ENVIRONMENTAL SOIL CHEMISTRY

Donald L. Sparks
Department of Plant and Soil Sciences
University of Delaware
Newark, Delaware

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2

INORGANIC SOIL COMPONENTS

INTRODUCTION

Soils are complex assemblies of solids, liquids, and gases. For example, in a typical silt loam soil that is ideal for plant growth the solid component in the surface horizon represents about 50% of the volume (about 45% mineral and 5% organic matter), gases (air) comprise about 20–30%, and water typically makes up the remaining 20–30%. Of course, the distribution of gases and water in the pore space component can change quickly depending on weather conditions and a host of other factors.

The median and range of elemental content of soils from around the world are given in Table 2.1. The elements that are found in the highest quantities are O, Si, Al, Fe, C, Ca, K, Na, and Mg. These are also the major elements found in the earth's crust and in sediments (Table 2.1). Oxygen is the most prevalent element in the earth's crust and in soils. It comprises about 47% of the earth's crust by weight and greater than 90% by volume (Berry and Mason, 1959).

The inorganic components of soils represent more than 90% of the solid components. Their properties such as size, surface area, and charge behavior, greatly affect many important equilibrium and kinetic reactions and processes in soils.

The inorganic components of soils include both primary and secondary minerals (defined below), which range in size (particle diameter) from clay-sized colloids ($< 2\ \mu m$ or 0.002 mm) to gravel (> 2 mm) and rocks. Table 2.2 lists the major primary and secondary minerals that are found in soils. A mineral can be defined as a natural inorganic compound with definite physical,

TABLE 2.1. Contents of Elements in Soils, The Earth's Crust, and Sediments

	Soils (mg kg^{-1})					
Element	Median[a]	Range[a]	Median[b]	Range[b]	Earth's crust (mean)[c]	Sediments (mean)[c]
Al	72,000	700–<10,000	71,000	10,000–300,000	82,000	72,000
As	7.2	<0.1–97	6	0.10–40	1.5	7.7
B	33	<20–300	20	2–270	10	100
Ba	580	10–5,000	500	100–3,000	500	460
Be	0.92	<1–15	0.30	0.01–40	2.6	2
Br	0.85	<0.5–11	10	1–110	0.37	19
C, Total	25,000	600–370,000	20,000	7,000–500,000	480	29,400
Ca	24,000	100–320,000	15,000	700–500,000	41,000	66,000
Cd	—	—	0.35	0.01–2	0.11	0.17
Cl	—	—	100	8–1,800	130	190
Co	9.1	<3–70	8	0.05–65	20	14
Cr	54	1–2,000	70	5–1,500	100	72
Cs	—	—	4	0.3–20	3	4.2
Cu	25	<1–700	30	2–250	50	33
F	430	<10–3,700	200	20–700	950	640
Fe	26,000	100–>100,000	40,000	2,000–550,000	41,000	41,000
Ga	17	<5–70	20	2–100	18	18
Ge	1.2	<0.1–2.5	1	0.10–50	1.8	1.7
Hg	0.09	<0.01–4.6	0.06	0.01–0.50	0.05	0.19
I	1.2	<0.5–9.6	5	0.10–25	0.14	16
K	15,000	50–63,000	14,000	80–37,000	21,000	20,000
La	37	<30–200	40	2–180	32	41
Li	24	<5–140	25	3–350	20	56
Mg	9,000	50–>100,000	5,000	400–9,000	23,000	14,000
Mn	550	<2–7,000	1,000	20–10,000	950	770
Mo	0.97	<3–15	1.2	0.1–40	1.5	2
N	—	—	2,000	200–5,000	25	470
Na	12,000	<500–100,000	5,000	150–25,000	23,000	5,700

(Continues)

chemical, and crystalline properties. A primary mineral is one that has not been altered chemically since its deposition and crystallization from molten lava. Examples of common primary minerals in soils include quartz and feldspar. Other primary minerals that are found in soils in smaller quantities include pyroxenes, micas, amphiboles and olivines. Primary minerals occur primarily in the sand (2–0.05 mm particle diameter) and silt (0.05–0.002 mm particle diameter) fractions of soils but may be found in slightly weathered clay-sized fractions. A secondary mineral is one resulting from the weathering of a primary mineral; either by an alteration in the structure or from reprecipitation of the products of weathering (dissolution) of a primary mineral. Common secondary minerals in soils are the ①aluminosilicate minerals such as kaolinite and montmorillonite, ②oxides such as gibbsite, goethite, and birnessite, ③amorphous materials such as imogolite and allophane, and sulfur and

TABLE 2.1 *Continued*

	Soils (mg kg^{-1})					
Element	Median[a]	Range[a]	Median[b]	Range[b]	Earth's crust (mean)[c]	Sediments (mean)[c]
Nb	11	<10–100	10	6–300	20	13
Nd	46	<70–300	35	4–63	38	32
Ni	19	<5–700	50	2–750	80	52
O	—	—	490,000	—	474,000	486,000
P	430	<20–6,800	800	35–5,300	1,000	670
Pb	19	<10–700	35	2–300	14	19
Rb	67	<20–210	150	20–1,000	90	135
S, Total	1,600	<800–48,000	700	30–1,600	260	2,200
Sb	0.66	<1–8.8	1	0.20–10	0.2	1.2
Sc	8.9	<5–50	7	0.50–55	16	10
Se	0.39	<0.1–4.3	0.4	0.011	0.05	0.42
Si	310,000	16,000–450,000	330,000	250,000–410,000	277,000	245,000
Sn	1.3	<0.1–10	4	1–200	2.2	4.6
Sr	240	<5–3,000	250	4–2,000	370	320
Th	9.4	2.2–31	9	1–35	12	9.6
Ti	2,900	70–20,000	5,000	150–25,000	5,600	3,800
U	2.7	0.29–11	2	0.70–9	2.4	3.1
V	80	<7–500	90	3–500	160	105
Y	25	<10–200	40	10–250	30	40
Yb	3.1	<1–50	3	0.04–12	3.3	3.6
Zn	60	<5–2,900	90	1–900	75	95
Zr	230	<20–2,000	400	60–2,000	190	150

[a] From U.S. Geological Survey Professional Paper 1270 (1984), with permission. Represents analyses from soils and other surficial materials from throughout the continental United States (regoliths including desert sands, sand dunes, loess deposits, and beach and alluvial deposits containing little or no organic matter).

[b] From Bowen (1979) and references therein, with permission. Represents soil analyses from throughout the world.

[c] From Bowen (1979) and references therein, with permission.

carbonate minerals. The secondary minerals are primarily found in the clay fraction of the soil but can also be located in the silt fraction.

PAULING'S RULES

Most of the mineral structures in soils are ionically bonded and their structures can be predicted based on Pauling's Rules (Pauling, 1929). Ionic bonds are formed when an ion interacts with another ion of opposite charge in the mineral structure to form a chemical bond. Covalent bonds are those which result from a sharing of electrons. Most chemical bonds have a combination of ionic and covalent character. For example, the Si–O bond is equally ionic and covalent. The Al–O bond is approximately 40% covalent and 60%

TABLE 2.2. Common Primary and Secondary Minerals in Soils[a]

Name	Chemical formula[b]
	Primary minerals
Quartz	SiO_2
Muscovite	$KAl_2(AlSi_3O_{10})\ (OH)_2$
Biotite	$K(Mg, Fe)_3(AlSi_3O_{10})\ (OH)_2$
Feldspars	
Orthoclase	$KAlSi_3O_8$
Microcline	$KAlSi_3O_8$
Albite	$NaAlSi_3O_8$
Amphiboles	
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
Pyroxenes	
Enstatite	$MgSiO_3$
Diopside	$CaMg(Si_2O_6)$
Rhodonite	$MnSiO_3$
Olivine	$(Mg, Fe)_2SiO_4$
Epidote	$Ca_2(Al, Fe)_3Si_3\ O_{12}(OH)$
Tourmaline	$(Na, Ca)\ (Al, Fe^{3+}, Li, Mg)_3Al_6(BO_3)_3(Si_6O_{18})\ (OH)_4$
Zircon	$ZrSiO_4$
Rutile	TiO_2
	Secondary minerals
Clay minerals[c]	
Kaolinite	$Si_4Al_4O_{10}(OH)_8$
Montmorillonite	$M_X\ (Al, Fe^{2+}, Mg)_4Si_8O_{20}(OH)_4$ (M = interlayer metal cation)
Vermiculite	$(Al, Mg, Fe^{3+})_4(Si, Al)_8O_{20}(OH)_4$
Chlorite	$[M\ Al\ (OH)_6](Al, Mg)_4(Si, Al)_8\ O_{20}(OH, F)_4$
Allophane	$Si_3Al_4O_{12} \cdot nH_2O$
Imogolite	$Si_2Al_4O_{10} \cdot 5H_2O$
Goethite	$FeOOH$
Hematite	$\alpha\text{-}Fe_2O_3$
Maghemite	$\gamma\text{-}Fe_2O_3$
Ferrihydrite	$Fe_{10}O_{15} \cdot 9H_2O$
Bohemite	$\gamma\text{-}AlOOH$
Gibbsite	$Al\ (OH)_3$
Pyrolusite	$\beta\text{-}MnO_2$
Birnessite	$\delta\text{-}MnO_2$
Dolomite	$Ca\ Mg(CO_3)_2$
Calcite	$CaCO_3$
Gypsum	$CaSO_4 \cdot 2H_2O$

[a] Adapted from Mineralogy: Concepts, Descriptions, Determinations by Berry, Mason, and Dietrich. Copyright © 1959 by W. H. Freeman and Company and Hurlbut, C. S., Jr., and Klein, C. (1977). "Manual of Mineralogy" 19th ed. Copyright © 1977 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

[b] An explanation for the chemical formula can be found in the text.

[c] Formulas are for the full-cell chemical formula unit.

ionic (Sposito, 1989). Pauling's Rules (1929) are provided below with a brief description of their meaning in soil mineral structures.

