts in general. A variety of analyses is available for Onondaga chert, allowing some comparisons among methods of analysis and among laboratories doing the same type of analysis. Three different analysts who presented thin section data on Onondaga chert agree that dolomite rhombs and calcite inclusions are the most common impurities, but they differ somewhat as to the presence, absence, and abundance of the other contaminants (see appendix B). Most of these disagreements probably result from analysis of slightly different samples. The Onondaga cherts vary both laterally and vertically, and extensive sampling is necessary to characterize them thoroughly.

Three sets of chemical data are available for Onondaga chert. Luedtke (1976) and Jarvis (1988) used neutron activation analysis, and their data agree well. For the four elements analyzed by both (sodium, bromine, barium, and uranium), each of the means falls well within the other's standard deviation. Given that these analyses were done in different laboratories and calibrated to different standards, the agreement is quite satisfactory. Ozol (1963) obtained his data by means of classical chemical analysis, and these data do not agree as well. All of his values are higher than those obtained by Jarvis and Luedtke, and while his sodium and calcium values do fit within their standard deviations, his means are outside their standard deviations for aluminum, magnesium, potassium, titanium, and iron. This discrepancy is unlikely to be because of sampling bias because all three of the analysts primarily sampled the western end of the Onondaga formation. The fact that Ozol's iron and titanium values are extremely high, well up in the range usually characteristic of jaspers, raises the possibility that some of his samples may have become contaminated during the crushing process.

In comparison with other cherts, the Onondaga chert is high in carbonate and salt-related elements, such as sodium, bromine, calcium, strontium, and magnesium. It is medium for elements associated primarily with clays, metals and other detritus (aluminum, potassium, cesium, rubidium, iron, cobalt, chromium, zinc, titanium, vanadium, the rare earth elements, barium, thorium, hafnium, scandium), and it is relatively low for antimony, manganese, and uranium.

#### **BEDDED CHERTS**

A number of analyses are available for the Monterey formation, but it is doubtful that any of them can be considered thoroughly characteristic of the chert from this very widespread and highly variable formation. One oft-cited value (for example, Cressman 1962:6) actually represents cherty shale, said to fracture along bedding planes (Bramlette 1946:13) and therefore obviously not of artifact quality. In addition, many other values represent various types of diatomite or opal-CT, which are quite different from true cherts. Gross chemical changes accompanied diagenesis in this formation; many elements were expelled as the silica

dissolved and reprecipitated, and proportions of others were diluted as silica was deposited (Brueckner and Snyder 1985:559). Therefore, chemical data for the earlier stages of diagenesis will certainly not be representative of the final chert.

One analysis of "opaque flint," provided by the classic reference for this formation (Bramlette 1946:13), reports only aluminum and calcium, both of which are present in fairly large quantities. More recently, Brueckner and Snyder (1985) analyzed five samples of black chert from the Santa Marta area. They describe no obvious contaminants other than a fibrous carbonized organic material identified in thin sections, but they mention that carbonates, apatite, feldspar, residual clay, and zeolites are present in other siliceous rocks of the Monterey formation. Compared to other cherts, these samples are high in molybdenum, chromium, zinc, and zirconium. The molybdenum, chromium, and zinc are apparently controlled by organic matter, and zirconium is said to be detrital (Brueckner and Snyder 1985:56). These cherts have medium quantities of aluminum, iron, nickel, copper, cadmium, vanadium, and sodium, and low amounts of magnesium, phosphorus, potassium, calcium, titanium, manganese, strontium, barium, cesium, and rubidium, suggesting relatively little clay or carbonate contribution. Again, we do not know how typical these values are of other Monterey formation cherts or of bedded cherts in general. Brueckner and Snyder (1985:559) point out that these are young cherts and suggest that only the relatively pure siliceous sediments may have had sufficient time to be altered to quartz.

Data concerning other bedded cherts suggest that cherts formed in close association with shales are often much higher in most contaminants than the Monterey cherts analyzed by Brueckner and Snyder. For example, thin sections of Cocksackie chert from New York indicate a rich variety of impurities, including clastic quartz, muscovite mica, clays, chlorite, pyrite, hematite, dolomite rhombs, calcite, and organic carbon (Wray 1948:34, Prothero 1983:385-389). These descriptions agree well with the chemical data; of all the cherts in the Michigan sample, Cocksackie chert most often produced the highest element values. For example, Cocksackie had double the amount present in the next highest chert for sodium, rubidium, scandium, cerium, cobalt, and thorium and was also quite high in cesium, hafnium, lanthanum, europium, and lutetium. Most of these values represent elements associated with clays; the high sodium value may be due in part to nearby volcanoes (Ruedemann and Wilson 1936). Cocksackie chert is low only in bromine and uranium. Lack of bromine may be because of low salinity levels in the deep waters in which this chert is believed to have formed. The lack of uranium is more surprising since there is considerable evidence in the associated shale for abundant organic life and reducing conditions.

Pollock's data (1987) for the Munsungen shale cherts of Maine, which are similar to Cocksackie chert in appearance and

formed under rather similar conditions, also indicate high values for virtually all the elements studied. Sodium, magnesium, aluminum, potassium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, and strontium were very high; calcium, nickel, and barium were present in moderate quantities; and only lithium was relatively low. Chemical data on cherts from Costa Rica (Hein et al. 1983) and Japan (Matsumoto and Iijima 1983) suggest that cherts forming in areas near many active volcanoes may have unusually high levels of many impurities, especially metals. Not all bedded cherts have high proportions of impurities, however; for example, Arkansas novaculite is very low in many elements, except zirconium, hafnium, and the rare earth elements.

### JASPERS

Jaspers are rich in iron by definition, and in many other metals, especially copper, cobalt, and nickel, which are strongly associated with iron. Many jaspers form through the action of hydrothermal fluids (Lovering 1972), which also affects their chemistry. Thin section analyses of Pennsylvania jasper show residual quartz, hematite, limonite, and small amounts of biotite mica and feldspars (Prothero 1983:351–355). Carbon and clay were specifically reported as being absent; so, it is not surprising that this jasper is low in such clay-related elements as cesium, rubidium, chromium, hafnium, and thorium, and the highly soluble sodium and bromine. Uranium, barium, and the rare earth elements were present in moderate to fairly high proportions. As would be expected, Pennsylvania jasper is very high in iron, cobalt, and antimony.

Hatch and Miller (1985:229) also present elemental data for Pennsylvania jasper and, again, their means fall within my standard deviations and vice versa (see appendix B). They also analyzed several other types of jasper, all of which show the same high proportions of metals, although they vary considerably with regard to other elements. Finally, both Pennsylvania and Limerock jasper data demonstrate a pattern that may be typical of cherts formed in part through hydrothermal activity: high antimony values coupled with low sodium values. As discussed previously, a number of elements, including antimony, are often enriched by hydrothermal processes, while sodium is markedly reduced, especially in comparison with potassium. This is presumably because sodium is highly soluble in hot water and stays in solution, while other minerals, especially iron oxides and silica, precipitate (Lovering 1972:30–31; Holland et al. 1988).

### AGATE AND CHALCEDONY

The chemical data from several Serra Geral agates show considerable internal variability, even between different bands of the same agate, and there is no obvious pattern to this variability (Flörke et al. 1982). This limited sample cannot demonstrate that horizontal layers or milky layers have more (or fewer) trace elements than the concentric or translucent layers. This situation supports the

authors' suggestion that each layer was independently deposited by waters of varying composition (Flörke et al. 1982:326). All values are low compared to other cherts, however, with the exception of sodium, which is present in moderate quantities in most of these agates. These chemical data support the authors' statement that no crystalline impurities are visible in thin sections (Flörke et al. 1982:327).

Other analyses, such as Maxwell's for a chalcedony nodule from Virginia (Maxwell 1963) and mine for the chalcedony phase of Lambrix chert (Luedtke 1976), support the conclusion that chalcedonies usually contain very low quantities of most impurities, unless they have been subjected to secondary staining. As suggested in chapter 3, this relative lack of impurities may be a function of the specific circumstances under which fibrous quartz forms.

### SILICIFIED WOOD

Silicified woods vary greatly in chemical composition, depending on the plant species represented, the nature of the sediments enclosing the wood, and the kinds of fluids participating in diagenesis. As described in chapter 3, the petrified wood of the Chinle formation occurs in several different stratigraphic positions, and its color and texture differences suggest considerable chemical variability. Unfortunately, only a few chemical analyses are available. Maxwell (1963) analyzed one sample which he described as being light gray to grayish white. Thin section analysis showed fine calcite dust and scattered dolomite rhombs as being the primary impurities. Classic chemical analysis indicated high proportions of carbon, calcium, strontium, manganese, and lithium; medium amounts of magnesium and germanium; and low quantities of the predominantly clay and metal elements aluminum, iron, sodium, potassium, titanium, phosphorus, manganese, arsenic, molybdenum, and copper. The lack of clay is interesting, considering the important role played by volcanic ash in providing the silica for these and many other silicified woods. In contrast, Stein (1982) found that nearly all of her samples showed evidence of clay. Perhaps Maxwell's sample came from wood that had been deposited within one of the sandstone or carbonate lenses within the Chinle Formation.

Sigleo's data derived from the Petrified Forest samples indicate that chemical composition may vary widely within a single fragment, suggesting another explanation for Maxwell's findings (Sigleo 1979). She analyzed a cross section of a single branch of silicified wood and compared the composition of the black carbonaceous core, the reddish middle portion, and the beige outer portion. Clays, mostly montmorillonite but including some illite and chlorite, were the most abundant impurities in all parts of the branch but were especially concentrated in the outer portion. Aluminum, magnesium, calcium, sodium, potassium, cobalt, cesium, hafnium, scandium, samarium, europium, terbium, lutetium, and thorium increased from the inner to the outer

parts of the branch. Carbon, silicon, antimony, zirconium, and uranium were enriched in the center and decreased toward the outer part of the branch. The largest amounts of iron and manganese were found in the reddish portion. Sigleo concluded that the clays had precipitated from water diffusing into the wood while organic matter was breaking down and dissolving. Proportions of several other elements, including iron, were controlled by the different oxidizing and reducing conditions in the various parts of the branch. In comparison with other cherts, Sigleo's samples are high in aluminum and sodium, medium in iron and calcium, and low in potassium. Carbon and magnesium cannot be compared because they varied so much across the branch.

Other organic materials can also become silicified. Knife River flint, a silicified lignite from North Dakota, provides an interesting comparison to the silicified wood data. Lignite is a carbonized peatlike material, and Clayton et al. (1970) say abundant detrital plant debris and cellular microstructures are visible in thin sections of the chert, although they do not mention the presence of any other minerals. Chemically, Knife River flint is indeed low in clay minerals, metals, and salts (sodium, bromine, iron, cesium, lanthanum, hafnium, rubidium, scandium, cobalt, chromium, and thorium). It has medium amounts of the rare earth elements and is high in barium, uranium, and antimony, probably resulting from the reducing conditions and high organic content of the original lignite.

#### MAGADI-TYPE CHERTS

I found no quantitative analyses for East African magadi-type cherts. Thin section data, however, indicate that the most common impurities are finely disseminated calcite, zeolites, feldspars, and clays (Schubel and Simonson 1990). In addition, limited information was available for two magadi-type cherts formed in Pliocene lakes in Nevada and Oregon (Weis and Wasserburg 1987:972). The Nevada sample is gratifyingly high in sodium, as one would hope for a chert that began as sodium-rich magadiite, and is moderately high in iron and potassium. It is low to very low in magnesium, aluminum, phosphorus, calcium, rubidium, strontium, and samarium. The Oregon sample was analyzed only for rubidium, strontium, and samarium and is low in all three. Obviously, many more analyses are necessary to determine just how typical this pattern is for magadi-type cherts.

#### Comparisons among cherts of the same mode of origin

The data above indicate that mode of origin does play an important role in determining the chemical characteristics of a chert type but that the nature of adjacent sediments is not the only relevant factor. For example, both Onondaga chert and Grimes Graves flint formed in close association with carbonates, but the former chert type has considerably higher proportions of carbonate-related elements, presumably owing to different conditions during diagenesis. In other words, the chemical composition of a chert is

partially but not entirely predictable from knowledge of its mode of origin, and cherts that formed in the same general way may still differ in some or many aspects of their chemical composition. This latter point can be further explored by examining data for a subset of eighteen of the Michigan project cherts, all of which formed in Paleozoic limestones or dolomites in the Great Lakes region of North America. Though age, location, and mode of origin are roughly similar for all these cherts, they still vary in a number of other ways and are therefore chemically different.

#### DETRITUS

To examine variability among these eighteen chert types, I constructed a matrix showing the correlations among element means (table 4.5). All values above 0.535 are significant at the 0.01 level (one tail test,  $df = 16$ ). Obviously, many of these elements are highly correlated. The pattern of correlations suggests that a major portion of the total variability can be accounted for by the amount of detritus present, including clays, metallic oxides, and perhaps organic matter. Some of these cherts, such as Plum Run and Zaleski, have consistently high levels of many detritus-related elements. Others, such as Flint Ridge and Burlington, have relatively low levels of most impurities. The rare earth elements, thorium, scandium, barium, and hafnium, correlate fairly well with both clay and metal elements, suggesting that they occur primarily as adsorbed ions. The clay and metal elements do not correlate as highly with each other, however. A scatterplot of cobalt means against rubidium means (fig. 4.1) shows that these elements, associated with metals and clays, respectively, are somewhat independent.

Figure 4.1 also illustrates a technical problem concerning these data: occasionally a chert type, such as Plum Run in this case, has much higher proportions of certain elements (specifically chromium, iron, cobalt, zinc, antimony, or uranium) than the rest of the cherts. Because of the mathematics of regression equations, a single very high value can completely alter the correlation coefficient, in some cases from a significant correlation to no correlation or vice versa (although none of the values in table 4.1 changed from a significant positive to a significant negative correlation or vice versa). Therefore, I determined the correlation coefficient both with and without the very high values. If both correlation coefficients were either significant or not significant, I listed the correlation coefficient of the total sample. If the correlation changed from significant to not significant (or vice versa) with the addition of the high value, however, I listed the correlation coefficient obtained without the high value. This value is assumed to be a better representation of the relationship among the elements for the majority of the cherts in this sample. Such coefficients are underlined in table 4.5.

The carbonate cherts in this sample with more detrital impurities may have formed closer to land, or more sediments may have washed into the basins where they formed because of local uplift and mountain building or because of weathering conditions

on the adjacent landmasses. Several of the cherts with high proportions of detritus also appear to have formed under reducing conditions, which can affect their chemistry.

#### REDUCING/OXIDIZING CONDITIONS

For reducing conditions to exist, atmospheric oxygen must be lacking and decaying plant and animal debris, which produces methane, hydrogen sulfide, and other reducing agents, must be present (Krauskopf 1979:253). Cherts formed under such conditions may contain minerals, such as pyrite, which precipitate only under reducing conditions. They should retain relatively large amounts of carbonaceous organic matter, which will often result in darker colors, and they may have higher levels of the elements often associated with organic matter, such as uranium. On the other hand, cherts that formed under oxidizing conditions should contain a different suite of minerals, organic matter other than calcium carbonate should have decayed and escaped as  $\text{CO}_2$ , and the resulting chert should be lighter colored than cherts formed under reducing conditions.

The proportion of uranium in carbonate cherts is plotted in figure 4.2 against their darkness or lightness as measured in terms of color value on the Munsell chart. Circled points indicate those for which pyrite was reported as an impurity. In general, the predictions outlined above are supported. Cherts with minerals typical of reducing environments are also generally darker and higher in uranium, presumably because of their higher organic content. Cherts without pyrite are generally lighter colored and low in uranium. The correlation is not perfect because darkness/lightness in cherts is not determined by their organic content only; in this case, some of the darker cherts are high in metals and clays as well. In addition, uranium is not solely controlled by organic matter but can be detrital in origin. For example, the Front Range of the Rocky Mountains in Colorado is a well-known source of uranium ores (Wedepohl 1969–1978:90–E–11). Cherts from the Colorado/Wyoming area for which I have data are relatively high in uranium, regardless of color or organic content.

#### SALINITY

Differences in salinity may also be responsible for some of the variability among carbonate cherts. Jarvis found a strong correlation among the proportions of sodium, chlorine, and bromine in his study of Onondaga chert (Jarvis 1988:41). Sodium and bromine are also correlated within the Burlington chert (Luedtke and Meyers 1984). This would suggest that these two elements are present primarily in the form of salts and that their proportions are a function of the salinity of the waters within which the different cherts formed. Thus, it was somewhat surprising to find that sodium and bromine were not significantly correlated (table 4.5). A scatterplot of these points (fig. 4.3) shows a tendency for a positive correlation between the two elements, but that the pattern is broken by two clusters of chert types lying nearly perpendicular to the general trend.

Examination of the correlation between sodium and bromine within each carbonate chert reveals that there is a significant correlation between the two elements for ten of the cherts and no correlation, or in one case a significant negative correlation, for the other eight. The latter are primarily the cherts shown in figure 4.2 as having formed under reducing conditions. In these cases, the sodium is apparently present in a different mineral form, since it correlates with clay and metal elements rather than with bromine. When these latter chert types are removed from the sample, the correlation between sodium and bromine for the remaining ten is 0.814.

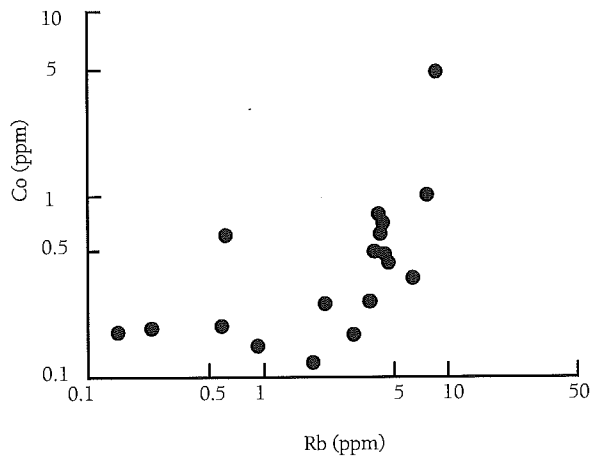
Thus, it appears that the salinity of the water in which the chert formed affected the proportions of several impurities in some of these carbonate cherts. Whether these apparent differences in salinity reflect the saltiness of the seawater in which the siliceous sediments were first deposited or that of later waters involved in diagenesis is open to question. For others of these cherts, sodium is predominantly present as some mineral other than a soluble salt; and in these cases, sodium levels are not related to salinity.

#### RARE EARTH ELEMENT PATTERNS

The patterning of rare earth elements varies for this sample of cherts (fig. 4.4 through 4.8). These elements are displayed in the standard format, normalized with regard to chondrite values and listed in order by atomic number. Chondrite values given in Brownlow (1979:16) were used here; others are also available (Glascok 1988:115), but the differences among these various references do not appear to be great enough to affect the results significantly. More problematical is the fact that these data are not corrected for uranium concentration, which can affect the proportions of some rare earth values. Nevertheless, these factors should have little effect on general trends. The absolute concentration of the rare earth elements in these cherts (as table 4.5 indicates) is correlated with the amount of detritus and can vary considerably; Plum Run has the highest proportions, while Cordell has the lowest.

All plots show a pattern of decrease from left to right; that is, the light rare earth elements are enriched relative to the heavier ones. This pattern is typical of terrestrial and shallow marine sediments in which the light rare earth elements are preferentially adsorbed on the surfaces of clays, iron oxides, organics, or carbonates. They are quickly deposited into sediments (Fleet 1984:305), while the heavy rare earth elements stay in solution and are carried out to the deeper ocean basins (DeBaar et al. 1985). Figure 4.9 shows a plot of composite data for 40 North American shales (Haskin et al. 1968), demonstrating this trend.

Most cherts in the sample show the small negative anomaly for europium that is also characteristic of terrestrial sediments. Europium tends to stay in solution a little better than the other rare earth elements (DeBaar et al. 1985). The only chert type in this

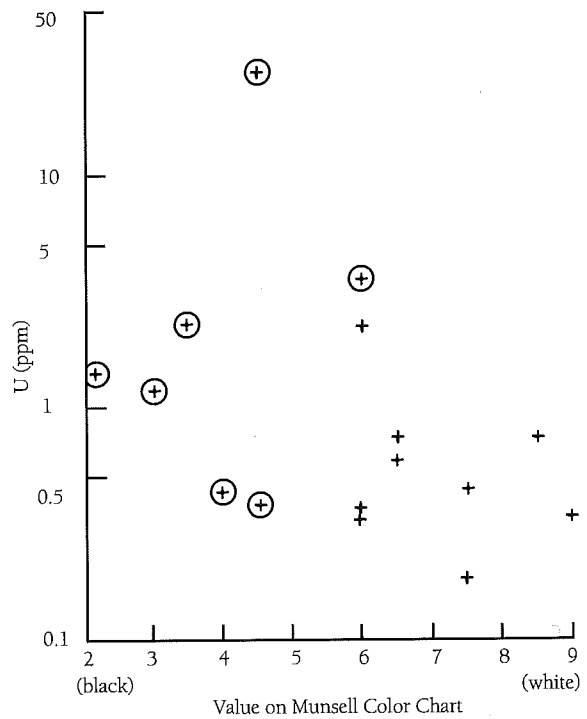


**Figure 4.1**

Scatterplot of cobalt versus rubidium trace element values for Midwest carbonate cherts.

sample with a positive europium anomaly is Flint Ridge. This may be because of the presence of minerals such as feldspars, which are usually enriched in europium (Cullers and Graf 1984). Alternatively, DeBaar et al. (1985) state that hydrothermal events often produce a strong positive europium anomaly, and this may be the case here. Although the geological literature on this formation does not mention hydrothermal activity in the area, Flint Ridge chert also shows the pattern of relatively high antimony and low sodium that appears to be typical of cherts that have undergone hydrothermal alteration.

These cherts have varying cerium anomalies, although none are strongly anomalous with regard to this element. Cerium is easily oxidized under normal surface conditions and then can become separated from the rest of the rare earth elements (Haskin et al. 1968). Cerium usually shows a positive or weak negative anomaly in well-oxygenated waters and the sediments formed in such waters but is depleted in deep-sea sediments. Shimizu and Masuda (1977) demonstrated that the Deep Sea Drilling Project cherts showed marked negative cerium anomalies, whereas cherts that formed in shallower waters and are now exposed on land did not. The carbonate cherts in the sample formed under various oxidizing and reducing conditions, as discussed previously, but there is no obvious correlation between this factor and cerium anomalies. That is, cherts that formed under oxidizing or reducing conditions did not consistently have either negative or positive anomalies. All the cherts formed in relatively shallow continental



**Figure 4.2**

Scatterplot of uranium trace element values versus color values for Midwest carbonate cherts.

seas, and it is possible that their rare earth element patterns were simply inherited, without much alteration, from the parental terrestrial sediments.

This hypothesis is supported by the observation that cherts which formed close in space and time show rather similar overall patterns. Although total proportions vary, the Silurian cherts (fig. 4.4) show similar trends, even though the Stoney Creek and Cordell sources are more than 500 km apart. The Devonian cherts are displayed in figures 4.5 and 4.6 for clarity and also because two different patterns seem to be evident. The steep decline in the light rare earth elements typical of the Michigan Silurian cherts (fig. 4.4) is also apparent for the Devonian cherts from Michigan (fig. 4.5). Devonian cherts from surrounding states show a slightly different pattern (fig. 4.6), however. Note especially the gratifyingly close correspondence between the closely related Amherstburg and Onondaga cherts. The Mississippian cherts (fig. 4.7) are from widely different areas and show little similarity in rare earth element pattern, although Indiana hornstone and Bayport do seem to be roughly parallel. The Pennsylvanian cherts, all from Ohio, again show similar patterns, with the notable exception of Flint Ridge, which is peculiar in many ways (fig. 4.8).

Finally, figure 4.9 shows, for comparison, the rare earth element pattern for a composite of 40 North American shales and for cherts of noncarbonate origins. In general, of all the cherts in the Michigan sample, the jaspers produced the oddest patterns, perhaps because of the hydrothermal alteration often involved in



Table 4.5 Correlation Matrix for Carbonate Cherts

	La	Ce	Sm	Eu	Yb	Lu	Th	Sc	Co	Zn	Fe	Cr	Ba	Rb	Cs	Hf	Sb	Na	U	Br
La	1.000																			
Ce	0.789	1.000																		
Sm	0.878	0.581	1.000																	
Eu	0.920	0.750	0.949	1.000																
Yb	0.899	0.830	0.950	0.906	1.000															
Lu	0.762	0.893	0.868	0.796	0.886	1.000														
Th	0.882	0.868	0.864	0.792	0.894	0.775	1.000													
Sc	0.738	0.742	0.905	0.788	0.928	0.794	0.875	1.000												
Co	0.592	0.641	0.880	0.730	0.786	0.689	0.736	0.902	1.000											
Zn	<u>0.800</u>	<u>0.726</u>	0.829	0.669	0.719	0.596	0.657	0.858	0.984	1.000										
Fe	0.825	0.569	<u>0.737</u>	<u>0.745</u>	<u>0.755</u>	<u>0.558</u>	<u>0.796</u>	<u>0.779</u>	<u>0.696</u>	<u>0.661</u>	1.000									
Cr	0.661	0.746	0.880	<u>0.452</u>	0.836	0.798	0.816	0.912	0.935	0.909	<u>0.619</u>	1.000								
Ba	0.796	0.749	0.718	0.776	0.773	0.858	0.673	0.552	<u>0.774</u>	<u>0.766</u>	0.100	<u>0.660</u>	1.000							
Rb	0.606	0.692	0.643	0.533	0.764	0.604	0.821	0.840	0.652	0.589	<u>0.714</u>	0.737	0.399	1.000						
Cs	0.467	0.426	0.566	0.421	0.660	0.482	0.642	0.786	<u>0.370</u>	0.299	0.208	<u>0.528</u>	0.187	0.878	1.000					
Hf	0.570	0.723	0.482	0.413	0.594	0.754	0.600	0.454	<u>0.670</u>	<u>0.614</u>	0.182	<u>0.947</u>	0.734	0.486	0.389	1.000				
Sb	<u>0.750</u>	0.608	<u>0.670</u>	<u>0.769</u>	<u>0.655</u>	0.653	<u>0.500</u>	0.168	0.127	0.041	0.082	0.303	<u>0.722</u>	0.045	0.061	<u>0.397</u>	1.000			
Na	0.498	0.388	0.491	0.503	0.550	0.496	0.431	0.511	<u>0.516</u>	<u>0.606</u>	0.471	0.446	0.480	0.578	0.608	0.362	0.131	1.000		
U	0.117	0.511	0.344	0.018	0.245	<u>0.369</u>	0.198	0.238	0.418	0.290	-0.072	<u>0.525</u>	0.437	0.066	0.096	<u>0.456</u>	<u>0.484</u>	0.138	1.000	
Br	-0.240	-0.343	-0.311	-0.322	-0.205	-0.398	-0.198	-0.135	-0.219	-0.242	0.053	-0.162	-0.453	0.240	0.442	-0.109	-0.516	0.325	-0.247	1.000

Chert types in sample (see appendix B): Amherstburg, Bayport, Bois Blanc, Brush Creek, Burlington, Cordell, Delaware, Flint Ridge, Indiana hornstone, Kettle Point, Norwood, Onondaga, Plum Run, Put-in-Bay, Stoney Creek, Tennile Creek, Upper Mercer, Zaleski.

their formation and/or the mineralogy of the host rocks where they formed (Michard 1989). It should be noted that cherts formed in different depositional environments from those discussed here may have rather different rare earth element patterns. Murray et al. (1990) suggest that cherts formed in association with metals and close to spreading undersea ridges have large negative cerium anomalies, with the anomaly decreasing regularly with distance to the continental margin. They also found that cherts forming under conditions of rapid deposition tended to be low in total rare earth elements because the high sedimentation rates allowed little time for the rare earth elements to be adsorbed from the seawater.

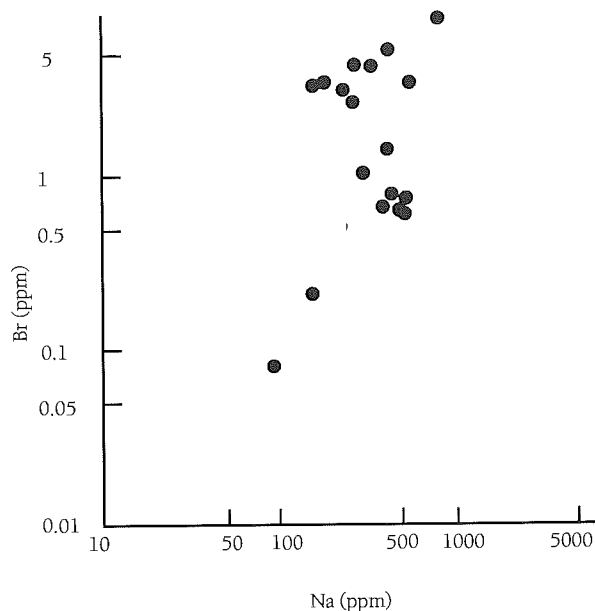
### SUMMARY

Even though a series of cherts form in relatively similar ways in the same general region, their chemistry can still differ considerably. The proportion of detritus, kinds of detritus, presence of oxidizing or reducing conditions, and salinity are only a few of the possible influences. Of course, the more similar cherts are in their histories, the more chemically similar they are likely to be. For example, Upper Mercer and Zaleski cherts are both black cherts of Pennsylvanian age, which were formed in close association with coal beds and which outcrop only about 100 km apart in southeastern Ohio. These two cherts are also chemically similar, with similar proportions of many detrital elements and parallel rare earth element patterns. However, Upper Mercer and Zaleski cherts vary in their appearance, their thin section characteristics (Stout and Schoenlaub 1945:47, 69), and their chemistry. In fact, it is highly unlikely that any two cherts would ever be chemically identical, because any differences in their histories should be reflected in at least some aspect of the resulting chert mineralogy and geochemistry.

### Chemical Variation Within Formations

The causes of chemical variability within chert types include many of the same factors that are responsible for differences among chert types. Deposition conditions were probably not the same over an entire basin, nor are other conditions likely to have remained constant over the long formative periods. Parts of a formation that were closer to the source of sediments, were covered by shallower water, or were deposited in waters having somewhat different pH or oxidizing/reducing conditions differ in some ways from the rest of the formation, though they are similar in other ways.

Such intraformational variability can be both a boon and a problem, depending on one's goals. For those investigators attempting to characterize a chert type chemically, variability means that more samples must be analyzed and that they must be representative of all parts of the formation. It also often means that more complex statistics are necessary to differentiate sources and assign artifacts to them. For those attempting to determine as precisely as possible where an archaeological artifact originated, intraformational variability is welcome because it allows discrimi-



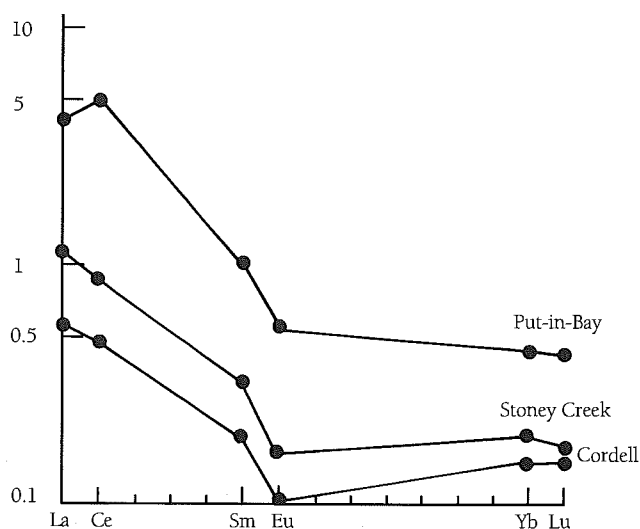
**Figure 4.3**

Scatterplot of sodium versus bromine trace element values for Midwest carbonate cherts.

nation of specific quarries and outcrops within the larger formation.

Intraformational variability occurs on more than one scale. On the smallest scale, that visible in thin sections, it is evident that many impurities are not evenly spread throughout a fragment of chert but rather are clumped into discrete crystals, localized around fossils, or concentrated along laminations, etc. Thus, chemical variability will usually be great if only tiny portions of a fragment of chert are sampled but should decrease if larger samples are analyzed or if samples are pooled. Some elements seem to be inherently more variable than others in this regard, probably because of differences in the way they occur in the cherts. For example, Sieveking et al. (1972:156) have suggested that elements adsorbed on the surfaces of mineral impurities should be more variable than elements incorporated within minerals because the former are not rigidly held and are thus more mobile during diagenesis.

I calculated  $V$ , the coefficient of variability ( $V=sd/x$ ), for each element at each source in the Michigan sample and then ranked the elements of each source in order of increasing  $V$ . Grouping the rankings produces the pattern shown in table 4.6. All elements were more variable in some cherts than in others, but the proportions of uranium and iron nearly always varied a great deal more within most chert types than did other elements. Both uranium and iron could be occurring in part as adsorbed ions, as Sieveking et al. suggested, but other factors are also likely to be responsible. Iron minerals are often visibly unevenly distributed in thin sections and are also strongly affected by chemical conditions that can change over short distances in areas where chert is forming. For



**Figure 4.4**

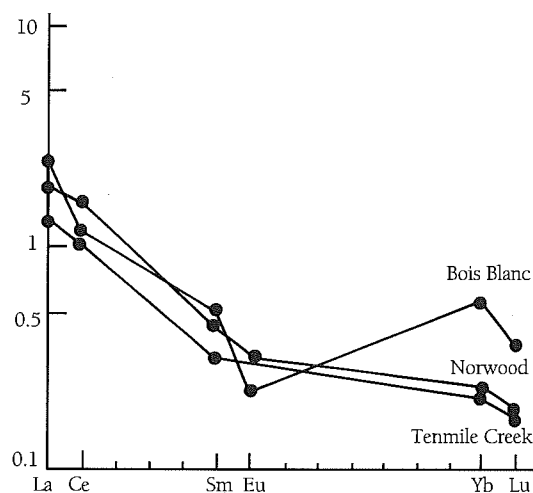
Chondrite-normalized rare earth element values for carbonate cherts of Silurian age from Michigan.

example, Clayton (1986:51) reports higher concentrations of iron on the lower side of the chalk flint nodules he studied, where reducing conditions had existed, and less iron on the upper side, which formed under more oxidizing conditions. Uranium is also highly susceptible to variations in reducing and oxidizing conditions; it might also be expected to concentrate around fossils because of its association with organic matter.

At the other extreme, sodium and bromine are usually distributed rather evenly within these cherts. Both of these elements may be present in many cherts as salts, either dissolved in water or in solid form; this may explain their even distribution. Clayton states that sodium is present primarily as salt in the pore water of the chalk flint he studied and that "almost all of the sodium in flint can be removed if the finely ground sample is leached with distilled water" (Clayton 1986:50). Of course, where sodium or bromine is present in some other form, V is likely to be higher.

Chemical variability is also evident on a larger scale, correlated with variability in the visible characteristics of cherts. This should not come as a surprise because many of these visible characteristics are caused by impurities (chap. 5). Sigleo's correlation of chemical with color differences in silicified wood was described previously (Sigleo 1979). In another example, I found that the concentric bands in Bayport chert differed slightly in chemistry, presumably reflecting different local conditions as each band formed (Luedtke 1978). In general, the proportions of organic-related elements (uranium, barium), metals (iron, cobalt, antimony), and rare earth elements were highest in the center of the nodules and decreased toward the outer bands, while clay-related elements (rubidium, cesium, chromium, thorium, scandium, sodium) showed the opposite trend.

Cherts that vary in translucence and color appear to have



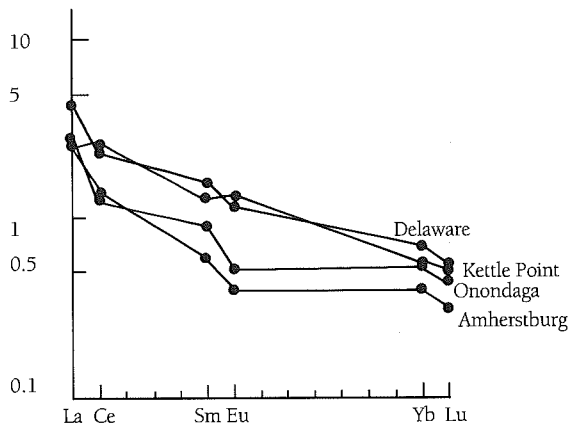
**Figure 4.5**

Chondrite-normalized rare earth element values for carbonate cherts of Devonian age from Michigan.

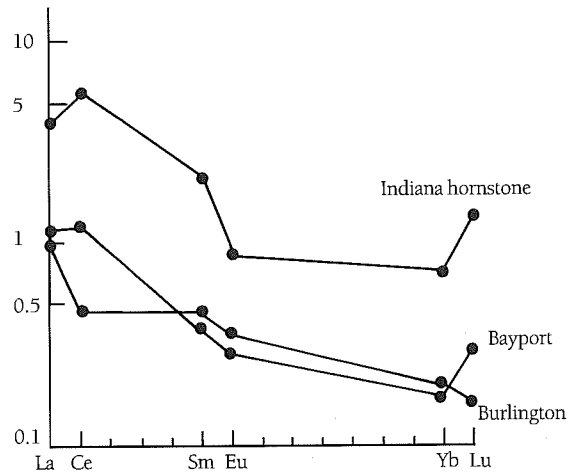
even more dramatic chemical variability. For example, Lambrich chert grades from opaque sandy brown to opaque gray and finally to a pale gray translucent botryoidal chalcedony that lines the interior of cavities (Luedtke 1978). Chemical variability among these three varieties of Lambrich chert indicates a strong dilution effect. Most elements decrease at virtually the same rate from high values in the sandy chert to low values in the chalcedony. The only exceptions are bromine, uranium, and sodium. Bromine and uranium are slightly enriched in the chalcedony, while sodium is found in nearly constant proportions in all three. It seems that the solution from which the varieties of Lambrich chert formed became increasingly pure but that bromine, uranium, and sodium stayed in solution until the final stages of precipitation.

Limerock jasper from Rhode Island also varies considerably in appearance: from opaque dark brown or ocher yellow to translucent pale pinkish white chert (Luedtke 1987). The opaque variety is greatly enriched in iron and cobalt relative to the translucent variety; the two sets of standard deviations do not even overlap. The opaque chert is also enriched in most other elements, but the standard deviations do overlap with those of the translucent chert for these elements. This is not just a dilution effect since the ratios among elements in the two varieties are not similar. On the other hand, the proportion of uranium is almost the same in both varieties, and sodium, thorium, and antimony are somewhat enriched in the translucent variety. Again, these differences appear to result from differences in the solubility of the minerals involved, probably under hydrothermal conditions. In general, then, the more extreme the visible differences within a chert type, the more extreme the chemical variability.

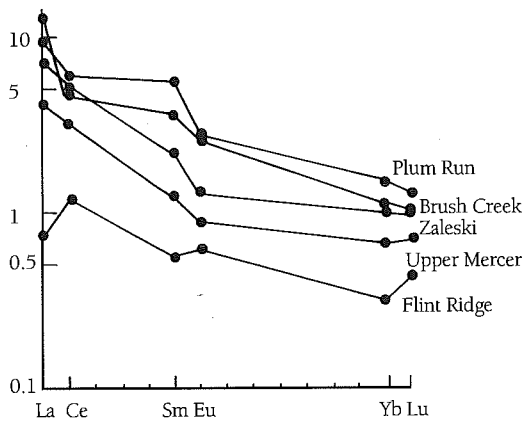
Finally, at the largest scale, different parts of a chert-bearing formation can vary chemically because of slight differences in the basin of deposition. For example, Norwood chert outcrops in



**Figure 4.6**  
Chondrite-normalized rare earth element values for carbonate cherts of Devonian age from Ohio, Ontario, and New York.

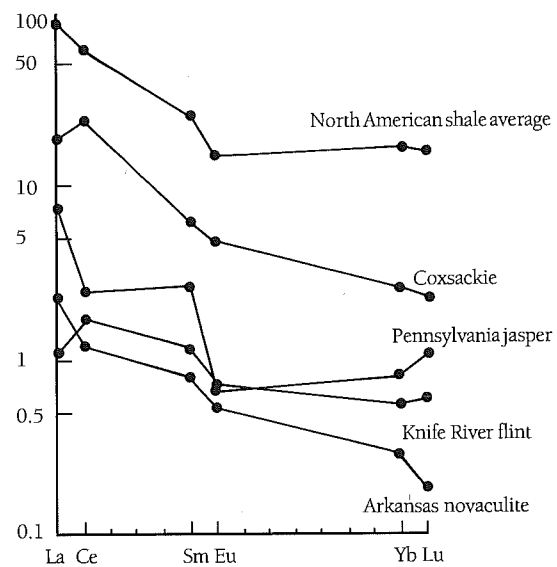


**Figure 4.7**  
Chondrite-normalized rare earth element values for carbonate cherts of Mississippian age from Indiana, Illinois, and Michigan.



**Figure 4.8**  
Chondrite-normalized rare earth element values for carbonate cherts of Pennsylvanian age from Ohio.

three places in a band only 27 km in length, yet cherts from these three outcrops are chemically different (Luedtke 1978). Specifically, clay-related elements decrease from west to east, but metals decrease and then increase again to the east. The trend of the rare earth elements follows that of the metals, although not as markedly. Even within the main Norwood quarry area, six bluffs stretching for 0.5 km along the shore of Lake Michigan, detritus-related elements appear to decrease from north to south. Since the formation also dips in that direction, this variability may actually reflect changes over time rather than space.



**Figure 4.9**  
Chondrite-normalized rare earth element values for several non-carbonate cherts.

A 13-km stretch of chert-rich Burlington limestone along the Lower Illinois River Valley represents the most thoroughly and systematically sampled chert outcrop in the Michigan sample. Trend surface analysis showed that proportions of most elements changed slightly with either space or time (Luedtke and Meyers 1984). Elements associated with clays and metals were most abundant in the lower chert lenses and decreased over time, whereas uranium showed the opposite trend. A spatial trend was also evident, running from northwest to southeast. This information agrees with Harris and Meyers' (1987) statement that the

**Table 4.6 Element Variability (by quarter)**

	Top	2nd	3rd	Bottom
Na	17	2	1	2
Br	13	3	4	2
Cr	9	7	3	3
Th	6	10	4	2
Hf	5	11	2	4
Sc	6	9	5	2
Ba	7	5	3	7
Sb	4	8	5	5
Cs	3	8	6	5
Eu	6	6	6	4
La	4	8	8	2
Ce	4	6	12	0
Sm	3	5	9	5
Yb	2	7	8	5
Lu	4	4	8	6
Co	3	3	11	5
Rb	4	4	4	10
Fe	5	2	6	9
U	5	2	5	10

Burlington limestone was deposited on a shallow but open continental shelf, with a shoreline to the northwest and a drop-off to deeper waters to the southeast. Sodium and bromine decrease from northwest to southeast, presumably reflecting gradual deepening of the water and lower salinity levels. Antimony also decreases somewhat in this direction, for less obvious reasons. On the other hand, barium and cobalt show the opposite trend, increasing from northwest to southeast, possibly reflecting an increase in organic activity in the slightly deeper waters. The rare earth elements did not show a clear pattern, although they are somewhat correlated with clays and metals. They may be adsorbed on clays, metals, carbonates, and even organic matter in the Burlington chert and thus do not correlate well with any one component.

Other researchers have found that different outcrops of the same formation can be discriminated. The variability among chalk flint outcrops has already been mentioned. Jarvis (1988) separated six different outcrops of the Onondaga formation on the basis of chemical variability, apparently reflecting distance from the source of sediments and changes in salinity. Hatch and Miller were relatively successful in discriminating four different quarries of Pennsylvania jasper (Hatch and Miller 1985:229), and Hein et al. (1983:160) found differences among different chert sources in Costa Rica.

Although most of the variability discussed here is apparently related to differences in conditions at the time the cherts formed, postdepositional processes may also cause intraformational variability. For example, the eastern end of the Arkansas novaculite all probably formed under relatively similar conditions (Jones and

Knauth 1979), but within this zone the area around Magnet Cove was subjected to intense metamorphism and hydrothermal action as a result of the intrusion of an igneous ring dike sometime after the chert had formed. Chert close to the intrusion was metamorphosed to quartzite, while chert further away was recrystallized (Keller, Stone, and Hoersch 1985). This recrystallization apparently caused chemical changes as well; compared to Magnet Cove chert, the more distant Caddo Gap outcrop has higher proportions of all the elements identified in the Michigan project except iron, uranium, and antimony. For all elements but cobalt and cesium the chert from Caddo Gap produced values twice as high as Magnet Cove. Thus, hydrothermal activity apparently resulted in rather thorough flushing of many elements from Arkansas novaculite, but enrichment of some metals.

Intraformational variability will not prevent accurate chemical characterization of chert types if enough samples are analyzed. The coefficient of variability used to determine which elements vary most and least can also be used to determine which chert types vary most and least. For example, the mean V for each formation in the Michigan sample ranged from 0.28 to 0.89, the average being 0.504 (sd = 0.182). Cherts showing less variability tended to be homogeneous in appearance or occurred only in a restricted geographic area. On the other hand, cherts with greater chemical variability demonstrated more varied visible properties or outcropped over a large area. How these findings relate to the amount of sampling necessary to characterize a chert type is discussed in appendix A.

