

CLAY MINERALS

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INTRODUCTION

Clay minerals refers to a group of hydrous aluminosilicates that predominate the clay-sized ($<2 \mu\text{m}$) fraction of soils. These minerals are similar in chemical and structural composition to the primary minerals that originate from the Earth's crust; however, transformations in the geometric arrangement of atoms and ions within their structures occur due to weathering. Primary minerals form at elevated temperatures and pressures, and are usually derived from igneous or metamorphic rocks. Inside the Earth these minerals are relatively stable, but transformations may occur once exposed to the ambient conditions of the Earth's surface. Although some of the most resistant primary minerals (quartz, micas, and some feldspars) may persist in soils, other less resistant minerals (pyroxenes, amphiboles, and a host of accessory minerals) are prone to breakdown and weathering, thus forming secondary minerals. The resultant secondary minerals are the culmination of either alteration of the primary mineral structure (incongruent reaction) or neof ormation through precipitation or recrystallization of dissolved constituents into a more stable structure (congruent reaction). These secondary minerals are often referred to as phyllosilicates because, as the name implies (Greek: *phylon*, leaf), they exhibit a platy or flaky habit, while one of their fundamental structural units is an extended sheet of SiO_4 tetrahedra.

STRUCTURE OF CLAY MINERALS

The properties that determine the composition of a mineral are derived from its chemical foundation, geometric arrangement of atoms and ions, and the electrical forces that bind them together (1). Given that there are eight elements that constitute over 99% of the Earth's crust (Table 1), the inclusion of these in the elemental makeup

of soil minerals is understandable. Notwithstanding, the prevalence of silicon and oxygen in the phyllosilicate structure is logical. The SiO_4 tetrahedron is the foundation of all silicate structures. It consists of four O^{2-} ions at the apices of a regular tetrahedron coordinated to one Si^{4+} at the center (Fig. 1). An interlocking array of these tetrahedral connected at three corners in the same plane by shared oxygen anions forms a hexagonal network called the tetrahedral sheet (2). When external ions bond to the tetrahedral sheet they are coordinated to one hydroxyl and two oxygen anion groups. An aluminum, magnesium, or iron ion typically serves as the coordinating cation and is surrounded by six oxygen atoms or hydroxyl groups resulting in an eight-sided building block termed an octahedron (Fig. 1). The horizontal linkage of multiple octahedra comprises the octahedral sheet. The minerals brucite $\text{Mg}(\text{OH})_2$ and gibbsite $\text{Al}(\text{OH})_3$ are similar to the octahedral sheets found in many clay minerals; however, phyllosilicates may contain coordinating anions other than hydroxyls. Cations in the octahedral layer may exist in a divalent or trivalent state. When the cations are divalent (Mg , Fe^{2+}), the layer exhibits a geometry similar to brucite, such that electrical neutrality is maintained. In this arrangement the ratio of divalent cations to oxygens is 1:2 and all three possible cation sites in the octahedron are occupied. This configuration and the respective sheet formed from an array of such as octahedral are referred to as trioctahedral. When the cations are trivalent (Al , Fe^{3+}), the charge balance is maintained by leaving one of every three octahedral cation sites empty. Under this configuration, the ratio of trivalent cations to oxygens is 1:3 and the layer exhibits a gibbsite-like dioctahedral arrangement. A combination of tetrahedral and di- or trioctahedral sheets bound by shared oxygen atoms forms aluminosilicate layers that comprise the basic structural units of phyllosilicates (Fig. 2). Sheet arrangement within the aluminosilicate layers varies between clay mineral types resulting in variable physical and chemical properties that differentiate the clay mineral classes.

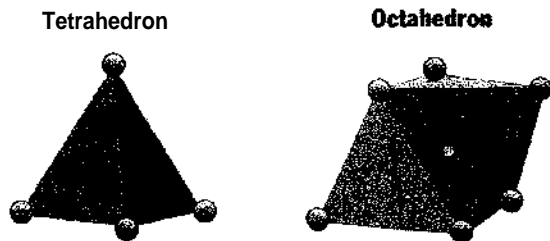
Table 1 Common elements in Earth's crust and ionic radius

Element	Crustal average (gkg~')	Ionic radius (nm)	Volume (%)
O^{2-}	466.0	0.140	89.84
Si^{4+}	277.2	0.039	2.37
Al^{3+}	81.3	0.051	1.24
Fe^{2+}	50.0	0.074	0.79
Mg^{2+}	20.9	0.066	0.60
Ca^{2+}	36.3	0.099	1.39
Na^{2+}	28.3	0.097	1.84
K^{+}	25.9	0.133	1.84

(AdapCed from Ref. 1.)