Rule 1: *A coordinated polyhedron of anions is formed about each cation, the cation–anion distance being determined by the radius sum (sum of cation and anion radii) and the coordination number of the cation by the radius ratio.*

Ionic radii (IR), of cations and anions commonly found in inorganic soil minerals and the coordination number and radius ratio (assuming oxygen is the dominant anion) of the common cations are given in Table 2.3. The coordination number (CN), which is a function of the radius ratio, is the number of nearest anions surrounding the cation in a mineral. In soils, cations in mineral structures have coordination numbers of 4, 6, 8, or 12. The radius ratio is the ratio of the cation radius to the anion radius. Cations having ionic radii less than a critical minimum radius ratio can fit between closely packed anions having different configurations (Fig. 2.1). For elements in the same group of the periodic table the IR increase as the atomic number increases. For positive ions of the same electronic structure the IR decrease with increasing valence. For elements that exist in multiple valence states such as Mn, the IR decrease with increasing positive valence.

Figure 2.1 shows the relationship of radius ratio, coordination number, and the geometrical arrangements of nearest anions around a central cation. The IR of the oxygen ion in minerals is assumed to be 0.140 nm. Based on Fig. 2.1 one can see that the Si^{4+} cation would occur in fourfold or tetrahedral coordination with 0^{2-} (the radius ratio would be 0.039/0.140 = 0.279), i.e., four

TABLE 2.3. Ionic Radius (IR), Radius Ratio, and Coordination Number (CN) of Common Cations and Anions in Inorganic Soil Minerals[a]

	IR (nm)	Radius ratio[b]	CN
O^{2-}	0.140	—	—
F^-	0.133	—	—
Cl^-	0.181	—	—
Si^{4+}	0.039	0.279	4
Al^{3+}	0.051	0.364	4,6
Fe^{3+}	0.064	0.457	6
Mg^{2+}	0.066	0.471	6
Ti^{4+}	0.068	0.486	6
Fe^{2+}	0.074	0.529	6
Mn^{2+}	0.080	0.571	6
Na^+	0.097	0.693	8
Ca^{2+}	0.099	0.707	8
K^+	0.133	0.950	8,12
Ba^{2+}	0.134	0.957	8,12
Rb^+	0.147	1.050	8,12

[a] Adapted from Hurlbut and Klein (1977).

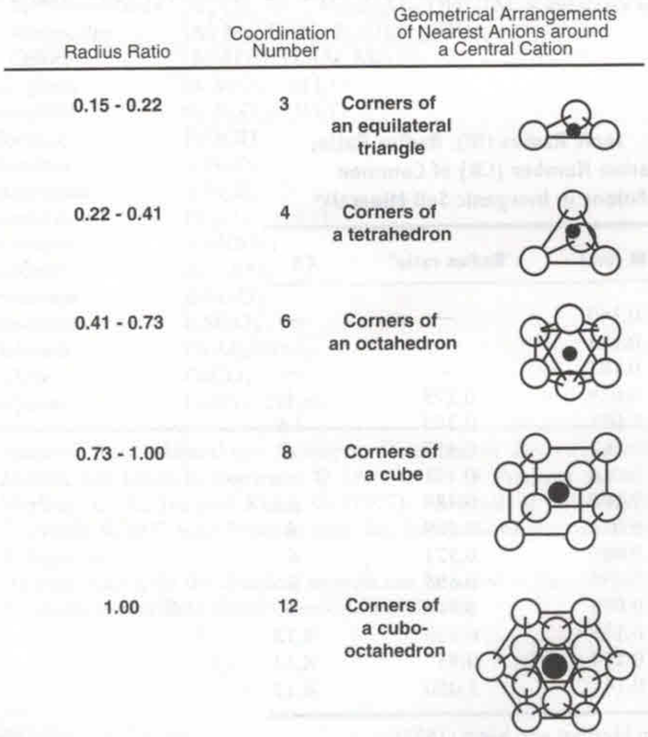
[b] Ratio of cation radius to O^{2-} radius (O^{2-} radius = 0.140 nm).

oxygen anions can surround the cation and result in a tetrahedral coordination configuration such as that shown in Fig. 2.1. Aluminum (Al^{3+}) could also occur in fourfold coordination with 0^{2-} since the radius ratio is 0.051/0.140 = 0.364. In fact, Al^{3+} can occur in either four- or sixfold coordination depending on the temperature during crystallization of the mineral. High temperatures cause low coordination numbers, i.e., fourfold coordination, while at low temperatures sixfold coordination is favored.

Based on the information given in Fig. 2.1, Fe^{2+} (0.074 nm), Fe^{3+} (0.064 nm) and Mg^{2+} (0.066 nm) would occur in octahedral coordination. As noted above, Al^{3+} could also occur in octahedral coordination. The coordination number of these cations is 6, so that six O groups arrange themselves around the cation, as shown in Fig. 2.1.

Rule 2: *In a stable coordination structure the total strength of the valency bonds which reach an anion from all neighboring cations is equal to the charge of the anion.*

This rule is known as the Electrostatic Valency Principle. This can be expressed as $s = Z/CN$, where s is the electrostatic bond strength to each coordinated anion, Z is the valence of the cation, and CN is the coordination number (Pauling, 1929). Thus, for Si in tetrahedral coordination, the electrostatic bond strength would be $Z(4^+)$ divided by CN(4) which equals 1. For Al in octahedral coordination the electrostatic bond strength would be $Z(=3^+)$



Radius Ratio	Coordination Number	Geometrical Arrangements of Nearest Anions around a Central Cation
0.15 - 0.22	3	Corners of an equilateral triangle
0.22 - 0.41	4	Corners of a tetrahedron
0.41 - 0.73	6	Corners of an octahedron
0.73 - 1.00	8	Corners of a cube
1.00	12	Corners of a cubo-octahedron

FIGURE 2.1. Relationship of radius ratio, coordination number, and geometrical arrangement of nearest anions around a central cation. Adapted from Dennen (1960), with permission.

divided by CN(= 6) or 0.5. If Al substitutes for Si in the tetrahedral layer, the electrostatic bond strength would be $Z(=3^+)$ divided by CN(= 4) or 0.75, not 1. On the other hand, if Mg^{2+} substitutes for Al^{3+} in the octahedral layer then the electrostatic bond strength is $2^+/6$ or 0.33, not 0.5.

Rule 3: *The existence of edges, and particularly of faces, common to the anion polyhedra in a coordinated structure decreases its stability; this effect is large for cations with high valency and small coordination number, and is especially large when the radius ratio approaches the lower limit of stability of the polyhedron.*

Rule 3 is a statement of Coulomb's Law for cations and indicates that there are three ways for tetrahedra and octahedra polyhedra (Figs. 2.2A and 2.2B, respectively) to bond: point-to-point, the most stable configuration, edge-to-edge, and face-to-face, the least stable configuration (Fig. 2.3). With cations with high valence such as Si^{4+} the tetrahedra are bonded point-to-point and with cations of lower valence such as Al^{3+} the octahedra are bonded edge-to-edge. Polyhedra are not bonded face-to-face.

Rule 4: *In a crystal containing different cations those of high valency and small coordination number tend not to share polyhedron elements with each other.*

This rule is saying that highly charged cations stay as far from each other as possible to lessen their contribution to the crystal's Coulomb energy (Pauling, 1929).

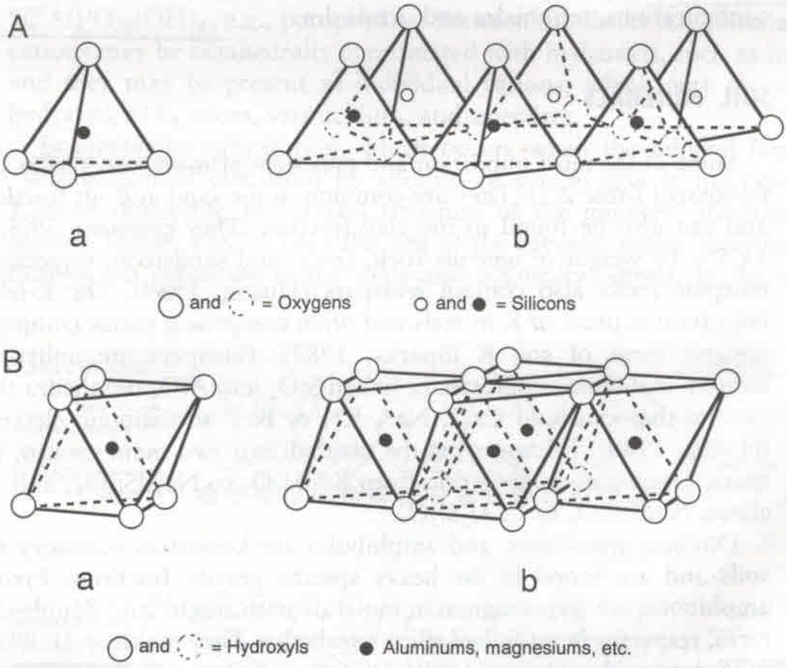


FIGURE 2.2. (A) Diagrammatic sketch showing (a) single SiO_4 tetrahedron and (b) sheet structure of tetrahedra arranged in a hexagonal network. (B) Diagrammatic sketch showing (a) single octahedral unit and (b) sheet of octahedral units. From Grim R. E. (1968). "Clay Mineralogy." Copyright 1968 McGraw-Hill. Reproduced with permission of McGraw-Hill, Inc.

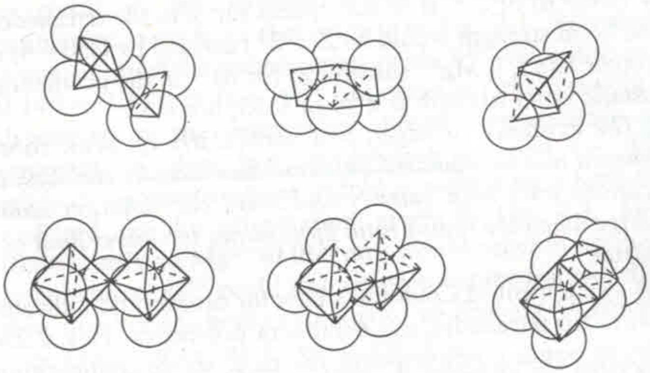


FIGURE 2.3. The sharing of a corner, an edge, and a face by a pair of tetrahedra and by a pair of octahedra. From Pauling, L. (1940). "The Nature of the Chemical Bond" 3rd ed. Copyright © 1940 Cornell University. Used by permission of the publisher, Cornell University Press.

