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Susan Trolier-McKinstry , Robert E. Newnham
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1 Introduction to Bonding, Structure, and Structure–Property Relations

The goal of this book is to explore how a knowledge of bonding, crystal structure, and structure–property relations can be used in materials science and engineering to design and utilize materials whose properties match those required in a given application. This field is sometimes referred to as *crystal chemistry*. Crystals are groups of atoms that repeat periodically in space. A knowledge of how the atoms are arranged in space, and the strength of the bonds holding them together, in turn, provides direct insight into properties as diverse as refractive index, cleavage, thermal conductivity, ionic conductivity, and many others.

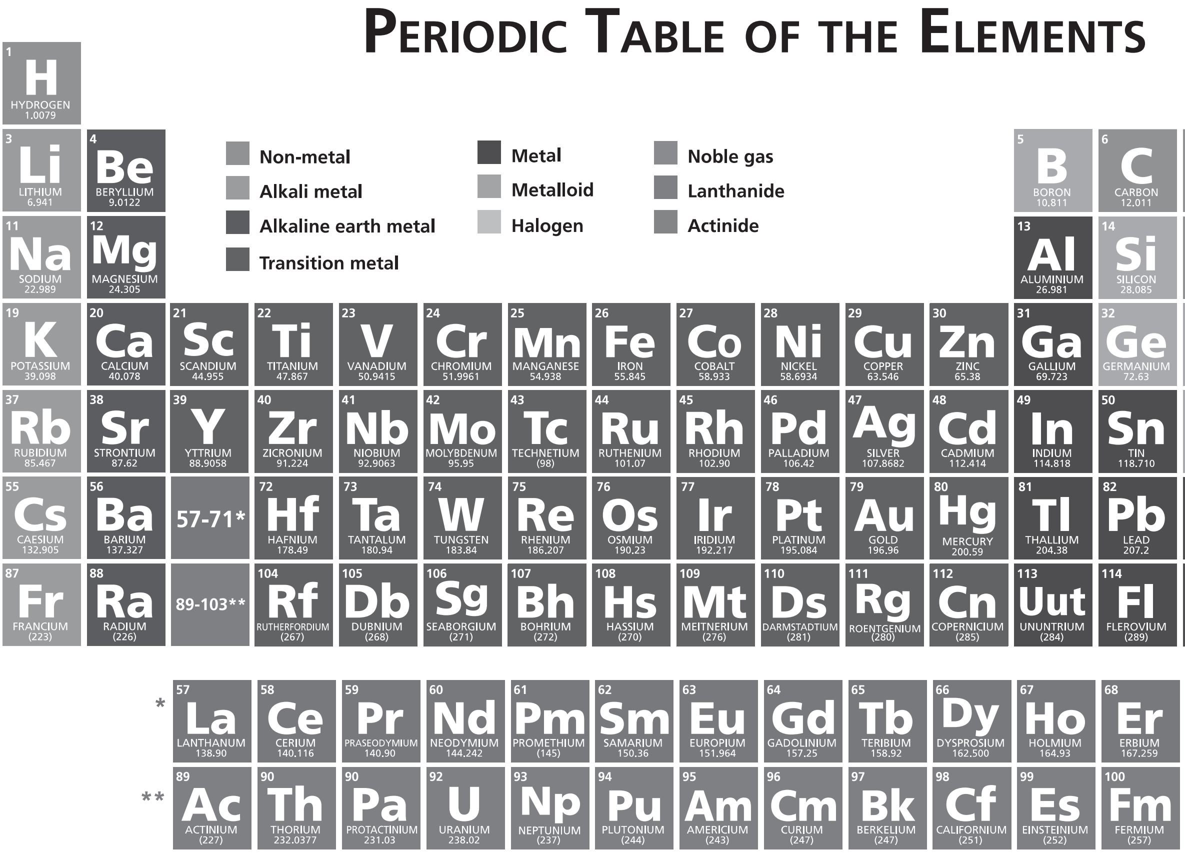
For many problems of interest in materials engineering, it is helpful to ask the following questions:

