

## INORGANIC SOLID PHASE

Soil consists of inorganic and organic solids, the soil solution, soil air, and living organisms. Soil chemistry is primarily concerned with the solid and liquid phases and their interactions. This chapter deals with the inorganic solid phase of soils, primarily the clay fraction, and its important properties. The clay fraction ( $<2 \mu\text{m}$  in size) carries out most of soil chemistry. The larger sand ( $50\text{--}2000 \mu\text{m}$ ) and silt ( $2\text{--}50 \mu\text{m}$ ) fractions are much less chemically active and are composed largely of quartz ( $\text{SiO}_2$ ), which is rather inert.

Inorganic soil particles range in size from colloidal particles ( $<2 \mu\text{m}$ ) to gravel ( $>2 \text{mm}$ ) and rocks. Inorganic components exert the major effect on most soil properties and on the overall suitability of soil as a plant growth medium. Organic components include plant and animal residues at various stages of decomposition, cells and tissues of soil organisms, and substances synthesized by the soil population. Organic components, although usually present in much smaller amounts than inorganic components, affect soil properties significantly because of their high reactivity.

Most inorganic soil components are crystalline compounds of definite structure called minerals. The sand and silt fractions are largely *primary minerals*, minerals formed at elevated temperatures and inherited unchanged from igneous and metamorphic rocks, sometimes after passing through one or more sedimentary cycles. Primary minerals occur in the clay fraction of weakly weathered soils but are minor constituents of the clay fraction of most agricultural soils. The most abundant primary minerals in soils are quartz ( $\text{SiO}_2$ ) and the feldspars ( $\text{MAlSi}_3\text{O}_8$ ), where M is a combination of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ . Micas, pyroxenes, amphiboles, and other primary minerals are also common, but in smaller amounts.

Minerals of the clay fraction of soils are largely secondary, that is, formed by low-temperature reactions and either inherited from sedimentary rocks or formed directly in the soil by weathering. These *secondary (authigenic) minerals* in soils commonly

include the layer silicates, Al and Fe hydroxyoxides, and carbonates and sulfur compounds. Early workers assumed that clay minerals formed in soils were amorphous, noncrystalline spheres. X-ray diffraction revealed that many clay minerals are instead crystalline. The aluminosilicate clay minerals are layered, similar to mica, and have the same relative dimensions as a stack of postage stamps.

Other important constituents of the clay fraction are the so-called *free oxides*. These are Al, Fe, Mn, and Ti hydroxyoxides that accumulate in the soil as weathering removes silicon. The free oxides range from amorphous to crystalline and are often the weathered outer layer of soil particles. The hydroxyoxides, plus amorphous aluminosilicates such as *allophane*, are the most important clay-sized nonlayer minerals in soils.

The most abundant carbonate in soils is calcite ( $\text{CaCO}_3$ ), although pure calcite rarely precipitates directly from the soil solution. Calcium carbonate is common in semiarid and arid region soils and is often present in humid region subsoils derived from calcareous parent material. Ca carbonate accumulates in loose and porous to strongly indurated and rock-like layers in semiarid and arid soils. *Gypsum* ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) occurs in semiarid and arid region soils. The major sulfur mineral is *pyrite* ( $\text{FeS}_2$ ). Pyrite is frequently associated with shales and coal beds and may form in soils under reducing conditions.

## 5.1 CRYSTAL CHEMISTRY OF SILICATES

Layered aluminosilicates are the most important secondary minerals in the clay fraction of soils. When layer silicate minerals are clay or colloidal size ( $<2 \mu\text{m}$  effective diameter), their large surface area greatly influences soil properties. Most of the important clay minerals have similar silicate structures. Inasmuch as clay minerals are such important clay components, and as different clay minerals can change soil properties greatly, an understanding of soil properties begins with an understanding of silicate structures.

