

G

GABION

A wire-mesh container filled with stones. They are used in modular fashion to build retaining walls to fortify slopes and minimize erosion there on. Being porous, they allow the fortified slope to drain, thus preventing the buildup of hydrostatic pressure. A further advantage is their flexibility, which allows them to adjust to minor earth movements.

GELIFLUCTION

The creep of a surface layer of thawed, water-saturated soil downhill over frozen ground. A characteristic type of mass movement in periglacial (permafrost) environments.

Cross-references

Cryosols
Ice Erosion

GEOCHEMISTRY IN SOIL SCIENCE

Geochemistry in soil science differs from the classical geochemistry of rock formations because soil differs fundamentally from weathered rock (Singer and Munns, 1991). Soils are open, multi-component biogeochemical systems that undergo biological, chemical, and physical transformations leading to a characteristic morphological feature – the soil horizons – which reflect the unique influences of percolating waters and living organisms acting over millennia. These transformations also serve to link soils with the atmosphere and hydrosphere, as illustrated for the element nitrogen (N) in Figure G1, a flow diagram which applies to natural soils at spatial scales ranging from pedon to

landscape. Soil N flows are similar to those for soil C, in that humus (“soil organic matter”) 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 , being of environmental concern because of its very strong absorption of terrestrial infrared radiation (greenhouse gas). The source of these gases is dissolved inorganic N, whose transformation 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 Figure G1. 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 a flooding event 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 being 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/N ratios are applied to these soils as fertilizers, since rapid microbial mineralization of such materials is favored.

This example illustrates the typical way in which geochemistry in soil science includes within its purview the transformations and cycling of chemical elements as affected by atmospheric, biological and hydrological agents.

Geochemical patterns in soils

The major elements in soils are those whose concentrations exceed 100 mg kg^{-1} , all others being termed trace elements.

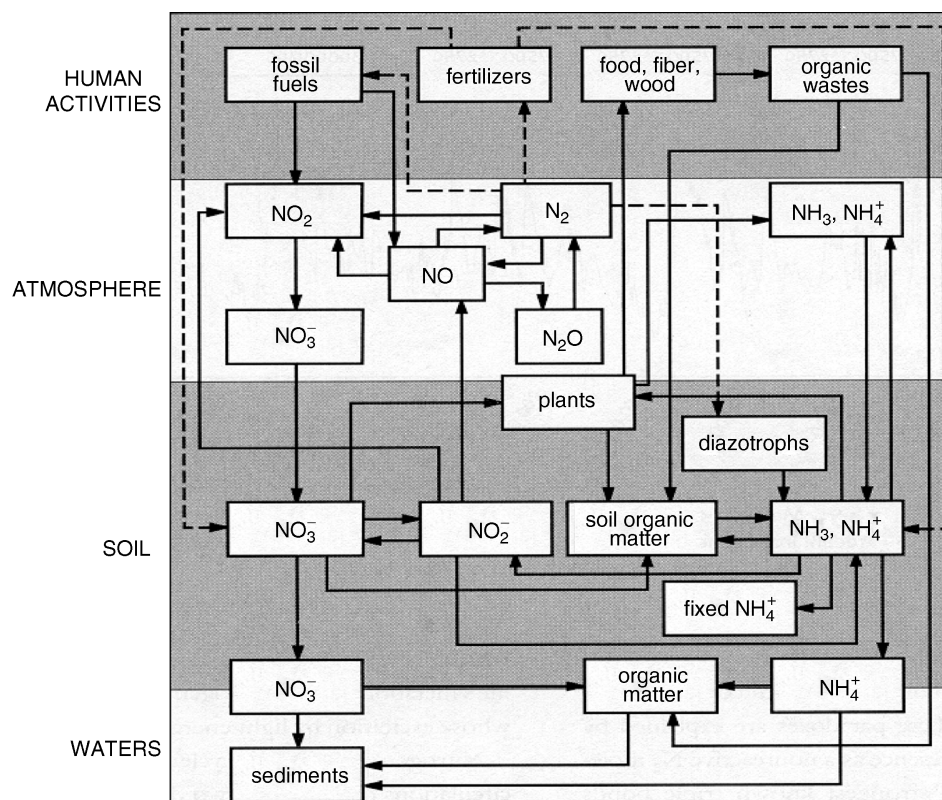


Figure G1 Main reservoirs and flows in the biogeochemical cycle of nitrogen (Smil, 2000).