### **Chemical Variation Between Source Samples and Archaeological Artifacts**

Archaeologists usually deal with chert in the form of artifacts, which further complicates the task of characterizing cherts on the basis of their chemistry. Chemical differences can exist between artifacts and source samples, either because of sampling bias or because the artifacts have been chemically altered by weathering or exchanges with the soils in which they were deposited. In the first case, a nonrepresentative sample may have been selected by the archaeologist, by the stone tool maker, or by both. If the archaeologist has not systematically or thoroughly sampled a chert source, the resulting data may not represent the full range of chemical variation for that chert type. Thus, artifacts made of that chert might appear to fall outside the range of variation for that chert type (though they will probably be closer to the true source than to other sources).

It is also possible that the archaeologist's sample is unbiased but that the people who made the artifacts were selective in their choice of raw material. They may have sought out varieties with particular physical or visible properties that happen to correlate with chemical differences. For example, if they deliberately chose darker varieties of a particular chert type, they would probably be

choosing a sample that is higher in metals, carbon, or clay minerals than the average for the whole formation. If, however, the source as a whole has been characterized adequately by the archaeologist, this should not be a serious problem. Artifact values should still fall within the range of variability, though they might cluster in a limited part of that range.

Artifact makers might also have chosen a biased sample because they obtained their chert from one specific part of a formation, presumably the most accessible part. Again, such bias should be no problem if the entire formation has been characterized accurately; artifact sample values should still fall within the range of variability for the formation. Sampling bias on the part of the stone tool makers would present a real problem only if the area they sampled was markedly different chemically and could not be sampled by the archaeologist because it has been quarried out, destroyed by modern development, or drowned by rising sea or lake levels.

Even when there are no sampling biases, chemical differences can exist between artifact and source samples because the artifact has been chemically altered by weathering and/or by exchanges with the soil. Archaeologists and geologists are quite aware that the outer surfaces of rocks exposed on the earth's surface or buried in soil alter over time; consequently, they normally choose samples from the interior of a fragment, where no visible signs of weathering are evident. However, those who wish to analyze archaeological artifacts cannot always be so choosy. Some artifacts are weathered throughout, while for others, the portion that we are allowed to sample has significant weathered areas. Such weathering is especially a problem for analytical techniques that analyze the surface of a fragment rather than its bulk composition.

Chemical changes brought about by weathering are discussed in greater detail in chapter 7. In general, weathering can oxidize or reduce minerals on the surface of an artifact, and groundwater may then dissolve some elements and carry them away. Groundwater also may deposit other elements in the more porous weathered rind of an artifact. The extent of these changes varies considerably by element and chert type. I examined trace element data from 41 artifacts made of four different chert types in the Michigan sample and found that the only consistent differences between sources and artifacts were for sodium and uranium. Thirty-eight of the 41 artifacts fell below the mean of their source for sodium, and 22 of these were more than one standard deviation below the source mean. Jarvis also found that artifacts made of Onondaga chert were depleted in sodium relative to source samples (Jarvis 1988:46); presumably, sodium is easily mobilized and removed from cherts by groundwater. On the other

hand, 34 of the 41 artifacts were above the mean of their source for uranium, and 17 of these were more than one standard deviation above. Uranium is probably associated with organic matter in the soils in which the artifacts have lain; terrestrial organic matter concentrates uranium even more effectively than marine organic matter (Hein et al. 1987:158).

The extent of both of these chemical alterations may be affected by the chert's physical characteristics (and probably by soil type). Two of the chert types from which these artifacts were made, Norwood and Bayport cherts, are relatively porous and coarse grained compared to the dense and fine-grained Upper Mercer and Indiana hornstone cherts. All of the artifacts in which sodium was depleted more than one standard deviation, and 13 of the artifacts in which uranium was enriched more than one standard deviation, were made of the more porous cherts. In addition, 13 of 17 Norwood chert artifacts were depleted more than one standard deviation in iron, whereas none of the other cherts showed this depletion. Clearly, different cherts weather differently, and some minerals are more susceptible to weathering than others. Therefore, investigators should analyze only unweathered portions of artifacts and/or avoid the more mobile elements.

## Summary

While many of the conclusions in this chapter are based on relatively small samples and must still be considered preliminary, it is encouraging to find that much of the geochemistry of chert conforms quite well to the general geochemical principles developed through studies of other sedimentary rocks. All cherts contain at least some impurities, and the kinds and quantities of these impurities are a function of each chert's mode of origin in general and its specific history in particular. A wide range of factors can affect the chemistry of cherts, including the adjacent rock types, the amount and kinds of terrigenous sediments transported to the area where the chert is forming, the chemical characteristics of the waters involved in chert formation, and various diagenetic influences. These same factors can cause the proportions of impurities to differ within a chert type, but such variability is generally less than the variability among chert types. This outcome is not really surprising since two cherts should have exactly the same impurities only if they have had exactly the same history. Such a coincidence is far more likely within a single geological formation than among formations.

Differences in the kinds and quantities of impurities may be useful in determining exactly how cherts formed. Impurities are also relevant to many of its properties, including most notably its visible properties.



# 5

## Visible Properties

**C**hert is extraordinarily variable in its appearance. It comes in every color of the spectrum and in patterns ranging from solids to spots to stripes to the “miniature landscapes” known as picture agates. Some cherts are translucent, others appear to be completely opaque. Some have a luster as glossy as satin, others are dull as chalk. This rich variety is even more surprising since quartz, the major constituent of chert, is colorless, transparent, and glassy. Thus the diversity must result largely from impurities and, to a lesser extent, from microstructural differences.

The visible characteristics of chert have always been of interest to people who make and use stone tools. As will be discussed in chapter 6, modern stoneworkers frequently use these visible properties to judge the quality of a chert type and to estimate how it is likely to respond to knapping and to use; their prehistoric counterparts surely did the same. Furthermore, visible properties may sometimes have had ideological or aesthetic significance and were undoubtedly used to determine whether a given item was of local or exotic origin. That is, a stoneworker would surely know all local and many distant chert types by their appearance and would make trade or exchange decisions on that basis.

Archaeologists have also paid a good deal of attention to the visible properties of chert, in part because they are the only attributes that can be determined easily and inexpensively. Ascertaining the chemical or mechanical properties of a material requires complex equipment and expertise, but anyone with adequate vision can look at a piece of chert and describe it. Thus, most people who analyze a lithic assemblage routinely sort the artifacts into raw material types on the basis of their visible properties; in fact, most of the identifications of chert types that

abound in the archaeological literature are based on visible properties alone. Many of these identifications are surely correct, but others are wrong and there are few ways to be certain which is which. Appendix A further addresses this issue.

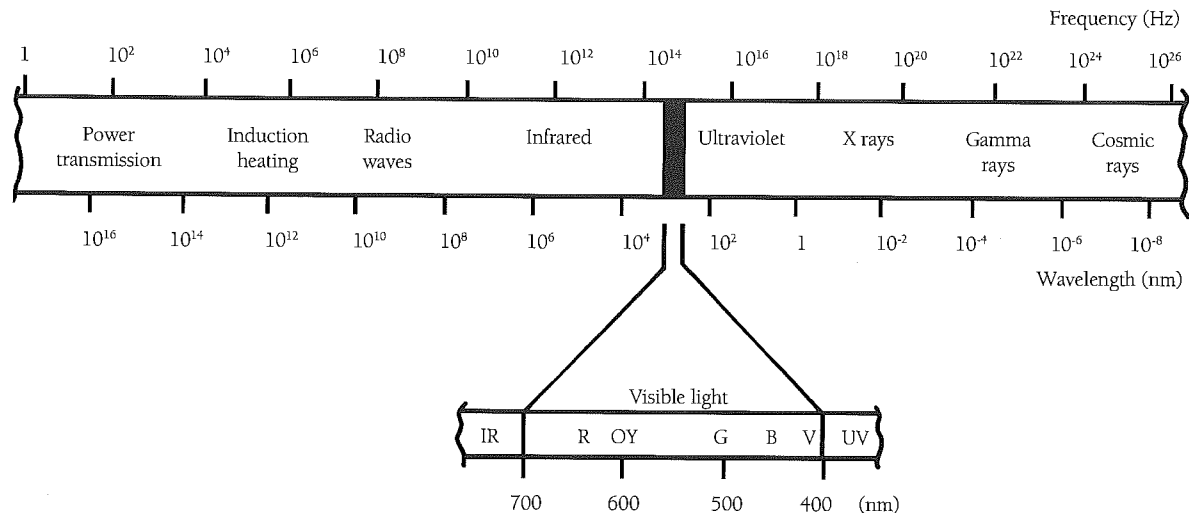
A third group of people concerned with the visible properties of chert are jewelers and gem dealers. Many semiprecious gems are varieties of microcrystalline quartz and thus fall into the broad category of chert as defined here. Jasper, moss agate, chrysoprase, prase, sard, carnelian, plasma, heliotrope, bloodstone, and banded agate are all cherts with specific visible characteristics that gem dealers have valued since antiquity. All are defined in the glossary.

### Light and Chert

“Visible properties,” as used here, include those properties in artifacts and hand samples that are visible to the eye—such as color, translucency, luster, texture, and structure—and those, such as grain size, that are visible only under magnification. Though different in scale, both the macroscopic and microscopic properties of a material result from the interactions between light and matter; so, a brief discussion of light is necessary before we can proceed.

Light is a form of energy or, more precisely, a form of electromagnetic radiation, that travels in straight lines with wave-like motion. In fact, light is one small portion of a range of energy types that grade into one another (fig. 5.1). At one end of this range are those forms of radiation with very long wavelengths and correspondingly low frequency and energy, such as radio waves. At the other end are forms of radiation with very short wavelengths, high frequency and high energy, such as cosmic rays. In





**Figure 5.1**

The spectrum (after Nassau 1983:18).

between these extremes fall infrared radiation, visible light, ultraviolet radiation, X rays, and gamma rays. The human eye can see only those forms of energy with wavelengths between about 0.380 and 0.780  $\mu$  (usually expressed as 380 to 780 nm) (De Grandis 1986:11). Within this narrow range, we see light of the shorter wavelengths as purple or blue, medium wavelengths as shades of green and yellow, and longer wavelengths as orange and red. When we see all of these wavelengths together, we perceive the light as white.

When light strikes matter, the light can either pass through (that is, be transmitted by) the material, be absorbed, or be reflected, depending on the properties of the material. It is the reflected light that we perceive with our eyes (unless we hold the specimen between our eyes and a light source, in which case we will see transmitted light). If all the light passes through, the material is perceived as colorless and transparent, or clear. If most of the light is absorbed, the material appears black. If more than 80% of the light is reflected, we perceive the material as white (De Grandis 1986:55). If part of the spectrum of visible light is absorbed and the rest is reflected, we see colors.

The chemistry and crystalline structure of a material determine how light will behave when it strikes the material. To simplify greatly, if a material is constructed on the molecular level in such a way that all the atoms are tightly bound to one another, with no extra electrons or unfilled electron shells, then all the light that is not reflected off the surface will pass through the material. Quartz has such a structure when it is pure and flawless, and this is why quartz crystals are usually clear. On the other hand, if the crystal structure of a material is such that it has unsatisfied electrons, then it will absorb energy from the light. Usually, only light of certain wavelengths is absorbed, depending on what electron shell is being affected. The light of other wavelengths is transmitted or

reflected, thus making the material appear to be colored. Materials with an atomic structure resulting in many unbound and highly mobile electrons—that is, metals—absorb most of the light. However, this causes an electrical current to begin on the surface of the metal, and the energy is remitted almost immediately as light. Thus, polished metals have highly reflective surfaces (Nassau 1983:164-165).

Cherts are made of minerals with a variety of chemical and structural properties, and thus light behaves in a complex manner when it interacts with chert. Figure 5.2 shows schematically what happens when a ray of light strikes a flake of chert. If the surface of the chert is relatively smooth, part of the light is reflected at an angle equal to the angle of incidence, resulting in specular, or mirror-like, reflection of mostly white light. If the surface is less even, some of the light penetrates just into the surface layer of molecules and is then reflected more diffusely. Depending on the impurities present, some of the spectrum will have been absorbed and thus the reflected light will appear colored. If the flake surface is very rough, the light is scattered completely, no color penetration occurs, and the chert appears chalky white. The light not immediately reflected off the surface of the flake enters the body of the flake, where much of it is absorbed, scattered, or internally reflected. The remaining light is transmitted through the flake.

The ray of light shown in figure 5.2 bends slightly when it enters the flake and again when it exits. Called refraction, this phenomenon occurs whenever light moves from a medium of one density into a medium of different density. The amount of refraction, or bending, depends on characteristics of both the light and the material it enters. Light of shorter wavelengths is bent more than light of longer wavelengths; thus, blue light is refracted more than red light. This is the reason a prism can separate white light into a spectrum of colors.

The amount of bending is also affected by the density of the

material the light enters: the denser the material, the more the light is bent. This property is measured by a value known as the refractive index. The refractive index is sometimes also defined in terms of the speed at which light moves through a material; light moves fastest through a vacuum and is slowed in any other medium, with speed decreasing with density. The more light is slowed and bent by a material, the higher that material's refractive index will be. Refractive indexes of most solids range between 1.4 and 2.0 (Berry et al. 1983:138). Of the minerals, opal has one of the lowest refractive indices at 1.435, and many common minerals have refractive indices between 1.5 and 1.7. Diamond, a relatively dense mineral, has a refractive index of 2.42, and hematite has one of the highest values at 3.22 (Klein and Hurlbut 1985:568).

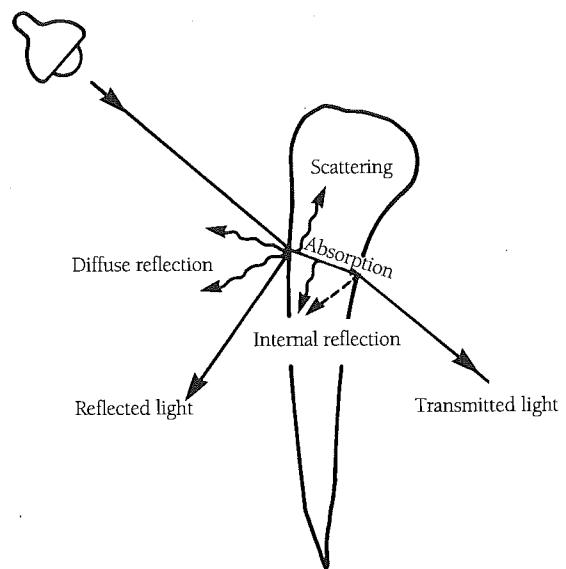
Many minerals have more than one refractive index, depending on the orientation of their crystals; these are said to be optically anisotropic. Quartz is such a mineral, with refractive indexes of 1.5533 parallel to the *a* axes and 1.5442 parallel to the *c* axis. As discussed in chapter 2, silicon and oxygen atoms are a little more closely packed along the *c* axis in quartz and slightly less densely packed along the *a* axes. Therefore, light vibrating parallel to *c* is slower relative to light vibrating parallel to the other axes. The refractive indices of cherts are usually slightly less than that of pure quartz because of the pore spaces and bubbles in the former. Flint has been measured at 1.537 (Midgley 1951:179), and chalcedonies range from 1.534 (Midgley 1951:179) to 1.543 (Flörke et al. 1982:328).

The refractive index is one chert property that obviously derives primarily from quartz. For many of the other visible properties of chert, however, the quartz simply provides a blank canvas upon which impurities and microstructure work to produce striking visual effects. The following discussion considers the visible properties of chert and the factors that cause them and suggests ways to standardize description of these properties to facilitate comparisons.

## Color

Color is the most obvious visible property and often is assumed to be one of the more typical characteristics of a chert type. Quartz is normally colorless, but chert is always colored, largely owing to the inevitable impurities. In my experience, the majority of cherts fall somewhere in the range from white through gray to black. Golds, reds, and browns are also very common; less common are greens, blues, purples, and yellows.

On a molecular level, the processes that cause us to see colors are rather complex. Nassau (1983) defined thirteen separate processes relevant to minerals and rocks, some of which overlap and most of which seem to require considerable background in physics and chemistry to understand fully. For our purposes, I group them into two broad types, the electronic processes and the physical processes. The electronic processes are the most impor-



**Figure 5.2**

Light striking a flake of chert.

tant, and all involve interactions between light and the electrons in a material. If there are no unbound electrons, light does not interact at all; thus, colorless minerals are those in which all electrons are nicely paired and in filled shells. However, many materials have “unsatisfied” electrons in their structure, sometimes because of the nature of the constituent elements and especially the connections among them and sometimes because of atomic substitutions or flaws in the structure. Such unsatisfied electrons are capable of absorbing energy, usually just of certain wavelengths, and the rest of the light is then reflected as color. Most rock and mineral colors result from such processes (Loeffler and Burns 1976).

The physical (or optical) processes involve the bending and scattering of light within materials (DeSautels 1965). This occurs when light encounters grain boundaries, cracks, flaws, or minerals of different refractive indices. Light of different wavelengths is bent or scattered to different degrees. The blue end of the spectrum is more strongly scattered than the red end, causing the “fire,” or flashes of color, typical of faceted diamonds (DeSautels 1965:55). The play of color typical of precious opals also results from the diffraction of light by an orderly three-dimensional array of silica spheres (DeSautels 1965:54). In general, though, “color involving geometrical and physical optics plays a relatively small role in minerals and gemstones” (Nassau 1983:336).

Geologists, physicists, and artists have sought ways to describe colors objectively and all have found it necessary to distinguish three aspects of color, each of which may derive from different characteristics of the material (Hurst and Kelly 1961). The first aspect is usually called *hue* (sometimes *tonality*) and refers to the part of the color spectrum that is being reflected. Thus red, yellow, and blue are different hues corresponding to light of

different wavelengths.

The second aspect of color is usually called *value*, though it is also referred to as lightness, brightness, or luminous intensity. Value describes a color in relation to the extremes of black and white. Thus, a light blue and a dark blue may both be the same hue, but they are of different values because the former is closer to white and the latter is closer to black. Presumably, then, value is related to the proportion of the light that is reflected rather than absorbed.

The third aspect of color is *chroma*, also referred to as the purity or the degree of saturation of the color. It describes the extent to which the dominant color is mixed with other colors. Thus, a pure or saturated color, one of high chroma, reflects a relatively narrow segment of the color spectrum. Many artificial paints or dyes are of very high chroma, but most colors found in nature represent more than one small part of the color spectrum and thus appear "muddier." We often call such colors "earth tones"; a color of very low chroma is close to a gray (De Grandis 1986:181).

These three aspects of color should be familiar to archaeologists because they are the same dimensions used in the organization of the Munsell color charts. The different pages of the chart represent different hues; within a page, the colors vary in value from top to bottom and in chroma from left to right. Munsell charts are used routinely to describe soil types; they are also the most sensible means of describing rock colors. Granted, the Munsell chart is not a perfect, unambiguous instrument, as Ives (1984:6–8) has pointed out. Some soils and rocks do not seem to match any of the color chips especially well, and colors can also appear to vary depending on the amount of moisture present, the time of the day, the kind of light, and the eyes of the observer. This is all very well known to anyone who has spent time in a hot test pit arguing with a digging partner about whether the soil in level three is closer to 10YR5/8 or to 10YR6/8. Munsell charts have the advantage, however, of being widely available to archaeologists. They are certainly a better means of describing chert colors than using such qualitative terms as "bright reddish yellow," which will surely bring different images to mind for different people.

Since color is caused by a material's chemistry and physical structure, one might think that it would be easy to explain why a rock has the color it does. Unfortunately, this is often not the case. In fact, for some gems, the cause of the color could not be explained until the gem was synthesized in the laboratory after much trial and error (Nassau 1983:99). There are three reasons for this. First, many different processes cause color. Nassau (1983: color fig. 1) shows a color plate of six deep-blue gemstones, all of which appear to be the same color but all of which owe their color to a different process. Second, there is no simple one-to-one correlation between colors and specific elements because color is a function of the bonding and interactions among atoms, not the kinds of atoms themselves. For example, different iron minerals produce a wide range of colors (table 5.1). Third, sometimes a tiny

quantity of one impurity can make a big color difference, while larger quantities of other impurities do not affect color. For example, the normally colorless mineral corundum remains colorless despite the incorporation of a few hundred parts per million of titanium. If a similar amount of iron is present, the corundum is a pale yellow color. If a few hundred parts per million of both titanium and iron are present, however, the corundum takes on a deep blue color and is known as a sapphire (Nassau 1983:140).

Thus, "the cause of the color of a substance cannot always be deduced directly from knowing the composition" (Nassau 1983:97). One cannot simply assume that the color is due to the predominant impurity, and in many cases several color-causing mechanisms are present at the same time. In other words, we really do not know exactly what causes many rock colors. For this reason, most of the causes of particular chert colors that are usually given in the literature, and which will be discussed below, are based more on common sense than on actual experimental evidence.

It is not even easy to say what factors in chert cause the different aspects of color. Hurst and Kelly (1961:251–252) stated that the hue of a chert is determined by the kind of impurity, and chroma by the amount of that impurity; value is determined by the grain size, texture, and overall amount of impurities. I agree that hue results from the predominant color-causing impurity but suggest that chroma or saturation is more likely to be determined by the presence or absence of other impurities, as well as the nature of the color-causing mineral itself. Value is probably caused in part by grain size but may also be affected by the amount of the predominant color-causing impurity: the smaller the quantity, the closer the color should be to white. To what degree the impurity is dispersed may also affect value. Clayton et al. point out that specimens of Knife River flint with highly dispersed organic matter are darker. "Samples with the best developed internal sedimentary structures are the lightest colored because the organic material was least dispersed" (Clayton et al. 1970:287). On the other hand, too finely divided pigments tend to lose their color (Nassau 1983:240). Clearly, this issue needs more research.

There is no such thing as a perfectly clear or colorless chert. By definition, chert is made up of tiny grains of quartz, and the interfaces among these grains cause much of the incoming light to be reflected or scattered rather than transmitted. In addition, the water inclusions typical of most cherts also reflect light (Folk 1974:80). The end result of these physical processes is white, which can be considered the "base" color of chert. For a chert to appear white, it must be relatively free of colored impurities, though it is possible it may contain substantial quantities of colorless or white minerals, such as calcite and some clays. Chemical analyses indicate that white or pale-colored cherts, such as Burlington, Cordell, and some Flint Ridge and Arkansas novaculite, are at the low end of the range for many elements (see appendix B).

Gray is probably the most common chert color, if one includes the full range from pale to dark and those tinged with tan, blue, pink, and other colors. These colors are especially hard to explain because so many phenomena can be responsible. Some common impurities (that is, certain clays, feldspars, and metallic minerals) are gray, and relatively small amounts of black impurities in a fundamentally white chert can produce gray. Tarr (1917:413), for example, attributes the gray varieties of Burlington chert, which is generally white, to organic matter or finely divided pyrite. Two minerals of complementary colors present in relatively equal proportions result in gray: if one mineral reflects the red segment of the spectrum and the other reflects green, the two colors cancel each other out (Nassau 1983:12).

Black is often caused by organic carbon and is especially typical of cherts formed under reducing conditions, as discussed in chapter 4. Ruedmann and Wilson (1936:1544) suggest that considerable amounts of carbon can override colors that would otherwise predominate. Some black cherts derive their color from manganese minerals. In addition, the combination of iron and titanium, which causes some minerals to appear blue, can cause other minerals to be black (Nassau 1983:335). The black color typical of much English Chalk flint is said to be an optical effect caused by the scattering of light within the physical structure (Shepherd 1972:23); this flint does contain organic matter, however. The black color of Stevns chert, another chalk flint, has been attributed primarily to finely dispersed amorphous carbon (Micheelsen 1966:309).

Minerals made of metallic elements (especially copper, iron, manganese, chromium, nickel, cobalt, vanadium, and titanium) are a major cause of many colors in chert. Of these, iron is by far the most important because it is normally present in much greater proportions than any other metal. Iron minerals come in a wide variety of colors (see table 5.1) but many are uncommon. Hematite, goethite, limonite, and pyrite, the usual iron minerals in chert, are responsible for many red, gold, and brown hues. Some iron minerals can be easily altered. For example, the oft-noted change from gold to red when jaspers are heated results from goethite being altered to hematite (Schindler et al. 1982:528). Gem dealers take advantage of this fact by heat-treating carnelian and sard to improve their reddish color, which is caused by finely dispersed hematite (Fron del 1962:206). Other forms of iron minerals are less likely to cause visible color. For example, some cherts that are normally white will turn pink when heat-treated. This implies that the iron is normally present in these cherts as a mineral that has little effect on color but that the same amount of iron in the form of hematite can cause visible color.

Chemical data suggest a few generalizations about iron in non-heat-treated cherts. According to the Michigan project data, cherts that appear pure white generally have less than 150 ppm of iron, pink cherts generally contain between 100 and 1,000 ppm, and red cherts contain at least 1,000 ppm. However, one light gray

**Table 5.1 Colors of Various Iron Minerals**  
(from Pough 1976)

Color	Mineral	Composition
White	Loellingite	FeAs <sub>2</sub>
Light yellow	Pyrite	FeS <sub>2</sub>
White-gray to brown	Siderite	FeCO <sub>3</sub>
Light brass yellow	Marcasite	FeS <sub>2</sub>
Bronze	Pyrrhotite	Fe <sub>1-x</sub> S
Ocher yellow to black	Limonite	FeO(OH)nH <sub>2</sub> O
Yellow or brown to black	Goethite	HFeO <sub>2</sub>
Red to black	Hematite	Fe <sub>2</sub> O <sub>3</sub>
Green to brown	Fayalite	Fe <sub>2</sub> SiO <sub>4</sub>
Green	Ferrous iron	Various
Purple	Heterosite	(Fe, Mn)PO <sub>4</sub>
Steel gray	Native iron	Fe
Black	Magnetite	FeFe <sub>2</sub> O <sub>4</sub>

chert had over 4,000 ppm, presumably in the form of one of the less colorful iron minerals, and green Cocksackie chert averages nearly 18,000 ppm.

Other colors in chert are caused by a wide range of minerals. For example, green is often caused by chlorite (Pollock 1987). Fron del states that the pale green of chrysoprase is attributable to hydrated nickel silicate, the darker green of plasma to chlorite or celadonite, and the "leek green" of prase to hornblende fibers and/or chlorite (Fron del 1962:218–219). Spielbauer (1976:165) says that blue can be caused by certain copper minerals and that manganese minerals can be responsible for a lilac-pink color. The pale blue color typical of many chalcedonies is attributed to Tyndall scattering, a physical mechanism in which blue light is scattered while red light is transmitted (Fron del 1962:198). Tyndall scattering may also be responsible for the pale brown of chalcedony in transmitted light (Pelto 1956:35).

## Translucency

Materials vary in the degree to which light passes through without being absorbed or reflected. This aspect is called diaphaneity. Materials are described as transparent if they allow almost all light through (for example, window glass); as opaque if they do not allow any light through (for example, most metals); and as translucent if they allow some light through. Diaphaneity is not an absolute property because it varies with the material's thickness. Thus, gold is normally perceived as opaque but is translucent when very thin, and a sufficient thickness of glass becomes translucent rather than transparent. All cherts are actually translucent, although this property is sometimes apparent only in very thin flakes or thin sections.

Perhaps because diaphaneity is so strongly affected by thickness, there is no generally accepted way in which to measure or quantify it. Ahler (1983) has suggested a good, practical

measure that I found helpful and simple to use. To quantify translucency in Knife River flint, he held flakes at the edge of the shade of a desk lamp, 8 cm from a 75-watt bulb. He saw that the translucency varied, with the thin edges appearing highly translucent and the thick spine appearing opaque. A relatively clear line marked where the chert changed from translucent to opaque, and Ahler measured the thickness of the flake at that point. I tested this procedure first on Knife River flint and was pleased to find that my measurements agreed well with his. Results were also quite consistent when different parts of the same flake were measured or when measurements were taken on different flakes of the same material. Best of all, this procedure produces a satisfactorily wide spread of values, from about 0.5 mm for very opaque cherts to 20 mm or more for chalcedonies and very translucent cherts. This procedure was used to obtain translucency values for many of the cherts used in this study, and their values are given in appendix B. I found, as did Ahler, that translucency can vary within a chert type; therefore, several measurements should be taken and the results presented as a range.

The causes of diaphaneity in minerals are well known. Berry et al. (1983:143) state that most pure minerals are either transparent or opaque. Transparent minerals are those in which all the electrons are satisfied and bound up, so that most of the light passes through (unless the specimen is very thick or made up of more than one crystal, in which case some of the light is absorbed or scattered, making the material appear translucent). The opaque minerals are primarily the native metals and metallic sulfides and oxides, although even some of these are translucent in extremely thin fragments. They appear opaque because they either absorb or reflect all the light. The minerals that make up chert vary considerably in diaphaneity. Quartz, the predominant mineral, is transparent in its pure crystalline form. Of the common impurities, water is also transparent, the carbonates are transparent to translucent, and organic materials are generally translucent. Clays are subtranslucent to opaque, and metallic oxides and sulfides are opaque (Berry et al. 1983).

The translucency of chert depends largely on the impurities. Cherts that are pure quartz are highly translucent, whereas those that have large amounts of opaque minerals are less translucent. The kind of impurity, its quantity, and its distribution affect translucency. As would be expected, impurities that are themselves translucent do not decrease chert translucency much. For example, Blatt et al. (1972:536) state that, even though many limestone cherts contain large amounts of carbonate minerals, they are still fairly translucent. Similarly, Knife River flint has considerable organic content, yet is quite translucent (though translucency is less for the lighter colored varieties in which organic matter is not well dispersed [Ahler 1986:3]).

Clay would be expected to reduce translucency more than carbonates, but it is hard to separate the effects of clay from those of metallic oxides, with which it is often closely associated.

Metallic minerals, being the most common opaque impurity in cherts, would be expected to decrease translucency the most. I attempted to test the proposition that translucency should decrease as the amount of iron increases by comparing these variables within a single chert type, so that at least some of the other possible variables would be constant. Thus, I correlated translucency (measured by the method described above) and iron content for twenty-four samples of Arkansas novaculite, which varies considerably in both translucency and trace element content. The correlation between translucency and iron content was  $-0.473$ , significant at the 0.01 level and higher than the correlation between translucency and any of the other elements measured in the Michigan project.

Grain size may also affect translucency. Every time light encounters a grain boundary, some of it is scattered or absorbed. Thus, one might predict a priori, as do Hurst and Kelly (1961), that fine-grained cherts would be less translucent than coarse-grained cherts. Grain size may not be an independent variable, however. As suggested in chapter 3, cherts may tend to have smaller grains if they form in the presence of many impurities that can act as centers of nucleation. Therefore, the lesser translucency of fine-grained cherts might be because of impurity content, not grain size. Furthermore, the Hurst and Kelly prediction does not always hold true. For example, English Chalk flint is generally black and translucent, but many nodules have zones of less translucent gray or brown flint, assumed by some analysts to represent zones of recrystallization. Iler (1963) compared the two varieties and found that the less translucent gray flint was composed of grains two to ten times larger than the translucent black flint.

The distribution of impurities in chert may sometimes be as important as their quantity. Jaspers are usually not very translucent because of their high iron content, but many are translucent in parts because the iron oxides settled in clumps and streaks. In the case of English flint, the distribution of impurities might explain differential translucency if the lighter areas have indeed recrystallized. It is reasonable to assume that if recrystallization occurred within a chert nodule after it formed, all the impurities could not be expelled; they might then become concentrated along grain boundaries. A given amount of impurity concentrated on a two-dimensional plane might present more of a barrier to light than the same amount of impurity scattered through a three-dimensional volume (as seems to be the case with various varieties of Knife River flint). More of the light being reflected back by such impurity layers would explain both the decreased translucency and the lighter color of the gray chalk flint.

## Luster

Some of the light that strikes a material is reflected from its surface, and the appearance of this reflected light is called *luster*. Luster is

a function of both the mineralogy and the surface characteristics of a material and is usually described by a bewildering variety of subjective terms such as silky, greasy, pearly, or waxy. Berry, Mason, and Dietrich (1983:141) pointed out that the four basic qualitative types of luster show good correlation with the refractive index, though they admit that the dividing lines among these types are not exact. Thus, materials with metallic luster, such as gold, have refractive indexes greater than 3. Minerals with refractive indexes between 2.6 and 3, such as cinnabar, generally have submetallic luster. Diamond and other minerals with refractive indexes between 1.9 and 2.6 have adamantine luster, while minerals such as quartz with refractive indexes from 1.3 to 1.9 have vitreous, or glassy, luster. Berry et al. (1983) state that most of the other terms for luster are the result of surface modifications of these four basic types. For example, diamonds with microscopically rugged surfaces appear to have greasy luster, roughened quartz appears waxy, and fibrous materials such as chalcedony look silky.

To further complicate the issue, luster refers not only to the quality but also to the quantity of light reflected. Such terms as bright, shiny, and dull refer primarily to the intensity of the reflected light. This aspect of luster is largely a function of the evenness of the surface. The smoother the surface, the more evenly and intensely light is reflected.

Because chert is made predominantly of quartz, one would expect its "base" luster to be vitreous, though, in reality, few cherts would be described as such. This is because the quartz takes the form of small grains. When chert is fractured, it usually breaks around these grains, resulting in a microscopically uneven surface from which light is reflected in many directions. Light is not reflected back at an angle equal to the angle of incidence, as it is from the smooth surface of a quartz crystal. In general, then, cherts made of small quartz grains appear shinier because their surfaces are flatter and light is reflected more evenly. Cherts made of larger grains have rougher surfaces that reflect light less evenly and thus do not appear as shiny.

Grain size is not the only factor affecting luster in cherts. Roughened, porous, or pitted surfaces, such as those resulting from certain wear and weathering processes, appear dull irrespective of grain size. On the other hand, other weathering processes deposit silica on the surface of the chert, making the surface more even and shiny. Also, abrasion can polish the surface so that it appears shiny. The glassy surfaces of the semiprecious varieties of chert used in jewelry are prepared this way, and such polish can also develop as a result of wear (Kamminga 1979). Another process that can alter the luster of a chert is heat-treating. This process causes a fracture to cut across the grains rather than around them. The resulting surface is more even, making the chert appear shinier than it did before it was heated (see chapter 7).

Finally, the kind and quantity of impurities in a chert may affect luster. Schindler et al. (1982) suggest that some of the

increase in luster that is typical of heat-treated jasper is due to the alteration of goethite, the predominant iron mineral in the unheated jasper, to hematite. Goethite has a dull, earthy luster, and its alteration results in an "increase in reflection of light from the well-defined facets of the hematite crystals" (Schindler et al. 1982:535). Presumably, large amounts of clay in a chert might also dull its luster.

Quantifying luster proved to be far more difficult than quantifying color and translucency. I tried two methods suggested in the literature. Rick (1978:16–17) describes a technique involving the angle at which light is reflected from the surface of a sample, but I was unable to put this method into operation. Keeley (Hayden 1979:193–194) uses a light meter to measure the amount of light reflected up through a microscope. Using Keeley's method, I obtained numbers that expressed color value as well as luster; pale cherts reflected more light than dark cherts. For cherts of the same approximate value, however, those described as shiny did produce higher readings than those described as dull. Unfortunately, neither the Munsell color chart nor the light meter used in this experiment were sensitive enough to allow me to sort out these two factors. Therefore, in appendix B I fall back on the qualitative terms of shiny, medium, and dull to describe the cherts.

Further work along the lines suggested by Rick and Keeley might well result in a successful method for quantifying luster. Additional research might also follow up an observation I made while adjusting the cherts under the microscope. I noted that cherts with dull luster reflected the same amount of light no matter how they were oriented, while shiny flakes reflected a great deal more light at certain orientations. To a large extent, this is also what makes us perceive such flakes as being shiny when we hold them. Thus, some measure of the amount of difference between the most reflective and least reflective orientations might provide a useful way to quantify luster.

## Texture

Archaeologists frequently describe cherts as being fine grained or coarse grained. Even the largest quartz grains are only 50  $\mu$  (0.05 mm) in diameter, however, too small to be seen without a microscope. It is likely that what we are actually describing is the fracture surface, not the quartz grains. If this fracture surface is visibly uneven at a scale greater than that of the individual quartz grains, we say the chert is coarse grained. There appears to be no objective means of quantifying this attribute, though Rick (1978:15) suggests a rough typology of chert textures based on the appearance and feel of a chert when one scratches it with a fingernail.

Variations in the smoothness of fracture surfaces could be caused by a number of factors. First, texture may be a function of porosity, or the frequency of holes and cavities, with porous cherts appearing coarse grained and nonporous cherts appearing fine

grained. Second, texture may pertain to the presence or absence of clusters of quartz grains, perhaps resulting from the replacement of opal-CT spherulites or fossils. If such clusters exist in a chert and fractures tend to go around rather than through them, the resulting fracture surfaces might appear uneven. A third possibility is that texture is, indeed, a function of grain size, even if it is not equivalent to grain size. A growing crack or fracture moving through a chert normally makes many small detours around the grains (see chap. 6). It is possible that larger grains deflect the fracture enough to produce a fracture surface that is much rougher than that of the individual grains. In fact, all these factors may operate to create the phenomenon we perceive as texture, as will be discussed below.

## Structure

Uneven distribution of color, luster, texture, and translucency creates structure, also called fabric or pattern, often a highly distinctive aspect of a chert type. These variations in visible properties can be gradual or abrupt, regular or irregular. They produce striped, spotted, streaked, or irregularly splotched or mottled cherts. With a few exceptions, the terminology for describing rock structure has not been standardized, but qualitative descriptions, combined with appropriate measurements, are probably quite adequate for this visible attribute. Structure in chert results from replacement of features present in the original sediments or from chert diagenesis.

## Replacement features

Many cherts result from replacement of preexisting sediments; in such cases, original structures are often reproduced. Thus, many limestones or marls were deposited in flat layers, resulting in banding (layers greater than 1 cm thick) or laminations (layers less than 1 cm thick). These structures are sometimes faithfully reproduced in the chert lenses or nodules enclosed in these carbonates. In fact, it is sometimes possible to follow a single bedding plane from the matrix into the chert and out again (Bramlette 1946:50). Although layers may differ in luster or translucency, mostly they differ in color because nonsilica minerals are concentrated along the bedding planes. For example, most Norwood chert has a finely laminated structure, sometimes with crossbedding. The laminations, which are reddish tan against a cream background, result from iron oxide concentrations on the original bedding surfaces. In general, such laminations indicate that the sediment was deposited in quiet waters below the wave base; the laminations would be convoluted if currents exerted shear stress on the beds (Pettijohn 1975:102).

Much of the irregular mottling and splotching that appears on some cherts is also a replacement phenomenon. For example, Onondaga chert is typically gray and mottled, but it can also be featureless or homogeneous. Ozol (1963) demonstrates that the

structure of Onondaga chert is essentially that of the surrounding limestone. Where the limestone is mottled and fossiliferous, the chert shows much mottling and variation in visible properties. On the other hand, "The replacement of homogeneous even grained limestone with few fossils gives rise to a homogeneous even grained fabric in the chert, which is free of variations in grain size and areas of contrasting texture" (Ozol 1963:220). Again, the structure of the limestone reflects the depositional history of the specific basin of deposition, including the amount of burrowing by animals and the amount of wave action.

Oolitic cherts are also the result of replacement. Oolites are tiny spheres of inorganic origin that form primarily in marine environments where strong bottom currents agitate carbonate sediments. This agitation causes calcium carbonate to precipitate in concentric layers around a sand grain or fossil nucleus (Blatt 1982:248). The resulting oolites, usually 1 to 2 mm in diameter, can become silicified, resulting in a distinctive chert that looks as if it is made up of tiny beads (for example, Blatt 1982:386).

Fossils are common features of replacement origin. In extreme cases, such as silicified wood, coral, or bone, the structure of the chert is that of the fossil itself. More often, though, fossils appear as small inclusions in the chert, some easily visible and identifiable with the naked eye (for example, crinoids, corals, and bryozoans) and others visible only as small spots (for example, diatoms, radiolarians, and many foraminifera). They are often a slightly different color than the body of the chert, and sometimes exist only as casts, in which case the original material of the fossil has dissolved, leaving a cavity in the chert.

Finally, visible bits of other rocks or minerals can become incorporated into chert as it forms. For example, some cherts fully enclose small patches of limestone or dolomite, relics of the original sediments. Rounded grains of detrital quartz, which were originally sand grains, are another example.

## Structures resulting from chert diagenesis

The process of chert formation can create structures that were not present in the original sediments. An example is concentric banding or lamination, in which layers form parallel to a chert nodule's surface rather than flat and parallel to the original bedding plane of the sediments. Concentric banding results when numerous layers of silica are deposited on the interior surface of a cavity, as with the Serra Geral agates described in chapter 3. Concentric banding may also develop from the center out as chert nodules grow. For many nodular cherts, silicification begins in one small area and spreads outward. If there are temporary halts in the growth of the nodule or changes occur in the chemistry of the fluid or sediments, concentric layers may form. These layers are usually slightly different in color and may also differ in luster, texture, and translucency.

Some horizontal laminations can also result from diagenesis rather than from depositional processes. For example, the in-

creased pressures and temperatures resulting from overlying sediments can cause silica to dissolve locally, leaving a thin layer of insoluble residues behind. The resulting "pinstripe" can resemble a depositional layer but is of diagenetic origin (Pollock 1987:77).

Sometimes minerals other than quartz form in crystals that are large enough to be part of the chert's visible structure. For example, small crystals of pyrite are visible as speckles in some cherts. Dendrites are another example. These little branching structures often appear fernlike or mosslike but are actually of inorganic origin. They are usually made of manganese dioxide, or sometimes of iron oxides, and they often form along cracks or flaws in cherts. They may also form while the silica is in a colloidal or gel-like state, at which time they can diffuse into the silica (Fronde1 1962:209).

The chert breccias, mentioned in chapter 3, are distinctive structures of diagenetic origin. In this case, the original chert was broken and fragmented and then cemented together again by silica that is often of a different color or texture (for example, Kolodny 1986). This process creates a chert that resembles a conglomerate. Finally, many cherts contain visible cracks, veins, or cavities that have been filled with other materials. Chalcedony and quartz crystals are common in such fissures, but they may also be filled with calcite, hematite, or other minerals.

An obvious change in color, luster, and texture appears on the outer surface of nodules, beds, and lenses of most cherts. This outer layer, the "cortex," is also a diagenetic feature. Unfortunately, archaeologists use the term cortex to refer to outer layers of two very different origins. We call the surface layer of a chert nodule or bed while it is in its surrounding matrix its cortex, but we also use this term for the weathered zone that forms over time on chert fragments or artifacts (see chap. 7, this vol.). Both of these surface layers involve marked changes in visible properties, both have mechanical and chemical properties that differ from those in the main body of the chert, and both must usually be removed before knapping can begin. Thus, the dorsal surface of a decortication flake can show the chalky surface typical of a nodule, the battering and percussion marks typical of a rock taken from a stream-bed, or the dull, bleached surface typical of a cobble that has been lying on the surface of a quarry.

It would be preferable to distinguish these two types of surfaces, although the dual usage is deeply entrenched in the literature. I suggest that "weathering rind" is the most appropriate term to describe the layer that forms on chert as a result of weathering processes. "Cortex" could then refer to the layer that forms on the outer surface of a nodule or bed during diagenesis.

The cortex is a transition zone between the chert and its matrix, and it is distinct from either. It is usually between 0.5 mm and 1 cm thick, is often a lighter color than the chert, and is generally less translucent, duller in luster, and coarser in texture. The cortex often resembles the surrounding matrix, but it is

usually not identical to it. For example, the cortex on nodules of English Chalk flint is often a different color from the surrounding chalk (Shepherd 1972:23). In many cases, there is a rather sharp transition between chert and cortex (for example, Micheelsen 1966:288), but sometimes this transition is gradual (for example, Ozol 1963:35). The cortex is also chemically intermediate between chert and matrix. For example, Ozol (1963:35) found that the cortex of Onondaga chert nodules had less silica than the chert but more calcium, magnesium, and carbon; on the other hand, the cortex had more silica and dolomite than the surrounding limestone. Some cortexes also have considerable amounts of opal-CT (for example, Flörke et al. 1982:326). There is not yet enough research to determine whether the cortex is a zone in which chert is still forming or is the point at which chertification stopped because of insufficient silica or too many impurities. Given the diversity of ways in which chert can form, it seems likely that chert cortexes also originate in more than one way.

## Microscopic Properties

Entire chert artifacts are often examined under either low (10x to 100x) or high (100x to 500x) magnification in order to study the traces of wear that tell how the artifact was used (for example, Hayden 1979). To study chert as a raw material rather than as a tool, however, one usually cuts a thin section for microscopic analysis. This involves sawing off a flat fragment and grinding it down to a uniform thickness of about 30  $\mu$  after which it is mounted on a glass microscope slide. At this thickness, all cherts are translucent and can be studied with transmitted light using petrographic microscopes. When one examines such thin sections, one sees (1) a great deal of silica, (2) other minerals in varying proportions and distributed in various ways, and (3) the microfabric.

Much of the silica is microcrystalline quartz, which appears speckled and grayish because the grains are too small to be resolved by ordinary light microscopes. After all, a grain of quartz 1  $\mu$  in diameter must be magnified 1,000 times to appear 1 mm across, and this is the top of the magnification range for light microscopes. Individual grains are also very difficult to see or measure with light microscopes because the average thin section is considerably thicker than the average quartz grain in chert. Thus, we are always viewing grains superimposed on top of one another.

