

## CHAPTER 7: TRACE ELEMENTS

$\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$  (and  $\text{H}_2\text{O}$ , of course) can be considered a trace constituent, though  $\text{Sr}^{2+}$ ,  $\text{HBO}_3^-$ , and  $\text{Br}^-$  are sometimes considered major constituents also (constituents or species is a better term here than elements). These, including the last three, constitute over 99.99% of the total dissolved solids in seawater. Trace elements in seawater and in rocks do have one thing in common: *neither affect the chemical or physical properties of the system as a whole to a significant extent*. This might serve as a definition. However, trace (or at least minor) elements can determine the color of a mineral (e.g., the green color of chrome diopside), so even this definition has problems. And  $\text{CO}_2$ , with a concentration in the atmosphere of only 360 ppm, profoundly affects the transparency of the atmosphere to infrared radiation, and, as a result, Earth's climate. At even lower concentrations, ozone in the upper atmosphere controls the atmospheric transparency to ultraviolet radiation. So this definition is not satisfactory either.

Yet another possible definition of a trace element is: *an element whose activity obeys Henry's Law in the system of interest*. This implies sufficiently dilute concentrations that for trace element A and major component B, A-A interactions are not significant compared to A-B interactions.

There is perhaps no satisfactory quantitative definition of a trace element that will work in every situation. For our present purposes, any of these definitions might do, but bear in mind that a trace element in one system need not be a trace element in another.

## 7.2 BEHAVIOR OF THE ELEMENTS

### 7.2.1 Goldschmidt's Classification

No matter how we define the term "trace element", most elements will fall into this category, as is illustrated in Figure 7.1. That being the case, this is a good place to consider the geochemical characteristics of the elements. Goldschmidt\* recognized four broad categories: atmophile, lithophile, chalcophile, and siderophile (Figure 7.2, Table 7.1). *Atmophile* elements are generally extremely volatile (i.e., they form gases or liquids at the surface of the Earth) and are concentrated in the atmosphere and hydrosphere. *Lithophile*, *siderophile* and *chalcophile* refer to the tendency of the element to partition into a silicate, metal, or sulfide *liquid* respectively. *Lithophile* elements are those showing an affinity for silicate phases and are concentrated in the silicate portion (crust and mantle) of the earth. *Siderophile* elements have an affinity for a metallic liquid phase. They are depleted in the silicate portion of the earth and presumably concentrated in the core. *Chalcophile* elements have an affinity for a sulfide liquid phase. They are also depleted in the silicate earth and may be concentrated in the core. Many sulfide ore deposits originated from aqueous fluids rather than sulfide liquid. A chalcophile element need not necessarily be concentrated in such deposits. As it works out, however, they generally are. Most elements that are siderophile are usually also somewhat chalcophile and visa versa.

There is some basis for Goldschmidt's classification in the chemistry of the elements. Figure 7.2 shows that the lithophile elements occur mainly at either end of the periodic table, siderophile elements are mainly group 8, 9 & 10 elements (and their neighbors), chalcophile elements are mainly group 11, 12 and the heavier group 13-16 elements, while the atmophile elements are mainly the noble gases. The distribution of the electropositive elements (those that give up an electron more readily than they accept one) among metal, sulfide, and silicate phases is controlled by the free energies of formation of the corresponding sulfides and silicates. By comparing the free energies of formation with those of ferrous

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\* Victor Goldschmidt (1888-1947) is often considered the 'father of geochemistry'. Goldschmidt earned a Ph.D. from the University of Oslo in 1911 and remained there until 1929, when he assumed the directorship of the Geochemisches Institut at the University of Göttingen. Because of the worsening political situation in Germany, he returned to Oslo in 1935. He was for a time imprisoned in a concentration camp after Germany invaded Norway in 1940. In 1942 he fled to Sweden and eventually to England. He returned to Oslo in 1946 but never fully recovered from the effects of imprisonment and died a year later. The Geochemical Society has named its most prestigious medal after him and co-sponsors, along with the European Association of Geochemistry, annual Goldschmidt Conferences.

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TABLE 7.1. GOLDSCHMIDT'S CLASSIFICATION OF THE ELEMENTS

Siderophile	Chalcophile	Lithophile	Atmophile
Fe*, Co*, Ni*	(Cu), Ag	Li, Na, K, Rb, Cs	(H), N, (O)
Ru, Rh, PdZn, Cd, Hg	Be, Mg, Ca, Sr, Ba	He, Ne, Ar, Kr, Xe	
Os, Ir, Pt	Ga, In, Tl	B, Al, Sc, Y, REE	
Au, Re <sup>†</sup> , Mo <sup>†</sup>	(Ge), (Sn), Pb	Si, Ti, Zr, Hf, Th	
Ge*, Sn*, W <sup>‡</sup>	(As), (Sb), Bi	P, V, Nb, Ta	
C <sup>‡</sup> , Cu*, Ga*	S, Se, Te	O, Cr, U	
Ge*, As <sup>†</sup> , Sb <sup>†</sup>	(Fe), Mo, (Os)	H, F, Cl, Br, I	
	(Ru), (Rh), (Pd)	(Fe), Mn, (Zn), (Ga)	

\*Chalcophile and lithophile in the earth's crust

<sup>†</sup>Chalcophile in the earth's crust

<sup>‡</sup>Lithophile in the earth's crust

sulfide and ferrous silicate, it is possible to deduce which elements are siderophile, those which are chalcophile and which are lithophile. For historical reasons, namely lack of  $\Delta G_f^\circ$  data on silicates, the point is generally illustrated using the enthalpy of formation,  $\Delta H_f$ , of the oxide. Since 'oxyphile' could arguably be a better term than lithophile, this is not such a bad thing. Table 7.2 gives some examples. Elements whose oxides have high  $-\Delta G_f$  are lithophile. Why this is the case should be clear from our understanding of thermodynamics. States with the lowest free energy are the most stable: a high  $-\Delta G_f$  indicates the oxide is much more stable than the metal. Elements whose oxides have  $-\Delta G_f$  similar to that FeO combine with oxygen only about as readily as Fe, and are generally siderophile. Those elements whose oxides have low  $|\Delta G^\circ|$  are generally chalcophile.

Lithophile elements also have either very low electronegativities or very high ones and tend to form ionic bonds (although the basic silicate bond, the Si—O bond, is only about 50% ionic, metal–oxygen bonds in silicates are dominantly ionic). Siderophile and chalcophile elements have intermediate electronegativities and tend to form covalent or metallic bonds.

