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The Chemical Composition of Soils

1.1 Elemental Composition

Soils are porous media created at the land surface through weathering processes mediated by biological, geological, and hydrological phenomena. Soils differ from mere weathered rock, however, because they show an approximately vertical stratification (the *soil horizons*) that has been produced by the continual influence of percolating water and living organisms. From the point of view of chemistry, soils are open, multicomponent, biogeochemical systems containing solids, liquids, and gases. That they are open systems means soils exchange both matter and energy with the surrounding atmosphere, biosphere, and hydrosphere. These flows of matter and energy to or from soils are highly variable in time and space, but they are the essential fluxes that cause the development of soil profiles and govern the patterns of soil quality.

The role of soil as a dynamic reservoir in the cycling of chemical elements can be appreciated by examining tables 1.1 and 1.2, which list average mass concentrations of important nonmetal, metal, and metalloid chemical elements in continental crustal rocks and soils. The rock concentrations take into account both crustal stratification and the relative abundance of sedimentary, magmatic, and metamorphic subunits worldwide. The soil concentrations refer to samples taken approximately 0.2 m beneath the land surface from uncontaminated mineral soils in the conterminous United States. These latter concentration data are quite comparable with those for soils sampled worldwide. The average values listed have large standard deviations, however, because of spatial heterogeneity on all scales.

Table 1.1

Mean content (measured in milligrams per kilogram) of nonmetal elements in crustal rocks and United States soils.

Element	Crust ^a	Soil ^b	Element	Crust ^a	Soil ^b
B	17	26	P	757	260
C	1990	16,000	S	697	1200
N	60	2000	Cl	472	100
O	472,000	490,000	Se	0.12	0.26

^aWedepohl, K. H. (1995) The composition of the continental crust. *Geochim. Cosmochim. Acta* 59: 1217.

^bSchacklette, H. T., and J. G. Boerngen. (1984) *Element concentrations in soils and other surficial materials of the conterminous United States*. U.S. Geological Survey Professional Paper 1270.

Table 1.2

Mean content (measured in milligrams per kilogram) of metal and metalloid elements and their anthropogenic mobilization factors (AMFs).

Element	Crust ^a	Soil ^b	AMF ^c	Element	Crust ^a	Soil ^b	AMF ^c
Li	18	20	3	Cu	25	17	632
Be	2.4	0.6	2	Zn	65	48	115
Na	23600	5900	2	As	1.7	5.2	27
Mg	22000	4400	<1	Sr	333	120	3
Al	79600	47000	<1	Zr	203	180	4
Si	288000	310000	<1	Mo	1.1	0.6	80
K	21400	15000	<1	Ag	0.07	0.05	185
Ca	38500	9200	2	Cd	0.1	0.2	112
Ti	4010	2400	1	Sn	23	0.9	65
V	98	58	14	Sb	0.3	0.5	246
Cr	126	37	273	Cs	3.4	4.0	12
Mn	716	330	10	Ba	584	440	4
Fe	43200	18000	16	Hg	0.04	0.06	342
Co	24	7	4	Pb	14.8	16	127
Ni	56	13	56	U	1.7	2.3	12

^aWedepohl, K. H. (1995) The composition of the continental crust. *Geochim. Cosmochim. Acta* 59:1217.

^bSchacklette, H. T., and J. G. Boerngen. (1984) *Element concentrations in soils and other surficial materials of the conterminous United States*. U.S. Geological Survey Professional Paper 1270.

^cAMF = mass extracted annually by mining and fossil fuel production ÷ mass released annually by crustal weathering and volcanic activity. Data from Klee, R. J., and T. E. Graedel. (2004) Elemental cycles: A status report on human or natural dominance. *Annu. Rev. Environ. Resour.* 29:69.

The *major elements* in soils are those with concentrations that exceed 100 mg kg^{-1} , all others being termed *trace elements*. According to the data in tables 1.1 and 1.2, the major elements include O, Si, Al, Fe, C, K, Ca, Na, Mg, Ti, N, S, Ba, Mn, P, and perhaps Sr and Zr, in decreasing order of concentration. Notable among the major elements is the strong enrichment of C and N in soils relative to crustal rocks (Table 1.1), whereas Ca, Na, and Mg show significant depletion (Table 1.2). The strong enrichment of C and N is a result of the principal chemical forms these elements assume in soils—namely, those associated with organic matter. The average C-to-N, C-to-P, and C-to-S ratios (8, 61, and 13 respectively) in soils, indicated by the data in Table 1.1, are very low and, therefore, are conducive to microbial mineralization processes, further reflecting the active biological milieu that distinguishes soil from crustal rock.

The major elements C, N, P, and S also are *macronutrients*, meaning they are essential to the life cycles of organisms and are absorbed by them in significant amounts. The global biogeochemical cycles of these elements are therefore of major interest, especially because of the large anthropogenic influence they experience. Mining operations and fossil fuel production, for example, combine to release annually more than 1000 times as much C and N, 100 times as much S, and 10 times as much P as is released annually worldwide from crustal weathering processes. In soils, these four elements undergo biological and chemical transformations that release them to the vicinal atmosphere, biosphere, and hydrosphere, as illustrated in Figure 1.1, a flow diagram that applies to natural soils at spatial scales ranging from pedon to landscape. The two storage components in Figure 1.1 respectively depict the litter layer and *humus*, the organic matter not identifiable as unaltered or partially altered biomass. The microbial transformation of litter to humus is termed *humification*. The content of humus in soils worldwide varies systematically with climate, with accumulation being favored by low temperature and high precipitation. For example, the average humus content in desert soils increases by about one order of magnitude as the mean annual surface temperature drops fivefold. The average humus content of tropical forest soils increases approximately threefold as the mean annual precipitation increases about eightfold. In most soils, the microbial degradation of litter and humus is the process through which C, N, S, and P are released to the contiguous aqueous phase (the *soil solution*) as inorganic ions susceptible to uptake by the biota or loss by the three processes indicated in Figure 1.1 by arrows outgoing from the humus storage component.

