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Francis Albarede
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Introduction

Geochemistry utilizes the principles of chemistry to explain the mechanisms regulating the workings – past and present – of the major geological systems such as the Earth's mantle, its crust, its oceans, and its atmosphere. Geochemistry only really came of age as a science in the 1950s, when it was able to provide geologists with the means to analyze chemical elements or to determine the abundances of isotopes, and more significantly still when geologists, chemists, and physicists managed to bridge the chasms of mutual ignorance that had separated their various fields of inquiry. Geochemistry has been at the forefront of advances in a number of widely differing domains. It has made important contributions to our understanding of many terrestrial and planetary processes, such as mantle convection, the formation of planets, the origin of granite and basalt, sedimentation, changes in the Earth's oceans and climates, and the origin of mineral deposits, to mention only a few important issues. And the way geochemists are perceived has also changed substantially over recent decades, from laboratory workers in their white coats providing age measurements for geologists or assays for mining engineers to today's perception of them as scientists in their own right developing their own areas of investigation, testing their own models, and making daily use of the most demanding concepts of chemistry and physics. Moreover, because geochemists generate much of their raw data in the form of chemical or isotopic analyses of rocks and fluids, the development of analytical techniques has become particularly significant within this discipline.

To give the reader some idea of the complexity of the geochemist's work and also of the methods employed, we shall begin by following three common chemical elements – sodium (Na), magnesium (Mg), and iron (Fe) – on their journey around system Earth. These three elements were created long before our Solar System formed some 4.5 billion years ago, in the cores of now extinct stars. There, the heat generated by the gravitational collapse of enormous masses of elementary particles overcame the repulsive forces between protons and triggered thermonuclear fusion. These reactions allowed particles to combine forming ever larger atomic nuclei of helium, carbon, oxygen, sodium, magnesium, and iron. This activity is still going on before our very eyes as the Sun heats and lights us with energy released by hydrogen fusion. When, after several billion years, the thermonuclear fuel runs out, the smaller stars simply cool: the larger ones, though, collapse under their own weight and explode in one of the stellar firework displays that nature occasionally stages, as with the appearance of a supernova in the Crab nebula in AD 1054. The matter scattered by such explosions drifts for a while in interstellar space as dust clouds similar to the one that can be observed in the nebula of Orion. Turbulence in the cloud and collisions between the particles make the system unstable and the particles coalesce to form small rocky bodies known as planetesimals. Chondritic meteorites give us a pretty good idea of what these are like. Gravitational chaos amplifies very rapidly and the planetesimals collide to form larger and larger bodies surrounding a new star: a Solar System is born.

As the planet forms and evolves, our three chemical elements meet different fates. Sodium is a volatile element with a relatively low boiling point (881 °C) and large amounts of it are therefore driven off into space by the heat generated as the planet condenses. Iron, which is initially scattered within the rock mass, melts and collects at the heart of the planet to form the core, which, on Earth, generates the magnetic field. Magnesium has a boiling point of 1105 °C and behaves in an un-extraordinary way assembling with the mass of silicate material to form the mantle, the main bulk of the terrestrial planets, and residing in minerals such as olivine (Mg_2SiO_4), the pyroxenes ($Mg_2Si_2O_6$ and $CaMgSi_2O_6$), and, if sufficient pressure builds up, garnet ($Mg_3Al_2Si_3O_{12}$).

The chemical histories of the planets are greatly influenced by their magmatic activity, a term that refers to all rock melting processes. On our satellite, the Moon, the formation of abundant magmas in the first tens of millions of years of its history has left its mark in the surface relief. The crust, composed of the mineral plagioclase ($CaAl_2Si_2O_8$), is so light that it floats on the magma from which it crystallized, forming the lunar highlands that rise above the Moon's marias. The sodium that did not vaporize migrated with the magma toward the lunar surface and combined readily in the plagioclase alongside calcium. On Earth, water is abundant because temperatures are moderate and because the planet is massive enough for gravity to have retained it. The action of water and dissolved carbonates is another significant factor in the redistribution of chemical elements. Water causes erosion and so is instrumental in the formation of soils and sedimentary rocks. The presence of chemically bound water in the continental crust promotes metamorphic change and, by melting of metamorphosed sedimentary rocks, the formation of granite that is so characteristic of the Earth's continental crust. A substantial fraction of the sodium that did manage to enter into the formation of the early crust was soon dissolved and transported to the sea, where it has resided for hundreds of millions of years. Some marine sodium entered sediment and then, in the course of magmatic processes, entered granite and therefore the continental crust.

