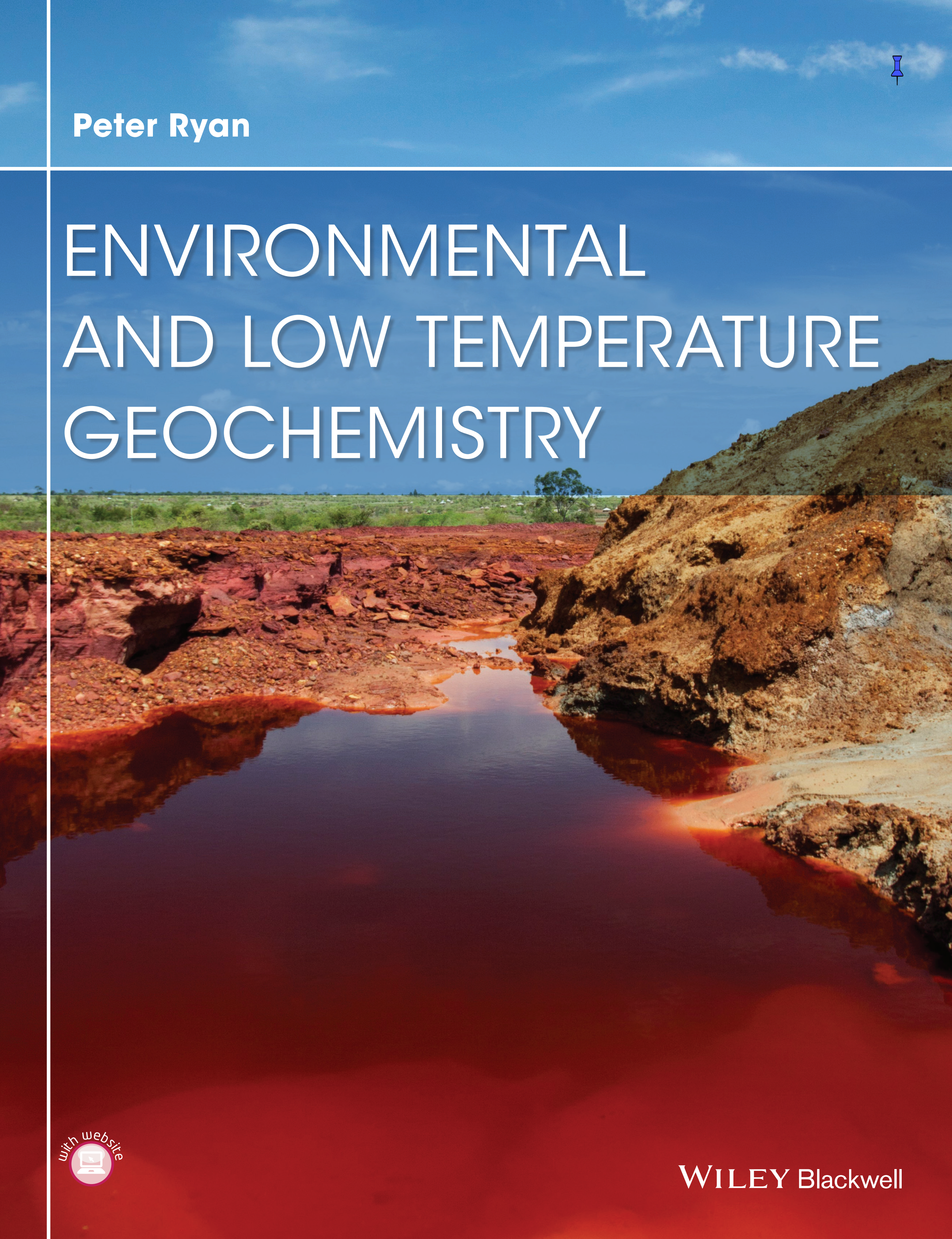

Peter Ryan

ENVIRONMENTAL AND LOW TEMPERATURE GEOCHEMISTRY

with website

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Environmental and Low Temperature Geochemistry

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About the Companion Website

This book is accompanied by a companion website:
www.wiley.com/go/ryan/geochemistry

The website includes:

- Powerpoints of all figures from the book for downloading
- PDFs of tables from the book

1

Background and Basic Chemical Principles: Elements, Ions, Bonding, Reactions

1.1 AN OVERVIEW OF ENVIRONMENTAL GEOCHEMISTRY – HISTORY, SCOPE, QUESTIONS, APPROACHES, CHALLENGES FOR THE FUTURE

> “The best way to have a good idea is to have a lot of ideas.” (Linus Pauling)
>
> “All my life through, the new sights of nature made me rejoice like a child.” (Marie Curie)

Environmental geochemistry encompasses research at the intersection of geology, environmental studies, chemistry and biology, and at its most basic level, is designed to answer questions about the behavior of natural and anthropogenic substances at or near the surface of Earth. The scope includes topics as diverse as trace metal pollution, soil formation, acid rain and sequestration of atmospheric carbon, and most problems in environmental geochemistry require understanding of the relationships among aqueous solutions, geological processes, minerals, organic compounds, gases, thermodynamics, kinetics, and microbial influences, to name a few. A good example is the fate and transport of lead in the environment. In some areas much of the lead in the Earth surface environment is (was) derived from combustion of leaded gasoline, because even after it had been banned, Pb tends to persist in soil. The original distribution of Pb was controlled at least in part by atmospheric processes ranging from advection to condensation and precipitation.

The fate and transport of Pb deposited on the land surface is controlled by the interactions and relationships among lead atoms, solids compounds (e.g. inorganic minerals or organic matter), potential for uptake into plants or other organisms, and the composition of water in soils, lakes or streams (including dissolved gases like O_2 and CO_2). In cases where Pb falls on soils bearing the carbonate anion (CO_3^{-2}), the formation of lead carbonate ($PbCO_3$) can result in sequestration of lead in a solid state where it is largely unavailable for uptake by organisms. If the $PbCO_3$ is thermodynamically stable, the lead can remain sequestered (i.e. stored), but changes in chemical regime can destabilize carbonates. For example,

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acidic precipitation that lowers the pH of soil can cause dissolution of $PbCO_3$, but how much of the carbonate will dissolve? How rapidly? Much like the melting of ice at 10 °C, geochemical processes are kinetically controlled (some more than others), so even in cases where phases exist out of equilibrium with their surroundings, we must know something about rate laws in order to predict how fast reactions (e.g. dissolution of $PbCO_3$) will occur.