Important losses of C from soils occur as a result of leaching, erosion, and runoff, but most quantitative studies have focused on emissions to the atmosphere in the form of either CO_2 or CH_4 produced by respiring microorganisms. The CO_2 emissions do not arise uniformly from soil humus, but instead are ascribed conventionally to three humus “pools”: an *active pool*, with C residence times up to a year; a *slow pool*, with residence times up to a century, and a *passive pool*, with residence times up to a millennium. Natural

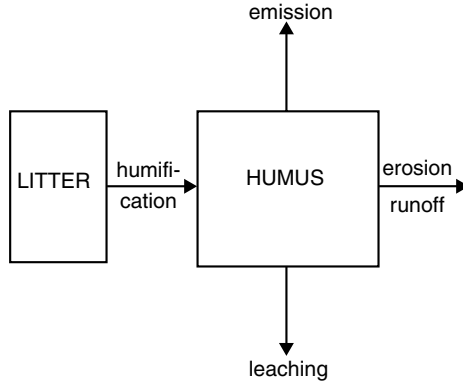


Figure 1.1. Flow diagram showing storage components (boxes) and transfers (arrows) in the soil biogeochemical cycling of C, N, P, and S.

soils can continue to accumulate C for several millennia, only to lose it over decades when placed under cultivation. The importance of this loss can be appreciated in light of the fact that soils are the largest repository of nonfossil fuel organic C on the planet, storing about four times the amount of C contained in the terrestrial biosphere.

The picture for soil N flows is similar to that for soil C, in that humus is the dominant storage component and emissions to the atmosphere are an important pathway of loss. The emissions send mainly N_2 along with N_2O and NH_3 to the atmosphere. The N_2O , like CO_2 and CH_4 , is of environmental concern because of its very strong absorption of terrestrial infrared radiation (*greenhouse gas*). Unlike the case of CO_2 and CH_4 , however, the source of these gases is dissolved *inorganic* N, the transformation of which is termed *denitrification* when N_2 and N_2O are the products, and *ammonia volatilization* when NH_3 is the product. Denitrification is typically mediated by respiring microorganisms, whereas ammonia volatilization results from the deprotonation of aqueous NH_4^+ (which itself may be bacterially produced) under alkaline conditions. Dissolved inorganic N comprises the highly soluble, “free-ion” chemical species, NO_3^- , NO_2^- , and NH_4^+ , which can transform among themselves by electron transfer processes (*redox reactions*), be complexed by other dissolved solutes, react with particle surfaces, or be absorbed by living organisms, as illustrated in the competition diagram shown in Figure 1.2, which pertains to soils at the ped spatial scale. Natural soils tend to cycle N without significant loss through leaching (as NO_3^-), but denitrification losses can be large if soluble humus, which is readily decomposed by microorganisms, is abundant and flooding induces anaerobic conditions, thereby eliminating O as a competitor with N for the electrons made available when humus is degraded. Cultivated soils, on the other hand, often show excessive leaching and runoff losses of N, as well as significant emissions—both of which are of

major environmental concern—because of high inputs of nitrate or ammonium fertilizers that artificially and suddenly increase inorganic N content. A similar problem occurs when organic wastes with low C-to-N ratios are applied to these soils as fertilizers, because rapid microbial mineralization of such materials is favored.

Sulfur flows in soils that form outside arid regions or tidal zones can be described as shown in Figure 1.1, with humus as the dominant reservoir and losses through leaching, runoff, and emission processes. Mineralization of organic S in humus usually produces SO_4^{2-} , which can be leached, react with particle surfaces, or be absorbed by living organisms (Fig. 1.2). In flooded soils, soluble H_2S and other potentially volatile sulfides are produced under microbial mediation from the degradation of humus or the reduction of sulfate (electron transfer to sulfate to produce sulfide). They can be lost by emission to the atmosphere or by precipitation along with ferrous iron or trace metals as solid-phase sulfides. The competition for aqueous SO_4^{2-} in soil peds thus follows the paradigm in Figure 1.2, with the main differences from NO_3^- being the much stronger reactions between sulfate and particle surfaces and the possibility of precipitation as a solid-phase sulfide, as well as emission to the atmosphere, under flooded conditions.

Phosphorus flows in soils follow the diagram in Figure 1.1 with the important caveat that inorganic P reservoirs—phosphate on particle surfaces and in solid phases—can sometimes be as large as or larger than that afforded by humus, depending on precipitation. Leaching losses of soil P are minimal, and gaseous P emissions to the atmosphere essentially do not occur from natural

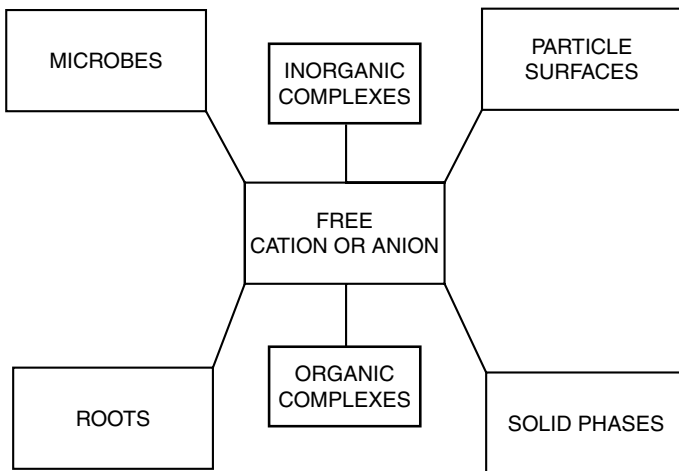


Figure 1.2. Competition diagram showing biotic and abiotic sources/sinks for aqueous species (inner three boxes) in a soil ped. Coupling among the four sources/sinks is mediated by the free ionic species of an element.

soils. Mineralization of humus and dissolution of P from solid phases both produce aqueous PO_4^{3-} or its proton complexes (e.g., H_2PO_4^-), depending on pH, and these dissolved species can be absorbed by living organisms or lost to particle surfaces through adsorption reactions, which are yet stronger than those of sulfate, and through precipitation, along with Ca, Al, or Fe, as a solid-phase phosphate, again depending on pH. As is the case with N, fertilizer additions and organic waste applications to soils can lead to P losses, mainly by erosion, that pose environmental hazards.

