CLAY MINERALS

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Introduction

The clay-size fraction of soils consists of mineral particles that are less than 2 μm in equivalent diameter. This is the realm of exceedingly small, crystalline particles dominated by planar arrays of SiO_4 structural units and many structural hydroxyls and water. These 'clay minerals' crystallize in the aqueous environment at the Earth's surface from the constituent ions released by dissolving (weathering) 'primary minerals' such as olivines, pyroxenes, feldspars, micas, quartz, and others that were formed under extreme heat and pressure deep within the Earth. Clay minerals are responsible for many of the soil's most important and characteristic physical and chemical properties. Fundamental soil properties such as cation exchange and shrink–swell properties, as well as practical considerations such as how well a particular soil will attenuate a specific pollutant, or how much fertilizer phosphorus will be fixed and unavailable to crops, are all influenced by molecular-scale differences in soil clay minerals.

Clay minerals are distinguished on the basis of their different crystal structures, and there is a close relationship between the crystal structure and the corresponding bulk physical and chemical properties of a particular type of clay. We begin by considering some of the properties of the major chemical elements that make up the clay minerals.

Major Element Composition of Clay Minerals

Most of the mass and volume of the Earth's crust is made up by only a few chemical elements. O and Si alone account for almost 75% of the mass, with most of the remainder, in order of decreasing abundance, consisting of Al, Fe, Ca, Na, K, Mg, Ti, H, P, and Mn. On a volume basis, oxygen alone accounts for more than 90% of the total volume. O, as O^{2-}, is the only abundant anion, while the other abundant elements are all cations. Most of these cations have only one stable oxidation state at the Earth's surface (Al^{3+}, Ca^{2+}, Na^+, K^+, Mg^{2+}, Ti^{4+}, H^+, P^{5+}); Fe (Fe^{2+}, Fe^{3+}) and Mn (Mn^{2+}, Mn^{3+}, Mn^{4+}) are the exceptions. The O^{2-} anions are much larger than most of the positively charged cations. The Earth's crust, therefore, can be characterized as large O atoms in an approximately close-packed arrangement held together by attraction to smaller cations located in the interstitial space.

Most of the elements in the crust and in soils occur in minerals, and the elements listed above are major constituents of the most abundant minerals, including clay minerals. Building on the concept of packing O atoms in space, we will consider atoms as rigid spheres, realizing that this is an oversimplified but convenient model for developing the key structural concepts.

Basic Structural Concepts

Tetrahedra and Octahedra

Two distinct structural features occur within the crystal structures of soil clay minerals as a consequence of packing the large O^{2-} ions together in space. The first consists of four O^{2-} ions packed closely together, and can be described as three O^{2-} ions arranged in a triangle with the fourth O^{2-} occupying the dimple formed by the other three (**Figure 1**). The centers of the four O^{2-} ions form the apices of a regular tetrahedron, and the small space in the center is called a 'tetrahedral site.' Cations located in tetrahedral sites are in fourfold or tetrahedral coordination, because they are surrounded by and bonded to four O^{2-} ions.

The second structural feature consists of six closely packed O^{2-} ions. Three of them are arranged in a triangle in one plane, and the other three, also in a triangle but rotated 60° relative to the first three, are in a second plane so that the two triangular groups intermesh (**Figure 1**). The centers of the six O^{2-} ions form the apices of a regular octahedron, and the small space in the center is called an 'octahedral site.' Cations located in the octahedral site are said to be in sixfold or octahedral coordination because they are surrounded by and bonded to six O^{2-} ions.

Tetrahedral and octahedral sites differ in another important way. The space that can be occupied by a cation in a tetrahedral site is smaller than the space that can be occupied in an octahedral site. Since cations vary in size, smaller cations tend to occur in tetrahedral sites, somewhat larger cations tend to occur in octahedral sites, and the largest cations must fit into spaces that are even larger than octahedral sites. Cations with sizes intermediate between the optimum for two sites can occur in either site. The Al^{3+} ion, for example, can occur in either octahedral or tetrahedral sites. **Table 1** summarizes the structural sites in which cations tend to occur in clay minerals.
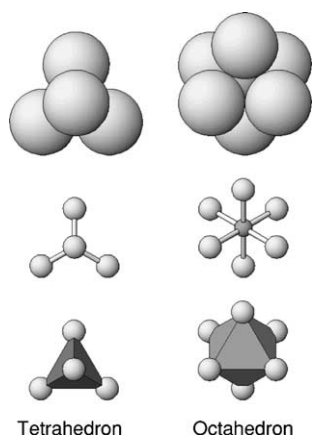
Figure 1 Spheres closely packed to form a tetrahedron and an octahedron. Note the appearance for the three different ways of drawing the model: as a sphere-packing model (top row), ball-and-stick model (middle row), and a polyhedral model (bottom row). (Adapted from Schulze DG (2002) An introduction to soil mineralogy. In: Dixon JB and Schulze DG (eds) *Soil Mineralogy with Environmental Applications*, pp. 1–35. Madison, WI: Soil Science Society of America, with permission.)