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 (Schacklette and Boerngen, 1984). Notable among the major elements is the strong enrichment of C and N in soils relative to crustal rocks, whereas Ca, Na, and Mg show significant depletion. 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/N, C/P, and C/S ratios, 8, 61, and 13, respectively, in soils are very low and, therefore, 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 one thousand times as much C and N, one hundred times as much S, and ten 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 was illustrated for N in Figure G1.

A simple geochemical parameter with global environmental significance is the anthropogenic mobilization factor (AMF), 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. If AMF is well above 10, an element is said to have significant anthropogenic perturbation of its global biogeochemical cycle (Klee and Graedel, 2004). 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.

The chemical elements essential to plant growth in soil are: H, B, C, N, O, Mg, P, S, Cl, K, Ca, Mn, Fe, Cu, Zn, and Mo (Singer and Munns, 1991). Of these elements, B, Cl, Mn, Fe, Cu, Zn, and Mo are micronutrients (absorbed in trace amounts) and Mg, S, and Ca are secondary nutrients (absorbed in small, but not trace, amounts). The remaining six elements are macronutrients. The 16 essential elements – with the exception of Mo – have the distinguishing property that their atomic number ≤ 30 (Frausto da Silva and Williams, 1991). Thus, they are among the “light elements” that have relatively small crystallographic ionic radii. The biological significance of this property can be appreciated by reference to two important geochemical parameters that are applied to the metal elements (Frausto da Silva and Williams, 2001).

The first is the ionic potential (IP), which is the valence of a metal cation divided by its crystallographic ionic radius expressed in units of nanometers. Metal cations with $IP < 30 \text{ nm}^{-1}$ tend to be found in circumneutral waters without significant concentrations of complexing ligands as solvated chemical species (“free cations”); those with $30 > IP > 100 \text{ nm}^{-1}$ tend to hydrolyze

readily in circumneutral waters; and those with $IP > 100 \text{ nm}^{-1}$ tend to be found as oxyanions. Examples of these three classes are: Na^+ ($IP = 9.8 \text{ nm}^{-1}$), Al^{3+} ($IP = 56 \text{ nm}^{-1}$), and Cr^{6+} ($IP = 231 \text{ nm}^{-1}$). If a metal element has different valence states, it may fall into different classes: Cr^{3+} ($IP = 49 \text{ nm}^{-1}$) hydrolyzes, whereas hexavalent Cr forms an oxyanion species in aqueous solution. 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+} ($IP = 46 \text{ nm}^{-1}$)), 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 to 100 nm^{-1}) is the signature of metal elements that are not expected to be soluble at circumneutral pH in the absence of complexing ligands.

The second important geochemical property of metal elements is their Class A or Class B behavior. A metal cation is Class A if it (1) has low polarizability (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 oxygen-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 are the “heavy metals” Ag, Cd, Hg, and Pb, while 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.

The description of metals according to these two parameters 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 toxicants. 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^+). 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 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 non-availability 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. Large AMF values 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.

One of the most important geochemical properties of soils is their content of trace elements (Adriano, 2001). Soil minerals containing trace elements serve as reservoirs for the elements, releasing them slowly into the soil solution as weathering continues. If a trace element is also a micronutrient, then the rate of mineral weathering becomes a critical factor in soil fertility. For example, the ability of soils to provide Co to plants depends on the rate at which this element is transformed from an Mn oxide constituent to a soluble chemical form. Soil chemical properties, like pH, electrode potential, and water activity, will affect the rate of this transformation and thus control Co solubility. Similarly, the weathering rate of soil minerals containing Cd as a trace element will determine in part the potential hazard of this toxic element to plants.

