



Water-Quality Principles

QW1022–TEL

Lesson 4—Governing Principles of Aqueous Systems

Source: Berner, E.K., and Berner, R.A., 1966, *Global environment: Water, air, and Geochemical Cycles*: North Haven, Conn., Prentice-Hall, Inc., p. 148–153. Electronically reproduced with permission of the authors.

U.S. Department of the Interior
U.S. Geological Survey

CHEMICAL WEATHERING

Minerals Involved in Weathering

The chemical weathering of rocks and minerals has been alluded to throughout the previous discussion without detailing exactly what rocks and minerals are involved. As a guide we present in Tables 4.3 and 4.4 lists of the most common minerals involved in weathering. Primary minerals (Table 4.3) are those undergoing destruction by weathering, while secondary minerals (Table 4.4) are those formed by weathering. (Technically speaking, all minerals can undergo destruction by weathering, but the secondary minerals are the most resistant.) In interpreting Table 4.3, those with no geological background may find it helpful to visualize rocks simply as aggregates of minerals. There are three basic types of rock: igneous, sedimentary, and metamorphic. Igneous rocks are formed by crystallization from a melt at high temperature and include the common rock types, granite (Na plagioclase feldspar, K-feldspar, quartz, biotite) and basalt (Ca-plagioclase feldspar, pyroxenes, olivine). Sedimentary rocks are deposited in water at the

TABLE 4.2 Concentrations of Na⁺, K, Ca⁺⁺, and Al in Soil Waters of a Watershed Forested with Aspen Trees, Sangre de Cristo Mountains, New Mexico, and in Rainfall and Throughfall in the Same Area

Water	Depth (cm)	Concentration (μg/l)			
		Na ⁺	K ⁺	Ca ⁺⁺	Al
Rainfall	—	67	120	360	5
Throughfall	—	85	2800	780	10
Soil water	30	710	2200	4400	350
Soil water	100	1600	430	1300	30
Soil water	150	3100	350	1050	38
Soil water	200	3800	510	2450	11

Source: Graustein 1981.

TABLE 4.3 Common Primary Minerals That Undergo Weathering

Mineral	Generalized Composition	Weathering Rock Type(s)	Main Reaction
Olivine	$(\text{Mg,Fe})_2\text{SiO}_4$	Igneous	Oxid. of Fe Cong. diss. by acids
Pyroxenes	$\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$ or $(\text{Mg,Fe})\text{SiO}_3$	Igneous	Oxid. of Fe Cong. diss. by acids
Amphiboles	$\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ (also some Na and Al)	Igneous Metamorphic	Oxid. of Fe Cong. diss. by acids
Plagioclase feldspar	Solid solution between $\text{NaAlSi}_3\text{O}_8$ (albite) and $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite)	Igneous Metamorphic	Incong. diss. by acids
K-feldspar	KAlSi_3O_8	Igneous Metamorphic Sedimentary	Incong. diss. by acids
Biotite	$\text{K}(\text{Mg,Fe})_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	Metamorphic Igneous	Incong. diss. by acids Oxid. of Fe
Muscovite	$\text{KAi}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	Metamorphic	Incong. diss. by acids
Volcanic glass (not a mineral)	Ca,Mg,Na,K,Al,Fe-silicate	Igneous	Incong. diss. by acids and H_2O
Quartz	SiO_2	Igneous Metamorphic Sedimentary	Resistant to diss.
Calcite	CaCO_3	Sedimentary	Cong. diss. by acids
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	Sedimentary	Cong. diss. by acids
Pyrite	FeS_2	Sedimentary	Oxid. of Fe and S
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Sedimentary	Cong. diss. by H_2O
Anhydrite	CaSO_4	Sedimentary	Cong. diss. by H_2O
Halite	NaCl	Sedimentary	Cong. diss. by H_2O

Note: cong. = congruent; incong. = incongruent; diss. = dissolution; oxid. = oxidation.

earth's surface and include eroded debris from preexisting rocks (e.g., quartz and feldspar), as in sandstones; fine-grained secondary minerals formed by weathering (e.g., iron oxides and clays), as in shales; the skeletal remains of organisms (mainly CaCO_3), as in limestones; and precipitates from seawater (gypsum and halite), as in evaporites. Metamorphic rocks form by the recrystallization and alteration of sedimentary and igneous rocks at elevated temperatures and pressures (but without melting) and contain many different minerals, including amphiboles, muscovite, biotite, quartz and feldspar.