Magnesium, by contrast, tends to remain in the dense refractory minerals. It lingers in solid residues left after melting or precipitated during crystallization of basalt at mid-oceanic ridges or at ocean island volcanoes. Where it does enter fluids, it subsequently combines with olivine and pyroxene, which precipitate out as magma cools. Magnesium is resistant to melting and is predominant in the mantle, which has ten to thirty times the magnesium content of the crust.

The Earth is a complex body whose dynamics are controlled by mechanisms that commonly work in opposing directions: differentiation mechanisms, on the one hand, maintained by fractionation of elements and isotopes between the phases arising during changes of state (melting, crystallization, evaporation, and condensation), and, on the other hand, mixing mechanisms in hybrid environments such as the ocean and detrital rocks that tend to homogenize components derived from the various geological units (rain water, granite, basalt, limestone, soil, etc.). By fractionation we mean that two elements (or two isotopes) are distributed in unequal proportions among the minerals and other chemical phases present in the same environment.

It can be seen then that the elements must be studied in terms of their properties in the context of the mineral phases and fluids accommodating them and in the context of the processes that govern changes in these phases (magmatism, erosion, and sedimentation). By mineral phase is meant all the crystals from a small neighborhood (mm to cm) that belong to the same mineral species. We will start by discussing some useful rules of organic and nuclear chemistry that illuminate the geochemical properties of elements. An understanding of transport mechanisms is very important in geochemistry. The term "cycle" is sometimes employed but we will see later that its meaning needs to be clarified. Conversely, the terminology used above, which emphasizes that sodium resides for a long time in the ocean or that magnesium lingers in solid residues of melting, illustrates that transfers among the different parts of the globe, such as the core, mantle, crust, and oceans, are to be considered kinetically, or, more loosely, dynamically, in terms of flows or transport rates. We will next turn our attention to the mysterious field of stable isotopes, with the idea of clarifying the principles of their fractionation in nature. Radioactive decay, which alters the atomic nucleus and therefore the nature of certain elements at rates that are unaffected by the physical, crystallographic, or chemical environment in which they occur, will allow us to include the incessant ticking of these "clocks" in our study of radioactive processes.

The book then moves on to the essential study of the dynamics and evolution of the mantle and continental crust, and the study of marine geochemistry and its implications for paleoclimatology and paleoceanography. Two new chapters on biogeochemistry and environmental geochemistry have been added to the second edition. A last chapter deals with the geochemical properties of a number of elements. Most students deplore the lack of such a systematic approach in the literature; what is supposed to be common knowledge is never taught, simply because the odds of being inaccurate, unbalanced, and superficial are too great. An appendix provides an overview of a number of methods for analyzing chemical elements and isotopes.

I have been asked so many times by genuinely motivated colleagues from other disciplines where a compact description of geochemistry could be found. I hope this short textbook will meet this demand. It will probably be found that this book relies more heavily on equations than most other geochemistry textbooks. I maintain that a proper scientific approach to our planet must use all the available tools, especially those of physics and chemistry, to supplement purely descriptive and analytical approaches. I therefore ask readers to persevere despite the superficial difficulty of some of the equations, which are, after all, nothing more than a means of encoding concepts that ordinary language is powerless to convey with adequate precision. Oscar Wilde said that " . . . nothing that is worth knowing can be taught." A collection of observations is no more science than a dictionary is literature. Above all, I have made every attempt to avoid turning the reader of this book into a stamp collector.

But the devil is in the detail and I occasionally had to cut corners: some concepts, definitions, and proofs could have benefited from more rigor and from more detailed supporting arguments. I very much wanted to keep this book short, so I hope that my specialist colleagues will forgive the short-cuts used to this effect.