Even this brief summary of the soil cycles of C, N, S, and P can serve to illustrate their biogeochemical similarities in the setting provided by Figures 1.1 and 1.2. Humus is their principal reservoir (with P sometimes as an exception), and all four elements become *oxyanions* (CO_3^{2-} , NO_3^- , SO_4^{2-} , PO_4^{3-} , and their proton complexes) when humus is mineralized by microorganisms under aerobic conditions at circumneutral pH. The affinity of these oxyanions for particle surfaces, as well as their susceptibility to precipitation with metals, has been observed often to increase in the order $\text{NO}_3^- < \text{SO}_4^{2-} \leq \text{CO}_3^{2-} \ll \text{PO}_4^{3-}$. This ordering is accordingly reversed for their potential to be lost from soils by leaching or runoff processes, whereas it remains the same for their potential to be lost by erosion processes.

1.2 Metal Elements in Soils

Table 1.2 lists average crustal and soil concentrations of 27 metals and three metalloids (Si, As, and Sb) along with their *anthropogenic mobilization factors* (AMFs). The value of AMF is calculated as the mass of an element extracted annually, through mining operations and fossil fuel production, divided by the mass released annually through crustal weathering processes and volcanic activity, with both figures being based on data obtained worldwide. If AMF is well above 10, an element is said to have significant anthropogenic perturbation of its global biogeochemical cycle. A glance along the fourth and eighth columns in Table 1.2 reveals that, according to this criterion, the transition metals Cr, Ni, Cu, Zn, Mo, and Sn; the “heavy metals” Ag, Cd, Hg, and Pb; and the metalloids As and Sb have significantly perturbed biogeochemical cycles. Not surprisingly, these 12 elements also figure importantly in environmental regulations.

Metal elements are classified according to two important characteristics with respect to their biogeochemical behavior in soils and aquatic systems. The first of these is the *ionic potential* (IP), which is the valence of a metal cation divided by its ionic radius in nanometers. Metal cations with $\text{IP} < 30 \text{ nm}^{-1}$ tend to be found in circumneutral aqueous solutions as solvated chemical species (*free cations*); those with $30 < \text{IP} < 100 \text{ nm}^{-1}$ tend to hydrolyze readily in circumneutral waters; and those with $\text{IP} > 100 \text{ nm}^{-1}$ tend to be found as oxyanions. As examples of these three classes, consider Na^+ ($\text{IP} = 9.8 \text{ nm}^{-1}$), Al^{3+} ($\text{IP} = 56 \text{ nm}^{-1}$), and Cr^{6+} ($\text{IP} = 231 \text{ nm}^{-1}$). (See Table 2.1 for a listing of

ionic radii used to calculate IP.) If a metal element has different valence states, it may fall into different classes: Cr^{3+} ($\text{IP} = 49 \text{ nm}^{-1}$) hydrolyzes, whereas it has just been shown that hexavalent Cr forms an oxyanion species in aqueous solution. The physical basis for this classification can be understood in terms of coulomb repulsion between the metal cation and a solvating water molecule that binds to it in aqueous solution through ion–dipole interactions. If IP is low, so is the positive coulomb field acting on and repelling the protons in the solvating water molecule; but, as IP becomes larger, the repulsive coulomb field becomes strong enough to cause one of the water protons to dissociate, thus forming a hydroxide ion. If IP is very large, the coulomb field then becomes strong enough to dissociate both water protons, and an oxyanion forms instead.

Evidently any monovalent cation with an ionic radius larger than 0.033 nm will be a solvated species in aqueous solution, whereas any bivalent cation will require an ionic radius larger than 0.067 nm to be a solvated species. The alkali metal in Table 1.2 with the smallest cation is Li (ionic radius, 0.076 nm) and the alkaline earth metal with the smallest cation is Be (ionic radius, 0.027 nm), followed by Mg (ionic radius, 0.072 nm). Thus alkali and alkaline earth metals, with the notable exception of Be, will be free cations in circumneutral aqueous solutions. The same is true for the monovalent heavy metals (e.g., Ag^+) and the bivalent transition metals and heavy metals (e.g., Mn^{2+} and Hg^{2+}), although the bivalent transition metals come perilously close to the IP hydrolysis threshold. Trivalent metals, on the other hand, tend always to be hydrolyzed [e.g., Al^{3+} , Cr^{3+} , and Mn^{3+} ($\text{IP} = 46 \text{ nm}^{-1}$)], and quadrivalent or higher valent metals tend to be oxyanions. The soluble metal species in circumneutral waters are either free cations or free oxyanions, whereas hydrolyzing metals tend to precipitate as insoluble oxides or hydroxides. Thus, falling into the middle IP range (30–100 nm^{-1}) is the signature of metal elements that are not expected to be soluble at circumneutral pH.

The second important characteristic of metal elements is their *Class A* or *Class B* behavior. A metal cation is *Class A* if (1) it has low polarizability (a measure of the ease with which the electrons in an ion can be drawn away from its nucleus) and (2) it tends to form stronger complexes with O-containing ligands [e.g., carboxylate (COO^-), phosphate, or a water molecule] than with N- or S-containing ligands. A metal is *Class B* if it has the opposite characteristics. If a metal is neither *Class A* nor *Class B*, it is termed *borderline*. The *Class B* metals in Table 1.2 are the heavy metals Ag, Cd, Hg, and Pb, whereas the *borderline* metals are the transition metals Ti to Zn, along with Zr, Mo, and Sn, each of which can behave as *Class A* or *Class B*, depending on their valence and local bonding environment (*stereochemistry*). All the other metals in Table 1.2 are *Class A*. We note in passing that *Class A* metals tend to form strong *hydrophilic* (water-loving) complexes with ligands in aqueous solution through ionic or even electrostatic bonding, whereas *Class B* metals tend to form strong *lipophilic* (fat-loving) complexes with ligands in aqueous solution through more covalent bonding. *Hydrophilic* complexes seek polar molecular

environments (e.g., cell surfaces), whereas lipophilic complexes seek nonpolar environments (e.g., cell membranes). These tendencies are a direct result of (1) the polarizability of a metal cation (with high polarizability implying a labile “electron cloud,” one that can be attracted toward and shared with a ligand) and (2) the less polar nature of N- or S-containing ligands, which makes them less hydrophilic than O-containing ligands.