Also included in Table 4.3 are the principal weathering reactions that each primary mineral undergoes. Weathering reactions are classified here according to the nature of the attacking substance and whether the primary mineral simply dissolves or whether a portion of it reprecipitates to form a secondary mineral or minerals. Simple dissolution is referred to as *congruent dissolution*, and dissolution with reprecipitation of some of the components of the mineral is called *incongruent dissolution*. Attacking substances are separated into soil acids, dissolved oxygen, and water itself. Dissolved oxygen attacks only those minerals that contain reduced forms of elements, principally iron and sulfur, and that undergo oxidation to form new minerals.

TABLE 4.4 Common Secondary Minerals Formed by Weathering in Soils

Mineral	Composition
Hematite	Fe_2O_3
Goethite	HFeO_2
Gibbsite	$\text{Al}(\text{OH})_3$
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Smectite	$(\frac{1}{2} \text{Ca, Na}) \text{Al}_2\text{MgSi}_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ (average composition)
Vermiculite	Basically biotite or muscovite composition with K^+ replaced by hydrated cations
Calcite	CaCO_3
Opaline silica (not a mineral)	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Although most minerals are attacked mainly by soil acids, a few very soluble ones simply dissolve in water. This is shown in Table 4.3. In addition, these soluble minerals may also reprecipitate under arid conditions. This is why gypsum, for example, appears in Tables 4.3 and 4.4 as both a primary and a secondary mineral.

Minerals can be listed in order of their degree of resistance to weathering. In other words, if two minerals are present in the same soil and are attacked by the same acids for the same length of time, one will be destroyed faster than the other. On the basis of observations of partly weathered rocks and soils and of responses to different climatic conditions, a table has been prepared (Table 4.5) of minerals listed in order of increasing resistance to weathering. This table is similar to those prepared by others (e.g., Goldich 1938; Loughnan 1969; Carroll 1970) and is based largely on this older work. Although some reordering can occur in different soils, overall the order shown is considered to be well established. Goldich (1938) noted that the order shown for igneous silicate minerals parallels their temperature of formation from molten magma. In other words, the silicate minerals that weather fastest (e.g., olivine) are those that originally formed at the highest temperatures. The reason for this correlation is not clear, but a common explanation (e.g., Goldich 1938) is that minerals formed under conditions more distantly removed from those at the earth's surface are less stable there and thus weather faster. This explanation agrees with the position of the common secondary minerals at the bottom of the list but does not account for the high weatherability of nonsilicates, such as halite, gypsum, calcite, and pyrite, which also form under earth surface conditions.

Mechanism of Silicate Dissolution

Of all mineral groups, silicates have received the most attention in weathering studies because they make up the most abundant rock types. How primary silicates dissolve during weathering, however, is not well known. One theory is that silicate dissolution occurs by means of the formation of a protective surface layer of altered composition on each mineral grain (e.g., Luce et al. 1972; Paces 1973; Busenberg and Clemency 1976; Chou and Wollast 1984; Muir and Nesbitt

TABLE 4.5 Mineral Weatherability (Decreasing from Top to Bottom)

Halite
Gypsum-anhydrite
Pyrite
Calcite
Dolomite
Volcanic glass
Olivine
Ca-plagioclase
Pyroxenes
Ca-Na plagioclase
Amphiboles
Na-plagioclase
Biotite
K-feldspar
Muscovite
Vermiculite, smectite
Quartz
Kaolinite
Gibbsite, hematite, goethite

Note: Minerals are listed in order of increasing resistance to weathering. (Exact positions for some minerals can change one or two places due to effects of grain size, climate, etc.) See also Goldich 1938; Loughnan 1969; and Carroll 1970.

1992). This layer is assumed to be so tight that it severely inhibits the migration of dissolved species to and from the surface of the primary mineral, and in this way is protective. The layer forms from components of the underlying primary mineral and, as weathering proceeds, it increases in thickness. It was invoked originally to explain the results of laboratory dissolution experiments (simulating weathering), where rates of dissolution were seen to decrease with time, due presumably to the thickening of a protective surface layer. However, when applied to most mineral grains taken from actual soils (e.g., Berner and Holdren 1979; Berner and Schott 1982; Blum et al. 1991) or to the surfaces of mineral grains from experiments at neutral pH (e.g., Holdren and Berner 1979; Casey et al. 1989), attempts to prove the existence of a layer with any appreciable thickness greater than a few nanometers, using both electron microscopic and surface chemical techniques, have proven to be negative. Much recent experimental and theoretical work (e.g., Casey et al. 1989) has emphasized layer formation, but it is based almost entirely on results for low-pH experiments outside the normal pH range found in most soils.