Readers may e-mail any queries, criticisms and – who knows – words of encouragement to the author (albarede@ens-lyon.fr).

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1 The properties of elements

The 92 naturally occurring chemical elements (90, in fact, because promethium and technetium are no longer found in their natural state on Earth) are composed of a nucleus of subatomic nucleons orbited by negatively charged electrons. Nucleons are positively charged protons and neutral neutrons. As an atom contains equal numbers of protons and electrons with equal but opposite charges, it carries no net electrical charge. The mass of a proton is 1836 times that of an electron. The chemical properties of elements are largely, although not entirely, determined by the way their outermost shells of electrons interact with other elements. Ions are formed when atoms capture surplus electrons to give negatively charged anions or when they shed electrons to give positively charged cations. An atom may form several types of ions. Iron, for example, forms both ferric (Fe^{3+}) ions and ferrous (Fe^{2+}) ions, while it also occurs in the Fe^0 elemental form.

A nuclide is an atomic nucleus characterized by the number Z of its protons and the number N of its neutrons regardless of its cloud of electrons. The mass number A is the sum of the nucleons $N + Z$. Different interactions act in the nucleus and explain its binding: the short-range (nuclear) strong force, the long-range electromagnetic force, and the mysterious intermediate weak force. Two nuclides with the same number Z of protons but different numbers N of neutrons will be accompanied by the same suite of electrons and so have very similar chemical properties; they will be isotopes of the same element. The "chart of the nuclides" (Fig. 1.1) shows that in order to be stable, nuclides must contain a specific proportion of neutrons and protons. The semi-empirical formula for the energy of a nucleus is:

$$E = aA - bA^{2/3} + c\frac{(N-Z)^2}{A} - d\frac{Z^2}{A^{1/3}} \tag{1.1}$$

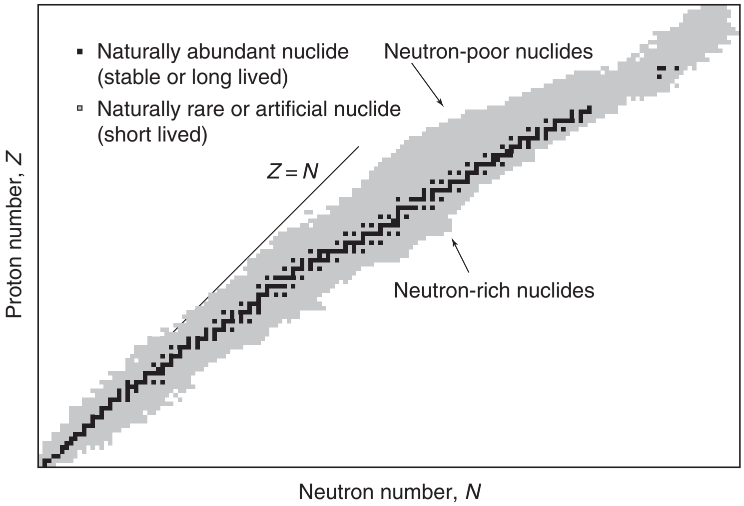

Figure 1.1 **Chart of the nuclides (overview). The light stable elements have approximately the same number *Z* of protons and number *N* of neutrons but the heavier stable elements deviate towards the neutron-rich side according to (1.2): this relationship defines the valley of stability. Elements that depart significantly from this rule are unstable (radioactive).**

and this describes the so-called "liquid drop" model of the nucleus. The constants a, b, c, and d can be adjusted to fit laboratory data. As a first approximation, the volume of the nucleus is proportional to A, its radius to $A^{1/3}$, and its surface area to $A^{2/3}$. The first term on the right-hand side expresses the volume energy, which is proportional to the number of nucleons; the second term is the surface energy, which subtracts the uncompensated attraction of the nucleons located near the surface of the nucleus; the third term expresses that, for a given A, the nuclear attraction between proton and neutron is slightly stronger than proton–proton and neutron–neutron attraction; the fourth term accounts for electrostatic energy which is inversely proportional to the distance between the neighboring charges of the protons. The locus of minimum energy, in the N, Z plot of Fig. 1.1, which is known as the "valley of stability," is obtained by minimizing (1.1) with respect to Z, and is conveniently represented by the equation:

$$Z = \frac{2A}{4 + 0.031A^{2/3}} \tag{1.2}$$

For light elements ($Z < 40$), the term in A at the denominator is very small, so $Z \approx A/2$ and therefore $N \approx Z$. At higher masses, electrostatic repulsion between protons gets stronger and $N > Z$. One easily finds that for ^{238}U, $Z = 92$ which is correct.