## 7.2.2 THE GEOCHEMICAL PERIODIC TABLE

Goldschmidt's classification is relevant mainly to distribution of elements in meteorites and to how elements distribute themselves between the Earth's major geochemical reservoirs: the core, the mantle and crust, and the hydrosphere and atmosphere. Since there is an overabundance of O in the outer part of the Earth, metallic liquids do not form, and siderophile elements have little opportunity to behave as such. Similarly, sufficient S is rarely available to form more than trace amount of sulfides. As a result, siderophile elements such as Ni and chalcophile elements such as Pb occur mainly in silicate phases in the crust and mantle.

We can, however, group the elements based on how they behave in the silicate portion of the Earth, the mantle and crust. Figure 7.3 illustrates this grouping. We first note that we have added sodium to those 6 elements whose molar abundance exceeds 1 percent (Figure 1), to form the group called major elements, and which we will not discuss in this chapter. Although the elements K, Ti, Mn, and P are often reported in rock analyses as major elements, we will include them in our discussion of trace elements. Let's now briefly examine the characteristics of the remaining groups.

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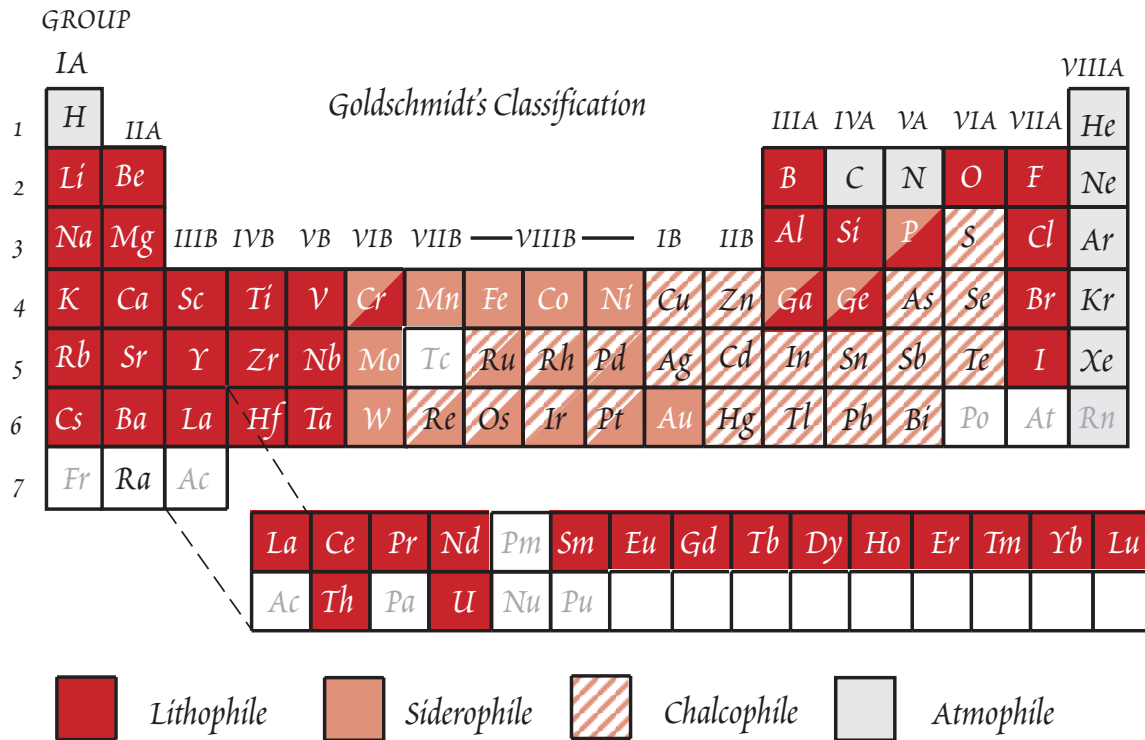


Figure 7.2. Goldschmidt's classification of the elements.

7.2.2.1 THE VOLATILE ELEMENTS

The defining feature of the noble gases is their filled outer electron shell, making them chemically inert as well as volatile. Hence, they are never chemically bound in rocks and minerals. Furthermore, except for He, they have rather large radii and cannot easily be accommodated in either cationic or anionic lattice sites of many minerals. Thus they are typically present at very low concentrations. Their concentrations are usually reported in STP cm<sup>3</sup>/g at (i.e., cm<sup>3</sup>/g at standard temperature and pressure: 273 K and 01.MPa; 1 cm<sup>3</sup>/g = 4.46 × 10<sup>-5</sup> moles/g). Concentrations in silicate rocks and minerals are

TABLE 7.2. FREE ENERGY OF FORMATION OF SOME OXIDES

Oxide	-ΔG <sub>f</sub> <sup>o</sup> (kJ/mole/oxygen)	Oxide	-ΔG <sub>f</sub> <sup>o</sup> (kJ/mole/oxygen)
CaO	604.0	In <sub>2</sub> O <sub>3</sub>	304.2
ThO <sub>2</sub>	584.6	SnO <sub>2</sub>	260.0
MgO	569.4	FeO	245.9
Al <sub>2</sub> O <sub>3</sub>	527.3	WO <sub>3</sub>	247.3
ZrO <sub>2</sub>	521.6	CdO	221.9
CeO <sub>2</sub>	512.6	NiO	211.6
TiO <sub>2</sub>	444.7	MoO <sub>3</sub>	215.4
SiO <sub>2</sub>	428.1	Sb <sub>2</sub> O <sub>3</sub>	207.9
Na <sub>2</sub> O	398.3	PbO	189.3
Ta <sub>2</sub> O <sub>3</sub>	374.0	As <sub>2</sub> O <sub>3</sub>	180.1
MnO	362.8	Bi <sub>2</sub> O <sub>3</sub>	168.8
Cr <sub>2</sub> O <sub>3</sub>	353.1	CuO	127.6
ZnO	318.4	Ag <sub>2</sub> O <sub>3</sub>	10.9