When atoms combine, the bond between them changes the electron distribution from that of the atomic state. The type of bond depends on the electronic structure of the combining atoms. *Ionic* or *electrostatic bonding* occurs between oppositely charged ions such as  $\text{Na}^+$  and  $\text{Cl}^-$ . Such ions are formed by the complete loss or gain of electrons to form positive or negative ions having an electron structure like an inert gas. The formation of  $\text{Na}^+$  and  $\text{Cl}^-$  from Na and Cl atoms is, for example,

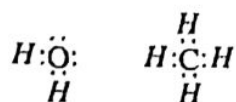


where the dots denote electrons in the outermost, or valence, shell. Alkali and alkaline earth metals and the halogens tend to gain or lose electrons readily and are the most likely to form ionic bonds.

—Ionic bonding is strong, and ionic-bonded compounds tend to be hard solids and have high melting points. Ionic bonding is also undirected—exerted uniformly in all

directions. The valence of a given ion is shared by the surrounding ions of opposite charge. The number of such neighbors is determined by their size relative to the size of the central ion. Ionic bonds predominate in many inorganic crystals, including the silicates.

*Covalent bonding* (shared electron pairs) is common between identical atoms or atoms having similar electrical properties, such as in H<sub>2</sub>O, F<sub>2</sub>, CH<sub>4</sub>, and C (diamond). In covalent bonding the electrons are shared between atoms so that each atom attains the inert gas electronic structure. For example,



Covalent bonding is strong, but directional. Bond angles in covalently bonded structures are determined by the geometric positions of the electron orbitals (orbitals) involved. Covalently bonded molecules have little tendency to ionize. Bonding within ionic radicals, or complex ions, such as SO<sub>4</sub><sup>2-</sup>, is frequently covalent.

*Hydrogen bonding* occurs between H<sup>+</sup> and ions of high electronegativity, such as F<sup>-</sup>, O<sup>2-</sup>, and N<sup>3-</sup>. The hydrogen bond is essentially a weak electrostatic bond and is important in crystal structures of oxy compounds, such as the layer silicates. Summed over many atoms, the individually weak hydrogen bonds can strongly bond adjacent structures.

The weak electrostatic force between residual charges on molecules is *van der Waals* bonding. Residual charges may result from natural dipoles of unsymmetrical molecules, polarization dipoles, or vibrational dipoles. These van der Waals forces are generally obscured by stronger ionic and covalent bonds but may dominate the properties of some molecules.

Each type of chemical bond imparts characteristic properties to a substance. If more than one type of bond occurs in a crystal, the physical properties such as hardness, mechanical strength, and melting point are generally determined by the weakest bonds. These are the first to yield under mechanical or thermal stress. Thus, the physical properties of layer silicates are determined largely by the strength of the bonds between their layers.

Although differences in the types of bonds may seem clear-cut, bonding in most crystals is somewhere in between. For example, the Si-O bond in the silicates is intermediate between purely ionic and purely covalent bonding. The degree of ionic nature of the Si-O bond is sufficient, however, to apply the rules for ionic bonding to silicate structures.

**Bonding within the silicate layers is predominantly ionic. As a result, forces are undirected and ion size plays an important role in determining crystal structure.** Table 5.1 shows the crystal radii of common ions in silicates. The distance between two adjacent ions in a crystal can be measured accurately by x-ray methods. From a series of such measurements between different ions, the effective contributing radius of each ion can be determined. An ion has no rigid boundary; an ion's radius depends on the number of its orbital electrons and on their relative attraction to the ion's nucleus. The radius of Fe ions, for example, decreases from 0.074 to 0.064 nm

**Table 5.1. Crystal ionic radii of selected cations, and coordination numbers for cations with oxygen**

Ion	Crystal Ionic Radius <sup>a</sup> (nm)	Coordination Number with Oxygen	
		Observed	Predicted
Si <sup>4+</sup>	0.042	4	4
Al <sup>3+</sup>	0.051	4, 6	4
Fe <sup>3+</sup>	0.064	6	6
Mg <sup>2+</sup>	0.066	6	6
Fe <sup>2+</sup>	0.074	6	6
Na <sup>+</sup>	0.097	6, 8	6
Ca <sup>2+</sup>	0.09	8	8
K <sup>+</sup>	0.133	8, 12	8
NH <sub>4</sub> <sup>+</sup>	0.143	8, 12	—
O <sup>2-</sup>	0.132	—	—

<sup>a</sup>Reprinted with permission from *Handbook of Chemistry and Physics*, 50th ed. Chemical Rubber Co. Inc. Cleveland, OH (1969–1970).

as the valence changes from Fe(II) to Fe(III). The ion radius also depends on the configuration of the ion structure.