In attempting to avoid the problem of superimposed grains, a few investigators have made thin sections of cherts that were only 3  $\mu$  thick and they report that grain boundaries are still indistinct (Micheelsen 1966:291). Micheelsen attributes this phenomenon to the presence of the slightly misaligned crystal plates within the grains, but it is also possible that grain boundaries are strained because of the pressure of the surrounding grains.

Not all the silica in chert is in the form of microcrystalline



quartz. Some of it occurs as very large grains, sometimes referred to as megaquartz, and as crystals lining cavities. Detrital quartz, usually in the form of sand grains, can be recognized by the rounded shape, clear grain boundaries, and large size relative to other chert grains. Chalcedony is extremely common in many cherts, and its fibrous structure is clear in thin section. It may form short, thick bundles or long, thinner ones, which are often described as plumose (plume-like) or flamboyant. These bundles often radiate out from a surface or may form spheres. Chalcedony often fills cracks or fossil shells and may also cement quartz grains in the body of a chert (Bradley and Clayton 1987). Finally, a small proportion of the silica in chert is in the forms of cristobalite and opal. The early literature often states that cherts contain rather large amounts of opal, but subsequent research has proven this assumption false (Pelto 1956).

Though most of the chert is composed of these various forms of silica, impurities are invariably present as well. In fact, these minerals are often the primary focus of the petrographer's interest when cherts are studied in thin section. They can be identified by a series of properties, including their crystal form, cleavage, grain shape, and the manner in which they reflect, bend, or absorb light (Klein and Hurlbut 1985:239–252). Petrographers generally attempt to identify all these minerals, estimate their quantities, and describe how they are distributed within the chert.

As discussed in chapter 4, the major types of impurities in chert are carbonates, clays, iron oxides, and organic compounds. The most common carbonates are calcite and dolomite. These minerals appear as irregular patches that represent unreplaced matrix, as well-shaped crystals, or as finely disseminated dust. A wide variety of clay minerals has been observed in cherts, and they usually are very finely disseminated or else concentrated around the edges of such features as fossils. Some clay-type minerals do occur in larger sizes; mica is often seen as small plates or scales, and chlorite as spherules (Wray 1948). The iron minerals often appear as finely scattered dust-sized fragments but can also occur as discrete crystals. Carbonaceous or organic matter may be visible as relic organic structures but is often present as tiny, scattered, structureless fragments.

The spatial distribution of all the different minerals and kinds of silica in a chert could be called its microfabric. In many cases, this is largely a close-up view of features that were also visible at the macroscopic level, but other features are only visible under the microscope. As with the macroscopic features, some result from replacement of previous sediments and others from the process of chert formation itself.

A good deal of the microscopic structure in many cherts is organic in origin and consists of marine fossils and fossil fragments. Under the microscope, their mineralogy is clear. Some, such as diatoms or sponge spicules, were siliceous to begin with, though the opal-A of which they were originally composed has now been converted to quartz. In some cases, these siliceous

fossils have dissolved and show only as "ghosts" outlined by impurities (Blatt 1982:385). The majority of fossils were originally calcareous; some of them retained their original mineralogy, but most were replaced entirely by quartz. Under some circumstances, fossils may be only partially silicified. Ozol (1963:137) describes fossils in Onondaga chert that extend across the interface between chert and limestone and are composed of silica on one side and calcite on the other. The exterior of other fossils has been replaced by silica, but the interior remains calcareous. In many cases, fossils were replaced by chalcedony, a process that often appears to have preceded the formation of the body of the chert (Heath and Moberly 1971:996; Clayton 1986:53). Under the microscope, some of these fossils are identifiable as to genus. Thus, they are useful indicators of the age of the chert and sometimes are diagnostic of specific chert types (for example, Reid 1984).

Nonmarine fossil features in chert include those of petrified wood, lignite, and bone. In some instances these materials have been replaced so perfectly that cell structures can still be studied, but in others the cells have been obliterated by decay and/or the replacement process (Blatt, Middleton, and Murray 1972:537). Some features observable in thin sections are of uncertain origin. These include the rounded or elongated black or brown blobs apparently made of carbonaceous matter which occur in some chalk flints (Micheelsen 1966:289).

The inorganic microstructures present in some cherts often provide additional information concerning structures that are also visible in hand samples. Thus, the fine reddish laminations of Norwood chert appear as alignments of iron and clay minerals under the microscope. The concentric structure of oolitic cherts is evident in thin section. In the center of the oolite one can often see the little grain of sand or bit of fossil that served as the nucleus. Cherts of unusual origin may show the textures of the rocks they replaced. For example, relic gabbro texture can be observed in thin sections of Newark jasper (Lavin 1983:144), and quartzite grains outlined by opaque minerals are visible in Pennsylvania jasper (Lavin 1983:140).

### **Properties Visible Under the Scanning Electron Microscope**

Additional visible information can be obtained by examining chert under a scanning electron microscope (SEM). These microscopes operate most often in the 20x to 20,000x range, but can reach 500,000x. SEMs operate on different principles than do light microscopes, however, and thus provide rather different kinds of information. Instead of transmitting light through a specimen of chert, the SEM bounces a beam of electrons off the surface, which is coated with a thin layer of a conducting material such as graphite, gold, or palladium. Thus, the SEM gives a detailed picture of the surface topography. Some minerals can also be identified by their crystal shapes, but this information is usually

more easily obtained from thin sections.

Archaeologists frequently use SEMs to examine the surfaces of artifacts. For example, these microscopes have been very useful in investigating the different kinds of wear that various activities produce on tools (for example, Del Bene 1979). SEMs are also especially well adapted for studying fracture surfaces and thus have been used extensively to study fracture mechanics (for example, Lawn and Marshall 1979) or the effects of heat-treating (for example, Mandeville 1973). Unfortunately, the interpretation of such photographs is still somewhat subjective, and there is a great need to standardize terminology and procedure. Anyone who has examined many of the often murky SEM photographs published in archaeological publications must wonder if they have become the archaeologist's Rorschach test. Sometimes our interpretations may reveal more about our own thought processes than about the artifacts themselves.

The SEM is especially well suited for examining the quartz grains in chert. An early study defined two "endpoints of surface morphology," plus a transitional form (Folk and Weaver 1952:502). One endpoint was called the "novaculite" type of surface, named after the Arkansas novaculite in which it was first observed. The individual quartz grains are unusually clear in such cherts (fig. 5.3); they look like "sharply defined equant polyhedral blocks" (Folk and Weaver 1952:502). The other endpoint was called the "spongy" type of surface, typified by many small hemispherical holes and vague tubules but no discrete grains. The intermediate surfaces had characteristics of both endpoints (figs. 5.4 and 5.5) and, in fact, were sometimes markedly bimodal (fig. 5.6).

Folk and Weaver found the spongy surface type to be typical of chalcedony. (Surprisingly, the characteristic chalcedony fibers are usually not visible under the SEM.) This has left the impression that the novaculite surface is the "normal" surface for microcrystalline quartz (Blatt 1982:387), but subsequent studies have shown that this is not the case. For example, Ozol found that "transitional" surfaces were typical of Onondaga chert, with the novaculite surface present only in one small area of one sample (Ozol 1963:160). My own sample of twenty-four chert types examined under the SEM showed that the novaculite surface was the exception, not the rule. In fact, Keller et al. (1985) argue that the well-developed grains and "triple point polygonal textures" of novaculite-type surfaces are primarily characteristic of metamorphosed and recrystallized cherts. Such surfaces do occasionally occur, however, in unmetamorphosed contexts as well; perhaps this surface is simply characteristic of very well-crystallized chert, which is most likely to occur as a result of metamorphism or hydrothermal recrystallization.

The term "transitional surfaces" actually encompasses a rather wide variety of textures. Since most chert microspheres appear to fall into this category, it would surely be useful to devise a means of subdividing it, or at least of describing the various aspects in a standardized and meaningful way.

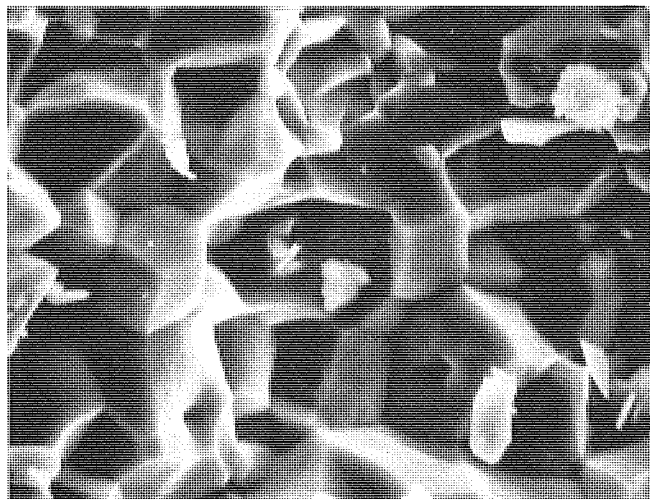
The SEM is also well suited for studying the scale just above grain size, the actual fracture surface for many cherts, and the relevant scale for texture. These surfaces are often made clearer by being etched with hydrofluoric acid to remove the more soluble silica between the clumps of quartz grains (Bradley and Clayton 1987:81). When this is done, relic spherulites and silicified fossils are easily visible.

## Correlations Among Various Visible Properties

A limited number of factors, most notably impurities and grain size, have been mentioned repeatedly as being probable causes of the various visible properties of chert. If these few factors are as important as implied, then we would expect that at least some of the visible properties of chert would be correlated. Table 5.2 represents an attempt to test this prediction by using samples of various cherts. Admittedly, some of the attributes are defined less objectively than others, but all measurements and descriptions were done independently, usually some months apart, to control observer bias as much as possible. In most cases, the correlation coefficients are based on a sample of thirty-one items, but some tests were done on a slightly different sample so that N is twenty-seven or even sixteen.

*Texture* was determined subjectively by arranging samples of each chert type in order by increasing coarseness and then assigning values on a 5-point scale, with 1 being finest and 5 being coarsest. *Luster* was determined similarly by arranging samples in order of increasing dullness and applying a 4-point scale, with 1 assigned to the shiniest flakes and 4 to the most dull and chalky flakes. *Value* was determined from the colors previously assigned using the Munsell chart and was included as a rough measure of the quantity of impurities. *Translucency* was measured using Ahler's method as described above.

*Porosity* was determined by soaking freshly struck flakes of the various cherts in a rock dye prepared by dissolving one tablet of red fluorescent dye (manufactured by Formulabs Inc. and available from Ward's Scientific) in one quart of water. A dye concentration of 240 ppm resulted. The flakes were soaked for 24 hours, removed from the solution, and dried without being rinsed. Each flake was then broken in half, and the depth to which the dye had penetrated was measured with calipers. This depth varied considerably, with some cherts showing no visible penetration while others were dyed to depths of 3 or 4 mm. Porosity is usually measured by heating a rock in a vacuum to remove all water and then exposing it to a gas and measuring how much gas is absorbed (Micheelsen 1966:310). The dye method of measuring porosity is not necessarily equivalent to the gas absorption method, and, in fact, the relationship between the two measures is unknown. If this method were to be adapted for wider use, some procedure for driving off water should certainly be included.

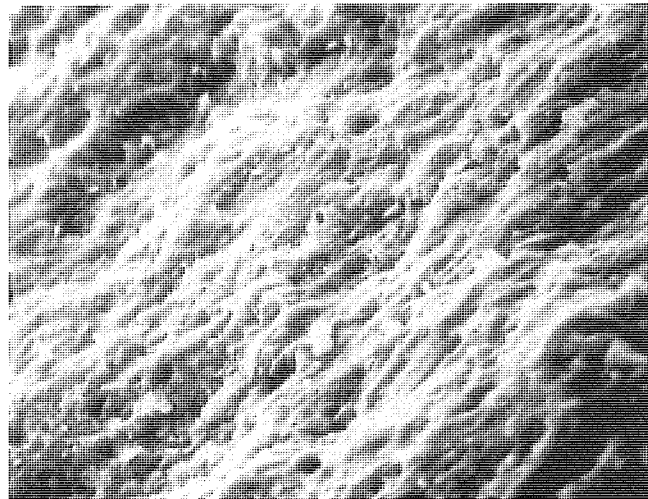
**Figure 5.3**

Scanning electron micrograph of fracture surface of light gray Arkansas novaculite from Magnet Cove, Arkansas (5000x).

Scanning electron micrographs were taken of many of the cherts at a standard magnification of 5000x; all identifying information was written on the back of the photograph. The micrographs were sorted in two different ways many months later to define different aspects of the fracture surfaces. First, they were sorted on the basis of how flat the fracture surface appeared to be; *SEM smoothness* is then a rank ordering from most flat to most irregular. Much later, the same micrographs were sorted by apparent grain, or *SEM grain size*. In most cases, the individual grains are difficult to discern, much less measure, so micrographs were simply sorted into four groups ranging from those that appeared to have the smallest grains to those with the largest grains. Figure 5.3 shows the sample with both the largest grain size and the most irregular surface, and figure 5.4 shows a sample that was judged to be relatively flat and whose grains ranked in the smallest size category.

The result of correlating all these measures is most interesting. Texture correlates significantly and positively with luster, porosity, SEM smoothness and grain size, and even value. In other words, the fine-grained cherts in this sample also tend to be lustrous and low in porosity, to appear flat and small grained under the SEM, and to be dark in color. This all makes considerable sense if grain size is indeed a key variable influencing other visible attributes, and if grain size is determined in part by the presence of impurities. Luster is also correlated significantly with porosity and with value, but neither luster nor porosity are significantly correlated with the SEM measures. Not unexpectedly, the two SEM measures correlate strongly with each other.

Translucency is not correlated with any of the other attributes, suggesting that grain size is not nearly as significant an influence on translucency as are impurities. Furthermore, the kind of impurities appears to be more important than absolute

**Figure 5.4**

Scanning electron micrograph of fracture surface of grey "wall flint" from Grimes Graves quarry area, Norfolk County, UK (5000x).

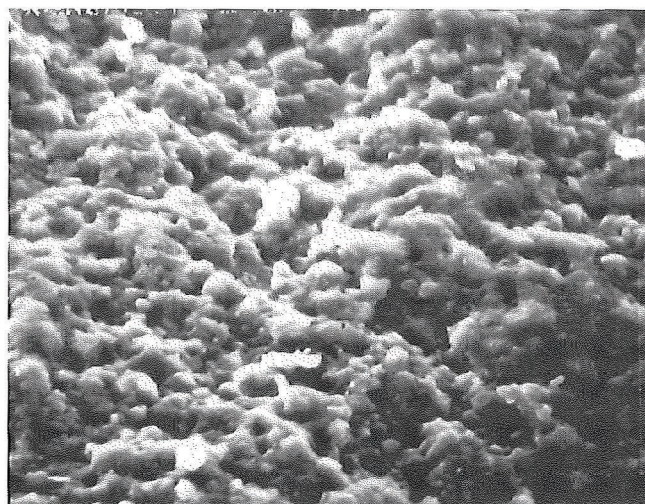
quantity. For example, two of the cherts, English Chalk flint and Knife River flint, contain small amounts of most impurities, and both are dark but translucent. A little organic carbon appears to make a big difference in color value without much affecting translucency. On the other hand, the jaspers are full of opaque impurities and are therefore low in transparency, but they are not very dark because limonite, the predominant impurity, is a relatively light color. Interestingly, the most translucent cherts did not fall at either the high or the low end of the luster and texture scales, but were all in the middle range.

The correlations observed make sense in terms of the physical processes and factors assumed to cause the visible attributes. Much more work will be needed to determine whether these correlations hold true for cherts in general or are simply an accident resulting from the characteristics of this particular sample.

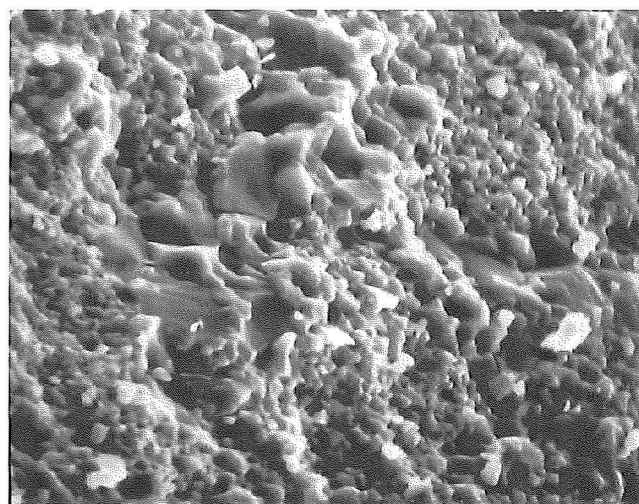
### Variability in Visible Properties

All cherts show at least some variation in their visible properties, but not all visible properties are equally variable within a particular chert type. For example, Flint Ridge chert is highly variable in color but is rather uniform in luster and texture. On the other hand, many varieties of Burlington chert are about the same color, but the quantity of fossils they contain varies a great deal. The scale of variability may also differ. For example, Bayport chert shows considerable variability within a given nodule, but nodules are rather similar wherever they occur.

Variability is not confined to macroscopically visible properties. Ozol examined thin sections of nine samples of chert from different parts of the widespread Onondaga formation. He found a great deal of variability from area to area and even within a single sample. In fact, he believed that the individual members could be



**Figure 5.5**  
Scanning electron micrograph of fracture surface of black Upper Mercer chert from Coshocton County, Ohio (5000x).



**Figure 5.6**  
Scanning electron micrograph of fracture surface of pale gray Arkansas novaculite from Caddo Gap, Arkansas (5000x).

distinguished (Ozol 1963:220). Other analysts have reported similar variability in thin sections from the same chert type (Prothero 1983:345–453). This variability may also be partly responsible for the fact that analysts rarely agree completely in their thin section descriptions of the same chert type (for example, see the description of Onondaga chert in appendix B). Variability is also surely present in the properties visible under the SEM, as demonstrated for Onondaga chert (Ozol 1963).

One might expect that highly localized cherts would vary less in their visible properties than would widespread cherts, but this is not always true. For example, Norwood chert, which only outcrops over approximately 27 km, varies from finely laminated and crossbedded in the west to convoluted or featureless in the east. Similarly, cherts of the Cordell formation range in color from pale gray to chocolate brown in a single outcrop, though other visible attributes are relatively constant. In both cases, the visual variability appears to be greater than the chemical variability. At the other extreme, the visible properties of English Chalk flint, which outcrops across much of southern England, vary little from location to location.

### Summary

The visible properties of cherts are due in large part to impurities since quartz itself is colorless, featureless, transparent, and of glassy luster. Color is primarily caused by impurities, though grain size also plays a role. (The Munsell color charts are recommended as a standard means for describing chert colors.) Translucency is also affected by impurities and to a lesser extent by grain size and is easily quantified using the method recommended in Ahler (1983). Luster and texture appear to be influenced strongly by grain size; however, objective means of measuring these two attributes are still lacking. The distribution of all these properties results in chert's structure, which can probably be conveyed adequately by qualitative descriptions.

Visible properties can be a rich mine of information about a chert and its history, especially when information is available at all the different scales: macroscopic, microscopic, and scanning electron microscopic. Color is an important, although not definitive, clue to the impurities present, and translucency is also indicative of the kind and amount of impurities in a chert. Luster

**Table 5.2 Correlations Between Visible Attributes\***

	Texture	Luster	Porosity	SEM smoothness	SEM grain size	Value	Translucency
Texture	1.000						
Luster	<u>0.799</u>	1.000					
Porosity	<u>0.658</u>	<u>0.633</u>	1.000				
SEM smoothness	<u>0.632</u>	0.369	0.476	1.000			
SEM grain size	<u>0.609</u>	0.340	0.534	<u>0.845</u>	1.000		
Value	<u>0.427</u>	<u>0.593</u>	<u>0.541</u>	0.277	0.204	1.000	
Translucency	-0.186	-0.054	-0.120	-0.134	0.024	0.211	1.000

\*Underlined values are significant at the 0.01 level or less.

and texture are closely related to grain size and to the characteristics of the fracture surface, both of which are relevant to mechanical properties. Structure provides valuable clues as to the history of the chert including how it formed, the microfauna and flora in the area, and how it was altered by diagenetic forces. Further detail on all these aspects can be obtained by examining cherts under the light microscope and the scanning electron microscope. In particular, thin sections can provide information

on the various siliceous and nonsiliceous minerals in chert, which can be helpful in interpreting elemental data and also in determining the history of the chert. Scanning electron microscopes provide detailed views of chert fracture surfaces and are extremely useful for understanding how fractures occur at the microstructural level. Because visible properties can be an important bridge to other chert properties, they deserve further study.

# 6

## Mechanical Properties

Chert's importance to people throughout history is based primarily on the way it breaks. It is one of a relatively few rock types that can be broken in a controlled manner to form a sharp, yet durable, edge. This fracturing process, called flaking, chipping, or knapping, is the principal way in which chert was worked into useful items, although chert can also be ground or abraded into desired shapes. Both stone-working methods make use of, and are constrained by, the mechanical properties of chert, especially its strength, hardness, uniformity, and elasticity. Though the mechanical properties of chert should thus be of particular interest to archaeologists, they are difficult to investigate. For various reasons, there seems to be a large gap between our knowledge of stone tools themselves and our understanding of the mechanical processes involved in their manufacture and use.

The mechanical properties of the raw material most certainly are not the most important factor in the manufacture of stone tools. Inspection of almost any assemblage will show that prehistoric stoneworkers used a wide variety of stone materials, some of them of shockingly poor quality. Skilled stoneworkers can do excellent work on even poor materials because of their control over other more significant variables, such as the shape of the core, how the core is held, the type and shape of the flaking implement, platform preparation, placement of the flaking implement on the core, and the force used, including its direction and the kind of "follow through" (Callahan 1979).

Stoneworkers' skills allowed them to use inferior materials, and they sometimes chose to do so for a number of reasons. One obvious factor is availability; an inferior stone material available nearby would be used more frequently than a superior material

that had to be brought from a distance. Size is another consideration because knapping is a subtractive process; one cannot make a big tool from a small pebble. Sometimes less than optimal materials may have been used simply because they were available in large chunks. Aesthetic considerations may have played a role. Gould et al. (1971:161) reported that some Australian stone tool users "place an aesthetic value on cherty materials of different colors and textures." Even symbolic or ideological factors may have contributed to raw material selection decisions. For example, strikingly colored Upper Mercer chert has strong associations with ritual contexts in early Late Woodland Michigan (Luedtke 1976:373). Indeed, some Australian Aborigines placed high value on certain raw materials of no special color or quality simply because they were obtained from locations of totemic significance (Gould et al. 1971:161-2).

Raw materials can only be judged superior and inferior with regard to the specific tasks or functions they serve. The mechanical properties that are most desirable for a circumcision knife are probably not the same as those for an axe head. Nevertheless, all other factors being equal, present day stoneworkers do make judgments about raw material quality and usually attempt to select the best material available to them. Differences in mechanical properties must have influenced prehistoric stoneworkers' choices of raw materials as well as the procedures they used to knap each material. Furthermore, these mechanical properties influence the ways in which stone tools become worn and damaged during use, an area of special concern to use-wear analysts (Greiser and Sheets 1979; Bradley and Clayton 1987:88).

Thus it is well worth studying the mechanical properties of

chert, but the reader must bear in mind that this is only one small facet of a much larger and more complex issue, that of how stone tools are actually made and used. The most significant aspects of this larger issue, fracture mechanics and procedures for making or interpreting stone tools, will barely be mentioned. The focus of this chapter is deliberately narrow, and only those aspects of the larger issue that are considered indispensable for an understanding of the mechanical properties of chert will be dealt with here. The advantages and disadvantages of two major approaches to studying the manufacture and use of stone tools are considered next, and several important concepts relevant to the processes of fracture and abrasion are introduced. Each of the major rock properties relevant to these processes is discussed, followed by a presentation of specific data that illustrate the range of values for these properties as exhibited by different chert types.

### **Approaches to the Study of Stone Tool Manufacture and Use**

There are currently two general approaches to the study of how stone tools are made and used, which I will call the practitioner approach and the experimental approach. Practitioners include both traditional stoneworkers and replicators, all those people who actually make and use stone tools. Their primary goal is the end product, an artifact of desired shape and attributes, though the replicators are also often concerned with the procedures used to reach that goal. Experimenters, on the other hand, are primarily interested in determining the physical and mechanical principles that underlie the process of making or using stone tools and with the mathematical constants and relationships that describe these principles. They work toward this goal through the use of carefully controlled experiments, often involving mechanical equipment. There is not always a clear dichotomy between the practitioner and experimental approaches, and some people do both, but the distinction is useful as a heuristic device.

The practitioners have undoubtedly had great success in meeting their goals. The ancient art of stoneworking has never entirely died out and persists to the present day in a number of traditional societies around the world. It has perhaps been best documented in Australia but has also been studied by ethnoarchaeologists in New Guinea, Cyprus, Ethiopia, and Highland Guatemala (for example, Hester and Heizer 1973:26–29). Flint knapping was also being practiced in England for a few specialized purposes, primarily the production of gunflints, as late as the 1980s, although the heyday for these activities was the eighteenth and nineteenth centuries (Clarke 1935; Shepherd 1972; Skertchly 1984). Studies of such traditional stoneworkers, for whom stoneworking was simply a normal part of making a living, have produced numerous insights for archaeologists interested in the manufacture and use of stone tools.

In addition, there have been a few individualists within non-

stone-using societies who have taught themselves to make stone tools. They found stoneworking to be a fascinating challenge and a tangible link with the prehistoric people whose tools they have found in plowed fields or eroding out of river banks (for example, Pond 1930). It was not until the 1960s, however, that stone-tool replication entered the mainstream of archaeology, largely through the efforts of Francois Bordes in Europe and Don Crabtree in the United States. The making of stone tools now flourishes again among archaeologists, and many of these modern flintknappers can achieve results equal to the best work produced by the professional stoneworkers of prehistory. The work of these two men is well documented in books, articles, movies, and videotapes, thus affording detailed study. Replication now plays an irreplaceable role in determining how stone tools were made, understanding site formation processes, performing use-wear studies, and generally maximizing the cultural information we derive from lithic remains.

The weakness of the practitioner approach is that it resists objective description. The making (and to some extent the using) of stone tools involves complex motor habits that are built up through a process of feedback after months and years of practice (Callahan 1979:37–38). Much of what good stoneworkers do thus becomes largely subconscious, and it is difficult for them to explain exactly what they are doing. Perhaps as a result, the terminology used by practitioners to describe their work is not well standardized, is sometimes inconsistent, and is often impressionistic or even metaphorical. Despite the best efforts of many replicators, stoneworking remains a skill that must be learned apprentice fashion or by trial and error.

The experimental approach, on the other hand, uses the methods and insights of engineering and materials science in order to study stoneworking. The goal is to define the major variables and to express the relationships among them mathematically (for example, Speth 1972; Faulkner 1972; Tomenchuk 1985). Experimenters use the findings of materials science to suggest which variables are likely to be most important. Then they attempt to structure experiments in which as many variables are controlled as possible so that the relationships among the remaining variables become clear. Because of this need to simplify, they often use standardized test equipment (for example, Bonnichsen's "Stainless Steel Indian" [1977:78–80]) and unretouched flakes or artificial materials, such as glass shaped to geometric forms, rather than actual stone tools. Such experiments are often very remote from the actual conditions under which stone tools were made and used. Furthermore, simply because so many variables are involved in stone working and each must usually be tested individually, the experimental approach is necessarily time-consuming.

An additional difficulty of this approach is its inherent interdisciplinary nature. An archaeologist starting out in this direction is confronted by formidable terminological and conceptual barriers. The literature of rock mechanics and engineering is

full of unfamiliar terms (many of which are defined by mathematical expressions rather than words alone). In addition, a number of these terms are used rather differently by materials scientists who work on different materials. Even worse, familiar words are used in unfamiliar ways; some common words are used in very narrow and restricted senses, while others are subdivided into a bewildering variety of properties or processes. For example, the first definition of the word *hard* in the New World Dictionary (2nd ed.) is, "not easily dented, pierced, cut, or crushed; resistant to pressure; firm and unyielding to the touch; rigid; solid and compact." This definition includes at least seven different mechanical properties as defined by engineers, some of which are closely related but others which are not.

To add to the confusion, most of these properties can be measured by more than one test, but the results of the different tests are not directly comparable. Furthermore, several different notational systems for expressing the results of these tests are in simultaneous use, some based on the metric and some on the English measuring system. No wonder all but the most intrepid archaeologists are inclined to flee from the experimental approach!

A less obvious concern is that some materials scientists deal with problems that are at quite different scales from those with which archaeologists are concerned. The findings of materials scientists working with glass and ceramics are often similar in scale to archaeological problems. However, most engineers and materials scientists who study stone are interested in either engineering and mining applications (stone used for construction, stone through which mines and tunnels must be built, and stone as a footing for buildings, and dams) or in structural geology (how rock bodies respond to earthquakes, faulting, and mountain building) (Jaeger and Cook 1979:1). While their laboratory experiments are necessarily based on small pieces of stone, they are primarily interested in the behavior of rock in large volumes, often bedrock, and with large forces and pressures. There is growing recognition that the behavior of materials under stress may even conform to different mathematical models at different scales (Ingraffea 1987). Thus, some of the conclusions rock mechanics researchers reach may not always translate easily to an archaeologist's problems, which usually involve relatively small fragments of rock under lesser pressures. For example, the behavior of a particular stone type under the pressure of a bridge abutment may be irrelevant to the behavior of that same stone type when it is pressed by an antler flaker.

To some extent, the strengths and weaknesses of the practitioner and experimental approaches are complementary, and the projects that make the best progress successfully combine both. Practitioners are likely to have useful ideas about what variables are most important for a given problem and are needed to keep projects firmly anchored in the reality of stoneworking in the face of the experimentalists' tendency to drift off into abstraction. On

the other hand, experimenters are needed to define variables unambiguously, to measure them accurately, and to discover how they relate to one another.

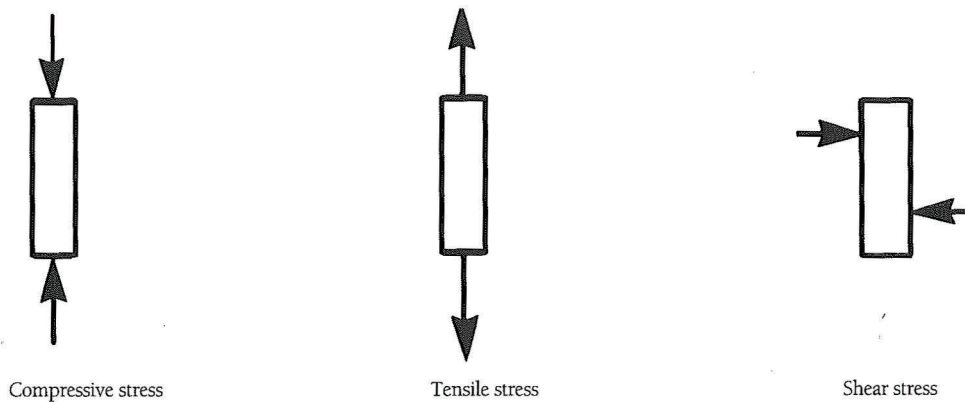
## Fracturing Chert

The most important mechanical properties for our purposes are those governing the way chert breaks. For this discussion, I assume that the reader has a basic understanding of the major processes of stoneworking and the descriptive terminology used by archaeologists at the level obtainable by reading Crabtree (1972) or almost any introductory text. All other terms are defined when they are first used in the text; most are also in the glossary. Fracturing is discussed on a generalized level without specifying what is being broken or what has caused the breakage. Thus, the object being fractured could be a chert nodule at a quarry, a prepared core, a projectile point being resharpened, or a scraper being worn during use. Similarly, the object whose pressure or impact breaks the chert object could be a hammerstone, an antler tine, a wooden or antler billet, a piece of wood being worked into a spear, or even a bit of grit caught in a hide.

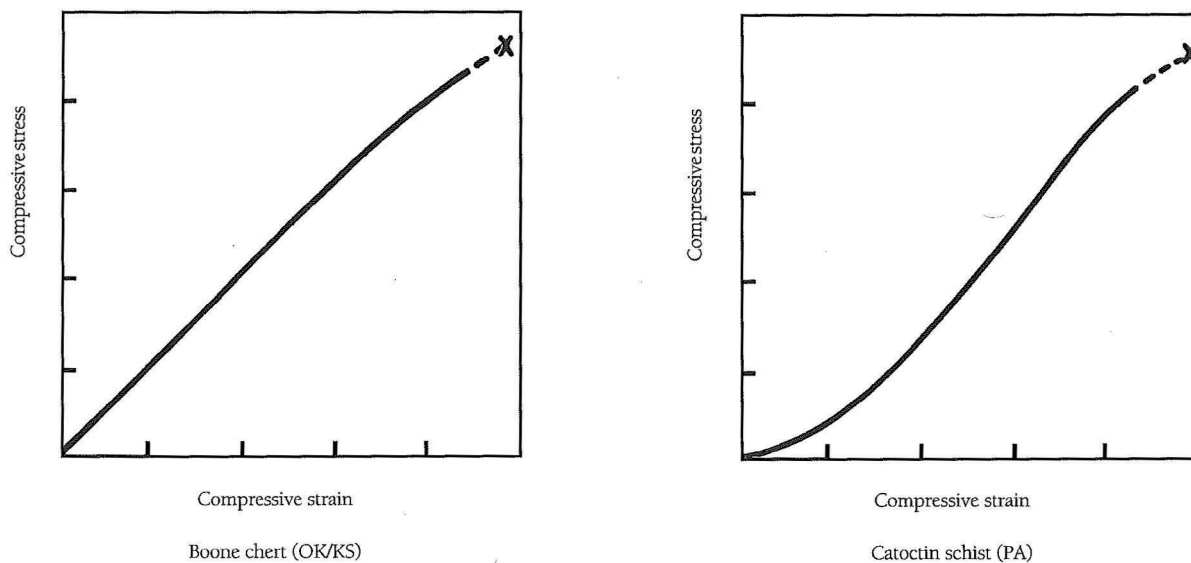
Whenever two objects are pressed together, whether it be an antler tine flaker against a biface or a scraper against a hide, they are placed under stress. Stress, defined as "the force exerted on an object per unit area," is generally measured either in some multiple of grams per square centimeter or in pounds per square inch. For a given force, stress increases as the area affected decreases; a heavy weight stresses your body much more when it is suspended by a string from your finger than when carried in a backpack. Stress can be either static or dynamic, and materials often respond differently to these two forms. Static stress is constant or slowly changing and relatively long term, such as that exerted by a building on its foundation. Dynamic stress is sudden and short term, such as that exerted by an explosive charge in rock or by a sledgehammer striking an outcrop. Pressure flaking is an example of quasi-static stress, while percussion flaking, which can be associated with velocities of impact in the range of 300 to 1,000 cm/sec. (Speth 1972:45), could be considered dynamic stress. The difference in velocities involved in these two methods of flaking stone may not be great enough, however, to affect the mechanical properties of the stone significantly (Cotterell and Kamminga 1987:680).

Materials respond differently not only to the duration of stress, but to the direction and kind of stress. Stress can be compressive, tensile, or shear (fig. 6.1). Compressive stress presses inward on an object from two or more directions, such as the stress exerted by a vise. Tensile stress occurs in stretching, as when an object is pulled apart. Shear stress distorts a material without stretching or compression by causing contiguous parts of the object to slide across each other. While all three kinds of stress are present in any stone tool flaking situation, tensile stress is the most important to archaeologists. Chert is a brittle material, and brittle



**Figure 6.1**

Compressive, tensile, and shear stresses.

**Figure 6.2**

Examples of stress strain diagrams. (left) Response of a brittle elastic material, Boone chert from the Oklahoma/Kansas area. (right) Response of a more deformable schist from Pennsylvania. (Both diagrams after Blair 1955:43X)

materials are least resistant to tensile stresses. Therefore, chert usually breaks because of the tensile stresses exerted upon it and is less affected by compression and shearing stresses.

Materials placed under stress can respond in three different ways. If they undergo a reversible (and usually temporary) change of shape, their response is said to be elastic. If they change shape or deform irreversibly, their response is said to be inelastic. The terms plastic and ductile are often used to describe inelastic responses, with the latter term being used primarily for materials that elongate, as do many metals. The change in the form of an object as a result of stress is called strain, and it is measured as the ratio of the change in length to the original length of the object. Strain applies to both temporary and permanent deformation. When the stress becomes too great for the material to withstand,

the material breaks.

Most materials respond differently to different levels and kinds of stress. A rubber band normally behaves elastically under tensile stress, but will break if the stress becomes too great. Metals often behave elastically under low stress, become ductile after a certain point called "yield stress," and ultimately break. Stress/strain diagrams are used to show how a specific material behaves under increasing stress (fig. 6.2). These diagrams are determined empirically by making standard size cylinders of a material (usually about 2 inches long and 0.5 inch in diameter) and subjecting them to increasing levels of stress. Strain is measured at the same time by strain gauges or by the change in length divided by the original length.

On the whole, chert shows little inelastic response to stress.

Kamminga (1979:148) has argued that the very surface of quartz crystals or grains may behave plastically under low stresses because of the presence of a layer of disordered silica only about  $0.01 \mu$  thick. He suggested that this plastic response may be relevant to the formation of some polishes on stone tools. In addition, there is a zone of stress at the tip of an expanding crack that apparently does not behave in a perfectly elastic manner (Atkinson and Meredith 1987:12). However, the rest of the chert behaves elastically under low stress; primarily, it absorbs the stress through adjustments on the molecular level, without permanently altering its shape (Faulkner 1972:37). Chert does not bend or stretch as visibly as does rubber, but its elasticity can be demonstrated. Indeed, a remarkable series of high-speed photographs of blades being removed from polyhedral cores includes several good examples of what certainly appears to be slight elastic bending in glass, a similarly brittle material (Crabtree 1968).

Chert breaks when it undergoes more stress than it can handle elastically. Materials that break at or near yield stress, without inelastic deformation, are said to be brittle; thus, chert is often referred to as a brittle elastic solid.

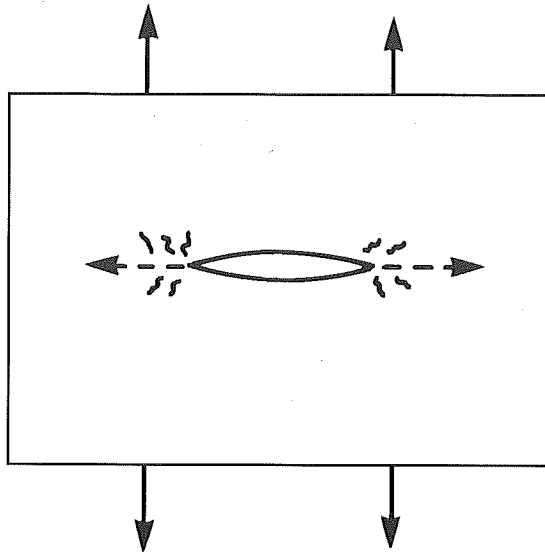
When materials break they either cleave or fracture, depending upon the nature of the atomic bonds in the material and the kind of force exerted. Some materials have lines of weakness built into their crystalline structure because the atomic bonds are stronger in some directions than in others. Breakage that results in smooth, flat planes along these crystal faces is called *cleavage*. For example, mica cleaves into flat plates, and galena into cubes. Quartz has very weak cleavage along several of its crystal faces (Fronde1 1962:104), and this is part of the reason crystal quartz is a difficult material to knap (Crabtree 1967:10–11). When a material breaks along surfaces that do not coincide with a crystal face, they are said to have fractured. Fractures are usually described as being either splintery, hackly, irregular, or conchoidal (curved and shell-like), the last being typical of many materials. Some materials have both cleavage and fracture; for example, fluorite has octahedral cleavage and conchoidal fracture. Chert only fractures, usually conchoidally.

For any type of breakage to occur in a material, the bonds between atoms must be broken. Therefore, the fracture strength of a material should be equal to the amount of stress needed to break its weakest atomic bonds. Theoretically, we should thus be able to calculate the strength of any material for which we know the chemistry and crystalline structure. In reality, however, no material is even close to its theoretical strength. In the 1920s, A. A. Griffith suggested that, for glass, this discrepancy between the theoretical and actual strength was caused by tiny cracks on the surface and inside the material. Such cracks can weaken a material significantly, just as a glass cutter weakens a pane of glass with a thin scratch enabling the pane to break exactly where wanted under relatively light stress. These so-called Griffith cracks are not visible macroscopically, but they can be seen on etched glass

surfaces. They may be on the order of  $0.01 \mu$  wide and  $0.1 \mu$  deep (Jaeger and Cook 1979:327). Some cracks form when the surface of glass is damaged, while others develop as the glass weathers.

Cracks are now viewed as being crucial to the mechanical properties of many other materials as well. In rocks, Griffith cracks are assumed to be about equal in length to the grain diameters, most often from 1 to  $100 \mu$  in length (Lawn and Marshall 1979:66); they are inherent in the structure of the material. McClintock and Walsh (1962) modified Griffith's theory to take into account the fact that some cracks close under pressure, thereby increasing the strength of the material. In general, the mathematical expression of this modified Griffith theory agrees well with actual strength values for many brittle materials (although it is less successful in explaining why undamaged glass is also weaker than it theoretically should be). The Griffith theory also provides a good explanation for the size effect, whereby small fragments of a material are generally found to give higher strength values than do larger fragments of the same material. For example, the tensile strength of a glass fiber 5 mm long is  $150 \text{ kg/mm}^2$ , but that of a glass fiber 90 mm long is only  $76 \text{ kg/mm}^2$  (McClintock and Argon 1966:491). Put simply, the larger the fragment, the greater the chance that it will contain cracks of dangerous size and shape, and the more easily it will break.

Chert, with its inherent lines of weakness between quartz grains and along fossils, veins, and other inhomogeneities, should have numerous Griffith cracks. Since fracture nearly always starts at cracks on or near the surface of a material (Tomenchuk 1985:60), procedures such as the grinding of striking platforms introduce even more cracks that are especially likely to weaken the material. Cracks are so critical to fracture because many kinds of stress can cause a high level of tensile stress to become concentrated at the tips of cracks in the material (fig. 6.3). Thus, even when the stress exerted on the object as a whole is relatively low, the stress affecting the material just at the edge of a crack can be very high. If stress exceeds a critical amount, the crack will begin to enlarge or propagate. As the crack grows, a fracture surface is created. This surface has elastic energy because the atoms just at the surface are not fully bonded to surrounding atoms. Once crack propagation begins, for example as a flake begins to separate from its core, "...the stress concentration due to the elongating crack steadily increases, and the released elastic energy exceeds the surface energy by increasing amounts, so that the fracture process accelerates and reaches very high speeds in a short time" (McClintock and Argon 1966:500). However, if the general stress field away from the crack does not remain constant the crack cannot accelerate so rapidly, and this may often be the case in knapping situations (Tsirk, personal communication). Faulkner has determined that fracture velocities of 28 to 230 m/sec are typical in cracks resulting from pressure flaking and up to 1,500 m/sec in cracks caused by percussion flaking (Faulkner 1972:121). This latter speed is relatively close to the 2,000 m/sec



**Figure 6.3**

A crack, propagating perpendicular to the axis of tensile stress.

velocities produced by explosive dynamic loading (Shockey et al. 1974:314). Cotterell and Kamminga (1979:107) argue, however, that characteristics of surface features indicate that most cracks propagate at lower velocities, less than 1,000 m/sec.

When chert is stressed all the inherent cracks and flaws within the zone under stress are affected to some degree, though exactly how they respond depends on their size, shape, and orientation. When such cracks begin to propagate, they grow in the general direction that is perpendicular to the greatest tensile stress (Lawn and Marshall 1979:66). Along this general trajectory, a crack will attempt to follow the line of least resistance, where atomic bonds are weakest. Cracks coalesce and join wherever possible. In chert, cracks usually go around quartz grains rather than through them (Folk and Weaver 1952; Mandeville 1973; Purdy 1974; Griffiths et al. 1987). This is probably owing partly to impurities, which are concentrated along grain boundaries, and partly to the characteristics of the grains. As discussed in chapter 2, "When a crystal consists of highly polarizable anions of large size, together with small, highly charged cations, then the anions will be pushed to the surface of the crystals and the cations will be recessed. Thus in a microcrystal of quartz oxygen ions predominate at the surface, while the silicon ions are depressed. It is believed that each microcrystal of quartz then "has a negatively charged 'skin', and effectively repels adjacent randomly oriented microcrystals" (Folk and Weaver 1952:507–508).

If a crack develops enough velocity to propagate all the way across a body of chert to the outer surface, the chert will fracture. The overall shape of a fragment produced by fracture is controlled by the distribution of stresses within the core or tool. As mentioned previously, all three kinds of stress are generally present in stoneworking or use situations. For example, pressure flaking first

involves compression, which inevitably results in tensile stresses (fig. 6.4) and shear stresses (not shown) that are perpendicular to the other two. These stresses are distributed differently depending on what is being done to the tool or core. Faulkner (1972) used a photoelastic polymer to show how stresses were distributed in a core from which blades were being removed by pressure flaking, but one can visualize very different stress lines in a nodule being quartered by percussion, a knife edge encountering a tendon, or a blade that is stepped on while it lies on a concrete lab floor.

