CHAPTER 1: INTRODUCTION

GEOCHEMISTRY

The term "geochemistry" was first used by the Swiss chemist Schönbein in 1838. You might guess, merely from the etymology of the word, that the field of *geochemistry* is somehow a marriage of the fields of *geology* and *chemistry*. That would be a good guess. But just how are chemistry and geology combined within geochemistry; what is the relationship between them? Perhaps the best explanation would be to state that *in geochemistry, we use the tools of chemistry to solve geological problems; that is, we use chemistry to understand the Earth and how it works*. The Earth is part of a family of heavenly bodies, our Solar System, that formed simultaneously and are closely related. Hence, the realm of geochemistry extends beyond the Earth to encompass the entire Solar System. The goals of geochemistry are thus no different from those of other fields of earth science; just the approach differs. On the other hand, while geochemists have much in common with other chemists, their goals differ in fundamental ways. For example, our goals do not include elucidating the nature of chemical bonding or synthesizing new compounds, although these may often be of interest and use in geochemistry. Though geochemistry is a subdiscipline of earth science, it is a very broad topic. So broad in fact that no one can really master it all; geochemists invariably specialize in one or a few aspects, such as atmospheric chemistry, geochemical thermodynamics, isotope geochemistry, marine chemistry, trace element geochemistry, soil chemistry, etc.

Geochemistry has flourished in the quantitative approach that has dominated earth science in the second half of the twentieth century. This quantitative approach has produced greater advances in the understanding of our planet in the last 50 years than in all of prior human history. The contributions of geochemistry to this advance have been simply enormous. Much of what we know about how the Earth and the Solar System formed has come from research on the chemistry of meteorites. Through geochemistry, we can quantify the geologic time scale. Through geochemistry, we can determine the depths and temperatures of magma chambers. Through geochemistry, mantle plumes were recognized. Through geochemistry, we know that sediments can be subducted into the mantle. Through geochemistry, we know the temperatures and pressures at which the various metamorphic rock types form and we can us this information, for example, to determine the throw on ancient faults. Through geochemistry, we know how much and how fast mountain belts have risen. Through geochemistry, we are learning how fast they are eroding. Through geochemistry, we are learning how and when the Earth's crust formed. Through geochemistry, we are learning when the Earth's atmosphere formed and how it has evolved. Through geochemistry, we are learning how the mantle convects. Through geochemistry, we are learning how cold the ice ages were and what caused them. The evidence of the earliest life, 3.8 gigayears (billion, or 10^9 years, which we will henceforth abbreviate as Ga), is not fossilized remains, but chemical traces of life. Similarly, the tenuous evidence that life existed on Mars about the same time is also largely chemical. Not surprisingly, instruments for chemical analysis have been key part of probes sent to other heavenly bodies, including Venus, Mars, Jupiter. Geochemistry lies at the heart of environmental science and environmental concerns. Problems such as acid rain, the ozone hole, the greenhouse effect and global warming, water and soil polution are geochemical problems. Addressing these problems requires a knowledge of geochemistry. Similarly, most of our non-renewable resources, such as metal ores and petroleum, form through geochemical processes. Locating new sources of these resources increasing requires geochemical approaches. In summary, every aspect of earth science has been advanced through geochemistry.

Though we will rarely discuss it in this book, geochemistry, like much of science, is very much driven by technology. Technology has given modern geochemists tools that allow them to study the Earth in ways that pioneers of the field could not have dreamed possible. The electron microprobe allows us to analyze mineral grains on the scale of microns in minutes; the electron microscope allows

us to view the same minerals on almost the atomic scale. Techniques such as X-ray diffraction, nuclear magnetic resonance, and Raman and infrared spectroscopy allow us to examine atomic ordering and bonding in natural materials. Mass spectrometers allow us to determine the age of rocks and the temperature of ancient seas. Ion probes allow us to do these things on micron scale samples. Analytical techniques such as X-ray fluorescence and inductively coupled plasma spectrometry allow us to perform in minutes analyses that would days using "classical" techniques. All this is done with greater precision and accuracy than was possible just a few decades ago. Mega-computers with megahertz of power and megabytes of memory allow us to perform in seconds thermodynamic calculations that would have taken years or lifetimes half a century ago; the giga-computers just around the corner will offer us even more power. New instruments and analytical techniques now being developed promise even greater sensitivity, speed, accuracy, and precision. Together, these advances will bring us ever closer to our goal understanding the Earth and its cosmic environment.

This Book

The intent of this book is to introduce you to geochemistry and to further your understanding of the Earth through it. To do this, we must first acquire the tools of the trade. Every trade has a set of tools. Carpenters have their saws and T-squares; plumbers have their torches and wrenches. Psychologists have their blot tests, physicians their stethoscopes, accountants their balance sheets, geologists have their hammers, compasses, and maps. Geochemists too have a set of tools. These include not only a variety physical tools such as analytical instruments, but interpretative tools that allow them to make sense of the data these instruments produce. The first part of this book, entitled *The Geochemical Toolbox*, is intended to familiarize you with the tools of geochemistry. These include the tools of thermodynamics, kinetics, aquatic chemistry, trace element geochemistry, and isotope geochemistry. Once we have a firm grip on these tools, we can use them to dissect the Earth in the second part of the book, entitled *Understanding the Earth*. We begin at the beginning, with the formation of the Earth and the Solar System. We then work our way upward through the Earth, from the mantle and core, through the crust and hydrosphere, and finally into the atmosphere.

In filling our geochemical toolbox, we start with the tools of physical chemistry: thermodynamics and kinetics. Thermodynamics is perhaps the most fundamental tool of geochemistry; most other tools are build around this one. For this reason, Chapters 2, 3, and 4 are devoted to thermodynamics. Thermodynamics allows us to predict the outcome of chemical reactions under a given set of conditions. In geochemistry we can, for example, predict the sequence of minerals that will crystallize from a magma under given conditions of temperature and pressure. The mineral assemblage of the resulting igneous rock, however, will not be stable at some other temperature and pressure. Thermodynamics allows us to predict the new suite of minerals that replace the original igneous ones. Thus thermodynamics provides enormous predictive power for the petrologist. Since geologists and geochemists are more often concerned with understanding the past than with predicting the future, this might seem to be a pointless academic exercise. However, we can also use thermodynamics in the reverse sense: given a suite of minerals in a rock, we can use thermodynamics to determine the temperature and pressure conditions under which the rock formed. We can also use it to determine the composition of water or magma from which minerals crystallized. This sort of information has been invaluable in reaching our understanding of how the Earth has come to its present condition. We can use this information to determine the amount of uplift experienced by a mountain range, the temperature at which an ore deposit formed, or the composition of ancient seas.

Thermodynamics has an important limitation: it is useful only in equilibrium situations. The rate at which chemical systems achieve equilibrium increases exponentially with temperature. Thermodynamics will be most useful at temperatures relevant to the interior of the Earth, say 500° C and above, because equilibrium will be closely approached in most cases. At low temperatures, that is, temperatures relevant to the surface of the Earth, many geochemical systems will not be in equilibrium and are governed by partly or largely by kinetics, the subject of Chapter 5. Kinetics deals with the rates and mechanisms of reactions. In this chapter, we will also touch upon such topics as diffusion and mineral surfaces. We will see that kinetics is intimately related to thermodynamics.

CHAPTER 1: INTRODUCTION

In Chapter 6, we see how tools of physical chemistry are adapted for use in dealing with natural solutions, the subject of aquatic chemistry. Much of the Earth's surface is covered by water, and water usually is present in pores and fractures to considerable depths even on the continents. This water is not pure, but is instead a solution formed by interaction with minerals. In Chapter 6, we acquire tools that allow us to deal with the interactions among dissolved species, including both among themselves and with the solids with which they come in contact. These interactions include phenomena such as dissolution and precipitation, complexation, adsorption and ion exchange. Clays are often the products of water-rock interaction and they have some very interesting chemical properties, so we will have a particularly close look at this group of minerals. The tools of aquatic chemistry are essential to understanding processes such as weathering and precipitation of sedimentary minerals, as well as dealing with environmental problems.

In Chapter 7, we move on to trace element geochemistry. In this chapter we will see that trace elements have provided remarkable insights into the origin and behavior of magmas. Without question, their value to geochemists far outweighs their abundance. There are several reasons for this. Their concentrations vary much more than do those of the more abundant elements, and their behavior tends often to be simpler and easier to treat than that of major elements (a property we will come to know as Henry's Law). Geochemists have developed special tools for dealing with trace elements; the objective of Chapter 7 is to become familiar with them.

Chapters 8 and 9 are devoted to isotope geochemistry. In Chapter 8, we learn that radioactive decay adds the important element of time; radioactivity is nature's clock. By learning to read this clock, we now know the age of the Earth and the continents, and we have gained some perspective on the rate and manner of evolution of the Earth. We can also use the products of radioactive decay, "radiogenic elements", as tracers. By following these tracers much as we would dye in fish tank, we can follow the evolution of a magma, the convection pattern of the mantle, and the circulation of the oceans. The isotopes of another set of elements vary not because of radioactive decay, but because of subtle differences in their chemical behavior. These "stable isotopes" are the subject of Chapter 9. The subtle differences in isotopic abundances of elements such as H, C, N, O, and S have, among other things, revealed the causes of the ice ages, provided insights into the composition of the ancient atmosphere, and reveal the diets of ancient peoples. Stable isotope geochemistry is the last of our geochemical tools.

With our toolbox full, we examine the Earth from the geochemical perspective in the second part of the book. We begin in Chapter 10 by looking at "the big picture": the cosmos and the Solar System. We learn how the chemical elements were formed, and how they, in turn, formed our Solar System and the Earth. We will find the tools of thermodynamic and isotope geochemistry particularly valuable in this Chapter. We will focus particularly closely on meteorites, because the chemistry of these objects provides the best record of the early history of the Solar System. Meteorites also provide essential information about the composition of the Earth as a whole, which will in turn be valuable to us in the following chapter.

In Chapter 11, we begin our inside-out geochemical tour of the Earth. First, we consider the composition of the Earth as a whole, then see how the Earth has differentiated into two major reservoirs: the mantle and core. We pay particular attention to the mantle. Though remote, the mantle is hardly irrelevant. It is important for several reasons. First, it constitutes 1/2 of the mass of the Earth. Second, the reservoirs we are most familiar with, the crust, the hydrosphere, and the atmosphere, have all formed from the mantle. Third, most geologic processes are ultimately a result of processes occurring within the mantle, processes such as convection and melting. In Chapter 12, we return to more familiar territory: the Earth's crust. We will find that geochemistry has provided much of our knowledge of how the crust has formed and how it has differentiated. We will find the tools of isotope and trace element geochemistry particularly useful in our examination of the solid Earth.