- What are the atoms involved and how are they arranged?
- How does this arrangement lead to certain mechanisms of electronic or atomic motion?
- How do these mechanisms give rise to the observed properties?
- How are these properties represented in equation form?
- How does symmetry modify the coefficients appearing in these equations?
- What controls the magnitudes of the coefficients? Are there useful trends and “Rules of Thumb”?
- Based on these structure–property relationships, when are exceptionally outstanding properties likely to develop?
- What are the important applications? How can engineers use these ideas?

Relationships between crystal structures and physical properties are described in this book, emphasizing the application of structure–property relations to engineering problems. Faced with the task of finding new materials with useful properties, the reader of this book should be able to use atomic/ionic radii, crystal fields, the arrangement of bonds, understanding of the bond type, and symmetry arguments as criteria for the materials selection process.

This field synthesizes a large amount of information, so that trends can be identified. It provides guidelines on:

- which materials might have interesting and useful properties,
- structure predictions as a function of temperature, pressure, and composition,
- crystalline solubility limits, and
- the nature and kinetics of solid state reactions.



PERIODIC TABLE OF THE ELEMENTS

▨ Non-metal
▨ Alkali metal
▨ Alkaline earth metal
▨ Transition metal
▨ Metal
▨ Metalloid
▨ Halogen
▨ Noble gas
▨ Lanthanide
▨ Actinide

1 H HYDROGEN 1.0079													
3 Li LITHIUM 6.941	4 Be BERYLLIUM 9.0122											5 B BORON 10.811	6 C CARBON 12.011
11 Na SODIUM 22.989	12 Mg MAGNESIUM 24.305											13 Al ALUMINIUM 26.981	14 Si SILICON 28.085
19 K POTASSIUM 39.098	20 Ca CALCIUM 40.078	21 Sc SCANDIUM 44.955	22 Ti TITANIUM 47.867	23 V VANADIUM 50.9415	24 Cr CHROMIUM 51.9961	25 Mn MANGANESE 54.938	26 Fe IRON 55.845	27 Co COBALT 58.933	28 Ni NICKEL 58.6934	29 Cu COPPER 63.546	30 Zn ZINC 65.38	31 Ga GALLIUM 69.723	32 Ge GERMANIUM 72.63
37 Rb RUBIDIUM 85.467	38 Sr STRONTIUM 87.62	39 Y YTTRIUM 88.9058	40 Zr ZICRONIUM 91.224	41 Nb NIOBIUM 92.9063	42 Mo MOLYBDENUM 95.95	43 Tc TECHNETIUM (98)	44 Ru RUTHENIUM 101.07	45 Rh RHODIUM 102.90	46 Pd PALLADIUM 106.42	47 Ag SILVER 107.8682	48 Cd CADMIUM 112.414	49 In INDIUM 114.818	50 Sn TIN 118.710
55 Cs CAESIUM 132.905	56 Ba BARIUM 137.327	57-71*	72 Hf HAFNIUM 178.49	73 Ta TANTALUM 180.94	74 W TUNGSTEN 183.84	75 Re RHENIUM 186.207	76 Os OSMIUM 190.23	77 Ir IRIDIUM 192.217	78 Pt PLATINUM 195.084	79 Au GOLD 196.96	80 Hg MERCURY 200.59	81 Tl THALLIUM 204.38	82 Pb LEAD 207.2
87 Fr FRANCIUM (223)	88 Ra RADIUM (226)	89-103**	104 Rf RUTHERFORDIUM (267)	105 Db DUBNIUM (268)	106 Sg SEABORGIUM (271)	107 Bh BOHRIUM (272)	108 Hs HASSIUM (270)	109 Mt MEITNERIUM (276)	110 Ds DARMSTADTIUM (281)	111 Rg ROENTGENIUM (280)	112 Cn COPERNICIUM (285)	113 Uut UNUNTRIUM (284)	114 Fl FLEROVIUM (289)