The ion radius of oxygen (O<sup>2-</sup>) is much larger than that of most cations found in silicates. The oxygen ion constitutes 50–70% of the mass, and over 90% of the volume, of most common silicate minerals. Silicate structures are largely determined by the manner in which the oxygen ions pack together.

An ion surrounds itself with ions of opposite charge. The number of anions that pack around a central cation depends on the ratio of the cation and anion radii and is called the *coordination number* of the central ion. Because O<sup>2-</sup> is virtually the only anion in soil minerals, our interest centers on the different cations. Assuming that ions act as rigid spheres, the stable arrangements of cations and anions can be calculated from the packing geometry of their crystal radii (Table 5.2).

**Table 5.2. Spatial arrangement of rigid spheres in relation to radius ratio and coordination number**

Radius Ratio ( $r_{\text{cation}}/r_{\text{anion}}$ )	Arrangement of Anions Around Cations	Coordination Number of Central Cation
0.15–0.22	Corners of an equilateral triangle	3
0.22–0.41	Corners of a tetrahedron	4
0.41–0.73	Corners of an octahedron	6
0.73–1	Corners of a cube	8
1	Closest packing	12

Ions are held together rigidly in a crystal structure, as determined by geometry and by electrical stability. More than one structure may meet the necessary requirements, but the most stable form will be the one having the lowest potential energy. The requirement of electrical neutrality means that the sum of positive and negative charges must be zero. Ions of opposite charge do not pair off to achieve neutrality. Instead, the cation's positive charge is divided among surrounding anions. The number of oxygen ions around each cation is determined by the coordination number, or radius ratio, of the cation and  $O^{2-}$ , rather than by the charge of the cation.

Table 5.2 shows the predicted and observed coordination numbers of common cations with  $O^{2-}$ . The  $Si^{4+}$  cation occurs in fourfold or *tetrahedral coordination*. Aluminium is generally found in sixfold or *octahedral coordination* but also occurs in tetrahedral coordination in igneous minerals. Where the radius ratio is near the boundary between two types of coordination, the cation may occur in either coordination, depending on conditions during crystallization. High crystallization temperatures generally favor low coordination numbers. In high-temperature minerals Al tends to assume fourfold coordination and to substitute for Si. At lower temperatures Al tends to occur in sixfold coordination and Al substitution for Si is rare.

The tetrahedral and octahedral units formed around Si and Al are basic to the structures of silicate minerals. Crystallography developed centuries ago, before ions were known. Crystallographers very cleverly deduced that crystals were formed by the packing of simple structures like tetrahedra and octahedra. Since they did not know about ions, their concern was about shapes. The number and arrangement of ions in a structure is more fundamental than the number of faces of the structure, but the old crystallographic nomenclature persists. The tetrahedral structure (Fig. 5.1a) is four  $O^{2-}$  ligands coordinated around one  $Si^{4+}$ , giving the unit  $SiO_4^{4-}$ . The electrostatic bond strength (ion charge divided by the number of bonds to the ion) for the tetrahedral unit is 1. In fourfold coordination, the hole between the four  $O^{2-}$  ions is 0.225 times the  $O^{2-}$  radius, or 0.030 nm, if the ions are rigid spheres. In reality, cations ranging from 0.029 to 0.052 nm radius occur in fourfold oxide coordination. The radius of  $Si^{4+}$  in fourfold coordination is about 0.042 nm, indicating that the ions are not completely rigid spheres.