The next three chapters focus on processes at the surface of the Earth. Here water is the dominant substance, and the tools of thermodynamics, kinetics, and aquatic chemistry will be of great use. In Chapter 13, we will take a close look at the interaction between water and the Earth's surface, and processes such as weathering and soil formation. We will see how these processes control the chemis-

CHAPTER 1: INTRODUCTION

try of streams, rivers, and lakes. Life is also an important force in shaping the face of our planet. The chemistry of living organisms is part of biochemistry and not geochemistry, so we will treat intracellular processes only very briefly. However, organisms produce a vast array of chemicals that find their way into the physical environment. In Chapter 14, we will examine the role these organic chemicals play in aquatic chemistry. We will also see how these chemicals are transformed into substances of great geological and societal interest: oil, gas, and coal. Most of the water at the surface of the Earth is in the oceans, so we devote Chapter 15 to marine chemistry. We will find that oceans are a fascinating example of an "open" geochemical system, with material constantly flowing both into and out. We will see that in the face of this constant change, geological and biological processes together produce a solution with very uniform concentrations of the major species, but highly variable concentrations of the minor ones.

Before we begin our study of geochemistry, we will devote the remainder of the chapter to reviewing some "fundamentals". First, we briefly examine the philosophy and approach that is common to all science. Then we review the most fundamental aspects of chemistry: how matter is organized into atoms and how these atoms interact to form compounds. Finally, we review a few fundamental aspects of the Earth.

The Philosophy of Science

This book will concentrate on communicating to you the body of knowledge we call geochemistry. Geochemistry is just part of a much larger field of human endeavor we call science. Science is certainly among humanity's greatest successes; without it, our current civilization would not be possible. Among other things, it would simply not be possible to feed, cloth, and shelter as many people as live today. This phenomenal success is due in large part to the philosophy of science.

Science consists of two parts: the knowledge it encompasses and the approach or philosophy that achieves that knowledge. The goal of all science is to understand the world around us. The arts and humanities also seek understanding. Science differs from those fields as much by its approach and philosophy as by its body of knowledge.

A common approach and philosophy unite the great diversity of fields that we collectively call science. When one compares the methods and tools of a high energy physicist with those of a behavioral biologist, for example, it might at first seem that they have little in common. Among other things, their vocabularies are sufficiently different that each would have difficulty communicating his research to the other. In spite of this, they share at least two things. The first is a criterion of "understanding". Both the physicist and the behavioral biologist attempt to explain their observations by the application of a set of rules, which, by comparison to the range of phenomena considered, are both few and simple. Both would agree that a phenomenon is understood if and only if the outcome of an experiment related to that phenomenon can be predicted beforehand by applying those rules to measured variables*. The physicist and biologist also share a common method of seeking understanding, often called the "scientific method".

Building Scientific Understanding

Science deals in only two quantities: *observations* and *theories*. The most basic of these is the *observation*. Measurements, data, analyses, experiments, etc. are all observations in the present sense. An observation might be as simple a measurement of the dip and strike of a rock formation or as complex as the electromagnetic spectrum of a star. Of course, it is possible to measure both the dip of rock strata and a stellar spectrum incorrectly. Before an observation becomes part of the body of scientific knowledge, we would like some reassurance that it is right. How can we tell whether observations are right or not? The most important way to verify an observation is to *replicate* it *independently*. In

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* Both would admit that chance, or randomness, can affect the outcome of any experiment (though the affect might be slight). By definition, the effect of this randomness cannot be predicted. Where the effects of randomness are large, one performs a large collection, or ensemble, of experiments and then considers the average result.

CHAPTER 1: INTRODUCTION

the strictest sense, 'independent' means by a separate observer, team of observers, or laboratory, and preferably by a different technique or instrument. It is not practicable to replicate every observation in this manner, but critical observations, those which appear to be inconsistent with existing theories or which test the predictions of newly established ones should be, and generally are, replicated. But even replication does not guarantee that an observation is correct.

Observations form the basis of *theories*. Theories are also called models, hypotheses, etc. *Scientific understanding is achieved by constructing and modifying theories to explain observations.* Theories are merely the products of the imagination of scientists, so we also need a method of sorting out 'correct' theories from 'incorrect' ones. Good theories not only explain existing observations, but make predictions about the outcome of still unperformed experiments or observations. *Theories are tested by performance of these experiments and comparison of the results with the predictions of the theory.* If the predictions are correct, the theory is accepted and the phenomenon considered to be understood, at least until a new and different test is performed. If the predictions are incorrect, the theory is discarded or modified. When trying to explain a newly discovered phenomenon, scientists often reject many new theories before finding a satisfactory one. But long-standing theories that successfully explain a range of phenomena can usually be modified without rejecting them entirely when they prove inconsistent with new observations.

Occasionally, new observations are so inconsistent with a well-established theory that it must be discarded entirely and a new one developed to replace it. Scientific 'revolutions' occur when major theories are discarded in this manner. Rapid progress in understanding generally accompanies these revolutions. Such was the case in physics in the early 20th century when the quantum and relativity theories replaced Newtonian theories. The development of Plate Tectonics in the 1960's and 1970's is an excellent example of a scientific revolution in which old theories were replaced by a single new one. A range of observations including the direction of motion along transform faults, the magnetic anomaly pattern on the sea floor, and the distribution of earthquakes and volcanoes were either not predicted by, or were inconsistent with, classical theories of the Earth. Plate tectonics explained all these and made a number of predictions, such as the age of the seafloor, that could be tested. Thus scientific understanding progresses through an endless cycle of observation, theory construction and modification, and prediction. In this cycle, theories can achieve "acceptance", but can never be proven correct, because we can never be sure that it will not fail some new, future test.

Quite often, it is possible to explain observations in more than one way. That being the case, we need a rule that tells us which theory to accept. When this occurs, the principle is that the theory that explains the greatest range of phenomena in the *simplest* manner is always preferred. For example, the motion of the Sun across the sky is quite simple and may be explained equally well by imaging that the Sun orbits the Earth as visa versa. However, the motions of the planets in the sky are quite complex and require a very complex theory if we assume they orbit the Earth. If we theorize that the Earth and the other planets all orbit the Sun, the motions of the planets become simple elliptical orbits and can be explained by Newton's three laws of motion. The geocentric theory was long ago replaced by the heliocentric theory for precisely this reason. This principle of simplicity, or elegance, also applies to mathematics. Computer programmers call it the KISS (Keep It Simple, Stupid!) Principle. In science, we can sum it up by saying: *don't make nature any more complex than it already is*.

THE SCIENTIST AS SKEPTIC

Though we often refer to "scientific facts", there are no facts in science. A fact, by definition, cannot be wrong. Both observations and theories can be, and sometimes are, wrong. Of course, some observations (e.g., the Sun rises each morning in the East) and theories (the Earth revolves around the Sun) are so oft repeated and so well established that they are not seriously questioned. But remember that the theory that the Sun revolves around the Earth was itself once so well established that it was not seriously questioned.

One of the ways science differs from other fields of endeavor is that *in science nothing is sacred*. It is best to bear in mind the possibility, however remote, that any observation or theory can be wrong.

W. M. White   Geochemistry

CHAPTER 1: INTRODUCTION

Conversely, we must also accept the possibility that even the wildest observations and theories might be correct: in quantum physics, for example, there is a great range of well-replicated observations that can only be labeled as bizarre (see, for example, Gribbin, 1984). 'Intuition' plays a greater role in science that most scientists might be willing to admit, even though scientific intuition is often very useful. Nevertheless, our intuition is based largely on our everyday experience, which is very limited compared to the range of phenomena that science attempts to understand. As a result, our intuition often deceives us. Sometimes we must put it aside entirely. That a clock will run slower if it moves faster, or that an electron can behave both as a wave and a particle, or that continents move great distances are all very counter-intuitive observations, but all are (apparently) correct. Thus *skepticism is one of the keys to good science.* In science, *never totally believe anything, but never totally disbelieve anything either.*

ELEMENTS, ATOMS, AND CHEMICAL BONDS: SOME CHEMICAL FUNDAMENTALS

THE PERIODIC TABLE

We'll begin our very brief review of chemical fundamentals with the Periodic Table. In Dmitri Mendeleyev's[‡] day, chemistry and geochemistry were not as distinct as they are today. Chemists were still very much occupied with discovering new elements, and they generally sought them in natural materials. For a variety of reasons, therefore, the Mendeleyev's periodic table provides a good point of departure for us.

Mendeleyev's periodic table of the elements was the sort of discovery that produces revolutions in

Figure 1.1. The Periodic Table showing element symbols and atomic numbers. Many older periodic tables number the groups as IA-VIIIA and IB-VIIB. This version shows the current IUPAC Convention.

[‡] Dmitri Ivanovich Mendeleyev was born in Tobolsk, Russia in 1834. He became professor of chemistry at St Petersburg in 1866. His periodic table was the sort of discovery that noble prizes are awarded for, but it came before the prize was established. He was honored, however, by having element number 101, medelevium, named for him. Mendeleyev died in 1906.

CHAPTER 1: INTRODUCTION

science. Chemistry had evolved tremendously through the first half of the nineteenth century. Between the publication of Lavoisier's *The Elements of Chemistry*, often considered the first modern text in chemistry, in 1789 and Mendeleyev's 1869 paper, the number of known elements had increased from 23 to 67. The concepts of the atom and the molecule were well established, and role of electromagnetic forces in chemical interactions was at least partly understood. Nevertheless, the structure of atoms, and how this structure governed chemical properties of the atom were to be twentieth century discoveries (though there were some interesting prescient theories). Mendeleyev's great contribution was to show that properties of the elements are a periodic function of atomic weights. Like all good scientific theories, this one made predictions: Mendeleyev was not only able to predict the discovery of then unknown elements, such as B, Sc, Ga, and Ge, but also their characteristics and probable mode of discovery. The periodic table led the way not only to the discovery of the remaining elements, but also to understanding the fundamental controls on chemical behavior.

Figure 1.1 shows the periodic table as we know it today. Like most theories, Mendeleyev's has gone through some revision since it was first proposed. Most importantly, we now organize the periodic table based on *Atomic Number* rather than atomic weight. The atomic number of an element is its most important property, and is determined by the number of protons in the nucleus (thus the terms *atomic number and proton number* are synonymous). The number of protons in turn determines both the number of electrons and how these electrons are organized.

The mass of an atom is a function of both the proton number and the *neutron number*, i.e., the number of neutrons in the nucleus*. Generally, several possible numbers of neutrons can combine with a given number of protons to form a stable nucleus (we will discuss nuclear stability in greater detail in Chapter 8). This gives rise to different isotopes of the same element, i.e., atoms that have the same atomic number but different masses. For example, helium has 2 stable isotopes: ^3He and ^4He. Both ^3He and ^4He[†] have 2 protons (and a matching number of electrons), but ^4He has 2 neutrons while ^3He has only 1.

The *atomic weight* of an element depends on both the masses of its various isotopes and on the relative abundances of these isotopes. This bedeviled nineteenth century chemists. William Prout (1785-1850), an English chemist and physiologist, had noted in 1815 that the densities of a number of gases were integer multiples of the density of hydrogen (e.g., 14 for nitrogen, 16 for oxygen). This law appeared to extend to many elemental solids (e.g., 12 for C, 28 for Si) as well, and it seemed reasonable that this might be a universal law. But there were puzzling exceptions. Cl, for example, has an atomic weight of 35.45 times that of hydrogen. The mystery wasn't resolved until Thompson demonstrated the existence of 2 isotopes of Ne in 1918. The explanation is that while elements such as H, N, O, C, and Si consist almost entirely of a single isotope, and thus have atomic weights very close to the mass number of that isotope, natural Cl consists of about 75% ^{35}Cl and 25% ^{37}Cl[‡].