The description of metals according to these two characteristics can be applied not only to understand the behavior of metals in terms of solubility and complex formation, but also to predict their status as plant (and microbial) *toxigants* (see the flow diagram in Fig. 1.3). For a given metal cation, if $IP < 30 \text{ nm}^{-1}$ and the metal is Class A, then it is unlikely to be toxic (e.g., Ca^{2+}), except possibly at very high concentrations (e.g., Li^+ , Na^+). Moving toward the right in Figure 1.3, we see that if $IP > 100 \text{ nm}^{-1}$, or if $IP < 30 \text{ nm}^{-1}$ and the metal is borderline, then it is quite possibly toxic, examples being Cr^{6+} in the first case and bivalent transition metal cations in the second case. If, instead, $30 < IP < 100 \text{ nm}^{-1}$, or the metal cation is Class B, then it is *very* likely to be toxic, examples being Be^{2+} and Al^{3+} in the first case; and Ag^+ , Hg^+ , along with the bivalent heavy metals in the second case. The chemistry underlying these conclusions is simple: If a metal tends to hydrolyze in aqueous solution or has covalent binding characteristics, it is very likely to be toxic, whereas if it tends to be solvated in aqueous solution and has ionic

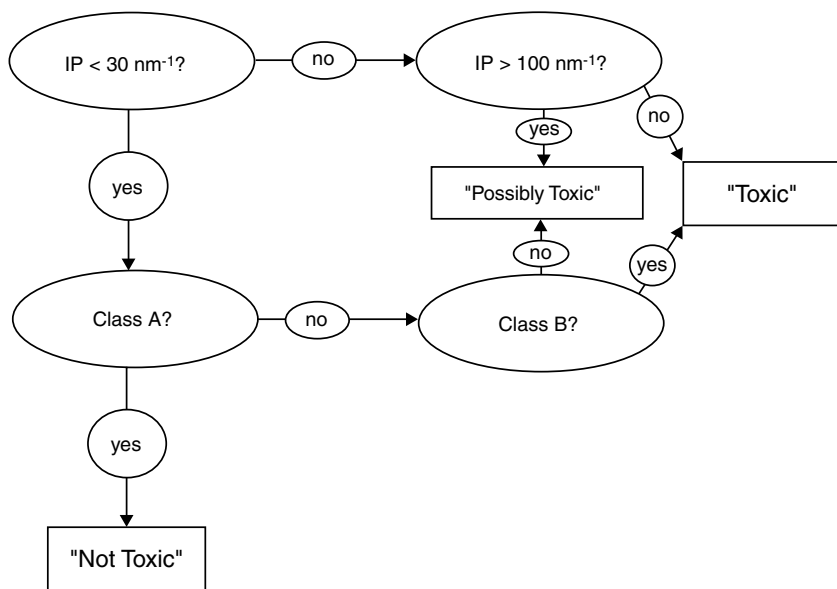


Figure 1.3. Flow diagram (beginning at upper left corner) for the toxicological classification of a metal cation at circumneutral pH using the criteria of ionic potential (IP) and Class A or B character.

or electrostatic binding characteristics, it is not as likely to be toxic. Toxicity is thus associated with insoluble metal cations and with those that tend to form covalent bonds in complexes with ligands. The first property evidently reflects low abundance in aquatic systems and, therefore, the nonavailability of a metal element as life evolved, whereas the second property is inimical to the relatively labile metal cation binding that characterizes most biochemical processes. Indeed, borderline metals become toxicants when they displace Class A metals from essential binding sites in biomolecules, bonding to these sites more strongly, and Class B metals are always toxicants, simply because they can displace either borderline metals (which often serve as cofactors in enzymes) or Class A metals from essential binding sites through much more tenacious bonding mechanisms. Note that the large AMF values in Table 1.2 are associated with borderline and Class B metals, implying, unfortunately, that human perturbations of metal biogeochemical cycles have enhanced the concentrations of toxicant metals in soil and water environments.

1.3 Solid Phases in Soils

About one half to two thirds of the soil volume is made up of solid matter. Of this material, typically more than 90% represents inorganic compounds, except for Histosols (peat and muck soils), wherein organic material accounts for more than 50% of the solid matter. The inorganic solid phases in soils often do not have a simple stoichiometry (i.e., they do not exhibit molar ratios of one element to another which are rational fractions), because they are actually in a metastable state of transition from an inhomogeneous, irregular structure to a more homogeneous, regular structure as a result of weathering processes. Nonetheless, a number of solid phases of relatively uniform composition (*minerals*) has been identified in soils worldwide. Table 1.3 lists the most common soil minerals along with their chemical formulas. Details of the atomic structures of these minerals are given in Chapter 2.

According to Table 1.1, the two most abundant elements in soils are oxygen and silicon, and these two elements combine chemically to form the 15 silicates listed in Table 1.3. The first nine silicates in the table are termed *primary minerals* because they are typically inherited from parent material, particularly crustal rock, as opposed to being precipitated through weathering processes. The key structural entity in these minerals is the Si–O bond, which is a more covalent (and, therefore, stronger) bond than typical metal–oxygen bonds (see Section 2.1). The relative resistance of any one of the minerals to decomposition by weathering is correlated positively with the Si-to-O molar ratio of its fundamental silicate structural unit, as a larger Si-to-O ratio means a lesser need to incorporate metal cations into the mineral structure to neutralize the oxygen anion charge. To the extent that metal cations are so excluded, the degree of covalency in the overall bonding arrangement will be greater and the mineral will be more resistant to decomposition in the soil environment.

Table 1.3
Common soil minerals.