Rule 5: *The number of essentially different kinds of constituents in a crystal tends to be small.*

This is because all substances tend to form the lowest possible potential energy. Many kinds of constituents would result in a complex structure that would be characterized by strains which would cause a high potential energy and instability. The different kinds of constituents refer to crystallographic configurations, tetrahedra and octahedra.

PRIMARY SOIL MINERALS

Some of the most important and prevalent primary minerals in soils are the feldspars (Table 2.2). They are common in the sand and silt fractions of soils and can also be found in the clay fraction. They comprise 59.5, 30.0, and 11.5% by weight of igneous rock, shale, and sandstone, respectively. Metamorphic rocks also contain feldspars (Huang, 1989). The K-feldspars are important sources of K in soils and often comprise a major component of the mineral form of soil K (Sparks, 1987). Feldspars are anhydrous three-dimensional aluminosilicates of linked SiO_4 and AlO_4 tetrahedra that contain cavities that can hold Ca^{2+}, Na^+, K^+, or Ba^{2+} to maintain electroneutrality (Huang, 1989). Feldspars can be divided into two main groups, alkali feldspars, ranging in composition from $KAlSi_3O_8$ to $NaAlSi_3O_8$, and the plagioclases, $NaAlSi_3O_8$ to $CaAl_2Si_2O_8$.

Olivines, pyroxenes, and amphiboles are known as accessory minerals in soils and are found in the heavy specific gravity fractions. Pyroxenes and amphiboles are ferromagnesian minerals with single- and double-chain structures, respectively, of linked silica tetrahedra. They make up 16.8% by weight of igneous rocks (Huang, 1989). Olivines are green neosilicates in which Mg^{2+} and Fe^{2+} are octahedrally coordinated by O atoms. They are prevalent in igneous rocks, are sources of soil micronutrients, and are generally present in smaller quantities than pyroxenes and amphiboles (Huang, 1989).

SECONDARY SOIL MINERALS

Phyllosilicates

Clay is a general term for inorganic material that is $< 2\ \mu$m in size, whereas clay mineral refers to a specific mineral which mainly occurs in the clay-sized fraction of the soil (Moore and Reynolds, 1989). Without question, the secondary clay minerals (phyllosilicates) in soils play a profound role in affecting numerous soil chemical reactions and processes as we shall see in this chapter and in following chapters.

Clay minerals are assemblages of tetrahedral and octahedral sheets (Fig. 2.4). The silica tetrahedral sheet is characterized by a number of properties. The Si–O bond distance is about 0.162 nm, the O–O distance is about 0.264 nm, the tetrahedra are arranged so that all tips are pointing in the same direction and the bases of all tetrahedra are in the same plane, and tetrahedra are bonded point-to-point.

The aluminum octahedral sheet has an O–O distance of 0.267 nm and the OH–OH distance is 0.294 nm. Bonding of Al octahedra occurs via edges.

When one tetrahedral sheet is bonded to one octahedral sheet a 1 : 1 clay mineral results. Thus, the full-cell chemical formula for an ideal 1 : 1 clay would be $\mathrm{Si}_4^{IV}\mathrm{Al}_4^{VI}\mathrm{O}_{10}(\mathrm{OH})_8$, where the superscripts represent four- and sixfold coordination in the tetrahedral and octahedral sheets, respectively. When two tetrahedral sheets are coordinated to one octahedral sheet, a 2 : 1 clay mineral results. The ideal full-cell chemical formula for a 2 : 1 clay would be $\mathrm{Si}_8^{IV}\mathrm{Al}_4^{VI}\mathrm{O}_{20}(\mathrm{OH})_4$, e.g., pyrophyllite. Between the sheets (i.e., interlayer space) cations may be octahedrally coordinated with hydroxyls, such as in chlorites, and they may be present as individual cations, which may or may not be hydrated, as in micas, vermiculites, and smectites.

Isomorphous substitution, which occurs when the mineral forms, is the "substitution of one atom by another of similar size in the crystal lattice without disrupting the crystal structure of the mineral" (Glossary of Soil Science Terms, 1987). Thus the size of the cationic radius determines which cations can substitute in the silica and octahedral sheets. In the tetrahedral

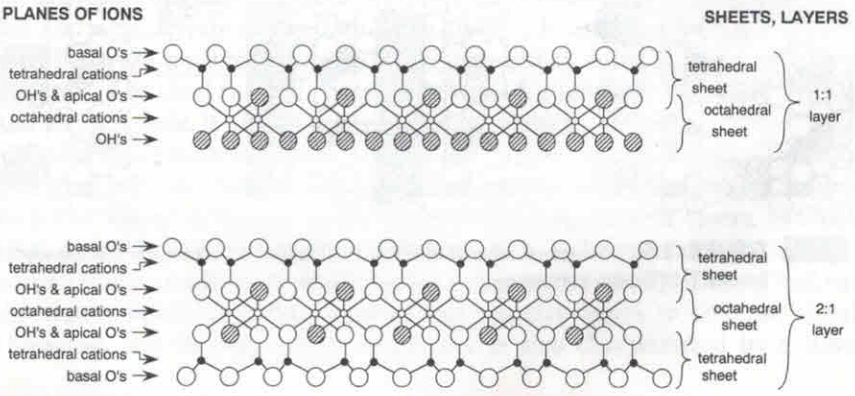


FIGURE 2.4. Phyllosilicate nomenclature. From Schulze (1989), with permission.

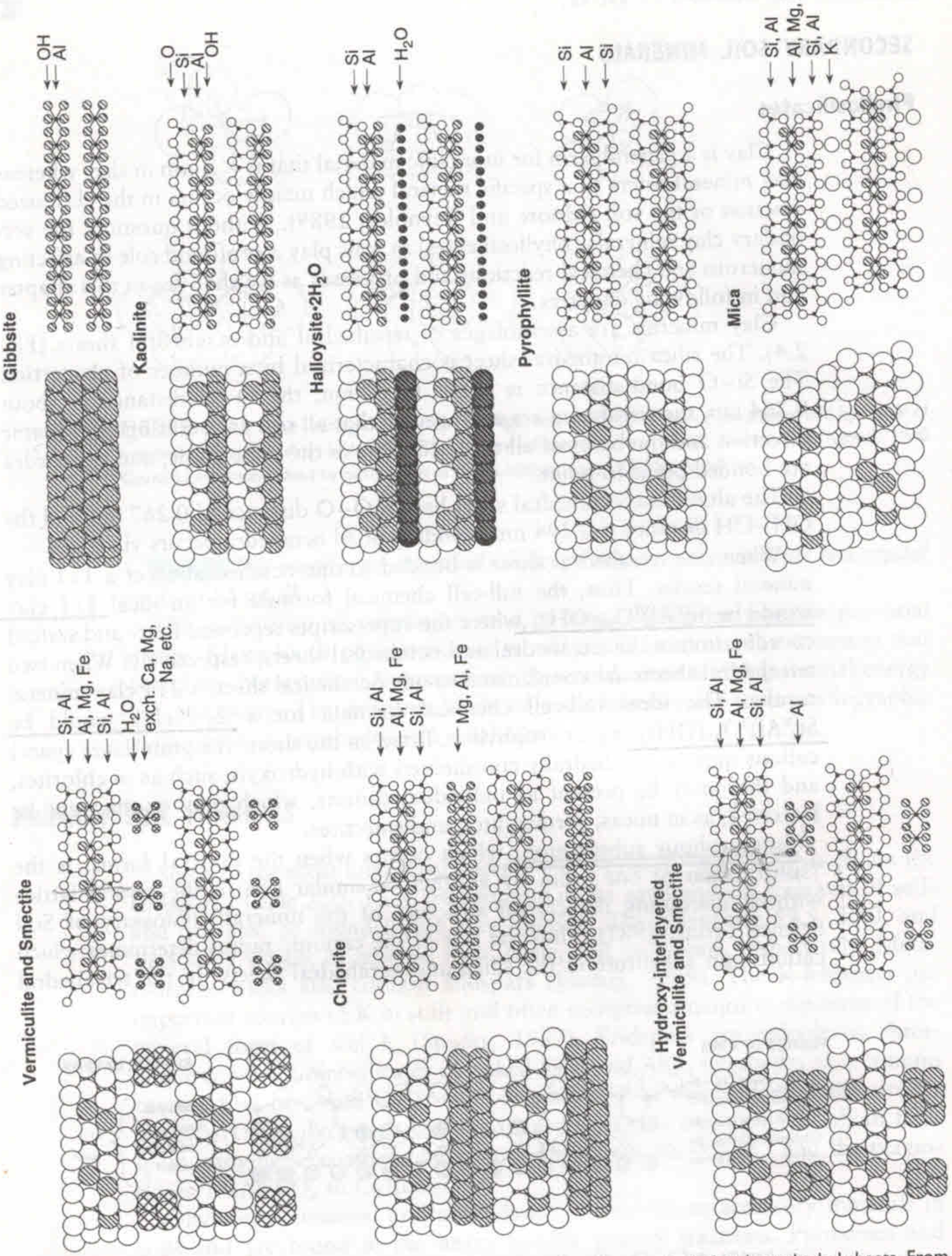


FIGURE 2.5. Structural scheme of soil minerals based on octahedral and tetrahedral sheets. From Schulze (1989), with permission.

sheet Al^{3+} usually substitutes for Si^{4+} but P can also substitute. In the octahedral sheet Fe^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Zn^{2+}, or Cu^{2+} can substitute for Al^{3+}. Thus, a cation with coordination number of 4 could substitute for Si^{4+} in the tetrahedral sheet and a cation of coordination number 6 could substitute for Al^{3+} in the octahedral sheet. As a result of this isomorphous substitution, a net negative charge develops which is associated with the 6 oxygens or hydroxyls of the octahedrons and with the 4 oxygens of the tetrahedrons.