ELECTRONS AND ORBITS

We stated above that the atomic number of an element is its most important property. This is true because the number of electrons is determined by atomic number, as it is the electronic structure of an atom that largely dictates it chemical properties. The organization of the elements in the periodic table reflects this electronic structure.

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* The neutron mass and proton mass are almost identical.

† By convention, the mass number, which is the sum of protons and neutrons in the nucleus, of an isotope is written as a preceeding superscript. However, for historical reasons, one says "helium–4". Note also that the atomic number or proton number can be readily deduced from the chemical symbol (atomic number of He is 2). The neutron number can be found by subtracting the proton number from the mass number. Thus the symbol '4He' gives a complete description of the nucleus of this atom.

‡ The actual mass of a atom depends on the number of electrons and the nuclear binding energy as well as the number of protons and neutrons. However, the mass of the electron is over 1000 times less than the mass of the proton and neutron, which are about equal, and the effect of nuclear binding energy on mass was too small for 19th century chemists to detect.

CHAPTER 1: INTRODUCTION

The electronic structure of atoms, and indeed the entire organization of the periodic table, is determined by quantum mechanics and the quantization of energy, angular momentum, magnetic moment, and spin of electrons. Four quantum numbers, called the principal, azimuthal, magnetic, and spin quantum numbers and conventionally labeled n, l, m, and m_s, control the properties of electrons associated with atoms. The first of these, n, which may take values 1, 2, 3, ..., determines most of the electron's energy as well as mean distance from the nucleus. The second, l, which has values 0, 1, 2, ... n-1, determines the total angular momentum and the shape of the orbit. The third, m, which may have values -l, ...0...l, determines the z component of angular momentum and therefore the orientation of the orbit. The fourth, m_s, may have values of $-\frac{1}{2}$ or $+\frac{1}{2}$ and determines the electron's spin. The first three quantum numbers result in the electrons surrounding the nucleus being organized into *shells*, *subshells*, and *orbitals**. The *Pauli Exclusion Principle* requires that no two electrons in an atom may have identical values of all four quantum numbers. Because each orbital corresponds to a unique set of the first 3 quantum numbers, only 2 electrons may occupy a given orbital, and then only if they have different spins. In Chapter 8 we will see that the properties of the nucleus are also dictated by quantum mechanics, and that the nucleus may also be thought of as having a shell structure.

Each shell corresponds to a different value of the principal quantum number. The periodic nature of chemical properties reflects the filling of successive shells as additional electrons (and protons) are added. Each shell corresponds to a 'period', or row, in the periodic table. The first shell (the K shell) has one subshell, the *1s*, consisting of a single orbital (with quantum numbers n=1, l=0, m=0. The *1s* orbital accepts up to 2 electrons. Thus period 1 has 2 elements: H and He. If another electron and proton are added, the electron is added to the first orbital, *2s*, of the next shell (the L shell). Such a configuration has the chemical properties of Li, the first element of period 2. The second shell has 2 subshells, *2s* (corresponding to l=0) and *2p* (corresponding to l=1). The *p* subshell has 3 orbitals (which correspond to values for m of -1, +1, and 0), p_x, p_y, and p_z, so the L shell can accept up to 8 electrons. Thus period 2 has 8 elements.

There are some complexities in the filling of orbitals beyond the L shell. In the M shell, which corresponds to period 3, there is the possibility of putting electrons in the *d* subshell (l=2), but this is energetically less favorable than electrons going in the subsequent shell. Thus the *3d* subshell is vacant in period 3 element in their ground states, and in the first 2 elements of period 4. Only when the *4s* orbital is filled do electrons begin to fill the *3d* orbitals. The 5
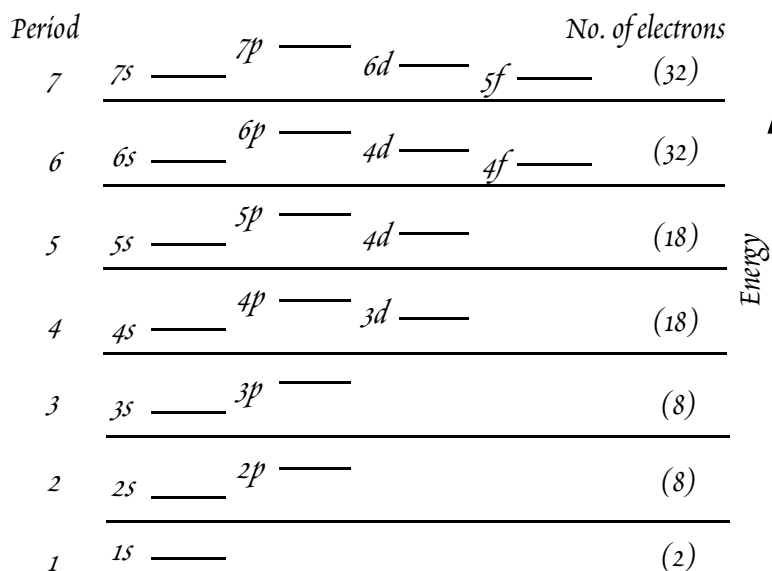

Figure 1.2. The predicted sequence of orbital energies for electrons in atoms. *S* levels can hold 2 electrons, *p*, *d*, and *f* can hold 6, 10, and 14 respectively.

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*It is often convenient to think of the electrons orbiting the nucleus much as the planets orbit the Sun. This analogy has its limitations. The electron's position can not be precisely specified as can a planet's. In quantum mechanics, the Schrödinger Wave function, ψ (or more precisely, ψ^2) determines the probability of the electron being located in a given region about the atom. As an example of failure of the classical physical description of the atom, consider an electron in the *1s* orbital. Both quantum number specifying angular momentum, l and m, are equal to 0, and hence the electron has 0 angular momentum, and hence can not be in an orbit in the classical sense.

W. M. White — Geochemistry

CHAPTER 1: INTRODUCTION

H $1s^1$																	He $1s^2$
Li $2s^1$	Be $2s^2$											B $2s^22p^1$	C $2s^22p^2$	N $2s^22p^3$	O $2s^22p^4$	F $2s^22p^4$	Ne $2s^22p^6$
Na $3s^1$	Mg $3s^2$											Al $3s^23p^1$	Si $3s^23p^2$	P $3s^23p^3$	S $3s^23p^4$	Cl $3s^23p^4$	Ar $3s^23p^6$
K $4s^1$	Ca $4s^2$	Sc $4s^23d^1$	Ti $4s^23d^2$	V $4s^23d^3$	Cr $4s^23d^5$	Mn $4s^23d^5$	Fe $4s^23d^6$	Co $4s^23d^7$	Ni $4s^23d^8$	Cu $4s^23d^9$	Zn $4s^23d^{10}$	Ga $4s^24p^1$	Ge $4s^24p^2$	As $4s^24p^3$	Se $4s^24p^4$	Br $4s^24p^4$	K $4s^24p^6$
Rb $5s^1$	Sr $5s^2$	Y $5s^24d^1$	Zr $5s^24d^2$	Nb $5s^24d^3$	Mo $5s^24d^4$	Tc $5s^24d^5$	Ru $5s^24d^6$	Rh $5s^24d^7$	Pd $5s^24d^8$	Ag $5s^24d^9$	Cd $5s^24d^{10}$	In $5s^25p^1$	Sn $5s^25p^2$	Sb $5s^25p^3$	Te $5s^25p^4$	I $5s^25p^4$	Xe $5s^25p^6$
Cs $6s^1$	Ba $6s^2$	La $6s^25d^1$	Hf $6s^25d^2$	Ta $6s^25d^3$	W $6s^25d^4$	Re $6s^25d^5$	Os $6s^25d^6$	Ir $6s^25d^7$	Pt $6s^25d^9$	Au $6s^25d^1$	Hg $6s^25d^{10}$	Tl $6s^26p^1$	Pb $6s^26p^2$	Bi $6s^26p^3$	Po $6s^26p^4$	At $6s^26p^4$	Rd $6s^26p^6$
Fr $7s^1$	Ra $7s^2$	Ac $7s^26d^1$															

La $6s^25d^1$	Ce $6s^23d^14f^1$	Pr $6s^24f^3$	Nd $6s^24f^4$	Pm $6s^24f^5$	Sm $6s^24f^6$	Eu $6s^24f^7$	Gd $6s^25d^14f^7$	Tb $6s^24f^9$	Dy $6s^24f^{10}$	Ho $6s^24f^{11}$	Er $6s^24f^{12}$	Tm $6s^24f^{13}$	Yb $6s^24f^{14}$	Lu $6s^25d^14f^{14}$
Ac $7s^26d^1$	Th $7s^26d^2$	Pa $7s^26d^15f^2$	U $7s^26d^15f^3$	Np $7s^26d^15f^4$	Pu $7s^25f^6$									

Figure 1.3. The Periodic Table showing the electronic configuration of the elements. Only the last orbitals filled are shown, thus each element has electrons in the orbitals of all previous group 18 elements (noble gases) in addition to those shown. Superscripts indicate the number of electrons in each subshell.

3d orbitals are filled as one passes up the first transition series metals, Sc through Zn. This results in some interesting chemical properties, which we will consider in Chapter 7. Similarly, the second and third transition series metals correspond to filling of the *4d* and *5d* orbitals. The *Lanthanide* and *Actinide* rare earth elements correspond to the filling of the 4f and 5f shells are filled (again result-ing in some interesting properties, which we will consider subsequently). The predicted sequence in which orbitals are filled and their energy levels are shown in Figure 1.2. Figure 1.3 shows the elec-tronic configuration of the elements.

FINDING THE ELECTRON: ATOMIC STRUCTURE AND THE SCHRÖDINGER EQUATION

The modern atomic theory of matter was first proposed by Dalton at the beginning of the 19th cen-tury, but it was not until the beginning of the 20th century that the structure atoms began to be re-vealed. In 1910 Ernest Rutherford proposed, based on α-particle scattering experiments, that atoms consisted of dense, small, positively charged nuclei surrounded by orbiting elections. Three years later, Niels Bohr introduced some aspects of the new quantum theory into the description of electron orbits. He was able to predict successfully the energy of the electron in the orbit of the hydrogen atom and thus to explain the electromagnetic emission spectrum of hydrogen. But the Bohr theory failed to describe the spectra of more complex atoms. A more satisfactory description of the electronic structure of atoms was not made until Erwin Schrödinger and Werner Heisenberg, building on a theory of Louis de Broglie, developed a fully quantum mechanical theory in 1926.