If Pb is dissolved into an aqueous form, additional questions of fate and transport must be addressed – will the Pb remain in solution, thus facilitating its uptake by plants? Or will it be carried in solution into a nearby surface water body, where it could be consumed by a fish or amphibian? Or will other soil solids play a role in its fate? Will it become adsorbed to the surface of a silicate clay or organic matter, transported downstream until it ultimately desorbs in lake sediments? We also need to consider the possibility that the $PbCO_3$ does not dissolve, but rather is physically eroded into a stream or lake, where it might dissolve or remain a solid, possibly becoming consumed by a bottom feeder, from which point it could biomagnify up the food chain.

Environmental geochemistry has its origins in ground-breaking advances in chemistry and geology ushered in by the scientific breakthroughs of the late 19th and early 20th centuries, particularly advances in instrumental analysis. The Norwegian Victor M. Goldschmidt is considered by many to be the founder of geochemistry, a reputation earned by his pioneering studies of mineral structures and compositions by X-ray diffraction and optical spectrograph studies. These studies led Goldschmidt to recognize the importance and prevalence of isomorphous substitution in crystals, a process where ions of similar radii and charges can substitute for each other in crystal lattices.

Goldschmidt's peer, the Russian Vladimir I. Vernadsky, had come to realize that minerals form as the result of chemical reactions, and furthermore, that reactions at the Earth surface are strongly mediated by biological processes. The application of geochemistry applied to environmental analysis mainly arose in the 1960s and 1970s with growing concern about contamination of water, air and soil. The early 1960s saw publication of Rachel Carson's *Silent Spring*, and early research on acid rain at Hubbard Brook in New England (F.H. Bormann, G.E. Likens, N.M. Johnson, and R.S. Pierce) emphasized the interdisciplinary thinking required for problems that spanned atmospheric, hydrologic, soil, biotic and geologic realms.

Current research in environmental geochemistry encompasses problems ranging from micrometer-scale (e.g. interactions between minerals and bacteria or X-ray absorption analysis of trace metal speciation), local-scale (e.g. acid mine drainage, leaking fuel tanks, groundwater composition, behavior of minerals in nuclear waste repositories) to regional (acid rain, mercury deposition, dating of glacier retreat and advance) and global (climate change, ocean chemistry, ozone depletion). Modern environmental geochemistry employs analytical approaches ranging from field mapping and spatial analysis to spectrometry and diffraction, geochemistry of radioactive and stable isotopes, and analysis of organic compounds and toxic trace metals. While the explosion of activity in this field makes it impossible to present all developments and to acknowledge the research of all investigators, numerous published articles will be cited and highlighted in throughout the text, and a case study that integrates many concepts is presented in Appendix I.

1.2 THE NATURALLY OCCURRING ELEMENTS – ORIGINS AND ABUNDANCES

The chemical elements that comprise Earth were mainly produced during the Big Bang approximately 12−15 billion years ago. The early universe was extremely hot (billions of degrees) and for the first few seconds was comprised only of matter in its most basic form, quarks. After about 15 s, the atomic building blocks known as neutrons, protons, electrons, positrons, photons and neutrinos began to form from quarks, and within moments after the Big Bang, the first actual atoms formed. Protons combined with neutrons and electrons to form hydrogen ($^{1}_{1}H$) and its isotope deuterium ($^{2}_{1}H$, or D), which rapidly began to form helium (He) through fusion, a process in which the nuclei of smaller atoms are joined to create larger, heavier atoms: 2H → He + energy, or to be more precise:

$$^{1}_{1}H + ^{2}_{1}H = ^{3}_{2}He + \gamma + E \qquad (1.1)$$

where γ is the symbol for gamma radiation emitted during nuclear fusion. (note: basic principles of atomic theory are presented in Section 1.3).

Small amounts of lithium were probably also produced in the first few minutes or hours after the Big Bang, also by fusion (in a simple sense represented as H + He = Li). From a graph of the abundances of elements in the solar system (Fig. 1.1), it is clear that H and He are the most abundant, and that, for the most part, element abundance decreases exponentially with increasing atomic number up to atomic number 50, and beyond that elements are quite rare.

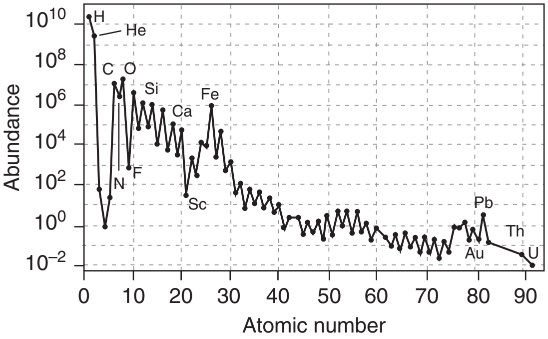

Fig. 1.1 Abundance of elements in the solar system normalized to Si = 10^6 on a logarithmic *y*-axis – this is a standard means of normalizing and plotting values for this type of data set.

It is also clear that some elements (e.g. Li, Be, B, Sc) appear to be anomalously uncommon as compared to their neighbors, whereas others seem to be present in anomalously high concentrations (e.g. Fe, Ni, Pb). It is also interesting to note the sawtooth pattern produced by alternation of relatively abundant even-numbered elements as compared to neighboring odd-numbered elements (a phenomenon described by the Oddo–Harkins rule). How do these observed trends relate to the processes that formed the elements? The answer lies in basic principles of nuclear fusion.

Elements larger than He were formed by fusion in stars in the first few million to hundreds of millions of years after the Big Bang by a process generally referred to as **stellar nucleosynthesis**. Gravitational forces had produced a contracting, spinning disc-like mass of primordial H and He known as the solar nebula that contained the energy necessary to form heavier elements by fusion as follows:

$$^{4}_{2}He + ^{4}_{2}He = ^{8}_{4}Be + \gamma \qquad (1.2)$$

$$^{4}_{2}He + ^{8}_{4}Be = ^{12}_{6}C + \gamma \qquad (1.3)$$

$$^{12}_{6}C + ^{12}_{6}C = ^{20}_{10}Ne + ^{4}_{2}He \qquad (1.4)$$

This process skipped over $_{3}Li$ and $_{5}B$ and the $^{8}_{4}Be$ that formed was very unstable and was either rapidly transformed to ^{12}C before it decayed (see middle reaction above) or was destroyed by radioactive decay.