The octahedral (eight-sided) structure is formed by six anions coordinated around a central cation (Fig. 5.1b). The electrostatic bond strength is 1/2 if the central ion is trivalent, or 1/3 if the central ion is divalent. Ions commonly found in octahedral

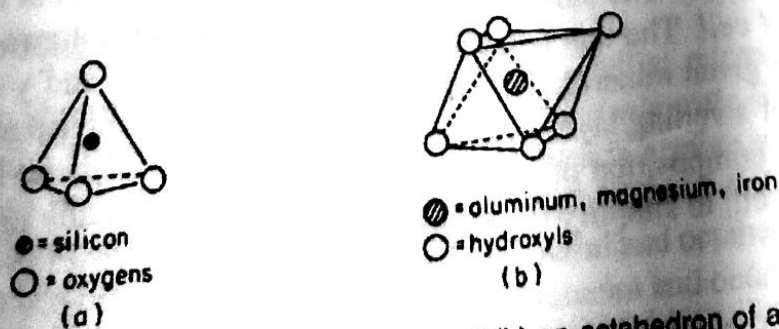


FIGURE 5.1. Diagram of (a) a silica tetrahedron, and (b) an octahedron of aluminum, magnesium, or iron.

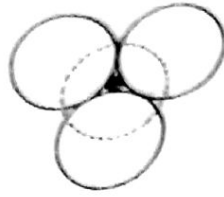


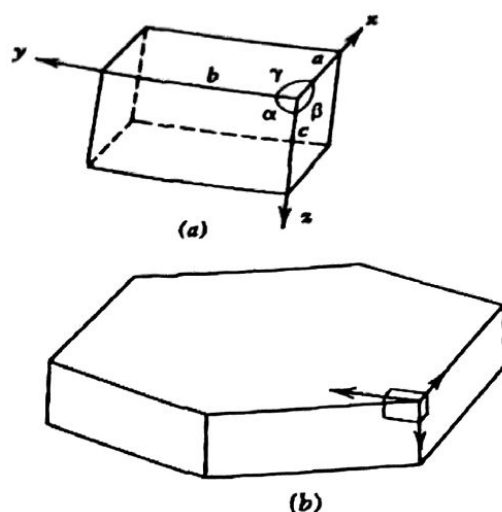
FIGURE 5.2. Silica tetrahedron showing position and relative size of oxygen  $\circ$  and silicon  $\bullet$  ions.

coordination in layer silicates are  $\text{Al}^{3+}$  (radius 0.051 nm in this coordination),  $\text{Mg}^{2+}$  (0.066 nm), and  $\text{Fe}^{2+}$  (0.074 nm). Figure 5.1 and all subsequent drawings of mineral structures greatly exaggerate bond lengths to point out structural features. Also, the size of the  $\text{O}^{2-}$  ions is reduced to show the relative positions of each ion. Figure 5.2 shows a silicate tetrahedron more accurately.

Minerals vary widely in chemical composition. Substitution of one element for another in mineral structures is common; pure minerals are rare in nature. *Isomorphic substitution*, *isomorphism*, *atomic substitution*, and *solid solution* all refer to the substitution of one ion for another without changing the structure of the crystal. Such substitution takes place during crystallization and does not change afterward. Isomorphic substitution can occur between many ions of the same charge, but the size of the ions, rather than the charge, is more important than the charge. Electrical neutrality is maintained by simultaneous substitution of ions elsewhere in the structure, or by retaining ions on the outside of the structure. Isomorphic substitution generally takes place only between ions differing by less than about 10 to 15% in crystal ionic radii.

The more common isomorphic substitutions in silicate structures are  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in tetrahedral coordination, and  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$  for  $\text{Al}^{3+}$  in octahedral coordination. Substitution between ions of unequal charge in layer lattice silicates leaves negative or positive charges within the crystal that are neutralized by ions on the surface of the lattices. The common substitutions in soils produce a net negative charge and contribute to the *cation exchange capacity* of soils. Some areas of soil clay particles have a net positive charge and an *anion exchange capacity*. The anion exchange capacity is usually less than the cation exchange capacity and may result from  $\text{Ti}^{4+}$  substituting for  $\text{Al}^{3+}$ .