Quantum mechanics treats the electron as a wave. Any wave, be it a displacement wave on a taut string or an electromagnetic wave, traveling in direction *x* must satisfy the wave equation:

$$\frac{\partial^2 F}{\partial x^2} = \frac{1}{\omega^2}\frac{\partial^2 F}{\partial t^2} \qquad 1.1$$

where F is the wave function (for example, the displacement of the string from equilibrium or the electric or magnetic field), and ω is the wavespeed. For an electron bound to an atom, it can be shown that this becomes (in 1 dimensional space):

CHAPTER 1: INTRODUCTION

$$\frac{h^2}{8\pi^2 m}\frac{d^2\Psi}{dx^2} + (E - V)\Psi = 0 \qquad\qquad 1.2$$

where h is Planck's constant, m is the mass of the electron, E is its kinetic energy, Ψ is the electron's wave function, and V is the potential energy: $V = Ze^2/r$ (e is the charge of the electron, r is the distance of the electron from the nucleus, and Z is the atomic, or proton, number and is 1 for hydrogen). Equation 1.2 is known as the *Schrödinger Equation*. What is the significance of the wave function Ψ? This question puzzled even Schrödinger, who suggested it was related to charge density. The correct answer was provided by Max Born shortly after publication of Schrödinger's paper, who proposed that it was related to the probability of finding the electron. Specifically, Born suggested that the probability of finding the electron, P, in a given interval *dx* at time *t* was given by:

$$P = \Psi(x, t)^2 \, dx \qquad\qquad 1.3$$

Ψ is sometimes called the *probability amplitude*.

The full (non-relativistic, time-independent) Schrödinger equation for 3-dimensional space is:

$$\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right) + (E - V)\Psi = 0 \qquad\qquad 1.4$$

where $\hbar = h/2\pi$; *h* is Planck's constant. In general, however, it is more convenient to write it in spherical coordinates:

$$\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial\psi}{\partial r}\right] + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\psi}{\partial\theta}\right] + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right)\frac{\hbar^2}{2m} + (E - V)\psi = 0 \qquad 1.5$$

where $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, and $z = r\cos\theta$. A sketch of the spherical coordinate system is shown in Figure 1.4.

The problem now becomes one of 'guessing' functions for E and $\Psi(r, \theta, \phi)$ that satisfy equation 1.3. This task can be simplified if we use our physical and mathematical knowledge to constrain our guesses. As a first step, we can recall that the Bohr model successfully explains the electromagnetic emission spectrum of the hydrogen atom, so we might adopt a value for E for hydrogen matching that of the Bohr model. We can also expect that energy levels will be quantized, so an integer quantum energy number, *n*, should enter somewhere. Indeed, work in the 19th century had already suggested that *n* should occur in the energy expression as an inverse square term. Thus we might guess at that the energy term will be:

$$E = \frac{me^4}{2\hbar^2 n^2} = \frac{e^2}{n^2 \, 2r_0} \qquad\qquad 1.6$$

where r_0 is the Bohr radius ($r_0 = 0.529$ Å, where Å is ångstroms, 10^{-8} cm).

What about Ψ? As a first guess, we might try a spherically symmetric solution, i.e., one in which the $\partial\Psi/\partial\theta$ and $\partial\Psi/\partial\phi$ terms are 0. This will clearly simplify equation 1.3. An electron bound to a hydrogen atom is unlikely to be found at great distance from the nucleus, so Ψ should go to 0 for large r. Thus we might try a solution of the form $\Psi(r) = ae^{-br}$, where a and b are constants. Setting $n = 1$ in equation 1.6, we find a solution when $a = (1/\pi)^{1/2}(1/r_0)^{3/2}$ and $b = 1/r_0$. Thus:

$$\psi(r) = \frac{1}{\pi^{1/2}}\left(\frac{1}{r_0}\right)^{3/2}e^{-r/r_0} \qquad\qquad 1.7$$

As it turns out, there is a whole family of spherically symmetric solutions that may be obtained by setting $n = 1, 2, 3, ...$; for example, for $n = 2$,

$$\psi(r) = \frac{1}{4(2\pi)^{1/2}} \left(\frac{1}{r_0}\right)^{3/2} \left(2 - \frac{r}{r_0}\right) e^{-r/r_0} \qquad 1.8$$
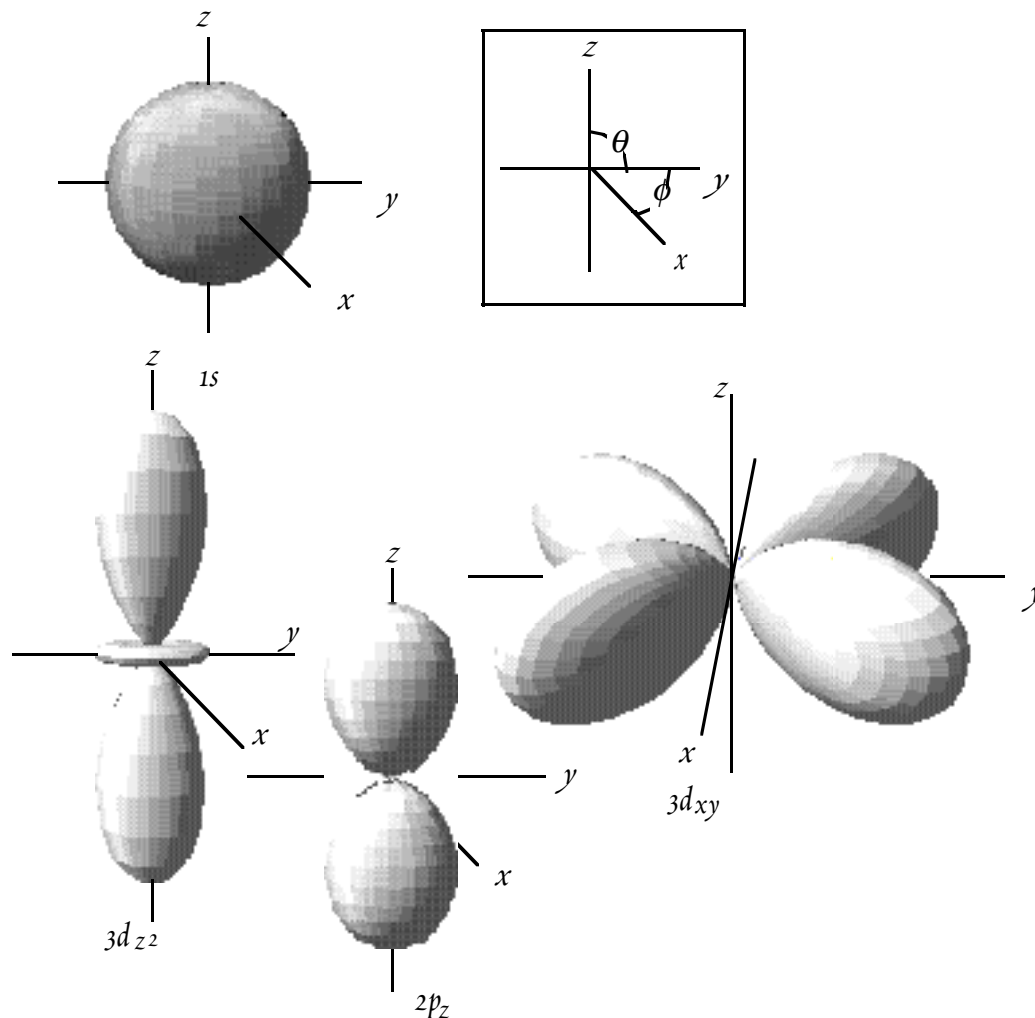

Figure 1.4. Spherical coordinates and 3 dimensional plots of probability density for the *1s, 2pz, 3d_{xy}*, and *3d_{z2}* orbitals of hydrogen.

Solutions of this form are designated Ψ_{1s}, Ψ_{2s}, etc., where the *s* indicates a spherically symmetric solution[‡] and the 1, 2, etc., are the principal quantum numbers.

What will such an orbital 'look like'? The orbital is independent of θ and ϕ and will therefore have spherical symmetry, as in Figure 1.4. Figure 1.5a shows Ψ plotted versus radial distance from the nucleus. The probability of finding the electron in spherical shell of radius r and thickness, *dr*, is given by $4\pi r^2 \Psi^2$ dr. Figure 1.5b shows the probability function $P = 4\pi r^2 \Psi^2$ plotted against radial distance. In Figure 1.5a, we see that the probability amplitude is highest close to the nucleus, but the volume of a spherical shell is small, so the probability is low. Far away from the nucleus, the volume of a shell is large, but Ψ is small, so P is also small. Reassuringly, the maximum of P occurs a t

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[‡] Actually, the letters s, p, d, f are originally of spectroscopic origin and stood for *sharp, principal, diffuse,* and *fundamental*.

Chapter 1: Introduction

$r = r_0$, the Bohr radius. Thus the Schrödinger Equation predicts that an electron in the 1s orbital will most likely be found at the Bohr radius.
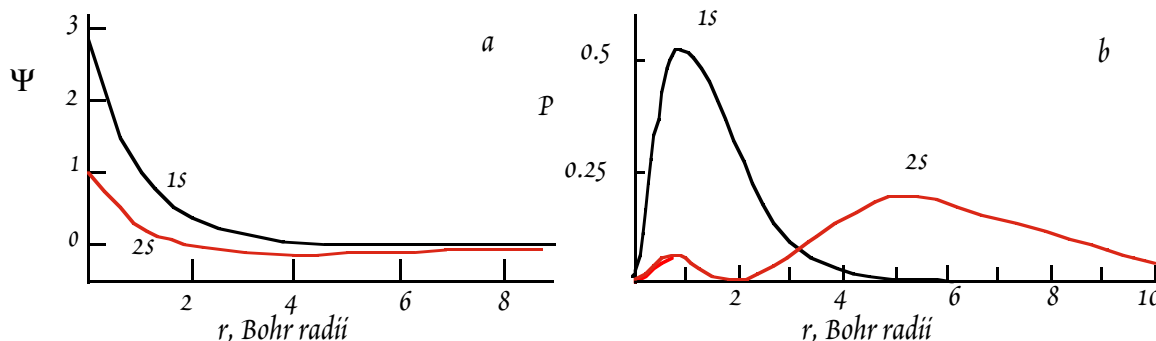

Figure 1.5. Plot of (a) Ψ (r) and (b) $P = 4\pi r^2 \Psi^2$ versus radial distance from the nucleus for the *1s* and *2s* orbitals. Scale for Ψ is arbitrary. Scale for P is normalized such that the probability of finding the electron somewhere is 1.