Fractures in chert can result from impact, pressure, bending, thermal shock, and a variety of other processes. Exactly how these different processes operate is a complex issue that is dealt with in the literature of fracture mechanics (for example, Cotterell and Kamminga 1987). The different types of fractures resulting from these processes can often be differentiated by their shapes, locations, and patterns of fracture markings such as ripple marks, hackles, or Wallner lines remaining on fracture surfaces (Cotterell and Kamminga 1979). While most of these fracture characteristics result primarily from factors extrinsic to raw material properties, raw material type may sometimes play a role. Most flake features certainly show up more clearly on fine-grained materials, and some features are not even manifested on certain other materials. In addition, fracture type may sometimes be influenced by grain size (Hayden and Kamminga 1979:7), and flake terminations are apparently affected by the material. Some raw materials appear to be more prone to hinge fractures than others (for example, Tsirik 1979:92), as will be discussed later. In general the relationship between fracture form and raw material type remains an area for further investigation.

## Abrasion of Chert

The only other important process by which chert can be worked is abrasion or grinding. This was done most often to form the bits of axes and adzes but was also used to create ornamental or decorative objects. Abrasion also occurs during use, as the tool rubs against its haft or against the material being worked. Chert can also be abraded by wind or water action or as a result of trampling by animals or machinery. Abrasion removes material from the surface of chert through several processes, including microfracture, removal of individual quartz grains through attrition or adhesion, and separation of chemical bonds that allows individual quartz molecules to break free (Rabinowicz 1965).

Abrasion can either roughen or smooth a surface, depending on surface characteristics of both the object and the abrader. The process is affected by numerous factors, including the size, hardness, and angularity of the abrading particles; the hardness of the material being abraded; and the presence of water, fat, or other fluids in the system (Kamminga 1979:152). Besides the obvious scratches and smoothing that result from abrasion, the surfaces of individual quartz grains are altered. Abraded quartz surfaces develop a thin layer of strained and disoriented silica about 0.03

$\mu$  thick or more (Fron del 1962:111–112). This layer is partly crystalline but has some of the properties of amorphous or hydrous silica, and is much more easily dissolved than intact quartz.

Abrasion can produce polish on chert surfaces, but polish is probably not due only to abrasion. It has been argued that some polish results when silica adheres to the surface of a tool. There is increasing support for the belief that some polish results from a chemical reaction between chert and silica-bearing plants which causes the surface of the chert to partially dissolve (Del Bene 1979; Unger-Hamilton 1984). The extent to which either polish or abrasion is affected by the mechanical properties of chert is virtually uninvestigated.

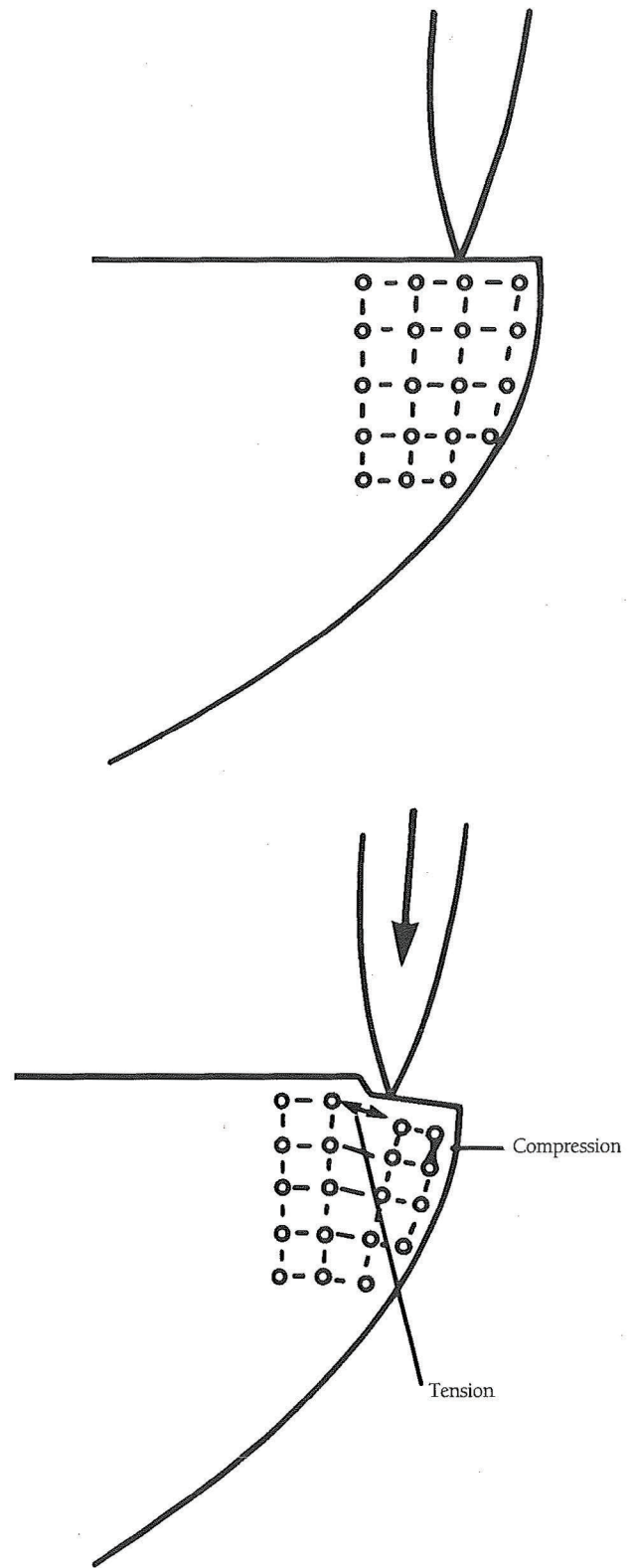
## Mechanical Properties

Some cherts fracture and abrade more easily or controllably than others, indicating that mechanical properties vary among cherts. Both traditional stoneworkers and replicators have definite and strong opinions as to what qualities make a material good for knapping. The commonalities in their accounts concerning these qualities provide a framework for discussing material properties. Each quality is introduced, correlated with the relevant properties defined by materials scientists, and related to other aspects of cherts. Numerical values will be given in the last section of this chapter.

### Homogeneity and isotropy

Homogeneity is usually the first property stoneworkers mention. As Crabtree says, the ideal lithic material "...must be of an even texture and relatively free of flaws, cracks, inclusions, cleavage planes and grains" (Crabtree 1967:8). The best material should have no surprises. Inhomogeneities cause fractures to be deflected as they move through the material, resulting in broken flakes, broken tools, hinge fractures, and general unpredictability of flaking. Large flaws make fracture more likely in some directions and places than in others; they make it much harder for the knapper to control the fracture process.

Practitioners often recommend testing for homogeneity by simply breaking open the material and looking at it. Sound is also commonly used in testing. For example, Clarke reports that the Brandon flintknappers tapped nodules lightly with a hammer to judge the quality of the chert under the cortex or "coat": "If the hammer falls dull and jumps, the stone is double-coated or of mixed color beneath the coat. If the stone is cracked, it flies to pieces. If on the other hand the coat is hard and the flint sound, the hammer rings" (Clarke 1935:49). Crabtree (1967:9) also suggests tapping a nodule lightly and listening to the sound it makes. If one hears a dull tone, the stone has flaws, but if it has a sharp ring, it is probably good. Binford and O'Connell (1984) describe how Australian Aborigines use a similar procedure to



**Figure 6.4**

Compressive and tensile stresses in a core being pressure flaked.

judge the quality of quartzite, suggesting that this procedure may have been used by stoneworkers worldwide. Material scientists find that the velocity of sound waves in rock is indeed affected by elastic properties and density, and especially by the presence of cracks and fissures (Goodman 1980:39).

Isotropy differs from homogeneity. A homogeneous material has the same properties at each location within it, while an isotropic material has mechanical properties the same in all directions. For example, a homogeneous chert nodule would have no flaws or cavities, while an isotropic chert nodule would have the same strength no matter how it was oriented in the testing equipment. On the other hand, if a material is anisotropic, orientation matters a great deal. For example, shale has greater compressive strength perpendicular to its bedding plane than parallel to its bedding plane. Because of its crystal structure, quartz is slightly anisotropic for most mechanical properties as it is for some visible properties (see chap. 2, this vol.). However, if the quartz grains are assumed to be randomly oriented, chert should be isotropic.

There are a number of reasons why some cherts are less homogeneous and/or less isotropic than others. Some have large internal fissures and flaws, some have unevenly distributed fossils, and others have large patches of other minerals, such as unreplaced matrix. Cherts exposed on the ground surface may be frost fractured. Laminations owing to heavy concentrations of impurities along deposition planes may cause a material to be weaker in some directions than in others, and thus both inhomogeneous and anisotropic. For example, some varieties of Knife River flint have "weak irregular parting along former bedding planes," making them unsuitable for knapping (Clayton et al. 1970:287). Silicified wood fractures preferentially parallel to the long axis of the original branch or trunk (Sigleo 1978:1399). In some cherts, grain texture varies considerably. Callahan (1979:150) has pointed out that areas of coarser grain texture appear to slow the velocity of fracture.

Some cherts may be slightly anisotropic even when they appear to be visually homogeneous. For example, Clarke (1935) reports that the Brandon flintknappers believed some nodules of English Chalk flint had a "grain" that caused them to fracture more easily in some directions than in others. Chalcedony ought to be anisotropic because of its fibrous structure, though this premise has not been tested to the best of my knowledge. Some of us who have worked with cherts having a banded or laminated structure have noted that the main axis of many prehistoric tools made of these cherts is either parallel or perpendicular to this banding. This orientation could be for aesthetic purposes, but may also be a response to mild anisotropy. Jones and Knauth (1979:593) report that "Preferential orientation of the  $c$ -axis of chert grains parallel with bedding is common in eastern [Arkansas] novaculite samples," probably due to silicification produced under significant pressure from overburden. Laboratory experiments also

suggest that metamorphism may cause the alignment of quartz grains in chert (Green 1967). Such nonrandom orientation of chert grains should result in anisotropism for some mechanical properties.

On the other hand, not all visually inhomogeneous materials are mechanically anisotropic. In one of the few cases where isotropism in chert has actually been tested, a block of Arkansas novaculite with what appeared to be obvious parallel flaws was tested both parallel and perpendicular to the plane of the flaws. No significant difference was found. "We conclude that the dynamic tensile strength of Arkansas novaculite is insensitive to the orientation of the pre-existing flaws" (Shockey et al. 1974:305). Unfortunately, the authors do not report exactly where the test specimen was obtained. Some Arkansas novaculite at the eastern end of its outcrop area has been subjected to metamorphism, and it would not be surprising if this heat and pressure had "healed" the flaws that originally existed in the material. Crabtree also points out that some apparent flaws, such as the chalcedony veins in certain jaspers, have approximately the same mechanical properties as the matrix and thus do not cause trouble for the knapper (Crabtree 1967:12).

Even if some cherts are anisotropic, the differences may be subtle enough so that knappers can compensate for them without even necessarily being aware of them. Mewhinney (1957:30) insists that he has not detected a "grain" even in concentrically banded nodules. Nevertheless, given the variability in chert origins, chemistry, and structure, it is probably not wise to assume that all cherts are as perfectly isotropic as they may appear to be.

## Strength

Strength, also called toughness or tenacity, is a measure of how much force must be applied to produce a fracture or, as Crabtree (1967:9) says, "The amount of resistance to the necessary force required for detaching a flake." On the whole, most practitioners seem to prefer that this quality be low, presumably in part to save wear and tear on muscles, but more importantly to allow greater control. A stone that has to be hit very hard cannot be hit as accurately as one that requires less force. In addition, certain stoneworking techniques, such as pressure flaking, cannot be performed on very strong materials. On the other hand, a material that fractures too easily will be prone to unwanted fracture during manufacture; it will also fracture easily during use. Thus, the knapper who is judging materials for strength must perform a balancing act in which the task for which the tool is intended plays an important role. Tools that will be subjected to a great deal of stress, such as axes and hoes, must be of stronger chert, while those for which a thin, sharp edge is desired will usually require a weaker and finer-grained chert.

This rather ambivalent attitude toward strength is well reflected in Callahan's (1979:16) table of raw material types, arranged in order based on "ease of workability." Strength peaks in

the middle of the range rather than at either end. The most workable materials, at the low end of his scale, are relatively weak. They should be worked with softer billets or flakers, and they require special procedures to keep platforms from collapsing. Materials at the high end of Callahan's scale, the least workable, are also somewhat less strong and are prone to hinge and step fractures. Presumably, fractures start easily in materials at this end of the scale but do not propagate all the way through the stone, as desired.

Most practitioners state that "workability" is a function of how fine grained (or fine textured, or smooth textured) the material is. Fracture in such materials is said to be easily controlled and results in very sharp edges (Crabtree 1967:15). Thus the best materials appear lustrous. For example, Mewhinney (1957:27) recommends that the prospective knapper "Knock off a flake and rub the scar with your thumb. The slicker it feels, or the shinier it looks, the better the flint will be." Crabtree (1967:9) suggests judging the quality of stream cobbles by looking for little percussion marks on their surfaces. He says that cobbles without such marks will be too coarse to be worked easily.

While workability (as defined by the practitioners) is not identical with strength, strength clearly plays a major role in determining how easily a material can be worked. Strength is also one of the most important properties of a material from an engineering standpoint, because so many of the situations with which they deal involve questions of whether or not a material will break. Unfortunately, there is no single measure of strength for a material because materials respond differently to different kinds of stress, as discussed above.

Brittle materials, such as chert, are nearly always strongest under compressive stress. Compressive strength is also the easiest kind of strength to measure. Blocks or cylinders of a material are simply squeezed in a machine much like a vise and put under increasing pressure until they break. The compressive strength of a brittle material is usually eight to ten times greater than its tensile strength (McClintock and Argon 1966:491). Tensile strength is much harder to measure because of the difficulty in devising a way to grip the sample securely so it can be pulled apart by pure tensile stress. Most testing apparatuses introduce extraneous stresses around the part of the sample that is gripped by the machine, and the first fractures occur in these areas. Thus, many values for tensile strength are actually determined indirectly by applying a formula to the values obtained from certain tests of compressive strength or by calculating from the results of bending or flexural tests. Shear strength appears to be even more difficult to measure and is rarely discussed, probably for that reason.

According to the rock mechanics literature, the major intrinsic factors controlling rock strength are (1) mineralogy, (2) grain size, (3) the extent to which grains are interlocked, (4) cracks and pores, and (5) the presence or absence of water. (Rock strength is also a function of extrinsic factors such as impact velocity, size

effect, and the size of the area being stressed, but these will not be discussed here.) Quartz is relatively strong because of its tight crystalline structure, and, in general, the more quartz a rock has, the stronger it is (Vutukuri et al. 1974:61). Cherts, with their high quartz content, generally fall within the range of compressive strengths engineers label as high to very high (Hatheway and Kiersch 1982:306).

The tensile strength of rocks is also strongly affected by the strength of the individual mineral grains, as well as that of the cement between them (Winkler 1973:41). Although there is no way to test this premise with the available data, I predict that the tensile strength in chert is partially affected by the proportion of impurities, most of which are weaker than quartz. As for shear strength, the limited data available suggest that silica-rich rocks have unusually high shear strength. Handin (1966) found that quartzite, obsidian, and even opal (normally quite a weak rock) have very high shear strength. Lundborg (1968), who tested "flintstone" from Skåne, Sweden, found it is more than twice as strong in shear as the next highest material he tested, a granite.

With regard to grain size, both compressive and tensile strength generally increase with decreasing grain size (Winkler 1973:41; Stagg and Zienkiewicz 1968:303). Materials with larger grains have larger inherent flaws along the grain boundaries, and large grains also absorb stress less effectively than small grains. On the whole, fine-grained rocks with many small flaws evenly distributed throughout the material resist fracture better than coarse-grained rocks or rocks with irregular grain sizes. However, some large-grained materials resist crack propagation because the fracture must change direction at each grain boundary (Lawn and Wilshaw 1975:116). In addition, materials in which the grains are interlocked are generally stronger; cracks are continually retarded as they search for a way around or through the grains (Lawn and Marshall 1979:66). The chemical and physical changes resulting from weathering also tend to blunt the ends of cracks.

Cracks, pores, and other openings are extremely important strength-controlling features because they concentrate tensile stresses at their edges and are very prone to fracture. Thus, pores (more or less spherical cavities) and cracks (flat cavities) weaken a rock considerably (Howarth 1987; Vutukuri et al. 1974:115). The shape, size, and orientation of these openings are important. Pores and cracks with round ends do not break easily, but cracks with sharp ends do. Longer cracks are also more dangerous than short ones; breaking strength is inversely proportional to the square root of the crack length (McClintock and Argon 1966:491). The orientation of cracks can also affect strength, an effect noted by glass researchers (Mecholsky et al. 1977) and flintknappers (Tsirk 1981:3).

Most cherts have many types and sizes of openings. Some openings, often the holes left where fossils or calcite crystals have dissolved, are macroscopically visible, but most are much smaller. For example, Purdy (1974:51) reported that only 0.14% of the

openings in her medium-grained Ocala chert were greater than  $370.8\ \mu$  in diameter, and 28% were less than  $23\ \mu$  in diameter. These smaller openings include tiny spherical bubbles that apparently occur primarily on the faces of the quartz grains and that may contain fluids. The largest are 1 to  $2\ \mu$  in diameter but most are about  $0.1\ \mu$  in diameter (Folk and Weaver 1952:502). Some of the pores and micropores are interconnected. Midgley (1951:183) calculates that these vary from about 0.02 to  $0.28\ \mu$  in diameter. Chalcedony also has coalescing tubules parallel to the fibers, most of which are about  $0.1\ \mu$  in diameter. Porosity from all these causes generally increases with weathering and decreases with age and depth of burial as openings are filled (Goodman 1980:23).

In general, cracks are considered more important than pores in influencing strength because they are more angular. Most cracks are assumed to be roughly round and flat, or "penny shaped," and to vary from less than 1 to more than  $20\ \mu$  in diameter. Many are inherent in the structure of the chert and coincide with grain boundaries. Sprunt and Brace (1974:140) found that most of the natural cracks in unstressed rocks have blunt or rounded ends and thus are relatively resistant to fracture.

Cracks can also be induced in chert. Callahan (1979:88) has noted that the working of chert can initiate cracks which later fracture, and Bonnichsen (1977:110) notes that most knappers, practicing a "conservation of energy" approach, start by hitting a stone as lightly as possible and gradually increase the force as needed, thus making it very likely that at least some new cracks are introduced. On the whole, cracks that have been induced by heating or mechanical pressure are sharper and longer than natural ones (Sprunt and Brace 1974:147) and therefore more likely to fracture.

The presence or absence of water affects the strength of chert. Cherts usually contain about 1% water by weight, some of it located in cracks and pores and the rest within the structure of the quartz and other minerals. Quartz becomes much weaker when tested in water (Frondele 1962:109), and its strength diminishes with increasing porosity (Broch and Franklin 1972:687). The primary reason for this effect is that water bonds to the surfaces of quartz plates and grains, with hydroxyl ions joining to the silicon ions. With one of these bonded layers on each quartz surface, the quartz layers are joined only by a relatively weak bond between two OH molecules instead of the much stronger Si:O bond; it is therefore much easier for fractures to start (Kirby and McCormick 1984:145). High temperatures increase this effect, but it also operates to a lesser extent at low temperatures.

Cracks may propagate more easily if water is present in the system. In dry chert, a fresh fracture creates two surfaces with numerous unbonded silicon and oxygen ions that tend to rejoin, thus limiting crack propagation. Water, on the other hand, bonds with the silicon ions and allows the fracture to proceed (Sieveking and Clayton 1986:288). Water on the surface of a core, in

particular, helps cracks to start, although it does not affect propagation because the surface water cannot spread as fast as the crack is moving (Kerkhof and Müller-Beck 1969; Tsirk 1981:12). Water may also affect strength through a variety of other mechanisms. Under relatively static loading, water can develop pressure that causes further weakening (Goodman 1980:79). Also, according to Patterson and Sollberger (1979:50) water "fills voids and pores in the physical structure with a liquid that acts as a hydraulic medium to allow more uniform transmission of force."

There are numerous ethnographic accounts of stoneworking people, including the Brandon flintworkers (Clarke 1935:49), who consider the moisture content of chert to be important to its knapping qualities. For example, the Lacondan Maya judge moisture content by the color of the chert. They will carefully soak or dry chert nodules in the sun to bring them to just the right condition for knapping (Clark 1982). Impressive quarry pits and even mineshafts in areas where the same chert is also available on or closer to the ground surface provide concrete proof that prehistoric people considered buried chert, moist and unweathered, to be superior enough to justify expending considerable effort to obtain it.

On the other hand, several other practitioners, most notably Mewhinney (1957), Skavlem (Pond 1930), and Callahan (1979:64), have argued that moisture content does not affect the quality of chert. This difference in perception is likely to reflect variability in cherts. Some cherts are simply less porous, or the pores do not interconnect; therefore, they do not gain or lose water easily. For example, Skavlem buried Tennessee flint in the mud of a spring for 2 years. At the end of that time, he saw a color change where moisture had penetrated about 6.3 mm into the surface, but he did not detect improvement in flakeability (Pond 1930:23). After soaking samples of a number of different types of chert, Patterson and Sollberger (1979) found no change in the workability of a glossy chert from Georgetown, Texas, or of heat-treated chert.

Other relatively porous cherts can gain and lose water rather rapidly (Purdy 1974:37-41; Mandeville 1973:199). Patterson and Sollberger (1979:50) reported soaking six 1 to 3-cm-thick flakes of "chalky textured" Belton Lake chert in a green dye for one week; the dye penetrated throughout. This soaking markedly improved workability, but the chert dried out and became less workable after only eight to twenty-four hours in the air, or even less time in direct sunlight.

In general, then, differences in the strength of different cherts are owing to a number of factors, including quartz grain size and shape, the number and shape of cracks and pores, water content, and perhaps the quantity and kinds of impurities. Some of these factors are intrinsic in the cherts whereas others, especially water and crack content, can be manipulated to some degree by stoneworkers. Research is still necessary to determine which of these factors influences strength the most.

## Elasticity

The third property often mentioned by practitioners is variously called elasticity, flexibility, or pliancy. Most practitioners associate elasticity specifically with the ability of a lithic material to resist unwanted fractures, such as end shock or step and hinge fractures. Elasticity is an especially confusing property because we normally use the word elastic to refer to materials that stretch, like rubber. Chert, and rocks in general, are clearly not stretchy. In rock mechanics, however, elasticity simply means the ability to deform without a permanent change in shape. Deformation is said to be elastic if strain returns to zero after the stress is removed. Note also that elastic may be used by materials scientists in two ways: to refer to a state of deformation or to characterize a material (as more or less elastic than another material). Although we cannot actually see the deformation chert undergoes when it is stressed, such changes do occur and can be measured.

Elasticity is measured by several different parameters, all of which essentially deal with different aspects of the change in shape that accompanies elastic behavior. The simplest of these is Young's modulus, also known as the modulus of elasticity, the modulus of deformation, or the modulus of deformability. It is defined as the ratio of stress to strain as measured on stress/strain diagrams such as those shown in figure 6.2. The larger this value, the stiffer or less elastic a material is and the more resistant it is to being strained. The other commonly used elastic constant is Poisson's ratio, which is based on the observation that when most materials are stretched, they expand lengthwise along the axis of tension and contract sideways. The ratio of the contraction sideways to the expansion lengthwise is Poisson's ratio; in general, the higher this value, the less deformable and more elastic it is.

Several other elastic constants are less consistently measured but are useful for specific purposes. Two of these deal with the changes in volume that accompany the changes in shape typical of elastic behavior. The bulk modulus, or the modulus of compressibility, describes the change in volume that occurs when a material is subjected to hydrostatic stress. For some engineering purposes, the reciprocal of this value is used, and this is called compressibility. All the elastic constants discussed thus far describe materials under tensile or compressive stress; the shear modulus measures the ratio of stress to strain for a material under shear stress. Finally, there are several obscure elastic parameters, such as Lamé's constants, that are closely related to some of the parameters already described. In fact, most of these constants are so closely related that formulas have been developed allowing one to be calculated from the others.

These various measures of elasticity are affected rather differently, however, by intrinsic and extrinsic factors. For example, Young's modulus is lower under conditions of static loading than it is under dynamic loading, but Poisson's ratio is higher under static loading. Also, if a material has crack surfaces that can slide past one another, Young's modulus decreases but Poisson's ratio

increases (Jaeger and Cook 1979:194).

In general, the elastic properties of a rock are determined by its mineralogy, grain size, and cracks. When different minerals are compared, elasticity is closely related to the type of bonding among the atoms of the mineral (Berry, Mason, and Dietrich 1983:153). The bonding between silicon and oxygen makes quartz fairly elastic; quartz is also somewhat anisotropic with regard to elasticity. Granular materials are generally more elastic than single crystals; so, chert is more elastic than crystal quartz. In addition, fine-grained rocks are usually more elastic than coarse-grained rocks (Winkler 1973:43).

Pores or other equidimensional holes have little effect on the elastic properties of rocks because they do not close up, but cracks are very significant (Walsh 1965a, 1965b). An increase in the number of cracks lowers both Young's modulus and Poisson's ratio because cracks allow greater deformation, or strain, to occur. In addition, the more cracks a material has the more compressible it is. Compressive stresses increase Young's modulus, though, because the cracks close up. Water does not affect elasticity much, at least in quartz.

In summary, chert does indeed have elasticity, and fine-grained cherts, or those with many internal cracks, should be the most elastic. Again, the effect of impurities on elastic properties has not been investigated for cherts.

## Hardness

Hardness is not especially relevant to the manufacture of stone tools by flaking, but it is certainly relevant to abrasion and to wear during use. Hardness is defined as the resistance of a material to abrasion, scratching, or penetration by an indenter and is apparently a composite property affected by strength, elasticity, and cleavage (Fron del 1962:113). There are numerous ways of measuring hardness, but the most familiar to archaeologists is the Mohs scale, established by the German mineralogist Friedrich Mohs in 1822; this scale is included in virtually every field guide to rocks and minerals. The Mohs scale ranges from 1 (the hardness of talc) to 10 (the hardness of diamond). Each rock or mineral's position on the scale is determined by testing which of the diagnostic minerals it can scratch or be scratched by. The Mohs scale is relative rather than absolute; the difference between steps 6 and 7, for instance, is much less than the difference between steps 9 and 10. Table 6.1 shows correlations between the Mohs scale and several other measures of hardness.

Hardness is a function of the molecular properties of a material, of grain size, and of the presence or absence of water. Hardness is greater for materials composed of small ions with high electrical charges that can be packed tightly (Berry, Mason, and Dietrich 1983:154–155). This is why quartz is so hard, with only a little variation in hardness values on the different crystal faces (Fron del 1962:113). Only a few relatively rare minerals are harder than quartz. Most cherts also test at or near 7 on the Mohs scale.



Hardness increases with decreasing grain size, at least for indentation hardness (Winkler 1973:35). Indentation hardness is also significantly higher for dry minerals than for those tested in water or moist air (Kirby and McCormick 1984:146).

### Miscellaneous Properties

A number of other mechanical and quasi-mechanical properties are discussed here for the sake of completeness and because some will be relevant later. The first of these is the coefficient of friction, measured as the force parallel to the surfaces needed to start a block of material moving across a plate of the same material, divided by the force perpendicular to the surfaces. This property is relevant to both strength and elasticity because the walls of cracks in materials with low coefficients of friction are able to move easily against one another (Jaeger and Cook 1979:53), thus making such materials more elastic and less strong. The coefficient of friction is low for quartz, 0.11, primarily because friction characteristics are determined more by surface finish than by rock type (Jaeger and Cook 1979:73), and quartz has very smooth crystal faces. For comparison, diamond has a similarly low value, 0.1 to 0.3, quartzite ranges from 0.48 to 0.67, and dolerite from 0.64 to 0.95 (Jaeger and Cook 1979:59). I found no values for chert but suspect it is somewhat less than for quartzite because the quartz grains are less tightly interlocked in chert. Interestingly, water acts as an antilubricant for this property of quartz although it acts as a lubricant for many other materials in this regard. Wet quartz has a coefficient of friction of 0.42. However, this antilubricating effect declines rapidly with increasing surface roughness (Horn and Deere 1962); so, it is unlikely to have an important effect on crack dynamics in chert.

The thermal properties of a material, especially its thermal conductivity and rate of thermal expansion, are relevant to any situation in which the material is exposed to high temperatures. For our purposes, this occurs when cherts are accidentally burned in fires or when they are intentionally subjected to heat-treating. Mirkovich (1968) has stated that the heat fracture characteristics of a material can be predicted from its thermal properties alone, regardless of strength and elasticity. Again, I did not find data on cherts in particular, but much is known about the thermal properties of quartz.

Thermal conductivity is a measure of the ease with which the energy of heat is transmitted from a warm to a cool area. The denser a material and the more rigidly its molecules are bonded, the more easily it can conduct heat. Diamond is highly conductive, at 290 to 390  $\times 10^{-3}$  calories/cm sec $^{\circ}$ C, and pyrite is also high at 90.6. Most rocks run between 6 and 9, with shale low at 3.26 and sulfur the lowest at 0.65 (Clark 1966). Quartz is higher than most minerals, at 27.3 parallel to the *c* axis and 16.3 perpendicular to that axis (Deer, Howie, and Zussman 1963:199). Quartzite, with its high quartz content, ranges between 10.1 and 16.05 (Clark

**Table 6.1 Various Measurements of Hardness**

Material	Mohs	Vickers <sup>a</sup>	Knoop <sup>b</sup>	Abrasive <sup>c</sup>	Drilling <sup>c</sup>
Talc	1	10	—	0.003	—
Gypsum	2	40	32	1.25	8.3
Calcite	3	100	135	4.5	50
Fluorite	4	200	163	5.0	143
Apatite	5	500	430	—	—
Orthoclase	6	750	560	37	4665
Quartz	7	1300	820	120	7648
Topaz	8	1700	1340	194	28,867
Corundum	9	2400	2100	1000	188,808
Diamond	10	—	7000	140,000	—

a = Gribble and Hall (1985:27)

b = Zoltai and Stout (1984:16)

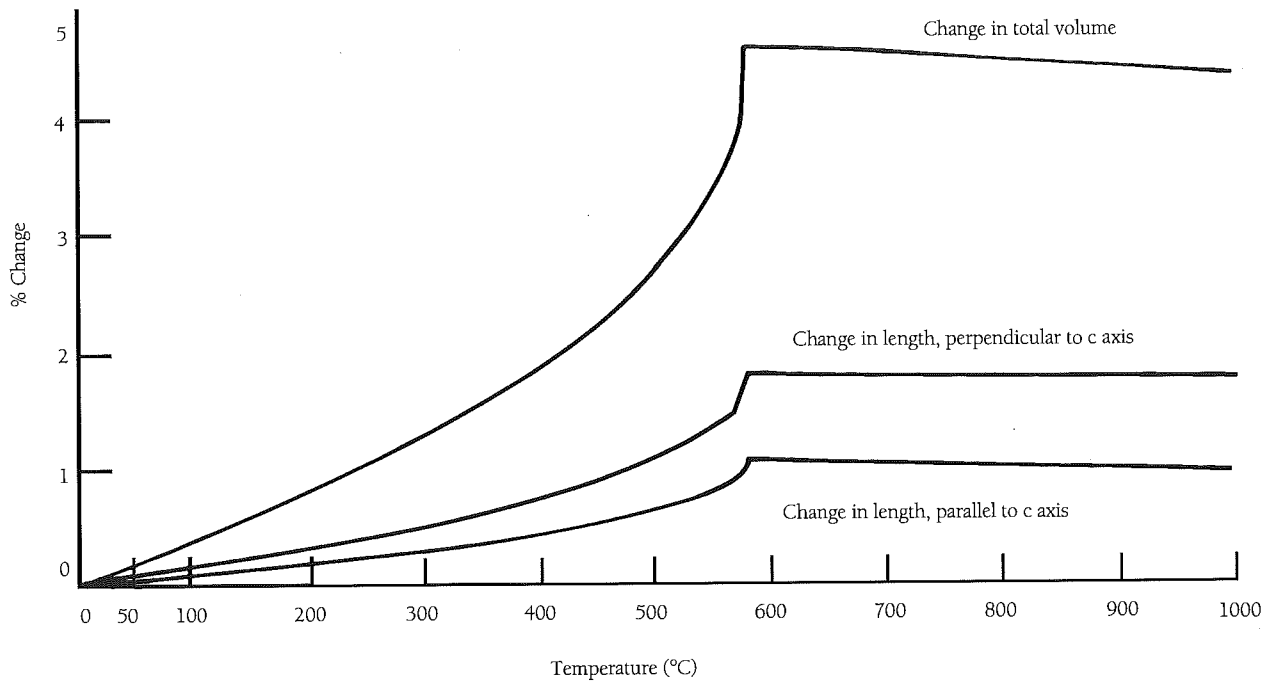
c = Winkler (1973:38)

1966), and chert is probably similar. Cherts with more cracks and pores, or with high proportions of impurities, should be lower in conductivity (Winkler 1973:45) and therefore more susceptible to thermal fracture because of uneven heating.

Quartz has an unusually high coefficient of volume thermal expansion compared to other minerals. It is therefore considered the most critical mineral in a rock under conditions of heating (Winkler 1973:171). This expansion is greater in the direction perpendicular to the *c* axis. Data concerning thermal expansion in quartz are shown in figure 6.5. Quartz undergoes a 3.76% expansion in volume when it is heated from room temperature to 570 $^{\circ}$  C (Winkler 1973:175). At about 573 $^{\circ}$  C, it changes from normal  $\alpha$  quartz to  $\beta$  quartz, and its volume declines again. The volume increase that quartz undergoes at lower temperatures can produce internal pressures as high as 1 to 2.5 kbars (Winkler 1973:171). Sumino and Anderson (1984:45) say the exact coefficient of volume thermal expansion for quartz is 33.43 to 34.96  $\times 10^{-6}$  K $^{-1}$  and that this property is inversely related to the bulk modulus.

Because quartz is a slightly better conductor than many minerals, one might expect it to be resistant to thermal shock since damaging steep thermal gradients are less likely to occur. However, quartz's high coefficient of thermal expansion apparently outweighs this advantage, causing quartz, and rocks made of quartz, to be highly susceptible to thermal fracture. High temperatures are even more damaging because they transform quartz into different silica minerals with very different crystalline structures. Thermal properties are discussed further in chapter 7.

These thermal properties are apparently unrelated to chert's ability to make sparks when it is struck against iron or steel. In fact, I was unable to find a definitive statement as to the cause of this phenomenon. Shepherd (1972:181) says that the sharp hard flint tears off minute white-hot fragments from the steel or metal, but Brown (1980:71) implies that the flint itself gives off sparks. The



**Figure 6.5**

Expansion of quartz with temperature. (Data plotted from values given in Skinner 1966: 91)

fact that the earliest self-striking gunlocks used marcasite, a form of iron pyrite, in place of flint (Brown 1980:53) would imply that quartz itself is not crucial to the process. Perhaps any material of suitable hardness and resistance to fracture would do.

Quartz is piezoelectric, and although this property is apparently unrelated to stone tool manufacture or use, it is the basis for most of the important industrial uses of quartz. Piezoelectricity is typical of most minerals such as quartz whose crystal structure lacks an axis of symmetry. Pressure exerted along one of the *a* axes of a quartz crystal causes a flow of electrons that produces a negative electric charge at one pole and a positive charge at the other. This process works in reverse, too; if you apply a current to the pole of a thin slice of quartz, it will flex (Hurlbut and Klein 1977:193). The intensity of this response is measured by *Q*, “a measure of the relative efficiency of transfer of energy back and forth between strain and motion...the ratio of energy stored to energy dissipated per cycle” (Deer et al. 1963:204). Quartz has the highest values of *Q* known; this property has resulted in many industrial applications, ranging from crystal radios, in which thin quartz crystals are used to stabilize radio frequencies, to quartz watches and applications in laser technology. The desire to produce extremely pure quartz crystals in large quantities for such purposes has spurred much research regarding the formation, crystal structure, and mechanical properties of quartz.

### Mechanical Properties of Specific Chert Types

Because mineralogy, grain size, and cracks are important influ-

ences on so many mechanical properties, it is not surprising that strength, elasticity, and hardness are broadly correlated across rock types (Hendron 1968:36). That is, rocks that are strong are also generally stiff and hard. Books on rock mechanics are full of formulas relating each of these material constants to the others (for example, Jaeger and Cook 1979). There is scatter in the data, however, and correlations are not perfectly predictable. For example, chalk is very stiff, with a high Young’s modulus, but it is neither strong nor hard. Jade has much higher tensile strength than chert, but with a Mohs hardness of 6, it is more easily scratched. Diamond is, of course, the hardest mineral known, but it is not very strong in tension. Therefore, at this point, it appears unlikely that we will be able to measure one mechanical property for a chert type and assume that we can reliably predict all the other properties from that value.

Until we have a much better understanding of the relative importance of the different determinants of chert’s mechanical properties we must conduct a great deal of empirical testing. Archaeologists have generated data concerning mechanical properties since the 1940s when Goodman (1944) performed standard mechanical tests on several stone-tool materials. Additional values are available in the literature of engineering and rock mechanics. Rather than compiling all such values and attempting to determine the average mechanical properties for chert, it is more useful to explore the range of variability, and especially to search for trends in the data that might suggest relationships among different chert attributes and mechanical properties. Table 6.2 lists mechanical and other properties for a series of specific chert types, arranged roughly in order of “workability.”

Table 6.2 Mechanical Properties of Cherts

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Material	Callahan grade	Murata & Norman index	Grain size ( $\mu$ )	Subgrain size ( $\mu$ )	Internal surface area ( $m^2/g$ )	Density (g/cc)	Moisture (% by wt.)	Water (% by wt.)	Young's modulus ( $N/m^2 \times 10^{10}$ )	Poisson's ratio	Compressive strength	Tensile strength ( $MN/m^2$ )	Fracture toughness ( $MN/m^{3/2}$ )	Transverse bending ( $MN/m^{3/2}$ )	Hardness (Shore scler.) strength ( $MN/m^2$ )
"Quartz"	4	9.8-10.2	>1000		0	2.651		0-0.39	9.6	0.075-0.077	167-329		10.37-13.86	1.002	
High Springs (4)					4.64		0.34-0.67	1.33			173.1	17.7			
English Chalk flint (gray) 4		5.7-9.8	2-10	>0.5		2.622		1.44						117.9	
Arkansas novaculite	3.5/4		10	0.075-0.2	4.86	2.64	0.32	1.12			365.5	41.0	1.04		
Ocala (3.5/4)				0.070			0.102-0.53						45.5-112.4		
Burlington (3.5/4)					5.39		0.23	1.55				21.2	2.0		
Johnson Lake (3.5)							0.23	2.23							
Bald Eagle Jasper (3.5)							0.23	1.38	5.3	0.09-0.16	360	35.8		162.1-165.5	103.4
"Chalcedony" (3.5)		<1.0-4.7	1x100	0.05-0.1	0.43	2.59	0.79	1.27							
Stevens (3.5)			7.5	0.03-0.06	0.31	2.594	0.27	1.27							
Onondaga (3.5)			3-9			2.57-2.64	0.05-0.16								
Flint Ridge (3.5)			<5			2.60		0.44							99.6
Indiana hornstone 3.5				0.0541			0.158								
English Chalk flint (black) 3		<1.0	<1	0.12		2.58	0.14							186.2	102.1-105.1
"Obsidian" 1		(Noncrystalline)					2.373	0	0	6.80	0.15	214.5-345.5	12.9-13.4	0.8	94.8

## Notes

## Material

## "Quartz"

## High Springs

## English Chalk flint (gray)

## Arkansas novaculite

## Ocala

## Burlington

## Johnson Lake

## Bald Eagle Jasper

## "Chalcedony"

## Stevens

## Onondaga

## Flint Ridge

## Indiana hornstone

## English Chalk flint (black)

## "Obsidian"

## References

## 6 Midgley (1951); 7 Frondel (1962); 9 Deer et al. (1963); 10, 12 Lama and Vutukuri (1978); 11 Sumino and Anderson (1984); 13 Savanick and Johnson (1974); 14 Kirby and McCormick (1984)

## 6, 8, 9, 12, 13 Purdy (1974)

## 4, 5, 15 Iler (1963); 7, 9 Weymouth and Williamson (1951)

## 4 Atkinson (1980); 5 Micheelsen (1966); 7 Grady and Kipp (1979); 13, 14 Shockey et al. (1974)

## 6, 8, 9, 12 Purdy (1974)

## 5 Weymouth and Mandeville (1975); 8, 15 Rick (1978)

## 6, 9, 13 Purdy (1974)

## 8, 9, 14 Schindler et al. (1982)

## 4 Folk (1974); 5, 7, 8, 9 Florke et al. (1982); 6 Midgley (1951); 10 Hatheway and Kiersch (1982); 11, 12, 13 Lama and Vutukuri (1978); 15 Iler (1963); 16 Greiser and Sheets (1979)

## 4, 5, 6, 7, 8, 9 Micheelsen (1966)

## 4, 7, 8 Ozol (1963)

## 4 Carlson (1987); 7, 16 Goodman (1944); 9 Stout and Schoenlaub (1945)

## 5 Weymouth and Mandeville (1975); 8 Mandeville (1973)

## 4, 5, 15 Iler (1963); 7, 16 Goodman (1944); 8 Purdy (1974)

## 7, 11 Speth (1972); 8, 9, 12, 13 Purdy (1974); 10 Tomenchuk (1985); 14 Cotterell and Kamminga (1987); 16 Greiser and Sheets (1979)

Values in parentheses are estimates.

There are several problems concerning the data in table 6.2. First, not many mechanical property measurements are available for chert, largely because chert is of minor interest to engineers and geologists. Values for chert are given in many publications, but careful scrutiny reveals that most are simply quoted from earlier studies; in fact, many of the values given in recent compilations were initially determined in the 1950s (for example, Carmichael 1982). Procedures and standards for determining mechanical properties have changed since then, making some of these data suspect. Also, most studies determine only a few properties so that not all the possible mechanical properties have been measured for the materials listed in table 6.2.

Another problem with the available chert data is that sampling has not been taken seriously (where it is even discussed). The exact source of a sample is rarely given, and the literature is full of values representing such materials as "Chalcedony, probably from California" or "Tennessee chert" (for example, Blair 1956:5 and Pelto 1956:44). I found no case in which an effort was made to sample the full range of variation of a chert type. A few studies involve tests on multiple samples of the same material, but more often analysts performed multiple repetitions of the same test on a single nodule or fragment. Disconcertingly often, the value given is based on a single test of a single sample of chert which is tacitly assumed to be typical of the entire formation (and sometimes of chert in general!). What appears to an archaeologist to be a shockingly cavalier attitude toward sampling may simply be due to the fact that ballpark figures are perfectly adequate for the kinds of questions rock mechanics people deal with. However, if we archaeologists are going to attempt to make the fine distinctions between material types necessary for applications to problems of lithic manufacture and use wear, we will need to be much more careful about sampling. In one of the few studies that involved a healthy sample, Rick found a wide range of values for the tensile strength of Burlington chert and concluded that "the point load strength of a single sample of chert from a formation is not representative of the formation" (Rick 1978:40).

Obviously, then, the data in table 6.2 vary in reliability, and it is probably best to treat them all as approximations. I attempted to increase reliability wherever possible. Where more than one value was available from different sources, I used the value based on the most measurements. Where an average of several measurements was given in the original source, the value is reported in table 6.2. Where no average was calculated in the original source, I usually give the range of values reported. I do not include sample sizes or standard deviations, partly because so few are available, but primarily because they might lend an air of spurious precision to the table. The significance of this table should be based on the general trends evident in the data, not the exact values.

Those persons seeking the original data will be appalled to discover that the information is given in at least five different units of measurement, and that one is assumed to know what all the

abbreviations mean. Most recent publications use the SI (Système International or Standard International) notation based on the metric system. I strongly support any effort to achieve uniformity in data reporting; so, I have used SI here. Thus most strength values are given in megaNewtons per square meter ( $\text{MN}/\text{m}^2$ ), with a Newton defined as the force necessary to give 1 kg an acceleration of 1 m per second squared. To convert megaNewtons per square meter to pounds per square inch (psi), the notation used most often in older sources, multiply the values in table 6.2 by 145.

Column 1 of the table lists material type. I included as many different cherts as possible but limited the table to reasonably well-defined types for which more than one measurement is available and for which I had enough information to estimate their positions with regard to column 2, Callahan grade. Categories in quotation marks are generic and include measurements for more than one material. Thus "quartz" refers to clear quartz crystals whenever possible, but sometimes it represents measurements on large quartz grains within granites. This row in the table is assumed to represent the mechanical properties of the mineral quartz, which theoretically should not vary much; it is included as a baseline against which to compare chert values. "Obsidian," a non-crystalline silica or natural glass, is also treated as a generic material. Although there is no theoretical reason to assume that all obsidians have the same mechanical properties, at least one experienced stoneworker has expressed the opinion that variability is minimal compared to cherts (Kamminga 1979:297). Also, obsidian variability is simply not a concern of this book. It was hoped that the categories "quartz" and "obsidian" would act as end members and would bracket the range of variability for cherts. "Chalcedony" is treated as a generic category because the proveniences of the samples tested were almost uniformly vague and because no one analyst presented enough different measurements. I am unwilling to exclude chalcedony entirely because its microstructure is so different from that of most cherts (see chapter 2), and this difference must surely affect its mechanical properties. Therefore, values for different chalcedonies are combined here in the hope that this material does not possess outrageous variability relative to other cherts.