*	57 La LANTHANUM 138.90	58 Ce CERIUM 140.116	59 Pr PRASEODYMIUM 140.90	60 Nd NEODYMIUM 144.242	61 Pm PROMETHIUM (145)	62 Sm SAMARIUM 150.36	63 Eu EUROPIUM 151.964	64 Gd GADOLINIUM 157.25	65 Tb TERIBIUM 158.92	66 Dy DYSPROSIUM 162.500	67 Ho HOLMIUM 164.93	68 Er ERBIUM 167.259
**	89 Ac ACTINIUM (227)	90 Th THORIUM 232.0377	90 Pa PROTACTINIUM 231.03	92 U URANIUM 238.02	93 Np NEPTUNIUM (237)	94 Pu PLUTONIUM (244)	95 Am AMERICIUM (243)	96 Cm CURIUM (247)	97 Bk BERKELIUM (247)	98 Cf CALIFORNIUM (251)	99 Es EINSTEINIUM (252)	100 Fm FERMIUM (257)

Fig. 1.1 Periodic table of the elements.

Learning crystal chemistry and crystal physics is an excellent way of developing an understanding of the structure–property relations underpinning materials science and engineering. While *crystal physics* determines which property coefficients are zero, based on symmetry arguments, *crystal chemistry* provides guidance on which property coefficients should be large or small.

Both of these fields, of course, require a strong understanding of crystal structures. Three-dimensional models and computer visualization software are both very helpful tools in understanding these. This book is extensively illustrated to facilitate an understanding of the three-dimensional nature of structures; the interested reader is strongly encouraged to seek out modeling kits, or one of the many programs that allow crystal structures to be plotted and rotated into various orientations.

The other part of crystal chemistry is *chemistry*. This textbook presumes a knowledge of the periodic table. There is a reasonably good chance that any material you make or utilize over the course of your career will be composed of elements on the periodic table. Therefore, it behooves any student in this field to have a firm grasp of the periodic table, including a working knowledge of the abbreviations for various elements, the location of different elements on the table, their electron configurations, and their common oxidation states. The periodic table itself is illustrated in Fig. 1.1 located on page 2.

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2 Raw Materials

Common engineering materials are made from common minerals, which come mostly from common rocks. This is a comforting thought for materials scientists, for we will never run out of them.

2.1 Abundance of Elements

The continental crust is about 30 km thick, and is made up chiefly of silicates. Estimated abundances of the major elements in the continental crust are listed in Table 2.1. Seven of the eight common elements are cations. Oxygen is the *only* common element that is an anion. Hence, most minerals (and most ceramics) are oxides.

2.2 Common Minerals

The most abundant of the thousands of different minerals found in the Earth's crust are listed in Table 2.2. The Earth consists of three main parts: (1) a central iron–nickel *core*, (2) an intermediate oxide *mantle* composed of dense iron and magnesium silicates, and (3) a thin outer *crust* enriched in aluminosilicates, alkali elements, and calcium. The minerals used in making ceramics and metals come from this outer crust.

As expected, the list is dominated by silicates. In nearly all silicates, silicon is bonded to four oxygens, with a Si–O bond length of ~1.6 Å. As discussed later, silicate structures are often classified according to the way in which the SiO_4^{4-} tetrahedra link together. Among the common minerals, the feldspars and quartz are network silicates in which the tetrahedra link together via the oxygens on the corners to form a three-dimensional network. Micas and clays are layer silicates with strong bonding in two dimensions, and pyroxenes and amphiboles are chain silicates with one-dimensional linkages. The silicate tetrahedra in olivine are discrete; that is, they bond to other ions in the structure, rather than forming Si–O–Si linkages. In much the same way, the CO_3^{2-} groups in carbonate minerals are distinct. These structural differences have a strong influence on the chemical and physical properties of minerals.