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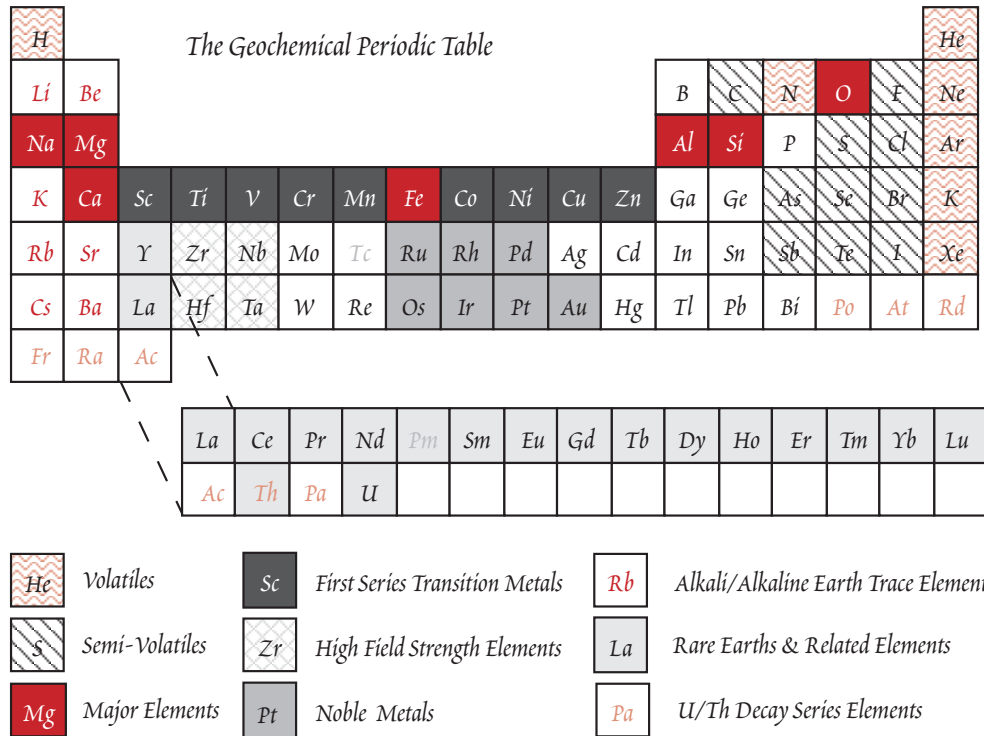


Figure 7.3. The Geochemical Periodic Table, in which elements are grouped according to their geochemical behavior.

typically  $10^{-4}$  to  $10^{-12}$  STP  $\text{cm}^3/\text{g}$  ( $10^{-1}$  to  $10^{-9}$  ppm). Their solubility in silicate melts is a strong function of pressure, as well as both atomic radius and melt composition as is illustrated in Figure 7.4. Although they cannot form true chemical bonds with other atoms, they can be strongly adsorbed to crystal surfaces through van der Waals forces.

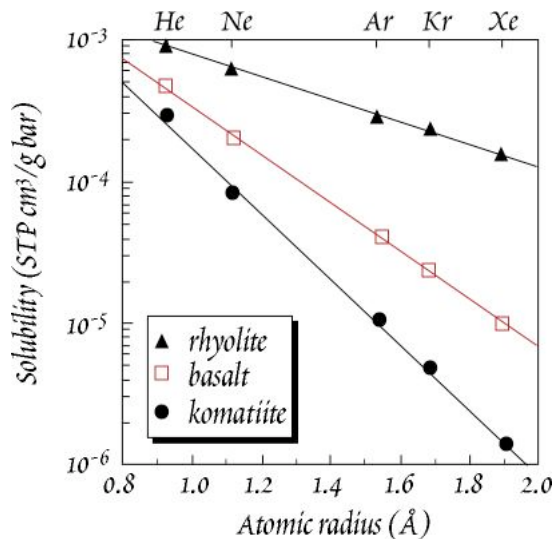


Figure 7.4. Solubility of the rare gases in melts of varying composition at 1200° to 1400° C. Solubility is a strong function of atomic radius and melt composition, but only a weak function of temperature. From Carroll and Draper (1994).

The very strong nature of the N-N bond makes nitrogen relatively unreactive once molecular nitrogen forms; consequently it, like the rare gases, is strongly partitioned into the atmosphere. However, it is quite capable of forming strong covalent bonds with other elements. In silicate minerals, N is probably primarily present as the ammonia ion rather than  $\text{N}_2$ . As such, it readily substitutes for  $\text{K}^+$ . As ammonia, it is highly soluble in aqueous fluids and is therefore readily transported by them. Ammonia, like  $\text{N}_2$ , is quite volatile, so both species partition readily into the gas phase of magmas. In aqueous solution, nitrogen will be present as nitrate (and trace amounts of ammonia, produced by breakdown of nitrogen-bearing organic compounds), as well as  $\text{N}_2$ . Nitrogen is a component of proteins and nucleic acids and as such is vital to all organisms. However, most plants can utilize only “fixed” nitrogen, that is nitrate or ammonia. In many natural waters, nitrate concentrations are held at very low concentrations because of biological utilization.

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## 7.2.2.2 THE SEMI-VOLATILES

The shared characteristic of this group is that they partition readily into a fluid or gas phase (e.g., Cl, Br) or form compounds that are volatile (e.g.,  $\text{SO}_2$ ,  $\text{CO}_2$ ). Not all are volatile in a strict sense (volatile in a strict sense means having a high vapor pressure or low boiling point; indeed, carbon is highly refractory in the elemental form).

The partitioning of sulfur between liquid and gas phases is a strong function of  $f_{\text{O}_2}$ . At high oxygen fugacities, sulfur is present primarily as  $\text{SO}_2$ , but at low  $f_{\text{O}_2}$  it is present primarily as sulfide. The solubility of sulfide in silicate liquids is, however, low. At sufficiently high sulfur concentrations in magmas, sulfide and silicate liquids will exsolve. Sulfide liquids are rich in Fe and Ni and other chalcophile metals and are the source of many economically important ore deposits. Large volumes of sulfide liquid are rare, but microscopic droplets of sulfide liquids commonly occur in mid-ocean ridge magmas.

Similarly, the solubility of  $\text{CO}_2$  in silicate magmas is limited and is a strong function of pressure. At low  $\text{CO}_2$  concentrations,  $\text{CO}_2$  exsolves from magmas to form a  $\text{CO}_2$ - $\text{H}_2\text{O}$  gas phase. However, at higher  $\text{CO}_2/\text{H}_2\text{O}$  ratios and total  $\text{CO}_2$  concentrations, carbonatite magmas can form in which  $\text{CaCO}_3$  is the dominant component. On the whole, carbonatites are rare, but over the course of geologic history they have erupted on every continent. In certain localities, such as the modern East Africa Rift, they can be fairly common.