Nuclei with N and Z too far from this valley of stability are unstable and are said to be radioactive. An isotope is radioactive if its nucleus undergoes spontaneous change such as occurs, for instance, when alpha particles (two protons and two neutrons) or electrons are emitted. It changes into a different isotope, referred to as radiogenic, by giving out energy, usually in the form of gamma radiation, some of which is harmful for humans. Several internet sites provide tables of all stable and radioactive nuclides. The vast majority of

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natural isotopes of naturally occurring elements are stable, i.e. the number of their protons and neutrons remains unchanged, simply because most radioactive isotopes have vanished over the course of geological time. They are therefore not a danger to people.

1.1 The periodic table

The atomic number of an element is equal to the number of its protons. We have seen before that the atom's mass number is equal to the number of particles making up its nucleus. The Avogadro number $\mathcal{N}$ is the number of atoms contained in 12 g of the carbon-12 isotope. The atomic mass of an isotope is the weight of a number $\mathcal{N}$ of atoms of that isotope. Dimitri Mendeleev's great discovery in 1871 was to demonstrate the periodic character of the properties of elements when ordered by ascending atomic number (Fig. 1.2). Melting point, energy of formation, atomic radius, and first ionization energy all vary periodically as we work through Mendeleev's table. The geochemical properties of elements are reflected by their position in this table. The alkali metals (Li, Na, K, Rb, Cs), alkaline-earth metals (Be, Mg, Ca, Sr, Ba), titanium group elements (Ti, Zr, Hf), but also the halogens (F, Cl, Br, I), inert gases (He, Ne, Ar, Kr, Xe), rare-earths (lanthanides), or actinides (uranium family) all form groups sharing similar chemical properties; these properties are indeed sometimes so similar that it was long a challenge to isolate chemically pure forms of some elements such as hafnium (Hf), which was only separated from zirconium (Zr) and identified in 1922.

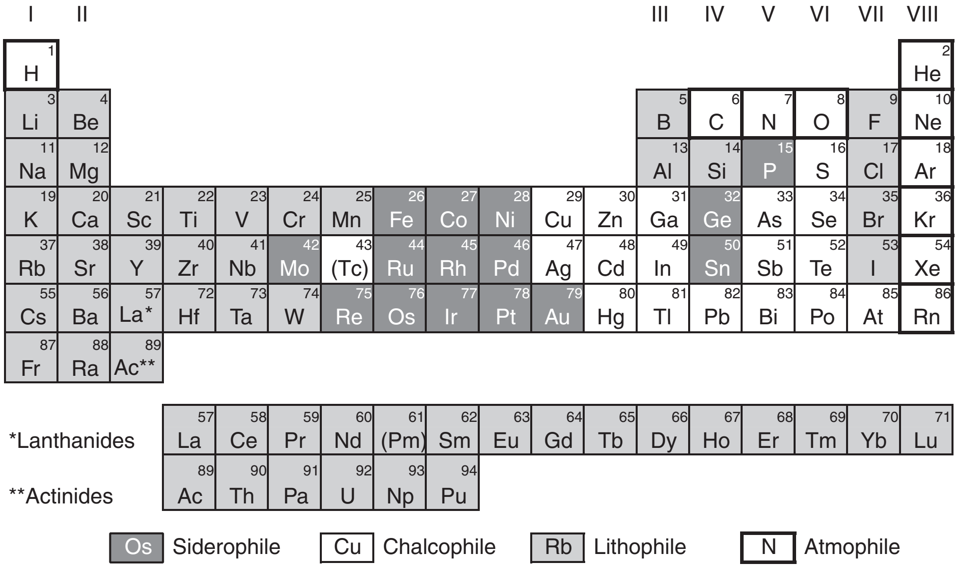

Figure 1.2 Mendeleev's periodic table of the elements and their geochemical classification after Goldschmidt. The elements in parentheses do not occur naturally on Earth. The atomic number of each element is given. Roman numerals over columns indicate groups.