What really appears to happen during weathering of most silicate minerals (at least for feldspars, pyroxenes, and amphiboles) is that soil solutions penetrate through permeable (non-protective) clay layers right to the bare surfaces of the primary mineral grains and there react with them. Dissolution does not occur at all places on the surface so as to produce general rounding of the grains, as predicted by the protective surface layer theory, but instead affects only those portions of the surface where there is excess energy, such as at outcrops of dislocations. (Dislocations are rows of atoms in a crystal that are slightly out of place and therefore more energetic.) As a result of selective etching, distinct crystallographically controlled etch pits form on the mineral surface and, upon growth and coalescence, form interesting features. Some examples

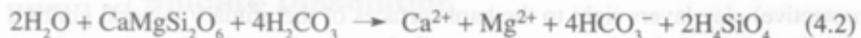
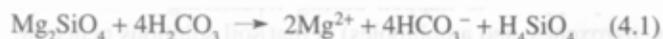
taken from our studies of soil feldspars and pyroxenes are shown in Figure 4.3. These etch pits reflect the crystal structure of the underlying mineral and therefore are regular in shape and aligned in certain directions. [For a general discussion of the microscopic study of soil minerals, consult Nahon (1991).]

For some minerals, principally the garnets, a protective surface layer dissolution mechanism may be operative. Velbel (1993b) has shown that the ratio of the molar volume of secondary weathering products to the molar volume of the primary mineral undergoing dissolution is a key factor in whether dissolution via a protective layer is possible. For most primary minerals, all reasonable weathering products (e.g., clay minerals and hydrous aluminum and iron oxides) have insufficient volume, during mole-for-mole weathering, to cover the primary mineral surfaces and thus provide a protective layer. Only the garnets, among common minerals, seem to fulfill the necessary criterion for total covering of the surface. In agreement with this prediction is the finding by Velbel of a lack of etch pitting and a tight covering of gibbsite and goethite on the surfaces of almandine garnet grains in soils from the southern Appalachian Mountains.

Dissolution of primary minerals, therefore, occurs via etch pit formation and growth of the pits. If the pits are located primarily at outcrops of dislocations, then a fundamental controlling factor on dissolution of a given mineral during weathering is the density of dislocations. (Dissolution of different minerals is still controlled by differences in chemical composition.) This can help to explain different rates of dissolution of minerals of similar composition under the same soil conditions. For example, the work of Holdren and Berner (1979) has shown that adularia, KAlSi_3O_8 , reacts in the laboratory with hydrofluoric acid (as a simulator of soil acids) much more slowly than does microcline, which has essentially the same chemical composition, KAlSi_3O_8 . The major difference between the two minerals is the presence of numerous twinning dislocations in microcline and very few in adularia. In addition, electron microscope studies (Berner and Schott 1982) show that coexisting hypersthene and augite (two pyroxene minerals in the same soil) weather at different rates, mainly because of differences in dislocation density. This is illustrated in Figure 4.3.

Silicate Weathering Reactions: Secondary Mineral Formation

Because silicate minerals constitute the fundamental components of most major rock types, it is important to inquire in detail into how they weather and to what they weather. As noted in Table 4.3, some weathering reactions involve simple congruent dissolution by water or acids. In the case of silicate minerals, congruent dissolution is rare and confined only to olivine, amphiboles, and pyroxenes that are relatively free of iron. (Congruent quartz dissolution is also rare.) In this case we have the following reactions, assuming that attack is by carbonic acid:



[Note that dissolved silica is represented here as H_4SiO_4 , which closely represents the actual form found in solution. It is sometimes also represented by the alternative formula $\text{Si}(\text{OH})_4$. We shall not represent silica in solution by SiO_2 , as is commonly done, because it can be confused with quartz.]

Most other silicate minerals, especially those containing aluminum, dissolve incongruently with the consequent formation of iron oxides and/or clay minerals. ("Clay minerals" is a common term

applied to fine-grained aluminosilicates and includes kaolinite, smectite, and vermiculite as well as other minerals, such as chlorite, that are not discussed here). The most abundant silicate mineral in the earth's crust, which also readily undergoes weathering, is plagioclase feldspar. On this basis we begin our discussion of weathering reactions using Na-plagioclase or albite.