Table 1.1. Quantum numbers and Example solutions to the Schrödinger Equation

orbital	n	ℓ	m	Ψ
1s	1	0	0	$\dfrac{1}{\pi^{1/2}}\left(\dfrac{1}{r_0}\right)^{3/2} e^{-r/r_0}$
2s	2	0	0	$\dfrac{1}{4(2\pi)^{1/2}}\left(\dfrac{1}{r_0}\right)^{3/2}\left(2-\dfrac{r}{r_0}\right)e^{-r/r_0}$
2p$_z$	2	1	0	$\dfrac{1}{4(2\pi)^{1/2}}\left(\dfrac{1}{r_0}\right)^{3/2}\left(2-\dfrac{r}{r_0}\right)e^{-r/r_0}\cos\theta$
2p$_x$	2	1	-1	$\dfrac{1}{4(2\pi)^{1/2}}\left(\dfrac{1}{r_0}\right)^{3/2}\left(2-\dfrac{r}{r_0}\right)e^{-r/r_0}\sin\theta\,\sin\phi$
2p$_y$	2	1	+1	$\dfrac{1}{4(2\pi)^{1/2}}\left(\dfrac{1}{r_0}\right)^{3/2}\left(2-\dfrac{r}{r_0}\right)e^{-r/r_0}\sin\theta\,\cos\phi$
3d$_{z^2}$	3	2	0	$\dfrac{1}{81(2\pi)^{1/2}}\left(\dfrac{1}{r_0}\right)^{3/2}\left(\dfrac{r}{r_0}\right)^2 e^{-r/3r_0}(3\cos^2\theta-1)$
3d$_{xy}$	3	2	-1	$\dfrac{1}{81(2\pi)^{1/2}}\left(\dfrac{1}{r_0}\right)^{3/2}\left(\dfrac{r}{r_0}\right)^2 e^{-r/3r_0}\sin\theta\,\cos\theta\,\sin\phi$

Now let's look for non-spherically symmetric solutions. First consider the energy term. The *s* orbitals, being spherically symmetric, have no angular momentum. In the general case, there will be some contribution from the angular momentum to the energy. We need to modify our energy term to take account of this. Perhaps it should come as no surprise that angular momentum is also quantized. Possible angular momentum values are given by:

$$L = \ell(\ell+1)\hbar^2 \qquad\qquad 1.9$$

where l is an integer between 0 and *n*-1. Thus nonsymmetric solutions are only possible for $n > 1$. The angular momentum contribution to energy is:

$$E_L = \frac{\ell(\ell+1)\hbar^2}{2mr^2} \qquad\qquad 1.10$$

As a first guess as to the form of Ψ, one might try a form of the exponential expression for the symmetric case. For example:

$$\psi = x \cdot ae^{-br} \qquad\qquad 1.11$$

It turns out that this and the equivalent y and z forms are solutions. A third quantum number, m, determines the orientation of the angular momentum. m may take values –l ... +l. Table 1.1 summarizes solutions to the Schrödinger Equation in terms of the 3 quantum numbers, n, l, and m. Figure 1.4 gives a few examples of the appearance of these orbitals.

Though the Schrödinger equation and electronic structure ultimately govern virtually all chemical interactions, much of geochemistry concerns itself with phenomena on a scale where these details need not be considered. However, as geochemists construct increasingly exact and detailed models, the Schrödinger Equation comes increasingly into play. We will see an example in chapter 6 how the geometry of the *3d* orbitals plays an important role in governing the geochemical behavior of the first transition series metals.

SOME CHEMICAL PROPERTIES OF THE ELEMENTS

It is only the most loosely bound electrons, those in the outermost shells, that participate in chemical bonding, so elements sharing a similar outermost electronic configuration tend to behave simi-
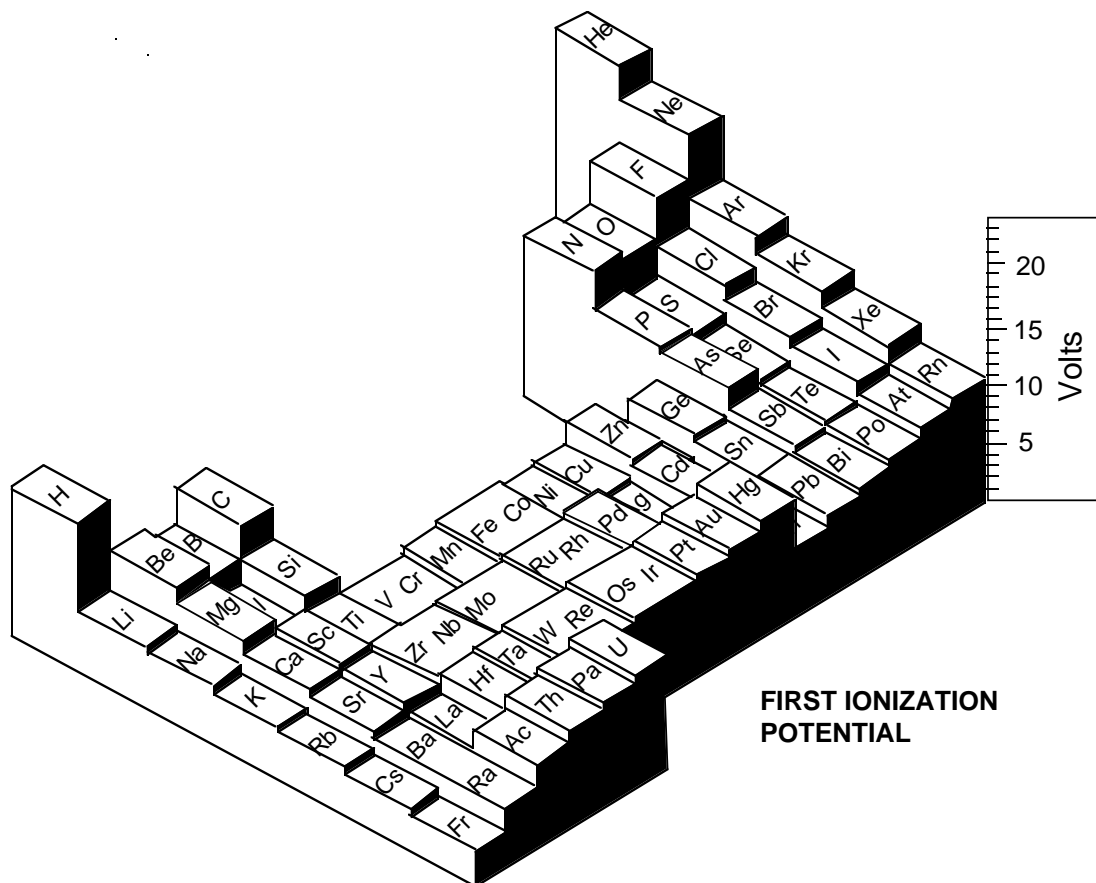

Figure 1.6. First ionization potential of the elements.

CHAPTER 1: INTRODUCTION

larly. Elements within the same column, or *group*, share outer electronic configurations and hence behave in a similar manner. Thus the elements of group 1, the *alkalis*, all have 1 electron in the outermost *s* orbital, and behave in a similar manner. The group 18 elements, the *noble, or rare, gases*, all have a filled *p* subshell, and behave similarly.

Let's now consider several concepts that are useful in describing the behavior of atoms and elements: *ionization potential*, *electron affinity*, and *electronegativity*. The *First Ionization Potential* of an atom is the energy required to remove (i.e., move an infinite distance away) the least tightly bound electron. This is energy absorbed by the electron in reactions such as:

$$Na \rightarrow Na^+ + e^- \qquad\qquad 1.12$$

The *Second Ionization Potential* is the energy required to remove a second electron, etc. The first ionization potential of the elements is illustrated in Figure 1.6.

The *electron affinity* is the energy given up in reactions such as:

$$F + e^- \rightarrow F^- \qquad\qquad 1.13$$

Electronegativity is another parameter that is often used to characterize the behavior of the elements. It is a relative, unitless quantity determined from the differences in bond energy between an A-B molecule and the mean energies of A-A and B-B molecules. *Electronegativity quantifies the tendency of an element to attract a shared electron when bonded to another element.* For example, F has a higher electronegativity than H (the values are 3.8 and 2.5 respectively), thus the bonding electron in hydrogen fluoride, HF, is more likely to be found in the vicinity of F than of H. It is also useful in characterizing the nature of chemical bonds between elements, as we shall see in a subsequent section. Electronegativities of the elements are shown in Figure 1.7.

In general, first ionization potential, electron affinity, and electronegativities, increase from left to right across the periodic table, and to a less degree from bottom to top. This reflects the shielding of outer electrons, particularly those in *s* orbitals, by inner electrons, particularly those in *p* orbitals, from the charge of the nucleus. Thus the outer *3s* electron of neutral sodium is effectively shielded from the nucleus and is quite easily removed. On the other hand, the *2p* orbitals of oxygen are not very effectively shielded, and it readily accepts 2 additional electrons. With the addition of these 2 electrons, the *2p* orbital is filled and the *3s* orbital effectively shielded, so there is no tendency to add a third electron. With the outer *p* (and *s*) orbitals filled, a particularly stable configuration is

Figure 1.7. Electronegativities of the elements.

CHAPTER 1: INTRODUCTION

reached. Thus Ne has little tendency to either add or give up an electron.

The number of electrons that an element will either give up or accept is known as its *valence*. For elements in the 'wings' of the periodic table (i.e., all except the transition metals), valence is easily determined simply by counting how far the element is horizontally displaced from Group 18 in the periodic table. For Group 18, this is 0, so these elements, the noble gases, have 0 valence. For group 1 it is 1, so these elements have valence of +1; for group 17 it is -1, so these elements have valence of -1, etc. Valence of the transition metals is not so simply determined, and these elements can have more than 1 valence state. Most, however, have valence of 2 or 3, though some, such as U, can have valences as high as 6.

A final characteristic that is important in controlling chemical properties is *ionic radius.* This is deduced from bond length when the atom is bonded to one or more other atoms. Positively charged atoms, or *cations*, have smaller ionic radii than do negatively charged atoms, or *anions*. Also, ionic radius decreases as charge increases. This decrease is due both to loss of electrons and to shrinking of the orbits of the remaining electrons. The latter occurs because the charge of the nucleus is shared by fewer electrons and hence has a greater attractive force on each. In addition, ionic radius increases downward in each group in the periodic table, both because of addition of electrons to outer shells and because these outer electrons are increasingly shielded from the nuclear charge by the inner ones. Ionic radius is important in determining important geochemical properties such substitution in solids, solubility, and diffusion rates. Large ions need to be surrounded, or *coordinated*, by a greater number of oppositely charged ions than do smaller ones. The ionic radii of the elements are illustrated in Figure 1.8.