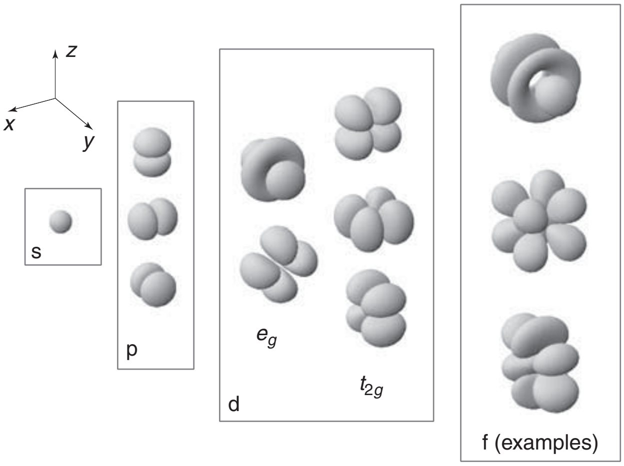

Figure 1.3 Examples of orbital geometry. Shown here are the surfaces of maximum probability of electron localization around the nucleus corresponding to various orbitals. s, p, d, f are the quantum numbers. Note the two types of d orbitals. Drawn using Orbital Viewer (Dave Manthey).

It is therefore very important to understand how elements are ordered in the periodic table. Put simply, an atom can be represented as a point-like nucleus containing the mass and charge of the nuclear particles and by mass-less electrons orbiting this point. The heavy nucleus is normally assumed to be immune to fluctuations in the more volatile electron clouds and is treated as stationary (Born-Oppenheimer approximation). Quantum mechanics requires the different forms of electron energy to be distributed discretely, i.e. at separate energy levels. It also requires that the different forms of momentum be quantized, not only the linear form of gas molecules bouncing around in a box, but also the angular momentum of the electrons on their atomic orbitals and around their spin axis. The angular momentum L plays the same role with respect to angular velocity ω as linear momentum $p = mv$ plays with linear velocity v: the familiar expression defining the linear kinetic energy as $p^2/2m$ becomes $L^2/2I$ for rotational kinetic energy, with the moment of inertia I playing for rotational energy the role of mass m for linear translation.

The Heisenberg principle states that the uncertainty of the position and the velocity of a particle vary inversely to one another and therefore prevents the exact calculation of electron orbits around the nucleus. An orbital is a complex function used by quantum mechanics to describe the probability of the presence of an electron around the nucleus but it is often reduced to a three-dimensional surface meant to represent the locus of maximum probability. It is denoted (Fig. 1.3) by a set of integers known as quantum numbers. The four levels of quantization are as follows:

1. The first (principal) quantum number n characterizes the total energy level of the electron and can take positive values 1, 2, 3, . . . It defines the main electron shells, which are sometimes represented by the letters K, L, M, . . .
2. The second (orbital) quantum number l characterizes the total orbital angular momentum L of the electron; it ranges from 0 to $n - 1$ and defines the number of lobes of the orbitals of each shell, which are usually designated by the letters s, p, d, f.