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Table 2.1 Major chemical elements in the Earth's crust and their abundance

Element	Weight%	Atomic%	Atomic #	Atomic wt. (amu)	Valence
Oxygen (O)	46.6	62.6	8	16.00	–2
Silicon (Si)	27.7	21.2	14	28.09	+4
Aluminum (Al)	8.1	6.5	13	26.98	+3
Iron (Fe)	5.0	1.9	26	55.85	+2, +3
Calcium (Ca)	3.6	1.9	20	40.08	+2
Sodium (Na)	2.8	2.6	11	22.99	+1
Potassium (K)	2.6	1.4	19	39.10	+1
Magnesium (Mg)	2.1	1.8	12	24.31	+2

Table 2.2 Mineral abundance in the continental crust

Mineral	Abundance	
Feldspars		58%
Orthoclase	$KAlSi_3O_8$	
Albite	$NaAlSi_3O_8$	
Anorthite	$CaAl_2Si_2O_8$	
Pyroxenes and amphiboles		13%
Diopside	$CaMgSi_2O_6$	
Enstatite	$MgSiO_3$	
Tremolite	$Ca_2Mg_4Si_8O_{22}(OH)_2$	
Quartz	SiO_2	11%
Micas, clays		10%
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	
Kaolinite	$Al_2Si_2O_5(OH)_4$	
Carbonates		3%
Calcite	$CaCO_3$	
Dolomite	$CaMg(CO_3)_2$	
Olivines		3%
Forsterite	Mg_2SiO_4	
Other Minerals		2%

2.3 Feldspars

The crystal structure of sodium feldspar (albite = $NaAlSi_3O_8$) is illustrated in Fig. 2.1. As pointed out in Table 2.2, feldspars are by far the most abundant mineral family in the Earth's crust. Their chemical compositions are given by $(K_{1-x-y}Na_xCa_y)(Al_{1+y}Si_{3-y})O_8$, where x and y range between 0 and 1. The end members are the minerals orthoclase ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$), and anorthite ($CaAl_2Si_2O_8$). Orthoclase also exists in slightly different high and low temperature forms known as sanidine and microcline.

The feldspar crystal structure consists of AlO_4^{5-} and SiO_4^{4-} tetrahedra linked together to form a three-dimensional framework, as shown in Fig. 2.1. Charge balance is maintained through the presence of alkali or alkaline earth cations in cavities in the tetrahedral framework.