Representing Crystal Structures

Octahedra and tetrahedra are commonly represented using different types of models, each of which portrays the same concept, but highlights different structural features. Sphere-packing models give an impression of the space occupied by the atoms, ball-and-stick models highlight the bonds, while polyhedral models emphasize the tetrahedral and octahedral units (Figure 1). There is some ambiguity associated with each representation, and it is important to understand the correspondence between, and limitations of, each type of model. Polyhedral models are used here, along with some sphere-packing models.

Tetrahedral and Octahedral Sheets

The most common and abundant clay minerals belong to a group of minerals called phyllosilicates (from Greek 'phyllon,' meaning 'leaf') or sheet silicates. A common structural theme in all phyllosilicates is the presence of SiO_4 tetrahedra arranged into sheets. Octahedra arranged into sheets are also present in the structures of phyllosilicates and in some hydroxide minerals as well. Different combinations of the two sheets give rise to the different clay mineral structures.

Tetrahedral Sheet

The tetrahedral sheet consists of SiO_4 tetrahedra arranged such that three of the four O^{2-} ions of each tetrahedron are shared with three nearest-neighbor tetrahedra (Figure 2). These shared O^{2-} ions are all

Table 1 Type of structural sites in which common cations tend to occur in phyllosilicate mineral structures

Type of site	Cation
Tetrahedral only	Si^{4+}
Tetrahedral or octahedral	Al^{3+}, Fe^{3+}
Octahedral only	Mg^{2+}, Ti^{4+}, Fe^{2+}, Mn^{2+}
Interlayer sites	Na^+, Ca^{2+}, K^+

in the same plane and are referred to as basal oxygens. Note that adjacent tetrahedra share only one O^{2-} between them (the tetrahedra share apices or corners). The fourth O^{2-} ion of each tetrahedron is not shared with another SiO_4 tetrahedron and is free to bond to other polyhedral elements. These unshared O^{2-} ions are referred to as apical oxygens. Since each basal oxygen contributes a charge of -1 to each Si^{4+} ion, the addition of H^+ ions to the apical oxygens to form hydroxyls should result in an electrically neutral tetrahedral sheet. Such individual tetrahedral sheets do not form stable mineral structures by themselves and only occur in combination with octahedral sheets, as described below.

Figure 2 shows all of the apical oxygens pointing in the same direction, namely, out of the plane of the paper toward the reader. This is the most common arrangement, but structures also occur in which the apical oxygens point alternately in opposite directions.

Octahedral Sheet

Analogous to the tetrahedral sheet, we can consider the octahedral sheet illustrated in Figure 3 as an assemblage of octahedra in which adjacent octahedra share two oxygens with one another. In other words, adjacent octahedra share edges. For the arrangement of octahedra shown in Figure 3, the octahedral sites are occupied by trivalent cations, typically Al^{3+}, and for charge balance, a proton (H^+) must be associated with each O^{2-}. (The H^+ takes up very little space, and the OH^- ion can be considered a sphere of roughly the same size as an O^{2-} ion.) Each OH^- contributes one-half a negative charge to each cation because each OH^- is shared between two octahedra. Each Al^{3+} cation is therefore effectively surrounded by $6 \times 0.5 = 3$ negative charges and the sheet is electrically neutral. Note the pattern of empty and filled octahedral sites. Two of every three possible octahedral sites are filled when trivalent cations are present in the octahedral sites. This arrangement is called dioctahedral and is the most common in soil clay minerals. If the octahedral sites are filled with divalent cations such as Mg^{2+} then every possible octahedral site must be occupied to produce an electrically
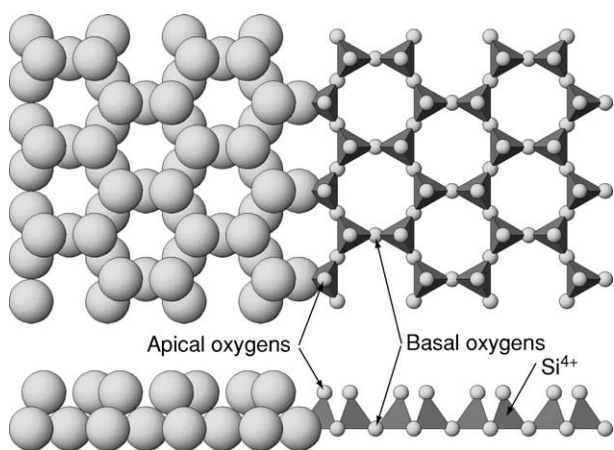
Figure 2 The tetrahedral sheet as a sphere-packing model (left half) and a polyhedral model (right half). (Adapted from Schulze DG (2002) An introduction to soil mineralogy. In: Dixon JB and Schulze DG (eds) *Soil Mineralogy with Environmental Applications*, pp. 1–35. Madison, WI: Soil Science Society of America, with permission.)
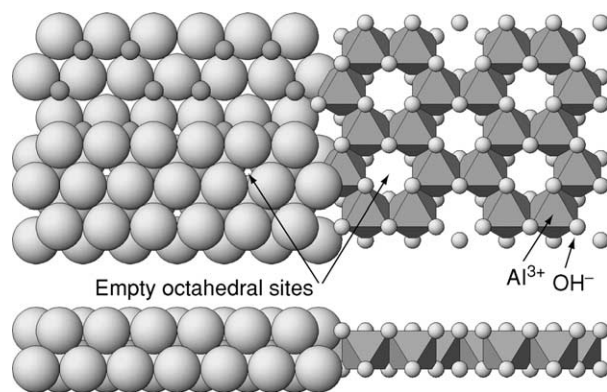