Fusion was able to form elements up to iron ($^{56}_{26}Fe$), but beyond Fe no heat is produced during fusion – that is, the process is no longer exothermic when fusing nuclei heavier than Fe. In fact, the iron nucleus is so stable that fusion reactions involving iron actually consume energy (it is an endothermic process), so without the heat needed to fuel fusion reactions, another process had to take over to form the heavier elements. This process is known as neutron capture and can be represented like this:

$$^{56}_{26}\mathrm{Fe} + ^{1}_{0}\mathrm{n} = ^{57}_{26}\mathrm{Fe} \quad (1.5)$$

$$^{57}_{26}\mathrm{Fe} + ^{1}_{0}\mathrm{n} = ^{58}_{26}\mathrm{Fe} \quad (1.6)$$

$$^{58}_{26}\mathrm{Fe} + ^{1}_{0}\mathrm{n} = ^{59}_{26}\mathrm{Fe} \quad (1.7)$$

The Fe^{59} atom is unstable and undergoes spontaneous radioactive decay by beta emission as follows:

$$^{59}_{26}\mathrm{Fe} = ^{59}_{27}\mathrm{Co} + \beta^{-} \quad (1.8)$$

In this case, the negatively charged beta particle (sometimes written as $^{0}_{-1}e$ or e^{-}) effectively represents the transformation of a neutron ($^{1}_{0}\mathrm{n}$) to a proton ($^{1}_{1}\mathrm{p}$). Neutron capture combined with radioactive decay then formed progressively heavier elements up to the heaviest naturally occurring element, uranium. Some elements such as $^{56}\mathrm{Ni}$ and $^{56}\mathrm{Co}$ are unstable and undergo radioactive decay to form stable $^{56}\mathrm{Fe}$, helping to explain the relative abundance of Fe as compared to elements with similar atomic number.

Neutron capture (equations 1.5–1.7) takes place via two main mechanisms. The **r-process** ("r" is for rapid) takes place in core-collapse supernovae, where there is a high flux of neutrons and extremely high temperatures (e.g. $> 10^9$ K), and nucleosynthesis involves a rapid series of neutron capture reactions starting (typically) with $^{56}\mathrm{Fe}$ – the r-process explains the origin of ~50% of atoms heavier than Fe. The other main means by which heavy elements can be produced is known as the **s-process** ("s" is for secondary), in which nucleosynthesis occurs by means of slow neutron capture. The difference is that s-process neutron-capture nucleosynthesis occurs in asymptotic giant branch (AGB) stars, which have lower temperatures (e.g. 10^3–10^4 K) than supernovae, and thus the s-process requires pre-existing (hence the "secondary" nature) heavy isotopes that can function as seed nuclei.

Getting back to fusion, it is clear that progressive fusion reactions involving atoms with even numbers of protons will lead to the sawtooth pattern in Fig. 1.1, but there is also another contributing factor to this pattern. The **Oddo–Harkins rule** states that atoms with an even number of protons in their nuclei are more stable than their odd-numbered counterparts. This is because, during nucleosynthesis, nuclei with an unpaired proton were more likely to capture an additional proton, producing a more stable proton arrangement in the nucleus of atoms with even numbers of protons. For additional information on nucleosynthesis and the origin of the elements, the reader is referred to the accessible and more-detailed presentation in Gunter Faure's text *Principles and Applications of Geochemistry*.

As the universe continued to cool, galaxies and solar systems began to form. The solar nebula that was to form our solar system cooled and began to solidify into small masses known as chondrites and eventually larger masses known as planetesimals (on the order of tens of km in diameter). Those bodies closest to the early sun were more enriched in heavier elements (especially Si, Al, Mg, Fe, Ca, Na, K), in part because centrifugal forces effectively flung lighter elements (H, He) preferentially to the farther reaches of the solar system (other important influences include temperature, pressure, redox conditions and nebular density, but these factors that will not be covered here). The end result is that the inner planets are terrestrial and rocky (Mercury through Mars) and enriched in heavier elements, whereas the outer planets are gaseous (Jupiter and beyond) and enriched in lighter elements (think of the possibility of methane oceans or methane ice on Jupiter's moon Titan).

Planets ultimately formed when gravitational forces caused accretion of planetesimals. The accretion of what was to become Earth produced heat that left the proto-planet in a molten or semi-molten state and allowed relatively dense Fe and nickel (Ni) to sink to the **core of the Earth**, whereas relatively light silicon (Si), aluminum (Al), magnesium (Mg), calcium (Ca), sodium (Na) and potassium (K) floated to the top to form **Earth's crust**, leaving the Fe-Mg-Ni-Cr-Si **mantle** in between core and crust. While this is a broad generalization, the result is a differentiated Earth (Table 1.1), one where average continental crust (~ between 25–60 km thick) has a felsic composition much like that of granite, whereas oceanic crust (~ between 5 and 10 km thick) is compositionally mafic (or basic) and comprised mainly of basalt, rock that is less silica-rich and relatively enriched in Fe, Mg and Ca relative to continental crust. The mantle is comprised of rock types like peridotite and dunite and has an ultramafic (or ultrabasic) composition.

One example of how compositional differentiation of the Earth is important in an environmental sense is related to soils formed by weathering of rocks derived from the mantle – these ultramafic soils tend to be depleted in plant nutrients such as Ca and K, and enriched in the trace metals Ni and Cr (and in some places, arsenic). Finally, the primordial atmosphere of Earth was comprised of CO_2, H_2O and N gases derived from volcanic eruptions. Oxygen in its form as O_2 gas is a relatively

Table 1.1 Chemical differentiation of Earth with major elements and selected trace elements. Major elements (SiO_2 through P_2O_5) are presented in units of wt% oxides and the trace elements are presented in concentrations of parts per million (ppm, or mg/kg). Data sources are as follows: granite is the United States Geological Survey granite standard "G-2"; basalt and ultramafic data are averages from Turekian and Wedepohl (1961) and Vinogradov (1962); sandstone and carbonate rock data are unpublished analyses of early Paleozoic sedimentary rocks from northwestern Vermont performed by the author; and shale is the North American Shale Composite (Gromet et al., 1984). Trace element values with asterisks are averages from Turekian and Wedepohl (1961) and Vinogradov (1962). Additional resource include the text *The Continental Crust: Its Composition and Evolution* by Taylor and McLennan (1985) and the chapter by Rudnick and Gao (2003) in *Treatise on Geochemistry*.