A *crystal* is an arrangement of ions or atoms that is repeated at regular intervals in three dimensions. The smallest repeating three-dimensional array of a crystal is called the *unit cell*. The unit cell dimensions  $a$  and  $b$  (the  $x$  and  $y$  dimensions) are constant for a given mineral; the  $c$  (or  $z$ ) dimension is also constant, except for the special case of swelling layer silicates (Fig. 5.3). The *basal plane* is the  $a$ - $b$  plane. The chemical composition of layer silicate minerals is normally expressed as one-half of a unit cell, to simplify the chemical formulas.



**FIGURE 5.3.** The unit cell of a crystal. It is a parallelepiped with angles  $\alpha$ ,  $\beta$ , and  $\gamma$  and edges  $a$ ,  $b$ , and  $c$ . Positions of atoms in the crystal are usually given as  $x$ ,  $y$ , and  $z$  coordinates scaled as fractions of the corresponding cell edges  $a$ ,  $b$ , and  $c$ . (a) Cell for kaolinite. (b) The outline of a crystal of kaolinite showing the orientation of one of its unit cells. The unit cell is  $a = 0.515$  nm,  $b = 0.85$  nm,  $c = 0.715$  nm,  $\alpha = 91.8^\circ$ ,  $\beta = 104.8^\circ$ , and  $\gamma = 90.0^\circ$ . The crystal is about 9.0 nm wide, 10.3 nm long and 2.1 nm thick, about 10 cells by 20 cells by 3 cells, or 600 cells in all. This crystal is at the smaller end of the range of kaolinite crystals found in soils. (From D. S. Greenland and U. H-B. Hayes, eds. 1978. *Chemistry of Soil Constituents*. Wiley, New York.)

## 5.2 STRUCTURAL CLASSIFICATION OF SILICATES

The Si–O bond is so strong that the tetrahedral arrangement of four oxygen anions about the silicon cation appears to be universal in silicate structures. Different silicate structures arise from the various ways in which the  $\text{SiO}_4$  tetrahedra combine with one another. Silicate structures range from single, separate tetrahedra to those in which all corners of the tetrahedron are linked through oxygen to other  $\text{SiO}_4$  tetrahedra. Table 5.3 gives a structural classification of the silicates. This chapter is limited to the silicate structures distinctive to soils.

### 5.2.1 Layer Silicates

Layer silicates, sheet-like phyllosilicates such as the familiar micas, are in primary rocks and in soils. The soil minerals are often called *clay minerals*. Since other components can also be in the clay fraction, layer silicates is a more accurate term. A typical layer silicate is a combination of a layer of Al–, Mg–, or Fe(II)–O octahedra plus one or two layers of Si–O tetrahedra. The tetrahedral and octahedral sheets bond together by sharing oxygens at the corners of the tetrahedra and octahedra. Layer silicate minerals are differentiated by (1) the number and sequence of tetrahedral and octahedral sheets, (2) the layer charge per unit cell, (3) the type of interlayer bor

Table 5.3. Structural classification of silicates<sup>a</sup>

Structural Type	Classification	Structural Arrangement	Si:O Ratio	Mineral Examples
Single tetrahedra	Nesosilicates	Single tetrahedra	1:4	Olivine, garnet
Diosilicates	Sorosilicates	Two tetrahedra sharing one corner	2:7	Hemimorphite
Ring structures	Cyclosilicates	Closed rings of tetrahedra sharing two oxygens	1:3	Beryl
Single chains	Inosilicates	Continuous single chains of tetrahedra sharing two corners	1:3	Pyroxene (augite)
Double chains	Inosilicates	Continuous double chains of tetrahedra sharing alternately two and three oxygens	4:11	Amphiboles (hornblende)
Sheet structures (layer silicates)	Phyllosilicates	Continuous sheets of tetrahedra each sharing three oxygens	2:5	Micas, montmorillonite
Framework structures	Tectosilicates	Continuous framework of tetrahedra each sharing all four oxygens	1:2	Quartz, feldspars, zeolite

<sup>a</sup>Reprinted with permission from James D. Dana. 1959. *Manual of Mineralogy*, 17th ed. (C. S. Hurlbut, ed.). Wiley, New York.

and interlayer cations, (4) the cations in the octahedral sheet, and (5) the type of stacking along the *c* dimension.