Figure 3 The octahedral sheet as a sphere-packing model (left half) and a polyhedral model (right half). The top three rows of spheres have been omitted from the sphere-packing model so that the underlying cations, represented here as Al^{3+}, can be seen more easily. The dioctahedral arrangement is shown here, in which two-thirds of the possible octahedral sites are filled with cations and one-third are empty. (Adapted from Schulze DG (2002) An introduction to soil mineralogy. In: Dixon JB and Schulze DG (eds) *Soil Mineralogy with Environmental Applications*, pp. 1–35. Madison, WI: Soil Science Society of America, with permission.)

neutral structure. This arrangement is called trioctahedral.

Octahedral sheets, stacked one on top of the other and held together by hydrogen bonds, make up the structure of gibbsite, $Al(OH)_3$, an aluminum hydroxide mineral that occurs in intensively leached soils. The structure of gibbsite is the simplest in a series of structures containing octahedral sheets.

Phyllosilicate Minerals Common In Soil Clays

Phyllosilicates are divided into two groups, 1:1- and 2:1-type minerals, based on the number of tetrahedral and octahedral sheets in the layer structure.

1:1-Type Minerals

1:1 Layer structure   The 1:1 layer structure consists of a unit made up of one octahedral and one tetrahedral sheet, with the apical O^{2-} ions of the tetrahedral sheets being shared with (and part of) the octahedral sheet (**Figure 4**). There are three planes of anions (**Figure 4b**). One plane consists of the basal O^{2-} ions of the tetrahedral sheet, the second consists of O^{2-} ions common to both the tetrahedral and octahedral sheets (marked 'a' in **Figure 4a**) plus OH^- belonging to the octahedral sheet ('b' in **Figure 4a**), and the third consists only of OH^- belonging to the octahedral sheet.

Kaolinite   The structure of kaolinite consists of 1:1 layers stacked one above the other. Kaolinite contains Al^{3+} in the octahedral sites and Si^{4+} in the tetrahedral sites (**Figure 5**). The 1:1 layer is electrically neutral and adjacent layers are held together by hydrogen bonding between the basal oxygens of the tetrahedral sheet and the hydroxyls of the exterior plane of the adjacent octahedral sheet.

Kaolinite is a common mineral in soils and is the most common member of this subgroup. It tends to be particularly abundant in more weathered soils such as Ultisols and Oxisols. Kaolinites have very little isomorphous substitution in either the tetrahedral or octahedral sheets and most kaolinites are close to the ideal formula $Al_2Si_2O_5(OH)_4$. The 1:1 layer has little or no permanent charge because of the low amount of substitution. Consequently, cation exchange capacities and surface areas are typically low. Soils high in kaolinite are generally less fertile than soils in which 2:1 clay minerals dominate.

Kaolinite can form in soils from Al and Si released by the weathering of primary and other secondary minerals. For example, feldspars often weather to kaolinite in soils formed from igneous rocks. Kaolinite can also be inherited from clayey, sedimentary soil parent materials.

Halloysite   Halloysite has a 1:1 layer structure similar to kaolinite except that the 1:1 layers are separated by a layer of H_2O molecules when fully hydrated (**Figure 5**). This water is probably present as hydration shells around a small number of interlayer cations (cations that reside between two adjacent 1:1 or 2:1 layers), although the presence of interlayer
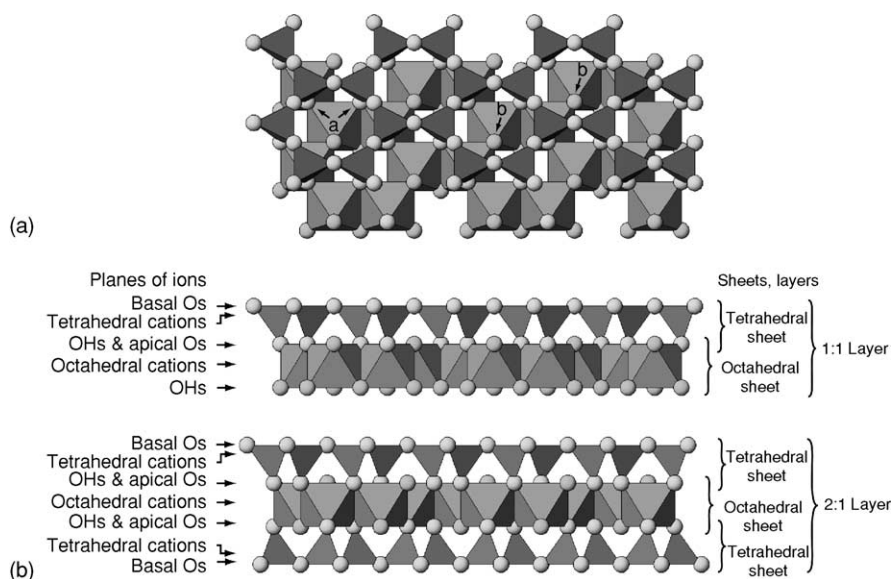
Figure 4 (a) Oblique view of the 1:1 layer structure illustrating the relationship between the tetrahedral and octahedral sheets. Note that adjacent apical oxygens of the tetrahedral sheet (arrows 'a') also define corners of octahedra in the octahedral sheet. Arrows marked 'b' point to OHs that lie directly in the center of the hexagonal rings of tetrahedra, although they appear off-center in this oblique view. (b) Edge view of the 1:1 and 2:1 layer structures, illustrating phyllosilicate nomenclature. (Adapted from Schulze DG (2002) An introduction to soil mineralogy. In: Dixon JB and Schulze DG (eds) *Soil Mineralogy with Environmental Applications*, pp. 1–35. Madison, WI: Soil Science Society of America, with permission.)