Name	Chemical formula	Importance
Quartz	SiO_2	Abundant in sand and silt
Feldspar	$(\text{Na}, \text{K})\text{AlO}_2[\text{SiO}_2]_3$ $\text{CaAl}_2\text{O}_4[\text{SiO}_2]_2$	Abundant in soil that is not leached extensively
Mica	$\text{K}_2\text{Al}_2\text{O}_5[\text{Si}_2\text{O}_5]_3\text{Al}_4(\text{OH})_4$ $\text{K}_2\text{Al}_2\text{O}_5[\text{Si}_2\text{O}_5]_3(\text{Mg}, \text{Fe})_6(\text{OH})_4$	Source of K in most temperate-zone soils
Amphibole	$(\text{Ca}, \text{Na}, \text{K})_{2,3}(\text{Mg}, \text{Fe}, \text{Al})_5(\text{OH})_2$ $[(\text{Si}, \text{Al})_4\text{O}_{11}]_2$	Easily weathered to clay minerals and oxides
Pyroxene	$(\text{Ca}, \text{Mg}, \text{Fe}, \text{Ti}, \text{Al})_2(\text{Si}, \text{Al})_2\text{O}_6$	Easily weathered
Olivine	$(\text{Mg}, \text{Fe})_2\text{SiO}_4$	Easily weathered
Epidote	$\text{Ca}_2(\text{Al}, \text{Fe})\text{Al}_2(\text{OH})\text{Si}_3\text{O}_{12}$	} Highly resistant to chemical weathering
Tourmaline	$\text{NaMg}_3\text{Al}_6\text{B}_3\text{Si}_6\text{O}_{27}$ $(\text{OH}, \text{F})_4$	
Zircon	ZrSiO_4	
Rutile	TiO_2	} Abundant in soil clay fractions as products of weathering
Kaolinite	$\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_8$	
Smectite	$\text{M}_x(\text{Si}, \text{Al})_8(\text{Al}, \text{Fe}, \text{Mg})_4\text{O}_{20}(\text{OH})_4$	
Illite	M = interlayer cation	
Vermiculite	$0.4 \leq x \leq 2.0 = \text{layer charge}$	
Chlorite		
Allophane	$\text{Si}_y\text{Al}_4\text{O}_{6+2y} \cdot n\text{H}_2\text{O}$ $1.6 \leq y \leq 4, n \geq 5$	Abundant in soils derived from volcanic ash deposits
Imogolite	$\text{Si}_2\text{Al}_4\text{O}_{10} \cdot 5 \text{H}_2\text{O}$	Abundant in leached soils
Gibbsite	$\text{Al}(\text{OH})_3$	
Goethite	FeOOH	Abundant Fe oxide in temperate soils
Hematite	Fe_2O_3	Abundant Fe oxide in aerobic soils
Ferrihydrite	$\text{Fe}_{10}\text{O}_{15} \cdot 9 \text{H}_2\text{O}$	Abundant in seasonally wet soils
Birnessite	$\text{M}_x\text{Mn}(\text{IV})_a\text{Mn}(\text{III})_b\text{O}_2$ M = interlayer cation, $x = b + 4c = \text{layer charge}, a + b + c = 1$	Most abundant Mn oxide
Lithiophorite	$\text{LiAl}_2(\text{OH})_6\text{Mn}(\text{IV})_2\text{Mn}(\text{III})\text{O}_6$	Found in acidic soils
Calcite	CaCO_3	Most abundant carbonate
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Most abundant sulfate

For the first six silicates listed in Table 1.3, the Si-to-O molar ratios of their fundamental structural units are as follows: 0.50 (quartz and feldspar, SiO_2), 0.40 (mica, Si_2O_5), 0.36 (amphibole, Si_4O_{11}), 0.33 (pyroxene, SiO_3), and 0.25 (olivine, SiO_4). The decreasing order of the Si-to-O molar ratio is the same as the observed decreasing order of resistance of these minerals to weathering in soils (see Section 2.2).

The minerals epidote, tourmaline, zircon, and rutile, listed in the middle of Table 1.3, are highly resistant to weathering in the soil environment. Under the assumption of uniform parent material, measured variation in the relative number of single-crystal grains of these minerals in the fine sand or coarse silt fractions of a soil profile can serve as a quantitative indicator of mass changes in soil horizons produced by chemical weathering.

The minerals listed from kaolinite to gypsum in Table 1.3 are termed *secondary minerals* because they nearly always result from the weathering transformations of primary silicates. Often these secondary minerals are of clay size and many exhibit a relatively poorly ordered atomic structure. Variability in their composition through the substitution of ions into their structure (*isomorphic substitution*) also is noted frequently. The layer-type aluminosilicates, smectite, illite, vermiculite, and chlorite, bear a net charge on their surfaces (*layer charge*) principally because of this variability in composition, as shown in Section 2.3. Kaolinite and the secondary metal oxides below it in the list—with the important exception of birnessite—also bear a net surface charge, but because of proton adsorption and desorption reactions, not isomorphic substitutions. Birnessite, a layer-type Mn oxide, also bears a surface charge, mainly because of vacancies in its structure (quantified by an x subscript in the chemical formula) where Mn^{4+} cations should reside. Secondary metal oxides like gibbsite and goethite tend to persist in the soil environment longer than secondary silicates because Si is more readily leached than Al, Fe, or Mn, unless significant amounts of soluble organic matter are present to render these latter metals more soluble.