We can now summarize a few of the more important chemical properties of the various groups in the periodic table. Group 18, does not participate in chemical bonding in nature, hence the term 'noble gases'. Group 1 elements, the alkalis, readily accept an electron (they are *electropositive*) and hence are highly reactive. They tend to form *ionic bonds* rather than *covalent* ones and hence tend not to form bonds that are as strong as other elements. They tend to be quite soluble in aqueous solutions. Because they have only a +1 charge, their ionic radii tend to be larger than other cations. Group 2 elements, the *alkaline earths*, have these same characteristics, but somewhat moderated. Group 17 elements, the *halogens*, are highly electronegative and readily accept an electron, are highly reactive, form ionic bonds, and are quite soluble. Their ionic radii tend to be larger than more highly charged anions. Elements of Groups 13-16 tend to form bonds that are predominantly covalent. As a result, they tend to be less reactive and less soluble (except where they form soluble radicals, such as SO_4^{2-}) than Group 1, 2, and 17 elements. Finally, the transition metals are a varied lot. Many form strong bonds (generally with O in nature) and are fairly insoluble, particularly the highly charged ones.
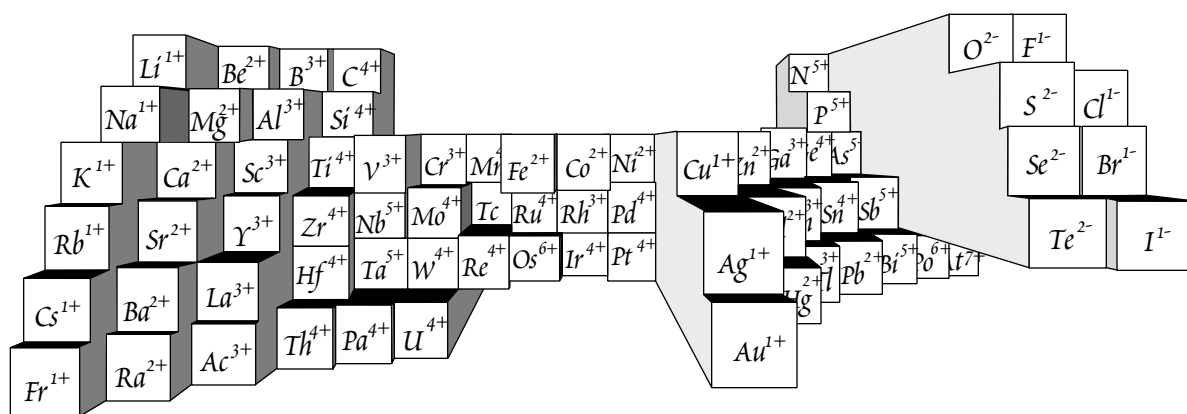
Ionic Radii

Figure 1.8. Ionic radii of the elements.

CHAPTER 1: INTRODUCTION

Some, the 'noble metals' (Ru, Rh, Pd, Os, Ir, Pt) in particular, tend to be very unreactive and insoluble. The rare earths are of interest because all have 2 electrons in the *6s* outer orbital, and vary only by the number of electrons in the 4*f* shell. Their bonding behavior is thus quite similar. They vary systematically in ionic radius, which makes them of great geochemical interest.

CHEMICAL BONDING

Covalent, Ionic, and Metal Bonds

Except for the noble gases, atoms rarely exist independently: they are generally bound to other atoms in molecules, crystals, or ionic radicals. Atoms bind to one another through transfer or sharing of electrons, or through electrostatic forces arising from uneven distribution of charge in atoms and molecules. A bond that results from the total transfer of electrons from one atom to another is known as an *Ionic Bond*. A good example is the bond between Na and Cl in a halite crystal. In this case, the Na atom (the electropositive element) gives up an electron, becoming positively charged, to the Cl atom (the electronegative element), which becomes negatively charged. Electrostatic forces between the Na^+ and the Cl^- ions hold the ions in place in the crystal. When electrons are shared between atoms, such as in the H_2O molecule or the SiO_4^{4-} radical, the bond in known as covalent. In a *Covalent Bond*, the outer electrons of the atoms involved are in hybrid orbits that encompass both atoms.

The ideal covalent and ionic bonds represent the extremes of a spectrum: most bonds are neither wholly covalent nor wholly ionic. In these intermediate cases, the bonding electrons will spend most, but not all, of their time associated with one atom or another. Electronegativity is useful in describing the degree of ionicity of a bond. Though there is no clear distinction between a covalent and ionic bond, a bond is considered ionic when the difference in the electronegativity of the two atoms involved is greater than 2. In Figure 1.7, we see that metals (generally those elements on the left hand side of the periodic table) tend to have low electronegativities while the non-metals (those elements on the right) have high electronegativities. Thus bonds between metals and non-metals (e.g., NaCl) will be ionic while those between non-metals (e.g., CO_2) will be covalent, as will bonds between two like atoms (e.g., O_2).

Another type of bond occurs in pure metal and metal alloy solids. In the metallic bond, valence electrons are not associated with any single atom or pair of atoms; rather they are mobile and may be found at any site in the crystal lattice. Since metals rarely occur naturally (iron meteorites and the Earth's core are notable exceptions), this type of bond is less important in geochemistry than other bonds.

Ionically bonded compounds tend to be good conductors of heat and electricity and have high melting temperatures. They also tend to be hard, brittle and highly soluble in water. Covalently bonded compounds tend to be good conductors of heat, but not of electricity. They are typically harder and less brittle than ionic solids but less soluble. In molecular solids, such as ice, atoms within the molecule are covalently bonded. The molecules themselves, which occupy the lattice points of the crystal, are bonded to each other through van der Waals and/or hydrogen bonds. Such solids are comparatively weak and soft and generally have low melting points.

Molecules in which electrons are unequally shared have an asymmetric distribution of charge and are termed *polar*. A good example is the hydrogen chloride molecule. The difference in electronegativity between hydrogen and chlorine is 0.9, so we can predict that bonding electron will be shared, but associated more with the Cl atom than with the H atoms in HCl. Thus the H atom will have a partial positive charge, and the Cl atom a partial negative charge. Such a molecule is said to be a *dipole*. The *dipole moment*, which is the product of one of the charges (the two charges are equal and opposite) times the distance between the charges, is a measure of the asymmetric distribution of charge. Dipole moment is usually expressed in debye units (1 debye = 3.3356×10^{-34} coloumb-meters).

Van der Waals Interactions and Hydrogen Bonds

Covalent and ionic bonds account for the majority of bonds between atoms in molecules and crystals. There are two other interactions that play a lesser role in interactions between atoms and molecules,

CHAPTER 1: INTRODUCTION
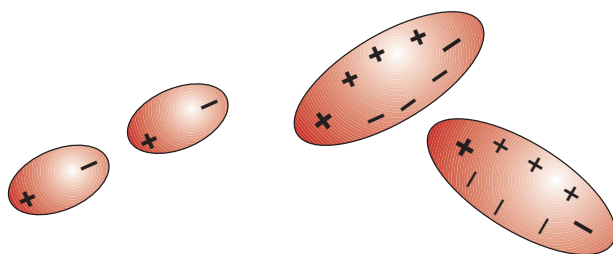
b. Dipole Interaction

b. The Induction Effect

Figure 1.9. Van der Waals interactions arise because of the polar nature of some molecules. Illustrated here are (a) dipole-dipole interactions, which occur when two dipolar molecules orient themselves so oppositely charged sides are closest, and (b) the induction effect, which arise when the electron orbits of one molecule are perturbed by the electromagnetic field of another molecule.

van der Waals interactions and hydrogen bonds. These are much weaker but nevertheless play an important role in chemical interactions, particularly where water and organic substances are involved.

Van der Waals interactions arise from asymmetric distribution of charge in molecules and crystals. There are three sources for van der Waals interactions: *dipole-dipole attraction*, *induction,* and *London dispersion* forces. As we noted above, many molecules, including water, have permanent dipole moments. When two polar molecules encounter each other, they will behave much as two bar magnets: they will tend to orient themselves so that the positive part of one molecule is closest to the negative part of another (Figure 1.9a). This results in a net attractive force between the two molecules. When the distance between molecules is large compared to the distance between charges within molecules, the energy of attraction can be shown to be:

$$U_{D-D} = -\frac{2}{3}\frac{\mu^4}{r^6}\frac{1}{k\,T} \qquad\qquad 1.14$$

where U_{D-D} is the interaction energy, μ is the dipole moment, T is temperature (absolute, or thermodynamic temperature, which we will introduce in the next chapter), k is a constant (Boltzmann's constant, which we shall also meet in the next chapter), and r is distance. We don't want to get lost in equations at this point; however, we can infer several important things about dipole-dipole interactions just from a quick glance at it. First, the interaction energy depends inversely on the sixth power of distance. Many important forces, such as electromagnetic and gravitational forces, depend on the inverse square of distance. Thus we may infer that dipole-dipole forces become weaker with distance very rapidly. Indeed, they are likely to be negligible unless the molecules are very close. Second, the interaction energy depends on the forth power of the dipole moment, so that small differences in dipole moment will result in large differences in interaction energy. For example, the dipole moment of water (1.84 debyes) is less than twice that of HCl (1.03 debyes), yet the dipole interaction
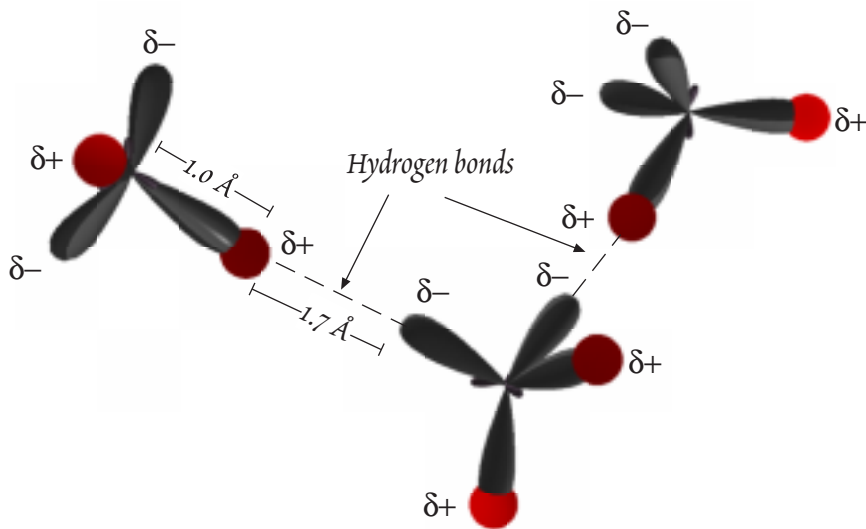

Figure 1.10. Hydrogen bonding between water molecules. Hydogen positions shown as red; sp^3 hybrid orbitals in oxygen shown as dark gray. The δ+ and δ– indicate partial positive and negative charges respectively.

CHAPTER 1: INTRODUCTION

energy between two water molecules (716 J/mol) is nearly 10 times as great as that between two HCl molecules (72.24 J/mol) at the same temperature and distance (298 K and 5Å). Finally, we see that dipole interaction energy will decrease with temperature.

Dipole molecules may also polarize electrons in a neighboring molecule and distort their orbits in such a way that their interaction with the dipole of the first molecule is attractive. This is known as the induction effect (Figure 1.9b). The induction energy also depends on the inverse sixth power of intermolecular distance, but only on the square of the dipole moment of the molecules involved. In addition, another parameter, the polarizability of a molecule, is also needed to describe this effect. In general, the attraction arising from induction is less important than from dipole-dipole interaction. However, because it depends only on the square of dipole moment, the induction attraction can be larger than the dipole-dipole attraction for some weakly dipolar molecules.

Finally, van der Waals forces can also occur as a result from fluctuations of charge distribution on molecules that occur on time scales of 10^{-16} seconds. These are known as London dispersion forces. They arise when the instantaneous dipole of one molecule induces a dipole in a neighboring molecule. As was the case in induction, the molecules will orient themselves so that the net forces between them are attractive.