ISOMORPHOUS SUBSTITUTION

The structural arrangement of the elements described above forms the template for the silicate clay minerals. However, the composition varies frequently due to substitution of ions within the mineral structure. Weathering allows for the substitution of Si^{4+} , Al^{3+} , and Mg^{2+} with cations with comparable ionic radii in their respective tetrahedral and octahedral sheets (Table 1). Consequently, Si^{4+} may be replaced by Al^{3+} in the center of the tetrahedron without changing the basic structure of the crystal. Moreover, cations such as $Fe^{3+/2+}$ and Zn^{2+} (ionic radius = 0.074 nm) may replace Al^{3+} and Mg^{2+} in the



- ⊙ Oxygen
- Silicon
- ⊙ Aluminum or Magnesium

Fig. 1 The basic structural components of clay minerals; a single four-sided tetrahedron, and a single eight-sided octahedron. (From Ref. 6.)

1:1 Clay Mineral (kaolinite)



2:1 Clay Mineral (pyrophyllite)

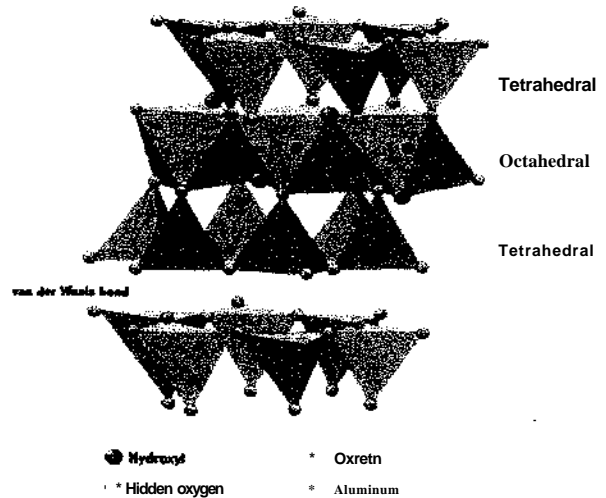


Fig. 2 Diagrammatic sketch of a 1:1 clay mineral consisting of one tetrahedral sheet bonded to an octahedral sheet (kaolinite); and a 2:1 clay mineral consisting of an octahedral sheet bound between two tetrahedral sheets (pyrophyllite). (From Ref. 6.)

octahedra. The process of replacing one structural cation for another of similar size is referred to as isomorphous substitution. This replacement represents the primary source of both negative and positive charges in clay minerals. For example, the substitution of one Al^{3+} for a Si^{4+} in the tetrahedron results in a gain of one negative charge.

Alternatively, replacement of a lower valence cation by one with a higher valence (Fe^{2+} by Fe^{3+}) results in a gain of one positive charge. Some clay minerals exhibit substitutions that result in both positive and negative charges. A balance of electron loss and gain within the structure determines the net charge of the mineral. In most soils, however, substitutions that result in net negative charge exceed those producing a positive charge.

Table 2 Properties of clay mineral groups

Group	Layer type	Net negative charge (cmolk ⁻¹)	Surface area (m ²)	Basal spacing (nm)
Kaolinite	1:1	2-5	10-30	0.7
Fine-grained mica	2:1	15-40	70-100	1.0
Smectite	2:1	80-120	600-800	1.0-2.0
Vermiculite	2:1	100-180	550-700	1.0-1.5
Chlorite	2:1:1	15-40	70-100	1.4

(Adapted from Ref. 5.)

CLAY MINERAL CLASSIFICATION

Clay minerals are generally classified into three layer types based upon the number and arrangement of tetrahedral and octahedral sheets in their basic structure. These are further separated into five groups that differ with respect to their net charge (Table 2).