As an example of this suppose that one Al^{3+} substitutes for one Si^{4+} in the tetrahedral sheet of an ideal 1 : 1 clay, $Si_4^{IV}Al_4^{VI}O_{10}(OH)_8$. After substitution the clay now has the formula $(Si_3Al_1)^{IV}Al_4^{VI}O_{10}(OH)_8$. The total negative charge is -28 and the total positive charge is $+27$. The net charge on the clay is -1, which is balanced by the presence of cations near the outer surface of the 1 : 1 clay.

Clays can be classified as dioctahedral or trioctahedral depending on the number of cation positions in the octahedral sheet that are occupied (Table 2.4). If two of the three positions are filled, then the clay is dioctahedral. If all three positions are filled, the clay is trioctahedral. For example, if Al^{3+} is present in the octahedral sheet, only two-thirds of the cation positions are filled (dioctahedral); for every 6 OH^- anions, only two Al^{3+} satisfy the anionic charge and a formula of $Al_2(OH)_6$ results. When Mg^{2+} is present, all three cation sites are filled since Mg is divalent and three atoms of Mg^{2+} would be necessary to satisfy the 6 OH^- ions (trioctahedral). The formula for this sheet would be $Mg_3(OH)_6$.

Trioctahedral minerals, which often contain Mg^{2+}, are found in areas with drier climates, while dioctahedral clays, which usually contain Al^{3+} in the octahedral sheet, are found in wet climates. Thus, in the United States, east of the Mississippi River the soils have predominately dioctahedral minerals, while the clay fraction of soils west of the Mississippi is dominated by trioctahedral minerals.

1 : 1 Clays (Kaolin–Serpentine Group). This group can be divided into dioctahedral kaolins and trioctahedral serpentines. The most common dioctahedral kaolin is kaolinite (Table 2.4, Fig. 2.5). Looking at the structure of kaolinite (Fig. 2.5), one sees that the basic structure consists of a silica tetrahedral sheet bonded to an aluminum octahedral sheet. Layers of kaolinite stack by hydrogen bonding (an electrostatic bond between a positively charged H^+ ion and a negatively charged ion such as O^{2-}, Klein and Hurlbut, 1985) and thus there are no interlayer spaces present, unlike what is found in 2 : 1 clay minerals. The ideal full-cell chemical formula for kaolinite is $Si_4^{IV}Al_4^{VI}O_{10}(OH)_8$ and there is little, if any, isomorphic substitution in kaolinite.

Other dioctahedral kaolins are dickite, nacrite, and halloysite (Table 2.4). The ideal full-cell chemical formula for these clays is the same as for kaolinite, with the major difference being the stacking sequence of layers. Halloysite (Fig. 2.5) has water molecules between each 1 : 1 layer and the ability to adsorb large quantities of monovalent cations such as NH_4^+. Drying will cause the water molecules to be removed and the clay layers to collapse together (Newman and Brown, 1987). Halloysite is also characterized by a tubular

TABLE 2.4. Partial Classification of Phyllosilicate Clay Minerals

Type	Group	Subgroup	Species	Composition (half-cell chemical formula unit)			
					Cations		
				Interlayer space	Tetrahedral sheet	Octahedral sheet	Anions
1:1	Kaolin	Kaolins	Kaolinite	—	Si_2	Al_2	$O_5(OH)_4$
	Serpentine	(dioctahedral)	Dickite	—	Si_2	Al_2	$O_5(OH)_4$
	$(x \sim 0)^a$		Nacrite	—	Si_2	Al_2	$O_5(OH)_4$
			Halloysite	$2H_2O$	Si_2	Al_2	$O_5(OH)_4$
		Serpentines (trioctahedral)	Antigorite	—	Si_2	Mg_3	$O_5(OH)_4$
			Chrysotile	—	Si_2	Mg_3	$O_5(OH)_4$
2:1	Pyrophyllite–talc	Pyrophyllite (dioctahedral)	Pyrophyllite	—	Si_4	Al_2	$O_{10}(OH)_2$
	$(x \sim 0)$	Talc (trioctahedral)	Talc	—	Si_4	Mg_3	$O_{10}(OH)_2$
	Smectite–saponite	Smectites	Montmorillonite	$(M_{0.33},H_2O)^b$	Si_4	$Al_{1.67}{}^c(Fe^{2+},Mg)_{0.33}$	$O_{10}(OH)_2$
	$(x \sim 0.2–0.6)$	(dioctahedral)	Beidellite	$(M_{0.33},H_2O)$	$(Si_{3.67}Al_{0.33})$	Al_2	$O_{10}(OH)_2$
			Nontronite	$(M_{0.33},H_2O)$	$(Si_{3.67}Al_{0.33})$	Fe_2^{3+}	$O_{10}(OH)_2$
		Saponite	Saponite	$(M_{0.33},H_2O)$	$(Si_{3.67}Al_{0.33})$	Mg_3	$O_{10}(OH)_2$
		(trioctahedral)	Hectorite	$(M_{0.33},H_2O)$	Si_4	$(Mg_{2.67}Li_{0.33})$	$O_{10}(OH)_2$

	Smectite–saponite	Smectites	Montmorillonite	$(M_{0.33},H_2O)$	Si_4	[illegible]	$O_{10}(OH)_2$
	($x \sim 0.2–0.6$)	(dioctahedral)	Beidellite	$(M_{0.33},H_2O)$	$(Si_{3.67}Al_{0.33})$	Al_2	$O_{10}(OH)_2$
			Nontronite	$(M_{0.33},H_2O)$	$(Si_{3.67}Al_{0.33})$	Fe^{3+}_2	$O_{10}(OH)_2$
		Saponite (trioctahedral)	Saponite	$(M_{0.33},H_2O)$	$(Si_{3.67}Al_{0.33})$	Mg_3	$O_{10}(OH)_2$
			Hectorite	$(M_{0.33},H_2O)$	Si_4	$(Mg_{2.67}Li_{0.33})$	$O_{10}(OH)_2$
	Vermiculite ($x \sim 0.6–0.9$)	Dioctahedral vermiculite	Dioctahedral vermiculite	$(M_{0.74},H_2O)$	$(Si_{3.56}Al_{0.44})$	$(Al_{1.4}Mg_{0.3}Fe^{3+}_{0.3})$	$O_{10}(OH)_2$
		Trioctahedral vermiculite	Trioctahedral vermiculite	$M_{0.70},H_2O$	$(Si_{3.3}Al_{0.7})$	Mg_3	$O_{10}(OH)_2$
	Illite ($x \sim <0.9> 0.6$)	Illite	Illite	$M_{0.74}$ (predominately K)	$(Si_{3.4}Al_{0.6})$	$(Al_{1.53}Fe^{3+}_{0.22}Fe^{2+}_{0.03}Mg^{2+}_{0.28})$	$O_{10}(OH)_2$
	Mica ($x \sim 1$)	Dioctahedral Mica	Muscovite	K	(Si_3Al_1)	Al_2	$O_{10}(OH,F)_2$
			Paragonite	Na	(Si_3Al_1)	Al_2	$O_{10}(OH,F)_2$
		Trioctahedral Mica	Biotite	K	$(Si,Al)_4$	$(Mg,Fe,Al)_3$	$O_{10}(OH,F)_2$
			Phlogopite	K	(Si_3Al_1)	Mg_3	$O_{10}(OH,F)_2$
			Lepidolite	K	$(Si,Al)_4$	$(Li,Al)_3$	$O_{10}(OH,F)_2$
	Brittle mica ($x \sim 2$)	Dioctahedral brittle mica	Margorite	Ca	(Si_2Al_2)	Al_2	$O_{10}(OH,F)_2$
		Trioctahedral brittle mica	Clintonite	Ca	$(Si_{1.3}Al_{2.7})$	$(Mg_{2.3}Al_{0.7})$	$O_{10}(OH,F)_2$
2:1:1	Chlorite (x is variable)	Di, dioctahedral chlorite	Donbassite	$(Mg_{0.3}Al_{1.9}OH_6)$	$(Si_{3.9}Al_{0.1})$	$(Al_{1.8}Mg_{0.2})$	$O_{10}(OH,F)_2$
		Di, trioctahedral chlorite	Cookeite	$(Li_1Al_{1.93}OH_6)$	$(Si_{3.51}Al_{0.49})$	$(Al_{1.78}Li_{0.22})$	$O_{10}(OH)_2$
		Tri, trioctahedral chlorite	clinochlore	$(Mg_2Al_1OH_6)$	(Si_3Al)	Mg_3	$O_{10}(OH)_2$

[a] x = Layer charge per half-cell formula unit.

[b] M = Metal cation.

[c] Represents a statistical average for isomorphic substitution.

morphology, whereas kaolinite, when examined with microscopic techniques, has a platy structure.

Two trioctahedral serpentines that are 1:1 clays are antigorite and chrysotile (Table 2.4). These clays have all three octahedral positions filled with Mg. There is also no substitution in either the tetrahedral or octahedral sheets, and thus they have no permanent negative charge.

2:1 Clays (Pyrophyllite–Talc Group). The ideal full-cell chemical formula for the dioctahedral 2:1 type clays is $Si_8^{IV}Al_4^{VI}O_{20}(OH)_4$ (pyrophyllite). The two representative clays of the pyrophyllite–talc group are pyrophyllite, a dioctahedral clay, and talc, a trioctahedral clay (Table 2.4). The layer charge per half-cell formula unit (full-cell forumula unit divided by 2), x, on these clays is 0 due to no apparent isomorphous substitution. In addition, there is no interlayer space in pyrophyllite and talc (Newman and Brown, 1987). However, even though there is little if any permanent negative charge on pyrophyllite, the edge sites that are present can have a significant influence on the retention of metals and on various physical properties of the clay (Keren and Sparks, 1994).