The structural unit of the *kaolin* group is formed by superimposing a tetrahedral sheet on an octahedral sheet. Such minerals are referred to as *1:1 layer silicates*. The top oxygens of the tetrahedral sheet are shared by the octahedral sheet, forming a

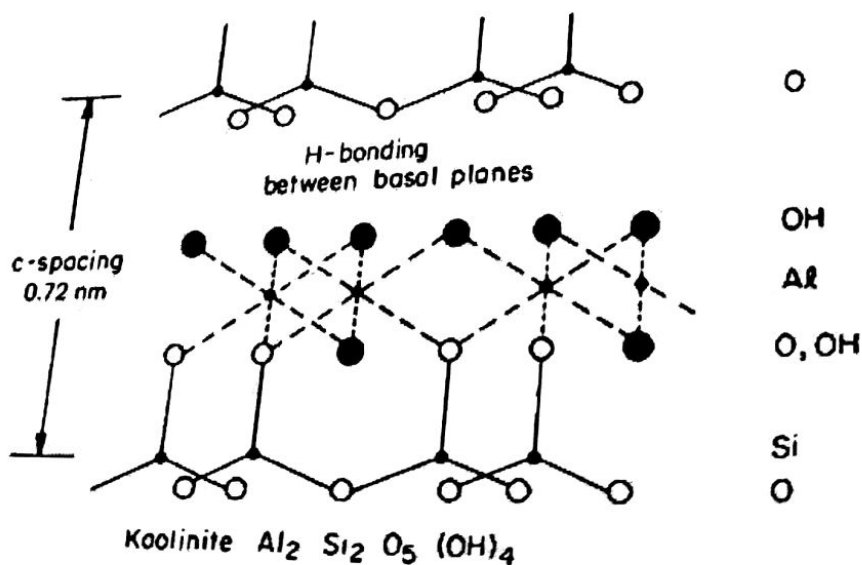


FIGURE 5.4. Schematic structure of kaolinite. (From F. E. Bear, ed. 1964. *Chemistry of the Soil*. ACS Monograph Series No. 160.)



common plane of oxygen ions within the structure (Fig. 5.4). In the shared plane, two-thirds of the oxygen ions are shared between Si and Al. The other one third of the oxygen ions have their remaining charge satisfied by  $H^+$ . The upper surface of kaolin is a layer of closely packed OH groups. The bottom surface is composed of hexagonally open-packed oxide ions, with an OH recessed within the hexagonal (ditrigonal) oxygens. The 1:1 minerals are apparently very inflexible in their structural requirements and allow little or no isomorphous substitution. The structure is electrically neutral. The 1:1 layers are held together strongly by the many hydrogen bonds between the OH groups of one sheet and the O ions of the next sheet.

The 2:1 layer silicates are made up of an octahedral sheet sandwiched between two tetrahedral sheets. These unit layers then stack in the  $c$  direction. Figure 5.5 shows the atomic arrangement of pyrophyllite, an electrically neutral 2:1 mineral. Soil 2:1 layer silicates, on the other hand, have the same structure, but have extensive isomorphous substitution, which leads to largely negative charges within the crystal. This charge must be balanced by other cations, either inside the crystal or outside the structure. The magnitude of charge per formula unit, when balanced by cations external to the unit layer, is called the *layer charge*. The 2:1 minerals are classified according to layer charge in Table 5.4.

The magnitude of layer charge plays a dominant role in determining the strength and type of bonding between the 2:1 layers. If the layer charge is zero, as in pyrophyllite, the 2:1 layers bond together by very weak van der Waals forces. If the layer charge is negative, the 2:1 sheets bond electrostatically and more strongly because cations enter between the unit layers. The greater the layer charge, the more cations, and the stronger the interlayer bond. *Smectites* (which include *montmorillonite* and *bentonite*) of low layer charge bond weakly so polar molecules, such as water, can enter between the sheets, and the minerals expand or swell as the soil becomes wet. In minerals of high layer charge, such as the micas (*muscovite* and *biotite*), the ionic bond of  $K^+$  between the sheets is so strong that polar molecules cannot enter, the minerals are nonswelling (nonexpanding), and the soil does not shrink and swell with changing moisture content. *Vermiculites* are intermediate in layer charge and also in-