The remaining elements in this group are always present in trace concentrations and never reach saturation in magmas and hence never exsolve as independent gas or fluid phases. Rather, they partition into gas phase formed by exsolution of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

## 7.2.2.3 THE ALKALI AND ALKALINE EARTH ELEMENTS

The alkali and alkaline earth elements have electronegativities less than 1.5 and a single valence state (+1 for the alkalis, +2 for the alkaline earths). The difference in electronegativity between these elements and most anions is 2 or greater, so the bonds these elements form are strongly ionic in character (Be is an exception, as it forms bonds with a more covalent character). Ionic bonds are readily disrupted by water due to its polar nature (see Chapter 3). The low ionic potential (ratio of charge to ionic radius) makes these elements relatively soluble in aqueous solution. Because of their solubility, they are quite mobile during metamorphism and weathering.

Because bonding is predominantly ionic, the atoms of these elements behave approximately as hard spheres containing a fixed point charge at their centers (these are among the group A or hard ions discussed in Chapter 6). Thus the factors that most govern their behavior in igneous rocks are *ionic radius and charge*. K, Rb, Cs, Sr, and Ba, are often collectively termed the *large-ion-lithophile (LIL) elements*. As the name implies, these elements all have large ionic radii, ranging from 118 picometers (pm) for Sr to 167 pm for Cs. The major minerals in basaltic and ultramafic rocks have two kinds of cationic lattice sites: small tetrahedral sites occupied by Si and Al (and less often by  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$ ) and larger octahedral ones usually occupied by Ca, Mg, or Fe and more rarely by Na. The ionic radii of the heavy alkali and alkaline earth elements are larger than the radii of even the larger octahedral sites. As a result, substitution of these elements in these sites results in local distortion of the lattice, which is energetically unfavorable. These elements thus tend to be concentrated in the melt phase when melting or crystallization occurs. Such elements are called *incompatible elements*. Incompatible elements are defined as those elements that partition readily into a melt phase when the mantle undergoes melting. Compatible elements, conversely, remain in the residual minerals when melting occurs. Over the history of the Earth, partial melting of the mantle and eruption or intrusion of the resulting magmas on or in the continental crust has enriched the crust in incompatible elements.

In contrast to the heavy alkaline earths, Be has an ionic radius smaller than most octahedral sites. Substitution of a small ion in a large site is also energetically unfavorable as the bond energy is reduced. Thus Be is also an incompatible element, though only moderately so. While Li has an ionic radius similar to that of Mg and  $\text{Fe}^{2+}$ , its substitution for one of these elements creates a charge imbalance that requires a coupled substitution. This is also energetically unfavorable, hence Li is also an incompatible element, though again only moderately so.

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## 7.2.2.4 THE RARE EARTH ELEMENTS AND Y

The rare earths are the two rows of elements commonly shown at the bottom of the periodic table. The first row is the *lanthanide* rare earths, the second is the *actinide* rare earths. However, the term “rare earths” is often used in geochemistry to refer to only to the lanthanide rare earths. We will follow that practice in this book, though we will discuss both the actinide and lanthanides in this section. Only two of the actinides, U and Th, have nuclei stable enough to survive over the history of the Earth. Y shares the same chemical properties, including charge and ionic radius, as the heavier rare earths, and as a result behaves much like them.

As the alkalis and alkaline earths, the rare earths and Y are strongly electropositive; the lanthanide have electronegativities of 1.2 or less, the actinides U and Th have slightly higher electronegativities. As a result, they form predominantly ionic bonds, and the hard charged sphere again provides a good model of their behavior. The lanthanide rare earths are in the +3 valence state over a wide range of oxygen fugacities. At the oxygen fugacity of the Earth’s surface, however, Ce can be partly or wholly in the +4 state and Eu can be partly in the +2 state at the low oxygen fugacities of the Earth’s interior. Th is always in a +4 valence state, but U may be in a +4 or +6 valence state, depending on oxygen fugacity (or  $p_e$ , if we chose to quantify the redox state that way). Unlike the alkali and alkaline earth elements, they are relatively insoluble in aqueous solutions, a consequence of their higher charge and high ionic potential and resulting need to be coordinated by anions. The one exception is U in its fully oxidized  $U^{6+}$  form, which forms a soluble oxyanion complex,  $UO_2^{2-}$ .

The rare earths are transition metals. In the transition metals, the *s* orbital of the outermost shell is filled before filling of lower electron shells is complete. In atoms of the period 6 transition elements, the *6s* orbital is filled before the *5d* and *4f* orbitals. In the lanthanide rare earths, it is the *4f* orbitals that are being filled, so the configuration of the valence electrons is similar in all the rare earth, hence all exhibit similar chemical behavior. Ionic radius, which decreases progressively from  $La^{3+}$  (115 pm) to  $Lu^{3+}$  (93 pm), illustrated in Figure 7.5, is thus the characteristic that governs their relative behavior.

Because of their high charge and large radii, the rare earths are incompatible elements. The degree of incompatibilities varies, however. Highly charged U and Th are highly incompatible elements, as are the lightest rare earths. However, the heavy rare earths have sufficiently small radii that they can be accommodated to some degree in many common minerals. The heaviest rare earths readily substitute for  $Al^{3+}$  in garnet, and hence can be concentrated by it. Eu, when in its 2+ state, substitutes for  $Ca^{2+}$  in plagioclase feldspar more readily than the other rare earths. Thus plagioclase is often anomalously rich in Eu compared to the other rare earths, and other phases in equilibrium with plagioclase become relatively depleted in Eu as a consequence.

The systematic variation in lanthanide rare earth behavior is best illustrated by plotting the log of the *relative abundances* as a function of atomic number (this sort of plot is sometimes called a Masuda, Masuda-Coryell, or Coryell plot, but most often is simply termed a rare earth plot or diagram). Relative abundances are calculated by dividing the concentration of each rare earth by its concentration in a set of normalizing values, such as the concentrations of rare earths in chondritic meteorites. Why do we use relative abundances? As we shall see in Chapter 10, the abundances of even numbered elements in the solar system (and most likely the cosmos) are greater than those of neighboring odd-

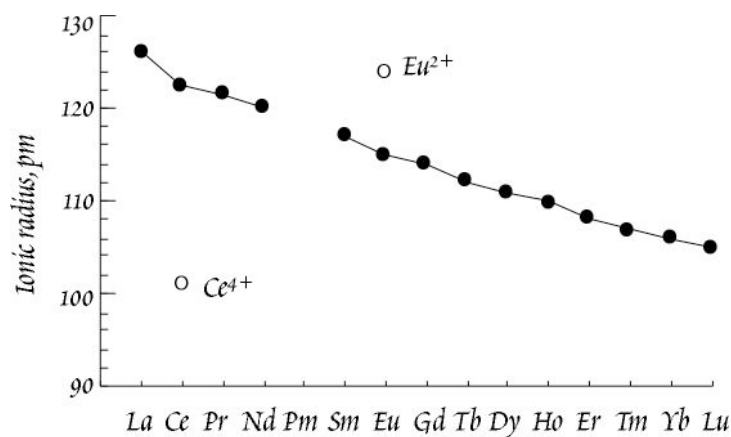


Figure 7.5. Ionic radii of the lanthanide rare earth elements (3+ state except where noted). Promethium (Pm) has no isotope with a half-life longer than 5 years.