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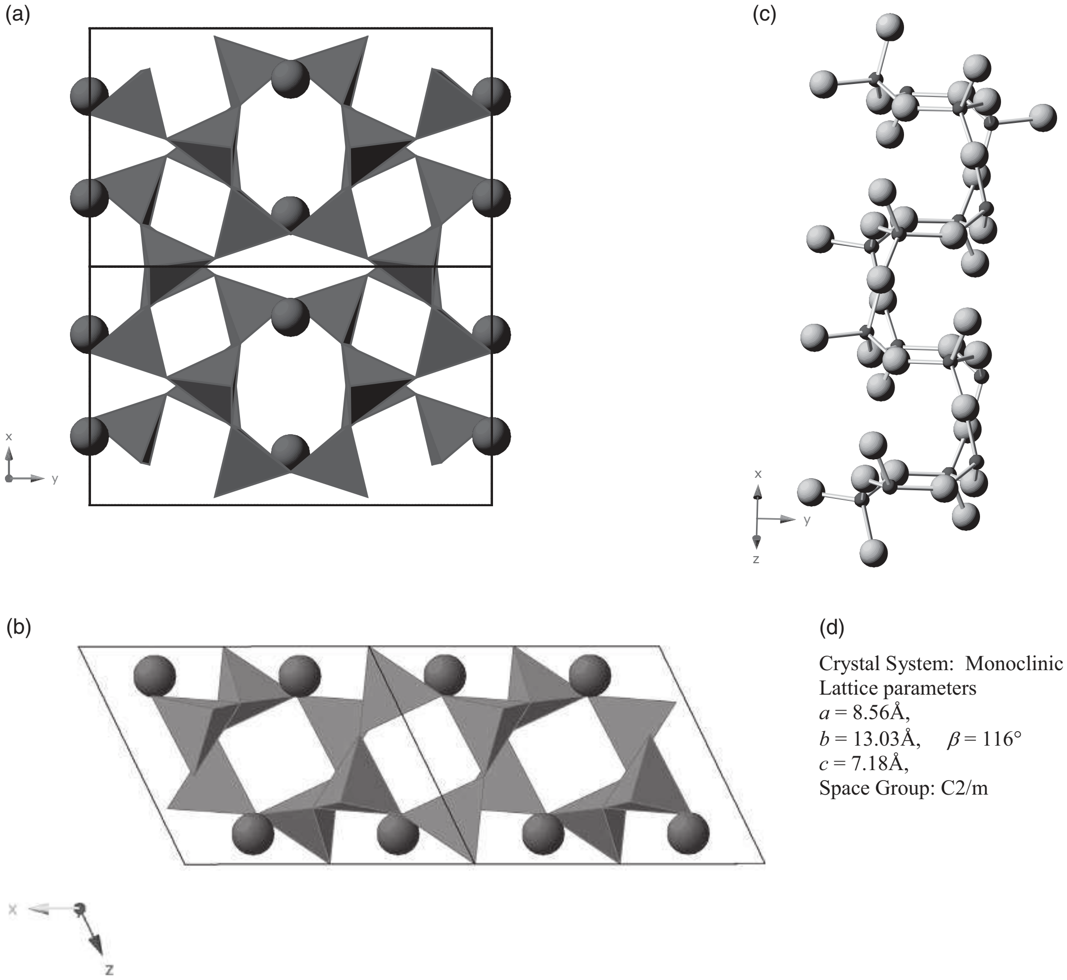

(d)

Crystal System: Monoclinic
Lattice parameters
$a = 8.56\text{Å}$,
$b = 13.03\text{Å}$, $\beta = 116°$
$c = 7.18\text{Å}$,
Space Group: C2/m

Fig. 2.1 Crystal structure of sanidine, $KAlSi_3O_8$. The aluminum and silicon tetrahedra (or atoms) are shown in a dark color, oxygen in large light spheres, and K as large dark spheres. (a) (001) projection, (b) (010) projection, (c) a portion of the aluminosilicate framework of the feldspars. Larger Na, Ca, or K ions fit into cavities within the framework. Si and Al atoms are bonded to four oxygens and each oxygen is bonded to two Si or one Si and one Al. Sanidine is the high temperature form of $KAlSi_3O_8$ in which aluminum and silicon are disordered on the tetrahedral sites, with an average bond length of 1.64 Å. Potassium is coordinated to nine oxygens at distances ranging from 2.70 to 3.13 Å. Sanidine is the prototype structure for the feldspars, an important family of minerals constituting almost 2/3 of the Earth's outer crust. The structures of most other feldspars are of lower symmetry than sanidine. The distortions can be traced to Al–Si ordering or to partial collapse around the large cation, or both.

The physical properties of the feldspars are readily understood in terms of the crystal structure. High hardness (6 on Mohs' scale) and high melting point (>800 °C) are related to the strong Al–O and Si–O bonds, which are cross-linked in all directions. Bonding is the strongest in the direction of the zig-zag chains shown in Fig. 2.1. Mechanical cleavage takes place on planes of lower bond density parallel to the chains.

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Feldspars are generally pale in color because iron, the most common coloring agent in minerals, does not fit into the structure well.

2.4 Common Elements and Their Oxides

When discussing ceramics, materials scientists and engineers use both common names and mineral names.