Organic matter is, of course, an important constituent of the solid phase in soils. The structural complexity of soil humus has thus far precluded the making of a simple list of component solids like that in Table 1.3, but something can be said about the overall composition of *humic substances*—the dark, microbially transformed organic materials that persist in soils (slow and passive humus pools) throughout profile development. The two most investigated humic substances are *humic acid* and *fulvic acid*. Their chemical behavior is discussed in Section 3.2. Worldwide, the average chemical formula for these two substances in soil is $\text{C}_{185}\text{H}_{191}\text{O}_{90}\text{N}_{10}\text{S}$ (humic acid) and $\text{C}_{186}\text{H}_{245}\text{O}_{142}\text{N}_9\text{S}_2$ (fulvic acid). These two average chemical formulas can be compared with the average C-to-N-to-S *molar* ratio of bulk soil humus, which is 140:10:1.3, and with the average chemical formula for terrestrial plants, which is $\text{C}_{146}\text{H}_{227}\text{O}_{123}\text{N}_{10}$. Relative to soil humus as a whole, humic and fulvic acids are depleted in N. Their C-to-N molar ratio is 30% to 50% larger than that of soil humus, indicating their greater resistance to

net microbial mineralization. Relative to terrestrial plants, humic and fulvic acids are enriched in C but depleted in H. The depletion of H, from roughly a 1.5:1 H-to-C molar ratio in plant material to roughly 1.3 in fulvic acid and 1.0 in humic acid, suggests a greater degree of aromaticity (e.g., H-to-C ratio is 1.0 in benzene, the prototypical aromatic organic molecule) in the latter materials, which is consistent with their resistance to microbial attack.

The 21 trace elements listed in Tables 1.1 and 1.2 seldom occur in soils as separate mineral phases, but instead are found as constituents of host minerals and humus. The principal ways in which important trace elements occur in primary and secondary soil minerals are summarized in tables 1.4 and 1.5. Table 1.5 also indicates the trace elements found typically in association with soil humus. The chemical process underlying these trace element occurrences is called *coprecipitation*. Coprecipitation is the simultaneous precipitation of a chemical element with other elements by any mechanism and at any rate. The three broad types of coprecipitation are *inclusion*, *adsorption*, and *solid-solution formation*.

Table 1.4
Occurrence of trace elements in primary minerals.

Element	Principal modes of occurrence in primary minerals
B	Tourmaline, borate minerals; isomorphic substitution for Si in micas
Ti	Rutile and ilmenite (FeTiO_3); oxide inclusions in silicates
V	Isomorphic substitution for Fe in pyroxenes and amphiboles, and for Al in micas; substitution for Fe in oxides
Cr	Chromite (FeCr_2O_4); isomorphic substitution for Fe or Al in other minerals of the spinel group
Co	Isomorphic substitution for Mn in oxides and for Fe in pyroxenes, amphiboles, and micas
Ni	Sulfide inclusions in silicates; isomorphic substitution for Fe in olivines, pyroxenes, amphiboles, micas, and spinels
Cu	Sulfide inclusions in silicates; isomorphic substitution for Fe and Mg in olivines, pyroxenes, amphiboles, and micas; and for Ca, K, or Na in feldspars
Zn	Sulfide inclusions in silicates; isomorphic substitution for Mg and Fe in olivines, pyroxenes, and amphiboles; and for Fe or Mn in oxides
As	Arsenopyrite (FeAsS) and other arsenate minerals
Se	Selenide minerals; isomorphic substitution for S in sulfides; iron selenite
Mo	Molybdenite (MoS_2); isomorphic substitution for Fe in oxides
Cd	Sulfide inclusions and isomorphic substitution for Cu, Zn, Hg, and Pb in sulfides
Pb	Sulfide, phosphate, and carbonate inclusions; isomorphic substitution for K in feldspars and micas; for Ca in feldspars, pyroxenes, and phosphates; and for Fe and Mn in oxides

Table 1.5

Trace elements coprecipitated with secondary soil minerals and soil humus.

Solid	Coprecipitated trace elements
Fe and Al oxides	B, P, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Mo, As, Se, Cd, Pb
Mn oxides	P, Fe, Co, Ni, Cu, Zn, Mo, As, Se, Cd, Pb
Ca carbonates	P, V, Mn, Fe, Co, Cd, Pb
Illites	B, V, Ni, Co, Cr, Cu, Zn, Mo, As, Se, Pb
Smectites	B, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb
Vermiculites	Ti, Mn, Fe
Humus	B, Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Cd, Pb

If a solid phase formed by a trace element has a very different atomic structure from that of the host mineral, then it is likely that the host mineral and the trace element will occur together only as morphologically distinct phases. This kind of association is termed *inclusion* with respect to the trace element. For example, CuS occurs as an inclusion—a small, separate phase—in primary silicates (Table 1.4).

If there is only limited structural compatibility between a trace element and a corresponding major element in a host mineral, then coprecipitation produces a mixture of the two elements restricted to the host mineral–soil solution interface. This mechanism is termed *adsorption* because the mixed solid phase that forms is restricted to the interfacial region (including the inter-layer region of layer-type minerals). Well-known examples of adsorption are the incorporation of metals like Pb and oxyanions like arsenate into secondary metal oxides (Table 1.5).

Finally, if structural compatibility is high and diffusion of a trace element within the host mineral is possible, a major element in the host mineral can be replaced sparingly but uniformly throughout by the trace element. This kind of homogeneous coprecipitation is *solid-solution formation*. It is enhanced if the size and valence of the substituting element are comparable with those of the element replaced. Examples of solid-solution formation occur when precipitating secondary aluminosilicates incorporate metals like Fe to replace Al in their structures (Table 1.5) or when calcium carbonate precipitates with Cd replacing Ca in the structure. Soil solid phases bearing trace elements serve as reservoirs, releasing the trace elements slowly into the soil solution as weathering continues. If a trace element is also a nutrient, then the rate of weathering becomes a critical factor in soil fertility. For example, the ability of soils to provide Cu to plants depends on the rate at which this element is transformed from a solid phase to a soluble chemical form. Similarly, the weathering of soil solids containing Cd as a trace element will determine the potential hazard of this toxic element to microbes and plants.

1.4 Soil Air and Soil Water

The fluid phases in soil constitute between one and two thirds of the soil volume. The gaseous phase, *soil air*, typically is the same kind of fluid mixture as atmospheric air. Because of biological activity in soil, however, the percentage composition of soil air can differ considerably from that of atmospheric air (781 mL N₂, 209 mL O₂, 9.3 mL Ar, and 0.33 mL CO₂ in 1 L dry air). Well-aerated soil contains 180 to 205 mL O₂ L⁻¹ soil air, but this can drop to 100 mL L⁻¹ at 1 m below the soil surface, after inundation by rainfall or irrigation, or even to 20 mL L⁻¹ in isolated soil microenvironments near plant roots. Similarly, the fractional volume of CO₂ in soil air is typically 3 to 30 mL L⁻¹, but can approach 100 mL L⁻¹ at a 1-m depth in the vicinity of plant roots, or after the flooding of soil. This markedly higher CO₂ content of soil air relative to that of the atmosphere has a significant impact on both soil acidity and carbonate chemistry. Soil air also contains variable but important contributions from H₂, NO, N₂O, NH₃, CH₄, and H₂S produced with microbial mediation under conditions of low or trace oxygen content.