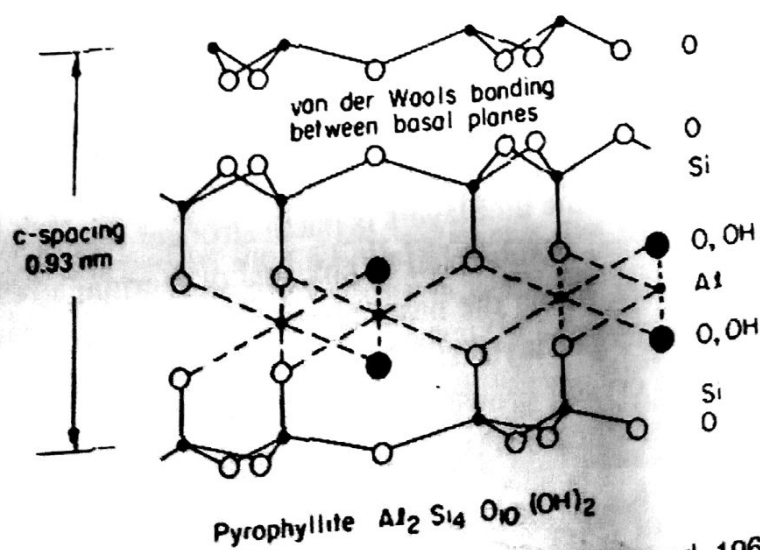


FIGURE 5.5. Schematic structure of pyrophyllite. (From F. E. Bear, ed. 1964. *Chemistry of the Soil*. ACS Monograph Series No. 160.)

Table 5.4. Typical 2:1 layer silicate minerals

Mineral Group	Layer Charge per Formula Unit in		Predominant Octahedral Cation	
	Tetrahedral Sheet	Octahedral Sheet	Al <sup>3+</sup> (Dioctahedral)	Mg <sup>2+</sup> (Trioctahedral)
Pyrophyllite-talc	0	0	Pyrophyllite	Talc
Smectites	0.25–0.6	0	Beidellite	Saponite
	0	0.25–0.6	Montmorillonite	Hectorite
Vermiculites	0.6–0.9	0	Vermiculite	Vermiculite
Micas	1	0	Muscovite	Biotite <sup>a</sup>

<sup>a</sup>Mg<sup>2+</sup> and Fe<sup>2+</sup> in octahedral coordination, K<sup>+</sup> in the interlayer position.

intermediate between micas and the smectites in their swelling properties. Within a given mineral group, specific minerals are defined by the predominant ion in the octahedral coordination. Table 5.4 gives names for common minerals having Al<sup>3+</sup> in octahedral coordination.

The 2:1 layer silicate minerals are sometimes defined on the basis of the number of octahedral positions occupied by cations. When two-thirds of the octahedral positions are occupied, such as in pyrophyllite (Al<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>), the mineral is called *dioctahedral*; when all three positions are occupied, such as in talc (Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>), the mineral is called *trioctahedral*. This difference in composition of layer silicates can be fairly easily determined by x-ray diffraction, because each substitution slightly changes the dimensions of the unit cell.

*Chlorites* are closely related to the micas and have about the same layer charge. In chlorite, the interlayer K<sup>+</sup> of mica is replaced by a positively charged octahedral *brucite* (Mg<sub>3</sub>(OH)<sub>6</sub>) sheet. The brucite sheet develops a positive charge when the Mg<sup>2+</sup> is partially replaced by Al<sup>3+</sup>. Such replacement is often about one-third of the Mg<sup>2+</sup> positions, to give the basic unit (Mg<sub>2</sub>Al(OH)<sub>6</sub>)<sup>+</sup> that fits into the interlayer position of 2:1 layer silicates to yield the 2:1:1 chlorite (Fig. 5.6). Chlorites are nonexpanding, have low cation exchange capacities, and are generally trioctahedral.