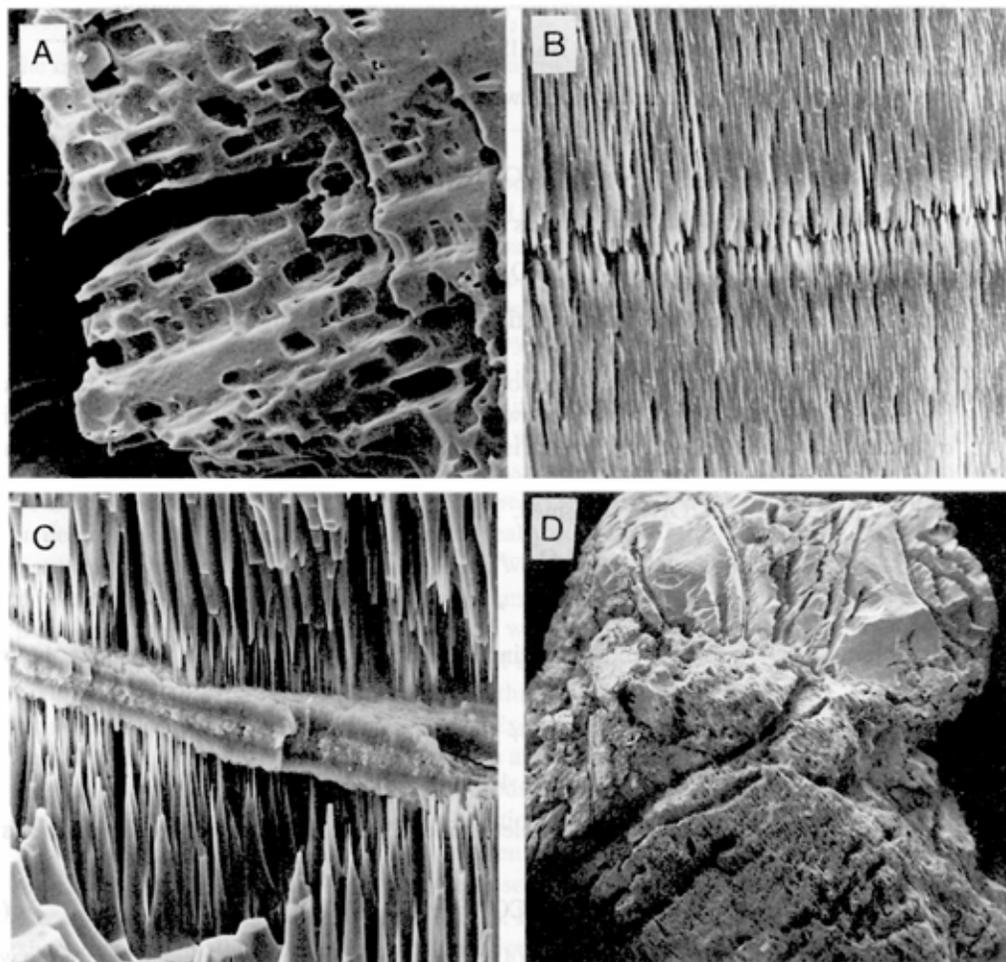


Figure 4.3. Scanning electron photomicrographs of partly weathered primary silicate mineral grains taken from soils. (A) Square-shaped ("prismatic") etch pits developed on dislocations in plagioclase feldspar (oligoclase from Piedmont, North Carolina). ($\times 3000$) (After R. A. Berner and G. R. Holdren. "Mechanism of Feldspar Weathering: Some Observational Evidence," *Geology*, 5, p. 372. © 1977 by The Geological Society of America. All rights reserved.) (B) Lens-shaped etch pits developed on dislocations in amphibole (hornblende from Ashe County, North Carolina). ($\times 3000$) (C) Clay-filled crack and surrounding "teeth" in hornblende formed by the coalescence of lens-shaped etch pits. ($\times 1000$) (D) Compound double pyroxene grain consisting of a single crystal of augite, $\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$, in lower portion of photo and a single crystal of hypersthene, $(\text{Mg,Fe})\text{SiO}_3$, in upper portion. Note greater degree of pitting of augite showing that it weathers faster because of a higher dislocation density. ($\times 50$) (B, C, D after R. A. Berner and J. Schott. "Mechanism of Pyroxene and Amphibole Weathering II: Observations of Soil Grains," *American Journal of Science*, 282, pp. 1219, 1222, 1223. © 1982 by the American Journal of Science, reprinted by permission of the publisher.)