	Granite	Basalt	Ultramafic	Sandstone	Shale	Carbonate
SiO_2	69.4	49.3	42.1	71.3	64.8	8.34
TiO_2	0.48	1.86	0.05	0.70	0.80	0.12
Al_2O_3	15.4	15.3	2.25	10.6	17.0	1.52
Fe_2O_3*	2.66	12.0	13.7	5.03	5.70	1.07
MnO	0.03	0.22	0.20	0.10	0.25	0.07
MgO	0.75	7.39	38.2	2.52	2.83	21.2
CaO	1.96	9.9	2.22	3.03	3.51	66.7
Na_2O	4.08	2.47	0.66	1.56	1.13	0.21
K_2O	4.48	0.98	0.02	4.61	3.97	0.55
P_2O_5	0.14	0.25	0.04	0.16	0.15	0.07
SUM	*99.4*	*99.7*	*99.4*	*99.7*	*100.1*	*99.8*
As	0.25	2.2	0.8	1.0	28	1.6
Ba	1880	315	0.7	595	636	99
Cr	10*	185	1800	20	125	10
Co	4.6	47	175	2.3	20*	3.6
Cu	11	94	15	2.5	45*	1.3
Ni	10*	150	2000	10.1	58	3.3
Pb	30	7	0.5	8.3	20*	2.8
Th	13*	3.5	0.005	4.4	12.3	0.54
U	3*	0.75	0.002	1.3	2.7	1.6
Zn	86	120	40	50	95*	13

recent addition to Earth's atmosphere, having begun to accumulate slowly and in a step-wise manner in the atmosphere after the appearance of photosynthetic algae 3 billion years ago.

1.3 ATOMS AND ISOTOPES: A BRIEF REVIEW

A schematic sketch of a carbon atom, consisting of a central positively charged nucleus surrounded by a negatively charged "cloud" of electrons, is presented in Fig. 1.2. All atoms consist of a nucleus that contains positively charged **protons** and neutral **neutrons**, subatomic particles with a mass of 1 atomic mass unit (1 amu, or 1 Dalton [Da]).

The actual mass of a proton is 1.6726×10^{-24} g, so it is more convenient to say that the mass of a proton is one amu or Da. The +1 charge on a proton = 1.602×10^{-19} coulomb. The number of protons in the nucleus is what distinguishes atoms of one element from another – hydrogen has 1 proton, helium has 2, carbon has 6, uranium has 92 protons, and so on. If there is a nucleus with some other number of protons than 92, it is not uranium. The number of protons is commonly referred to as the **atomic number** (Z).

The mass of a neutron is effectively the same as the mass of a proton (1 amu; 1.6749×10^{-24} g), and sum of protons and neutrons is the **atomic mass** or **mass number** or **atomic weight** – all are essentially synonymous terms, (see back inside cover for atomic weights chart). Virtually all of the mass of an atom is contained in its nucleus. The carbon atom in Fig. 1.2 contains a nucleus with 6 protons and 6 neutrons, a configuration represented in this text and in many other places as $^{12}_{6}C$. So, while the number of neutrons is not explicitly given in this notation, it is implied, and in the case of the most common form of uranium, $^{238}_{92}U$, there must be 146 neutrons in the nucleus along with 92 protons to produce the atomic mass of 238.

The carbon atom in Fig. 1.2 contains 6 protons and likely also contains 6 neutrons, but it could contain 7 or 8 neutrons. Differences in the number of neutrons (6, 7 or 8) give rise to the three **isotopes** of carbon. Carbon-12, or ^{12}C, is the most abundant isotope of carbon and it contains 6 neutrons; ^{13}C contains 7 neutrons and it is much rarer than ^{12}C (Chapter 10). ^{12}C and ^{13}C are both stable

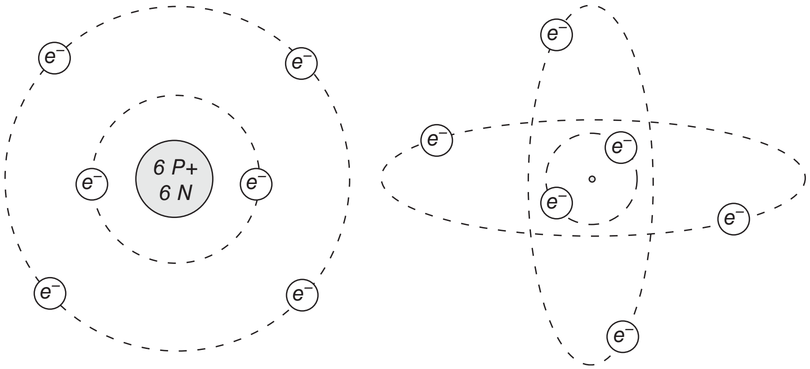

Fig. 1.2 Schematic sketches of Bohr models of a carbon atom (^{12}C) showing, on the left, 6 protons and 6 neutrons in the nucleus with 6 electrons in 2 separate orbitals, and on the right, an atom that attempts to show the actual size of the nucleus compared to the electron cloud, yet even here the nucleus is ~100 times larger than an actual nucleus. The example on the right also introduces the idea of separate orbitals in the outer electron "shell".

isotopes of carbon and the ratios of these two isotopes in plants, rocks, waters and sediments have proven very useful in environmental analysis. Carbon also has a **radioactive isotope**, ^{14}C, atoms of which are produced in the atmosphere in the presence of cosmic rays and ultimately undergo radioactive decay to nitrogen. This topic and many others in the field of isotope geochemistry are covered in Chapters 10 and 11.

Balancing the positive charge of the protons are **electrons** located in specified positions, or energy levels, outside of the nucleus. The charge on an electron is exactly opposite that of a proton – it is –1, or -1.602×10^{-19} coulomb, and neutrally charged atoms contain equal numbers of protons and electrons. Furthermore, while the "electron cloud" surrounding the nucleus is of a virtually negligible mass, it occupies a volume that is orders of magnitude larger than the volume of the nucleus (atoms are mostly open space).

For the purpose of this text and virtually all environmental geochemistry, the main concern to investigators is the outermost shell of electrons (the **valence shell**), because that is the part of the atom most intimately involved in bonding and ionization. Neutral atoms with atomic number (Z) < 20 contain somewhere between 1 and 7 electrons in their valence (outermost) shell; the noble gases Ne and Ar contain 8 valence-shell electrons. The most stable valence shell electron configuration for elements with Z < 20 is one that consists of 8 electrons, so all atoms with Z < 20 seek to produce ions or form bonds that result in eight valence electrons. This is done either by losing, gaining or sharing electrons (Section 1.6). In elements with Z > 20, the presence of d and f orbitals makes the **octet** rule inapplicable; nonetheless, heavier elements (Fe^{+2} and Fe^{+3}; Ni^{+2}; U^{+4} and U^{+6}) lose electrons in predictable manners to form more-stable configurations, and the forms of these ions are commonly known and enable prediction of their behaviors.

One convenient way to depict valence electrons is with **Lewis electron dot diagrams** (Fig. 1.3).