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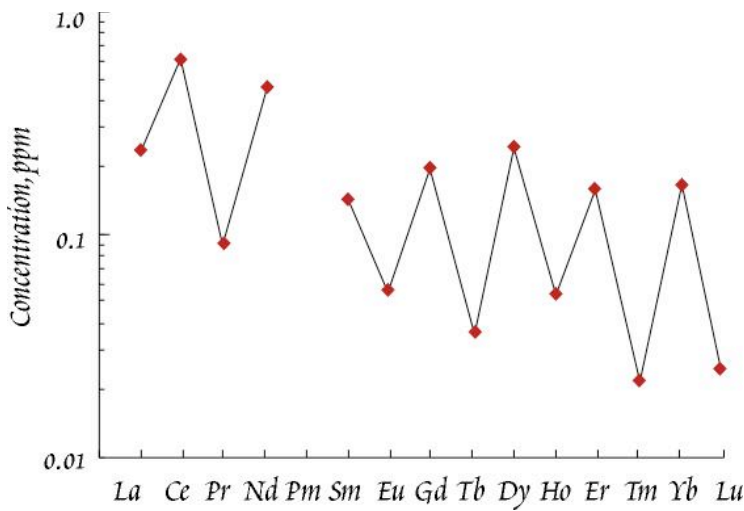


Figure 7.6. Concentrations of the rare earths in the carbonaceous chondritic meteorite Orgueil.

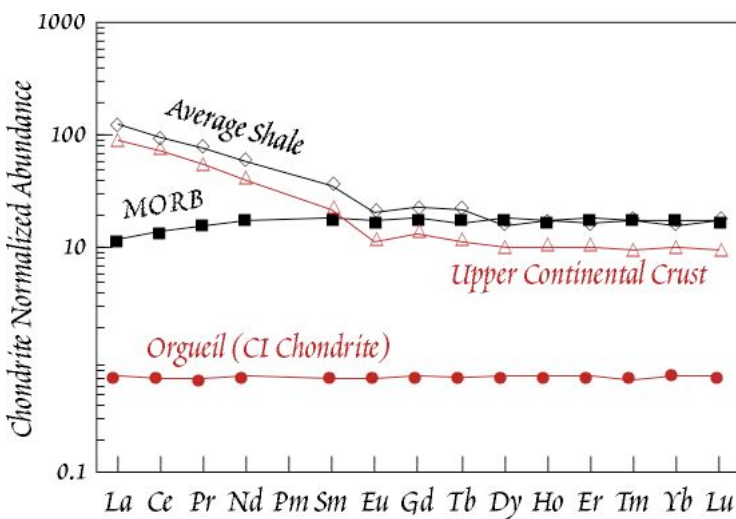


Figure 7.7. A rare earth plot showing rare earth patterns for average upper continental crust (Rudnick and Fountain, 1995), average shale, average mid-ocean ridge basalt, and the meteorite Orgueil. As a carbonaceous chondrite, Orgueil has lower rare earth concentrations than the average of ordinary chondrites used for normalization.

numbered elements. Furthermore, because of the way the elements have been created, abundances generally decrease with increasing atomic number. Thus a simple plot of abundances produces a saw tooth pattern of decreasing abundances. This can be seen in Figure 7.6, which shows rare earth abundances in the CI chondrite Orgueil (CI chondrites are a class of meteorites that are taken to be the best representative of the average concentrations of non-volatile elements in the solar system; see Chapter 10). “Normalizing” the rare earth abundances to those of chondritic meteorites eliminates effects related to nuclear stability and nucleosynthesis and produces a smooth pattern, such as those seen in Figure 7.7.

Though all igneous geochemists normalize rare earth abundances to some set of chondritic values, there is no uniformity in the set chosen. Popular normalization schemes include the CI chondrite Orgueil, an average of 20 ordinary chondrites reported by Nakamura (1974), and the chondritic meteorite Leedy (Masuda et al., 1973). Although the absolute values of the normalizing values vary (for example, the Nakamura values are about 28% higher than those of Orgueil), the relative abundances are essentially the same. Thus the normalized rare earth pattern should be the same regardless of normalizing values. Some sets of normalizing values are listed in Table 7.3. A more complete tabulation can be found in Rollinson (1993).

Rare earth patterns for upper continental crust and average mid-ocean ridge basalt (MORB) are also shown in Figure 7.7. MORB exhibits a *light rare earth-depleted* pattern; upper continental crust is *light rare earth-enriched* with a negative ‘Eu anomaly’. The light rare earth depletion of MORB reflects the incompatible element-depleted nature of the upper mantle from which these magmas are derived. This incompatible element depletion of the mantle is generally thought to have resulted from extraction of partial melts, in which the incompatible elements were concentrated. Those partial melts have crystallized to form the continental crust. If this is so, the complimentary nature of the rare earth patterns of MORB and continental crust is not coincidental. There are good reasons, which we will discuss in Chapters 10 and 11, to believe that the relative abundances of rare earths in the Earth as a whole are similar to those of chondrites, i.e., the rare earth pattern

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of the Earth should be flat. Mass balance therefore requires the sum of all the various rare earth reservoirs in the Earth have a flat rare earth pattern. If we assume the continental crust and the mantle are the only two reservoirs with significant concentrations of rare earth elements, and if the continental crust is light rare earth-enriched, then the mantle should be light rare earth-depleted.

A negative Eu anomaly is typical of many continental rocks, as well as most sediments and seawater. The Eu anomaly probably arises because many crustal rocks of granitic and granodioritic composition were produced by intracrustal partial melting. The residues of those melts were rich in plagioclase, hence retaining somewhat more of the Eu in the lower crust, and creating a complimentary Eu-depleted upper crust. Sediments and seawater inherit this Eu anomaly from their source rocks in the upper continental crust.

Many sedimentary rocks, and seawater, have rare earth patterns that are similar to each other, and to that of the continental crust. To accentuate the difference in rare earth patterns between sediments, low temperature geochemists often normalize rare earth abundances to the concentrations in average shale. Again, there are several sets of normalizing values (one set is given in Table 7.3, others may be found in Rollinson, 1993), but the relative abundances are all similar. Figure 7.8 shows examples of shale-normalized rare earth patterns.