1:1 Clay Minerals

The 1:1 layer minerals contain one tetrahedral and one octahedral sheet in their basic structural unit (Fig. 2.) This two-sheet mineral type is represented by the kaolin group, with the general formula $Al_2Si_2O_5(OH)_4$. Kaolinite, the most common mineral in this group, is dioctahedral, exhibiting Al^{3+} octahedral and Si^{4+} tetrahedral coordination. The sheets are held together by van der Waals bonds between the basal oxygens of the tetrahedral sheet and the hydroxyls of the octahedral sheet. Layers are held together tightly by hydrogen bonding, which restricts expansion and limits the reactive area to external surfaces. Isomorphic substitution for Si^{4+} and Al^{3+} in this mineral is negligible. As such, soils dominated by 1:1 minerals exhibit a low capacity for adsorbing cations and have low fertility. The serpentine group, with the general formula $Mg_3Si_2O_5(OH)_4$, represents the trioctahedral version of the 1:1 layer minerals.

2:1 Clay Minerals

The joining of two tetrahedral sheets (one from each side) to one octahedral sheet produces a three-sheet mineral type, which is called 2:1 and is represented by the mica, smectite, and vermiculite groups. Talc [$Mg_3Si_4O_{10}(OH)_2$] and pyrophyllite [$Al_2Si_4O_{10}(OH)_2$] are typical representatives of electrically neutral 2:1 type minerals in which adjacent layers are joined to each other by van der Waals

bonds (Fig. 2). Although these two minerals are found infrequently in soils (2), their structure serves as a model for discussing transitions leading to the formation of other more common 2:1 clay minerals.

The true micas have a similar structure to that of talc and pyrophyllite, except that substitution of Al^{3+} for Si^{4+} in every fourth tetrahedral site results in an excess of one negative charge per formula unit. The negative charge is satisfied by monovalent cations, primarily K^+ , that reside on interlayer sites between the 2:1 layers. The interlayer cation forms a strong bond between adjoining tetrahedral sheets, which limits expansion of the mineral. The mica group is subdivided into tri- and dioctahedral minerals according to cation substitutions in the octahedral sheet and within the interlayer. The trioctahedral group of micas contains interlayer K^+ cations and is represented by phlogopite [$KMg_3(AlSi_3O_{10})(OH)_2$], with Mg^{2+} occupying the octahedral sites, and biotite, which contains both Fe^{2+} and Mg^{2+} in the octahedron. Muscovite [$KAl_2(AlSi_3O_{10})(OH)_2$] is a dioctahedral mica containing Al^{3+} in the octahedral sheet and K^+ in the interlayer, while paragonite exhibits a similar dioctahedral coordination with interlayer K^+ and Na^+ cations. In most soils, micas are generally inherited from the parent material and occur in a relatively unweathered state in the sand and silt fractions. Mica in the clay fraction usually exhibits poorer crystallinity, lower K^+ content, higher water content, and possible substitutions of Fe^{2+} and Fe^{3+} in the octahedral sheets and Ca^{2+} in the interlayer. Manganese, vanadium, lithium, chromium, titanium, and several other cations are also known to occur in varying amounts in these fine-grained or clay-sized micas (1). Illite and glauconite (dioctahedral iron illites) are commonly associated with the clay-sized micas; however, the structures of these minerals are poorly defined and likely to be representative of a mixture of weathered micas. Expandable 2:1 clay minerals exhibit a similar layer structure to that described for mica, but vary widely in layer charge and interlayer spacing due to the

presence of weakly bound cations, water, or polar organic molecules in the interlayer region.

Smectites generally refer to a group of expandable dioctahedral 2:1 minerals with a charge of 0.2-0.6 per formula unit. Montmorillonite, the most common member of this group, derives its charge from the octahedral substitution of Mg^{2+} for Al^{3+} . Beidellite and nontronite, which are less abundant in soils, derive much of their charge from tetrahedral substitutions. Nontronite is distinguished from beidellite by the presence of iron in the octahedral sheet. The 2:1 layers in smectites are held together by van der Waals bonds and weak cation-to-oxygen linkages. The presence of exchangeable cations located between water molecules in the interlayer allows for expansion of the crystal lattice as the mineral hydrates. When the mineral is saturated with water, the basal spacing between layers can approach 2nm, while under dry conditions, the basal spacing may be reduced to less than 1 nm (Fig. 3). This expansion and contraction trait found in smectites, often

referred to as shrink-swell potential, is problematic to engineers and farmers alike due to the propensity for crack formation and general instability of the soil surface.