cations and the existence of layer charge to attract them has been difficult to confirm. Most clay silicates occur as thin plates, but halloysite often occurs as tubular or spherical particles.

Halloysite is usually found in soils formed from volcanic deposits, particularly volcanic ash and glass. It is a common clay mineral in the Andisol soil order. Halloysite forms early in the weathering process but it is generally less stable than kaolinite and gives way to kaolinite with time.

2:1-Type Minerals

In contrast to the 1:1 minerals, which are represented in soils by only two major minerals, the 2:1 minerals are structurally more diverse and are represented by several mineral species.

2:1 Layer structure   The 2:1 layer structure consists of two tetrahedral sheets, with one bound to each side of an octahedral sheet (**Figure 4b**). There are four planes of anions. The outer two consist of the basal oxygens of the two tetrahedral sheets, while the two inner planes consist of oxygens common to the octahedral sheet and the two tetrahedral sheets, plus the hydroxyls belonging to the octahedral sheet.

Pyrophyllite   The simple structure of pyrophyllite is a good starting point for discussing 2:1 structures. Pyrophyllite consists of 2:1 layers stacked one above

the other. The tetrahedral sheets contain only Si^{4+} and the octahedral sheet contains only Al^{3+}, resulting in the ideal formula $Al_2(Si_4)O_{10}(OH)_2$. The charge is balanced completely within the 2:1 layer, making the layer electrically neutral, and adjacent 2:1 layers are held together only by weak van der Waals forces. Pyrophyllite occurs only rarely in soils, usually only when it is inherited from low-grade metamorphic rocks.

Micas   Mica minerals have the 2:1 layer structure described for pyrophyllite but with two important differences. First, instead of having only Si^{4+} in the tetrahedral sites, one-quarter of the tetrahedral sites are occupied by Al^{3+}. Because of this substitution, there is an excess of one negative charge per formula unit in the 2:1 layer. Second, this excess negative charge is balanced by monovalent cations, commonly K^+, that occupy interlayer sites between two 2:1 layers (**Figure 5**). This gives an ideal formula of $KAl_2(AlSi_3)O_{10}(OH)_2$ for a mica mineral with Al in the octahedral sites.

The octahedral sheet can contain either Al^{3+} (the dioctahedral case; **Figure 3**) or Mg^{2+} (the trioctahedral case), and there are several different mica species, because Fe^{2+} and Fe^{3+} can substitute for Mg^{2+} and Al^{3+} in the octahedral sheet and Na^+ and Ca^{2+} can substitute for K^+ in the interlayer.