Because the rare earths are highly insoluble and immobile, rare earth patterns often remain unchanged during metamorphism. Hence rare earth patterns can provide information on the premetamorphic history of a rock. Indeed, even during the production of sediment from crystalline rock, the

TABLE 7.3. NORMALIZING VALUES USED FOR RARE EARTH PLOTS

	Ordinary Chondrites	Orgueil (CI Chondrite)	Leedy	BSE	Ave. Shale
La	0.329	0.236	0.378	0.648	41
Ce	0.865	0.619	0.976	1.675	83
Pr	0.130	0.09		0.254	10.1
Nd	0.630	0.463	0.716	1.25	38
Sm	0.203	0.144	0.23	0.406	7.5
Eu	0.077	0.0547	0.0866	0.154	1.61
Gd	0.276	0.199	0.311	0.544	6.35
Tb	0.055	0.0353		0.099	1.23
Dy	0.343	0.246	0.39	0.674	5.5
Ho	0.077	0.0552		0.149	1.34
Er	0.225	0.162	0.255	0.438	3.75
Tm	0.035	0.022		0.068	0.63
Yb	0.220	0.166	0.249	0.441	3.53
Lu	0.034	0.0245	0.0387	0.0675	0.61

"Ordinary chondrites" is modified from Nakamura (1974), Orgueil are the values tabulated by Anders and Grevesse (1989), Leedy, an ordinary chondrite, is from Masuda (1973), BSE is Bulk Silicate Earth from McDonough and Sun (1994), and Average Shale is from Piper (1974).

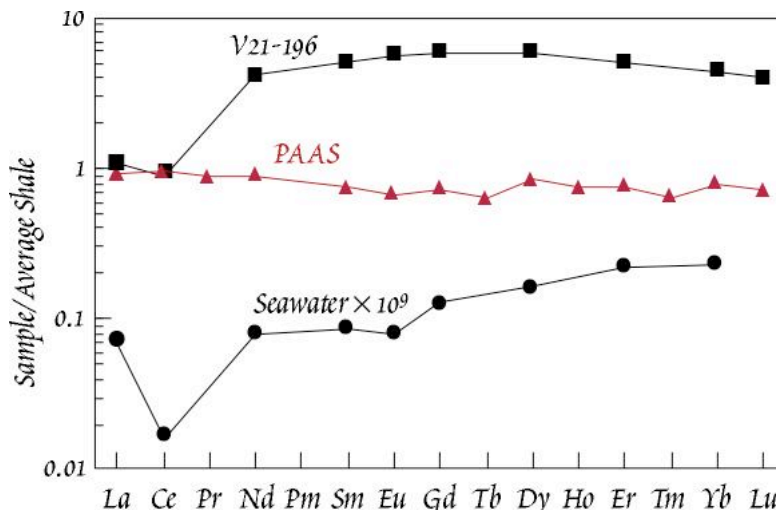


Figure 7.8. Shale-normalized REE earth patterns of a Pacific pelagic sediment (V21-196; Ben Othman et al., 1989), the Post-Archean shale composite (McLennan, 1989), and typical seawater (Elderfield and Greaves, 1982). Both the pelagic sediment and seawater display a negative Ce anomaly, a consequence of Ce being in the +4 oxidation state.



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rare earth patterns often remain little changed, and rare earth patterns have been used to identify the provenance, i.e., the source, of sedimentary rocks. Rare earth patterns have also become useful tools in chemical oceanography, now that modern analytical techniques allow their accurate determination despite concentrations in the parts per trillion range.

## 7.2.2.5 THE HFS ELEMENTS

The *high field strength (HFS) elements* are so called because of their high ionic charge: Zr and Hf have +4 valence states and Ta and Nb have +5 valence states. Th and U are sometimes included in this group. As we noted, Th has a +4 valence state and U either a +6 or +4 valence state. Because of their high charge, all are relatively small cations, with ionic radii of 64 pm for  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$ , and 72 and 76 pm for  $\text{Zr}^{4+}$  and  $\text{Hf}^{4+}$  respectively ( $\text{U}^{4+}$  and  $\text{Th}^{4+}$  are larger, however). Although they are of appropriate size for many cation sites in common minerals, their charge is too great and requires one or more coupled substitutions to maintain charge balance. As we noted earlier, such substitutions are energetically unfavorable. Thus Hf and Zr are moderately incompatible elements while Nb and Ta are highly incompatible elements. These elements are less electropositive than the alkalis, and alkaline and rare earths. That, as well as their high charge and the involvement of *d* orbitals (which are highly directional) in bonding in the case of Ta and Nb, means that there is a greater degree of covalency in the bonds they form. Thus the simple charged sphere is a less satisfactory model of their behavior.

As a consequence of their high ionic potential, or ionic charge to ionic radius ratio, the HFS elements are particularly insoluble. As a result, these elements tend to be very immobile during weathering and metamorphism. They are therefore particularly valuable in the study of ancient igneous rock suites as they can sometimes provide insights into the environment in which those rocks formed. Ta and Nb are present in anomalously low concentrations in magmas associated with subduction zones (indeed, this is considered a diagnostic feature of subduction-related volcanism). Although this depletion is not well understood, it is probably at least in part a consequence of the low solubility of these elements and the consequent failure of aqueous fluids generated by dehydration of the subducting oceanic crust to transport these elements into the magma genesis zone.

## 7.2.2.6 THE FIRST SERIES TRANSITION METALS

The chemistry of the transition elements is considerably more complex than that of the elements we have discussed thus far. There are several reasons for this. First, many of the transition elements have two or more valence states in nature. Second, the transition metals have higher electronegativity than the alkali and alkaline earths, so that covalent bonding plays a more important role in their behavior. Bonding with oxygen in oxides and silicates is still predominantly ionic, but bonding with other non-metals, such as sulfur, can be largely covalent. A final complicating factor is the geometry of the *d*-orbitals, which are highly directional and thus bestow upon the transition metals specific preferences for the geometry of coordinating anions, or ligands. We will discuss this aspect of their behavior in more detail in a subsequent section.

The solubility of the transition metals, though generally lower than that of the alkalis and alkaline earths, is quite variable and depends upon valence state and the availability of anions with which they can form soluble coordination complexes. Their behavior in magmas is also variable. They range from moderately incompatible (e.g., Ti, Cu, Zn) to very compatible (e.g., Cr, Ni, Co), but their exact behavior is generally a stronger function of composition (of both solid and melt phases) than that of the highly incompatible elements. With the exception of Mn, the first transition series metals are also siderophile and/or chalcophile.