Soil water is found principally as a condensed fluid phase, although the content of water vapor in soil air can approach 30 mL L⁻¹ in a wet soil. Soil water is a repository for dissolved solids and gases, and for this reason is referred to as the *soil solution*. With respect to dissolved solids, those that dissociate into ions (*electrolytes*) in the soil solution are most important to the chemistry of soils. The nine ion-forming chemical elements with concentrations in uncontaminated soil solutions that typically exceed all others are C (HCO₃⁻), N (NO₃⁻), Na (Na⁺), Mg (Mg²⁺), Si [Si(OH)₄⁰], S (SO₄²⁻), Cl (Cl⁻), K (K⁺), and Ca (Ca²⁺), where the principal chemical species of the element appears in parentheses or square brackets. [The neutral species Si(OH)₄⁰ is silicic acid.] With the exception of Cl, all are macroelements.

The partitioning of gases between soil air and the soil solution is an important process contributing to the cycling of chemical elements in the soil environment. When equilibrium exists between soil air and soil water with respect to the partitioning of a gaseous species between the two phases, and if the concentration of the gas in the soil solution is low, the equilibrium can be described by a form of *Henry's law*:

$$K_H = [A(\text{aq})]/P_A \quad (1.1)$$

where K_H is a parameter with the units moles per cubic meter per atmosphere of pressure, known as the *Henry's law constant*, $[A]$ is the concentration of gas A in the soil solution (measured in moles per cubic meter), and P_A is the partial pressure of A in soil air (measured in atmospheres). Table 1.6 lists values of K_H at 25 °C for 10 gases found in soil air. As an example of the use of this table, consider a flooded soil in which CO₂ and CH₄ are produced under microbial mediation to achieve partial pressures of 14 and 10 kPa respectively, as measured in the headspace of serum bottles used to contain the soil during

Table 1.6
The “Henry’s law constant” for 10 soil gases at 25 °C^a.

Gas	K_H (mol m ⁻³ atm ⁻¹)	Gas	K_H (mol m ⁻³ atm ⁻¹)
H ₂	0.78	NO	92
CO ₂	34.20	N ₂	0.65
CH ₄	1.41	O ₂	1.27
NH ₃	5.71×10^4	SO ₂	1.36×10^3
N ₂ O	24.17	H ₂ S	1.02×10^2

^aBased on data compiled from Lide, D. R. (ed.) (2004) *CRC handbook of chemistry and physics*, pp. 8-86–8-89. CRC Press, Boca Raton, FL.

incubation. According to Table 1.6, the corresponding concentrations of the two gases in the soil solution are

$$\begin{aligned}
 [\text{CO}_2(\text{aq})] &= 34.03 \frac{\text{mol m}^{-3}}{\text{atm}} \times \left(14 \text{ kPa} \times \frac{1 \text{ atm}}{101.325 \text{ kPa}} \right) \\
 &= 4.7 \text{ mol m}^{-3} \\
 [\text{CH}_4(\text{aq})] &= \frac{1.41 \text{ mol m}^{-3}}{\text{atm}} \times 0.0987 \text{ atm} = 0.14 \text{ mol m}^{-3}
 \end{aligned}$$

(The units appearing here are discussed in the Appendix.) The result for CO₂ is noteworthy, in that the concentration of this gas in a soil solution equilibrated with the ambient atmosphere would be 400 times smaller.

1.5 Soil Mineral Transformations

If soils were not open systems, soil minerals would not weather. It is the continual input and output of percolating water, biomass, and solar energy that makes soils change with the passage of time. These changes are perhaps reflected most dramatically in the development of soil horizons, both in their morphology and in the mineralogy of the soil clay fraction.

Table 1.7 is a broad summary of the changes in clay fraction mineralogy observed during the course of soil profile development. These changes are known collectively as the *Jackson–Sherman weathering stages*.

Early-stage weathering is recognized through the importance of sulfates, carbonates, and primary silicates, other than quartz and muscovite, in the soil clay fraction. These minerals survive only if soils remain very dry, or very cold, or very wet, most of the time—that is, if they lack significant throughputs of water, air, biota, and thermal energy that characterize open systems in nature. Soils in the early stage of weathering include Aridisols, Entisols, and Gelisols at the Order level in the U.S. Soil Taxonomy. Intermediate-stage

Table 1.7
Jackson–Sherman soil weathering stages.

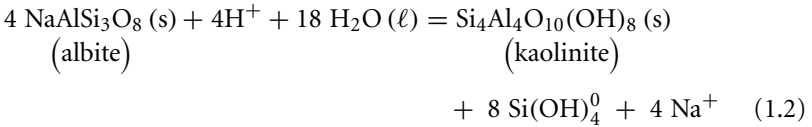
Characteristic minerals in soil clay fraction	Characteristic soil chemical and physical conditions	Characteristic soil properties ^a
<i>Early stage</i>		
Gypsum	Low water and	Minimally weathered soils: arid or very cold regions, waterlogging, recent deposition
Carbonates	humus content,	
Olivine/pyroxene/ amphibole	very limited	
Fe(II)-bearing micas	leaching	
Feldspars	Reducing environments, cold environments	
	Limited amount of time for weathering	
<i>Intermediate stage</i>		
Quartz	Retention of Na, K,	Soils in temperate regions: forest or grass cover, well-developed A and B horizons, accumulation of humus and clay minerals
Diocahedral mica/illite	Ca, Mg, Fe(II), and silica; moderate	
Diocahedral vermiculite/chlorite	leaching, alkalinity	
Smectite	Parent material rich in Ca, Mg, and Fe(II), but not Fe(II) oxides	
	Silicates easily weathered	
<i>Advanced stage</i>		
Kaolinite	Removal of Na, K,	Soils under forest cover with high temperature and precipitation: accumulation of Fe(III) and Al oxides, absence of alkaline earth metals
Gibbsite	Ca, Mg, Fe(II), and silica	
Iron oxides	Intensive leaching by fresh water	
Titanium oxides	Oxidation of Fe(II)	
	Low pH and humus content	

^aSoil taxa corresponding to these properties are discussed in Encyclopedia Britannica (2005) *Soil*. Available at www.britannica.com/eb/.