Silicon dioxide (silica) occurs in nature as the mineral quartz (SiO_2). Second only to oxygen in abundance, silicon occurs in a very large number of minerals. Silicon single crystals form the basis of the vast majority of integrated circuits. Amorphous SiO_2 films are essential in that application for their excellent insulating properties and high dielectric breakdown strength. Silica glass (SiO_2), silicon nitride (Si_3N_4), and silicon carbide (SiC) are important industrial products. Optical fibers based on SiO_2 are at the heart of the high-speed telecommunications industry.

Aluminum is the third most common element in the Earth's crust. The principal ore is bauxite, an impure mixture of diaspore (AlOOH) and gibbsite ($Al(OH)_3$). Aluminum oxide (alumina) occurs in nature as the mineral corundum (α-Al_2O_3). Ruby and sapphire are gem varieties of corundum, where the colors are introduced by transition metal impurities. Alumina ceramics are noted for their strength, hardness, and high melting point. China clay (kaolinite = $Al_2Si_2O_5(OH)_4$) is used in making whitewares. Kyanite (Al_2SiO_5) is an aluminosilicate used in refractories. As a metal, aluminum is widely used in packaging, and in applications where its light weight is an asset, as in aeronautical engineering.

Iron is the heaviest of the common elements. Steel (FeC_x) is a strong intermetallic alloy hardened by interstitial carbon atoms. Hematite (Fe_2O_3) and magnetite (Fe_3O_4) are ore minerals used for steel-making. Magnetic ceramics are made from ferrites such as $MnFe_2O_4$ and $BaFe_{12}O_{19}$.

Calcium oxide (lime = CaO) is usually obtained by heating limestone (calcite = $CaCO_3$) to drive off carbon dioxide. Apatite ($Ca_5(PO_4)_3OH$), dolomite ($CaMg(CO_3)_2$, gypsum ($CaSO_4 \cdot 2H_2O$), and anorthite feldspar are other common calcium minerals. Hydrated lime (portlandite = $Ca(OH)_2$), gypsum, and clay are key components of cement and concrete.

Sodium and sodium oxide (soda = Na_2O) are usually extracted from rocksalt (halite = NaCl). Trona ($Na_3(CO_3)(HCO_3) \cdot 2H_2O$ is another mineral source for the sodium used in glass-making. A more common occurrence in nature is the feldspar mineral albite = $NaAlSi_3O_8$.

Potassium is extracted from chloride minerals such as sylvite (KCl) and carnallite ($KMgCl_3 \cdot 6H_2O$). The oxide potash (K_2O)) is a major constituent of agricultural fertilizers and a minor additive in many glass compositions. Orthoclase ($KAlSi_3O_8$) is potash feldspar and muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$ is common mica.

Magnesium oxide (magnesia = MgO) is also known by its mineral name periclase. Mg enters into many rock-forming minerals including olivine (mostly Mg_2SiO_4) and pyroxenes such as diopside ($CaMgSi_2O_6$). Of greater economic importance are the carbonates magnesite ($MgCO_3$) and dolomite ($CaMg(CO_3)_2$) used in making refractories.

Hydrogen is widely distributed on the Earth's crust, not only as water and ice (H_2O), but also as partially hydrated minerals such as micas, clays, and amphiboles (tremolite =

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$Ca_2Mg_5(Si_4O_{11})_2(OH)_2$). Clean drinking water and abundant hydrogen fuel are major engineering objectives in the years ahead.

2.5 Ore Minerals

Metallic elements are often very specific in regard to the type of minerals they form. A few elements, such as platinum, palladium, and gold, occur primarily as *metallic alloys*, while others like copper and zinc are found primarily as *sulphides*. As expected, based on elemental abundances in the Earth’s crust, *oxides* are the most common ore minerals. Silicon, aluminum, magnesium, and iron are generally recovered from oxygen compounds. A few elements like the inert gases form no minerals at all. Geochemists classify these four groups as lithophile, chalcophile, siderophile, and atmophile (see Table 2.3).