## 7.2.2.7 THE NOBLE METALS

The platinum group elements (Rh, Ru, Pd, Os, Ir, Pt) plus gold are often collectively called the *noble metals*. These metals are so called for two reasons: first they are rare, second they are unreactive and quite stable in metallic form. Their rarity is in part a consequence of their highly siderophilic character. The concentration of these elements in the silicate Earth is only about 1% of their concentrations in

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chondrites. Presumably, the bulk of the Earth's inventory of these elements is in the core. As a result of their low concentrations, their behavior is still poorly understood.

These elements are all also chalcophile (i.e., all are enriched in sulfide liquids relative to silicate liquids), although to varying degrees. Ir appears to be the most chalcophile, Pt and Au the least. Considering the associations of their ore deposits, the platinum group elements (PGE) may be divided into two subgroups: the Ir group (Ir, Os, and Ru) and the Pd group (Rh, Pd, Pt). The former are often associated with chromites (chromite is  $(\text{Fe,Mg})\text{Cr}_2\text{O}_4$ , part of the spinel solid solution) in ultramafic rocks as native metal alloys or sulfide (e.g., the Stillwater Complex of Montana), while the latter are associated with magmatic sulfides of Fe, Ni, and Cu associated with gabbros (e.g., the Sudbury Complex of Ontario). Besides forming compounds with sulfur, these elements form a variety of chloride and other halide complexes. These complexes may play an important role in the formation of some PGE deposits and certainly do in many gold deposits.

These elements are transition elements and, like the first transition series, can exist in multiple valence states, ranging from 0 to +8, and have bonding behavior influenced by the *d*-orbitals. Thus their chemistry is complex. When in high valence states, some, Os and Ru for example, form oxides that are highly volatile.

The nature of the host phase for these elements in the mantle is unclear. Mitchell and Keays (1981) found that they were concentrated in minerals in the order garnet<olivine<orthopyroxene <clinopyroxene<spinel, but that the total inventory in all minerals was less than that in the bulk rock. They concluded that 60-80% of the PGE's were present in intergranular sulfides. An alternative host is native metal grains, such as osmiridium (an approximately 50-50 Os-Ir alloy), which have been found in peridotites. A study by Brüggmann et al. (1987) of komatiites revealed that the concentrations of Au and Pd increased with decreasing MgO while those of Ru, Os, and Ir decreased with decreasing MgO concentrations. This suggested that Au and Pd are moderately incompatible elements while Ru, Os, and Ir are highly compatible. Subsequent work has confirmed this conclusion and shown that Rh is compatible while Pt is incompatible. Recent studies suggest that the elements dissolve in silicate melts in low valence states, +2 for Ir (and perhaps Os), and +1 for the other elements. The solubility of these elements in silicate melts, relative to native metal alloys, appears to be quite low, but is probably not exceeded in nature.

In a manner analogous to the rare earths, PGE data are sometimes presented as plots of the chondrite-normalized abundance, as in Figure 7.9. In this case, however, elements are not ordered by atomic number, but rather by decreasing melting point. This, as it turns out, places them in order of decreasing compatibility. The dunite in Figure 7.9 has a relatively flat noble metal pattern, as do many mantle peridotites. The remaining samples show varying degrees of enrichment in the Pd group elements relative to the Ir group elements. The chromites and sulfides in Figure 9 are highly enriched in noble metals relative to the silicate magmatic rocks, consistent with their chalcophile nature and demonstrated affinity for oxide phases such as the spinels.

### 7.2.2.8 OTHER ELEMENTS

Of the elements that do not fit into any of the above groups, several deserve special comment as they are of particular interest in isotope geochemistry. The first of these is boron. The geochemistry of boron remains incompletely understood, but knowledge of it has grown since the mid-1980's when it was shown that the relative proportions of its two isotopes,  $^{10}\text{B}$  and  $^{11}\text{B}$ , vary in nature. Boron is only mildly electropositive, meaning that the bonds it forms generally have a substantial covalent component. In nature, it is most often bound to three oxygens to form the borate complex. Borate is quite soluble, making borate one of the major ions in seawater. Furthermore, borate is mobile and easily leached or added to rocks during weathering and metamorphism. In igneous systems it is mildly incompatible. Boron appears to be quite readily removed from subducting oceanic crust and sediment by fluids and enriched in subduction-related magmas.

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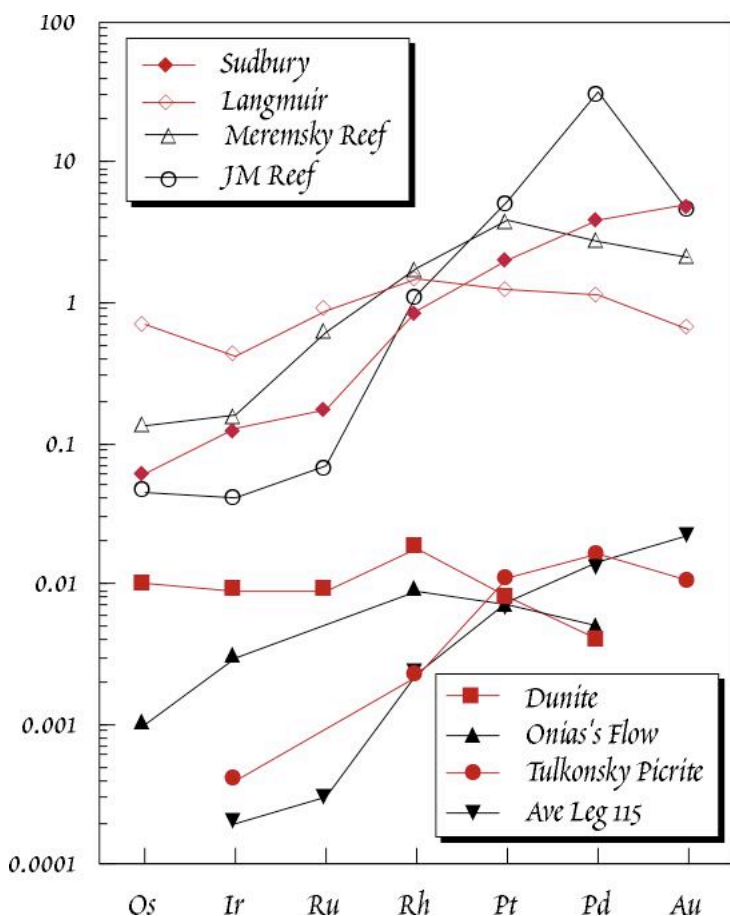