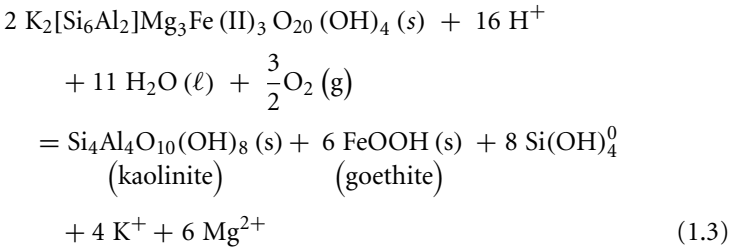
weathering features quartz, muscovite, and layer-type secondary aluminosilicates (*clay minerals*) prominently in the clay fraction. These minerals survive under leaching conditions that do not entirely deplete silica and the major elements, and do not result in the complete oxidation of ferrous iron [Fe(II)], which is incorporated into illite and smectite. Soils at this weathering stage include the Mollisols, Alfisols, and Spodosols. Advanced-stage weathering, on

the other hand, is associated with intensive leaching and strongly oxidizing conditions, such that only hydrous oxides of aluminum, ferric iron [Fe(III)], and titanium persist ultimately. Kaolinite will be an important clay mineral if the removal of silica by leaching is not complete, or if there is an invasion of silica-rich waters, as can occur, for example, when siliceous leachate from the upper part of a soil toposquence moves laterally into the profile of a lower part. The Ultisols and Oxisols are representative soil taxa.

The order of increasing persistence of the soil minerals listed in Table 1.7 is downward, both among and within the three stages of weathering. The primary minerals, therefore, tend to occur higher in the list than the secondary minerals, and the former can be linked with the latter by a variety of chemical reactions. Of these reactions, the most important is termed *hydrolysis and protonation*, which may be illustrated by the weathering of the feldspar *albite* or the mica *biotite*, to form the clay mineral *kaolinite* (Table 1.3). For albite the reaction is



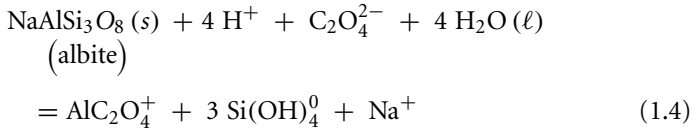
where solid (s) and liquid (ℓ) species are indicated explicitly, all undesigned species being dissolved solutes by default. The corresponding reaction for biotite is



in which the iron oxyhydroxide, goethite, is also formed. In both reactions, which are taken conventionally to proceed from left to right, the dissolution of a primary silicate occurs through chemical reaction with water and protons to form one or more solid-phase products plus dissolved species, which are then subject to leaching out of the soil profile. These two reactions illustrate an *incongruent dissolution*, as opposed to *congruent dissolution*, in which only dissolved species are products. The basic chemical principles underlying the development of eqs. 1.2 and 1.3 are discussed in Special Topic 1, at the end of this chapter.

The incongruent dissolution of biotite, which contains only ferrous iron [Fe(II)], to form goethite, which contains only ferric iron [Fe(III)], illustrates the electron transfer reaction termed *oxidation* (in the case of Eq. 1.3, the

oxidation of ferrous iron)—an important process in soil weathering. (Oxidation, the loss of electrons from a chemical species, is discussed in Chapter 6.) Another important weathering reaction is *complexation*, which is the reaction of an anion (or other ligand) with a metal cation to form a species that can be either dissolved or solid phase. In the case of albite weathering by complexation,



The organic ligand on the left side of Eq. 1.4, oxalate, is the anion formed by complete dissociation of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$, ethanedioic acid) at $\text{pH} \geq 4.2$. It complexes Al^{3+} released by the hydrolysis and protonation of albite. The resulting product is shown on the right side of Eq. 1.4 as a soluble complex that prevents the precipitation of kaolinite (i.e., the dissolution process is now congruent). Oxalate is a very common anion in soil solutions associated with the life cycles of microbes, especially fungi, and with the *rhizosphere*, the local soil environment influenced significantly by plant roots. Organic anions produced by microbes thus play a significant role in the weathering of soil minerals, particularly near plant roots, where anion concentrations can be in the moles per cubic meter range.

The three weathering reactions surveyed very briefly in this section provide a chemical basis for the transformation of soil minerals among the Jackson–Sherman weathering stages. With respect to silicates, a *master variable* controlling these transformations is the concentration of silicic acid in the soil solution. As the concentration of $\text{Si}(\text{OH})_4^0$ decreases through leaching, the mineralogy of the soil clay fraction passes from the primary minerals of the early stage to the secondary minerals of the intermediate and advanced stages. Should the $\text{Si}(\text{OH})_4^0$ concentration increase through an influx of silica, on the other hand, the clay mineralogy can shift upward in Table 1.7. This possible behavior is in fact implied by the equal-to sign in the chemical reactions in eqs. 1.2 through 1.4.

For Further Reading

- Churchman, G. J. (2000) The alteration and formation of soil minerals by weathering, pp. F-3–F-76. In: M. E. Sumner (ed.), *Handbook of soil science*. CRC Press, Boca Raton, FL. A detailed, field-oriented discussion of the chemical weathering processes that transform primary minerals in soils.
- Dixon, J. B., and D. G. Schulze (eds.). (2002) *Soil mineralogy with environmental applications*. Soil Science Society of America, Madison, WI. A standard reference work on soil mineral structures and chemistry.