Mica in soils is usually inherited from the parent rock and is likely to occur in soils derived from various
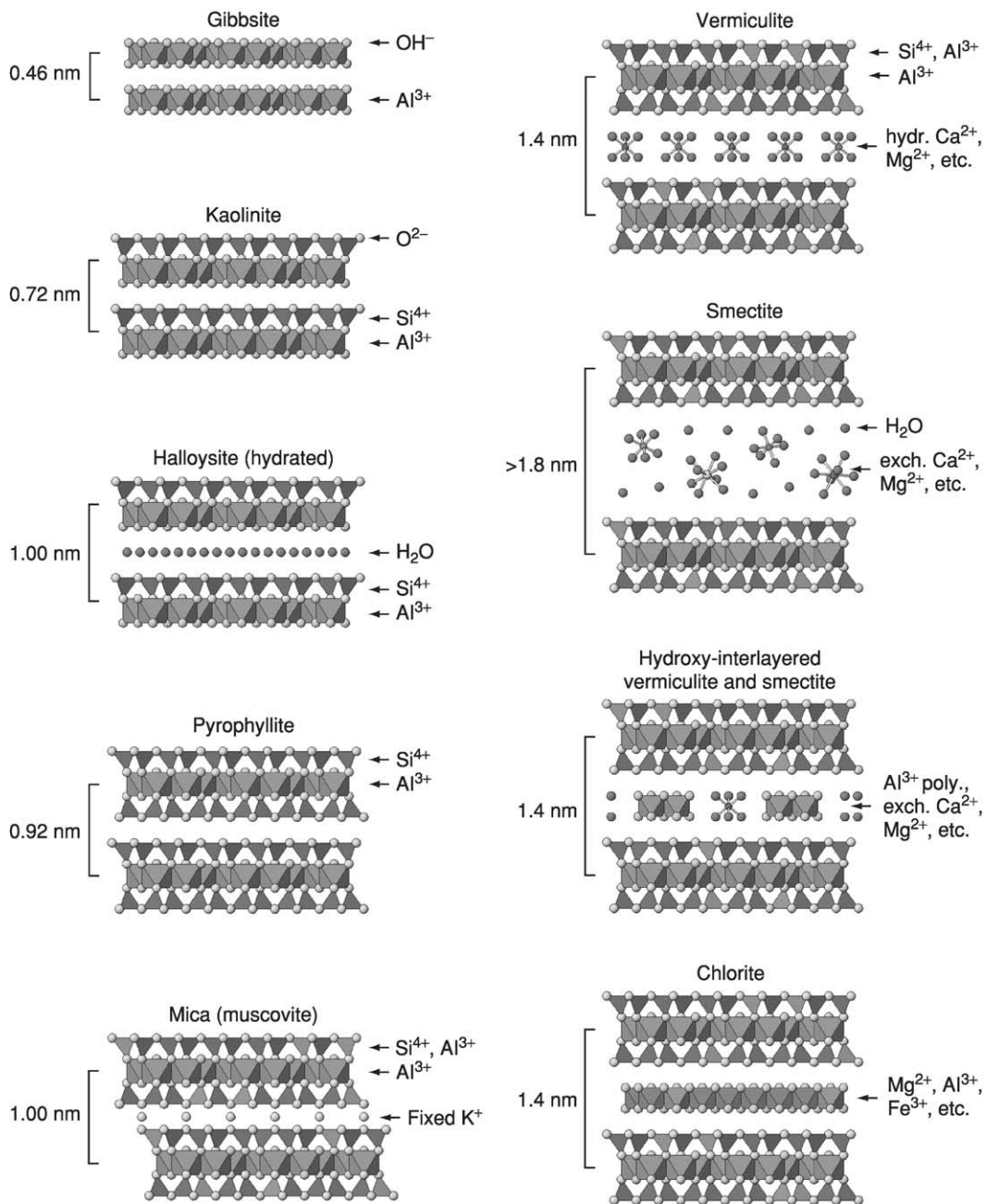
Figure 5 Structural scheme of soil minerals based on tetrahedral and octahedral sheets. (Adapted from Schulze DG (2002) An introduction to soil mineralogy. In: Dixon JB and Schulze DG (eds) *Soil Mineralogy with Environmental Applications*, pp. 1–35. Madison, WI: Soil Science Society of America, with permission.)

igneous and metamorphic rocks, as well as from sediments derived from them. Muscovite, biotite, and phlogopite are the three most common mica group minerals in rocks, and consequently in soils. All three contain K in the interlayer, but they differ in the composition of the octahedral sheet and whether they are di- or trioctahedral. Mica in the clay fraction of soils and sediments differs somewhat from the macroscopic muscovite mica it most closely

resembles. This clay-size mica is often referred to as illite. Glauconite is another mica mineral that is similar to illite, but it contains more Fe and less Al in its octahedral sheet than illite.

Micas weather to other minerals, particularly to vermiculites and smectites, and the K^+ released during weathering is an important source of K for plants. As a rule, the dioctahedral micas such as muscovite are more resistant to weathering than trioctahedral

micas. Thus, muscovite tends to be the most common mica mineral in soils.

Vermiculites Vermiculite has a 2:1 layer structure as described for mica, but, instead of having a layer charge of $\sim$1 per formula unit and K^+ in interlayer positions, vermiculite has a layer charge of 0.9–0.6 per formula unit and contains hydrated exchangeable cations, primarily Ca and Mg, in the interlayer (**Figure 5**). A typical formula for an idealized vermiculite weathered from muscovite is: $M^+_{0.75}$ $Al_2(Si_{3.25}Al_{0.75})$ $O_{10}(OH)_2$, where M^+ represents exchangeable cations. The high charge per formula unit gives vermiculite a high cation exchange capacity and causes vermiculte to have a high affinity for weakly hydrated cations such as K^+, NH_4^+, and Cs^+. Fixation of K^+ by vermiculite can be significant in soils that are high in vermiculite and that have not received large amounts of chemical fertilizers.

Vermiculites in soils are believed to form almost exclusively from the weathering of micas and chlorites. The weathering of micas to vermiculite (or smectite) is believed to occur by replacement of K^+ in the interlayer sites with hydrated exchangeable cations. The integrity of the 2:1 layer is preserved, but there is a reduction in the layer charge. Vermiculite does not swell as extensively as smectite and this is shown in **Figure 5** by the presence of only two planes of water molecules surrounding the hydrated cations in the interlayer space.

Smectites The smectite group consists of minerals with the 2:1 structure already discussed for mica and vermiculite, but with a still lower charge per formula weight, namely 0.6–0.2. As in vermiculite, the interlayer contains exchangeable cations (**Figure 5**). An idealized formula for a common soil smectite, the mineral beidellite, is: $M^+_{0.33}Al_2$ $(Si_{3.67}Al_{0.33})$ $O_{10}(OH)_2$, where M^+ represents exchangeable cations, typically Ca^{2+} and Mg^{2+}.