The weathering of mica, via replacement of interlayer K^+ with hydrated exchangeable cations, results in the formation of vermiculite. In soils, vermiculite exists as an Al^{3+} dominated dioctahedral and, to a lesser extent, Mg^{2+} dominated trioctahedral mineral. A charge of 0.6-0.9 per formula unit is derived in these minerals by tetrahedral substitution of Al^{3+} for Si^{4+} . Consequently, vermiculites exhibit a high cation exchange capacity, particularly for weakly hydrated cations such as K^+ , NH_4^+ , and Cs^+ (3). Because of the tetrahedral charge origin, water molecules and exchangeable cations—primarily Mg^{2+} and Ca^{2+} —are strongly adsorbed within the interlayer space of vermiculites. Unlike in smectites, the strong bonding of the interlayer cations holds the 2:1 layers together in vermiculites, thus limiting expansion of the basal spacing to 15 nm (Fig. 3).

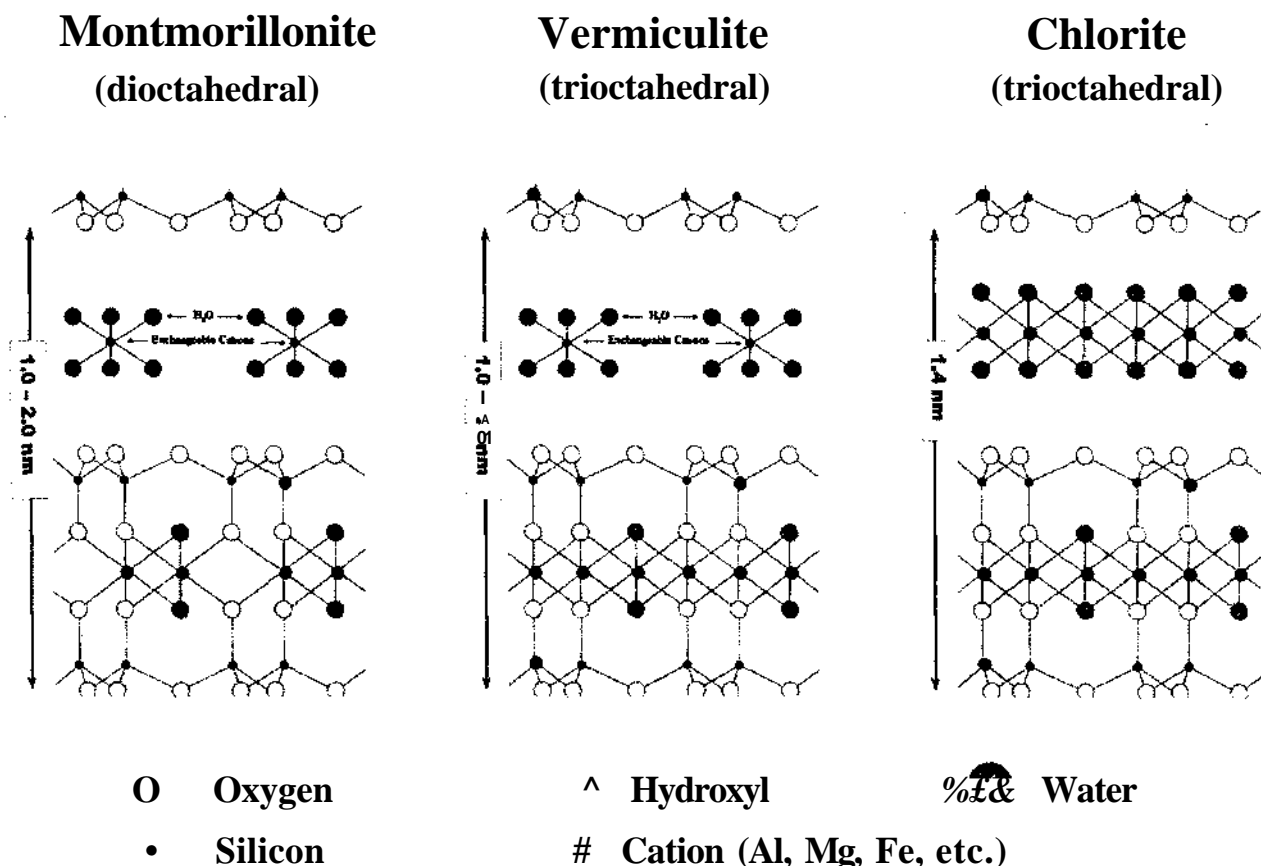


Fig. 3 Schematic representation of expandable dioctahedral montmorillonite and trioctahedral vermiculite, and nonexpandable trioctahedral chlorite.