The ways in which trace elements occur in primary and secondary soil minerals are summarized in Tables G1 and G2. (Table G2 also indicates trace elements found typically in

Table G1 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

association with soil humus.) The chemical process governing the trace element common also in primary silicates (Table G1); but, in this case, trace element occurrences described in these tables is coprecipitation, the simultaneous precipitation of a chemical element with other elements by any mechanism at any rate. The three broad types of coprecipitation are inclusion, adsorption and solid solution formation (Sposito, 1989).

If a pure solid phase that would be formed by a trace element has a very different atomic structure from that of a host mineral which coprecipitates with the trace element, then the host mineral and the trace element will occur together only as morphologically distinct solids. This kind of association is termed inclusion. For example CuS often occurs as a separate phase in primary silicates (Table G1). If there is some structural compatibility between a trace element and the corresponding major element in a host mineral, then coprecipitation can produce a mixture of the two elements at the mineral/soil solution interface. This mechanism is termed adsorption because the mixed solid phase is restricted to the interfacial region and its composition varies as the host mineral continues to precipitate from the soil solution (Stumm, 1992). Examples of adsorption are the surface accumulation of oxyanions, like borate, phosphate or molybdate, on secondary metal oxides (Table G2) and of transition metals, like Fe or Ni, on soil organic matter.

Table G2 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

Finally, if structural compatibility is high, and free diffusion of a trace element within a host mineral is possible, a major element in the host mineral can be replaced uniformly throughout by the trace element. This kind of homogeneous coprecipitation is solid solution formation. It is likely if the ionic size and valence of the substituting element are comparable to those of the element replaced. Solid solution formation occurs when secondary aluminosilicates precipitate and incorporate metals like Ni, Cu, and Zn to substitute for Al in their structures (Table G2), or when Ca carbonate precipitates with Cd substituting for Ca. "Isomorphous substitution" of this kind is common also in primary silicates (Table G1); but in this case, trace element substitution occurs as minerals crystallize from a silicate melt. As noted above, trace elements, even those that are micronutrients (e.g., Cu and Zn), can produce toxicity in plants (phytotoxicity) at sufficiently high concentrations in the soil solution.

Geochemical transformations in soils

The continual input and output of percolating water, biomass, and solar energy in soils makes them change with the passage of time. These changes are reflected in the morphological development of soil horizons, but they are also apparent in the mineralogy of the soil clay fraction as it changes from weathering.

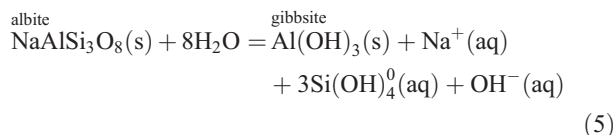
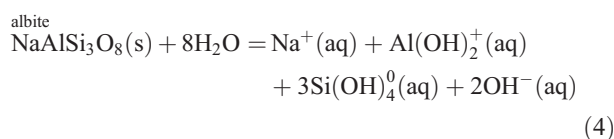
Table G3 provides a summary of typical changes in mineralogy observed in the clay fraction during soil profile development. These changes are known collectively as the Jackson-Sherman weathering stages, and they can be classified as "early stage," "intermediate stage," or "advanced stage," (Jackson and Sherman, 1953; Jackson, 1965). Early-stage weathering exhibits 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, for most of the time; i.e., for reasons of age or if they lack, the throughputs of water, air, and thermal energy that usually characterize open systems in nature (entisols, inceptisols, gelisols, and andisols). Intermediate-stage weathering features quartz, muscovite, and secondary aluminosilicates

Table G3 Jackson-Sherman soil weathering stages

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

prominently in the clay fraction. These minerals survive under conditions that do not deplete soluble silica $[\text{Si}(\text{OH})_4^0]$ and the macroelements, and that do not result in the complete oxidation of Fe^{II} incorporated into illite or smectite (aridisols, vertisols, mollisols, and alfisols). Advanced-stage weathering, on the other hand, is associated with intensive leaching and strongly oxidizing conditions, such that only hydrous oxides of Al, Fe^{III} , and Ti persist ultimately (ultisols and oxisols). Kaolinite will be an important clay mineral only 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 leachate from the upper part of a soil toposequence moves laterally into the profile of a lower part.