The most common smectite minerals range in composition between three end-members: montmorillonite, beidellite, and nontronite. All are dioctahedral, but they differ in the composition of the tetrahedral and octahedral sheets. Smectites do not fix K^+ as readily as do vermiculites because smectites have a lower layer charge, but smectites swell more extensively than vermiculite. This is illustrated in **Figure 5** by the larger spacing between the 2:1 layers.

Smectites are important minerals in temperate-region soils. Many plant nutrients are held in an available form on the cation exchange sites of soil smectites. Soils rich in smectite tend to be very effective at attenuating many organic and inorganic pollutants because of the high surface area and adsorptive

properties of the smectites. Smectites shrink upon drying and swell upon wetting. This shrink–swell behavior is most pronounced in the Vertisol order and in vertic subgroups of other soil orders. The shrink–swell properties lead to cracking and shifting problems when houses, roads, and other structures are built on smectitic soils.

Chlorites Like mica, chlorite minerals have a 2:1 layer structure with an excess of negative charge. In contrast to mica, however, the excess charge is balanced by a positively charged interlayer hydroxide sheet (**Figure 5**), rather than K^+. The interlayer hydroxide sheet is an octahedral sheet as shown in **Figure 3** and can be either di- or trioctahedral. Instead of being electrically neutral as in gibbsite, the hydroxide sheet has a positive charge caused by substitution of higher-valence cations for lower-valence ones, for example, $Mg_2Al(OH)_6^+$. Either octahedral sheet – the one that is part of the 2:1 layer or the interlayer hydroxide sheet – can be di- or trioctahedral, and can contain Mg^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Al^{3+}, Fe^{3+}, and Cr^{3+}, giving a large number of different mineral species.

Chlorite minerals in soils are often primary minerals inherited from either metamorphic or igneous rocks. They may also be inherited from sedimentary rocks such as shales, or from hydrothermally altered sediments. Chlorites are rather infrequent minerals in soils and when present they generally occur in small amounts. Chlorite weathers to form vermiculite and smectite, and the ease with which chlorites break down makes them sensitive indicators of weathering.

Hydroxy-interlayered vermiculite and smectite Hydroxy-interlayered vermiculite and smectite can be considered a solid solution with vermiculite or smectite as one end-member and chlorite as the other. Hydroxy-interlayered minerals form as Al^{3+} released during weathering hydrolyzes and polymerizes to form large polycations with a postulated formula of $Al_6(OH)_{15}^{3+}$ (or similar) in the interlayers of vermiculite and smectite. These polycations balance some of the charge of the 2:1 layer. The combination of a 2:1 layer with hydroxy Al in the interlayer gives a structure similar to that of chlorite (**Figure 5**). Thus, these minerals are also called secondary chlorites. The degree of filling of the interlayer with hydroxy Al can vary from none to almost complete, with properties of the clay varying accordingly. The interlayer hydroxy Al is not exchangeable, therefore it lowers the cation exchange capacity of smectite or vermiculite almost linearly as a function of the amount of Al adsorbed in the interlayer.

Interlayer hydroxy Al prevents smectite from shrinking and swelling as it normally would. In

vermiculite, it reduces K^+ fixation by lowering the exchange capacity and by preventing the interlayer from collapsing around the K^+. The positively charged hydroxy interlayers also provide potential sites for anion adsorption. Hydroxy-interlayered vermiculite and smectite are most common in Alfisols and Ultisols. Within a given profile, they tend to be most abundant near the soil surface.

Interstratification in phyllosilicates Because of the structural similarities of all of the phyllosilicate minerals just discussed, phyllosilicates in soils do not always occur as discrete particles of mica, vermiculite, smectite, chlorite, or kaolinite. For example, instead of being made up of a stack of identical 2:1 vermiculite layers, one physically discrete particle may consist of a mixture of both mica and vermiculite layers instead. Such minerals are referred to as 'mixed-layer' or 'interstratified minerals.'

Different types of interstratified minerals have been identified. Two-component systems include: mica-vermiculite, mica-smectite, mica-chlorite, kaolinite-smectite, and others. Three-component mixed layer systems can also occur. The sequence of layers can be either regular or random. A regularly interstratified mineral consisting of two types of layers denoted by A and B could have a sequence such as ABABAB..., or ABBABBABB..., or any other repeating sequence. In a randomly interstratified mineral, the sequence of layers is random – for example, ABBABAABBAAA.... Random interstratification of layer-silicates is more common in soils than regular interstratification, though regular interstratification, especially in weathering micas, is not rare.

Partial removal of interlayer K from micas or of interlayer hydroxide from chlorite is one way that interstratified minerals can form in soils. Other possibilities include (1) fixation of adsorbed K^+ by some vermiculite layers to give mica-like layers, and (2) the formation of hydroxide interlayers to produce chlorite-like layers.

Palygorskite and sepiolite Palygorskite and sepiolite are considered phyllosilicates, but are distinct structurally from the typical 1:1 and 2:1 layer structures. Both minerals have continuous tetrahedral sheets, but adjacent bands of tetrahedra within one tetrahedral sheet point in opposite directions rather than in one direction as in the 1:1 and 2:1 structures. The result is a structure that can be described as ribbons of 2:1 layers joined at their edges, as illustrated in Figure 6. Water molecules occur in the spaces between the ribbons. The 2:1 ribbons are wider in sepiolite than in palygorskite.