Table 1.1 Electronic configuration of the light elements

Element	Group	Quantum numbers				Configuration
		n	l	m	s	
H	I	1	0	0	+1/2	$1s^1$
He	VIII	1	0	0	−1/2	$1s^2 = [He]$
Li	I	2	0	0	+1/2	$[He]\ 2s^1$
Be	II	2	0	0	−1/2	$[He]\ 2s^2$
B	III	2	1	−1	+1/2	$[He]\ 2s^2\ 2p^1$
C	IV	2	1	−1	−1/2	$[He]\ 2s^2\ 2p^2$
N	V	2	1	0	+1/2	$[He]\ 2s^2\ 2p^3$
O	VI	2	1	0	−1/2	$[He]\ 2s^2\ 2p^4$
F	VII	2	1	+1	+1/2	$[He]\ 2s^2\ 2p^5$
Ne	VIII	2	1	+1	−1/2	$[He]\ 2s^2\ 2p^6 = [Ne]$
Na	I	3	0	0	+1/2	$[Ne]\ 3s^1$

3. The third (magnetic) quantum number m $(0, \pm 1, \ldots, \pm l)$ gives the part L_z of the angular moment which points along the rotation axis; it defines the shape of the orbital.
4. The fourth quantum number s describes the momentum associated with the spin of the electron and gives the direction of spin of the electron around its own axis relative to its orbital movement.

The Pauli exclusion principle states that no two electrons can have the same quantum numbers.

The periodic table can be constructed by assigning a unique set of quantum numbers to each element (Table 1.1) and the filling of the successive orbitals can now proceed from lower to higher energy levels until the number of electrons matches the number of protons in the nucleus. This holds for n, by definition, but also for l because of the electrostatic screening by electrons on lower orbitals (see below): for example, orbital 2p is filled after orbital 2s. The filling order is shown in Fig. 1.4 and can be exactly matched with the periodic table.

A number of Internet sites provide detailed periodic classifications, of which I can recommend http://www.webelements.com/, while Dave Manthey's excellent site http://www.orbitals.com/orb/ov.htm provides software to create very professionally drawn orbital pictures (Fig. 1.4).

In the periodic table, groups I (alkali metals) and II (alkaline-earth metals) correspond to the filling of s orbitals, and groups III to VIII to that of the p orbitals. The intermediate groups (transition elements such as iron and platinum) differ in the occupation of their d orbitals. When occupied, these d orbitals are normally closer to the nucleus than the s orbitals of the next shell out. Occupation of the orbitals is noted nx^i, where x represents the type of orbital (s, p, d, f), n its principal quantum number and i the number of electrons it contains. Most elements of the first series (e.g. V, Cr, Mn, Fe, Co, Ni, Cu, Zn) have an electron formula of the type $[Ne]3s^2\ 3p^6\ 3d^i\ 4s^2$, where [Ne] represents the fully occupied

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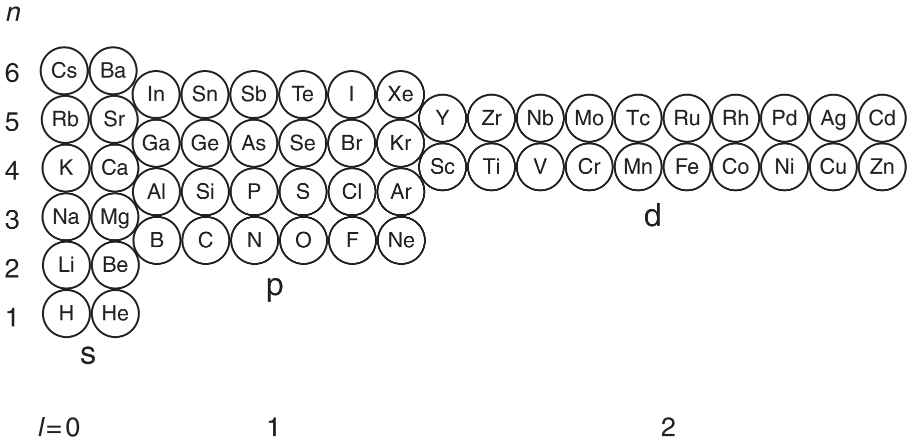


Figure 1.4 The filling order of the lowest orbitals of the elements in the periodic table. The vertical scale shows the energy levels.