Column 2 gives the Callahan grade for each material. Of all the practitioners, Errett Callahan (1979:16) has provided the most explicit ranking of lithic raw material types based on their ease of workability. His scale runs from 0.5 (opal), the most easily worked, to 5.5 (coarse quartzites and volcanics), the hardest to work. He characterizes materials graded from about 0.75 to 3.75 as elastic and those from 3.75 to 5.5 as tough. Those graded from about 2.5 to 3.75 are also characterized as strong. Callahan lists specific chert types that are examples of each grade, and, wherever possible, I included them. Values in parentheses are my estimates, based on my knowledge of the charts in question and how they compare with Callahan's examples. I used the Callahan grade to

establish the basic ordering of materials in the table; his ranking is assumed to reflect changes in mechanical properties that are of particular relevance to flintknapping.

Column 3 gives the Murata and Norman (1976) crystallinity index, which is based on the profiles of the X-ray diffraction peaks of the quartz in each material. This scale runs from less than 1.0 (weakly crystalline) to 10 (highly crystalline). Murata and Norman suggest that their scale is largely a function of crystal size but is also affected by crystal lattice distortion induced by mechanical stress or metamorphism. Not many values are available, but their order agrees well with the Callahan grades. In general, the more highly crystalline materials appear to be less workable than the less crystalline materials.

Column 4 gives the average size of the quartz grains in microns, as determined by microscopic inspection of thin sections or measurements from scanning electron microscope photographs. Again, there is generally good agreement between this measurement and both the Callahan and Murata and Norman scales, confirming the standard opinion of most flintknappers that fine-grained materials flake more easily than coarse-grained materials.

Column 5 gives the size of the quartz subgrains, the smaller crystals that make up the quartz grains (see chapter 2), again in microns. These values are determined by comparing the broadening of the X-ray diffraction peaks of the cherts to that of pure crystalline quartz and should therefore be related to the Murata and Norman scale. However, there is no clear pattern to the variability. Quartz subgrain size may be a characteristic that varies more within formations than we have assumed, or test conditions may be important. The fact that values from one source are all an order of magnitude higher than the rest suggests differences in testing procedures or interpretation. However, it is also possible that the size of subgrains is simply less directly relevant to mechanical properties than are other factors. In fact, there is evidence suggesting that subgrain size is not related to how coarse or fine grained a material appears. Weymouth and Mandeville (1975:66) present a series of values for subgrain size; if these values are compared with the descriptions of the same cherts in Mandeville (1973:191), it is clear that the fine-grained cherts are not always composed of small subgrains, and the coarse-grained cherts are not always composed of large subgrains.

Column 6 gives values for the interior surface area, measured in square meters per gram, which is determined by forcing gas under pressure into dry rock. Micheelsen (1966:310) has said that interior surface area should be a direct function of the surface area of the quartz grains (though it should also be affected by porosity and cracks). Since smaller grains have larger surfaces relative to their volume, interior surface area should increase as grain size decreases. This trend is indeed present for the top three values, but the other two are not consistent and seem to be different by an order of magnitude. Unfortunately, the three values were obtained

using helium, while the rest were obtained using nitrogen. It seems likely that this, or some other aspect of experimental procedure, is responsible for the discrepancy. It should not be surprising, though, to find that chalcedony has a larger surface area than chert because of the latter's loose, fibrous microstructure.

Column 7 is density in grams per cubic centimeter. For most materials density can be considered equivalent to specific gravity. Quartz, with a value of 2.65, is not especially dense; gold is very dense at 19.28, and opal is very low at 1.89. The mean for all minerals is 4.66, but the mean for rocks is 2.69, reflecting the importance of quartz as a rock-building mineral (Sumino and Anderson 1984:45). Most cherts will have lower densities than pure quartz, owing to impurities, pores, and water content. However, some jaspers may well have a higher density than pure quartz, because of their iron content. All iron oxides have higher densities than quartz (for example, hematite is 5.275), and some jaspers have a very high content of these minerals (see chap. 4). Table 6.2 shows that density declines as grain size decreases, presumably because of the increasing internal surface area.

Column 8 gives the percent of moisture, by weight, based on the amount of weight lost when a chert is heated to around 100° C and kept there for more than 24 hours. This is a measure of the free water present in cracks and cavities; it does not include water that is chemically bound to the silica or trapped in deep pores. Moisture declines roughly with grain size, which would seem to counter the previous suggestion that surface area increases with grain size. The two findings are not necessarily contradictory, though, because much of the increased surface area in a fine-grained chert may be too small to accommodate water molecules, which are larger than atoms of helium or nitrogen. Any trend at all is rather surprising, given that this particular value would seem to be especially susceptible to measurement error. Cherts were heated to slightly different temperatures for different lengths of time by the various researchers, and we have no way of knowing how much water might already have been lost through dehydration before testing took place.

Column 9 gives the total percentage of both free and chemically bound water by weight. This percentage is determined through chemical analysis and/or measurement of weight loss after the material received prolonged heating to temperatures greater than 600° C. Values determined through heating may be high because carbon dioxide is also being driven off as a result of the oxidation of carbon and carbonates, but most of the weight loss does represent water. There are no clear trends in the data, and it is possible that procedural differences were so great that they obscure any possible pattern. However, the data column does substantiate the oft-quoted generalization that cherts contain about 1% water.

Column 10 presents the first of the elastic constants, Young's modulus. It is usually determined by using electrical strain gauges

to measure the amount of strain (in Newtons per square meter) produced by different amounts of stress during triaxial compression tests, in which the sample is compressed from all sides (Hatheway and Kiersch 1984:304). Young's modulus is sensitive to test conditions; it is generally higher under compressive loading than in tension (Jaeger and Cook 1979:168), and measurements made under dynamic loading conditions generally run about 20% higher than measurements made under static loading conditions (Jaeger and Cook 1979:194). Since data compilations rarely report exactly how Young's modulus was measured, even more ambiguity is added to these values. In general, the higher Young's modulus is, the stiffer and more resistant to strain and deformation the material is. Pyrite, at 16.49, is very stiff, while slates and gneisses, with values as low as 0.25, are easily deformed. Engineers generally consider materials with a Young's modulus greater than 8.3 to have low deformability; values from 4.1 to 8.3, which represent the majority of rocks, are considered medium, and materials lower than 4.1 are considered highly compressible (Hatheway and Kiersch 1982:306). Cherts have been found to range from 3.5 to 10.3, with most falling between 5 and 6 (Tomenchuk 1985:400). The lack of data points in table 6.2 makes any further generalizations impossible.

Column 11 gives values for Poisson's ratio, the ratio between the lateral contraction and longitudinal expansion of an object in tension. It is usually determined indirectly through the use of electrical resistance strain gauges during compression tests in the laboratory or by sonic velocity tests in the field (Hatheway and Kiersch 1982:302). Poisson's ratio is a dimensionless measure, ranging from 0 to 0.5, with lower numbers indicating materials that can be easily deformed. Most rocks fall between 0.25 and 0.33 (Walsh 1965b); some dolomites are very stiff at 0.46 and schist is usually very deformable at 0.01. Poisson's ratio is not really a constant, as it can vary a great deal with pressure for rocks having many cracks (Walsh 1965b). Chert, along with most other rocks, shows a wide range of variability for this attribute, with values ranging from 0.001 to 0.34 (Speth 1972:52). However, most cherts are rather low, between 0.08 and 0.2 (Tomenchuk 1985:242; Speth 1972:52), presumably because many cherts have considerable internal porosity. Speth has suggested that Poisson's ratio may have special relevance to certain archaeological problems. He has argued on theoretical grounds that materials with Poisson's ratios below 0.27 possess a range of striking angles over which it is almost impossible to remove flakes (Speth 1972:51–54). Thus, materials with lower values for Poisson's ratio should be more difficult to flake.

Column 12 gives values for compressive strength, measured by subjecting a cylinder of a material to increasing compression, often from all sides (that is, triaxial compression), until it crumbles. Jaspillite, a banded jasper containing more than 25% iron, produced a very high value for compressive strength at 682.8 (Wuerker 1959:27), and quartzites generally range from 400 to 520. Most

rocks appear to fall between 10 and 100, and gypsum is very low at 1.25 (Hatheway and Kiersch 1982). For engineering purposes, compressive strength values greater than 220.7 are considered very high strength, while 110.3 to 220.7 is high strength (Hatheway and Kiersch 1982:306). The values shown indicate that chert is a very strong material and suggest that Callahan was right in indicating that strength peaked at the middle of his scale.

Column 13 gives values for tensile strength, theoretically the most interesting strength value for archaeologists because chert fractures first in tension. Tensile strength is rather difficult to measure. Traditional testing methods required either the machining of dog-bone shaped pieces or attachment of strong resins to the ends of cylinders so that test pieces could be pulled apart. Many values in the literature were determined indirectly through methods such as the Brazilian test or the point loading test, which involve compression (Hendron 1968). In addition, "the tensile strength of rock is more variable and more influenced by specimen size than any other mechanical property of rock" (Jaeger and Cook 1979:148); so, it is especially important to do repeated or multiple tests on the same chert. Just to add one more source of confusion, values obtained through dynamic testing tend to run six to ten times higher than those obtained in static tests (Lama and Vutukuri 1978:302). Cherts are relatively strong in tension, although we should expect much variability because of the considerable effect of cracks on this property. In comparison, diorite is stronger, at 50.3, while some shales test as low as 0.24. Again, data are scarce, but tensile strength seems to be greater for cherts in the middle of the range, just as Callahan predicted.

Column 14 gives values for fracture toughness, or stress intensity factor, which denotes a material's resistance to crack propagation and is a function of both tensile strength and characteristics of the cracks present in a material (Shockey et al. 1974). It can be measured in a number of ways, including the use of a Vickers microhardness indenter, under known pressure, to indent the surface of the material. Fracture toughness is calculated from the size of the indentation and the length of resulting cracks (Schindler et al. 1982:532). Window glass is low in this property, at 0.7, while gabbro is high for rock at 2.9 (Kirby and McCormick 1984).

Column 15 includes values for transverse bending strength. In this test, a block or cylinder of a material is supported on the ends and loaded in the middle, resulting in compressive stress at the point directly under the load and tensile stress on the opposite, or convex, side. This test tends to give values higher than those obtained in tensile strength tests because cracks open on the convex side, lowering Young's modulus and raising strength (Jaeger and Cook 1979:167–168). Broch and Franklin (1972:672) give data comparing findings for strength tests on marble, sandstone, and trachyte in direct tension and in bending. They found that bending strength values are about twice those determined in direct tension tests. The data in the table appear to indicate that,

for cherts, transverse bending strength is considerably higher than tensile strength.

Column 16 presents values for the only absolute measure of hardness represented by a number of available data points, the Shore scleroscope test. In this test, a small hammer is dropped onto the test material from a uniform height and the height of its rebound is measured. Winkler says the Shore scleroscope values are correlated with both elastic properties and with compressive strength (Winkler 1973:36). Comparable data are not available for many other materials, and, since all the values here are concentrated at the bottom of the table, it is difficult to discern a pattern. The references for each value reported are in the notes.

## Discussion

Over ten years ago Schiffer (1979:17) wrote, "We are going to have to begin thinking about the properties of raw materials that genuinely affect their use characteristics and patterns of modification, and define variables on that basis, rather than continuing to employ area-bound types, sometimes defined on specious criteria such as color. We need to determine as rapidly as possible those properties, for example, that affect the degree to which a specimen microflakes, striates, polishes, abrades, and absorbs amino acids under standardized test conditions." Elsewhere in the same book, Hayden and Kamminga (1979:10) called for the development of a few appropriate and inexpensive mechanical tests that would be especially relevant to archaeologists' problems. We still have a long way to go to meet either of these goals.

Table 6.2 demonstrates the considerable range of variation within chert and indicates the danger in using existing literature to obtain "average" values for its mechanical properties. Variability is not a problem confined to chert alone. "Workers in rock mechanics have often found [the traditional geological classifications] to be inadequate, or at least disappointing, in that rocks of the same lithology may exhibit an extremely large range in mechanical properties" (Deere 1968:3). If the table could be expanded and the gaps filled in, archaeologists wishing to estimate the mechanical properties of a chert type could select values typical of closely comparable types, but at this point the data are

far too incomplete.

It is hoped that the table will encourage more archaeologists to do their own testing, because the variability in chert mechanical properties shows a good deal of patterning. Even better, this patterning agrees with at least one practitioner's opinions about lithic material workability and with the general principles established by workers in rock mechanics. Obviously, the mechanical properties of quartz itself are the most important influence on the mechanical properties of chert, though the role of impurities is virtually unexplored. Grain size also plays a role in determining the mechanical properties of chert, and the role of cracks is likely to be significant. In general, though we cannot yet link the mechanical properties of different cherts to the ways in which they respond to manufacturing and wear processes, table 6.2 suggests that investigations of such links would be fruitful.

Other mechanical properties may be more relevant to our concerns than those presented in this table, which simply presents the properties most widely described in the literature. In addition, we are far from determining which of the many available mechanical tests are most relevant to our problems (Brown 1981). Archaeologists interested in the mechanical properties of materials such as ceramics (for example, Bronitsky 1986) and metals also are seeking such tests, and cooperation would surely be advantageous for all of us. Besides selecting appropriate mechanical tests, we must standardize test conditions because many measures are sensitive to differences in water content, temperature, confining pressure, rate of loading, and so on. It is also extremely important to sample our chert types adequately. Furthermore, we should perform the tests repeatedly to obtain accurate measures. For example, Broch and Franklin (1972) recommend performing a minimum of ten tests per sample, and 20 if the shape is irregular, and then averaging the results.

The mechanical properties of most materials are very complex, and chert is certainly no exception. However, these properties are relevant to many issues that are of considerable interest to archaeologists, and careful investigation of these properties could yield results that greatly increase our ability to draw inferences about past ways of life from the stone tools people made, used, and discarded.

# 7

## Altered Cherts

**T**he chemical, visible, and mechanical properties of cherts are not immutable; all can change as a result of cultural manipulation or natural processes. For example, stoneworkers sometimes alter mechanical properties by either soaking chert in water or drying it out. Even more dramatic changes can be achieved through heat-treating. Weathering also changes these properties in numerous ways. Finally, the sources of chert are sometimes altered by erosion and transport.

### Heat-treating

Heat-treating, also called thermal alteration, thermal pretreatment, and annealing, involves the intentional heating of chert to bring about desired changes, usually to improve its flaking properties. Heat-treating also produces dramatic color changes, which in some cherts may have been a secondary, or even a primary, goal.

This process was used rather commonly by prehistoric people, at least in North America (Purdy 1981; Griffiths et al. 1987), but it was only recently rediscovered by archaeologists. Don Crabtree, one of the earliest and most influential of the replicators, began to experiment with heat-treating when he became frustrated in his attempts to pressure flake Paleoindian projectile points out of certain raw materials (Crabtree and Butler 1964). He noted that prehistoric artifacts made of these same cherts appeared glossier than the quarry samples he had collected. Consequently he began heating raw materials to see if he could alter them. After much trial and error, Crabtree was successful. Once alerted to the possibility, archaeologists sought and found a number of descriptions of stoneworking peoples who were probably heat-treating chert,

though none of these accounts is very detailed and some may be garbled (Hester 1972; Mandeville 1973). In addition, there is a growing body of archaeological evidence for the use of this procedure.

### Procedures

When it is heat-treated, chert is subjected to slowly increasing heat until an optimal temperature is reached, kept at that temperature for some period of time, and then slowly cooled. Most experimenters have used kilns to achieve maximum control over temperature and to reach higher temperatures, but ovens and wood fires are also alternatives. Most kitchen ovens heat to at least 260° C (500° F), which is sufficient to heat-treat some cherts. Wood fires can reach temperatures as high as 900° C (Shepard 1971:79)—thermocouples track temperatures in such fires.

The trick is to heat the chert to the temperature needed to bring about the desired changes without incurring thermal shock, which results in fracture. Thermal shock occurs when part of the chert becomes much hotter or colder than the rest; the resulting difference in the rate of contraction or expansion causes the fragment to break. Many variables must be manipulated to achieve this balancing act, and they will be described step by step.

The fragment to be heated can vary from flake to cobble size, although several archaeologists have noted that cobbles require very slow rates of heating and cooling because they are especially susceptible to thermal shock (for example, Ahler 1983:5). Thin flakes appear to be the least susceptible to thermal shock, undoubtedly because they heat most evenly (Mandeville 1973:191). All the fragments should be about the same size; smaller and



thinner pieces can achieve the necessary temperature faster and may then begin to fracture while larger fragments have not yet been altered completely. Since most prehistoric people used heat treatment to produce raw material suitable for manufacture into bifacial tools, especially projectile points (Purdy 1981b:40; Schindler et al. 1982:536; Ahler 1983:6), preforms or large flakes would probably have been most commonly heat-treated. However, some modern stoneworkers in Australia have been observed to heat entire cores, while other members of the same group preferred to heat flakes (Tindale 1985:5).

Most experimenters have placed their chert in 1 or 2 cm of sand or soil to protect it from the direct heat that causes thermal shock. In campfire experiments, flakes have often been buried just under a fire, or a fire has been built in a pit and the flakes put in a thin layer of sand over the coals, sometimes with more coals over that. Other experimenters have found that no sand is needed as long as the chert is not in direct contact with heating elements, flames, or glowing embers. For example, Griffiths et al. (1987:47) had good success with dropping preforms directly onto beds of ash left by outdoor campfires when the ash had stopped glowing but embers were still glowing beneath.

There is also considerable variation in the rate at which temperatures are raised, with reported heat-up times ranging from a few minutes (Griffiths et al. 1987) to forty-eight hours (Ahler 1983:5). Several experimenters raised the heat in steps, increasing the temperature of the kiln or oven 25 to 50° at a time and then holding at each plateau for some length of time before raising the temperature again. Purdy (1974:42) held temperatures at each plateau for an hour. She found that this slow heating was especially important to avoid damage to cherts. Others raised the kiln temperature slowly at a steady rate, such as 50° per hour (Flenniken and Garrison 1975:126). On the other hand, Griffiths et al. (1987:45) put preforms directly into ovens preheated to 350° C without damage. The necessary heat-up time may be different for different chert types. Rick (1978:42) found that the maximum possible rate of temperature rise for white Burlington chert was about 30° per hour but darker varieties of the same chert could not be heated faster than 20° per hour without incurring damage.

The optimal maximum temperature varies for different cherts and is probably a function of both impurity content and grain size as well as water content. For each chert, there seems to be a temperature range below which no significant changes occur, no matter how long the chert is heated, and above which the chert sustains damage that renders it useless for knapping. The crucial range for most cherts appears to be between 250 and 450° C, well within the capabilities of a campfire. Some cherts must be heated to 600° C (Mandeville 1973; Purdy 1975), but this is probably the absolute maximum. At about 573° C the normal  $\alpha$  quartz of which most chert is composed begins to undergo a transition to high-temperature  $\beta$  quartz which involves a change in crystal structure (Fron del 1962:119). While this change is reversible, the strains

involved cause fractures to appear in quartz crystals (Fron del 1962:107) and therefore are likely to damage most cherts beyond use (for example, Purdy 1981b:34).

Table 7.1 shows the temperatures at which changes in color, luster, or workability occur for several different cherts as well as the temperatures at which damage was reported. This table supports the suggestion of several experimenters that fine-grained cherts are altered at lower temperatures than coarse-grained cherts. Purdy (1974:44) found, however, that her fine-grained Florida cherts altered at the same temperature as her coarser cherts, although the former altered more quickly than the latter. The amount and kind of impurities also appear to affect the optimal temperature, as is discussed below.

The length of time the chert must be kept at the optimal temperature also varies, with reported times ranging anywhere from half an hour (Griffiths et al. 1987:45) to 72 hours (Crabtree and Butler 1964). Most ethnographic accounts describe heating times of twenty-four hours or fewer (Hester 1972). Both Rick and Griffiths et al. found that, for their cherts, time and temperature were inversely related. That is, they could achieve the same degree of alteration either by heating a fragment at the low end of the critical temperature range for a long time or by heating it at the high end for a shorter time (Rick 1978:61; Griffiths et al. 1987:45).

Finally, all experimenters found that heated cherts must cool slowly or suffer thermal shock. Most simply allowed the cherts to cool along with the heat source, though other researchers cooled them outside the oven or kiln. The demonstrated necessity for the slow cooling of heated chert makes "drip flaking," an infamous piece of flintknapping folklore, especially improbable. Despite the existence of what purport to be firsthand observations of people manufacturing stone tools by dripping water on the edges of heated fragments of chert (Mandeville 1973:178–180), no one has replicated this method. It is either an extremely esoteric technique or the result of confusion in observers' minds between the process of heat-treating and the process of using fire and water at quarries as a means to break up large chunks of stone (for example, Purdy 1981b).

Two conclusions can be drawn from the wide range of variation in replicating heat-treating. First, each chert is a little different and requires experimentation to determine what method works best. Some cherts may not respond to heat-treating at all (Purdy 1975:134; Banks 1984:82), and others may not improve enough to make it worth the trouble (Crabtree and Butler 1964). Second, heat-treating does not appear to be an especially precise process. As long as limits on the rate of heating and maximum temperature are not exceeded, the same results can probably be obtained through various methods and by manipulating variables in different ways.

### Effect on Geochemistry

When chert is heated, the first change to occur is the loss of the free

**Table 7.1 Heat-treating Temperatures**

Temperature (°C)	Chert Types									
	1	2	3	4	5	6	7	8	9	10
600					D					
550					D		D			
500						D		D		
450			D		C					L
			D		C			D	L	
400	D		D		C	D	L		L	
	D		L		C	D	L	W	L	
350	D	D	L		C	D	L	WC		
	L	D	L		C			L		
300	L	D	L		CW	W		L	C	
	L		L	CL	C			L	C	
250	CLW	W	L	C	C		C		C	
					C				C	
200										
150										
100										

C = color change, L = luster change, W = best workability, D = heat damage

1 = Knife River flint (Abler 1983); 2 = South Mimms flint (Griffiths et al. 1987); 3 = Indiana hornstone (Mandeville 1973); 4 = Bayport chert (Ozker 1976); 5 = Bald Eagle jasper (Schindler et al. 1982); 6 = English Chalk flint (Griffiths et al. 1987); 7 = Florida cherts (Purdy 1974); 8 = Alibates chert (Joyce 1985); 9 = Burlington chert (Rick 1978); and 10 = Arkansas novaculite (Flenniken and Garrison 1975).

water located in pores and cracks. This loss generally begins at temperatures from just below 100 to about 150° C and results in a weight reduction of between 0.4 and 2% (Purdy 1974:39) which occurs well before any other alterations are perceptible. Rick suggests that this weight loss may happen slower in fine-grained cherts (Rick 1978:62), presumably because the water is less easily mobilized. Additional weight is lost when temperatures reach 350 to 500° C, at which point the chemically bound water is driven off (Purdy 1974:45; Griffiths et al. 1987:48).

Other impurities in chert are also altered as the temperature rises. Nonsilica minerals are especially likely to undergo oxidation, but they may also undergo reduction, decomposition, dehydration, inversion, and fusion (Shepard 1971:28). The exact temperature at which these changes take place depends in part on the porosity of the chert and in part on the other minerals present. For example, carbon oxidizes more readily than iron, and thus iron compounds may remain unaffected until the carbon is burned out (Shepard 1971:21). Some organic carbon compounds begin to oxidize at temperatures below 100° C (Yariv and Cross 1979:419), forming carbon monoxide or carbon dioxide, but most of the carbon is removed at temperatures above 500° C (Micheelsen 1966:296; Shepard 1971:21).

Once the carbonaceous matter is gone, sulfur and iron compounds can oxidize, with many beginning to oxidize in the range between 225 and 500° C where heat-treating occurs (Shepard 1971:21,22). For example, goethite oxidizes to hematite between

200 and 300° C (Schindler et al. 1982:529). Carbonates, also common impurities in chert, do not decompose to carbon dioxide and calcium oxide until temperatures reach 650° C (Micheelsen 1966:296; Shepard 1971:22). Therefore, Rick's report that the calcite peak disappeared from his X-ray diffraction patterns of Burlington chert heated to about 430 to 460° C is anomalous (Rick 1978:34).

Evidence suggests that carbonaceous impurities may accelerate the alteration process or allow it to occur at lower temperatures. Rick found that the darker varieties of Burlington chert must be heated more slowly and were altered at lower temperatures than the lighter varieties (Rick 1978:26). While I do not have trace element data from the exact samples Rick used or even samples that I am sure came from the same outcrops he used, I do have data that may allow a tentative conclusion as to what differentiates these two varieties of Burlington chert. Using data described in Luedtke and Meyers (1984), I took values for a subsample of quarry materials described in the field notes as being very white and another described as gray and compared the average proportions of several trace elements (table 7.2). Mean values were not significantly different for any element except uranium, which was enriched in the darker cherts (significant at the 0.01 level). As discussed in chapter 4, uranium is often associated with reducing conditions and the presence of carbonaceous organic material in cherts. Furthermore, uranium-rich Indiana hornstone is said to heat-treat at the unusually low temperature of 200° C (Mandeville

**Table 7.2 Trace Element Composition of Burlington Chert Varieties (ppm)**

	White Burlington (N=9)	Gray Burlington (N=8)	All Burlington (N=101)
Na	x=177.0 (SD=20.6)	x=154.6 (SD=45.6)	x=154.3 (SD=40.4)
Sc	x=0.186 (SD=0.100)	x=0.177 (SD=0.090)	x=0.154 (SD=0.091)
Cr	x=1.37 (SD=0.896)	x=0.954 (SD=0.316)	x=1.06 (SD=0.821)
Fe	x=144.0 (SD=86.6)	x=204.6 (SD=237.8)	x=144.7 (SD=142.2)
Co	x=0.102 (SD=0.045)	x=0.145 (SD=0.072)	x=0.148 (SD=0.137)
Br	x=0.227 (SD=0.059)	x=0.234 (SD=0.035)	x=0.228 (SD=0.061)
Rb	x=1.22 (SD=0.581)	x=0.853 (SD=0.409)	x=0.958 (SD=0.792)
Sb	x=0.060 (SD=0.026)	x=0.044 (SD=0.027)	x=0.049 (SD=0.027)
Cs	x=0.068 (SD=0.035)	x=0.052 (SD=0.030)	x=0.058 (SD=0.046)
Ba	x=10.4 (SD=4.09)	x=13.5 (SD=5.83)	x=14.7 (SD=8.50)
La	x=0.438 (SD=0.431)	x=0.496 (SD=0.405)	x=0.372 (SD=0.348)
Hf	x=0.041 (SD=0.016)	x=0.044 (SD=0.013)	x=0.038 (SD=0.019)
Th	x=0.155 (SD=0.118)	x=0.144 (SD=0.063)	x=0.134 (SD=0.119)
U	x=0.198 (SD=0.134)	x=0.432 (SD=0.171)	x=0.348 (SD=0.364)

1973:197), and Knife River flint, a silicified lignite, at 250° C (Ahler 1983). This effect may be due to some other coincidental factor, such as grain size, but it is also possible that oxidation of the carbonaceous matter releases heat, raising the internal temperature of these cherts above that of the surrounding fire.

Other minerals may interfere with the changes in silica associated with heat-treating. Purdy suggests that the presence of large amounts of calcium in a chert may retard heat-treating or prevent it altogether (Purdy 1974:46). Clay minerals retard recrystallization caused by metamorphism (Keller et al. 1985:1361), and it is worth investigating whether they may also make heat-treating more difficult. Also, the presence of muscovite mica may be deleterious because this mineral dehydrates at low temperatures. This alteration is accompanied by swelling as the water is converted to steam (Shepard 1971:31). Thus, one would expect that shale cherts containing mica might shatter before they can be effectively heat-treated.

In general, heat-treating causes few direct changes to chert

geochemistry. Some of the carbon, hydrogen, and oxygen are driven off as gases, but the proportions of all other elements stay the same. However, heat-treating can change the mineralogy of some impurities, resulting ultimately in indirect geochemical changes. When minerals are altered to other minerals, they may also change in volume, solubility, and susceptibility to weathering. Therefore, heat-treated artifacts made of certain cherts and deposited in certain soils weather differently than, and might differ chemically from, unheated artifacts made of the same chert (for example, Purdy and Clark 1979). On the other hand, artifacts made of other cherts or deposited under other soil conditions might show no chemical difference between heated and unheated varieties.

### Effect on Visible Properties

Color, translucency, and luster can all change when cherts are heat-treated, although none of these alterations occurs universally in all cherts. Perhaps most obvious is the color change that occurs for many cherts, often at a temperature lower than that which changes mechanical properties. Specifically, cherts frequently turn pink or red as various iron compounds oxidize to hematite. Purdy (1974:46) found that Florida cherts with 4,000 ppm iron changed to reddish brown, those with 2,500 ppm iron changed to pale red, and those with 1,100 ppm iron turned pink; cherts with less than 1,100 ppm iron did not change color. Gold and honey-colored jaspers, iron rich by definition, often turn a bright red when goethite oxidizes to hematite (Schindler et al. 1982). Snow (1980:132) has suggested that this "magical" transformation to a color similar to that of blood may have had ideological significance for some prehistoric hunters in the northeastern United States.

Many other cherts darken when they are heated. Ozker (1976:362) found that Bayport chert darkened by one value step on the Munsell scale, and Ahler (1983:3) found that Knife River flint also darkened when it was heated to low temperatures, although it turned a lighter mottled gray at temperatures above 500° C. Other cherts become lighter in color when heated; in some cases, this may be due to the oxidation of small amounts of carbonaceous matter, as in the gray Burlington (Rick 1978). In other cases, such as that of blue-black Stevns flint which becomes grayish with heating, the change was attributed to altered optical properties resulting from water loss (Micheelsen 1966:312). Since most of the color changes in heat-treated cherts are due to alterations in impurity minerals, cherts without many impurities, such as Arkansas novaculite, do not change color (Flenniken and Garrison 1975). However, Indiana hornstone, which is relatively rich in impurities, is also said to stay the same color when heat-treated (Mandeville 1973:191). Given the present state of our knowledge about the causes of color in chert, it is still best to test each chert type individually to determine whether it undergoes a color change when heated.

Some relatively translucent cherts, such as Knife River flint

and some varieties of Edwards Plateau chert, become less translucent when heated. Ahler (1983:4) found nearly a 20% decrease in translucency for Knife River flint when it was heated to 200° C and a 50% decrease when heated to 325° C. This effect may be due to a mineralogical change or to an increase in microfractures that could diffuse the incoming light and decrease translucency.

Though not all cherts change their color and translucency when heated, nearly all change their luster. Heat-treated chert is glossier than unheated chert of the same type (Crabtree 1967:14). This change does not occur on the original surface of the heated fragment but is visible only on flake scars made after heat-treating. The change in luster occurs at the same temperature as the change in fracture properties (discussed below), and often at a higher temperature than the color change. Several hypotheses have been offered to explain the luster change. Most often it is believed to be owing to the fact that in heated cherts, fractures propagate across quartz grains rather than around them (Purdy and Brooks 1971). In unheated chert, light is reflected in many directions from the irregular grain surfaces, but in heated chert the true luster of quartz can be seen as light is reflected off the fractured grains. Another explanation is that heated flints are glossy because of an increased number of fluid inclusions that reflect light and give a waxy sheen or luster (Griffiths et al. 1987:51). Schindler et al. stated that the increased luster of heat-treated jasper is due to the reflection of light from hematite crystals (Schindler et al. 1982:535). Whatever the cause, this change in luster is often the best indication of heat-treating in archaeological specimens, especially if part of an artifact still retains the original duller surface.

At the microscopic level, no change in quartz grain size or orientation has been detected in heat-treated chert (Purdy 1974:50; Schindler et al. 1982:530). Although metamorphic recrystallization of chert can apparently take place within this same general temperature range, metamorphism also involves greater pressures, amounts of associated fluids, and lengths of time than does heat-treating. Other visible changes are minimal; Purdy noted that some of her thin sections showed more cracks in the heated cherts, but this was not universally true. A decrease in the refractive index has also been noticed for heated cherts, associated with a decrease in density (Weymouth and Williamson 1951).

### **Effect on Mechanical Properties**

The most important change that occurs in heat-treated chert is an alteration in fracture properties: fractures propagate across quartz grains and microstructural features rather than around them. Numerous scanning electron micrographs show flatter fracture surface topography after heating than before. Two major models have been put forward to explain the cause of this change in fracture pattern. The first, here called the "silica fusion" model, believes that the quartz microcrystals somehow become more tightly connected. The pore spaces become filled in, making the chert more homogeneous and glasslike. Various mechanisms have

been suggested as the cause. Mandeville suggested that fibers of silica melt and fuse together (1973:201). Purdy and Brooks (1971:323) argue that impurities among quartz grains act as a flux to fuse the surfaces of the grains. Beauchamp and Purdy (1986:1966) suggest that the bound water among grains exists as a gel that becomes consolidated by heating. Griffiths et al. (1987:51) follow Micheelsen (1966:355–357) in arguing that the heating anneals crystal lattice faults in the quartz grains as the water migrates into an increased number of fluid inclusions.

The usual evidence put forth in support of this model is scanning electron micrographs which are said to show a "denser" structure for heated chert. Yet this change in appearance is not always clearly differentiated from the change in fracture properties described above, which also results in a more even fracture surface. Griffiths et al. (1987:51) indirectly support their model with evidence of more fluid inclusions in heated flint: a nuclear magnetic resonance signal for liquid water, not present at lower temperatures, appeared in their data for flint heated to 380° C. They also found that the chalcedony among relic lepispheres in heated flint was more susceptible to etching with hydrofluoric acid than was the chalcedony in unheated flint. They attributed this susceptibility to an increase in fluid inclusions (Griffiths et al. 1987:49–50).

Purdy (1974:51) used gas absorption to compare the porosity of a heated and an unheated sample of one of her chert types. Finding that the former was 60% less porous than the latter, she argued that the decrease resulted from the fusing of quartz grains. However, she performed this test on only two samples. In the absence of any information concerning to what degree porosity might vary within a chert type, it is difficult to know whether the difference was due to heat-treating or to some other factor. Other investigators have found that cherts increase in porosity when they are heated. English Chalk flint increased from 1.03% porosity for unheated flint to 2.12% for flint heated to 400° C, and density decreased from 2.622 to 2.593 over that same temperature range (Weymouth and Williamson 1951:582). Mandeville (1973:190) also reported a decrease in the density of cherts heated to about 300 to 400° C. Obviously, we need more testing and especially more information concerning the range of variability within chert types before we can consider this model to be adequately tested.

The silica fusion models present other problems. The melting point of silica is normally very high, about 1700° C, far above the range involved in heat-treating. Ceramists and glassworkers have demonstrated that the temperature at which silica melts can be lowered by the presence of fluxing ions, especially sodium, potassium, lithium, calcium, and magnesium, all of which are often present in cherts. "These ions when present lower the melting point of the system and, in particular react with silica at as low as 1000° C to form a viscous liquid, which on cooling does not crystallize but solidifies to form a glass, in which the fluxing ions occupy holes in the Si-O-network" (Worrall 1986:174). These

temperatures are still far above those involved in heat-treating. Even for glasses, which contain very large proportions of the fluxing ions so that the silica will be viscous at low temperatures, the relevant temperature ranges are from 600 to 700° C. It remains to be demonstrated that any of the impurities in chert can flux silica at temperatures between 250 and 450° C.

The second model regarding the cause of the change in fracture pattern induced by heat-treating, here called the "crack" model, argues that heating increases the number of microflaws in chert and/or distributes them more evenly. Thus, fractures occur more easily and are more controllable. Experimenters are not always explicit about whether these microflaws are located within or between grains. Logically, they should be within grains in order to produce the cross-grain fracturing that appears to be so typical of heat-treated cherts. Several experimenters have suggested that these microflaws are caused by the expansion of quartz when it is heated (for example, Flenniken and Garrison 1975:128). As discussed in chapter 6, quartz has the highest coefficient of thermal expansion of any common mineral (Skinner 1966:92), and it expands more in one crystallographic direction than the other. This uneven expansion could set up considerable stress in a system where quartz grains are randomly oriented. Griffiths et al. (1987) argue that hydraulic pressure may also play a role: the water in chert may expand when it is heated, resulting in microfracturing. Schindler et al. (1982:535) believe that cracks open up between quartz grains in jasper as goethite is oxidized to hematite, which forms smaller and denser crystals.

The decreases in strength typical of heat-treated cherts can be considered evidence in support of the crack model. Cracks are now viewed as extremely important strength-controlling features, and the sharp-ended cracks induced by heating and mechanical damage are especially likely to lead to fractures (Sprunt and Brace 1974). In further support of this model, Weymouth and Mandeville (1975:66) interpreted the broadening of X-ray diffraction peaks of heat-treated cherts as indicating a decrease in the size of the subgrains making up the quartz grains, presumably as a result of microfracturing. They found decreases ranging from 1 to 31% for a variety of cherts heated to 400° (Weymouth and Mandeville 1975:66). Micheelsen (1966:355–356), however, found just the opposite: the subgrain size of Stevns flint appeared to increase upon heating, which he attributes to the annealing of lattice flaws. Unfortunately, all of Micheelsen's experiments in the critical temperature ranges of 300 to 600° C also involved high pressures. These varying findings may result in part from differences in the size and shape of the original cracks or pores. Brantley et al. (1990) heated quartz crystals and found that small cracks healed faster than larger ones. Additional testing is surely necessary to determine exactly what happens to the particles in quartz grains when they are heated under low pressures.

The silica fusion and crack models are not necessarily mutually exclusive. Fusion and increased cracking could occur at the

same time, or each process could occur in some cherts but not in others. It should be fairly easy to devise tests of these models, and such research would be illuminating.

Whatever its cause, the change in fracture pattern is associated with changes in the strength of heat-treated cherts. The work of several researchers indicates that tensile strength decreases similarly in various heat-treated cherts. For example, Purdy (1974:49) found a reduction in point tensile strength of from 39 to 53% for Florida cherts, and heat-treated jasper had only half the fracture toughness of unheated jasper (Schindler et al. 1982:532). Rick (1978:40) found decreases in point tensile strength of from 11 to 55% for heated Burlington chert. Less explicably, Purdy reports an increase in the compressive strength of heat-treated chert, which she attributes to the tighter bonding of the quartz microcrystals (Purdy 1974:47–48). She also reports an increase in compressive strength for heated obsidian, which surely cannot be undergoing the same annealing process. This situation suggests that more research is needed to validate this finding.

To the best of my knowledge, Beauchamp and Purdy (1986) have published the only measurements of other mechanical properties that might be affected by heat-treating. In comparisons of heated and unheated Ocala chert, they found that fracture toughness decreased by nearly 68% after heating, Young's modulus increased, and Vickers hardness stayed the same.

A wealth of subjective evidence from flintknappers attests to the altered mechanical properties of heat-treated chert. Replicators report that heat-treated chert is less tough, more elastic, and therefore much easier to knap, and that it responds especially well to pressure flaking (Crabtree and Butler 1964). Ahler (1983:5) estimates that 50% less force is needed to detach flakes from heat-treated Knife River flint. In addition, flakes produced from heat-treated chert appear to be different from those produced from the same types of unheated cherts. More ripple marks are evident on flake scars (Ahler 1983:4; Rick 1978:51), and pressure flakes tend to be longer, larger, and better controlled, with more feather terminations and fewer step-and-hinge fractures (Flenniken and Garrison 1975:129). In addition, all replicators report that flake edges are noticeably sharper.

A decrease in chert strength is not entirely beneficial for stoneworkers. Ahler (1983:5) reports that heat-altered Knife River flint is more "fragile" and prone to lateral snap, reverse fracture, and platform collapse during percussion flaking. Rick (1978:53–54) also found that platforms had to be ground on heat-treated Burlington chert to avoid collapse and that flaked edges were less durable: "Because of the different properties of heat-treated and unaltered chert in tool use, heat-treated chert cannot be regarded simply as an improved raw material" (Rick 1978:62). Ahler (1983:6) agrees that heat-treating may not be appropriate for all tool types. At one prehistoric site, he found that projectile points showed the highest incidence of heat treatment. Although these points need not be extremely durable,

they do require the careful and controlled pressure flaking that heat-treating allows.

### Unintentional Heat Altering

Not all heat-altered chert has been heat-treated. Chert flakes and artifacts occasionally fell into hearths or were burned in house or forest fires. Chert was sometimes used as pot boilers or fire rock (Shepherd 1972:174). Some ethnographic stonetool users also used fire in quarrying, either to break up the surrounding matrix for removal (Mandeville 1973) or to break up pebbles, cobbles, or boulders for later use (Gregg and Grybush 1976:191; Binford and O'Connell 1984). Because these circumstances usually involved overly rapid heat-up times, direct contact between chert and fire, and/or excessive heating temperatures, they resulted in characteristic thermal damage.

Much of our information concerning heat damage in chert comes from heat-treatment replicators who often cause these kinds of damage in the course of determining the boundary conditions for heat-treating. In addition, some data are available from studies of flint that has been calcined—for example, heated to such high temperatures that it changes to cristobalite. Although the silica changes back to  $\alpha$  quartz upon cooling, the flint is whitened and severely damaged; thus, it is easy to crush and grind. Calcined flint was often used in the production of ceramics in England to prevent glazes from crazing (Weymouth and Williamson 1951).

The most common form of thermal damage is fracture, usually resulting in blocky, angular chunks with no bulbs of percussion (Purdy 1974:52). Even more distinctive of heating are “pot lid” fractures: small circular, convex fragments that appear to have popped off flat surfaces. Crazing and internal fracturing are often evident, sometimes accompanied by loss of color and luster (Ahler 1983:3). Many cherts become pale and chalky when heated too much, and some show “smoked” areas. Chert heated to very high temperatures can appear distorted because of shrinkage and apparent change in volume (Ahler 1983:4). Heat-damaged chert invariably is too badly flawed to be knapped; in fact, some cherts may become too brittle for knapping even before any damage is visible (Griffiths et al. 1987:44–45). It is likely that some of these types of damage are more often associated with certain improper heating conditions than with others (Purdy 1975). For example, Ahler (1983:5) has suggested that crazing is caused primarily by overly high temperatures and that pot lid fractures are associated with overly rapid heating and cooling.

When chert is heated, damage is especially likely to occur at several crucial points. Purdy (1974:431–442) noted that if her cherts were going to explode, they always did so between 350 and 400° C. Cherts could be rapidly heated and cooled with no ill effect as long as temperatures were kept below 350° C. In addition, the temperature of cherts that had been left at 350° C for twenty-four hours could then be safely raised to 400° C, but rapid heating to

400° C usually resulted in an explosion. Weymouth and Williamson (1951:587) also found that their flint often shattered at 365° C and pointed out that this is close to the “critical temperature” of water. Critical temperature is the temperature above which a gas cannot be liquefied under any amount of pressure. Water normally begins to boil, or turn into a gas, at 100° C, but when the water is under pressure, it will remain liquid until the critical temperature is reached. Thus, when chert is heated, much of its water begins to vaporize around 100° C, but the water deep in the rock is under pressure and remains liquid. If this water is not completely driven off by prolonged heating, it may turn to steam when the critical temperature is reached. The resulting increase in pressure may shatter the chert.

Another crucial point is 573° C, at which point the silica undergoes an inversion from normal low temperature  $\alpha$  quartz to high temperature  $\beta$  quartz, with an associated change in crystal structure. This inversion is reversible, but probably causes irreversible damage to the chert. Theoretically,  $\beta$  quartz should change to tridymite at about 870° C and to cristobalite at 1470° C, but in actuality quartz can turn to cristobalite at temperatures as low as 1030° C (Micheelsen 1966:313). Cristobalite becomes liquid at 1723° C, but the other varieties of silica can also become liquid directly if pressures are high enough. Most of these changes are relatively sluggish and affected by the presence of other minerals.

It is not always easy to tell whether an artifact was subjected to heat treatment or was heated by accident. Accidental heating can sometimes bring about the changes in color and luster associated with heat treatment, and intentional heat-treating can sometimes leave some of the chert damaged in the ways described above. Therefore, one must look at the patterning of heat alteration within an entire assemblage to determine whether heat treatment was intentional. If it can be demonstrated that heat alteration is preferentially associated with certain categories of tools or occurred at a specific stage in the manufacturing process, and especially if it can be demonstrated that knapping took place after alteration, then it is reasonable to infer that heat treatment took place.

### Dating Heated Chert

Both heat-treated and unintentionally heated chert can be dated by several methods. Most methods are based on the fact that chert, like other materials made of crystals, tends over time to trap electrons in its crystal structure. Radiation resulting from the decay of radioactive isotopes in the chert itself or in the surrounding soil matrix, or even from cosmic rays, interacts with the chert and knocks electrons free from their atoms (Göksu Ögelman 1986). Some of these electrons return to their original places and some migrate out of the chert. Other electrons become trapped in lattice flaws and accumulate in the chert over time unless they are released by being heated to between 350 and 500° C (or, for highly

translucent cherts, by strong sunlight). Thus, heating resets the "electron clock" to zero, and electrons begin accumulating again at a steady rate determined by the sources of radiation in the area. Thermoluminescence dating (TL) is the major method used to take advantage of this clock effect. Chert fragments that are judged to have been subjected to heat during the time the site was occupied are heated again in the laboratory, releasing the trapped electrons. As they escape, these electrons give off visible light, which can be measured. Because the amount of light is proportional to the amount of radiation to which the chert has been exposed, and the amount of radiation is partly a function of time, it is possible to determine how much time has passed since the sample was last heated. Göksu Ögelman (1986) provides a good discussion of the problems and prospects of this dating method. Although TL dating of chert is better accepted in Europe than in the United States (B. A. Purdy, personal communication), the results of this measuring technique, used at sites ranging in age from 2000 to 200,000 years, generally agree well with other dating methods. Thermoluminescence has also been used to determine whether chert artifacts have actually been heated. This is done by comparing the number of trapped electrons in the possibly heated specimen with the number in an artifact that is not believed to have been heated.