Palygorskite and sepiolite are often found in soils of arid and semiarid environments. Both minerals
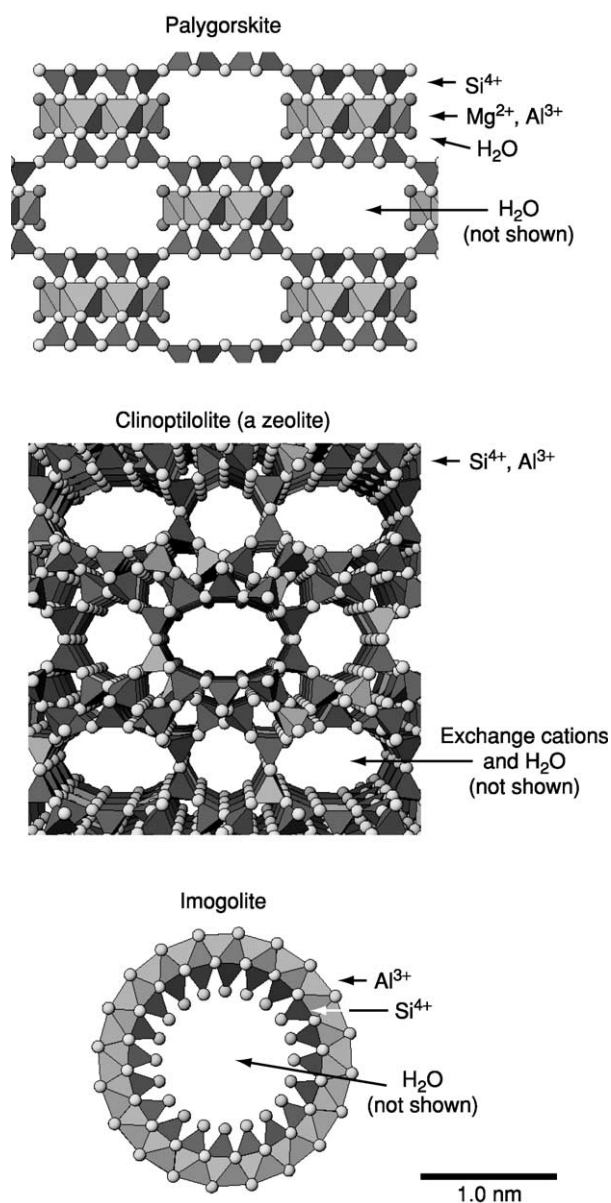

Figure 6 Structural models of representatives of three other aluminosilicate mineral groups that occur frequently in soils. All three are drawn to the same scale. (Adapted from Schulze DG (2002) An introduction to soil mineralogy. In: Dixon JB and Schulze DG (eds) *Soil Mineralogy with Environmental Applications*, pp. 1–35. Madison, WI: Soil Science Society of America, with permission.)

have a fibrous morphology in contrast to the platy morphology of most 1:1 and 2:1 minerals.

Other Minerals that Occur in Soil Clays

The phyllosilicate clay minerals described above are the most abundant and common in most soils, and they are the minerals that are usually considered to make up the 'clay minerals' group. Several additional minerals or mineral groups require mention as well. Some occur

only in particular soils, others occur in many soils, but usually only at low concentrations.

Zeolites

Zeolites are a large group of aluminosilicate minerals that consist structurally of SiO_4 tetrahedra arranged in ways that result in large amounts of pore space within the crystals (Figure 6). Aluminum substitutes for Si in the tetrahedral sites and, as a result, the $(Si,Al)O_4$ framework has a net negative charge. The charge is balanced by cations that reside in the channels and pores along with water molecules. Because the cations are exchangeable, zeolites have cation exchange properties similar to the phyllosilicates, but, because the tetrahedral framework of the zeolites is rigid and the size of the pores is fixed, small cations can move into and out of the pores freely, while larger cations are excluded. Thus, zeolites are often referred to as 'molecular sieves' because of their very selective cation exchange properties. Zeolites are relatively rare in soils because they weather easily in humid regions, but they occur in some soils in arid regions.

Allophane and Imogolite

The aluminosilicate minerals discussed above have three-dimensional crystal structures, with atoms packed together in a more or less regular manner over relatively long distances (10s of nanometers). They exhibit long-range order. Two other aluminosilicates, allophane and imogolite, exhibit short-range (or local) order. Structures with short-range order exhibit order over several nanometers, but on a larger scale the structure is disordered.

Allophane is a material consisting chemically of variable amounts of O^{2-}, OH^-, Al^{3+}, and Si^{4+}, and characterized by short-range order and a predominance of Si-O-Al bonds. It consists of small (3.5–5.0 nm) spheres, the structure of which has not been determined. The spheres clump together to form irregular aggregates. Imogolite consists of tubes several micrometers long with an outer diameter of 2.3–2.7 nm and an inner diameter of approx. 1.0 nm. The tubes consist of a single dioctahedral sheet with the inner surface OH replaced by SiO_3OH groups (Figure 6). Several individual tubes are arranged in bundles 10–30 nm across to give thread-like particles several micrometers long.