Fig. 1.3 Lewis electron dot diagrams showing valence electrons of sodium and oxygen in their ground states (left) and in the compound Na_2O (right), where each sodium has lost an electron to oxygen, resulting in two Na^+ and one O^{-2}.

Sodium, with one valence electron, and oxygen, with six, can be depicted as such:

Sodium satisfies the octet rule by losing an electron, becoming Na^{+1}. The neutral oxygen atom with six valence electrons can most easily satisfy the octet rule by gaining two electrons, producing O^{-2}, the most common form of oxygen in nature.

The **Aufbau principle** describes how electron orbitals are populated in a systematic manner. In brief, electrons occupy orbitals of fixed energy levels and tend to occupy the lowest energy levels possible to create a stable atom. Orbitals are filled in a relatively predictable, sequential manner, starting with the lowest quantum number ($n = 1$), for which there is only one orbital (the s-orbital) which can be occupied by two electrons (of opposite spin).

For a neutral hydrogen atom with only one electron the symbol is $1s^1$. For neutral He with 2 electrons, the notation is $1s^2$. Quantum number 2 ($n = 2$) contains both s- and p- orbitals, where the s-orbital again can be occupied by one electron pair and the p-orbital can host up to 3 electron pairs. For neutral lithium with 3 electrons, the notation is $1s^2\ 2s^1$. For neutral oxygen, the notation is $1s^2\ 2s^2\ 2p^4$. (to satisfy the octet rule, oxygen gains two electrons, producing O^{-2} with an electron configuration like that of neon: $1s^2\ 2s^2\ 2p^6$). The third quantum level ($n = 3$) contains s-, p- and d-orbitals, where the s- and p-orbitals can contain 1 and 3 electron pairs, respectively, and the d-orbital can host 5 electron pairs ($10e^-$s). However, the $3d$ orbital exists at a higher energy level than the 4 s orbital, so the 4 s orbital is filled before the $3d$.

The sequence in which these orbitals are filled is as follows:

$$1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p \rightarrow 5s \rightarrow 4d \rightarrow 5p \rightarrow 6s \rightarrow 4f \rightarrow 5d \rightarrow 6p \rightarrow 7s \rightarrow 6d$$

Two examples of larger atoms are calcium and iron. The notation for calcium is:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$. Note that the second and third quantum levels contain eight electrons, but that the fourth contains only two. What must calcium do to satisfy the octet rule when forming an ion? It loses two electrons, taking on an electron configuration like that of argon ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$) and becoming Ca^{+2}. The notation for iron is:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$ (26 electrons balance the 26 protons to produce a neutral Fe atoms). At this point the octet rule cannot be used to predict common oxidation states – iron tends to occur as Fe^{+2} or Fe^{+3} depending on redox conditions (more to come on redox later in this chapter).

1.4 MEASURING CONCENTRATIONS

Concentrations of elements or compounds are measured in a few common ways. Only in rare cases do scientists directly measure individual atoms/compounds, for even microscopic crystals of minerals at the micrometer scale such as hydroxides and silicate clays typically contain millions or billions of atoms.

1.4.1 Mass-based concentrations

One common means of measuring concentrations is by units such as milligrams per kilogram (mg/kg) for solids and milligrams per liter (mg/L) for liquids, or sometimes in units of micrograms (µg/kg or µg/L) or nanograms (ng/kg or ng/L) for trace elements. Note that mg/L = µg/mL. Weight percent is a common mass-based approach for expressing element concentration in cases where elements are in high concentrations (e.g. Table 1.1), a good example being Si, which comprises approximately 28% by weight (or mass) of the continental crust (or, as wt% oxide, approximately 59% of the crust – this conversion is presented below).

A few other useful facts to know about units of concentrations are:

For solids:

mg/kg is also known as parts per million (ppm), where mg is a milligram (10^{-3}g)
µg/kg is also known as parts per billion (ppb), where µg is a microgram (10^{-6}g)
ng/kg is also known as parts per trillion (ppt), where ng is a nanogram (10^{-9}g)

For liquids:

mg/L is also known as parts per million (ppm)
µg/L is also known as parts per billion (ppb)
ng/L is also known as parts per trillion (ppt)

Weight percent oxide is a common means of expressing major (abundant) elements in soils and rocks. Note in Table 1.1 that Si, Al, Fe and the other major elements are presented in units of SiO_2, Al_2O_3, Fe_2O_3 and so on. This is done partly by convention (or habit) and also because the major elements tend to occur in silicate minerals bonded to oxygen. The conversion factors for wt% element to wt% oxide for the common oxides are presented here in Table 1.2.

In the case of converting Ca to CaO, the conversion is determined as the molar mass of CaO divided by the molar mass of Ca, i.e. $56.08 \div 40.08 = 1.399$.

In the case of Al_2O_3, the conversion factor is determined as the molar mass of Al_2O_3 divided by the mass of the equivalent amount of Al in the oxide, i.e. $Al_2O_3 \div (2 * Al) = 101.957 \div (2 * 26.98) = 1.889$. For Na to Na_2O, the conversion is the molar mass of Na_2O divided by the molar mass of $2 * Na = 61.98 \div (2 * 22.99) = 1.348$.

For elements that can occur in more than one oxidation state (e.g. Fe^{+2}, Fe^{+3}), values may be

Table 1.2 Conversion factors for wt% element to wt% oxide.

Element	C.F.	Oxide
Al	1.889	Al_2O_3
Ca	1.399	CaO
Fe	1.286	FeO
Fe	1.430	Fe_2O_3
K	1.205	K_2O
Mg	1.658	MgO
Mn	1.291	MnO
Na	1.348	Na_2O
P	2.291	P_2O_5
Si	2.139	SiO_2
Ti	1.668	TiO_2

presented as either one of the oxidation states (i.e. either as FeO or Fe_2O_3), or as a combination of the two if the relative abundances of Fe^{+2} and Fe^{+3} are known. In many cases where iron oxidation state is not known, all iron is presented in terms of Fe_2O_3.

However, mass-based measurements like μg/L or wt% are not always the best way to express concentrations. Consider for example groundwater with 98.7 μg/L nickel (^{59}Ni) and 98.7 μg/L of uranium (^{238}U); i.e. both elements are present in equal concentrations of 98.7 ppb (evaporating the liter of water would leave 98.7 μg each of Ni and U). However, given that U atoms (238 g/mol) are ~4 times heavier than Ni (59 g/mol), there must be more Ni atoms – in fact, there are approximately four times as many Ni atoms as there are U atoms.