The geochemical character of an element is governed by the type of chemical bonding involved. *Lithophile* elements are readily ionized to form oxides or stable oxyanions such as silicates, carbonates, sulfates, or phosphates. The bonding has a strong ionic character. *Chalcophile* elements ionize less easily and tend to form covalent bonds with elements like S, Se, and Te. Chalcopyrite, an important ore of copper, is a typical chalcophile mineral (see Fig. 2.2), as is cinnabar, an important ore of mercury (Fig. 2.3). *Siderophile* elements are those for which metallic bonding is the normal condition.

2.6 The Oceans

Oceans cover about 70% of the Earth’s surface, some 1.5×10^{21} liters of seawater. Table 2.4 shows the concentration of eight elements, 3.5% of which consist of dissolved substances. Water is an excellent solvent for many ionic compounds because the dipole moment of water effectively shields the charged cations and anions from each other, as shown in Fig. 2.4.

For several centuries, scientists and engineers have been seeking ways of removing salts from seawater to augment the supply of freshwater. The three principal technologies for desalination are distillation, freezing, and reverse osmosis. *Distillation* is the oldest and most widely used method. The process involves vaporizing seawater and then condensing the purified water vapor. To reduce costs, solar radiation is used to evaporate the seawater in large “solar stills.” *Freezing* methods are also under development for desalination. When seawater is frozen, the solid ice is nearly pure H_2O. Much less energy is required to freeze seawater than to evaporate it, since the heat of fusion is only 6.01 kJ/mole, compared with 40.79 kJ/mole for vaporization. Even less energy is involved in the third method of desalination, *reverse osmosis*. No phase change is required for this method, making it potentially much less expensive. Reverse osmosis uses a high pressure of 30 atmospheres or more to purify seawater by forcing it through a semipermeable membrane. The main technical problem is development of inexpensive membranes that can be used for prolonged lifetimes under high-pressure conditions.

The ocean is also host to a large variety of raw materials in the continental shelf and ocean basins. These include mineral sands of titanium, manganese, and iron ores, phosphates, limestone, and diamonds. Bromine, magnesium, and sodium are recovered

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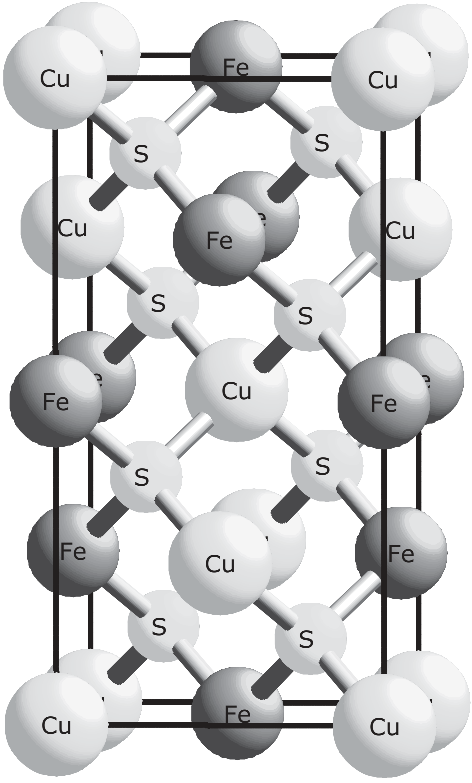
Table 2.3 Typical ore minerals