Another method that may be usable for dating is electron spin resonance spectroscopy. It is also based on the presence of free electrons, including both radiation-induced electrons and unpaired electrons present in some metal and rare earth element impurities. In this method, a sample of chert is placed in a strong magnetic field and bombarded with microwaves. The number and kinds of loose electrons can be determined by the kinds of microwaves absorbed at different wave lengths. As with TL, the quantity of free electrons is partially a function of time. This method has also been used to determine whether chert has been heated (Robins et al. 1978) and, in some cases, whether the maximum temperature was reached (Griffiths et al. 1986; Maniatis et al. 1989).

## Weathering

All rocks exposed to surface conditions begin to weather—that is, to alter in response to the atmosphere, temperature, and organisms in the surrounding environment. Geologists make a distinction between chemical and mechanical weathering, with the former involving changes in the minerals in a rock as a result of oxidation, reduction, solution, precipitation, hydration, and other chemical processes. Mechanical weathering involves breakdown of the rock, with little or no change in composition, as a result of trampling, crushing under the weight of sediments, the action of plant roots, or the expansion and contraction caused by temperature changes. In reality, it is not always easy to separate the effects of chemical and mechanical weathering. Chemical weathering

often makes rock surfaces more porous so that water and plant roots can penetrate and cause mechanical damage, while mechanical weathering opens up cracks in the rock along which chemical weathering can proceed. Therefore both types of weathering are discussed together here.

Chert, because of its relatively dense structure and stable mineral composition, resists weathering better than most other rocks. It does indeed weather, however, and this process is of interest to archaeologists for several reasons. First, weathering changes the chemical, visible, and mechanical properties of the rock surfaces, thus causing problems for certain kinds of archaeological analysis. Second, because the extent of weathering is partly a function of time, weathering phenomena are potential dating methods. Unfortunately for those interested in this latter possibility, weathering is an extremely complex process, defying easy generalization. It is a function of the interaction between the characteristics of a chert type and the characteristics of the surface environment to which the chert is exposed. Thus, two different cherts might weather differently in the same environment, and the same chert may weather differently in two different environments.

It is important to distinguish weathering rinds, sometimes called patinas, from cortexes. A cortex forms at the same time as the chert and is essentially a transition zone or interface between the chert and its surrounding matrix. Weathering rinds form much later as the result of irreversible chemical and mechanical changes in the chert. Weathering begins on the surface of a fragment and along any cracks or fissures. It can work its way throughout the body of the chert given enough time or extreme environmental conditions. During weathering, some of the silica may be removed either by solution or by the loosening of the quartz grains so that they fall out. Some of the impurities in the chert are also removed, and other minerals may be deposited in its pores or cracks.

These changes in the structure and chemical characteristics of the surface also result in changes in visible characteristics, often including an alteration in color. In addition, weathered surfaces are usually duller and coarser textured than fresh chert surfaces. The mechanical properties of weathered chert are also different. I know of no mechanical tests performed on weathered chert, but the fact that knappers usually remove the weathering rind as soon as possible suggests that it does not have desirable knapping properties. Tsirk has pointed out that mild weathering can lead to a decrease in the sharpness of flaws in obsidian, thus actually increasing its strength (Tsirk 1981:7). The same may be true of chert under some conditions.

## Effects of Chert Characteristics

Part of the variability in the ways cherts weather is due to factors inherent in the cherts themselves. Thus, fine-grained and even-textured cherts usually weather less easily than coarser cherts (Hurst and Kelly 1961), and smooth or polished surfaces resist

weathering better than rougher ones. In addition, cherts made of chalcedony are more susceptible to solution than those composed of more highly crystalline granular quartz (see chap. 3). Weathering properties can also vary within a chert type. Even within a single fragment, variations in texture and microstructure can result in uneven weathering (Hurst and Kelly 1961:255).

Porosity and water content greatly affect weathering. All cherts contain water, and the more porous cherts exchange water easily with their environment through capillary action. Micheelsen (1966:294) found that the water content of his Stevns flint was a continuous function of relative humidity. Mandeville noted that some cherts were capable of readily gaining and losing water under varying environmental conditions in the laboratory (Mandeville 1973:200). Water itself is chemically active, and it can also carry dissolved matter such as acids, bases, or humic substances, which can interact chemically with the chert. As water moves in and out of chert, it can cause oxidation and hydration, dissolution and leaching, precipitation, and chemical and mechanical disaggregation, especially of the nonsilica minerals (Hurst and Kelly 1961:253). For example, Rick (1978:26) noted that Burlington chert collected from streambeds was more likely to redden under heat treatment than was Burlington chert collected from outcrops, and he suggested that iron had been deposited in the streambed samples by the groundwater.

The minerals present as impurities in chert also affect the kind and rate of weathering. Some of these minerals are very stable, whereas others are susceptible to solution under some conditions and to precipitation under others. If these minerals are removed from between the quartz grains, the grains may become loosened. Impurity minerals may also expand or contract as they are altered, breaking up the surface of the chert and pushing quartz grains apart. Though cherts with high proportions of chemically unstable impurities will weather quickly, other impurities, such as organic matter, do not appear to accelerate patination (Hurst and Kelly 1961:254). Furthermore, Clark and Purdy (1979:523) suggest aluminum may retard weathering in cherts, perhaps by interfering with certain iron reactions.

Because the rate of weathering is so strongly affected by chert composition and structure, it is dangerous to assume that an artifact made of one chert is older than an artifact made of a different chert because the former has a thicker weathering rind. "Even limited study suffices to show that the patination rate may vary more with microstructure and mineralogical impurities than with age (Hurst and Kelly 1961:251).

### **Effects of Environmental Factors**

Weathering is also a function of the environment to which the chert is exposed, and, once again, many factors must be considered. If a flake of chert has lain on the ground for any length of time, it may have been affected by trampling, wind and sand blasting, ultraviolet light, or lichens that send little filaments into

the pores, dissolve certain minerals, and cause pitting and destroy patina (Ackerman 1964). If buried, it may have been damaged by plant rootlets, solifluction, or even glacial movement (Stapert 1976). Weathering is also affected by characteristics of the soil, such as its chemical make up, pH, temperature, permeability, and volume and rate of circulation of groundwater (Schmalz 1960). Most of the chemical reactions involved in weathering require water, and the rate of such reactions doubles for each 10° C rise in temperature. Thus, chemical weathering is greatest in warm, humid climates. Weathering can vary even over short distances. Many archaeologists have been surprised to discover that two artifact fragments from different parts of a site fit together, although they differ greatly in appearance. Such differences must be due to very local variations in weathering conditions.

### **Weathering Rinds**

Interactions between these factors and processes may be complex. The development of one kind of patina may subsequently prevent other kinds of weathering. On the other hand, weathering of one type may then encourage another type to begin. Finally, if the environment changes over time, artifacts may be subjected to different forms of weathering. Thus, it is nearly impossible to develop a typology of weathering rinds or patinas that will fit every case. Nevertheless, several broad categories have been defined and are described here as examples of the kinds of weathering that cherts can undergo. Subdivisions of some of these categories are described in the references cited.

#### **WHITE PATINA**

This type of weathering rind is sometimes called bleached patina. It is especially common on dark flints where it often begins as a bluish film, usually thicker on the upper surfaces than on lower ones, and becomes increasingly dull, chalky, and white or cream-colored over time (Stapert 1976:11–12). White patinas are sensitive to any inhomogeneity of the chert and may highlight banding or cracks in the material. They may also show the pattern of plant roots that lay against a fragment of chert. Scanning electron micrographs show that this patina has a pitted and porous surface, from which light is reflected in all directions (Stapert 1976:11–12). Though some older references say white patina is produced when silica is replaced by lime salts (for example, Goodwin 1960), more recent references state that it results when silica is removed from the surface of cherts buried in alkaline soils. In fact, white patina can be duplicated in the laboratory by soaking chert in sodium hydroxide for twenty-four hours (Schmalz 1960:60). "A deep patina might form, in all probability on an artifact exposed to sodium- or calcium-rich groundwater in less than a year" (Schmalz 1960:49). English Chalk flints are especially susceptible to such weathering because they generally lie in alkaline soils and because they contain a good deal of chalcedony, which is more soluble than granular quartz.

Some lighter colored cherts also develop a light weathering



rind to the leaching of other minerals and to the loss of silica. For example, carbonates are often easily leached from cherts (Krauskopf 1979:80). When iron compounds oxidize, they can change volume and may also contribute to acids that attack the clays, resulting in the loosening of quartz grains (Hurst and Kelly 1961:254). Clark and Purdy found that some Florida cherts formed a weathering rind consisting of an outer chalky white layer and an inner dark zone. Microprobe analysis showed that silicon and aluminum proportions did not vary greatly from the interior to the surface, but that iron was greatly depleted in the outer layer and considerably concentrated in the dark layer, relative to the unweathered chert (Clark and Purdy 1979:519–521).

#### **DARK PATINA**

Many cherts develop weathering rinds in various shades of brown ranging from yellow-brown to red or nearly black. Such patinas may have more than one origin. White patina is highly susceptible to staining by humic substances and iron in groundwater, and some dark patinas may also form in this way (Stapert 1976:12–13). Hurst and Kelly (1961:254–255) describe a goethite rind that can form on chert lying in stagnant and acid water: iron is leached from the chert and redeposited on its surface. On the other hand, Rottländer (1975) argues that some dark patinas result from oxidation rather than leaching of iron. He points out that such cherts show the same proportion of iron in the weathering rind as in the unweathered interior. The presence of iron does seem to be important for the development of a dark patina. One study of a Magadi-type chert noted that samples could weather white, yellow, or brown, and those that weathered brown contained three times more iron than the samples that weathered white (Stiles et al. 1974:289).

#### **GLOSSY PATINA**

Some cherts weather by developing a uniform translucent gloss over their entire surface as the result of silica deposition (Stapert 1976:12). Some of this silica may have been dissolved in the groundwater, but much of it probably comes from the chert itself. Rottländer (1975) duplicated glossy patina in the laboratory by soaking flint in peaty water (pH = 4) at 50° C for three weeks. During this time, the flint lost weight, and silica apparently dissolved from projections on the surface of the flint, which have high potential energy, and was redeposited in low areas, which have low potential energy (Rottländer 1975:108–109). When glossy patina forms, it seals off cracks and pores and makes the chert resistant to other forms of weathering (Stapert 1976:12).

Glossy patina forms a uniform coating, even into the hollows in the surface of a chert fragment. This appearance distinguishes it from glosses resulting from other processes, including wind and friction. Wind gloss results from mechanical polishing; it tends to have a greasy rather than glassy luster and generally affects one side of a fragment more than the other (Stapert 1976:14–19). Friction gloss is apparently caused by siliceous rocks rubbing

against one another in the soil, creating small patches of very high gloss (Stapert 1976:29–30). Harding et al. (1987) describe polish that can develop on the ridges and flat surfaces of chert bifaces as a result of fluvial transport in a gravel river bed. Finally, polish or gloss can form as a result of use wear, but this type of polish is normally localized on the working edge of a tool or on areas where the tool has rubbed against its haft.

#### **DESERT VARNISH**

Unlike the other weathering rinds that result from alteration and often destruction of the chert itself, desert varnish is actually deposited on the surface of chert by the wind, probably in conjunction with groundwater (Potter and Rossman 1977). Desert varnish is a hard, dark, glossy coating that can form on the exposed surfaces of most kinds of rocks in many different environments. It is especially common in deserts, though, where there is no vegetation to block the wind and the proper conditions exist for preserving the varnish once it forms. Desert varnish is made up largely of clay (at least 70%) in combination with iron and manganese oxides and small amounts of organic matter and trace elements (Potter and Rossman 1977:1447). Desert varnish forms extremely slowly. Deposits that have formed within the last hundred years occur in isolated patches only 1  $\mu$  thick (Dorn and DeNiro 1985:1474). Over a long enough time desert varnish can form a layer up to 100  $\mu$  (0.1 mm) thick over the entire exposed surface of a rock (Potter and Rossman 1977:1446).

#### **Frost Fracture**

Besides causing patinas or weathering rinds, weathering processes can also fracture chert. Probably the major form of mechanical damage is frost fracture, which can occur when temperatures drop below freezing. The term *frost fracture* actually covers several different types of damage, including fracture into angular blocky fragments, scaling of cortex from surfaces, and frost pits, convex fractures about 1 to 3 cm across that occur on flat surfaces, especially on relatively thin fragments of chert (Sieveking and Clayton 1986). Some cherts may also develop a distinctive texture; “. . . flakes [of English Chalk flint] that have a ‘soapy’ feel or appearance are regarded as frosted” (Sieveking and Clayton 1986:283). Scanning electron micrographs indicate that fractures cut across quartz grains and relic lepispheres in such flints and that the interstitial chalcedony in frosted flints is more easily etched (Sieveking and Clayton 1986).

Much of this information should sound familiar. Damage due to frost is in some ways similar to damage caused by heat, though there are differences that allow discrimination between these two forms of thermal damage. Frosted cherts do not usually change color, and many do not change luster. In addition, frost pits are bigger than pot lid fractures and usually have cortex on the back. Finally, frost fractures are usually parallel to the surface of the nodule or fragment. They sometimes appear to originate inside the body of the chert where concentric rings can sometimes be seen

spreading out from a fossil or other small inhomogeneity (Stapert 1976:20).

Freezing water is probably not responsible for all frost damage. The water in some cracks or large pores may freeze, but most of the water is spread so thinly that it is bound to the silica and cannot easily freeze (Sieveking and Clayton 1986:284). Therefore, thermal contraction probably causes most of the initial damage, especially where the difference in temperature between the weathered or cortex-covered surface and the unaltered interior of a chert fragment results in a steep thermal gradient. As the exterior contracts relative to the interior, scaling and frost pits develop (Sieveking and Clayton 1986:284). These stresses also cause internal fractures to develop, sometimes long before damage is visible on the surface of the chert. Once these cracks form, additional water is able to enter and freeze, producing further fracturing.

Numerous cycles of freezing and thawing are usually necessary to cause frost damage, but there is considerable variation and some fragments break almost immediately (Sieveking and Clayton 1986:283). Differences in porosity may account for some of this variability (Lautridou et al. 1986), and cherts with a great deal of moisture in them have been found to fracture more easily than dry cherts (Sieveking and Clayton 1986:283).

### **Implications for Archaeologists**

Weathering phenomena can complicate life for archaeologists in several ways. First, weathering can also interfere with the ability to recognize chert types. Changes in the mineral composition at the surface of weathered cherts may result in trace element differences between artifacts and source samples. Weathering can also dramatically change the visible properties of cherts, which could lead to misidentifications.

Weathering phenomena can also interfere with the ability to recognize artifacts as such. The various forms of mechanical weathering can fracture chert into "geofacts," which have sometimes been mistaken for tools (Shepherd 1972:148–150). Mechanical damage can "retouch" the edges of thinner flakes and tools (Stapert 1976:28–29). Weathering can prevent use wear analysis by obscuring or even obliterating the wear that originally existed on an artifact. Perhaps more confusingly, weathering can mimic wear on artifacts. Microfractures, scratches, and glossy areas can all be caused by natural, as well as cultural, processes (Stapert 1976). Wise use-wear analysts look for the clues that distinguish actual use wear from naturally occurring wear (Hayden 1979:283, 372).

A potential benefit of weathering is its use as a dating method. Archaeologists have been intrigued by this possibility for centuries, but progress has been hampered by the complexities of the weathering process in chert. Most archaeologists are reasonably comfortable using differential weathering of artifacts from the same chert type as a relative dating method within a site. For

example, differences in patination have sometimes proved useful for separating artifacts from two different components at sites with mixed stratigraphy (Michels 1973:28; Purdy and Clark 1987). However, no reliable method of absolute dating based on weathering has yet been developed for chert, although ingenious new approaches are continually being studied (Purdy 1981a).

For example, there have been recent attempts to use accelerator radiocarbon dating to determine the age of the organic matter in desert varnish (Dorn et al. 1986). Organic matter usually makes up less than 1% by weight of desert varnish and only the basal layer can be used, so 1,500 to 20,000 cm<sup>2</sup> of desert varnish must be scraped off to obtain enough material for analysis. The source of the carbon being dated is obviously a critical factor. In this test case, the carbon is believed to be derived primarily from local fungi, bacteria, microorganisms, and plant detritus that became airborne and were incorporated into the varnish (Dorn and DeNiro 1985). The rocks studied by Dorn et al. (1986:830) had no measurable organic carbon content of their own, and there were no obvious sources of older carbon in the environment that could have contaminated the desert varnish. Some cherts do contain considerable quantities of organic carbon, however, and it is not known what effect this might have on the technique (see chap. 3).

Recognizing that the quantities of desert varnish required make this technique impractical for most archaeological purposes, Dorn et al. (1986) suggest that the radiocarbon dates be used to calibrate a cation-leaching curve based on the fact that minor elements are leached at different rates from the desert varnish. Specifically, both potassium and calcium leach more rapidly than titanium, so the ratio of potassium plus calcium to titanium, as determined by proton induced X-ray emission spectroscopy, varies with the age of the varnish. This leaching curve appears to be different for different regions, though. Much basic background research is needed to make this method usable (Dorn et al. 1986). Other archaeologists have also attempted to make use of the leaching that often accompanies weathering as a dating method. For example, Clark and Purdy (1979) have suggested that iron may be leached from chert by a diffusion-controlled process and that the depth of leaching is proportional to time.

Other archaeologists have taken the opposite approach and examined the chemicals that might be diffusing into chert during weathering. For example Taylor (1975) has suggested that fluorine diffusion could be used to date chert and other rock types. Fluorine does not occur in large quantities in groundwater except in volcanic regions, but it is generally present, and fluorine-bearing water should diffuse along the grain boundaries in cherts exposed to groundwater. Controlling factors should be temperature of the area, chemical and physical properties of the rock, and time.

None of the weathering-related dating methods described above have been tested widely, and most archaeologists are

properly skeptical of all such methods. Unfortunately, we are unlikely to discover a method of dating weathering rinds on chert that is as widely applicable as obsidian hydration dating, which is based on the diffusion of water into natural silica glass during weathering. Anyone who is tempted, however, to dismiss the possibility entirely is encouraged to read a pioneering work on the application of science to archaeology, which concluded that obsidian hydration dating "should not be regarded as promising" (Heizer and Cook 1960:320, 321, 343). Dating chert on the basis of weathering phenomena may be complex and difficult, but it is not necessarily impossible. In addition, better methods for determining the chemical and physical properties of different chert types might go a long way toward making weathering-related methods of dating usable.

## Transport

Cherts are often moved from their original locations by erosion and transportation. The result is secondary chert sources that can greatly enlarge the zone within which a chert type is found. Some of these deposits were important to stone-using peoples. Such chert is sometimes battered and frost fractured, but part of it is of especially good quality because any weaknesses that originally existed have already fractured.

The distance a chert type is transported from its source depends on the nature of the transporting process. Residual cherts have usually moved the least. Residual deposits form when the surrounding bedrock, often a limestone or marl, has eroded or weathered away leaving the more resistant chert behind as a layer of nodules or fragments in loose sediments. Also, chert that has eroded out of an outcrop and fallen onto a talus slope does not move far from its source. Water is a more effective transporting agent, creating deposits of chert pebbles and cobbles in streambeds and on beaches and lakeshores. Glaciers can transport chert the farthest; thus, the factors and processes involved are worth considering in more detail.

In theory, a piece of chert could be transported hundreds of kilometers by a glacier and then somewhat farther by the rivers that drain it. In reality, though, transport is a destructive process, and a number of studies have shown that rocks tend to decrease in size exponentially as they are carried away from their sources (Krumbein 1937; Plumley 1948). Thus, the probability of finding chert in usable quantities and sizes decreases as one moves away from the primary source. The definition of a usable size fragment varies by culture. In Late Woodland Michigan, fragments as small as 3 cm in diameter were worked using bipolar percussion (Luedtke 1976:92). For most stone-using peoples, usable fragments were considerably larger.

Several factors influence the rate at which rocks are destroyed during transport by glaciers or streams. A crucial determinant is the size of the pieces initially quarried from the bedrock (Goldthwait

1971). Chert that originally formed in large nodules or massive beds will be carried farther than chert that formed in thin lenses or small nodules. Resistance to breakage is another factor. Being a relatively tough rock, chert is less vulnerable to breakage than rocks such as limestone or shale, though it is not as tough as quartzite or basalt. To the extent that cherts vary in mechanical properties such as brittleness and strength, they may also vary in their vulnerability to destruction during transport.

The rate of breakage also differs depending on where the rock is carried within the glacier. The most destructive is super-glacial transport, in which sediments that fall onto the tops of glaciers from surrounding mountains are destroyed quickly by the constant freezing and thawing that occurs there. Most rock, however, is gouged or plucked out of bedrock at the base of the glacier where it is subject to crushing, percussion, abrasion, frost action, and other destructive processes (Dreimanis and Vagners 1971). Occasionally, the glacier meets an obstruction such as a previous moraine or resistant bedrock. Then upshearing occurs, causing rocks to be carried to a position within the body of the glacier. Rocks undergoing englacial transport, as this is called, suffer the least destruction and are carried farthest in large size ranges.

Cherts also decrease in abundance relative to other types of rocks in the drift as they are spread out fanwise and diluted by materials continually being added to the glacial load. Fanning is the result of divergent flow within the glacier as it moves radially from the center of the lobe (Krumbein 1933). One study of "indicator fans" or boulder trains showed that the fanning forms an arc measuring 20 to 60° (Goldthwait 1971). Thus, chert can be spread some distance perpendicular to the major direction of the glacial flow.

The amount and rate of dilution depend on the strength and quarrying characteristics of the rocks downstream from the chert. The relative size of outcrop areas is important because a large outcrop will contribute more to till than a small outcrop. Some outcrops show greater resistance to erosion either for topographic reasons or because they are protected by a layer of previous drift (Krumbein 1933). Finally, different types of glacial deposits have varying proportions of distant materials. Terminal moraines have a higher proportion of distant materials than ground moraines because englacially transported rocks are generally deposited near the top of terminal moraines (Flint 1957; Dreimanis and Vagners 1969). Interlobate areas also tend to have high proportions of englacially transported materials.

Most studies have found that the pebble and cobble fraction of glacial till is predominantly local. Alden (1918) found that over 90% of the pebbles in the till he studied came from an average distance of less than 64 km from the collecting locality. Lotan and Shotron (1968) determined that over 92% of their pebbles were local. Crosby (1896) found that 50% of his pebbles came from less than 16 km away and that 90% came from less than 32 km. Goldthwait (1971) states that less than 0.1% of any lithology of

rocks survives beyond 34 km. It should be noted that all the above figures refer to pebble-size fragments or larger, as there is usually a greater volume of distant material in the smaller size.

Most cherts are unlikely to travel far in usable sizes and quantities. My own research in Michigan provides limited confirmation of this conclusion (Luedtke 1976:98–101). I was interested in how far Norwood chert, which occurs in lenses 2 to 15 cm thick, had been transported from its rather limited outcrop area in northwestern Michigan. I surveyed beach deposits, gravel quarries, and road cuts in the area around the outcrops to determine the availability of this material in secondary deposits. At each secondary deposit, the participants in the survey picked up every piece of Norwood chert over an inch in diameter that they could find within a two-minute period. The total number of pieces

collected at each locality determined the relative availability of the material, while the average length of fragments determined the rate of destruction during glacial transport. Both measures were in agreement, and they were confirmed by local rock hounds. Norwood chert was rarely found in usable sizes or quantities farther than 40 km south of its source.

Chert inevitably begins to alter once it is exposed at the earth's surface. Archaeologists are greatly interested in the alterations caused by human beings, including such processes as heat-treating, manufacture into tools, use, and transport from sources as a result of procurement or trade. Before we can deal with these culturally caused changes, we must first rule out the visible and mechanical properties of chert, fracture it, and transport it away from its primary sources.



# 8

## Summary

**W**hen I began the research for this book I hoped it would lead to several findings that would greatly simplify the lithic analyst's task. First, I hoped to find that the various properties of chert were interrelated in such a way that one could predict many of the properties on the basis of the others. I also hoped to find that a few of these properties were more central or critical than others and that these "key properties" would explain a large proportion of the variability in chert. Finally, I hoped to find simple and objective ways to measure the various properties of chert, especially the key properties. None of these hopes was fulfilled completely, but I do not believe that they are impossible goals. In fact, there are a great many intriguing research questions that may ultimately lead to their accomplishment.

This chapter highlights some of these research possibilities by returning to each major topic in this book and pointing out areas where we might profitably center our efforts, both to deepen our understanding of chert as a raw material and to obtain data that will bear directly on archaeological issues.

The nature of chert needs further exploration on several levels. First, because many archaeologists obviously prefer to subdivide the general category of chert into varieties such as flint and agate, we need a good, unambiguous typology. We must first accept the fact, however, that there are no inherent categories and that there is no consensus even among geologists as to how chert should be subdivided. In other words, a typology of cherts would be as arbitrary as any of the other typologies we deal with; a typology based on mode of origin would subdivide the chert universe differently from one based on visible, chemical, or mechanical properties. Therefore, as with our other typologies, we

must start by giving serious thought to the question of how we would want to use such a typology and what we would expect it to do.

A typology based only on obvious visible criteria, the kind most often devised by archaeologists, will not be adequate for any purpose other than description. Calling all red cherts "jasper" and all translucent cherts "chalcedony" only lends an air of spurious erudition to one's writing and can cause confusion for readers aware of other definitions of these terms. It would be far less misleading, and just as meaningful, to call them "red chert" and "translucent chert." A more useful typology would have categories that contain more than one kind of information. For example, cherts that are very high in iron (that is, jaspers) also usually have at least some distinctive visible, and perhaps mechanical properties. Cherts composed of fibrous quartz (that is, chalcedonies) are also similar in more than one property. We must therefore devise a typology that is both informed by geological reality and relevant to properties of interest to archaeology.

Second, the microstructure of chert requires further research. Micheelsen inferred—on the basis of a wide variety of physical tests on Stevns flint—the existence of smaller units of more uniformly ordered quartz within the grains composing chert. He pointed out, however, that some of his results were contradictory (Micheelsen 1966:344–346) and that his model for chert microstructure was not necessarily definitive (Micheelsen 1966:360). Surprisingly, though Micheelsen's work has been influential among chert analysts, few have followed up on his suggestions or attempted to duplicate his research using other types of chert. There is indisputable evidence that the quartz

grains in chert are made up of smaller units, but their exact shape and crystallographic characteristics are still only hypotheses. The distribution of water molecules on the surfaces of these smaller units is equally hypothetical. Surely, we should confirm or refine Micheelsen's model of chert microstructure before we make further use of it to explain the physical changes resulting from heat-treating, to interpret fracture surfaces viewed through the scanning electron microscope, and to evaluate other issues to which it may pertain.

The origin of chert is a third issue. In the last few years, geologists have made considerable progress in explaining how chert forms, and it is likely that this research will accelerate as momentum builds. We already have a good preliminary understanding of the conditions under which the different varieties of silica form. The origins of chalcedony are still confusing, but research is continuing on this topic as well. I hope to see increasing interest in the role played by impurities during chert formation. At this point, most research has focused on the undoubtedly crucial variables of silica concentration, temperature, pH, and time. It must be remembered, however, that impurities are invariably present when cherts form, and that many of the most common impurities significantly affect silica solution, precipitation, and crystallization.

The results of these geological investigations will surely be useful to us, but archaeologists, perhaps in collaboration with geologists, may have to initiate other types of research relevant to chert origins, because they are of greater interest to archaeologists than to geologists. For example, criteria for determining the mode of origin of cherts found out of geological context, as artifacts, would be useful. Since the mode of origin has an effect on chemical properties, the ability to determine mode of origin quickly would be helpful in sourcing. We may also need to initiate research dealing with the causes of variation in grain size since this issue does not seem to be a high priority for geologists. It seems very likely that grain size is one of the key properties mentioned at the start of this chapter; it is clearly relevant to both mechanical and visible properties and may be associated with certain chemical properties as well.

An understanding of the chemical properties of chert is obviously useful for chert source analysis. If the kinds and quantities of impurities in a chert are another key property, as is likely, then chemical properties may be found to be relevant to many other characteristics as well. Additional research on the major minerals occurring as contaminants in chert and the elements associated with them would be helpful in interpreting elemental data. It could also lead to increased understanding of how and why elements vary between and within formations.

Research concerning the role played by specific elements in chert would also be interesting and revealing. For example, uranium usually behaves according to the geochemical rules; it is frequently associated with organic matter and reducing condi-

tions, or with ore sources. It is anomalously low, however, for certain sources (that is, Cocksackie chert and Onondaga chert) for which there is good evidence of both high organic content and reducing conditions. This finding, together with the spread of the values shown in figure 4.2, indicates that additional factors must be involved in determining uranium concentrations. Antimony is another especially interesting element. Further research should make it possible to determine whether this element is indeed associated with hydrothermal fluids and why this is so.

It would be especially helpful to find interrelationships and correlations that would allow us to predict some of the more arcane properties of chert from visible properties, the easiest properties to determine. Some connections between visible and chemical properties can be suggested on the basis of the data available so far, but all require further testing. For example, white and/or translucent cherts appear to be generally low in most trace elements, especially metals, whereas dark, opaque cherts are generally high in many trace elements. Most gold, brown, and dark-red cherts have high proportions of iron, although some dark green and black cherts are also high in iron. Further work on the causes of color and translucency may help us make more such correlations.

Texture and luster defy easy quantification but are closely linked to a variety of mechanical properties and to weathering phenomena. Shiny, fine-grained cherts, long recognized by knappers as having superior flaking properties, may have distinct strength and elasticity. Texture and luster may also be linked to porosity, which affects weathering. Despite the potential significance of texture and luster, we do not yet understand what causes these attributes in chert. We need further research that will allow us to explain texture and luster and also to describe and quantify them on both the macroscopic and microscopic levels.

The mechanical properties of chert are directly relevant to many archaeological concerns, and they provide scope for a great deal of research. Table 6.2 suggests that there is indeed good agreement between important mechanical properties, including strength and elasticity, and chert characteristics such as grain size and density, and that all these properties are correlated with stoneworkers' opinions about what raw materials are best for knapping. These associations and correlations need further confirmation and refinement, however. Further work is also necessary to determine which properties of the raw material are the most important determinants of strength and elasticity in chert. For example, grain size seems to be quite important, but its exact contribution is not known. In addition, while it seems clear that the mechanical properties of chert are primarily those of quartz, it has yet to be determined whether impurities also play a role. It is possible that some impurities can modify strength and elasticity or affect the way fracture occurs. The role of water in chert also needs further exploration.

It would be interesting, and relatively simple, to test just how

isotropic chert really is. Isotropism has often been assumed for chert, but it has rarely been tested. Such a study could help settle the question of whether some cherts have a "grain"; it might also produce information that would be helpful in interpreting flaking patterns. It could also be significant for use-wear analysis; knowing whether some cherts do fracture and/or abrade more readily in some directions than in others would certainly affect wear patterning. In particular, it would be especially interesting to see whether chalcedony's fibrous structure affects its mechanical properties.

We must also determine which specific mechanical properties are most relevant to our concerns. Tensile strength is clearly more important to us than compressive strength, but the latter is more easily measured. Are the two well enough correlated in cherts so that we can calculate one from the other? Alternatively, it may be that fracture toughness is actually a more useful measure of "flakeability." Similarly, there are a number of different measures of elasticity and hardness, and we must determine which are most relevant to our concerns. We must also find the means for measuring these properties as simply and accurately as possible.

Once these issues are straightened out we will be in a better position to deal with such complex questions as how fracture types and features are affected by raw material characteristics. There is also little information available regarding how the processes of abrasion are affected by raw material characteristics. Such studies should help us in interpreting use-wear patterns and lithic-reduction strategies.

Heat-treating is another area of concern. A good deal of experimental evidence has resulted in consensus concerning the range of temperatures necessary for heat-treating, and considerable variability seems to be permissible for most of the other variables in this process. It is not surprising that heat-treating is a relatively imprecise procedure. If successful heat-treating took place only within a narrow range of temperatures and under highly controlled heating and cooling conditions, then it would not be worth doing given the technology available to most stone-tool-using people. It would be interesting to learn why some chert types can be heat-treated at considerably lower or higher temperatures than others. Is this due to their chemical composition, grain size and structure, or some other factor? Does high organic carbon content accelerate heat-treating and high carbonate content retard it, as suggested by some studies?

The most significant change produced by heat-treating is that fractures cut across, rather than around, quartz grains and other small-scale structures. This alteration in fracture pattern is apparently responsible for the changes in both mechanical properties

and luster which are so typical of heat-treated cherts, but there is no consensus as to its cause. It should be possible to devise tests between the major models to determine whether one or both of them is responsible for the pattern change. Heating also alters the color and translucency of many cherts. The color changes that occur with low-temperature heat-treating are apparently caused by alterations in impurities, especially the iron minerals. The change in translucency that occurs in some cherts has yet to be explained. Further research would be useful in understanding all these changes.

The various forms of thermal damage could also provide interesting research possibilities. It seems likely that heating chert to too high a temperature, raising the temperature too rapidly, and cooling too rapidly may each produce distinctive types of thermal damage. Discovery of such damage patterns could help us determine whether heat-damaged cherts from archaeological sites represent heat-treating errors, cherts burned by accident in open fires, chert used as fire rock, or chert used as potboilers.

How weathering affects chert is a final research possibility. The study of weathering phenomena will probably continue to be problematical, but it is worth persevering in this exploration because of the potential for developing new dating techniques and for understanding better the changes in mechanical, visible, and chemical properties that weathering can cause. One approach might be to focus on a single chert type to determine how it responds to varying environmental conditions, either in long-term studies or as simulated in the laboratory. It would also be interesting to compare a variety of cherts under the same conditions, to determine just how important certain characteristics, especially porosity, impurities, and grain size, are to weathering processes.

Some of the research projects I propose here should help us find answers to the questions we have traditionally asked about the lithic artifacts we find: How was this artifact made? How was it used? How old is it? Where did the raw material come from? A better understanding of the properties of chert could enable us to answer such questions as why this raw material was used instead of some other type. Why was this manufacturing process used instead of an alternative procedure? Is the technology of heat-treating related in any way to other technological processes that rely on the control of fire, such as ceramic firing and metallurgy? What are the social implications of all these technological issues? Although chert no longer plays a role in helping humans solve the vital everyday problems of obtaining food and shelter, it may still have untapped potential for helping us solve the more esoteric problems that face archaeologists in their efforts to decipher the complexities of the human past.





# Appendix A

## Chert Source Analysis

Lithic source analysis, the process of determining the original geographic source of a particular raw material, has enjoyed rapid development in recent decades. It is fast becoming an analysis that archaeologists feel obligated to include in their site reports and is also finding increasing application to problems of prehistoric cultural dynamics (for example, Luedtke 1976; Lavin 1983; Vehick 1985). Source analysis provides data archaeologists can use to examine such issues as trade and exchange processes, territory location and size, and the differential access to resources that is often associated with the development of social stratification or the beginning of craft specialization. Therefore, this appendix includes procedures for source analysis and suggests how a chert source data base might be structured to be of maximum use.

### Source Analysis Procedures

These are the necessary steps to be taken in a source analysis project.

#### STEP 1

Define the problem. A good source analysis is usually complex and expensive and should not be initiated merely as a fishing expedition in the vague hope that you might find something interesting. As with any other type of specialized analysis in archaeology, the results are only as meaningful as the questions asked. Furthermore, the amount of sampling required and the margin for error will vary depending on the nature of the problem. Most source analyses are either artifact-centered or material-centered; the former are concerned with identifying the source of a particular artifact of interest, whereas the latter are concerned with determining how a particular raw material is distributed. Obviously, very different size samples are involved depending on whether the question is "What is the source of this artifact from site X?" or "Which features at this site contain chert Y?" or "How far and in what proportions is chert Z distributed at archaeological sites away from its source?"

In addition, all source identifications have an inherent level of uncertainty. There are millions of chert sources on earth, and unless you control every one of them there is always the possibility that the artifact in question is actually made from a material outside your sampling universe. The more critical the source identification is to your larger interpretive concerns, the more you would want to reduce that uncertainty by increasing the number of sources considered. Above all, you must decide what you really hope to learn from the analysis and how much money and time you are willing to spend learning it. These parameters will help

you set priorities and make crucial decisions further along in the analysis.

#### STEP 2

Determine which chert types are possible sources for the artifact(s) of interest—and which other chert types might be confused with the type of interest. The archaeological and geological literature for the region should be consulted first, but it will probably be disappointing. Few regions have been thoroughly studied with regard to their chert resources, and information about even fewer regions has been published. Personal contacts are likely to be more fruitful; geologists and archaeologists who have worked in a region for any length of time will generally know of many sources. Rock hounds and owners of rock shops are also useful informants.

Not every chert type in a region is equally likely to be the source of the artifact in question. Visible properties can be used to narrow down the range of possibilities. In other words, if the artifact is white, it makes no sense to include a chert type that is always red or brown. To make these initial decisions it is absolutely vital that you know the full range of variation in visible properties for each chert type. All cherts vary in appearance, as in all other properties. There is usually a typical variety that is most common, or most distinctive, for a particular chert type.

All chert types also include variants that are usually less common and less distinctive. For example, typical Norwood chert is pale tan or gray with fine brown laminations. However, some Norwood chert is a dark mottled brown and some is a featureless dull pale gray. The latter variant is also common to a great many other Michigan chert types. Archaeologists are usually familiar with the typical varieties for their region, but they are rarely aware of all the variants unless they have spent time visiting quarries and outcrops. Furthermore, most cherts change at least some of their visible properties when they weather or are heat-treated, and these variants must also be known. Once an archaeologist's knowledge expands beyond the typical varieties and embraces the full range of variability, it becomes apparent that virtually all chert types have "look-alikes" from other formations. This is why visible criteria, which are useful in the initial sort, cannot be the sole criterion for making the final identification.

#### STEP 3

Learn as much as you can about each of your potential chert sources. The archaeological literature will often provide information concerning known quarries and the time periods during which they were exploited. It may also indicate what sorts of technical analyses have already been performed on that chert

type. The geological literature also includes technical analyses, the age of the formation, the rock types associated with the chert, the fossils present, the general outcrop area for the formation, and sometimes paleoenvironmental information relevant to the origin of the chert. Fieldwork will generally be needed to determine how far the material is distributed in such secondary deposits as streambeds or glacial till. If at all possible, this step should also include an actual visit to each source, as this is the best way to learn about a chert type and to be certain you know its full range of variation.

#### STEP 4

Based on the information you have gained in step 3, decide on the best way to determine the source of your artifact (or alternatively, to distinguish the material you are interested in from all possible look-alikes). The range of possible methods for doing this is great, and more techniques are being added all the time. A few practical considerations may constrain your choice of method. For example, you may be restricted as to what you can do with an artifact. You will rarely be allowed to thin section an artifact of display quality, and you may not even be allowed to remove a small sample for analysis. In such cases, you can use only nondestructive methods that analyze the whole artifact. The types of equipment to which you have access and the amount of money available for analysis may also influence your choice of analytical methods. In addition, if previous research has already provided one type of data about a source, it is far easier to continue with a method that gives compatible data than it is to start over from scratch.

In the absence of such constraints, the choice of analytical technique should be based on your judgment as to the type of information that will most likely differentiate your sources. If the chert types in question are of markedly different ages, you might consider differentiating them on the basis of their fossils (Reid 1984) or by such dating methods as rubidium/strontium (Rb/Sr), potassium/argon (K/Ar), or uranium decay (Brueckner and Snyder 1985). Oxygen isotope values may differentiate cherts formed in waters of different temperature or salinity. Cherts may differ in microstructure, which is visible in thin sections and perhaps in scanning electron micrographs.

Most cherts differ considerably in their impurity content, and a wide range of methods is available for detecting such differences. Petrographic analysis of thin sections, X-ray diffraction, Mössbauer spectroscopy, electron spin resonance spectroscopy, and nuclear magnetic resonance spectroscopy all can determine which specific minerals are present in a chert (for example, Symons 1986). Some of these techniques can also provide information concerning the proportions of these minerals. Elemental abundances can be determined through X-ray fluorescence, proton-induced X-ray emission, atomic absorption, or neutron activation analysis.

Harbottle (1982) discusses the strengths and weaknesses of many of these analytical methods.

No one technique will be suitable for all sourcing situations; any technique might work very well in one situation but poorly in another. In general, you will want to select the cheapest and simplest technique that is likely to produce results of suitable accuracy, given your particular archaeological problem. At this step you must decide how important it is to you that your identification be correct and how much time and money you are willing to spend on the analysis.

#### STEP 5

Perform the necessary tests or procedures. To do this, you will need data for both sources and artifacts. If the sources have already been characterized using the technique you have selected, you will only have to analyze the artifact or artifacts. More likely, there will have been no previous work and you will have to characterize sources and artifacts. Relying on existing type collections for your source samples is risky because these collections usually do not include the full range of variation for the chert type. It is far preferable to collect your own samples from the sources because you can then sample them systematically and thoroughly so as to include the full range of visible and spatial variability (for example, Meyers 1970).

The number of samples needed to characterize a source is a function of the amount of variability present and the level of precision desired. Table A.1 shows sample sizes necessary under specified conditions; this table is explained in greater detail elsewhere (Luedtke and Meyers 1984:289). Bear in mind the point made in chapter 4: cherts that outcrop over a very large area or that exhibit a great deal of variability in visible characteristics often have greater chemical variability than do more localized cherts or cherts that are visibly homogeneous.

#### STEP 6

Match artifacts to sources. In some cases, this may involve simple key-type logic: if fossil A is present in the artifact, it must have come from source R. In other cases, especially when multivariate chemical data are involved, more complex statistical procedures may be necessary. Luedtke (1979) discusses the advantages and disadvantages of some of the available procedures for matching artifacts with sources on the basis of chemical composition.

Some identification techniques are unavoidably subjective because the accuracy of identifications is dependent on the analyst's expertise, a quality not easily evaluated by those who are not personally acquainted with the analyst. Identifications based on macroscopic visible criteria are obviously of this type, but petrographic analyses of thin sections also involve subjective evaluations of whether a particular sample is similar enough to be from the source in question. Source analysts using such tech-

niques would be wise to emulate use wear analysts who face a similar credibility problem and who deal with it by performing blind tests. The results of these tests are published as a way of establishing the analysts' credentials as experts who can identify different wear patterns (for example, Odell and Odell-Vereecken 1980).

For source analysts, blind tests would involve having someone else select hand samples (or thin sections) collected from different chert sources, including both typical and unusual varieties. Artifacts should not be included, because their source is not absolutely certain, and the hand samples or thin sections should not be ones that the analyst has seen previously. The analyst should attempt to identify as many of the samples as possible and should publish the percentage of correct identifications obtained on this blind test.

### A Useful Data Base for Chert Sourcing

The process of determining the sources of cherts could be greatly facilitated by establishing a data base especially for this purpose and by organizing a procedure for using it systematically. To the best of my knowledge, no such data base exists, but archaeologists in many regions are collecting data that could eventually be used in this way. An optimal system of lithic source identification would make use of as many different kinds of information about chert types as possible, organized in such a way that new information could be added as it became available. It would also take full account of the variability in many, if not all, attributes of different chert types and would thus include both typical and variant forms of each. New variants could be added whenever they were defined.

A basic assumption of this proposed system is that in attempting to determine the source of an artifact, it is reasonable to look first at the geographically closest chert source that includes a type resembling the artifact. Then the next nearest source is looked at and so forth. This assumption does not imply that people will always use the closest available resource; it is simply a starting point—the artifact is considered local unless proven otherwise. After all, most archaeological assemblages are made up predominantly of local lithic materials, along with smaller proportions of exotic materials that have been traded or obtained elsewhere. Realistically, the source analyst's task is not to test each artifact against the total universe of chert types but rather to test between the two or three most likely sources. If each of these likely sources is considered in pairs, it should be possible to define relatively simple ways in which they differ, thus allowing a systematic progression through a testing procedure.

Perhaps the easiest way to explain how such a system would work is to demonstrate it with a hypothetical example from New England. First, we must assume the existence of a data base that describes each chert type in detail, including its geographical

**Table A.1 Sample Sizes Required, Given Different Amounts of Variation and Precision at the .95 Level of Confidence**

Precision	Mean coefficient of variation for all elements			
	V = 0.1	V = 0.3	V = 0.5	V = 0.7
0.20	1	9	24	47
0.10	4	35	96	188
0.05	15	138	384	753
0.03	43	384	1067	2092
0.01	384	3457	9604	18824

distribution, typical forms and variants, and bibliographic information. The starting point would be a series of regional maps indicating the locations of cherts with similar macroscopic properties. Color is likely to be an especially important determinant in many regions because it often varies among chert types, is easily observed, and can be described somewhat objectively by use of the Munsell color charts. However, other macroscopically visible characteristics, such as translucency or structure, may be better criteria for these maps in some regions.