The order of increasing persistence of the soil minerals listed in Table G3 is downward, both among and within the three stages of weathering. Primary minerals, therefore, tend to occur higher in the list than secondary minerals, and the former can be linked with the latter by five key geochemical transformations (Sposito, 1989). Of these, the most important is hydrolysis (reaction with water), illustrated by the chemical reactions:



In these reactions, the dissolution of the feldspar, albite, occurs through chemical reaction with water to form dissolved species (denoted by "aq"). Equation (4) describes a congruent dissolution process because only dissolved species make up the products, whereas Equation (5) describes an incongruent dissolution process because a solid-phase product-gibbsite is formed as well.

A convenient pictorial representation of congruent dissolution reactions can be developed through the construction of activity-ratio diagrams (Lindsay, 2001; Sposito, 1989). An activity-ratio diagram for three secondary minerals in an acidic soil is shown in Figure G2. The Jackson-Sherman weathering scenario (Table G3) indicates that, when soil profiles are leached free of silica with fresh water, 2:1 layer-type clay minerals (smectite, vermiculite, illite) are replaced by 1:1 layer-type clay minerals (kaolinite) and, ultimately, these are replaced by metal oxyhydroxides (e.g., gibbsite). This sequence of mineral transformations can be represented by the successive dissolution reactions of smectite, kaolinite, and gibbsite (Sposito, 1989):

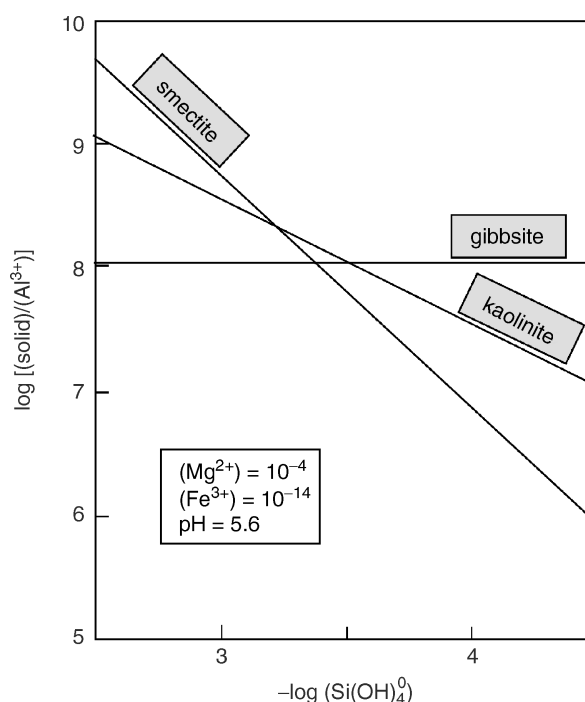
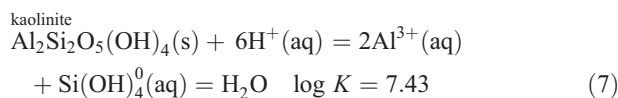
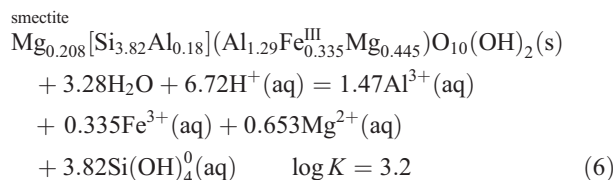
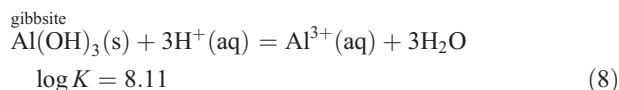


Figure G2 Activity ratio diagram for control of Al solubility by clay minerals and gibbsite (Sposito, 1989).