2:1 Clays (Smectite–Saponite Group). Clay minerals in the smectite–saponite group are characterized by a layer charge of 0.2–0.6 per half-cell formula unit (Table 2.4). The group includes the subgroups dioctahedral smectites and trioctahedral saponites. The dioctahedral smectites are represented by montmorillonite, beidellite, and nontronite. The ideal half-cell chemical formula for montmorillonite is $M_{0.33}$, $H_2OAl_{1.67}(Fe^{2+}, Mg^{2+})_{0.33}Si_4O_{10}(OH)_2$, where M refers to a metal cation in the interlayer space between sheets. The tetrahedral cations are Si^{4+} and the octahedral cations are Al^{3+}, Fe^{2+}, and Mg^{2+}. One can calculate the negative charge in the tetrahedral sheet as 0 and in the octahedral sheet as -0.33. Thus, the net negative charge is -0.33 that is balanced by exchangeable cations represented by $M_{0.33}$. The other feature that characterizes montmorillonite is the presence of water molecules in the interlayer space (Fig. 2.5). This causes montmorillonite to take on shrink–swell characteristics.

The major difference between montmorillonite and the other two dioctahedral smectites, beidellite and nontronite, is that isomorphous substitution in these minerals occurs in the tetrahedral sheet (i.e., Al^{3+} substitutes for Si^{4+}) rather than in the octahedral sheet. Nontronite also is an Fe-bearing mineral with Fe^{3+} being the predominant element in the octahedral sheet.

The trioctahedral members of the smectite–saponite group are saponite and hectorite. In saponite, substitution occurs in the tetrahedral sheet. In hectorite, a Li-bearing mineral, substitution occurs in the octahedral sheet (Table 2.4).

2:1 Clays (Vermiculite Group). Dioctahedral and trioctahedral vermiculites have a layer charge of 0.6–0.9 per half-cell formula unit. Dioctahedral vermiculite is characterized by substitution in both the tetrahedral and octahedral sheets, while trioctahedral vermiculite has substitution only in the tetrahedral sheet and all three of the octahedral cation positions are filled with Mg (Table 2.4).

While vermiculites are characterized by a platy morphology, similar to that for micas, they contain interlayer water (Fig. 2.5). Vermiculites form mainly from weathering of micas, particularly phlogopites and biotites, and interlayer

K^+ is replaced by other interlayer cations. However, vermiculites have a lower layer charge than micas and the Fe^{2+} in the octahedral sheet is oxidized to Fe^{3+} (Newman and Brown, 1987).

Let us take the half-cell chemical formula for dioctahedral vermiculite that is given in Table 2.4, since there is substitution in both the tetrahedral and octahedral sheets, and see how one would calculate the net layer charge on the clay.

$$M_{0.74}\ H_2O\ (Si^{4+}_{3.56}\ Al^{3+}_{0.44})(Al^{3+}_{1.4}\ Mg^{2+}_{0.3}\ Fe^{3+}_{0.3})\ O_{10}\ (OH)_2$$

The total positive charge on the clay is: Si^{4+} ($3.56 \times 4^+ = 14.24$) + Al^{3+} ($1.4 + 0.44 = 1.84 \times 3^+ = 5.52$) + Mg^{2+} ($0.30 \times 2^+ = 0.60$) + Fe^{3+}($0.30 \times 3^+ = 0.90$) = +21.26.

The total negative charge is O^{2-} ($10 \times 2^- = -20$) + OH^{-1} ($2 \times 1^- = -2$) = −22.

Thus, the net layer charge on dioctahedral vermiculite is + 21.26 + (−22) = −0.74.

This negative charge on the clay is balanced out by metal cations in the interlayer space that are represented as $M_{0.74}$ in Table 2.4. Please note that since H_2O is in the interlayer space and is not structural water, it is not considered in calculating the net layer charge.

2:1 Clays (Illite Group). Illite has a layer charge of about 0.8 per half-cell formula unit, intermediate between smectite and mica. Grim *et al.* (1937) developed the term illite to describe clay-size mica that was found in argillaceous rocks. Other terms that have been used in lieu of illite are hydromica, hydromuscovite, hydrous illite, hydrous mica, K-mica, micaceous clay, and sericite. Illite has more Si^{4+}, Mg^{2+}, and H_2O but less tetrahedral Al^{3+} and K^+ and water than muscovite. While K^+ is the predominant interlayer ion along with divalent ions such as Ca^{2+} and Mg^{2+}, NH_4^+ can also occur in illite.

2:1 Clays (Mica). Micas have a layer charge of about 1.0 per half-cell formula unit and are both dioctahedral, e.g., muscovite and paragonite, and trioctahedral, e.g., biotite, phlogopite, and lepidolite (Table 2.4). With the exception of paragonite, a Na-bearing mica, the other micas have K^+ in the interlayer positions to satisfy the negative charge resulting from isomorphous substitution. Thus, micas are major K-bearing minerals in soils and as they weather the nonexchangeable K is released for plant uptake. Weathering converts micas to partially expansible 2:1 clay minerals such as illite and vermiculite. The released K^+ from layer and edge weathering results in frayed edges and "wedge zones" (see Chapter 9 for a discussion of these) that play profound roles in K selectivity and K fixation (Sparks, 1987).

2:1:1 Clays (Chlorite Group). Chlorites are often referred to as 2:1:1 clays since they are 2:1 clays with a hydroxide interlayer, either gibbsite-like $[Al(OH)_x]$ or brucite-like $[Mg(OH)_x]$ where x is <3, that is continuous across the interlayer sheet and is octahedrally coordinated. This sheet is positively charged because there are fewer than $3OH^-$ per Al^{3+} in the sheet. The interlayer sheet is bound to the 2:1 clay electrostatically and the tetrahedral layer is bonded to the interlayer sheet by hydrogen bonding.

Chlorites can be trioctahedral in both octahedral sheets, i.e., the octahedral sheet of the 2:1 layer and the interlayer octahedral hydroxide sheet, and are referred to as tri,trioctahedral chlorites. Chlorites that are dioctahedral in the 2:1 layer and trioctahedral in the interlayer hydroxide sheet are referred to as di,trioctahedral chlorites.

2:1 Clays (Intergrade Clay Minerals). Intergrade clay minerals are intermediates between smectites and vermiculites. The interlayer space is composed of exchangeable cations and gibbsite-like or brucite-like islands that are not continuous as in chlorite. Accordingly, the interlayer space does not collapse on heating as readily as with smectites and vermiculites but it does collapse more easily than the complete interlayer hydroxy sheets in chlorite. A prominent intergrade clay mineral in many southeastern and mid-Atlantic United States soils is hydroxy-interlayered vermiculite (HIV), which is characterized by hydroxy-Al interlayers. The hydroxy-Al in these acid soils is an important source of nonexchangeable Al. In alkaline soils the interlayer material is hydroxy-Mg.

Interstratified Clay Minerals

Since the 2:1 and 1:1 layers of clays are strongly bonded internally but are weakly bonded to each other, layers can stack together to form interstratified clays. Examples include interstratified smectite with talc-type units and smectite and mica units such as 1:1 mica-dioctahedral smectite or hectorite. Another example would be interstratification of smectite or vermiculite with chlorite. For example, a 1:1 regularly interstratified chlorite–smectite structure would contain four tetrahedral sheets, two in each of the 2:1 layers, three octahedral sheets, one in each of the 2:1 layers and the other in the hydroxidic interlayer, and one expanding interlayer space containing the exchangeable cations. The anion content is $O_{40}(OH)_{20}$. Interstratification of smectite with kaolinite can also occur (Newman and Brown, 1987).

Allophane and Imogolite

Allophanes form from volcanic ash materials and are major components of volcanic-derived soils. They may also be found in the clay fraction of many nonvolcanically derived soils. Volcanic soils containing allophane usually contain significant organic matter and have low bulk densities. The SiO_2/Al_2O_3 ratio of allophanes varies from 0.84 to nearly 2, the characteristic ratio for kaolinite. Aluminum is in both tetrahedral and octahedral coordination. Imogolite has an almost constant SiO_2/Al_2O_3 ratio of 1 and Al is only in octahedral coordination; while it has little charge resulting from isomorphic substitution, imogolite can adsorb substantial quantities of monovalent cations, like halloysite (Newman and Brown, 1987). Microscopic analyses of imogolite reveal thread-like particles that are bundles of parallel tubes about 20 nm in diameter. Allophane exhibits spherical particles 30–50 nm in diameter (Brown, 1980).

Fibrous Clay Minerals

Palygorskite (previously referred to as attapulgite) and sepiolite are fibrous minerals that do not have continuous octahedral sheets. They contain ribbons of 2:1 phyllosilicates. One ribbon is linked to the next by inversion of SiO_4 tetrahedra along a set of Si–O–Si bonds.

Oxides, Hydroxides, and Oxyhydroxides

Aluminum, iron, and manganese oxides play extremely important roles in the chemistry of soils. While they may not be found in large quantities, they have significant effects on many soil chemical processes because of their high specific surface areas and reactivity.

The general term oxides refers to metal hydroxides, oxyhydroxides, and hydrous oxides (where nonstoichiometric water is in the structure). Some of the oxides found in soils are listed in Table 2.5. Oxides are ubiquitous in soils. They may exist as discrete crystals, as coatings on phyllosilicates and humic substances, and as mixed gels.

Aluminum-Oxides

A number of crystalline Al hydroxides, oxyhydroxides, and oxides are found in natural settings. The oxyhydroxides are less common than the hydroxides. Only two oxides are naturally formed in soils, gibbsite [$Al(OH)_3$, an Al hydroxide] and bohemite (γ-AlOOH, an oxyhydroxide). Diaspore (α-AlOOH) and corundum (α-Al_2O_3, an anhydrous Al oxide) can also be found, but are much less common (Table 2.5). The anhydrous Al oxides may be found in some igneous and metamorphic rocks.

TABLE 2.5. Oxides, Oxyhydroxides, and Hydroxides Found in Soils[a]

Aluminum oxides	
Bayerite	α-$Al(OH)_3$
Boehmite	γ-AlOOH
Diaspore	α-AlOOH
Gibbsite	γ-$Al(OH)_3$
Iron oxides	
Akaganeite	β-FeOOH
Ferrihydrite	$Fe_{10}O_{15} \cdot 9H_2O$
Feroxyhyte	δ-FeOOH
Goethite	α-FeOOH
Hematite	α-Fe_2O_3
Lepidocrocite	γ-FeOOH
Maghemite	γ-Fe_2O_3
Magnetite	Fe_3O_4
Manganese oxides	
Birnessite	δ-MnO_2
Pyrolusite	β-MnO_2
Titanium oxides	
Anatase	TiO_2
Rutile	TiO_2

[a] Adapted from Hsu (1989), McKenzie (1989), Schwertmann and Cornell (1991), and Taylor (1987).