1.4.2 Molar concentrations

Quantifying concentrations on a molar basis has its roots in the work of Italian scientist Amadeo Avogrado, who in 1811 realized that equal volumes of gases at identical pressures and temperatures contain equal numbers of atoms (or molecules in the case of gases like N_2 and O_2), even though their atomic masses differed. The term **mole** (abbreviated mol) describes the number of atoms of a given element required to form a mass equal to the atomic mass of the substance, in grams. For C, this mass is 12.011 grams. For U, this mass is 238.03 g, and so on. For all elements, the number of atoms required to form the atomic mass in grams is 6.0221×10^{23} atoms, a value known as **Avogadro's number**. 238.03 g of uranium (1 mol of U) contains 6.0221×10^{23} atoms; 4.002 g of helium (1 mol of He) contains 6.0221×10^{23} atoms.

The mole is a very useful concept in chemistry – most equations are expressed in terms of moles of reactants and products. In order to express Ni and U concentrations in terms of moles per liter (mol/L), or for trace elements like these, μmol/L, the mass concentration must be multiplied by the inverse of the molar mass (and a conversion for g to μg) as follows:

$$\text{For Ni}: \quad 98.7 \mu g/L * 1\,\text{mol}/58.693\,\text{g} * 1\,\text{g}/10^6 \mu g = 1.68 \times 10^{-6}\text{mol/L}$$

$$\text{For U}: \quad 98.7 \mu g/L * 1\,\text{mol}/238.03\,\text{g} * 1\,\text{g}/10^6 \mu g = 0.415 \times 10^{-6}\text{mol/L}$$

It is often helpful to express units in easy to communicate terms, so in this case mol/L would probably be converted to micromoles per liter (μmol/L), by multiplying mol/L by 10^6 μmol/mol:

$$1.68 \times 10^{-6}\text{mol/L} * 10^6 \mu\text{mol/mol} = 1.68 \mu\text{mol/L of U in the groundwater}$$

$$0.415 \times 10^{-6}\text{mol/L} * 10^6 \mu\text{mol/mol} = 0.415 \mu\text{mol/L of Ni in the groundwater}$$

In a solid (e.g. sediment or rock) with 1 mol/kg each of Fe (55.85 g/mol) and Al (26.98 g/mol): (1) there is an equal number of atoms of Fe and Al in the soil; and (2) Fe comprises a greater mass of the soil than Al (whether expressed as wt%, g/kg or mg/kg). Given that mass units are a common way of expressing concentration, it may be necessary to convert from molar units to mass units. A few algebraic calculations allow conversion from mol/kg to 3 common units, g/kg, mg/kg and wt%.

Given that 1 mol of Fe = 55.85 g:
55.85 g/mol * 1 mol/kg = 55.85 g/kg Fe
...***or*** 55.85 g/kg * 1000 mg/g = 55850 mg/kg Fe
... ***or*** 55.85 g/kg * 0.1 = 5.855% Fe (by weight)

1 mol of Al = 27 g; 27 g/mol * 1 mol/kg = 27 g/kg Al
... ***or*** 26.98 g/kg * 1000 mg/g = 26980 mg/kg Al
... ***or*** 26.98 g/kg * 0.1 = 2.698% Al (by weight)

1.4.3 Concentrations of gases

Atmospheric gas concentrations are typically expressed as the proportion of the total volume accounted for by a given gas. For example, the current atmospheric concentration of CO_2 is ~400 ppmv, indicating that 400 out of every one million molecules of gas in Earth's atmosphere is CO_2. At the onset of the industrial revolution atmospheric CO_2 was 280 ppmv. Less-abundant gases are often expressed in terms of ppbv or pptv (parts per billion or trillion, volumetrically), and the major components of the atmosphere like the fixed gases N_2, O_2 and Ar, are expressed in terms of percent (by vol): $N_2 = 78.1\%$, $O_2 = 20.9\%$ and $Ar = 0.9\%$ (the amounts vary depending on the amount of H_2O vapor in the air, which can range from 0 to 4% by volume). Expressed in this way, CO_2 comprises approximately 0.0400% percent of the atmosphere (vol%), but clearly units of ppmv are more useful for a gas like CO_2. Gases also dissolve in liquids, and units of concentration in these cases are commonly mg/L or mmol/L.

1.4.4 Notes on precision and accuracy, significant figures and scientific notation

A few important topics related to data analysis and presentation of results are encompassed by the concepts of precision and accuracy. Simply stated, **accuracy** describes how closely a measured value agrees with the actual value. The accuracy of chemical analyses can be tested by analyzing standards of known concentration. Consider a certified standard solution that contains 250 mg/L of aluminum (Al), and five analyses of this standard on your spectrometer produces results of 237, 271, 244, 262, and 240 mg/L. The mean of those five values is 251 mg/L – the average value is very close to the certified value of 250 mg/L. One way to express the accuracy of this test is as a percent difference from the certified value:

$$[(251\ \text{mg/L} - 250\ \text{mg/L}) \div 250\ \text{mg/L}] * 100 = 0.4\%$$

However, the five results are somewhat lacking in **precision**, which is basically a measure of the reproducibility of results – how closely do measured results agree with each other? It is conceivable to produce results with a high degree of precision that are lacking in accuracy. For example, after recalibrating the spectrometer and re-analyzing the Al standard, values now are 277, 281, 274, 278 and 275 mg/L. The mean value of 277 mg/L is farther from the certified value of 250 mg/L (the difference from the certified value is 10.8%), but the results are definitely more precise.

One way to calculate uncertainty is to determine the standard deviation of the data. The formula for standard deviation and details on its appropriate use can be found in a statistics textbook, but using Microsoft Excel's standard deviation formula produces σ values as follows:
For the values 237, 271, 244, 262 and 240 mg/L, $\sigma = 14.9$
For the values 277, 281, 274, 278 and 275 mg/L, $\sigma = 2.74$
Which are better, analyses with greater accuracy but less precision (251 + 14.9 mg/L), or greater precision but less accuracy (277 + 2.74 mg/L)? Precise values are easier to correct because there is less uncertainty than if you have to deal with

accurate values plagued by low precision. This emphasizes one of the reasons why it is important to run standards when making analytical measurements. Of course, the ideal situation is to use a well-calibrated instrument for which accuracy and precision are both high, but regardless, it is imperative that researchers seek to quantify both parameters when making measurements.

In addition to quantifying uncertainty, it is very important to present numerical results in a manner that relates to the sensitivity of the measurement, or the degree of confidence associated with that measurement, while also trying to avoid propagation of error. Every measurement has some limited number of **significant digits** (or **significant figures**). Measurements of pH made using litmus paper can only be reported to 1 significant figure (e.g. pH = 6), whereas measurements made with well-calibrated probes may be reported to 3 significant figures (e.g. pH = 5.87).