Lithophile elements	Symbol	Typical ore
Aluminum	Al	Bauxite, $Al_2O_3 \cdot 2H_2O$
Barium	Ba	Barite, $BaSO_4$
Beryllium	Be	Beryl, $Be_3Al_2Si_6O_{18}$
Boron	B	Borax, $Na_2B_4O_7 \cdot 10H_2O$
Calcium	Ca	Calcite, $CaCO_3$
Cerium	Ce	Monazite, $CePO_4$
Chromium	Cr	Chromite, $FeCr_2O_4$
Iron	Fe	Hematite, Fe_2O_3
Lithium	Li	Spodumene $LiAlSi_2O_6$
Magnesium	Mg	Magnesite, $MgCO_3$
Manganese	Mn	Pyrolusite, MnO_2
Niobium	Nb	Columbite, $FeNb_2O_6$
Phosphorus	P	Apatite, $Ca_5(PO_4)_3OH$
Potassium	K	Sylvite, KCl
Silicon	Si	Quartz, SiO_2
Sodium	Na	Halite, NaCl
Strontium	Sr	Celestite, $SrSO_4$
Sulphur	S	Gypsum, $CaSO_4 \cdot 2H_2O$
Tantalum	Ta	Tantalite, $FeTa_2O_6$
Tin	Sn	Cassiterite, SnO_2
Titanium	Ti	Ilmenite, $FeTiO_3$
Tungsten	W	Scheelite, $CaWO_4$
Uranium	U	Uraninite, UO_2
Zirconium	Zr	Zircon, $ZrSiO_4$
Chalcophile elements	**Symbol**	**Typical ore**
Antimony	Sb	Stibnite, Sb_2S_3
Arsenic	As	Arsenopyrite, FeAsS
Cadmium	Cd	Greenockite, CdS
Cobalt	Co	Cobaltite, CoAsS
Copper	Cu	Chalcopyrite, $CuFeS_2$
Lead	Pb	Galena, PbS
Mercury	Hg	Cinnabar, HgS
Molybdenum	Mo	Molybdenite, MoS_2
Nickel	Ni	Pentlandite (Ni,Fe)S
Silver	Ag	Argentite, Ag_2S
Zinc	Zn	Zincblende, ZnS
Siderophile elements	**Symbol**	
Gold	Au	
Platinum	Pt	
Palladium	Pd	
Atmophile elements	**Symbol**	
Helium	He	
Neon	Ne	
Argon	Ar	
Krypton	Kr	
Xenon	Xe	
Nitrogen	N_2	



Crystal System: Tetragonal
Lattice parameters
a = 5.24Å
c = 10.30Å
Space Group: $I\bar{4}2d$

Fig. 2.2 The unit cell of chalcopyrite, $CuFeS_2$. Iron and copper are bonded to four sulfurs in tetrahedral configuration. Each S is bonded to two Cu and two Fe.

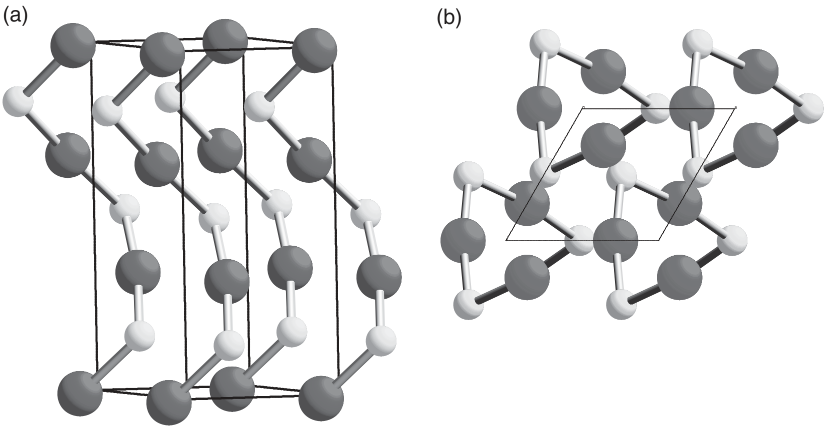


Fig. 2.3 Crystal structure of cinnabar, HgS. (a) Several chains of Hg and S atoms spiraling parallel to c. (b) Four spirals looking down the c axis. Crystal system: the crystal system is trigonal, with lattice parameters a = 4.149 Å, c = 9.495 Å, and space group: $P3_121$.