The solid-phase reactant in Equation (6) is montmorillonite, with Mg^{2+} as the interlayer exchangeable cation. Its dissolution reaction (at 298.15 K) is characterized by the equilibrium constant, K . The value of K for the dissolution of kaolinite (Equation (7)) reflects a well-crystallized solid phase. Poorly crystallized kaolinite – typical of intensive soil weathering conditions – would yield $\log K \approx 10.5$. In Equation (8), gibbsite also is assumed to be well crystallized; poorly crystallized gibbsite would yield $\log K \approx 9.35$.

Equations (6) to (8) can be used to construct an activity-ratio diagram in respect to $\text{Al}^{3+}(\text{aq})$ activity in the soil solution, shown conventionally between curved brackets, that is (Al^{3+}) , as influenced by the leaching of silicic acid (Sposito, 1989). At a given value of the soil-solution activity of silicic acid $[\text{Si}(\text{OH})_4^0]$, which is the independent variable (and under the assumption that all solid phases are in their Standard States), the solid that produces the largest value of the activity ratio, $[(\text{solid})/(\text{Al}^{3+})]$ is the one that is most stable and, therefore, the one that will be present at equilibrium. This conclusion follows because a solid phase that produces the smallest soil solution activity of a free ionic species will also control the solubility of that species. The effect of soil profile leaching at pH 5 is represented in the activity-ratio diagram by moving from left to right along its x-axis. Amorphous silica supports $(\text{Si}(\text{OH})_4^0) \approx 10^{-2.7}$. This condition, which reflects the intensive weathering of primary silicates in an acidic soil, leads to the prediction that smectite is the most stable solid phase with

respect to solubility control of Al. As leaching and the loss of silica proceed, the silicic acid activity will decrease, and when $(\text{Si}(\text{OH})_4^0) \ll 10^{-4}$ (the silicic acid activity supported by the dissolution of quartz, gibbsite becomes the most stable Al-bearing solid phase. This progression of minerals agrees with field observations as summarized in the Jackson-Sherman intermediate-to-advanced weathering stages (Table G3).

The geochemical interpretation of activity-ratio diagrams is influenced by the existence of varying degrees of crystallinity of soil minerals, with a corresponding variation in their solubility (Sposito, 1985). For example, in the case of Figure G2, poorly crystallized forms of gibbsite and kaolinite, alluded to above, would require replacing K by larger values, such that the gibbsite line would be plotted 1.24 units lower and the kaolinite line would be shifted downward by 1.53 units (Figure G3). The effect of these changes is to create “windows” of gibbsite and kaolinite stability, instead of single lines in the diagram, and thus to enlarge the range of silicic acid activity over which smectite can remain the most stable solid phase. This kind of variability and the typical value, $(\text{Si}(\text{OH})_4^0) \approx 8 \times 10^{-4}$, in acid soils suggests that smectite, kaolinite, and gibbsite commonly will coexist in these soil weathering environments.

Another important geochemical transformation is complexation (often inappropriately called “chelation”), the reaction of complexing anions with metals in soil minerals (Sposito, 1989):