As a rule, calculations should be carried out using all figures with each of their representative significant figures, and then the final result should be rounded at the end of the calculation. Using an example where the average concentration of uranium in groundwater in an aquifer is 14.3 μg/L, the aquifer volume is 1.241×10^8 m^3 and average porosity (and thus % water in the saturated zone) is 18%, the resulting mass of U in the aquifer is:

$$14.3\mu g/\mathrm{L} * 1.241 \times 10^8 \mathrm{m}^3 * 1000\,\mathrm{L/m}^3 * 0.018 = 3.2 \times 10^{11} \mu g\,\mathrm{U}$$

The final result is limited by the two significant figures in 18% (note that conversions involving liters to cubic meters, cm^3 to mL, etc. do not limit sig figs).

Also important to understand is the significance of zeros. Consider the following values: 7200, 700043, 0.0436, 0.043600. How many significant figures are reported for each, and why?

- 7200 is assumed to have 2 significant figures because any zero at the end of a number *and before a decimal point* is assumed to not be significant. How many significant figures does 847 000 possess? Three. 7200.0 contains 5 significant figures.
- 700 043 has 6 sig figs. Any zeros within a number are significant.
- 0.0436 has 3 sig figs because any zeros after a decimal point and before the first non-zero digit are not significant.
- 0.043600 has 5 significant figures because zeros that follow a non-zero digit after a decimal point are considered significant (as in 7200.0 example above).

Some of these examples serve to illustrate why scientists tend to express values in terms of **scientific notation**. Using scientific notation, the values above become:

7.2×10^3 (2 sig figs)
7.2000×10^3 (if we needed to report 7200 to 5 sig figs, this is how it would look)
7.00043×10^5 (6 sig figs)
4.36×10^{-2} (3 sig figs)
4.3600×10^{-2} (5 sig figs)

As a closing thought, one has to wonder about the precision of the road sign in southwestern Ecuador shown in Fig. 1.4. Being literal about significant figures, the distance to Engunga is precisely indicated as being between 14995 and 15005 m. (note: it is a very small town, so the precision may be justified).

1.5 PERIODIC TABLE

The Periodic Table of the Elements (front inside book cover) is one of the most useful tools to researchers and students of chemistry, geochemistry and biochemistry. First fully developed by the Russian chemist Dmitri Mendeleev in 1869 and refined ever since, it lists elements in order of atomic mass (from left to right in each row, and also from top to bottom in each column) and

Fig. 1.4 Road sign in southwestern Ecuador.

by similarities in chemical properties. Row 3 of the periodic table begins with sodium (atomic number $Z = 11$) and progresses to the right with increasing Z all the way up to Ar ($Z = 18$).

The atomic mass for each element represents a weighted average of the mass of the isotopes of that element, normalized to ^{12}C – observe that the atomic mass of sulfur (S, with $Z = 16$) is 32.065, reflecting weighted average of ^{32}S and heavier isotopes. The S atomic mass of 32.065 is derived from the abundances of the four stable S isotopes as is demonstrated in the following mass-balance calculation (data from Faure, 1986):

$$^{32}S = 95.02\% \quad ^{33}S = 0.75\% \quad ^{34}S = 4.21\% \quad ^{36}S = 0.02\%$$

$$\begin{aligned}
^{32}S &: 0.9502 * 31.97 = 30.377894\\
^{33}S &: 0.0075 * 32.97 = 0.247275\\
^{34}S &: 0.0421 * 33.97 = 1.430137\\
^{36}S &: 0.0002 * 35.97 = \underline{0.007194}\\
&\qquad \text{Sum} = 32.062500
\end{aligned}$$

Atomic masses are sometimes regarded as dimensionless numbers, but are also expressed in terms of amu (Daltons) and also in terms of gram molecular weights (i.e. the gram molecular weight, or mass of one gram of sulfur, is 32.065 g). All atomic masses are normalized to the mass of ^{12}C, and this is why the mass of ^{32}S is expressed as 31.97 g/mol.

Columns (or groups) of elements generally contain elements with similar valence electron configurations, that is, the outermost shell of electrons tends to behave in a similar manner for elements of a given row. Good examples are column 1, the alkali metals, all of which lose one electron when they form chemical bonds, resulting in a series of +1 charged ions including Na^+ and K^+; column 2, the alkaline-earth metals that form divalent cations (e.g. Ca^{+2}); and column 8, the noble gases, including elements like argon and neon with complete valence shells (as a result, they do not form chemical bonds in nature). Elements in column 7, the halogens, tend to gain one electron when forming chemical bonds, resulting in halide anions with a –1 charge (e.g. Cl^-).

It may not come as a surprise that alkali metals tend to form bonds with halides, such as:

$$Na^+ + Cl^- \rightarrow NaCl \tag{1.9}$$

The point to understand here is that the periodic table presents information in a systematic way that can help to predict the behavior of elements in environmental systems. Like Na^+, K^+ also can form bonds with chloride (Cl^-) to form a different salt, KCl (a substitute for NaCl in reduced-sodium diets). In fact, K^+ and Na^+ substitute for one another in many minerals. The periodic table also implies that arsenic (As) might substitute for phosphorous (P) in mineral structures, which it does.

In 2003, the environmental geochemist Bruce Railsback from the University of Georgia developed an innovative new periodic table for geologists known as *An Earth Scientist's Periodic Table of the Elements and Their Ions*, one where elements are organized according to their occurrences in geological environments (http://www.gly.uga.edu/railsback/PT.html). This new formulation is designed to predict how elements and ions behave in the environment. Unlike the conventional periodic table originally envisioned by Mendeleev, the Earth scientist's periodic table organizes elements by charge, so it shows many elements multiple times because many elements have numerous valence states. It also contains abundant information on abundance of different elements in soils, seawater, mantle vs. crust, ionic radii in crystals, and much more. For example, Fig. 1.5 shows the relative solubilities of oxides of various ions, and from this inset it is apparent that Al and Ti form insoluble oxides (corundum, Al_2O_3; rutile, TiO_2) but that Na, K, N and S do not (they are more likely to occur as soluble ions such as Na^+, K^+, NO_3^- and SO_4^{-2}).

The Earth scientist's periodic table also shows the numerous species of nitrogen that exist in natural systems (e.g. valence states and common molecules of N), predicted behaviors, attributes and affinities of the abundant and trace cations in natural systems, and more (Railsback, 2003).