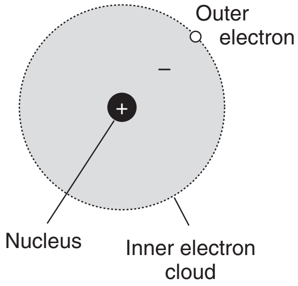
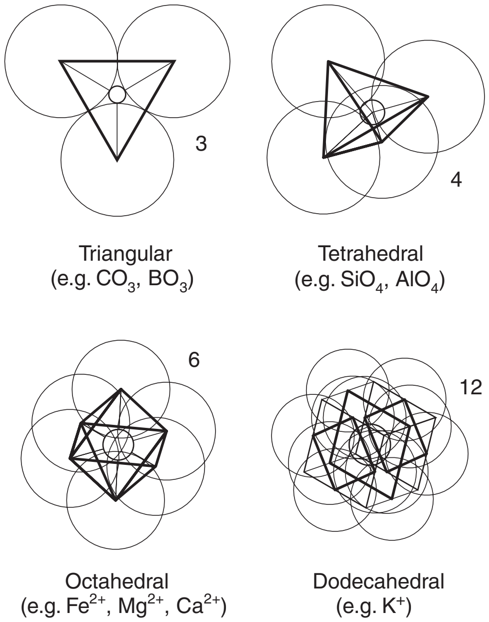


Figure 1.5 Shielding of the nuclear charge by the cloud of electrons orbiting between the outer electrons and the nucleus.

orbitals of a neon atom; and their divalent ions, such as Fe^{2+} and Cu^{2+}, have a configuration [Ne]$3s^2$ $3p^6$ $3d^i$. These transition elements differ only by the number i of electrons in orbital 3d but have an identical outer electron shell 4s, which explains why their chemical properties are so similar. This phenomenon is further amplified in the rare-earths (or lanthanides), such as La and Ce (shell 4f), and the actinides (5f), such as U and Th, where the s and p orbitals of the external shells are identical.

Simple rules hold for the prediction of atomic radii. First, the potential energy and atomic radius increase with n and therefore down each column of the periodic table. Second, the atomic radius decreases across each row. This is due to the reduction of electrostatic attraction of the outer electrons by the cloud of the inner electrons (Fig. 1.5), a phenomenon known as shielding. For the lanthanides and the actinides, the f electrons on their multilobate orbitals leave some parts of the nucleus exposed (Fig. 1.3) and therefore do not screen the increasing charge of the nucleus as efficiently as the more smoothly shaped lower-order orbitals. As a result, their atomic radii decrease smoothly with their increasing atomic number, a phenomenon known as lanthanide (and actinide) contraction.



Triangular (e.g. CO_3, BO_3)

Tetrahedral (e.g. SiO_4, AlO_4)

Octahedral (e.g. Fe^{2+}, Mg^{2+}, Ca^{2+})

Dodecahedral (e.g. K^+)

Figure 1.6 **The main ion coordination systems in naturally occurring minerals: triangular (three closest neighbors), tetrahedral (4), octahedral (6), and dodecahedral (12) coordination.**

The energy stored in silicates as chemical bonds depends on the nature of the cations and the crystal sites accommodating them. Depending on their ionic radius, cations may occupy sites of varying size and the number of oxygen neighbors with which they bond (coordination number) increases with the size of the site. Carbon and boron atoms combine with oxygen in a triangular arrangement (i.e. threefold coordination, Fig. 1.6), while silicon and aluminum atoms combine with oxygen to form a tetrahedron (fourfold coordination). However, medium-sized cations, such as Fe^{2+}, Mg^{2+}, or Ca^{2+}, will take up vacant octahedral sites (sixfold coordination) between SiO_4 tetrahedra while the biggest ions, such as K^+ or OH^- hydroxyl anions, require the most spacious sites, normally of twelvefold coordination.

1.2 Chemical bonding

Atoms and ions combine to form matter in its solid, liquid, or gaseous states. The importance of occupation of the outer electron shell can be illustrated by comparing the interaction between two atoms of helium, where two electrons occupy orbital 1s, with the interaction between two hydrogen atoms, each with a single electron only. When the two helium atoms come close together and their electron clouds interpenetrate, one atom's electrons cannot be accommodated by the orbital of the other as this would infringe the Pauli exclusion principle. They must therefore jump to the 2s orbital, at a cost in energy that penalizes the formation of such bonds. Two hydrogen atoms, however, can lend one another