The process begins with the excavation of a flake of bright red chert at a site on one of the Boston Harbor islands. I suspect the flake is made from an exotic material and is thus relevant to the question of whether the site's inhabitants participated in interregional trade. I go first to the map for red chert locations and find the source closest to my site, as well as the next closest source. Immediately, I encounter an issue that may or may not be unique to New England: several fine-grained siliceous materials can easily be mistaken for chert and should therefore be included in the data base. Source 5, Saugus "jasper," is actually a fine-grained igneous rock. Source 7, Limerock chert, is the next closest source; it is a true chert that is normally honey colored but can turn red when heat-treated.

I then consult a second data base which consists of comparisons among all the different chert types and variants, pair by pair. Table A.2 shows part of this hypothetical data base. The first column indicates which chert types are being compared. For example, the first section compares the typical variety of material 5, Saugus "jasper," with variant 1 of material 7, Limerock chert. The other three columns list the major differences between each pair of cherts (or chertlike materials).

When I look at the entry comparing the red varieties of types 5 and 7, I find a number of ways in which they differ. If my flake has chalcedony veins, it is definitely not from the Saugus source, and if it has opaque cream-colored veins, it probably is. If it is featureless and unweathered, however, I cannot decide on the basis of macroscopic properties alone whether it comes from Saugus or Limerock. These two types of rock are mineralogically different and undoubtedly petrographically distinct. At this time I do not have thin section data for both, but I do have chemical data for both. While these samples differ in many ways, there is an

**Table A.2 Example of Portion of Suggested Chert Data Base**

Sources	Major macroscopic differences	Major petrographic differences	Major chemical differences(ppm)
5 Saugus T	Uniform, opaque cream veins	Not available	Na R=27,000-38,000
7 Limerock V1	Often mottled, chalcedony veins common		Na R=28-95
6 Normanskill V3	Shaley, chalcedony rare	Chert Groundmass, clay and fossils	Sm R=.94-2.10 La R=4.5-11.8 Na R=1351-3811 Cs R=0.58-1.52
7 Limerock V1	Chalcedony veins common	Chalcedony Groundmass, no fossils, iron oxide blebs	Sm R=0.008-0.67 La R=0.05-0.71 Na R=28-95 Cs R=0-0.09
2 Berlin T	Flow banding	Not available	Na R=27,000-32,000
7 Limerock V1	No banding		Na R=28-95
4 Little Falls V3	Black pyrite spots	Granular Groundmass, fossils, dolomite rhombs	Not available
7 Limerock V1	No black spots	Chalcedony Groundmass, no fossils or dolomite	
7 Limerock V1		Chalcedony Groundmass, iron oxide blebs	La R=0.05-0.71, Co R=0.89-16.2
8 Pennsylvania V1	Virtually identical	Relict quartzite grains outlined by opaque minerals	La R=0.8-3.4, Co R=0.52-3.0

especially striking difference in the proportions of sodium. Although my data are derived from neutron activation analysis, virtually any chemical analysis should be able to detect differences this great.

Assuming Saugus is ruled out as the source of my red chert, I move on to compare Limerock chert with the next closest source, represented by a rare variant of Normanskill chert. Again, macroscopic differences may or may not help, but petrographic differences should, and the two sources also have nonoverlapping ranges for at least four trace elements. Source 2, Berlin "jasper," is another igneous rock that virtually always shows flowbanding; so, it can be easily ruled out on macroscopic grounds. Like the Saugus material, it also shows a pattern of extremely high values for sodium. Little Falls chert is the next closest source. Although I am not fully familiar with this chert type, Lavin's description suggests that it would be easily distinguishable, both macroscopically and petrographically, from Limerock chert (Lavin 1983).

The next pair to be considered would definitely require technical analysis because Limerock jasper and Pennsylvania

jasper can look alike. There are petrographic differences between the two cherts because they are of different origins, and they differ chemically as well. Good discrimination can be obtained with only two elements, and identifications are even more certain if more elements are included (Luedtke 1987).

Sources of red chert become more numerous to the south and west of New England, and one could keep testing pairs indefinitely. The decision as to when one has tested enough depends in part on the archaeological situation. For example, if my flake had been found at a Paleoindian site I would be well advised to continue testing more distant possibilities. In New England, as elsewhere, Paleoindian sites often include lithic materials brought from considerable distances. On the other hand, if the flake came from Late Woodland context, it would be less important to test distant sources, because such assemblages in this region consist primarily of local materials. I would also obviously be more conscientious in testing as many alternative chert types as possible if the implications of a particular identification were especially significant or controversial. Ultimately, the decision to stop testing

would depend on how comfortable I was with the identification.

This system, like all others for chert source analysis, is best used by people who have considerable familiarity with the chert sources in their region because elements of judgment are involved, both in making decisions along the way and in deciding when to stop. However, this is true of any method of chert identification; there is always a certain level of uncertainty because it is impossible to rule out the possibility that the artifact came from a source outside the sampling universe or that it represents an as yet unknown source or variant. The advantage of the procedure suggested here is not that it will always give accurate identifications but that the logic through which the identification was determined can easily be followed or duplicated by other analysts.

All well and good for a chert of an unusual color in a part of the world that is notoriously chert-free. But what about gray or light-brown cherts, which are ubiquitous in some areas? Obviously, it would be much more difficult to compile the type of data base I have described for a chert-rich area such as Kentucky. I don't want to minimize the time and labor which would be needed to construct the initial data base, although I can report that in the case of my jasper example, it was easier than I had expected.

This identification approach has several advantages over the systems generally used. First, it does not assume that chert types are homogeneous in any way; rather, it takes all forms of variation into account. Second, it is an open system; new variants and new criteria for discriminating among types can be added at any time. Unlike a key, it is also geographically open and infinitely expand-

able if circumstances should so require. Third, it provides a variety of options for discriminating among chert types, thus allowing a user to select the technique or techniques most appropriate to a specific archaeological problem or situation. This could potentially decrease the costs and increase the accuracy of chert source analysis, resulting in wider acceptance by the archaeological community. Fourth, it proceeds in a systematic and logical fashion, allowing anyone to follow the analyst's thought processes and to assess the validity of the resulting identifications. This can overcome the problem of the increasing numbers of perhaps correct, but completely unverifiable, chert source identifications accumulating in the literature today.

Archaeologists have been aware for a long time that significant conclusions can be drawn from data on the sources of lithic artifacts. The accuracy of the conclusions about prehistoric trade, exchange, economy, politics, or social organization, however, depends on the accuracy of the source identifications. Chert is a complex and variable material, and it is unlikely that there will ever be a cheap, simple technique that will identify chert types accurately in all situations. The best strategy would then be to make use of all the available procedures and kinds of information and to incorporate new techniques as they are developed. As we increase the sourcing options and become more aware of where each technique works best, we should be able to increase the reliability and number of chert source identifications, thus allowing us to spend more time dealing with the interesting archaeological questions source analyses are supposed to help us answer.



## Appendix B

### Specific Chert Types

Although this book is not about particular chert types, many of its conclusions rely heavily on data from a number of specific cherts, not all of which are familiar to all readers. Therefore, it seems imperative to include some basic information regarding the chert types that have provided much of the raw data used here to test hypotheses, thereby allowing other researchers to check the conclusions independently. Also, while some of the data are available elsewhere, others are printed here for the first time. These descriptions must be regarded as thumbnail sketches; far too much space would be required to describe each type thoroughly or to include information such as its archaeological significance.

The chert types are listed in alphabetical order by common or geological name. The same level of information is not available for all chert types, but the same general format has been used. Data that establish geological context are given first, including the formation within which the chert is found, the age of the formation, and roughly how and where the chert occurs. Next, the visible attributes of the most typical variety are provided, including structure, color, texture, luster, and translucency. Structure is described as being homogeneous, shaded, mottled, streaked, banded, or laminated. (Most of these terms are self-explanatory, but they are also defined in the glossary.) Color is specified in terms of the Munsell color chart. Texture and luster are not quantified; cherts are simply described as fine, medium, or coarse in the first case and shiny, medium, or dull in the second. Translucency is defined in terms of the test described in chapter 5: the higher the value, the more translucent the chert. The major nonsiliceous minerals are given next, usually from thin section data, followed by any additional information considered relevant or necessary. Finally, the references from which some of the specific facts were taken are listed.

Following the descriptions, chemical data for each chert type are supplied. The number of samples (N), analytical method (data type), and source of data (ref) are given as well. All data are specified in parts per million. Data originally published as oxides have been transformed to elemental values by using the conversion table in Glascock (1988:114). If an element is not listed or if the space for it is blank, it was not sought in that particular analysis. If "n.f." is shown, then the element was sought and either not detected at all or detected in such a small number of samples, relative to total sample size, that the resulting value is dubious. Trace element data are usually not normally distributed and are

therefore often log transformed before they are used in statistical procedures. The mean and standard deviation of the untransformed values are not entirely misleading measures of central tendency in most cases, however, and their use greatly facilitates comprehension and comparison with other data.

Most of the chemical data given here were generated by the University of Michigan Museum of Anthropology project. Some are reprinted (and corrected) from Luedtke (1976), and others are presented for the first time (indicated by ref=UMMA). The laboratory procedures and data analyses used are described elsewhere (Luedtke 1976; Meyers and DeNies 1972). An additional twenty-five or more chert types were also analyzed as part of this project. They have not been used here either because the sample size was considered too small, because too much of the data had been lost in the course of a destructive laboratory move in the mid-1970s, or because I do not know enough about the chert type or the conditions under which the samples were collected to interpret the findings meaningfully. No such restrictions were applied to other people's data; whatever was available is shown here.

The UMMA data are not perfect. First, this early project suffered from equipment problems that do not afflict more recent studies. Second, there was—and still is—no chert standard to which data can be calibrated; so, our data were calibrated against several different standards. Third, these data have not been corrected for some of the complex interactions among elements discussed by Miller (1982:34) or those resulting from uranium fission products discussed by Ives (1984:70–72); in general, these corrections would not significantly affect quantities. Finally, sample sizes are usually not as large as I now consider necessary, and not all chert sources were sampled systematically.

Despite these caveats, where comparisons are available, the UMMA data agree fairly well with data generated more recently by laboratories not working under some of the same handicaps we experienced. Also, these data are used here to draw very general conclusions, not to distinguish fine shadings of difference. Broad trends should be evident even from fuzzy data. The UMMA project was conceived as a pilot project, the point of which was to determine whether further research would be fruitful. It is hoped its results will provide justification for future projects to be conducted with the careful sampling and thorough data analysis necessary to produce data of the highest possible level of accuracy and precision.



## Amherstburg Chert

Amherstburg formation, Lower Devonian. Chert occurs as nodules or lenses 5 cm in diameter in limestone in southern Ontario, Canada. Structure is streaked, mottled, and flecked with fossils, with color typically light brown-gray, 10YR6/1 to 7/1, streaked with lighter cream colors. Texture is fine, luster is medium, and translucency is 1 to 1.5 mm. Very similar, especially at eastern end of distribution, to Onondaga chert. (See Luedtke 1976 and table B.1.)

**Table B.1 Trace Element Data for Amherstburg Chert**

(N=9; data type=NAA, ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 438.6	x 0.478	x 0.037	x 1.65	x 0.0094
sd 114.3	sd 0.227	sd 0.014	sd 0.559	sd 0.0037
R 310-592	R 0.270-0.890	R 0.020-0.060	R 1.05-2.41	R 0.005-0.016
Sc	Zn	Cs	Sm	Hf
x 0.320	x 2.42	x 0.258	x 0.134	x 0.161
sd 0.107	sd 0.903	sd 0.072	sd 0.067	sd 0.084
R 0.190-0.470	R 1.42-3.85	R 0.160-0.350	R 0.047-0.299	R 0.080-0.300
Cr	Br	Ba	Eu	Th
x 3.79	x 5.17	x 14.0	x 0.032	x 0.299
sd 0.706	sd 1.14	sd 5.60	sd 0.0067	sd 0.130
R 2.62-4.80	R 3.92-7.14	R 6.46-23.1	R 0.020-0.040	R 0.170-0.560
Fe	Rb	La	Yb	U
x 1706.9	x 4.36	x 0.985	x 0.069	x 0.587
sd 708.7	sd 1.82	sd 0.331	sd 0.026	sd 0.192
R 771-2581	R 1.70-6.95	R 0.660-1.76	R 0.030-0.110	R 0.310-0.980

## Arkansas Novaculite

Arkansas novaculite formation, Devonian to Lower Mississippian. Chert occurs as beds up to several meters thick interbedded with shales, sandstones, and limestones from central Arkansas to eastern Oklahoma, USA. Structure is homogeneous, banded or streaked, and colors are variable, ranging from white to black and including reds, pinks, golds, and grays. White, N8/, is probably most typical. Texture is medium, luster is dull, and translucency is from 0.5 to 14 mm, with most around 7.5 mm. East end of outcrop area has been metamorphosed by Mesozoic intrusives. (See Goldstein and Hendricks 1953; Jones and Knauth 1979; and table B.2.)

**Table B.2 Trace Element Data for Arkansas Novaculite**

(N=26; data type=NAA; ref=UMMA)

Na	Co	Cs	Sm	Hf
x 24.1	x 0.074	x 0.108	x 0.329	x 0.192
sd 21.6	sd 0.057	sd 0.104	sd 0.382	sd 0.172
R 5.80-80.0	R 0.021-0.251	R 0.023-0.468	R 0.044-1.52	R 0.032-0.754
Sc	Br	Ba	Eu	Th
x 0.371	x 0.047	x 29.8	x 0.082	x 0.216
sd 0.366	sd 0.031	sd 20.4	sd 0.099	sd 0.171
R 0.041-1.19	R 0.004-0.128	R 3.95-85.7	R 0.009-0.377	R 0.038-0.610
Cr	Rb	La	Yb	U
x 0.544	x 1.65	x 1.47	x 0.110	x 0.481
sd 0.436	sd 1.36	sd 1.75	sd 0.098	sd 0.440
R 0.038-1.51	R 0.060-4.72	R 0.185-7.58	R 0.035-0.467	R 0.008-1.78
Fe	Sb	Ce	Lu	
x 559.0	x 0.034	x 2.81	x 0.011	
sd 787.4	sd 0.030	sd 3.02	sd 0.0065	
R 12.0-3130.5	R 0.0075-0.134	R 0.310-11.1	R 0.004-0.026	

### Bald Eagle Jasper

Nittany formation, Lower Ordovician. Chert occurs in dolomite in central Pennsylvania, USA. Structure is homogeneous or banded, color is yellow to golden brown, and texture is variable. Major impurity is goethite. Also called Houserville jasper. May be the source of the jasper pebbles in the Upper Ordovician Bald Eagle conglomerate (Lavin 1983). (See Schindler et al. 1982; Hatch and Miller 1985, and table B.3.)

**Table B.3 Trace Element Data for Bald Eagle Jasper**

(N=9; data type=NAA; ref=Hatch and Miller 1985)

K	Mn	Cu	La
x 96.6	x 92.9	x 1.89	x 4.59
sd 35.8	sd 82.3	sd 1.12	sd 1.61
Sc	Fe	As	Sm
x 3.32	x 120771.0	x 29.7	x 1.82
sd 1.94	sd 62925.0	sd 12.8	sd 0.580

### Bayport Chert

Bayport formation, Upper Mississippian. Chert occurs as nodules up to 23 cm in diameter (and occasionally as thin lenses) in dolomite and limestone in eastern Michigan, USA. Structure is concentrically banded and highly fossiliferous, and typical color is gray, ranging from 10YR5/1 to 7/1. Texture is coarse, luster is dull to medium, and translucency is 0.5 mm. (See Luedtke 1976 and table B.4.)

**Table B.4 Trace Element Data for Bayport Chert**

(N=32; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 422.1	x 0.187	x 0.054	x 1.41	x 0.0092
sd 93.5	sd 0.104	sd 0.040	sd 0.419	sd 0.0046
R 328.5-515.6	R 0.083-0.290	R 0.015-0.093	R 0.990-1.83	R 0.0046-0.0138
Sc	Zn	Cs	Sm	Hf
x 0.149	x 5.11	x 0.074	x 0.085	x 0.174
sd 0.047	sd 4.41	sd 0.033	sd 0.040	sd 0.116
R 0.102-0.296	R 0.696-9.52	R 0.041-0.107	R 0.046-0.125	R 0.057-0.290
Cr	Br	Ba	Eu	Th
x 3.49	x 1.44	x 37.7	x 0.023	x 0.173
sd 1.75	sd 0.444	sd 15.3	sd 0.010	sd 0.054
R 1.74-5.24	R 0.994-1.88	R 22.4-53.0	R 0.013-0.033	R 0.118-0.227
Fe	Rb	La	Yb	U
x 612.0	x 2.50	x 0.456	x 0.031	x 3.65
sd 367.5	sd 1.11	sd 0.163	sd 0.016	sd 2.04
R 244-980	R 1.40-3.61	R 0.293-0.619	R 0.014-0.047	R 1.61-5.68

### Bois Blanc Chert

Bois Blanc formation, Lower Devonian. Chert occurs as nodules and lenses several centimeters in diameter in limestones and dolomites in northern Michigan, USA, and southern Ontario, Canada. Structure is homogeneous to mottled and sometimes banded, and tiny fossils and cavities lined with quartz crystals are common. Color is typically pale gray to white, N/7 to N/8. Texture is fine to coarse, luster is dull, and translucency is 0.5 mm. The chemical data are from Michigan sources only. (See Luedtke 1976 and table B.5.)

**Table B.5 Trace Element Data for Bois Blanc Chert**

(N=15; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 243.7	x 0.192	x 0.012	x 1.46	x 0.011
sd 42.2	sd 0.061	sd 0.0073	sd 0.293	sd 0.0031
R 187.6-305.5	R 0.100-0.260	R 0.002-0.021	R 1.13-1.69	R 0.007-0.014
Sc	Zn	Cs	Sm	Hf
x 0.534	x 3.04	x 0.344	x 0.120	x 0.248
sd 0.168	sd 0.885	sd 0.098	sd 0.029	sd 0.066
R 0.330-0.740	R 2.05-3.97	R 0.240-0.450	R 0.080-0.160	R 0.170-0.350
Cr	Br	Ba	Eu	Th
x 4.01	x 4.26	x 11.5	x 0.018	x 0.366
sd 1.20	sd 0.827	sd 3.20	sd 0.0045	sd 0.082
R 2.58-5.49	R 3.14-5.41	R 6.26-14.7	R 0.010-0.020	R 0.260-0.450
Fe	Rb	La	Yb	U
x 855.3	x 5.92	x 0.948	x 0.102	x 0.456
sd 278.9	sd 1.32	sd 0.222	sd 0.034	sd 0.135
R 471.5-1131.9	R 4.45-7.32	R 0.700-1.28	R 0.060-0.150	R 0.290-0.600

### Brush Creek Chert

Brush Creek formation, Upper Pennsylvanian. Chert occurs as nodules and lenses up to 60 cm thick in limestone in southern Ohio, USA. Structure is homogeneous with microfossils, and color is gray-brown, N3/ to N4/ to tan, 10YR5/1. Texture is fine to medium, luster is medium to shiny, and translucency is 0.5 mm. Major impurities are clay, mica, and limonite. (See Stout and Schoenlaub 1945; Luedtke 1976; and table B.6.)

**Table B.6 Trace Element Data for Brush Creek Chert**

(N=5; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 547.3	x 0.714	x 0.214	x 5.66	x 0.031
sd 118.0	sd 0.407	sd 0.069	sd 2.33	sd 0.0055
R 412.6-719.4	R 0.300-1.29	R 0.140-0.300	R 2.88-9.24	R 0.026-0.040
Sc	Zn	Cs	Sm	Hf
x 0.554	x 9.49	x 0.170	x 0.822	x 0.312
sd 0.229	sd 4.72	sd 0.127	sd 0.533	sd 0.102
Rv 0.370-0.940	R 5.38-17.0	R 0.080-0.380	R 0.404-1.72	R 0.200-0.470
Cr	Br	Ba	Eu	Th
x 5.15	x 0.632	x 232.9	x 0.216	x 0.712
sd 1.98	sd 0.136	sd 214.9	sd 0.147	sd 0.296
R 3.38-7.30	R 0.430-0.790	R 90.1-613.5	R 0.100-0.460	R 0.430-1.06
Fe	Rb	La	Yb	U
x 2598.2	x 4.23	x 5.07	x 0.200	x 2.33
sd 805.6	sd 3.19	sd 5.02	sd 0.068	sd 1.48
R 2044-4004	R 2.30-9.71	R 1.85-13.9	R 0.120-0.270	R 0.730-3.64

## Burlington Chert

Burlington formation, Middle Mississippian. Chert occurs as nodules and lenses up to 20 cm in diameter in limestone in western Illinois and northeastern Missouri, USA. Structure is usually homogeneous but also streaked, concentrically banded, or more rarely horizontally banded, and sometimes highly fossiliferous. Color is usually white N8/ or pale gray but can also be yellow, tan, darker gray, or even black. Texture is fine to coarse, luster is shiny to dull, and translucency is 2 to 4 mm. Impurities include calcite, pyrite, glauconite, and clay. The chemical data below represent samples collected systematically from a series of outcrops stretching for 13 km along the lower Illinois River Valley. (See Tarr 1917; Meyers 1970; Luedtke and Meyers 1984; and table B.7.)

**Table B.7 Trace Element Data for Burlington Chert**

(N=101; data type=NAA; ref=Luedtke and Meyers 1984)

Na	Co	Cs	Sm	Hf
x 154.3	x 0.148	x 0.058	x 0.099	x 0.038
sd 40.4	sd 0.137	sd 0.046	sd 0.087	sd 0.019
R 33.5-272.6	R 0.037-0.753	R 0.012-0.300	R 0.013-0.433	R 0.010-0.093
Sc	Br	Ba	Eu	Th
x 0.154	x 0.228	x 14.7	x 0.028	x 0.134
sd 0.091	sd 0.061	sd 8.50	sd 0.027	sd 0.119
R 0.029-0.446	R 0.081-0.421	R 1.52-43.8	R 0.005-0.152	R 0.026-0.917
Cr	Rb	La	Yb	U
x 1.06	x 0.958	x 0.372	x 0.035	x 0.348
sd 0.821	sd 0.792	sd 0.348	sd 0.028	sd 0.364
R 0.125-5.17	R 0.020-5.27	R 0.055-1.77	R 0.002-0.145	R 0.001-2.109
Fe	Sb	Ce	Lu	
x 144.7	x 0.049	x 0.542	x 0.005	
sd 142.2	sd 0.027	sd 0.433	sd 0.003	
R 19.6-933.8	R 0.012-0.150	R 0.084-2.12	R 0.001-0.020	

## Cordell Chert

Cordell formation, Middle Silurian. Chert occurs as lenses from 1.5 to 6 cm thick in dolomite in northern Michigan, USA. Structure is homogeneous to streaked with many light-colored fossils, and color is either dark brown, 10YR4/1, or medium to light gray, N7/. Texture is fine, luster is medium to shiny, and translucency is 1.5 to 2.5 mm. (See Luedtke 1976 and table B.8.)

**Table B.8 Trace Element Data for Cordell Chert**

(N=10; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 261.9	x 0.171	x 0.015	x 0.585	x 0.0047
sd 78.3	sd 0.052	sd 0.0087	sd 0.205	sd 0.0023
R 124.9-340.4	R 0.110-0.230	R 0.003-0.036	R 0.250-0.880	R 0.001-0.008
Sc	Zn	Cs	Sm	Hf
x 0.215	x 1.55	x 0.115	x 0.045	x 0.080
sd 0.038	sd 1.11	sd 0.030	sd 0.012	sd 0.011
R 0.140-0.270	R 0.470-3.60	R 0.080-0.170	R 0.028-0.053	R 0.070-0.100
Cr	Br	Ba	Eu	Th
x 1.88	x 2.51	x 7.56	x 0.008	x 0.328
sd 0.352	sd 1.10	sd 1.18	sd 0.0018	sd 0.050
R 1.44-2.62	R 1.02-4.52	R 5.78-9.99	R 0.006-0.011	R 0.280-0.400
Fe	Rb	La	Yb	U
x 950.4	x 2.97	x 0.215	x 0.028	x 0.354
sd 385.4	sd 0.618	sd 0.070	sd 0.012	sd 0.300
R 554-1682	R 2.12-4.01	R 0.090-0.300	R 0.010-0.050	R 0.010-0.760

## Coxsackie Chert

Normanskill or possibly Deepkill formation, Lower Ordovician. Chert occurs in beds ranging from 1 cm to 3 m thick, interbedded with siliceous green shales in eastern New York, USA. Structure is homogeneous or laminated, and color is blue-green to dark green, 5G5/1 to 5G4/1 to 5BG4/1. Texture is medium to fine, luster is dull to medium, and translucency is <0.5 but as much as 3 mm in a few places. Impurities include clays, mica, chlorite, clastic quartz, dolomite rhombs, calcite, organic carbon, pyrite, and fossils. (See Wray 1948; Luedtke 1976; Lavin 1983; and table B.9.)

**Table B.9 Trace Element Data for Coxsackie Chert**

(N=7; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 2536.4	x 13.6	x 0.460	x 27.8	x 0.070
sd 1053.6	sd 2.77	sd 0.181	sd 10.4	sd 0.012
R 1351.2-3810.9	R 8.08-16.5	R 0.240-0.700	R 16.3-42.9	R 0.060-0.090
Sc	Zn	Cs	Sm	Hf
x 3.27	x 9.56	x 0.946	x 1.37	x 0.727
sd 0.927	sd 2.60	sd 0.378	sd 0.392	sd 0.298
R 2.41-4.63	R 6.80-14.4	R 0.580-1.52	R 0.924-2.07	R 0.430-1.15
Cr	Br	Ba	Eu	Th
x 15.2	x 0.180	x 145.4	x 0.393	x 2.32
sd 7.99	sd 0.078	sd 22.0	sd 0.119	sd 1.08
R 8.35-27.5	R 0.090-0.330	R 116.7-173.7	R 0.240-0.580	R 1.16-3.90
Fe	Rb	La	Yb	U
x 17811.2	x 23.9	x 7.32	x 0.473	n.f.
sd 7159.3	sd 11.3	sd 2.66	sd 0.118	
R 7412-25539	R 9.98-39.5	R 4.47-11.8	R 0.370-0.690	

## Delaware Chert

Delaware formation, Middle Devonian. Chert occurs as nodules and lenses 8 to 15 cm thick in limestone in northern Ohio, USA. Structure is homogeneous to shaded, and color is dark brown, 10YR4/1 to 10YR5/1. Texture is fine, luster is medium to shiny, and translucency is 0.5 to 1 mm. Impurities include calcite and pyrite. (See Stout and Schoenlaub 1945; Luedtke 1976; and table B.10.)

**Table B.10 Trace Element Data for Delaware Chert**

(N=5; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 333.2	x 0.436	x 0.056	x 2.76	x 0.017
sd 43.5	sd 0.190	sd 0.011	sd 0.869	sd 0.005
R 287.4-382.5	R 0.270-0.690	R 0.040-0.070	R 1.90-4.06	R 0.009-0.021
Sc	Zn	Cs	Sm	Hf
x 0.448	x 4.01	x 0.230	x 0.349	x 0.260
sd 0.043	sd 0.482	sd 0.027	sd 0.152	sd 0.058
R 0.400-0.490	R 3.41-4.76	R 0.190-0.260	R 0.180-0.565	R 0.200-0.350
Cr	Br	Ba	Eu	Th
x 3.79	x 4.01	x 100.2	x 0.094	x 0.448
sd 0.518	sd 0.453	sd 65.0	sd 0.048	sd 0.075
R 3.39-4.69	R 3.37-4.62	R 31.9-190.6	R 0.040-0.160	R 0.360-0.540
Fe	Rb	La	Yb	U
x 1814.6	x 4.63	x 1.70	x 0.124	x 0.390
sd 526.8	sd 0.350	sd 0.508	sd 0.036	sd 0.277
R 1138-2451	R 4.30-5.19	R 1.19-2.43	R 0.090-0.180	R 0.110-0.760

## English Chalk Flint

Upper Chalk formation, Upper Cretaceous. Chert occurs primarily as nodules from 1 cm to 1 m in diameter and sometimes in tabular deposits in chalk in southeastern England. Structure is homogeneous to mottled black—N3/ to N4/—with areas of lighter colored and more granular gray chert, and often with fossils. Texture is fine, luster is medium, and translucency is 5 to 10 mm. Impurities include organic carbon, carbonate rhombs, calcite dust, and occasional grains of iron minerals. One sample was omitted when means and standard deviations were calculated for the chemical data in Sieveking et al.; Ca and P levels were so much higher for this sample than for the others as to suggest that the aberrant sample may have included some of the cortex. (See Sieveking et al. 1972; Aspinall and Feather 1972; Shepherd 1972; and table B.11.)

**Table B.11 Trace Element Data for English Chalk Flint  
(Grimes Graves quarry)**

Sieveking et al. 1972 N= 20; data type= AA		Aspinall and Feather 1972 N= 20; data type= NAA	
Li	P	Sc	Th
x 6.05	x 91.4	x .23	x .14
sd 1.28	sd 24.5	sd .04	sd .03
R 4.0-8.0	R 42.0-131.0		
Na	K	Cr	U
x 287.7	x 235.4	x .7	x .8
sd 41.7	sd 30.9	sd .2	sd .6
R 242-384	R 172-308		
Mg	Ca	Cs	
x 21.1	x 440.7	x .023	
sd 3.99	sd 105.9	sd .006	
R 14-29	R 269-740		
Al	Fe	Ta	
x 664.6	x 84	x .012	
sd 116.8	sd 20.2	sd .003	
R 495-863	R 34-115		

## Flint Ridge Chert

Vanport formation, Middle Pennsylvanian. Chert occurs as a single bed averaging 1.2 m in thickness among limestones and shales in central Ohio, USA. This material is variable in all its visible properties; structure can be homogeneous, shaded, laminated, mottled, streaked, or brecciated. Small veins and cavities lined with chalcedony or quartz crystals are very common. Color ranges from white to dark gray and includes yellows, pinks, reds, and blues. White and pale gray, N8/ and N7/, are probably most common. Texture is fine to medium, luster is shiny to medium, and translucency is 3 to 8 mm, with most about 5 mm. Most Flint Ridge chert has a luminous quality that is difficult to quantify but is quite distinctive among Midwest cherts. Impurities include finely disseminated carbonates and iron oxides. (See Luedtke 1976; Lavin 1983; Carlson 1987; and table B.12.)

**Table B.12 Trace Element Data for Flint Ridge Chert**

(N=23; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 89.8	x 0.180	x 0.137	x 1.47	x 0.013
sd 49.7	sd 0.156	sd 0.058	sd 1.36	sd 0.013
R 31.6-222.5	R 0.030-0.630	R 0.040-0.270	R 0.160-4.90	R 0.001-0.052
Sc	Zn	Cs	Sm	Hf
x 0.119	x 0.977	x 0.016	x 0.130	x 0.036
sd 0.066	sd 0.986	sd 0.0085	sd 0.135	sd 0.022
R 0.050-0.315	R 0.200-3.72	R 0.006-0.030	R 0.013-0.435	R 0.010-0.090
Cr	Br	Ba	Eu	Th
x 1.16	x 0.082	x 28.2	x 0.051	x 0.082
sd 0.776	sd 0.079	sd 14.4	sd 0.067	sd 0.051
R 0.110-2.66	R 0.009-0.298	R 7.83-59.9	R 0.003-0.280	R 0.010-0.180
Fe	Rb	La	Yb	U
x 634.6	x 1.58	x 0.284	x 0.056	x 0.757
sd 641.3	sd 1.53	sd 0.284	sd 0.061	sd 0.570
R 73.7-2471.9	R 0.070-4.90	R 0.037-0.933	R 0.008-0.249	R 0.196-2.09

## Indiana Hornstone

Ste. Genevieve formation, Middle Mississippian. Chert occurs as nodules or lenses 30 cm or more in diameter in limestone in southern Indiana, USA. Structure is homogeneous to concentrically banded, with cavities lined with pale blue chalcedony or quartz crystals, and color is typically medium blue-gray, 5B5/1. Texture is fine, luster is shiny, and translucency is 1 to 2 mm. Impurities include dolomite rhombs, calcite, pyrite, anthraxolite, and fluorite. Also called Harrison County chert and Wyandotte chert. (See Luedtke 1976; Tankersley 1984; and table B.13.)

**Table B.13 Trace Element Data for Indiana Hornstone**

(N=104; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 444.1	x 0.812	x 1.02	x 6.60	x 0.043
sd 100.7	sd 0.545	sd 0.445	sd 2.96	sd 0.030
R 280.5-714.2	R 0.210-2.47	R 0.240-2.19	R 3.20-18.3	R 0.015-0.157
Sc	Zn	Cs	Sm	Hf
x 0.501	x 6.48	x 0.212	x 0.475	x 0.476
sd 0.080	sd 3.50	sd 0.046	sd 0.378	sd 0.205
R 0.290-0.762	R 1.01-14.7	R 0.120-0.330	R 0.014-2.05	R 0.220-1.33
Cr	Br	Ba	Eu	Th
x 7.08	x 0.774	x 189.4	x 0.073	x 0.459
sd 1.17	sd 0.362	sd 117.7	sd 0.012	sd 0.078
R 4.28-11.0	R 0.423-2.97	R 39.1-542.2	R 0.050-0.110	R 0.250-0.630
Fe	Rb	La	Yb	U
x 830.5	x 4.29	x 1.53	x 0.129	x 27.8
sd 181.7	sd 1.80	sd 0.306	sd 0.039	sd 22.2
R 508.3-1651.6	R 1.06-11.5	R 1.05-2.94	R 0.074-0.266	R 3.43-104.8

## Kettle Point Chert

Ipperwash formation, Middle Devonian. Chert occurs as nodules and lenses 8 cm thick in gray shale and limestone in southwest Ontario, Canada. Structure is homogeneous to streaked or mottled, and color ranges from medium or dark gray, N5/ to N6/, to lighter gray or grayish purple, 7.5YR8/2. Texture is fine to medium, luster is medium to shiny, and translucency is 1 to 4 mm. Also called Port Franks chert. (See Luedtke 1976 and table B.14.)

**Table B.14 Trace Element Data for Kettle Point Chert**

(N=24; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 574.5	x 0.627	x 0.037	x 3.03	x 0.015
sd 203.0	sd 0.327	sd 0.018	sd 1.88	sd 0.0093
R 238.8-1046.8	R 0.200-1.32	R 0.010-0.080	R 0.940-8.07	R 0.004-0.044
Sc	Zn	Cs	Sm	Hf
x 0.387	x 4.50	x 0.159	x 0.297	x 0.099
sd 0.138	sd 3.16	sd 0.090	sd 0.200	sd 0.048
R 0.170-0.630	R 1.48-13.1	R 0.060-0.340	R 0.104-0.832	R 0.030-0.190
Cr	Br	Ba	Eu	Th
x 2.34	x 3.52	x 92.1	x 0.103	x 0.243
sd 1.29	sd 0.994	sd 173.6	sd 0.064	sd 0.082
R 0.520-4.79	R 2.08-6.45	R 8.15-687.3	R 0.040-0.290	R 0.120-0.420
Fe	Rb	La	Yb	U
x 2495.3	x 4.11	x 0.931	x 0.092	x 0.366
sd 983.1	sd 2.64	sd 0.459	sd 0.068	sd 0.229
R 1013.2-4071.6	R 0.030-9.53	R 0.480-2.62	R 0.020-0.340	R 0.050-0.930



## Knife River Flint

Golden Valley formation?, Eocene. Chert always found in alluvial, lag, and slope-wash deposits; so, the exact provenance is not known. However, most probably represents bed of silicified lignite, usually 10 to 20 cm thick, associated with sandstones, shales, and clays in western North Dakota, USA. Structure is homogeneous or finely laminated, and color is typically very dark brown, 10YR2/2 or 3/2. Texture is fine, luster is medium, and translucency is 5 to 11 mm. Impurities are mostly organic carbon; plant remains are visible in some cases. (See Clayton et al. 1970; Ahler 1986; Julig et al. 1988; and table B.15.)

**Table B.15 Trace Element Data for Knife River Flint**

(N=5; data type=NAA; ref=UMMA)

Na	Co	Cs	Sm	Hf
x 172.5	x 0.045	x 0.0065	x 0.279	x 0.040
sd 67.9	sd 0.018	sd 0.0042	sd 0.230	sd 0.027
R 118.8-274.8	R 0.034-0.075	R 0.0015-0.0119	R 0.134-0.684	R 0.011-0.077
Sc	Br	Ba	Eu	Th
x 0.282	x 0.074	x 110.5	x 0.060	x 0.134
sd 0.240	sd 0.032	sd 74.3	sd 0.066	sd 0.070
R 0.096-0.627	R 0.036-0.121	R 38.5-208.0	R 0.019-0.172	R 0.064-0.244
Cr	Rb	La	Yb	U
x 1.14	x 0.386	x 0.442	x 0.103	x 6.18
sd 1.43	sd 0.352	sd 0.341	sd 0.106	sd 2.83
R 0.250-3.26	R 0.062-0.761	R 0.119-1.009	R 0.022-0.281	R 3.30-10.8
Fe	Sb	Ce	Lu	
x 43.1	x 0.168	x 2.06	x 0.020	
sd 10.9	sd 0.095	sd 1.53	sd 0.014	
R 31.8-55.3	R 0.059-0.253	R 1.03-4.73	R 0.0038-0.041	

## Lambrix Chert

Coldwater formation?, Lower Mississippian. Chert occurs as nodules up to 30 cm in diameter in dolomites, limestone, and shale. The exact geological context of this chert is unclear because it is known only from glacial deposits overlying the contact between the Coldwater formation and the Marshall formation in western Michigan, USA. As the latter formation is not reported to have chert and the Coldwater is, this material is assumed to be from the Coldwater formation. Nodules range from a friable, fine-grained, cemented sandstone to sandy chert to solid chert, with botryoidal chalcedony and quartz crystals lining interior cavities. The sandy chert, gray chert, and chalcedony are treated here as three different phases. The sandy chert is streaked, and it is reddish brown, 10YR5/4–6/4. Texture is coarse, luster is dull, and translucency is 0.5 mm. The gray chert is homogeneous to slightly streaked or “dusty,” with color ranging from 10YR6/1 to 7/2; its texture is medium to fine, luster is medium, and translucency is 1 to 1.5 mm. The chalcedony is pale blue-gray, N6/ to N7; texture is fine, luster is shiny, and translucency is 6 mm. (See Luedtke 1976 and table B.16.)

**Table B.16 Trace Element Data for Lambrix Chert**

(data type=NAA; ref=Luedtke 1976)

	Sandy, N=9	Gray, N=13	Chalcedony, N=6
Na	x 654.7 sd 145.1 R 509.6-799.8	x 586.2 sd 114.7 R 471.6-700.9	x 463.8 sd 127.3 R 291.3-581.8
Sc	x 1.37 sd 0.994 R 0.380-2.37	x 0.596 sd 0.349 R 0.248-0.945	x 0.099 sd 0.036 R 0.060-0.160
Cr	x 5.88 sd 1.50 R 4.39-7.37	x 4.11 sd 1.04 R 3.06-5.15	x 0.455 sd 0.544 R 0.070-0.840
Fe	x 4159.5 sd 2313.2 R 1846-6473	x 1603.9 sd 818.8 R 885-2523	x 115.8 sd 52.5 R 69.9-206.0
Co	x 1.19 sd 0.701 R 0.485-1.89	x 0.525 sd 0.264 R 0.272-0.789	x 0.073 sd 0.036 R 0.020-0.110
Zn	x 5.90 sd 1.06 R 4.85-6.96	x 70.5 sd 85.4 R 0-155.9	x 3.99 sd 4.37 R 0.900-7.08
Br	x 1.93 sd 0.810 R 1.12-2.74	x 2.54 sd 1.07 R 1.47-3.61	x 3.63 sd 1.06 R 2.62-5.15
Rb	x 11.65 sd 8.10 R 3.54-19.8	x 6.63 sd 3.80 R 2.84-10.4	x 0.780 sd 0.250 R 0.490-1.13
Sb	x 0.054 sd 0.030 R 0.024-0.084	x 0.032 sd 0.014 R 0.018-0.046	x 0.012 sd 0.0067 R 0.006-0.020
Cs	x 0.548 sd 0.428 R 0.120-0.976	x 0.305 sd 0.169 R 0.137-0.474	x 0.027 sd 0.010 R 0.010-0.040

**Table B.16 Trace Element Data for Lambrix Chert (con't)**

(data type=NAA; ref=Luedtke 1976)

	Sandy, N=9	Gray, N=13	Chalcedony, N=6
Ba	x 48.8	x 30.1	x 22.2
	sd 33.2	sd 19.6	sd 9.90
	R 15.6-82.1	R 10.5-49.7	R 14.6-42.0
La	x 3.53	x 1.44	x 0.081
	sd 2.24	sd 0.576	sd 0.022
	R 1.29-5.77	R 0.867-2.02	R 0.048-0.110
Ce	x 6.14	x 3.02	x 0.545
	sd 3.08	sd 1.08	sd 0.191
	R 3.06-9.22	R 1.94-4.10	R 0.390-0.920
Sm	x 0.860	x 0.420	x 0.034
	sd 0.336	sd 0.154	sd 0.020
	R 0.524-1.20	R 0.265-0.574	R 0.015-0.060
Eu	x 0.221	x 0.135	x 0.0082
	sd 0.068	sd 0.057	sd 0.0029
	R 0.153-0.289	R 0.078-0.192	R 0.004-0.010
Yb	x 0.203	x 0.091	x 0.022
	sd 0.120	sd 0.041	sd 0.013
	R 0.083-0.322	R 0.050-0.132	R 0.002-0.036
Lu	x 0.030	x 0.015	x 0.003
	sd 0.018	sd 0.0084	sd 0.0021
	R 0.011-0.048	R 0.0069-0.024	R 0.0005-0.006
Hf	x 0.237	x 0.148	x 0.020
	sd 0.124	sd 0.067	sd 0.0089
	R 0.113-0.360	R 0.081-0.216	R 0.010-0.030
Th	x 1.01	x 0.514	x 0.015
	sd 0.536	sd 0.222	sd 0.010
	R 0.476-1.55	R 0.292-0.736	R 0.003-0.030
U	x 0.419	x 0.510	x 2.60
	sd 0.241	sd 0.410	sd 1.51
	R 0.178-0.660	R 0.100-0.920	R 1.49-5.60

## Limerock Jasper

Blackstone series, Precambrian. Chert occurs as boulders up to 1 m in diameter in a collapsed sinkhole in marble in northern Rhode Island, USA. Structure is streaked, and color is usually golden, 10YR6/4. Most material is opaque gold, but some is translucent and pale yellow (2.5Y7/4) or gray (N8/), and this variety has been analyzed separately. Texture ranges from coarse to medium, luster is medium to dull, and translucency is 1 to 3 mm for the opaque gold variety and 15 to 18 mm for the translucent variety. Impurities include clay and goethite. (See Luedtke 1987 and table B.17.)

**Table B.17 Trace Element Data for Limerock Jasper**

(data type=NAA; ref=UMMA)

	Opaque (N= 29)	Translucent (N= 11)		Opaque	Translucent
Na	x 44.3 sd 21.6 R 19.0-95.0	x 59.1 sd 35.6 R 23.0-117.0	Sb	x 0.699 sd 0.548 R 0.089-1.82	x 1.56 sd 2.01 R 0.199-6.80
Sc	x 0.732 sd 1.26 R 0.008-3.58	x 0.060 sd 0.042 R 0.011-0.126	Cs	x 0.073 sd 0.018 R 0.045-0.092	x 0.047 sd 0.024 R 0.022-0.072
Cr	x 5.15 sd 5.34 R 0.583-18.4	x 2.13 sd 1.12 R 0.294-3.60	La	x 0.237 sd 0.197 R 0.047-0.710	x 0.240 sd 0.236 R 0.027-0.731
Fe	x 24708.0 sd 13169.3 R 6590-58291	x 371.9 sd 244.5 R 100-827	Ce	x 9.00 sd 5.12 R 1.07-21.7	x 0.644 sd 0.558 R 0.139-1.80
Co	x 3.62 sd 3.21 R 0.891-16.2	x 0.285 sd 0.244 R 0.074-0.523	Sm	x 0.157 sd 0.210 R 0.0076-0.673	x 0.118 sd 0.110 R 0.022-0.376
Ni	x 21.8 sd 10.7 R 8.60-33.1	n.f.	Eu	x 0.092 sd 0.111 R 0.016-0.335	x 0.023 sd 0.013 R 0.008-0.046
Zn	x 17.5 sd 13.5 R 2.70-51.7	x 12.2 sd 9.80 R 2.95-31.0	Yb	x 0.251 sd 0.285 R 0.060-0.920	n.f.
As	x 1.12 sd 0.461 R 0.680-1.91	n.f.	Lu	x 0.051 sd 0.066 R 0.0082-0.211	x 0.010 sd 0.0067 R 0.003-0.021
Ag	n.f.	x 0.245 sd 0.131 R 0.089-0.476	U	n.f.	x 0.388 sd 0.278 R 0.130-0.997
Cd	x 11.0 sd 14.7 R 1.62-58.0	n.f.			

(n.f. in either variety: Br,Rb,Ba,Tb,Hf,Th)

### Magadi-type Chert

First sample is described as lake chert of Pliocene age found as a nodule 5 cm in diameter in zeolitized tuff in west central Nevada, USA. Visible properties are not described, except that texture varies. Second sample is described as lake chert of Pliocene age found as a smaller (2 cm), but macroscopically similar, nodule in southeastern Oregon, USA. (See Weis and Wasserburg 1987 and table B.18.)