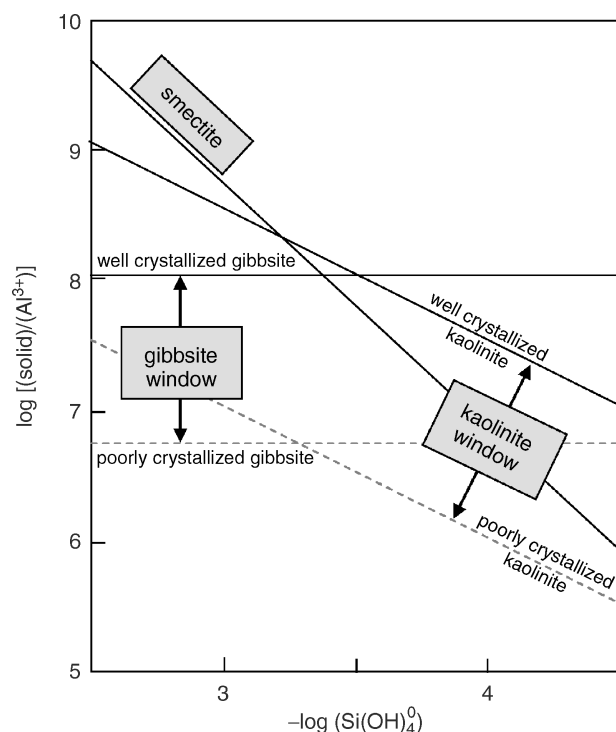
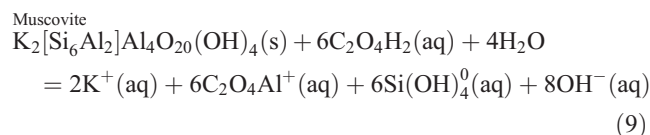
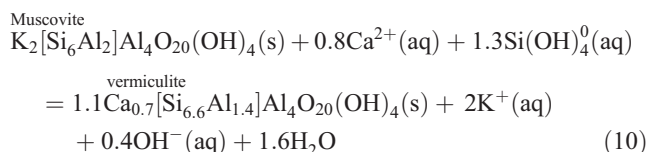


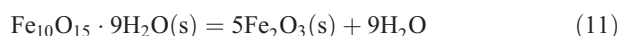
Figure G3 Gibbsite and kaolinite windows for the same conditions as Figure G2.

The second compound on the left side of Equation (9), oxalic acid (ethanedioic acid), dissociates and releases its anion, $\text{C}_2\text{O}_4^{2-}$, to form a soluble complex with Al^{3+} . This complex formation, in turn enhances the possibility of congruent dissolution for muscovite, since the soluble complex, $\text{C}_2\text{O}_4\text{Al}^+(\text{aq})$, helps to prevent the hydrolysis of Al that otherwise could lead to gibbsite precipitation, as in Equation (5).

Cation exchange, on the other hand, is a geochemical transformation associated with the incongruent dissolution of muscovite to form vermiculite in soils that retain both Ca^{2+} and $\text{Si}(\text{OH})_4^0$ (Sposito, 1989):



The Ca^{2+} ion exchanges with K^+ to occupy an interlayer position in vermiculite. This kind of reaction is favored for example, in an aridisol having abundant dissolved Ca (and silicic acid) in the soil solution. Incongruent dissolution is accompanied often by oxidation-reduction reactions, if Fe or some other “redox element” is involved in weathering. An example is the incongruent dissolution of biotite, which contains Fe^{II} , to form vermiculite, which contains both Fe^{II} and Fe^{III} , as well as goethite, which contains only Fe^{III} . Finally, hydration-dehydration can be added to complete this listing of significant geochemical transformations. An example of dehydration is the transformation of ferrihydrite to hematite:



Mineral dehydration reactions are favored as the relative humidity of soil water drops below 100%.

The geochemical transformations surveyed very briefly in this article provide a chemical basis for the cycling of elements through the weathering of soil minerals both within and between the Jackson-Sherman stages. In respect to silicates one “master variable” controlling these transformations is the activity of silicic acid in the soil solution. As the activity and therefore 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, as chemical principles would indicate, the mineralogy can be expected to shift upward in Table G3.

Finally, to restate a point stressed at the beginning of this article, the geochemistry of soils is largely distinguished from the geochemistry of rocks by the role played by organisms and humus. The integration of biology – particularly microbiology – into aqueous geochemistry has been one of the significant advances in the science in recent years (see e.g., Drever, 2004 page xvii).