The total energy of all three types of van der Waals interactions between water molecules is about 380 J/mol assuming an intermolecular distance of 5 Å and a temperature of 298 K (25° C). Though some interaction energies can be much stronger (e.g., CCl_4, 2.8 kJ/mol) or weaker (1 J/mol for He), an energy of a few hundred Joules per mole is typical of many substances. By comparison, the hydrogen-oxygen bond energy for each H—O bond in the water molecule is 46.5 kJ/mol. Thus van der Waals interactions are quite weak compared with typical intramolecular bond energies.

The *Hydrogen Bond* is similar to van der Waals interactions in that it arises from nonsymmetric distribution of charge in molecules. However, it differs from van der Waals interactions in a number of ways. First, it occurs exclusively between hydrogen and strongly electronegative atoms, namely oxygen, nitrogen and fluorine. Second, it can be several orders of magnitude stronger than van der Waals interactions, though still weak by comparison to covalent and ionic bonds. The exact nature of hydrogen bonds is not completely understood. They arise principally from electrostatic interactions. In the water molecule, binding between oxygen and hydrogen results in hybridization of s and p orbitals to yield two bonding orbitals between the O and two H atoms and 2 non-binding sp^3 orbitals on the oxygen. The latter are prominent on the opposite side of the O from the hydrogens. The hydrogen in one water molecule, carrying a net positive charge, is attracted by the non-binding sp^3 electrons of the oxygen of another water molecule, forming a hydrogen bond with it (Figure 1.10).

Hydrogen bonds typically have energies in the range of 20-40 kJ/mol. These are much higher than expected for electrostatic interactions alone and indeed approach values similar to intramolecular bond energies. Thus there is the suspicion that the some degree of covalency is also involved in the hydrogen bond. That is to say that the non-binding electrons of oxygen are to some degree shared by with the hydrogen in another molecule. Hydrogen bonds are perhaps most important in water, where they account for some of the extremely usual properties of this compound, such as its high heat of vaporization, but they can also be important in organic molecules and are present in HF and ammonia as well.

A Brief Look at the Earth

Structure of the Earth

The Earth consists of 3 principal layers: the core, the mantle, and the crust (Figure 1.11). The core, roughly 3400 km thick and extending about half way to the surface, consists of Fe-Ni alloy and can be subdivided into an inner and outer core. The outer core is liquid while the inner core is solid. The mantle is about 3000 km thick and accounts for about 2/3 the mass of the Earth; the core accounting for the other 1/3. The crust is quite thin by comparison, nowhere thicker than 100 km and usually much thinner. Its mass is only about 0.5% of the mass of the Earth. There are 2 fundamental kinds of crust: oce-
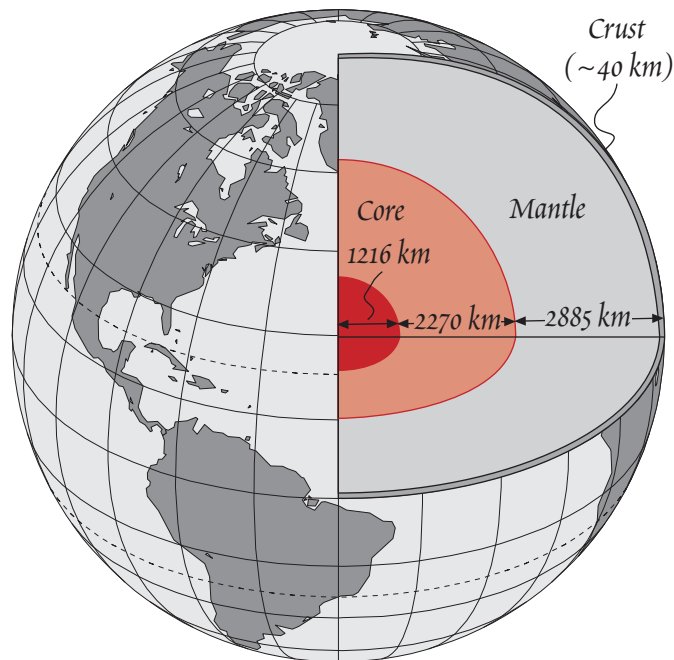
CHAPTER 1: INTRODUCTION

Figure 1.11. The Earth in cross-section. The outer rocky part of the planet, the mantle and crust, consists principally of silicates and is 2885 km thick. The core, divided into a liquid outer core and a solid inner core, consists of iron-nickel alloy and is 3486 km thick.

anic and continental. Ocean crust is thin (about 6 km) and is nowhere older than about 200 million years. The continental crust is thicker (about 35-40 km thick on average) and relatively permanent.

Both the crust and the mantle consist principally of silicates. The mantle is comparatively rich in iron and magnesium, so ferromagnesian silicates, such as olivine and pyroxenes, dominate. Rocks having these compositional characteristics are sometimes called *ultramafic*. The continental crust is poor in iron and magnesium, and aluminosilicates such as feldspars dominate. Rocks of this composition are sometimes referred to as *felsic*. The oceanic crust is intermediate in composition between the mantle and continental crust and has a *mafic* composition, consisting of a roughly 50-50 mix of ferromagnesian minerals and feldspar. These differences in composition lead to differences in density, which are ultimately responsible for the layering of the Earth, the density of each layer decreasing outward. The continental crust is the least of dense of these layers. The fundamental reason why continents stick out above the oceans is that continental crust is less dense than oceanic crust.

Plate Tectonics and the Hydrologic Cycle

Two sources of energy drive all geologic processes: solar energy and the Earth's internal heat. Solar energy drives atmospheric and oceanic circulation, and with them, the hydrologic cycle. In the hydrologic cycle, water vapor in the atmosphere precipitates on the land as rain or snow, percolates into the soil and, through the action of gravity, makes it way to the oceans. From the oceans, it is evaporated into the atmosphere again and the cycle continues. The hydrologic cycle is responsible for two very important geologic processes: weathering and erosion. Weathering, a topic we will consider in more detail in Chapter 13, causes rocks to breakdown into small particles and dissolved components. The particles and dissolved matter are carried by the flow of water (and more rarely by wind and ice) from high elevation to areas of low elevation. Thus the effect of the hydrologic cycle is to level the surface of the planet.

The Earth's internal heat is responsible for tectonic processes, which tend to deform the surface of the planet, producing topographic highs and lows. The internal heat has two parts. Some fraction of the heat, estimated to be between 25% and 75%, originated from the gravitational energy released when the Earth formed. The other fraction of internal heat is produced by the decay of radioactive elements, principally uranium, thorium, and potassium, in the Earth. The Earth's internal heat slowly decays over geologic time as it migrates to the surface and is radiated away into space. It is this migration of heat out of the Earth that drives tectonic processes. Heat causes both the outer core and the mantle to convect, as hot regions rise and cold regions sink. Convection within the outer core gives rise to the Earth's magnetic field, and may have other, as yet not understood, geologic consequences. Convection in the mantle is responsible for deformation of the Earth's crust as well as volcanism.
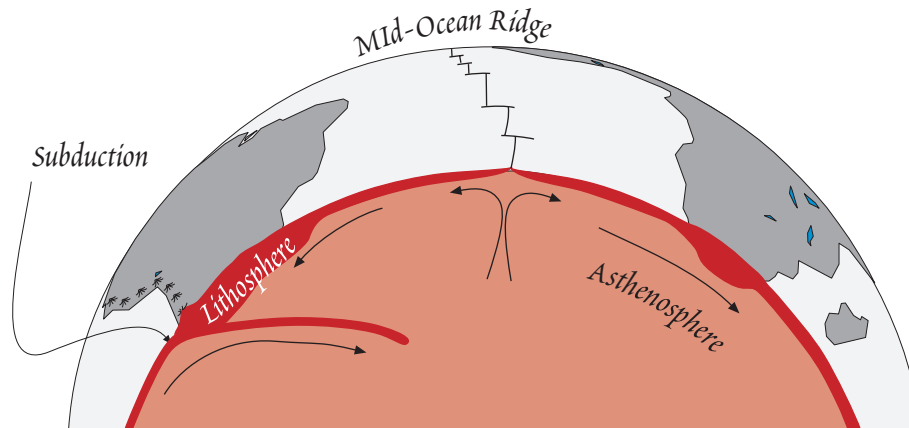
Figure 1.12. Cross section of the Earth illustrating relationships between lithosphere and asthenosphere and plate tectonic processes. Oceanic crust and lithosphere are created as plates diverge at mid-ocean ridges and are eventually subducted back into the mantle. Continental lithosphere is thicker and lighter than oceanic lithosphere and not easily subducted.

The great revolution in earth science in the 1960's centered on the realization that the outer part of the Earth was divided into a number of "plates" that moved relative to one and other. Most tectonic processes, as well as most volcanism, occur at the boundaries between these plates. The outer part of the Earth, roughly the outer 100 km or so, is cool enough (<1000 ° C) that it is rigid. This rigid outer layer is known as the lithosphere and comprises both the crust and the outermost mantle (Figure1.12). The mantle below the lithosphere is hot enough (and under sufficient confining pressure) that it flows, albeit extremely slowly, when stressed. This part of the mantle is known as the asthenosphere. Temperature differences in the mantle create stresses that produce convective flow. It is this flow that drives the motion of the lithospheric plates. The motion of the plates is extremely slow, a few tens of centimeters per year at most and generally much less. Nevertheless, on geologic time scales they are sufficient to continually reshape the surface of the Earth, creating the Atlantic Ocean, for example, in the last 200 million years.

Rather than thinking of plate motion as being driven by mantle convection, it would be more correct to think of plate motion as part of mantle convection. Where plates move apart, mantle rises to fill the gap. As the mantle does so, it melts. The melt rises to the surface as magma and creates new oceanic crust at volcanos along mid-ocean ridges (Figure 1.12). Mid-ocean ridges, such as the East Pacific Rise and the Mid-Atlantic Ridge, thus mark *divergent plate boundaries*. As the oceanic crust moves away from the mid-ocean ridge it cools, along with the mantle immediately below it. This cooling produces a steadily thickening lithosphere. As this lithosphere cools, it contracts and its density increases. Because of this contraction, the depth of the ocean floor increases away from the mid-ocean ridge. When this lithosphere has cooled sufficiently, after 100 million years or so, it becomes more dense than the underlying asthenosphere. The lithosphere may then sink back into the mantle in a process known as *subduction*. As the lithosphere sinks, it creates deep ocean trenches, such as the Peru-Chile Trench, or the Marianas Trench. Chains of volcanos, known as island arcs, invariably occur adjacent to these deep sea trenches. The volcanism occurs as a result of dehydration of the subducting oceanic crust and lithosphere. Water released from the subducting oceanic crust rises into the overlying mantle, causing it to melt. The island arcs and deep sea trenches are collectively called *subduction zones*. Subduction zones thus mark *convergent plate boundaries*. It is primarily the sinking of old, cold lithosphere that drives the motion of plates. Thus the lithosphere does not merely ride upon convecting mantle, its motion is actually part of mantle convection.