### 5.2.2 Relation of Structure to Physical and Chemical Properties

The interlayer bond has a big effect on the physical and chemical properties of layer silicates. Bonding within the unit layers is much stronger than between adjacent unit layers. When the mineral is subjected to physical or thermal stress, it fractures first between the unit layers, along the basal plane. This is the reason for the flake-like shape of most macroscopic layer silicate crystals. Also, the stronger the interlayer bond, the greater the crystal growth in the *c* dimension before fracture. Hence, the size and shape of layer silicate crystals is a direct consequence of the strength of their interlayer bonds.

The surface area of layer silicates is related to their expanding properties, and may be either external only or external plus internal. *External surface* refers to the

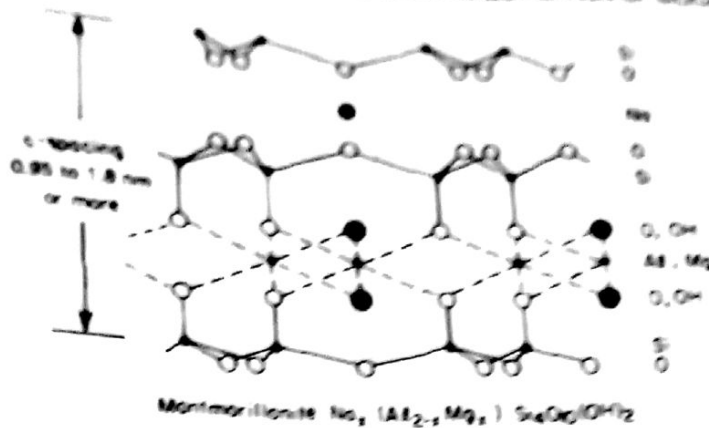


FIGURE 5.6. Schematic structure of chlorite. (From F. E. Bear, ed. 1964. *Chemistry of the Soil*. ACS Monograph Series No. 160.)

faces and edges of the whole crystal; *internal surface* is the area of the basal plane surfaces of each unit layer. Nonexpanding minerals exhibit only external surface; expanding minerals have both internal and external surface. The total surface area of montmorillonite can be as large as  $800 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$ . The surface area of kaolinite, a nonexpanding and 1:1 layer silicate, is usually only  $10 \text{ to } 20 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$ .

The *c* spacing of the layer silicates is determined by (1) the number of O—OH sheets per unit structure in the *c* dimension, and (2) the presence of ions and/or polar molecules in the basal plane. This spacing is conveniently measured by x-ray diffraction. Pyrophyllite has an electrically neutral lattice and hence no interlayer cations. Adjacent units of this mineral approach one another closely and form van der Waals bonds, preventing water entry. The resultant constant *c* spacing is 0.93 nm (Fig. 5.5). In minerals having weak interlayer bonds such as montmorillonite, cations and water or other polar molecules can enter between the basal planes, causing the *c* spacing to increase. The expansion varies greatly with the amount and type of polar molecule. In minerals with strong interlayer bonding, such as mica, chlorite and kaolinite, water, and other polar molecules cannot enter between the basal planes.

Adsorbed cations are held by layer silicates to balance the negative charge resulting from isomorphous substitution and from unsatisfied bonds on crystal edges. The magnitude of the exchange capacity of the crystal edge is related to the number of unsatisfied bonds, and therefore is a direct function of crystal size. In 2:1 layer silicates, the larger portion of the cations balancing this mostly negative charge is in the basal plane. Where the layer charge is high, such as in mica, the bond energy is so great, the adjacent layers are so tightly "collapsed," and the  $K^+$  fits so well into the hexagonal holes in the basal plane that the adsorbed cations are not exchangeable. The adsorbed cations of smectite minerals, on the other hand, are readily exchangeable. For vermiculite,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Na^+$  ions in interlayer position are exchangeable, but  $K^+$  and  $NH_4^+$  ions, because of their good fit, are not exchangeable by ordinary procedures. Thus, exchange capacity is directly related to layer charge until the charge becomes so large that the adsorbed cations cannot be removed.