Gibbsite is the most common Al oxide mineral. It is often found in highly weathered soils such as Oxisols in tropical areas and in Ultisols. The structure of gibbsite is shown in Fig. 2.6 (Hsu, 1989). There are two planes of closely packed OH$^-$ ions with Al^{3+} ions between the planes. The Al^{3+} atoms are found in two of the three octahedral positions (dioctahedral) and are in hexagonal rings. In the interior of gibbsite, each Al^{3+} shares six OH$^-$ with three other Al^{3+} ions and the OH$^-$ ion is bridged between Al^{3+} (Fig. 2.6). On the edge of gibbsite, each Al^{3+} shares only four OH$^-$ with two other Al^{3+} and the other two coordination sites are filled by one OH$^-$ and one H_2O; neither is bridged between Al^{3+} ions. Due to H-bonding, the OH$^-$ ions in a particular unit are directly above the OH$^-$ ions in another unit (Hsu, 1989).

Iron Oxides

The major Fe oxides and oxyhydroxides are listed in Table 2.5. The octahedron is the basic structural unit for all Fe oxides. Each Fe atom is surrounded by six oxygens or both O^{2-} and OH$^-$ ions. Goethite and hematite are called the α phases, while lepidocrocite and maghemite are the γ phases. The α phases are more stable than the γ phases. The Fe^{3+} can be replaced by Al^{3+}, Mn^{3+}, and Cr^{3+} via isomorphous substitution. Other cations such as Ni, Ti, Co, Cu, and Zn can also be found in the Fe oxide structure (Schwertmann and Cornell, 1991).

Goethite is the most common and thermodynamically stable Fe oxide in soils. It has double bands of FeO(OH) octahedra sharing edges and corners, the bands bonded partially by H bonds. Goethite exhibits needle-shaped crystals with grooves and edges. Hematite is the second most common Fe

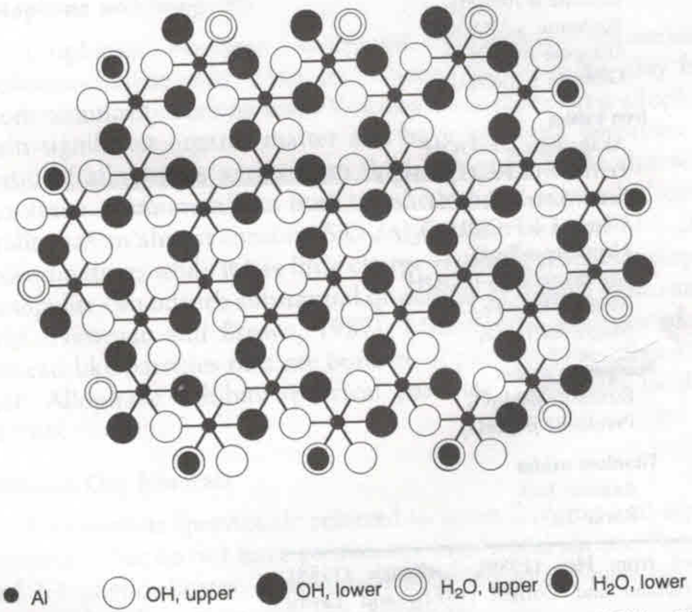


FIGURE 2.6. Schematic representation of the unit layer of $Al(OH)_3$. Edge, unshared OH may protonate as a function of pH to form H_2O. From Hsu (1989), with permission.

oxide in soils. It is common in highly weathered soils and gives many red soils their color. Its structure consists of FeO_6 octahedra which are connected by edge- and face-sharing. Other Fe oxides are maghemite, which is common in highly weathered soils, and ferrihydrite, a hydrated semicrystalline material (Schwertmann and Cornell, 1991).

Manganese Oxides

Manganese oxides (Table 2.5) are quite common in soils. They provide a source of Mn, an essential element for plants, they can adsorb heavy metals, and they are a natural oxidant of certain metals such as As^{3+} and Cr^{3+}. Manganese oxides occur in soils as coatings on soil particles, in cracks and veins, and as nodules as large as 2 cm in diameter. Most Mn oxides are amorphous. The most stable form of Mn oxide is pyrolusite but it is uncommon in soils. Birnessite is the most prevalent Mn oxide in soils (McKenzie, 1989).

Carbonate and Sulfate Minerals

The major carbonates found in soils are calcite ($CaCO_3$), magnesite [$MgCO_3$, which is very unstable and is transformed to $Mg(OH)_2$], dolomite [$CaMg(CO_3)_2$], ankerite [$(Ca,Fe,Mg)_2\ (CO_3)_2$], siderite ($FeCO_3$), and rhodochrosite ($MnCO_3$). The major sulfate mineral is gypsum, $CaSO_4 \cdot 2H_2O$. The carbonate and sulfate minerals are highly soluble compared to silica soil minerals and are most prevalent in arid and semiarid regions (Doner and Lynn, 1989).

SPECIFIC SURFACE OF SOIL MINERALS

An important physical property of secondary soil minerals is their high surface areas (Table 2.6). The total surface area of a secondary mineral depends on both internal and external surface areas.

TABLE 2.6. Specific Surface of Selected Soil Minerals

Mineral	Specific surface ($m^2\ g^{-1}$)
Kaolinite	7–30
Halloysite	10–45
Pyrophyllite	65–80
Talc	65–80
Montmorillonite	600–800
Dioctahedral vermiculite	50–800
Trioctahedral vermiculite	600–800
Muscovite	60–100
Biotite	40–100
Chlorite	25–150
Allophane	100–800

√ External Surface Area Measurement

External surface area is normally determined by measuring the adsorption of N_2 gas (the adsorbate) at temperatures near the boiling point of liquid N (77K). Surface area analysis is based on the Brunauer, Emmett, and Teller (1938) theory. The common linearized BET equation is (Carter *et al.*, 1986):

not for inter-layer area.

$$\frac{P}{V(P_0 - P)} = \left(\frac{1}{V_m c}\right) + \left[\left(\frac{(c-1)}{V_m c}\right)\left(\frac{P}{P_0}\right)\right], \tag{2.1}$$

where P = pressure (Pa) of a gas at equilibrium with a solid, P_0 = gas pressure (Pa) required for saturation at the temperature of the experiment, V = volume (m^3) of gas adsorbed at pressure P, V_m = volume (m^3) of gas required for monolayer coverage over the complete adsorbent surface, and $c = \exp[E_1 - E_2]/RT$, where E_2 is the heat of liquification of the gas, E_1 is the heat of adsorption of the first layer of adsorbate, R is the gas constant, and T is the absolute temperature.

If one plots $P/V(P_0 - P)$ vs. P/P_0, a linearized plot should result. The slope would equal $(c - 1)/V_m c$ and the intercept would equal $1/V_m$. Once the V_m is determined, the specific surface can be calculated according to Eq. (2.2) (Hiemenz, 1986),

$$E = N_a\, \sigma\, V_m / V_0, \tag{2.2}$$

where E = specific surface (m^2 g$^{-1)}$ of the adsorbent, N_a = Avogadro's number (6.02×10^{23} molecules mol^{-1}), σ = cross-sectional area (m^2) of the adsorbate, and V_0 = molar volume (m^3).

Other adsorbates can also be used in external surface area analysis, such as ethylene for solids having surface areas < 1000 cm^2 g^{-1} and krypton for solids with intermediate surface areas. Nitrogen is the most frequently used adsorbate, particularly with solids that have surface areas > 10 m^2 g^{-1}. It is not good to use N_2 with a clay mineral like montmorillonite since its surface area is primarily internal and nonpolar N_2 molecules do not penetrate the interlayer regions between the layer sheets.

√ Total Surface Area Measurement

Ethylene glycol monoethyl ether (EGME) is a common material that is used to measure the total surface area of a mineral. One applies excess EGME to the adsorbent that has been dried over a P_2O_5 desiccant in a vacuum desiccator and then removes all but a monolayer of the EGME from the mineral surface using a vacuum desiccator containing $CaCl_2$. Then, by plotting the weight of EGME retained on the solid as a function of time, one can determine when the weight of EGME becomes constant. At this point, one assumes that monolayer coverage has occurred. To calculate the specific surface, Eq. (2.3) can be used (Carter *et al.*, 1986),

$$A = W_g/(W_s)(0.000286), \tag{2.3}$$

where A = specific surface (m^2 g^{-1}), W_g = weight (g) of EGME retained by the sample after monolayer equilibration, and W_s = weight (g) of P_2O_5 (desiccant) dried sample; 2.86×10^{-4} g EGME is required to form a monolayer on 1 m^2 of surface. To obtain internal surface area (S_I),

$$S_T = S_E + S_I$$

or (2.4)

$$S_I = S_T - S_E,$$

where S_T = total surface area ($m^2\ g^{-1}$), S_E = external surface area ($m^2\ g^{-1}$), and S_I = internal surface area ($m^2\ g^{-1}$).

SURFACE CHARGE OF SOIL MINERALS

Types of Charge

Soil minerals can exhibit two types of charge, permanent or constant charge and variable or pH-dependent charge. In the remainder of the book, we will refer to these as constant and variable charge. In most soils there is a combination of constant and variable charge. Constant charge is invariant with soil pH and results from isomorphous substitution. Therefore, this component of charge was developed when the mineral was formed. Examples of inorganic soil components that exhibit constant charge are smectite, vermiculite, mica, and chlorite. The constant charge terminology is attributed to Schofield (1949). He found that the cation exchange capacity (CEC) of a clay subsoil at Rothamsted Experimental Station in England was relatively constant between pH 2.5 and 5, but increased between pH 5 and 7. He also showed that the CEC of montmorillonite did not vary below pH 6, but increased as pH increased from 6 to 9. He ascribed the constant charge component to isomorphous substitution and the variable component to ionization of H from SiOH groups on the clay surfaces. His conclusion about constant charge is still valid, if the clays are relatively pure. However, we now know that the contribution of SiOH groups to the creation of negative charge is not significant in most soils since the pK_a (see Box 2.1 for derivation and description of K_a and pK_a) of silicic acid is so high (about 9.5) that ionization of the SiOH group would occur only at very alkaline pH.