**Table B.18 Trace Element Data for Magadi-type Chert**

(data type=XRF; ref=Weis and Wasserburg 1987)

Nevada chert (N= 1)		Oregon chert (N= 1)	
Na= 1186.9	K= 829.9	Rb= 0.612	Rb= 0.490
Mg= 301.6	Ca= 571.8	Sr= 6.92	Sr= 1.89
Al= 423.3	Fe= 2306.0	Nd= 0.115	Nd= 0.272
P= 87.2		Sm= 0.026	Sm= 0.096

### Monterey Chert

Monterey formation, Miocene. Chert occurs as beds up to several centimeters thick interbedded with shale, mudstone, and sandstone, in western California, USA. Structure is often finely laminated, and color ranges from black to gray to white. I have access to only one sample, for which texture is medium, luster is medium to shiny, and translucency is 0.5 mm. Impurities include organic carbon, carbonates, apatite, feldspar, and clays. Table B.19 includes some values in which the ranges do not appear to agree with the means; these apparent misprints are in the original reference. (See Brueckner and Snyder 1985; Bramlette 1946.)

**Table B.19 Trace Element Data for Monterey Chert**

(N=5; data type=XRF, PES, ID; ref=Brueckner and Snyder 1985)

Na	Ca	Fe	Rb	Mo
x 445	x 143	x <2236	x 0.263	x 15
R 148-668	R 71.5-285.9	R 175-5800	R 0.226-0.397	R 9-21
Mg	Ti	Ni	Sr	Cd
x <36.2	x 43	x 21	x 2.16	x <7
R <6.03-120.6	R 35-56	R 7-52	R 1.08-3.14	R <2-7
Al	V	Cu	Y	Cs
x 2434	x 13	x <5	x 1	x 0.013
R 1799-3545	R 8-18	R <5-<5	R 1-2	R 0.0098-0.013
P	Cr	Zn	Zr	Ba
x 43.6	x 24	x 18	x 11	x 21
R 43.6-87.2	R 21-27	R 15-21	R 10-11	R 11.8-20.4
K	Mn			
x 191	x 31			
R 158-241	R 7.74-77.4			

## Norwood Chert

Whiskey Creek formation, Middle Devonian. Chert occurs as lenses ranging from 2 to 15 cm thick interbedded with marly shales, limestones, and dolomites in northern Michigan, USA. Structure is finely laminated, sometimes convoluted but often very regular and sometimes crossbedded, and often flecked with microfossils. Color is typically pale gray or tan, 10YR7/1, with laminations in darker colors, N7/ or 10YR6/1. Texture is medium to fine, luster is dull to shiny, and translucency is 0.5 mm. Also called Eastport chert. Although this material occurs at several locations, the most important source is the Piwangoning quarry, and the chemical data in table B.20 are from this source. (See Luedtke 1976; Kesling et al. 1974.)

**Table B.20 Trace Element Data for Norwood Chert**

(N=39; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 302.8	x 0.272	x 0.023	x 1.92	x 0.0057
sd 57.2	sd 0.082	sd 0.0085	sd 0.805	sd 0.0026
R 170.5-457.0	R 0.140-0.480	R 0.013-0.040	R 0.880-3.70	R 0.0003-0.012
Sc	Zn	Cs	Sm	Hf
x 0.262	x 1.64	x 0.147	x 0.100	x 0.103
sd 0.112	sd 0.233	sd 0.047	sd 0.035	sd 0.030
R 0.140-0.627	R 1.29-1.82	R 0.090-0.230	R 0.060-0.199	R 0.060-0.170
Cr	Br	Ba	Eu	Th
x 2.15	x 1.01	x 43.7	x 0.025	x 0.348
sd 0.527	sd 0.367	sd 12.8	sd 0.0067	sd 0.110
R 1.62-2.98	R 0.565-1.63	R 21.4-69.7	R 0.016-0.034	R 0.180-0.570
Fe	Rb	La	Yb	U
x 1846.5	x 3.58	x 0.757	x 0.041	x 0.098
sd 702.3	sd 1.61	sd 0.227	sd 0.018	sd 0.045
R 810-3786	R 1.89-7.79	R 0.460-1.37	R 0.0002-0.099	R 0.010-0.140

## Onondaga Chert

Onondaga formation, Lower to Middle Devonian. Chert occurs as nodules 1.3 to 1.5 cm in diameter in limestone and dolomite that outcrops across upstate New York, USA. Structure is usually mottled and streaked, with veins filled with chalcedony or quartz crystals, and color is typically very dark gray, N3/-N4/, to lighter gray, N5/-N6/. Texture is fine to medium, luster is shiny, and translucency is 1 to 1.5 mm. See table B.21; Prothero sometimes distinguishes between the eastern and western ends of the formation. Onondaga chert is similar to Amherstburg chert with which it is correlated. (See Ozol 1963; Luedtke 1976; Jarvis 1988; and table B.22.)

**Table B.21 Petrographic Data for Onondaga Chert**

	Wray (1948)	Ozol (1963)	Prothero (1983)
Dolomite rhombs	Fairly abundant	Abundant	Abundant
Dusty calcite	Abundant	Abundant	Present
Pyrite	Rare	Present	Abundant E, present W
Mica	Rare		Present
Clastic quartz		Present	Absent
Iron oxide		Present	Absent E, present W
Organic matter	Rare		Absent

**Table B.22 Trace Element Data for Onondaga Chert**

	Ref= Luedtke 1976 data type= NAA N= 15	Ref= Jarvis 1988 data type = NAA N= 120	Ref= Ozol 1963 data type= oxides N= 10	Luedtke	Jarvis
Na	x 793.7 sd 394.9 R 330.0-1435.3	x 700 sd 230	x 875 sd 296 R 519-1261	Sr x 22.4 sd 25.3	
Mg		x 2000 sd 620	x 5657 sd 1660 R 2895-34075	Sb x 0.031 sd 0.0099 R 0.020-0.050	
Al		x 4090 sd 820	x 5545 sd 1190 R 3492-7143	I x 0.135 sd 0.353	
Cl		x 1090 sd 430		Cs x 0.364 sd 0.091 R 0.180-0.500	
K		x 1010 sd 760	x 1826 sd 617 R 1245-2822	Ba x 30.8 sd 9.76 R 11.1-49.9	x 20.7 sd 12.5
Ca		x 16800 sd 11000	x 25919 sd 12302 R 4646-41959	La x 1.12 sd 0.527 R 0.298-2.14	
Sc	x 0.385 sd 0.128 R 0.195-0.586			Ce x 1.54 sd 0.569 R 0.540-2.61	
Ti		x 135 sd 48	x 647 sd 138 R 479-899	Sm x 0.197 sd 0.155 R 0.051-0.681	
V		x 4.75 sd 2.23		Eu x 0.041 sd 0.017 R 0.020-0.090	
Cr	x 3.77 sd 0.860 R 2.46-4.90			Dy x 0.151 sd 0.074	
Mn		x 16.2 sd 9.5		Yb x 0.094 sd 0.038 R 0.049-0.178	
Fe	x 1042.6 sd 228.7 R 594-1482		x 15905 sd 7023 R 8875-28441	Lu x 0.013 sd 0.0086 R 0.001-0.037	
Co	x 0.367 sd 0.081 R 0.220-0.470			Hf x 0.155 sd 0.034 R 0.080-0.200	
Zn	x 4.63 sd 1.93 R 2.33-8.81			Th x 0.288 sd 0.087 R 0.180-0.460	
Br	x 8.02 sd 3.72 R 4.15-14.0	x 11.3 sd 4.6		U x 0.436 sd 0.100 R 0.293-0.681	x 0.463 sd 0.109
Rb	x 6.23 sd 3.08 R 1.47-10.9				

## Pennsylvania Jasper

Hardyston formation, Lower Cambrian. Chert occurs as replaced masses in quartzite and argillaceous sandstone in southeastern Pennsylvania, USA. Structure is often mottled, sometimes has a wood-grain appearance, and contains many veins filled with quartz or chalcedony. Color is typically gold, 10YR5/4, but can also be brown, red, or paler colors. Texture is fine to medium, luster is medium to shiny, and translucency is <0.5 to 1 mm. Impurities include microcline, plagioclase, clastic quartz, biotite, hematite, limonite. (See Lavin 1983; Hatch and Miller 1985; Luedtke 1987; and table B.23.)

**Table B.23 Trace Element Data for Pennsylvania Jasper**

(data type=NAA)

	All PA jasper (N=28; ref UMMA)	Vera Cruz quarry (N= 16; ref=UMMA)	Vera Cruz quarry (N=20; ref= Hatch and Miller 1985)
Na	n.f	x 246.0 sd 55.2 R 207-285	
K			x 608 sd 315
Sc	x 0.415 sd 0.356 R 0.094-1.52	x 0.321 sd 0.206 R 0.133-0.738	x 0.380 sd 0.284
Cr	x 1.33 sd 0.460 R 0.538-2.23	x 1.31 sd 0.498 R 0.538-2.23	
Mn			x 48 sd 603.0
Fe	x 9452.0 sd 4459.7 R 1430 -18891	x 8675.8 sd 3517.3 R 3193-13325	x 13780 sd 14527
Co	x 1.54 sd 0.872 R 0.199-3.45	x 1.70 sd 0.898 R 0.524-3.45	
Cu			x 6.83 sd 3.68
Zn	x 24.4 sd 17.5 R 3.43-65.2	x 23.7 sd 16.0 R 3.43-51.1	
As	x 2.64 sd 1.10 R 0.885-4.08	x 2.64 sd 1.19 R 0.885-4.08	x 8.07 sd 7.19
Cd	x 7.72 sd 5.18 R 2.26-19.1	x 7.39 sd 5.84 R 2.26-19.1	
Sb	x 0.462 sd 0.354 R 0.041-1.24	x 0.488 sd 0.276 R 0.146-0.984	
Cs	n.f	x 0.114 sd 0.0075 R 0.106-0.122	
Ba	x 69.3 sd 41.6 R 26.5-179.8	x 54.8 sd 30.3 R 26.5-153.8	
La	x 3.80 sd 3.87 R 0.267-13.6	x 2.85 sd 3.62 R 0.819-12.6	x 3.90 sd 9.91



**Table B.23 Trace Element Data for Pennsylvania Jasper (cont'd)**

(data type=NAA)

	All PA jasper (N=28; ref UMMA)	Vera Cruz quarry (N= 16; ref=UMMA)	Vera Cruz quarry (N=20; ref= Hatch and Miller 1985)
Ce	x 5.46 sd 4.48 R 1.82-21.5	x 2.97 sd 0.804 R 1.82-4.04	
Nd	x 8.99 sd 5.14 R 2.20-15.8	n.f.	
Sm	x 1.02 sd 0.925 R 0.180-3.37	x 0.600 sd 0.556 R 0.180-2.31	x 1.34 sd 2.91
Eu	x 0.191 sd 0.205 R 0.014-0.602	x 0.057 sd 0.035 R 0.014-0.133	
Tb	x 0.226 sd 0.126 R 0.049-0.454	x 0.141 sd 0.096 R 0.049-0.288	
Yb	x 0.398 sd 0.500 R 0.053-1.99	x 0.145 sd 0.058 R 0.073-0.266	
Lu	x 0.060 sd 0.068 R 0.014-0.283	x 0.034 sd 0.017 R 0.014-0.083	
Hf	x 0.135 sd 0.060 R 0.057-0.283	x 0.143 sd 0.070 R 0.087-0.283	
Hg	x 0.938 sd 0.663 R 0.153-2.77	x 0.885 sd 0.553 R 0.283-1.96	
Th	x 0.283 sd 0.182 R 0.060-0.663	x 0.259 sd 0.199 R 0.060-0.663	
U	x 1.84 sd 1.28 R 0.777-5.97	x 1.74 sd 1.31 R 0.791-5.97	(Additional elements n.f. for UMMA data: Na,Ni,Br,Rb,Ag,Cs)

## Petrified Forest Silicified Wood

Chinle formation, Middle Triassic. Chert occurs as silicified wood at the Petrified Forest National Park in east central Arizona, USA. Color is highly variable, from pale gray to red to black, and texture, luster, and translucency also vary greatly. Impurities include calcite, dolomite, clay, and iron oxides. The samples identified below as black, red, and beige represent a cross section of a single branch, with the black sample taken from the center of the branch, the red sample from a middle ring, and the beige sample from the outer portion of the branch. (See Maxwell 1963; Sigleo 1979; Ash 1987; and table B.24.)

**Table B.24 Trace Element Data for Petrified Forest Silicified Wood**

Ref= Maxwell 1963; N=1; data type= oxides and emission spectroscopy		Ref= Sigleo 1979; N=3; data type= NAA		
		Black sample	Red sample	Beige sample
C	2347	18900	300	500
Na	74.2	667.6	964.3	1854.5
Mg	663.4	12.1	1326.8	3377.4
Al	105.8	4603.2	15978.8	23227.5
K	83.0	n.f.	83.0	166.0
Ca	11007.9	786.3	1000.7	1787.0
Fe	388.5	1397.6	4192.8	1886.8
Li	11	Ge	0.2	
P	13	As	0.8	
Ti	13	Sr	10-100	
Cr	1-10	Mo	0.4	
Mn	63	Ba	10-100	
Cu	0.1-1	(P= Be, V; n.f.=Sc,Co,Ni,Ga Sn)		

## Plum Run Chert

Vanport formation, Middle Pennsylvanian. Chert occurs as lenses in limestone in northeastern Ohio, USA. Structure is mottled and streaked, and color is generally blue gray, N4/, to tan, 2.5Y5/2. Texture is fine to medium, luster is medium to shiny, and translucency is 1.5 to 4 mm. Impurities include carbonates and pyrite. (See Stout and Schoenlaub 1945; Luedtke 1976; and table B.25).

**Table B.25 Trace Element Data for Plum Run Chert**

(N=5; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 553.6	x 4.62	x 0.128	x 7.20	x 0.043
sd 55.2	sd 3.04	sd 0.043	sd 3.98	sd 0.0085
R 484.8-616.7	R 1.01-7.84	R 0.070-0.190	R 3.64-12.5	R 0.035-0.052
Sc	Zn	Cs	Sm	Hf
x 1.38	x 108.4	x 0.440	x 1.28	x 0.220
sd 0.612	sd 131.5	sd 0.206	sd 1.23	sd 0.088
R 0.770-1.96	R 12.7-296.0	R 0.210-0.730	R 0.260-2.87	R 0.130-0.340
Cr	Br	Ba	Eu	Th
x 15.8	x 0.746	x 139.1	x 0.222	x 0.918
sd 10.9	sd 0.202	sd 21.6	sd 0.056	sd 0.421
R 4.19-31.7	R 0.490-0.970	R 107.6-155.4	R 0.170-0.280	R 0.450-1.40
Fe	Rb	La	Yb	U
x 4126.3	x 8.46	x 3.71	x 0.270	n.f.
sd 2244.0	sd 4.16	sd 0.775	sd 0.125	
R 2178-7020	R 4.72-12.2	R 3.01-4.47	R 0.140-0.440	

### Put-in-Bay Chert

Put-in-Bay formation, Upper Silurian. Chert occurs as small nodules or lenses in limestone in southeastern Michigan, USA. Structure is homogeneous to shaded, and color is cream, buff, or reddish buff, 10YR7/1 to 6/1. Texture is coarse to medium, luster is dull, and translucency is 0.5 mm. (See Luedtke 1976 and table B.26.)

**Table B.26 Trace Element Data for Put-in-Bay Chert**

(N=5; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 176.3	x 0.632	x 0.080	x 5.94	x 0.013
sd 59.6	sd 0.259	sd 0.017	sd 2.17	sd 0.0021
R 84.4-218.0	R 0.400-0.970	R 0.070-0.110	R 3.72-8.73	R 0.011-0.016
Sc	Zn	Cs	Sm	Hf
x 0.316	x 2.72	x 0.180	x 0.231	x 0.232
sd 0.064	sd 1.14	sd 0.080	sd 0.061	sd 0.033
R 0.230-0.400	R 1.40-4.25	R 0.100-0.310	R 0.125-0.280	R 0.180-0.270
Cr	Br	Ba	Eu	Th
x 4.97	x 3.44	x 37.1	x 0.046	x 0.576
sd 1.12	sd 0.412	sd 6.26	sd 0.014	sd 0.107
R 3.72-6.41	R 2.92-3.83	R 32.4-47.6	R 0.023-0.057	R 0.440-0.730
Fe	Rb	La	Yb	U
x 11600.4	x 6.22	x 1.62	x 0.080	x 2.32
sd 6214.3	sd 2.64	sd 0.488	sd 0.016	sd 3.07
R 4346-20598	R 2.61-9.13	R 0.910-2.11	R 0.060-0.100	R 0.450-7.77

### Serra Geral Agate

Serra Geral formation, Lower Cretaceous. Chert occurs as fillings in vesicles of basaltic lavas in southern Brazil. Agates are concentrically banded, horizontally laminated, or both, and color is typically bluish gray or white. Central cavities are often lined with quartz crystals. No obvious impurities reported, other than water. (See Flörke et al. 1982 and table B.27.)

**Table B.27 Trace Element Data for Serra Geral Agate**

(N=8; data type=AA and emission spectroscopy; ref=Florke et al. 1982)

Li	Mg	K	Fe
x 2.80	x 15.8	x 87.2	x 86.5
sd 2.10	sd 11.4	sd 76.1	sd 90.7
R 0.47-6.5	R 1.2-33.8	R 19.1-266.4	R 7.0-279.5
Na	Al	Ca	
x 260.6	x 183.2	x 112.6	
sd 206.3	sd 150.4	sd 40.8	
R 89.0-749.2	R 15.9-507.9	R 57.2-178.7	

## Stevns Flint

Stevns formation?, Cretaceous (Maastrichtian). Chert occurs as nodules ranging from 2 to 100 cm in diameter in chalk near Stevns in eastern Denmark. Structure is homogeneous to mottled, and color is typically bluish black, with the centers of nodules often light gray. The black chert is fine grained and nearly opaque, with "subvitreous luster," while the lighter gray chert is more granular. Some nodules have black rounded bodies 1 to 50 mm in size, and also small (2 to 50  $\mu$ ) irregularly shaped brownish bodies that are opaque and organic appearing. Amorphous carbon and calcite are major impurities. (See Micheelsen 1966 and table B.28.)

**Table B.28 Trace Element Data for Stevns Flint**

(N=1; data type=oxides; ref=Micheelsen 1966)

C= 521.1	P= 122.0	V= 1.12	Ni= 0.472	Ba= 0.896
Na= 0.022	Ca= 629.0	Cr= 0.684	Sr= 16.9	La= 0.853
Mg= 12.1	Sc= 0.065	Mn= <0.023	Y= 0.787	
Al= 169.3	Ti= 12.0	Fe= 54.4	Zr= 1.48	

## Stoney Creek Chert

Raisin River formation, Upper Silurian. Chert occurs as nodules and lenses up to 8 cm thick in tan dolomite in southeastern Michigan, USA. Structure is streaked and flecked with numerous light and dark fossils. Typical color is gray, N6/ to N7/, with streaks of darker brown, 10YR6/1. Texture is coarse to medium, luster is dull to medium, and translucency is 0.5 mm. (See Luedtke 1976 and table B.29.)

**Table B.29 Trace Element Data for Stoney Creek Chert**

(N=15; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 256.9	x 0.123	x 0.022	x 1.06	x 0.0053
sd 79.6	sd 0.051	sd 0.009	sd 0.406	sd 0.0031
R 138.9-359.2	R 0.030-0.210	R 0.008-0.040	R 0.420-2.00	R 0.0004-0.012
Sc	Zn	Cs	Sm	Hf
x 0.107	x 2.13	x 0.085	x 0.074	x 0.176
sd 0.047	sd 1.51	sd 0.042	sd 0.033	sd 0.111
R 0.020-0.170	R 0.570-5.87	R 0.010-0.140	R 0.029-0.101	R 0.010-0.370
Cr	Br	Ba	Eu	Th
x 3.39	x 3.03	x 9.59	x 0.013	x 0.178
sd 0.948	sd 1.17	sd 3.31	sd 0.0059	sd 0.063
R 2.31-5.87	R 0.980-4.81	R 4.77-15.6	R 0.003-0.027	R 0.030-0.290
Fe	Rb	La	Yb	U
x 1156.7	x 1.84	x 0.453	x 0.035	x 0.764
sd 872.6	sd 0.738	sd 0.167	sd 0.016	sd 0.230
R 110.2-3192	R 0.550-3.26	R 0.110-0.720	R 0.010-0.060	R 0.550-1.45

### Tenmile Creek Chert

Tenmile Creek formation, Middle Devonian. Chert occurs as nodules or lenses in limestone in northwestern Ohio, USA. Structure is homogeneous or mottled, with light colored flecks and fossils. Color is typically pale bluish gray to yellowish, 10YR7/1 to 7.5YR8/4. Texture is coarse to fine, luster is dull to medium, and translucency is 0.5 mm. (See Luedtke 1976 and table B.30.)

**Table B.30 Trace Element Data for Tenmile Creek Chert**

(N=10; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 155.2	x 0.260	x 0.025	x 1.26	x 0.005
sd 69.7	sd 0.101	sd 0.0071	sd 0.482	sd 0.0017
R 78.1-242.6	R 0.150-0.420	R 0.020-0.040	R 0.710-2.30	R 0.003-0.009
Sc	Zn	Cs	Sm	Hf
x 0.160	x 2.97	x 0.077	x 0.072	x 0.087
sd 0.058	sd 2.33	sd 0.030	sd 0.023	sd 0.028
R 0.090-0.250	R 0.740-6.47	R 0.040-0.120	R 0.051-0.115	R 0.040-0.140
Cr	Br	Ba	Eu	Th
x 1.07	x 3.19	x 16.9	x 0.025	x 0.156
sd 0.488	sd 0.926	sd 4.71	sd 0.0085	sd 0.052
R 0.440-1.68	R 2.04-4.42	R 10.7-22.6	R 0.010-0.040	R 0.080-0.220
Fe	Rb	La	Yb	U
x 1855.2	x 2.30	x 0.520	x 0.038	x 0.193
sd 1532.7	sd 0.682	sd 0.135	sd 0.011	sd 0.106
R 633-5803	R 1.18-3.38	R 0.300-0.740	R 0.020-0.060	R 0.020-0.330

### Upper Mercer Chert

Upper Mercer formation, Lower Pennsylvanian. Chert occurs as nodules and beds, some more than 15 cm thick, in limestones and shales in central Ohio, USA. Structure is homogeneous or mottled, with frequent veins of white or blue chalcedony, and color is typically black, N/2, to dark gray. Texture is medium to fine, luster is medium to shiny, and translucency is 0.5 to 1 mm. Impurities include carbon, pyrite, limonite, and ankerite. (See Stout and Schoenlaub 1945; Luedtke 1976; and table B.31.)

**Table B.31 Trace Element Data for Upper Mercer Chert**

(N=25; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 393.0	x 0.491	x 0.106	x 3.96	x 0.023
sd 166.2	sd 0.349	sd 0.062	sd 2.31	sd 0.011
R 203.7-858.6	R 0.080-1.33	R 0.010-0.240	R 1.20-9.44	R 0.008-0.045
Sc	Zn	Cs	Sm	Hf
x 0.358	x 3.64	x 0.087	x 0.286	x 0.286
sd 0.200	sd 3.75	sd 0.058	sd 0.171	sd 0.238
R 0.100-0.878	R 0.260-14.8	R 0.020-0.230	R 0.078-0.710	R 0.050-0.970
Cr	Br	Ba	Eu	Th
x 4.34	x 0.650	x 191.8	x 0.072	x 0.386
sd 1.57	sd 0.210	sd 146.1	sd 0.038	sd 0.219
R 1.23-6.91	R 0.311-1.11	R 34.4-459.9	R 0.020-0.170	R 0.100-0.930
Fe	Rb	La	Yb	U
x 1243.7	x 4.00	x 1.61	x 0.122	x 1.21
sd 937.3	sd 2.61	sd 0.864	sd 0.071	sd 1.23
R 180.4-3819.6	R 0.550-9.31	R 0.443-3.29	R 0.030-0.330	R 0.060-5.48

## Zaleski Chert

Zaleski formation, Middle Pennsylvanian. Chert occurs in 30 cm thick beds, along with limestone, calcareous shale, and iron ore in southern Ohio, USA. Structure is homogeneous with microfossils, and color is typically pitch black, N2/, to brownish black. Texture is fine to medium, luster is medium to shiny, and translucency is 0.5 mm. Impurities include carbon and pyrite. (See Stout and Schoenlaub 1945; Luedtke 1976; and table B.32.)

**Table B.32 Trace Element Data for Zaleski Chert**

(N=4; data type=NAA; ref=Luedtke 1976)

Na	Co	Sb	Ce	Lu
x 524.4	x 1.01	x 0.062	x 6.70	x 0.030
sd 80.3	sd 0.545	sd 0.015	sd 2.48	sd 0.0
R 451.8-634.5	R 0.530-1.75	R 0.050-0.080	R 4.77-10.3	R 0.030-0.030
Sc	Zn	Cs	Sm	Hf
x 0.772	x 10.7	x 0.242	x 0.503	x 0.275
sd 0.166	sd 3.07	sd 0.068	sd 0.194	sd 0.087
R 0.660-1.02	R 8.29-14.9	R 0.190-0.340	R 0.384-0.792	R 0.200-0.400
Cr	Br	Ba	Eu	Th
x 5.49	x 0.632	x 167.4	x 0.110	x 0.710
sd 2.05	sd 0.181	sd 37.1	sd 0.034	sd 0.234
R 4.15-8.54	R 0.370-0.780	R 138.8-220.5	R 0.090-0.160	R 0.560-1.06
Fe	Rb	La	Yb	U
x 4044.2	x 7.40	x 2.82	x 0.178	x 1.41
sd 2615.6	sd 2.26	sd 1.09	sd 0.017	sd 0.590
R 1748-7807	R 5.41-10.5	R 2.05-4.39	R 0.160-0.200	R 0.580-1.94



# Glossary

- abrasion** mechanical wearing, grinding, scraping, or rubbing away of rock surfaces by friction or impact
- adsorption** adherence of ions or molecules in solution to the surface of solids with which they are in contact
- agate** translucent variety of chert, often primarily composed of chalcedony, characterized by alternating bands or stripes of color, clouds, or moss-like forms; can be any color, though usually pale; commonly forms in cavities of other rocks
- $\alpha$  quartz** variety of silica that forms at temperatures and pressures typical of the earth's surface and is stable up to 573°C; also called low quartz
- amorphous** lacking in crystalline structure
- anisotropic** describes a material in which physical properties vary with direction; opposite of isotropic
- atom** smallest particle of an element that can exist alone
- banded** chert structure characterized by flat or concentric layers of different color, texture, or luster greater than 1 cm thick
- banded agate** gem variety of translucent chert characterized by alternating bands of various colors; layers are sometimes straight but more often wavy, zigzag, or concentric
- $\beta$  quartz** variety of silica that forms at higher temperatures than  $\alpha$  quartz and is stable between approximately 573 and 870°C; also called high quartz
- bloodstone** gem variety of translucent chert of leek-green or dark green color with red or brownish-red spots resembling drops of blood
- botryoidal** literally, having the form of a bunch of grapes; describes the surface of certain rocks and minerals, such as chalcedony, which can look like a series of interlocking spheres or bubbles
- breccia** a sedimentary rock made up of angular coarse fragments held together by a mineral cement or in a fine-grained matrix
- brittle** not flexible or ductile; prone to fracture easily under very slight bending or deformation
- bulk modulus** number that expresses a material's resistance to elastic changes in volume
- carbonate** minerals such as calcite, aragonite, or dolomite which have the carbonate ion  $\text{CO}_3$  as an important part of their chemical composition
- carnelian** gem variety of translucent chert of blood-red, reddish white, orange-red, reddish yellow, or brownish-red color
- chalcedony** variety of chert in which quartz particles take the form of fibers
- chelation** reaction between a metallic ion and an agent, generally organic, which results in the formation of a ring structure and the effective removal of the metallic ion from the system
- chert** sedimentary rock composed primarily of microcrystalline quartz along with lesser amounts of quartz crystals, opal, and impurities
- chert type** chert that occurs in a discrete geological deposit and exhibits a restricted range of variation in at least some properties; usually from a single geological formation
- chroma** aspect of color that expresses the extent to which the dominant color is mixed with other colors; also called purity or saturation
- chrysoprase** gem variety of chert; apple-green or pale yellowish-green
- clastic** pertaining to a rock or sediment composed primarily of broken fragments derived from preexisting rocks or minerals and transported some distance from their place of origin
- cleavage** in minerals, the property of being rather easily split parallel to one or more of the crystal faces characteristic of the mineral; also used to refer to splitting along bedding planes in rocks
- clouded agate** gem variety of translucent light-colored chert with irregular, indistinct, or more or less rounded spots or patches of darker gray resembling clouds
- coesite** variety of silica that forms under high pressures, stable above 20 kilobars; found naturally only in association with meteor impact craters
- colloid** any finely divided substance in suspension; particles are too small to be visible under an ordinary microscope and either do not settle out or settle very slowly
- compressibility** relative change in volume per unit change in pressure; reciprocal of the bulk modulus
- compressive stress** stress that tends to push together the material on opposite sides of a real or imaginary plane, as when an object is squeezed in a vise
- compressive strength** amount of compressive stress a material can withstand before it fractures
- conchoidal** used to describe a smoothly curved or shell-like fracture surface
- cortex** outer layer found on many cherts which formed as a transition zone between the chert and its bedrock matrix and which is visually and mineralogically distinct from either
- cristobalite** variety of silica that generally forms at very high temperatures and is stable between about 1470° and the melting point of silica at normal pressures, 1723° C
- cryptocrystalline** describes the texture of a rock consisting of crystals that are too small to be distinguished with the unaided eye or even with an ordinary microscope
- crystal** homogeneous solid made up of an element or chemical compound throughout which the atoms or molecules are arranged in a regularly repeated pattern, often resulting in outer surfaces composed of smooth surfaces meeting at angles
- crystalline** having a crystal structure or regular arrangement of atoms in a space lattice; also said of a mineral particle having the internal structure of a crystal but lacking well-developed crystal faces
- desert varnish** a dark, shiny film or coating composed mainly of iron oxide and clay, along with traces of manganese oxide and silica, which can form on rocks in some environments
- detritus** collective term for fragmental material, such as sand, silt, or clay, derived from older rocks and moved from its place of origin
- diagenesis** all the physical, chemical, and biological changes that a sediment undergoes after the grains are deposited and while it is becoming a rock, but before it is metamorphosed or weathered
- diaphaneity** the extent to which light is transmitted through a mineral



- diatomite** light colored, crumbly siliceous sediment composed chiefly of diatom shells
- ductile** capable of undergoing considerable deformation without breaking; especially characteristic of materials that elongate, such as metals
- dynamic loading** stress applied at a very fast rate, which must be measured because it can affect the mechanical properties of materials
- Eh** ability of a natural environment to bring about any oxidation or reduction process; also called redox potential or oxidation potential; an extremely oxidizing environment could give a value as high as 1.23 volts, while an extremely reducing environment could give a value as low as -0.6 volts
- elastic** capable of sustaining stress without permanent deformation; ability of a material to return to its original form after a load is removed
- electron** negatively charged particle that forms a part of all atoms
- element** any of the more than 100 fundamental substances that consist of atoms of only one kind and that either singly or in combination constitute all matter
- epigenetic theory** belief that chert formed late in diagenesis, probably as a result of groundwater action after the matrix had become rock and been uplifted
- euohedral** describes a crystal with well-developed crystal faces, whose growth was not restrained or interfered with by adjacent grains
- evaporite** nonclastic sedimentary rock composed primarily of minerals produced from a saline solution as a result of extensive or total evaporation
- fabric** distribution and orientation of the particles, crystals, and cement of which a rock is composed; also called petrofabric, rock fabric, and structural fabric
- flint** homogeneous high-quality chert, especially the dark gray or black cherts that formed in the Cretaceous chalks of Europe
- fluid inclusion** a tiny (1 to 100  $\mu$ ) cavity in a rock or mineral containing liquid and/or gas, formed by the entrapment in crystal irregularities of fluid, commonly that from which the rock crystallized
- flux** a substance added to a body to enable it to fuse more readily; in ceramics, fluxing agents lower the temperature at which silica melts during firing
- fractionation** separation of chemical elements in nature by processes such as preferential concentration of an element in a mineral during crystallization or differential solubility during rock weathering
- fracture** general term for breakage in rocks or minerals caused by mechanical failure; unlike cleavage, fracture is generally not parallel to crystal faces
- fracture toughness** ability of a material to absorb energy without fracturing
- gel** a translucent to transparent, semi-solid, apparently homogeneous substance in a colloidal state, generally elastic and jellylike, containing a dispersion of fine particles that have coalesced to some degree
- gelatinous precipitant** soft, nonhomogeneous mass that settles out of a solution
- geochemistry** branch of geology that studies the amounts and distribution of the chemical elements and isotopes in minerals, ores, rocks, soils, water, and the atmosphere; also, the study of the principles governing these distributions
- grain** a small particle of mineral or rock lacking well-developed crystal faces
- hardness** ability of a material to resist abrasion, scratching, or indentation
- heat treatment** process of intentionally heating chert in order to alter its mechanical and visible properties
- heliotrope** another name for bloodstone
- homogeneous** chert structure characterized by even distribution of color, texture, or luster throughout the sample
- hornstone** regional name for chert; sometimes used to refer to chert characterized by splintery or subconchoidal fracture; also sometimes used to refer to hornfels or silicified shale
- hue** aspect of a color that describes its position on the spectrum and permits it to be classed as red, yellow, green, blue, and so on
- hydrothermal** pertaining to action of heated or superheated water
- igneous** rocks that solidified from molten or partly molten material
- inclusion** either a solid (inorganic or organic, crystalline or amorphous), a liquid, or a gas included in a mineral or rock
- ion** atom or group of atoms combined in a molecule that carries a positive or negative charge as a result of having lost or gained one or more electrons
- isotope** one of two or more varieties of the same chemical element; isotopes have identical numbers of protons and electrons but different numbers of neutrons, and they often have slightly different physical and chemical properties because of the resulting differences in mass
- isotropic** describes materials for which optical, mechanical, and physical properties are the same in all directions; opposite of anisotropic
- jasper** a variety of chert containing iron oxide impurities that generally result in a characteristic gold, brown, or red color
- laminated** chert structure characterized by flat or concentric layers of different color, granularity, or luster less than 1 cm thick
- lens** a geologic deposit bounded by converging surfaces, so that it is thick in the middle and thins out toward the edges
- lepisphere** a tiny spheroidal aggregate of platy, blade-shaped crystals of opal-CT
- lignite** brownish-black variety of coal, in between peat and subbituminous coal
- lussatite** fibrous opal-CT
- luster** reflection of light from the surface of a mineral or rock, described by its quality and intensity
- lutecite** variety of chalcedony characterized by inclined extinction and by fibers that are elongated at an angle of about 30° to the *c* axis; also called lutecline and lutecin
- macrocrystalline** describes the texture of a rock consisting of crystals that are large enough to be visible to the unaided eye
- metamorphic** rocks derived from preexisting rocks by mineralogical, chemical, and/or structural changes which occurred essentially in the solid state and resulted from high temperatures and pressures
- microcrystalline** describes the texture of a rock consisting of crystals that are not visible to the unaided eye but which can be seen under a microscope
- mineral** naturally occurring, homogeneous substance or material formed by inorganic processes and having a characteristic set of physical properties, a definite range of chemical composition, and a molecular structure usually expressed in crystalline form
- mineralogy** branch of geology concerned with the study of minerals, including their formation, occurrence, properties, com-

- position, and classification
- mineraloid** naturally occurring, usually inorganic substance that has a definite range of chemical composition and a characteristic set of physical properties, but which is too amorphous to be crystalline
- modulus** formula or constant that defines a property of materials
- molecule** unit of matter that is the smallest particle of an element or compound that can exist in a free state and still retain the characteristics of the element or compound
- moss agate** gem variety of translucent chert containing inclusions (usually oxides of iron and manganese) that form dendritic patterns resembling trees, moss, or ferns
- mottled** chert structure characterized by abrupt and uneven variations in color and texture across the sample
- nodule** round or irregularly rounded knot, mass, or lump of a mineral or mineral aggregate
- novaculite** regional name for dense, hard, even-textured cherts in Arkansas and Oklahoma which were often used as whetstones
- nucleation** beginning of crystal growth at one or more points
- onyx** gem variety of semitranslucent chert with alternating bands of color, like agate, but with the bands always straight and parallel
- opal** mineraloid composed of hydrated silica, usually containing 3 to 9% but sometimes up to 20% water; occurs in all colors and is translucent, often having an iridescent play of colors
- opal-A** natural hydrous silica characterized by an X-ray diffraction pattern with very diffuse peaks, indicative of a highly disordered or nearly amorphous internal structure
- opal-C** natural hydrous silica that yields an X-ray diffraction pattern indicative of well-ordered alpha-cristobalite with only a small amount of tridymite stacking; often found in association with lava flows
- opal-CT** natural hydrous silica which yields an X-ray diffraction pattern indicative of disordered alpha-cristobalite and alpha-tridymite
- opaque** describes a material that does not allow visible light to pass through
- outcrop** that part of a geological formation or structure that is exposed at the surface of the earth
- oxidation** process of oxidizing, or state or result of being oxidized
- oxidize** to combine with oxygen; to add oxygen chemically to a substance often by means of a series of reactions
- patina** colored film or thin outer layer produced on the surface of a rock by weathering; also called weathering rind
- penecontemporaneous theory** belief that chert formed at the same time that its matrix was solidifying to rock
- petrography** branch of geology dealing with the description and systematic classification of rocks
- petrology** branch of geology dealing with the origin, occurrence, structure, and history of rocks
- pH** negative logarithm of the hydrogen-ion concentration, a value that represents how acid or basic a solution is—for example, a strong acid has a pH of 0, a pH of 7 is neutral, a strong base has a pH of 14
- piezoelectricity** development of an electric potential in certain crystallographic directions when mechanical stress is applied to a material or, alternatively, the development of a mechanical strain, hence vibration, when an electrical potential is applied to the material
- plasma** gem variety of translucent or semitranslucent chert of bright green, leek-green, or nearly emerald-green color, sometimes having white or yellowish spots
- plastic** capable of being deformed continuously and permanently in any direction without fracture
- Poisson's ratio** ratio of the transverse strain to the corresponding lateral strain in a body subjected to stress along a single axis; a measure of a material's elasticity
- polymer** natural or synthetic substance consisting essentially of giant molecules formed from smaller molecules of the same substance, often having a definite arrangement of the components of the giant molecules
- porcellanite** dull, light colored variety of impure chert having the general appearance of unglazed porcelain
- potlid fractures** small, round, convex fragments that pop off chert surfaces as a result of thermal stress
- prase** gem variety of translucent chert of dull leek-green or light-grayish yellow-green color
- precipitate** to cause a soluble substance to separate from a solution as a result of a chemical or physical change
- quartz** crystalline silica, an important rock-forming mineral that can occur either as transparent hexagonal crystals or as macrocrystalline or microcrystalline grains in rocks; the major mineral in chert
- quartzine** less common variety of chalcedony characterized by fibers that are elongated parallel to the *c* axis; also called length slow chalcedony
- rare earth elements** group of elements between atomic number 57 (lanthanum) and 71 (lutetium), plus yttrium, all of which are closely similar in chemical and physical properties
- reduce** to remove oxygen from a compound; to deoxygenate
- reduction** process of removing oxygen from a compound by chemical or electrochemical means, opposite of oxidation
- refraction** deflection of a ray of light due to its passage from one medium to another of differing density, which changes its velocity
- refractive index** number that expresses the ratio of the velocity of light in a vacuum to the velocity of light within a particular mineral
- rigidity** ability to resist applied stress that would tend to deform a material
- rock** aggregate of one or more minerals
- sard** gem variety of translucent chert of brown, reddish-brown, or deep orange-red color; sometimes classed as a variety of carnelian
- saturated** describes a solution having the greatest concentration of a dissolved substance that can remain in solution under given temperature, pressure, and chemical conditions
- sedimentary** rocks that formed at the surface of the earth, either by accumulation and cementation of fragments of rock, minerals, and organisms or by precipitation from seawater and other surface solutions
- shaded** chert structure characterized by gradual transitions in color, texture, and luster across the sample
- shear stress** stress applied from two directions so that parts of a material slide upon each other, moving apart in opposite directions
- silcrete** conglomerate consisting of surface sand and gravel cemented into a hard mass by secondary silica
- silex, silixite** French terms for flint and chert, respectively
- silica** silicon dioxide, SiO<sub>2</sub>, in all its crystalline, amorphous, hydrated, or hydroxylated forms including quartz, opal, cristobalite, tridymite, coesite, stishovite, and several other obscure minerals
- silicate** any of a large group of minerals whose crystal lattices contain SiO<sub>4</sub> tetrahedra, either isolated or joined through one or more of the oxygen atoms

- siliceous** describes a rock containing abundant silica, especially free silica
- silicic acid** any of several weakly acid substances resulting from the solution of silica in water, but especially  $H_4SiO_4$
- solubility** concentration of a substance in a solution saturated with respect to that substance at a given temperature and pressure; for example, the solubility of quartz in water at room temperature and pressure is 6 parts per million
- solution** homogeneous mixture consisting of one substance dissolved in another, usually a liquid
- source** location where a particular chert type can be obtained, either from a primary source such as an outcrop or a secondary source such as a stream bed or glacial deposit
- static loading** describes the situation in which stress is applied very slowly, increasing gradually from zero to the maximum value and then remaining constant
- stiffness** ability of a material to resist elastic deformation; proportional to the modulus of elasticity
- stishovite** extremely dense variety of silica that forms at very high pressures, greater than 100 kb, and is only found naturally in association with meteor impact craters
- strain** deformation resulting from applied force; within range where a material is responding elastically, strain is proportional to stress
- streaked** chert structure characterized by elongated mottles or lenses of different color, texture, or luster
- strength** amount of stress that a solid can withstand without failing by rupture or continuous plastic flow; ability of a material to resist fracture
- stress** force per unit area
- structure** macroscopic appearance of a rock, describing how color or texture or composition vary in neighboring parts; for example, banded structure, mottled structure
- subgrain** small units of quartz in which the crystal lattice is continuous and uniformly oriented; subgrains comprise the plates that make up the quartz grains in chert; also called crystallites or particles
- syngenetic theory** belief that chert formed very early in diagenesis, often precipitating as a gel in loose sediments on the ocean floor
- tensile stress** stretching load; forces that tend to pull an object apart
- tetrahedron** four-sided figure in which each face is a triangle
- texture** macroscopic or microscopic appearance of a rock, especially grain size, shape, and arrangement
- thermal conductivity** amount of heat that can pass through a given thickness of a material in a given amount of time
- thermal expansion** increase in linear dimensions of a solid because of a rise in temperature
- thermal shock** breakage of a material, especially a brittle material, due to the thermal stress of rapidly rising temperature
- thermal stress** stress in a material caused by extreme differences in the temperature of various parts of the object
- thermoluminescence** property of emitting light when heated, as a result of the release of energy stored as electron displacements in the crystal lattice
- thin section** slice of rock or mineral mechanically ground to a thickness of about 0.03 mm and mounted between glasses as a microscope slide; most rocks and minerals are transparent or translucent at this thickness, and so optical properties can be studied
- toughness** intermediate value between softness and brittleness; tough materials have high tensile strength plus moderate elasticity and are resistant to shock
- translucent** describes a material that is capable of transmitting light but is not transparent
- transparent** describes a material capable of transmitting light so well that an object can be seen through it
- triaxial stress** stress applied from three mutually perpendicular directions
- tridymite** variety of silica formed at high temperatures and normal atmospheric pressure, stable between 870 and 1470° C
- turbidite** sediment or rock deposited by a turbidity current (a relatively dense current carrying large quantities of clay, silt, and sand which flows down a submarine slope through less dense seawater); characterized by graded bedding, moderate sorting, and well-developed primary structures
- value** aspect of a color that describes how light or dark it is relative to the extremes of black and white; also called lightness, brightness, or luminous intensity
- vitreous** having a glassy luster
- weathering** destructive process or group of processes by which rocks exposed to atmospheric agents on or near the earth's surface undergo physical disintegration and chemical decomposition, resulting in changes in color, texture, composition, firmness, or form
- weathering rind** an outer crust or layer on a pebble, boulder, or other rock fragment formed by weathering; also called patina
- X ray** electromagnetic radiation of very short wavelengths between approximately 0.1 and 100 Ångstroms
- X-ray diffraction** process of characterizing minerals based on the pattern produced when a beam of X rays is diffracted by the regular three-dimensional arrangement of atoms in the mineral
- X-ray fluorescence** process of using X rays of short wavelengths to induce a substance to emit X rays of a longer wavelength that are characteristic of the elements in the substance
- Young's modulus** ratio of the tensile stress in a material to the corresponding tensile strain; also called modulus of elasticity
- zebraic chalcedony** chalcedony that shows alternating irregular black and white bands across the fibers when viewed under crossed nicols, giving a zebra-like appearance; results from the helical twisting of the quartz crystallites making up the fibers
- zeolite** generic term for a large group of usually white or colorless hydrous aluminosilicates that are analogous to feldspars in their composition and that are related to clays

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