2:1:1 Clay Minerals

Chlorites are a group of minerals that exhibits a basic 2:1 layer structure similar to that described for talc or pyrophyllite, but with an interlayer brucite- or gibbsite-like sheet, which forms a 2:1:1 structural arrangement. Isomorphic substitutions within the interlayer hydroxide sheet create a net positive charge that balances the negative charge arising from the 2:1 layers. A typical formula for the interlayer sheet is $(\text{MgFeAl})(\text{OH})_2$; however, a variety of cation species may exist in these brucite or gibbsite-like islands that contribute to a large number of mineral species within this group. There is no water adsorption within the interlayer space; thus, chlorites are considered nonexpansive minerals (Fig. 3).

Hydroxy-Al Interlayered Vermiculites and Smectites

Chlorites exist in soils as primary minerals that weather to form vermiculite and smectite. In contrast, hydroxy-Al interlayered vermiculites or smectites are considered to be exclusively secondary minerals forming as intermediate mineral weathering products, or from deposition of hydroxy-Al polymeric components within the interlayer space of expanding minerals (4). These hydroxy-Al polycations—with the general formula $\text{Al}_6(\text{OH})^+$ —balance a portion of the charge but they are not exchangeable. Because the level of hydroxy-Al occupancy within the interlayer space is variable, the CEC of the expandable 2:1 clays is reduced as a function of the quantity and valence of the hydroxy-Al polymer residing within the interlayer.

Mixed Minerals

In the soil environment, clay minerals rarely occur as homogeneous mixtures of single groups, types, or mineral phases. Instead, they comprise complex assemblages of primary minerals, and weathering intermediates of multiple structural and compositional combinations. The potential also exists for a discrete mineral grain to be composed of more than one clay type or contain components that are intermediate between two known minerals. These minerals are referred to as mixed-layer or interstratified minerals. Examples of such mixed-layer mineral sequences include mica-vermiculite, mica-smectite, chlorite-vermiculite, and kaolinite-smectite, among others. The sequence of differing layers making up the mixed mineral occurs at both regular and random intervals. Consequently, efforts to fully characterize clay

mineralogy within certain soils may be hindered considerably.

Other Clay Minerals

In addition to the phyllosilicates described, certain oxides, hydroxides, and hydroxy-oxides (sesquioxides) of Si, Al, Fe, as well as some poorly crystalline aluminosilicates, may also be found in small quantities in the soil clay fraction (7, 8). Typical representatives of Si-oxide minerals that are often found in the clay fraction are quartz—due to its high resistance to weathering—and opal—a poorly crystalline polymorph of quartz, which precipitates from Si-supersaturated solutions or is of volcanic or biogenic origin. Gibbsite ($\text{Al}(\text{OH})_3$) is the main Al-hydroxide representative in clay fractions of highly weathered soils, while goethite (FeOOH) is the most common clay fraction Fe-mineral. The poorly crystalline aluminosilicate clay minerals allophane and imogolite are typically found in clay fractions of soils derived from volcanic materials. Extensive discussions about these minerals and their properties are provided in other soil mineral sections of this encyclopedia.

Clay Mineral Identification and Quantification

The basic methods used for clay mineral identification and quantification involve X-ray diffraction (XRD) and thermal analyses (TA) (9). Electron microscopy (EM) is also employed for complementary mineral characterizations. In XRD analysis the basal spacing (or d-spacing) between equivalent crystal planes is measured from the specific angle at which they diffract X-rays of known wavelength according to Bragg's Law: $(d/n = A/2 \sin \theta)$ where d = basal spacing, n = order of diffraction, usually set to 1, A = X-ray wavelength, and θ = diffraction angle. Therefore, diffraction peaks at specific angles corresponding to fixed d-spacing characteristic of specific minerals are used for mineral identification, while diffraction peak intensities are utilized for quantitative estimations. The identification of minerals with overlapping d-spacing regions (smectite, vermiculite, chlorite) is based on specific diffraction peak shifts, following solvation with specific ions and/or heating treatments.

Thermal methods are based on characteristic temperature regions in which specific minerals lose their structural OH water (thermogravimetric analysis or TGA) and the enthalpy associated with the dehydroxylation reaction (differential scanning calorimetry or DSC). Mineral quantities are estimated from comparisons of the OH- or

enthalpy fractions that have been measured and standard quantities of representative pure minerals.

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