Figure 7.9. Chondrite-normalized abundances of the noble metals in a variety of igneous rocks and associated sulfides. "Sudbury" is the magmatic sulfide from the Little Stobie #1 Mine of the Sudbury intrusion (Naldrett et al., 1979), "Langmuir" is the sulfide of the Langmuir komatiite, Canada (Naldrett et al., 1979), "Meremsky Reef" is a composite of the Meremsky Reef chromite layer of the Bushveld Complex, South Africa (Heimstra, 1979), "JM Reef" is a chromite layer of the Stillwater Complex, Montana (Barnes et al., 1985), "Dunite" is a dunite from the Urals (Stockman, 1982), "Onias's Flow" is a komatiite flow from the Belingwe Greenstone Belt, Zimbabwe (Zhou, 1994), "Tulkonsky Picrite" is a picrite from the Siberia Traps (Brügmann et al., 1993), and "Ave Leg 115" is the average of basalts drilled from the Indian Ocean on ODP Leg 115 (Fryer and Greenough, 1982).

and it can be readily transported in metamorphic and hydrothermal solutions. Its ionic radius is 119 pm in octahedral coordination, virtually identical to that of Sr. In igneous systems it is moderately incompatible, as might be expected from its ionic radius and charge.

The concentration of phosphorus is sometimes high enough that it is treated as a major element. With a valence of +5 and being moderately electropositive, it is generally present in nature as the oxyanion  $\text{PO}_4^{3-}$ , in which it is doubly bound to one of the oxygens and singly bound to the others. In

Rhenium is of interest because it decays radioactively to Os. Though it is not one of the platinum group elements, Re is adjacent to them in the periodic table and shares many of their properties, including being highly refractory under reducing conditions, being both highly siderophile and chalcophile, having a variety of potential valence states, having a large  $E_{\text{H}}$ , so that the metal is relatively resistant to oxidation, and forming a volatile (though only moderately so) oxide species. In oxidized aqueous solutions at the Earth's surface it is present as the perrhenate ion,  $\text{ReO}_4^-$ , and is quite soluble. However, it is readily adsorbed from solution under reducing conditions, leading to its concentration in organic-rich materials such as black shales and coals. In igneous systems, it is incompatible, though details of its behavior are not understood.

Lead is of great interest not only because of its economic importance but also because it is the product of radioactive decay of  $^{232}\text{Th}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$  and is quite toxic. The latter is of concern because its widespread use, particularly in paint and gasoline, has led to widespread pollution. Pb is chalcophile, though not so much as the PGE's and Re, and perhaps slightly siderophile. It is also quite volatile. Pb is in the +2 state throughout virtually the entire range of natural redox conditions. Pb has an electronegativity of 1.9, indicating a greater degree of covalency in its bonding than for the alkalis, alkaline earths and rare earths. The solubility of Pb is reasonably low under most conditions, but it can form strong complexes with elements such as Cl

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rocks, it forms the common mineral apatite ( $\text{Ca}_3(\text{PO})_4(\text{OH},\text{F},\text{Cl})$ ) as well as rarer minerals such as monazite. It behaves as a moderately incompatible element in mafic and ultramafic igneous systems.

The elements of the U and Th decay series have no stable nuclei. They exist on the Earth only because they are continually created through decay of U and Th. They are of interest in geochemistry only because of their radioactivity. As we shall see in the next chapter, they can be useful geochronological tools. As radioactive substances, they represent potential environmental hazards and are of interest for this reason as well. Radon is perhaps the element that causes the greatest concern. As a noble gas, it is quite mobile. Relatively high levels of this gas can accumulate in structures built on uranium-rich soils and rocks. In this group we could also include the two "missing" elements, Tc and Pm. Like the U-decay series elements, they have no long-lived nuclei. They are, however, present in the Earth in exceedingly minute amounts, created by natural fission of U as well as by capture of fission-produced neutrons. Merely detecting them is a considerable challenge.

Ga and Ge can substitute, albeit with difficulty because of their larger radii, for their more abundant neighbors directly above them in the periodic table, Al and Si. Both are thus moderately incompatible elements. Their concentrations in the silicate Earth are somewhat low because of their siderophile nature. Germanium's greatest contribution to geochemistry may, however, be in experimental studies. Germanates created by substituting Ge for Si are used to simulate the properties of silicates at high pressures. This approach works because the oxygen ion is far more compressible than are cations. Thus the ratio of the ionic radius of oxygen to silicon at high pressure is similar to that of oxygen to germanium at low pressure. Such studies of "germanium analogs" considerably advanced the understanding of the Earth's deep interior decades before the technology for reproducing the pressure of the deep Earth in the laboratory existed. Studies of germanium analogs continue in parallel with ultrahigh pressure experiments.

The geochemistry of the remaining elements, particularly in igneous processes, is poorly understood. Because of their low abundances, there have been few analyses published of these elements. Progress is being made on this front, however. For example, Newsom et al. (1986) demonstrated that the behavior of the chalcophile element Mo closely follows that of the rare earth Pr. W appears to be highly incompatible and its behavior mimics that of Ba. In oxidizing solutions, Mo forms a very soluble oxyanion complex,  $\text{MoO}_4^{2-}$ , so that its concentration in seawater is relatively high. Tin (Sn) and antimony (Sb) behave as moderately incompatible elements, with behaviors in igneous systems that are similar to that of the rare earth Sm (Jochum et al., 1985, 1993). However, these elements appear to form soluble species so, unlike Sm, they can be relatively mobile. It appears, for example, that they are readily stripped from subducting oceanic crust and carried into the magma genesis zones of island arc volcanoes.

### 7.3 DISTRIBUTION OF TRACE ELEMENTS BETWEEN CO-EXISTING PHASES

#### 7.3.1 THE PARTITION COEFFICIENT

Geochemists find it convenient to define a *partition or distribution coefficient* as:

$$D_i^{\alpha-\beta} = \frac{C_i^\alpha}{C_i^\beta} \quad 7.1$$

where C is concentration, *i* refers to an element (or species) and  $\alpha$  and  $\beta$  are two phases. By convention, if one phase is a liquid, the concentration ratio is written solid over liquid, i.e.:

$$D_i^{s/\ell} = \frac{C_i^s}{C_i^\ell} \quad 7.2$$

where *s* refers to some solid phase and  $\ell$  refers to the liquid phase. The distribution coefficient is a convenient concept for relating the concentration of some element in two different phases. It is also readily measured, either experimentally or 'observationally'. In the former, two phases are equilibrated at the temperature and pressure of interest and the concentration of *i* is subsequently measured in both. In