Garrison Sposito

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Cross-references

Biogeochemical Cycles
Geology and Soils
Macronutrients
Micronutrients
Nitrogen Cycle
Phosphorus Cycle
Plant Nutrients
Sulfur Transformations and Fluxes
Trace Elements

GEOGRAPHY OF SOILS

The geography of soil is concerned with the distribution and variability of soils on terrestrial landscapes ranging from local to global scales. Birkeland (1999, chapter 10) gives a clear exposition of the conceptual framework, but see Bunting (1967), Boulaïne (1975), Cruickshank (1972) Steila and Pond (1989), and Foth and Schafer (1980) for earlier ideas. Of the soil forming factors, it is principally climate and the closely dependent variable vegetation that determine soil geography in this sense. For present purposes they are best considered as a linked variable. The remaining soil forming factors – parent material, topography and time – may be considered secondary determinants which modify the geographical regularities imposed by the linked variable climate-vegetation.

The classic 1938 Yearbook of Agriculture of the U.S. Department of Agriculture (USDA, 1938) made the concept explicit in terms of diagrams such as Figure G4, in which climatic gradients in temperature and rainfall are of primary importance in determining vegetation and hence soil variations over the land

surface. Not surprisingly, considering its provenance, this model follows fairly closely the pattern of soils on the North American continent (Figure G5), with the cold-hot gradient following a north-south axis, and the wet-dry gradient an east-west one. Reverse the north-south gradient and the model fits South America almost as well, allowing for the fact that the southern tip does not reach such high latitudes. Where differences exist between model and reality, they are explainable as being due to the effects of the other soil forming factors as previously stated. For example this is most obvious in the case of topography, with the Cordillera disrupting the simple latitudinal and longitudinal variations imposed by climate-vegetation.

A different perspective on the relationship of soil and weathering conditions to climate and vegetation is shown as a pole to equator transect in Figure G6.

The time factor

Tectonic events (including volcanism) and glaciations are the principal ways by which the pedogenetic clock is reset. Where such geological activity is of recent date, new lithospheric materials have been exposed to the weathering regime, and the soils that are forming are inevitably at an immature stage of development. Where recent tectonic or glacial activity is lacking, the soils can be expected to be more mature. As such maturity evolves the geographical distribution of soil types follows ever more closely the climate-vegetation zonation of a given area. This can be seen especially on the land surfaces of Australia and Africa, both of which contain geologically undisturbed peneplains of great age (order of 10^7 years or more). It is there that you find the ferralitic soils that have had the time to be winnowed down to simple chemical and mineralogical compositions represented by the residua system of weathering (Chesworth, 1992).

The organic factor

Jackson and Sherman (1953) draw a distinction between two compartments of the weathering zone: an upper (pedochemical) compartment, with a notable organic presence to influence weathering processes, and a lower (geochemical) compartment, in which this presence is, if not absent, much attenuated. Essentially the dividing line is the transition from the solum to the parent material. Since weathering in the parent material will be the least affected by any reactions and interactions between biotic and abiotic components, it will be relatively uniform throughout the world (leaving aside any consideration of differences in rates of weathering). Hydrolysis in the zone of geochemical weathering, will therefore largely be determined by the ability of the system H_2O-CO_2 to produce protons. Only in the solum will protons from an organic source make a significant difference. Pedogeochemical weathering in the solum therefore, can be expected to vary with the linked soil-forming factor climate-vegetation. How many distinctly different variations in pedogeochemical weathering this amounts to, depends upon how fine the distinctions are that are used in defining the zones. Pedro (1979) for example recognizes five zones worldwide, based on the type of hydrolysis that takes place. Gaucher (1977), taking other factors into account, distinguishes ten different types of soil-chemical environment. Chesworth's version (1992) is the basis of Figure G7.

Along these lines, an important geographical distinction relates to the acid soils to which the weathering system evolves in regions with a humid climate. In cold and temperate zones, where coniferous forests and ericaceous heaths are found, the



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