The variable charge component in soils changes with pH due to protonation and deprotonation of functional groups (Chapter 5) on inorganic soil minerals such as kaolinite, amorphous materials, metal oxides, oxyhydroxides, and hydroxides, and layer silicates coated with metal oxides and soil organic matter.

Cation Exchange Capacities of Secondary Soil Minerals

The negative charge on constant charge minerals that results from isomorphous substitution and on variable charge minerals that results from deprotonation of functional groups is balanced by positive charge in the form of exchangeable cations. While cation and anion exchange phenomena will be discussed in detail later (Chapter 6), it would be instructive at this point to

BOX 2.1. Calculation of Acid Dissociation Constants (K_a) and Derivation of the Henderson–Hasselbalch Equation

(I) Calculation of K_a and pK_a values.

Suppose that a 0.1 *M* CH_3COOH (acetic acid) solution is ionized 1.3% at 298K. What is the K_a for CH_3COOH?

$$\underset{\text{acid}}{CH_3COOH} + H_2O \overset{K_a}{\rightleftharpoons} H_3O^+ + \underset{\text{base}}{CH_3COO^-} \tag{2.1a}$$

or

$$\underset{\text{acid}}{CH_3COOH} \overset{K_a}{\rightleftharpoons} H^+ + \underset{\text{base}}{CH_3COO^-}$$

Brönsted and Lowry defined an acid as a proton donor and a base as a proton acceptor. According to Lewis an acid is an electron-pair acceptor and a base is an electron-pair donor. The definitions of Lewis are general and also include species that do not have a reactive H^+ (Harris, 1987). In Eq. (2.1a) CH_3COOH is an acid and CH_3COO^- is a base because the latter can accept a proton to become CH_3COOH. Acetic acid and CH_3COO^- are a conjugate acid–base pair. The K_a for the second reaction in Eq. (2.1a) is

$$K_a = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]}, \tag{2.1b}$$

where brackets indicate concentration in mol liter^{-1}, $[H^+] = 0.1$ mol liter$^{-1} \times 0.013 = 0.0013$ mol liter^{-1}, $[CH_3COO^-] = 0.1$ mol liter$^{-1} \times 0.013 = 0.0013$ mol liter^{-1}, and $[CH_3COOH] = (0.1000$ mol liter$^{-1}) - (0.0013$ mol liter$^{-1}) = 0.0987$ mol liter^{-1}. Substituting in these values in Eq. (2.1b),

$$K_a = \frac{[0.0013 \text{ mol liter}^{-1}][0.0013 \text{ mol liter}^{-1}]}{[0.0987 \text{ mol liter}^{-1}]}$$

$$= 1.071 \times 10^{-5} \text{ mol liter}^{-1} \tag{2.1c}$$

The higher the K_a, the more dissociation of the acid into products and the stronger the acid. Acetic acid has a low K_a and thus is slightly dissociated. It is a weak acid. One can also calculate a pK_a for CH_3COOH where

$$pK_a = -\log K_a = -\log 1.071 \times 10^{-5} \text{ mol liter}^{-1} \tag{2.1d}$$

$$pK_a = 4.77 \tag{2.1e}$$

The lower the pK_a, the stronger the acid. For example, hydrochloric acid (HCl), a strong acid, has p$K_a = -3$.

(II) Derivation of Henderson–Hasselbalch Equation

One can derive a relationship, known as the Henderson–Hasselbalch equation, between pK_a and pH that is very useful in studying weak acids and in preparing buffers. A buffer is a solution whose pH is relatively constant when a small amount of acid or base is added. Since soils behave as weak acids, the Henderson–Hasselbalch equation is useful in understanding how, if pH and pK_a are known, the protonation and deprotonation of functional groups [formally defined in Chapter 5; an example would be the carboxyl ($R{-}C{=}O{-}OH$, where R is an aliphatic group) functional group of soil organic matter in soils] can be assessed.

We know for CH_3COOH that the K_a can be derived from Eq. (2.1b). Taking the −log of both sides of Eq. [2.1b] results in

$$-\log K_a = \frac{-\log [H^+][CH_3COO^-]}{[CH_3COOH]}. \qquad (2.1f)$$

Rearranging,

$$-\log K_a = -\log [H^+] - \log \frac{[CH_3COO^-]}{[CH_3COOH]}. \qquad (2.1g)$$

Simplifying,

$$pK_a = pH - \log \frac{[CH_3COO^-]}{[CH_3COOH]}. \qquad (2.1h)$$

Rearrangement yields,

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]} \qquad (2.1i)$$

or

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}. \qquad (2.1j)$$

If $[CH_3COO^-] = [CH_3COOH]$, then

$$pH = pK_a + \log 1. \qquad (2.1k)$$

Since log 1 = 0, Eq. (2.1k) becomes

$$pH = pK_a. \qquad (2.1l)$$

Therefore, when the $pH = pK_a$, 50% of the acid is dissociated (CH_3COO^-) and 50% is undissociated (CH_3COOH). If one is studying the dissociation of a carboxyl functional group associated with soil organic matter, and the pK_a is 5, at pH 5, 50% would be in the undissociated carboxyl ($R{-}C{=}O{-}OH$) form and 50% would be in the dissociated, carboxylate ($R{-}C{=}O{-}O^-$) form.

briefly discuss the CEC of some of the important secondary minerals in soils. A major component of a soil's CEC is attributable to the secondary clay minerals. The other major component is the organic matter fraction that will be discussed in Chapter 3. The CEC of secondary minerals is very important in affecting the retention of inorganic and organic species.

Table 2.7 shows the CEC for some important secondary minerals. The measured CEC of kaolinite is variable, depending on the degree of impurities in the clay and the pH at which the CEC is measured. If few impurities are present the CEC should be very low, <2 cmol kg^{-1}, since most scientists agree that the degree of isomorphic substitution in kaolinite is small. Impurities of 0.1 to 10% smectitic, micaceous, and vermiculitic layers in kaolinite (Moore and Reynolds, 1989) and anatase, rutile, feldspars, quartz, and iron oxides are often present. Selective dissolution analysis of kaolinite and separation into fine fractions can be employed to determine the degree of impurities and whether isomorphous substitution is present (Newman and Brown, 1987). Another explanation for the often unexpected CEC that is measured for kaolinite is negative charge resulting from surface functional edge groups such as AlOH which are deprotonated when neutral pH extracting solutions (e.g., ammonium acetate) are employed in CEC measurements.

Halloysite, which also has little if any ionic substitution, can have a higher measured CEC than expected. This is attributable to the association of halloysite with allophane (which often has a high CEC) in soils and to the large quantities of NH_4^+ and K^+ ions (which will be assumed to be exchangeable) that are often present between the clay layers. These ions result in an inflation of the CEC when it is measured. When they are accounted for, the CEC of halloysite is close to that of kaolinite.

Montmorillonite has a high CEC that is due to substantial isomorphic substitution and to the presence of fully expanded interlayers that promote exchange of ions. Even though the layer charge of dioctahedral vermiculite is higher than that for smectites, the CEC is less. This is because the interlayer space of vermiculite is not fully open due to K^+ ions satisfying some of the negative charge. Because K^+ has a small hydrated radius compared to other

TABLE 2.7. Cation Exchange Capacity (CEC) of Secondary Soil Minerals

Mineral	CEC (cmol kg^{-1})
Kaolinite	2–15
Halloysite	10–40
Talc	<1
Montmorillonite	80–150
Dioctahedral vermiculite	10–150
Trioctahedral vermiculite	100–200
Muscovite	10–40
Biotite	10–40
Chlorite	10–40
Allophane	5–350

cations such as Ca^{2+} and Mg^{2+}, and because it has the proper coordination number, 12, it fits snugly into the interlayer space of vermiculites and micas. Since the coulombic attractive forces between the K^+ ion and the surfaces of the clay's interlayer are greater than the hydration forces between the individual K^+ ions, the interlayer space undergoes a partial collapse. The trapped K^+ is not always accessible for exchange, particularly when NH_4^+ is used as the index cation to measure CEC.

The measured CEC for dioctahedral vermiculite is also often affected by the presence of $Al(OH)_x$ material in the interlayer. This material often blocks the exchange of cations in the interlayer and consequently the measured CEC is lower than what would be expected based on the layer charge (see Chapter 9 for further discussion on effects of hydroxy-Al interlayer material on cation exchange). In trioctahedral vermiculite, the interlayer cations are usually Ca^{2+} or Mg^{2+} and there are no restrictions to complete cation exchange.

While micas have a higher layer charge than vermiculites, the measured CEC is lower because the exchangeable K^+ in the interlayer, which satisfies the negative lattice charge, is usually inaccessible to index cations used in CEC analyses since it is "fixed" tightly by hydrogen bonding.

The $Al-(OH)_x$ or $Mg-(OH)_x$ interlayer sheet of chlorite is positively charged, satisfying some negative charge. The interlayer sheet also blocks the exchange of cations. Both of these factors cause the measured CEC of chlorite to be lower than one might predict based on layer charge. Allophane has Al^{3+} substituting for Si^{4+} and a lot of edge sites that can create a very high CEC. The high CEC can also be due to salt absorption, like what occurs with halloysite.

IDENTIFICATION OF MINERALS BY X-RAY DIFFRACTION ANALYSES

Clay minerals and other secondary as well as primary minerals can be semiquantitatively identified by using x-ray diffraction analyses. If one wants to precisely quantify the mineral suites, then quantitative techniques including chemical, thermal, infrared, and surface area analyses must be employed.