The density of the continental crust is always lower than that of the mantle, regardless of how cold the crust becomes. As a result, it cannot be subducted into the mantle. The Indian-Eurasian plate

CHAPTER 1: INTRODUCTION

boundary is a good example of what happens when two continental plates converge. Neither plate readily subducts and the resulting compression has produced, and continues to uplift, the Himalayan Mountains and the Tibetan Plateau. This area of the continental crust is not only high, it is also deep. The crust beneath this region extends to depths of as much as 100 km, nearly three times the average crustal thickness. Rocks within this thickened crust will experience increased temperatures and pressures, leading to *metamorphism*, a process in which new minerals form in place of the original ones. In the deepest part of the crust, melting may occur, giving rise to granitic magmas, which will then intrude the upper crust.

The topographically high Himalayas are subject to extremely high rates of erosion, and the rivers draining the area carry enormous quantities of sediment. These are deposited mainly in the northern Indian Ocean, building the Ganges and Indus Fans outward from the continental margin. As the mountains erode, the mass of crust bearing down on the underlying asthenosphere is reduced. As a result of the decreased downward force, further uplift occurs.

The third kind of plate boundary is known as a transform boundary and occurs where plates slide past one and other. A good example of this type of plate boundary is the San Andreas Fault system of California. Here the Pacific Plate is sliding northward past the North American Plate. The passage is not an easy one, however. The two plates occasionally stick together. When they do, stresses steadily build up. Eventually, the stress exceeds the frictional forces holding the plates together, and there is a sudden jump producing an earthquake. Earthquakes are also common in subduction zones and along mid-ocean ridges. They are much rarer in the interior of plates.

Most volcanism and crustal deformation occur along plate boundaries. A small fraction of volcanos, however, is located in plate interiors and appears to be entirely unrelated to plate tectonic processes. Crustal uplift also occurs in association with these volcanos. Two good examples are Hawaii and Yellowstone. These phenomena are thought to be the result of mantle plumes. Mantle plumes are convective upwellings. In contrast to the convective upwelling occurring along mid-ocean ridges, which is typically sheet-like, mantle plumes appear to be narrow (~100 km diameter) and approximately cylindrical. Furthermore, it appears that mantle plumes rise from much deeper in the mantle, perhaps even the core-mantle boundary, than convection associated with plate motion.

EARTH MATERIALS

The most abundant elements in the Earth are O and Fe (both close to 32%), Mg (~15%), Si (~14%), Ni (~1.8%), Ca (1.7%), and Al (1.6%). The majority of the Earth's Fe and Ni are in the core. The remaining rocky part of the Earth, the mantle and crust, consists of ~44% O, ~23% Mg, 21% Si, 2.5% Ca, and 2.4% Al. As a consequence, the outer part of the Earth consists principally of compounds known as *silicates*. Silicates are compounds based on the silica tetrahedron, consisting of a silicon atom surrounded by four oxygens (Figure 11.13a). The bonds between the oxygens and silicon are about 50% covalent–50% ionic and are quite strong. The silicon atom shares an electron with each of the four oxygens. Since oxygen has two valence electrons, each oxygen can form an additional bond. There are two possibilities: the oxygen can form a second bond (which is usually more ionic) with another metal atom or it can form a bond with a second silicon. This latter possibility leads to linking of silica tetrahedra to form rings, chains, sheets, or frameworks. Oxygens bound to two silicons are called *bridging oxygens*.

In orthosilicates, the silica tetrahedra are either completely independent or form dimers, that is, two linked tetrahedra. A good example of a mineral of this type is olivine, whose structure is illustrated in Figure 11.13b. The chemical formula for olivine is $(Mg,Fe)_2SiO_4$. The notation (Mg,Fe) indicates that either magnesium or iron may be present. *Olivine* is an example of a solid solution between the Mg-end member, forsterite (Mg_2SiO_4), and the Fe-end member, fayalite (Fe_2SiO_4). Such solid solutions are quite common among silicates. As the formula indicates, there are two magnesium or iron atoms for each silica tetrahedra. Since each Mg or Fe has a charge of +2, their charge balances the –4 charge of each silica tetrahedra. Olivine constitutes roughly 50% of the Earth's upper mantle, and is thus one of the most abundant minerals in the Earth. At great pressures, it disproportionates to a Fe-

CHAPTER 1: INTRODUCTION

Mg oxide (magnesiowüstite) and $(Mg,Fe)SiO_3$ (Mg-perovskite). At the same time, silicon atoms become octahedrally coordinated (surrounded by 6 oxygens rather than 4 as in the silica tetrahedra).

In chain silicates, the silica tetrahedra are linked together to form infinite chains (Figure 1.13c), with one bridging oxygen per tetrahedra. Minerals of this group are known as *pyroxenes* and have the general formula $XSiO_3$ where X is some metal, usually Ca, Mg, or Fe, which is located between the chains. Two pyroxenes, orthopyroxene $((Mg,Fe)SiO_3)$ and clinopyroxene $(Ca(Mg,Fe)Si_2O_6$ are very abundant in the Earth's upper mantle as well as mafic igneous rocks. The pyroxenes wollastonite $(CaSiO_3)$ and jadite $(NaAlSi_2O_6)$ are found exclusively in metamorphic rocks.

In double chain silicates, an additional bridging oxygen per tetrahedra joins two chains together.

The Silica Tetrahedron

Sheet Structure

bridging oxygens

non-bridging oxygens

Olivine Structure

Oxygen   Silicon   Mg, Fe, etc.

Pyroxene Structure

Minerals of this group are known as *amphiboles*, which occur widely in both igneous and metamorphic rocks. Among the important minerals in this group are hornblende $(Ca_2Na(Mg,Fe)_4 Al_3Si_8O_{22}(OH)_2)$, tremolite-actinolite $(Ca_2(Mg,Fe)_5Si_8 O_{22}(OH)_2)$, and glaucophane $(Ca_2(Mg,Fe)_3Al_3Si_8O_{22}(OH)_2)$. These minerals all contain OH as an essential component (Cl or F sometimes substitutes for OH). They are thus examples of hydrous silicates.

Sharing of a third oxygen links the tetrahedra into sheets, forming the sheet silicates (Figure 1.13d). This group includes *micas* such as biotite $(K(Mg,Fe)_3AlSi_3O_{10}(OH)_2)$ and muscovite $(KAl_3Si_3O_{10} (OH)_2)$, talc $(Mg_3Si_4O_{10} (OH)_2)$, and *clay minerals* such as kaolinite $(Al_2Si_2O_5 (OH)_4)$. As in amphiboles, OH is an essential component of sheet silicates. These minerals can form through weathering and are thus primary sedimentary minerals. Many of them are found in igneous and metamorphic rocks as well.

When all four oxygens are shared between tetrahedra, the result is a framework. The simplest framework silicate is quartz (SiO_2), which con-
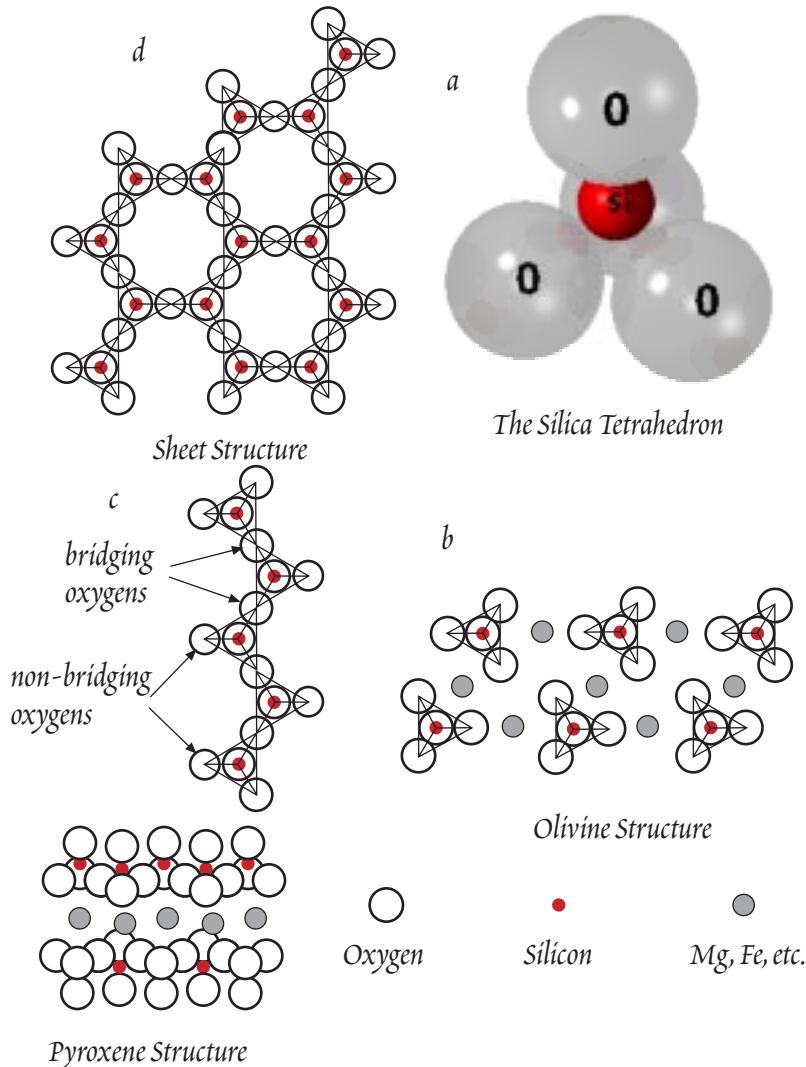
Figure 1.13. The silica tetrahedron and the structure of silicate minerals. a. The silica tetrahedron consists of a central silicon atom bound to 4 oxygens. b. In orthosilicates such as olivine, the tetrahedra are separate and each oxygen is also bound to other metal ions that occupy interstitial sites between the tetrahedra. c. In pyroxenes, the tetrahedra each share one oxygen and are bound together into chains. Metal ions are located between the chains. d. In sheet silicates, such as talc, mica, and clays, the tetrahedra each share 3 oxygens and are bound together into sheets.

CHAPTER 1: INTRODUCTION

sists solely of linked SiO_4 tetrahedra. The other important group of framework silicates are the *feldspars*, of which there are three end-members: sanidine ($KAlSi_3O_8$), albite ($NaAl\ Si_3O_8$), and anorthite ($Ca\ Al_2Si_2O_8$). The calcium and sodium feldspars form the plagioclase solid solution, which is stable through a large temperature range. Sodium and potassium feldspars, collectively called alkali feldspar, form more limited solid solutions. Feldspars are the most abundant minerals in the Earth's crust.

Silicates are the most abundant minerals in the Earth, but not the only ones. Other classes of minerals include oxides such as magnetite (Fe_3O_4) and ilmenite ($FeTiO_3$), carbonates such as calcite ($CaCO_3$), sulfates such as gypsum $CaSO_4 \cdot 2H_2O$, hydroxides such as gibbsite ($Al(OH)_3$), and sulfides such as pyrite FeS_2.

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