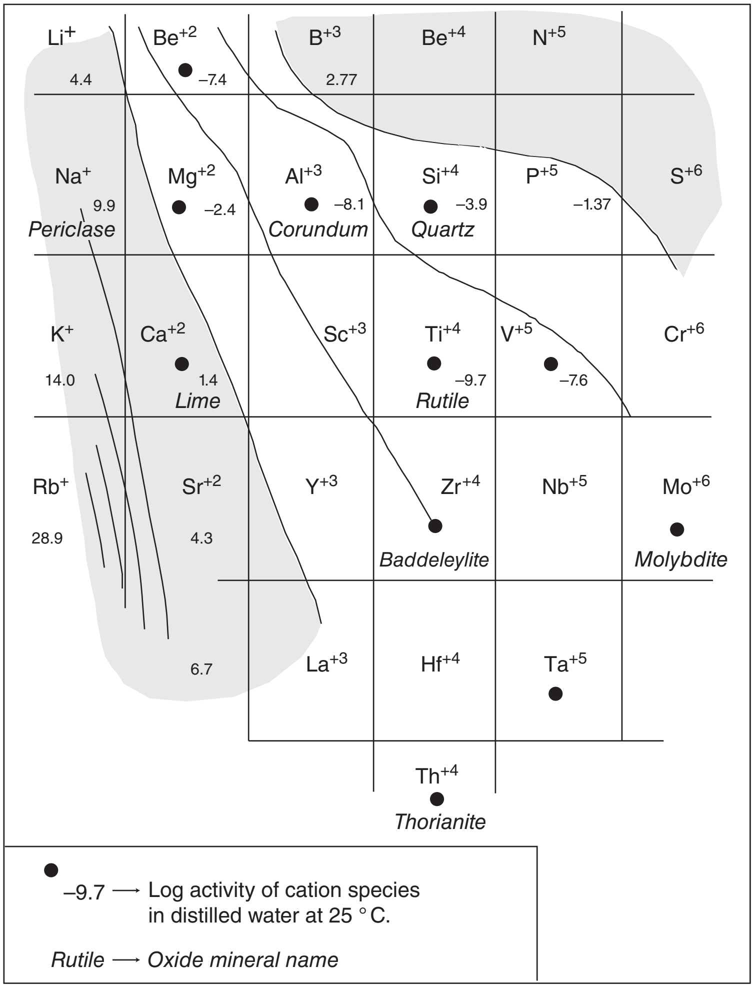

Fig. 1.5 Solubilities of ions as a function of ionic charge, from Inset 4 of *An Earth Scientist's Periodic Table of the Elements and Their Ions* (Railsback, 2003). Oxides of the elements are used as reference (e.g. lime, periclase, etc.). Note that low-charge base cations/alkali metals and cations of the alkaline Earth metals are relatively soluble, as are high-charge cations such as S^{+6} and N^{+5}, which form polytatomic anions (SO_4^{-2}, NO_3^-). Cations with +3 and +4 charges (e.g. Al^{+3}, Ti^{+4}, Zr^{+4}) are insoluble in most surficial environments, with activities in H_2O at 25 °C of $\sim 10^{-8}$ to 10^{-10}. (Railsback 2003.)

1.6 IONS, MOLECULES, VALENCE, BONDING, CHEMICAL REACTIONS

It is relatively rare to find elements in their native, neutral state in nature. A few examples include the diatomic gases hydrogen (H_2), oxygen (O_2) and nitrogen (N_2), solids like gold (Au) and graphite and diamond (both forms of C), and the noble gases (He, Ne, Ar, etc.). Most elements occur as ions, molecules or compounds in liquids (petroleum, alcohols, H_2O and the dissolved species it contains), solids (minerals, proteins, humus), and gases (CO_2, CH_4, NO_2). **Ions** are charged atoms, atoms that have either gained or lost one or more electrons from their neutral state. Examples of ions include the cation Na^{+1} and the anion S^{-2}. Most of the elements form cations, because metals generally lose electrons to form cations, and most of the elements are metals. A few common metal cations are Mg^{+2}, Al^{+3}, $Cr^{+3,+6}$, $Fe^{+2,+3}$ – note that some elements have more than one oxidation state. Generally only those elements in the upper right of the periodic table form anions (e.g. O^{-2}, N^{-3}, F^{-1}, etc). **Oxidation state** is a term for the charge on an ion: "the oxidation state of iron in swamps is generally +2 (divalent), whereas in streams iron tends to occur in the +3 (trivalent) oxidation state".

Molecules are formed when two or more atoms are joined by a chemical bond, and **compounds** are a specific type of molecule formed when two or more atoms of *different* elements are joined by chemical bonds. The gases H_2, O_2 and N_2 are comprised of molecules but they are not compounds (they are diatomic gases). Examples of compounds include NaCl, H_2O and C_8H_{18} (octane). Most substances in nature, other than some gases and a few metals, are compounds.

There are two main types of **chemical bonds** responsible for forming molecules and compounds, ionic bonds and covalent bonds. These two bond types represent polar ends of the bonding spectrum, but it is useful to consider each type separately, and then examine intermediate cases. We will also examine metallic bonds and Van de Waals bonds, but first will begin with ionic bonds.

Ionic bonding occurs between atoms of elements with very different valence electron configurations. Coulomb forces describe interactions between charged atoms or molecules (i.e. ions), and when the charges are opposite (i.e. involving cations and anions), the result is attraction (conversely, the Coulombic interaction between like-charged particles, e.g. 2 cations, causes repulsion).

The classic example of Coulombic attraction is the bond between an alkali metal cation (e.g. Na^+) and a halogen anion (e.g. Cl^-). The cation and anion are electrostatically attracted to each other and the result is formation of an ionic bond producing a solid, in this case cubic vitreous crystals of halite (NaCl).

Loss of an electron by sodium and its incorporation into the valence shell of chlorine can be viewed in the sense of a Lewis electron-dot diagram (Fig. 1.6):

The way this type of bond commonly forms in the natural world is when sodium and chloride ions are dissolved in water and ultimately become attracted to each other when their concentrations become sufficiently high to allow formation of solid crystals. (More details about the controls on aqueous processes are covered in detail in Chapters 4, 5, and 9).

1.6.1 Ionic bond strength

The strength of an ionic bond is largely controlled by the charges on the ions and by the ionic radii of the ions involved in the bonding – this is a concept that should be intuitively apparent because ions with higher (opposite) charges will be attracted

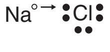

Fig. 1.6 Schematic representation of formation of an ionic bond by transfer of the Na valence electron to Cl.