To analyze and identify clay minerals by x-ray diffraction the patterns (diffractograms) are analyzed with particular emphasis on the peak's position, intensity, shape, and breadth. Values of 2θ are measured by employing Bragg's Law and d-spacings (interplanar or diffraction spacing) are calculated or obtained from 2θ-d tabulations. Bragg's Law can be expressed as (Brindley and Brown, 1980)

$$n\lambda = 2d \sin \theta, \tag{2.5}$$

where θ is the glancing angle of reflection or half the angle between the incident and diffracted beams, λ is the wavelength of the radiation, and n is the order of reflection which takes values 1, 2, 3, etc. For example, the reflection from the basal (00l) plane is described as the (001) reflection or the diffraction is of first-order. The experimentally measured parameter $d/n = \lambda/2\sin\theta$ is the d-spacing. More comprehensive details on x-ray diffraction theory are provided in several excellent references (Brindley and Brown, 1980; Newman, 1987; Moore and Reynolds, 1989).

Clay Separation and X-Ray Diffraction Analysis

Clays are usually separated by centrifugation after removal of carbonates with sodium acetate buffered to pH 5 and of organic matter with hydrogen peroxide or sodium hypochlorite. Iron oxides are then usually removed with a sodium dithionite ($Na_2S_2O_4$) solution, buffered at neutral pH with sodium bicarbonate($NaHCO_3$) and sodium citrate which is added as a complexing agent to keep the iron in solution (Kunze and Dixon, 1986).

The clays are usually segregated into either the <2-μm fraction or the 2- to 0.2-μm and <0.2-μm fractions by centrifugation. They are then saturated with K^+ and Mg^{2+} and excess salt is removed with deionized water. In the case of the Mg-saturated clays, a glycerol treatment is added. The glycerol solution aids in the identification of smectite. Clay is placed on a ceramic tile or on a glass slide or is transferred from a millipore filter to a glass slide for analysis. The clay samples are then heated at several temperatures and analyzed by x-ray diffraction. Clays will give characteristic d-spacings at different temperatures that are diagnostic for their identification. Also, by heating K-saturated samples, certain clay minerals will collapse and be unstable at high temperatures. Moreover, K^+ is not very hydrated and heating will cause it to collapse. With the K-saturated samples, temperatures of 298, 373, 573, and 823K should be used. For Mg-saturated samples, temperatures of 298 and 373K are employed. Diagnostic d(001) spacings for some common primary and secondary soil minerals are given in Table 2.8.

USE OF CLAY MINERALS TO RETAIN ORGANIC CONTAMINANTS

There are many industrial uses of clays (for example, in oil and chemical industries). Recently, there has been much interest in using clays, particularly smectites, because of their high surface areas, for removal of organic pollutants from water. However, natural clays contain exchangeable metal ions, which makes their surfaces hydrophilic, and consequently they are quite ineffective in sorbing nonionic organic compounds (NOC) from aqueous solution. However, it has been found that if the metal ions are exchanged with large surfactant cations, such as long-chain alkylamine cations, the clay surfaces become hydrophobic or organophilic. Such clays are referred to as organoclays and are very effective in sorbing organic pollutants such as NOC (Mortland, 1970; Mortland *et al.*, 1986). It also appears that the organoclay is a stable complex, i.e., the surfactants are not easily desorbed (Zhang *et al.*, 1993). Zhang and Sparks (1993) found that there was little adsorption of aniline and phenol on untreated montmorillonite, but that adsorption of both organics was significantly enhanced when the clay was modified with $HDTMA^+$ (hexadecyltrimethyl-ammonium).

Such organoclays could prove very advantageous in a number of settings. For example, clays that are employed as liners in landfills to diminish the transport of pollutants into water supplies could be modified, resulting in enhanced organic chemical retention and decreased mobility of the pollutants. Also, the organoclays could be used in wastewater treatment and spill control situations (Soundarajan *et al.*, 1990).

TABLE 2.8. Diagnostic d(001) Spacings (nm) of Soil Minerals as Determined from X-Ray Diffraction

	K saturation (K)[a]				Mg saturation (K)[a]	
	298	383	573	823	298	383
Kaolinite	0.715–0.720	0.715–0.720	0.715–0.720	No peak[b]	0.715–0.720	0.715–0.720
Montmorillonite	1.4	1.4	1.4	1.0	1.82	1.42
Vermiculite	1.4	1.4	1.0	1.0	1.4	1.4
Mica	1.0	1.0	1.0	1.0	1.0	1.0
Chlorite	1.4	1.4	1.4	1.4	1.4	1.4
Hydroxy-interlayered vermiculite	1.4	d-spacing decreases with increased temperature to near 1.0 nm if vermiculitic and to 1.2 nm if more chloritic[c]			1.4	1.4
Quartz	0.426 (001 reflection) 0.334 (002 reflection)					
Feldspars	0.318–0.330					
Birnessite	0.72					
Gibbsite	0.484					

[a] Degrees Kelvin.

[b] Kaolinite is not structurally stable above 573K.

[c] As temperature increases, the $Al(OH)_x$ interlayers become less stable and are removed.

BOX 2.2. Calculation of Structural Formulas and CEC of Clay Minerals

While x-ray diffraction can be used to semiquantitatively determine the mineral suites in soils and thermal and surface area analyses can be used to quantify soil minerals, these methods will not provide structural formulas. Such information can only be gleaned through chemical analyses. To obtain the necessary data, the mineral must first be broken down by acid dissolution. The procedure outlined below was first introduced by Ross and Hendricks (1945). In calculating the structural formulas it must be assumed that the SiO_2, Al_2O_3, etc., that are reported were a part of the clay mineral structure. While this may not be completely valid, it is usually true for clay minerals from natural deposits.

The analyses shown in Table 2.9 are for a 2:1 clay with an ideal formula of $Si_8Al_4O_{20}(OH)_4$. Thus, there are a total of 44 positive charges and 44 negative charges, assuming a full-cell chemical formula. To calculate the structural formula for this clay, the following assumptions are made: (1) a total of eight atoms can fit in the tetrahedral sheet which can contain Si^{4+} and Al^{3+}; (2) a total of four atoms can fit in the octahedral sheet with Al^{3+}, Fe^{3+}, Fe^{2+}, Mg^{2+}, and Li^+ able to fit in this sheet; and (3) larger cations such as K^+, Na^+, and Ca^{2+} occur as exchangeable cations and satisfy negative charge resulting from isomorphic substitution.

The data given in Table 2.9 indicate that there are only 7.844 Si^{4+} atoms present in the clay mineral; a total of 8 atoms can fit in the tetrahedral sheet. Therefore, the remaining 0.156 atoms in the tetrahedral layer will be Al^{3+}. Therefore, this sheet has the cationic composition $(Si^{4+}_{7.844}, Al^{3+}_{0.156})^{IV}$. The remaining Al^{3+} atoms (3.005 − 0.156 = 2.849) will go in the octahedral sheet plus enough Fe^{3+}, Fe^{2+}, and Mg^{2+} atoms, in that order, to yield 4 atoms. Thus,

TABLE 2.9. Structural Analysis for a 2 : 1 Clay Mineral

Oxide[a]	Weight %	Atomic weight (g)	g eq cations[b]	g eq cations in total[c]	Atoms per unit cell[d]
SiO_2	50.95	60.06	3.39	31.376	7.844
Al_2O_3	16.54	101.94	0.974	9.015	3.005
Fe_2O_3	1.36	149.69	0.055	0.509	0.170
FeO	0.26	71.85	0.007	0.065	0.033
MgO	4.65	40.30	0.231	2.138	1.069
CaO	2.26	56.08	0.081	0.750	0.375
Na_2O	0.17	61.98	0.006	0.056	0.056
K_2O	0.47	94.20	0.010	0.093	0.093

$\Sigma = 4.754$

[a] Total analyses of clay mineral expressed as oxides and based on a full-cell chemical formula unit.

[b] (Weight %/atomic weight) × (valence of cation) (numbers of atoms of the cation), e.g., for SiO_2 (50.95/60.06) (4).

[c] g eq cations × 44 (number of positive charges per unit cell)/(normalization factor). The normalization factor is Σ g eq cations, which for this example is 4.754.

[d] g eq cations in total/valence of cation.

the octahedral layer would have the cationic composition ($Al^{3+}_{2.849}$, $Fe^{3+}_{0.170}$, $Fe^{2+}_{0.033}$, $Mg^{2+}_{0.948}$)^{VI}. The remaining Mg atoms, 0.121 plus the 0.375 Ca, 0.056 Na, and 0.093 K atoms will go in the interlayer of the clay as exchangeable cations to satisfy the negative charge created in the tetrahedral and octahedral sheets. The complete structural formula for the clay would be

$$(Si^{4+}_{7.844}, Al^{3+}_{0.156})^{IV}\ (Al^{3+}_{2.849}, Fe^{3+}_{0.170}, Fe^{2+}_{0.033}, Mg^{2+}_{0.948})^{VI}$$

$$O_{20}(OH)_4\ (Mg^{2+}_{0.121}, Ca^{2+}_{0.375}, Na^{+}_{0.056}, K^{+}_{0.093}).$$

The overall positive charge is +31.844 in the tetrahedral sheet and +11.019 in the octahedral sheet. The total positive charge is thus (+31.844) + (+11.019) = +42.863. The total negative charge is [(20)(−2) + (4)(−1)] = −44. Therefore, the net charge on the clay is (+42.863) + (−44) = −1.137 or −1.14 equivalents (eq) unit cell^{-1}. This negative charge is balanced out by (0.121) (2) + (0.375)(2) + (0.056)(1) + (0.093)(1) = +1.141 or +1.14 eq unit cell^{-1} as exchangeable cations.

The cation exchange capacity of the clay can be calculated using the following formula:

$$\frac{\text{Net negative charge in eq unit cell}^{-1}}{\text{Molecular weight of the clay per unit cell}}\ (1000\ \text{meq eq}^{-1})\ (100\ \text{g})$$

$$= \frac{1.14\ \text{eq unit cell}^{-1}}{746.45\ \text{g}}\ (1000\ \text{meq eq}^{-1})\ (100\ \text{g}) = 152.72\ \text{meq}\ 100\text{g}^{-1}$$

$$= 152.72\ \text{cmol kg}^{-1}$$

kg cmol

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