Allophane and imogolite usually occur as weathering products of volcanic ash and are important minerals in the Andisol soil order. Imogolite has also been identified in the Bs horizons of Spodosols. Allophane and imogolite can specifically adsorb many inorganic and organic compounds. Andisols, for example, usually fix large amounts of phosphate, making it unavailable to plants, and the large

amounts of organic matter common in Andisols may be due, in part, to adsorption of organic molecules by allophane and imogolite. Soils containing large amounts of allophane and imogolite usually have unique physical properties such as a low bulk density, high water-holding capacity, high liquid and plasticity limits, and a thixotropic consistence.

Aluminum Hydroxide Minerals

Gibbsite, which has already been mentioned as simply a stack of octahedral sheets containing Al^{3+} in the octahedral sites (Figure 5), occurs in situations where weathering and leaching have been intense or long. Gibbsite often occurs in Ultisols and Oxisols and can be important in the fixation of phosphate fertilizers.

Iron Oxide Minerals

Fe is almost as abundant as Al in the Earth's crust, and one or more strongly colored iron oxide minerals are ubiquitous accessory minerals in almost all soil clays. Goethite (FeOOH) is the most common soil iron oxide mineral and accounts for the yellowish-brown colors of many soils. Hematite (Fe_2O_3) is common also and accounts for the red colors of many soils. Iron oxide surfaces are highly reactive and can sorb and fix phosphate, many transition metals, and organic compounds. Redox reactions are an important aspect of soil iron oxide mineralogy.

Manganese Oxide Minerals

Manganese is about 50 times less abundant in the Earth's crust than Fe, so minerals containing large amounts of Mn are proportionally less abundant. Nevertheless, some Mn oxide minerals occur in almost all soils, with birnessite $((Na,Ca)(Mn^{3+}, Mn^{4+})_7O_{14} \cdot 2.8H_2O)$ being one of the more common ones. The Mn^{4+} and Mn^{3+} in manganese oxide minerals is reduced to soluble Mn^{2+} under relatively mild reducing conditions, making Mn oxide minerals important in many soil redox reactions.

Titanium Oxide Minerals

Ti is slightly more abundant than Mn in the Earth's crust, and two Ti minerals, anatase and rutile (both TiO_2) occur widely in soil clays. The Ti-oxide minerals, however, are relatively inert chemically and have a negligible impact on most soil properties.

Carbonates, Sulfates, and Soluble Salts

In semiarid to arid climates, calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), and an array of evaporite minerals (minerals with solubilites greater than or equal to gypsum) often occur coassociated with the

aluminosilicate and oxide minerals discussed above. The impact of these minerals varies greatly, depending on the amount and type of mineral present.

List of Technical Nomenclature

Minerals   gibbsite, kaolinite, halloysite, pyrophyllite, mica, illite, glauconite, muscovite, smectite, montmorillonite, beidellite, nontronite, vermiculite, chlorite, hydroxy-interlayered smectite and vermiculite, interstratified clay minerals, allophane, imogolite, palygorskite, sepiolite, zeolites, iron oxide minerals, goethite, hematite, aluminum hydroxide minerals, manganese oxide minerals, birnessite, titanium oxide minerals, anatase, rutile, calcite, gypsum, evaporite minerals, biotite, phlogopite

See also: **Kinetic Models**; **Thermodynamics of Soil Water**

Further Reading

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CLIMATE CHANGE IMPACTS

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Introduction

Soils form through the interaction of a number of influences, including climate, relief and/or landscape, parent material, organisms (including fauna, flora, and humans) and time. The nature of this interaction varies in different parts of the world, resulting in several thousand types of soil worldwide. It takes thousands of years for a soil to form, and most soils are still evolving as a result of changes in some of these soil-forming factors, particularly climate and vegetation, over the past few millennia. Changes in any of the soil-forming factors, such as climate, will impact directly and indirectly on current soils, with important implications for their development and use.

Unraveling the likely extent and impact of climate change on soils is a complex process and one in which progress has been slow. It is made all the more complicated by the fact that not only can soils be strongly affected directly and indirectly by climate change, but soils themselves can act as both source and sink for greenhouse gases and thus have the potential for either positive or negative feedback to climate change. The lack of specificity of the global circulation models (GCMs) at present, combined with the complexity of the interaction of the various soil-forming processes and the fact that there is still a limited knowledge of many of them, particularly biological ones, makes it difficult to quantify the changes that will ensue. On the basis of current knowledge, it is only possible to describe the likely impacts of climate change on soils in a qualitative or semiquantitative way and highlight the key changes, their direction where there is adequate climate change information, and the implications of them.

Climate Change Predictions

Estimates of global climate change are continually being revised as models are being improved and new data collected. The current main sources of information available on the likely extent of climate change are the Third Assessment Reports of the Intergovernmental Panel on Climate Change (IPCC).

These reports conclude that the globally averaged surface temperature will increase by between 1.4 and 5.8°C over the period 1990 to 2100 and that nearly all land areas will warm by more than this global average, particularly in northern high latitudes in the cold season (**Table 1**). Increased summer continental drying and associated risk of drought is likely over most midlatitude interiors, the main areas for which the models are consistent with one another.