KAOLIN-SERPENTINE GROUP

Minerals of this groups are 1:1 layer silicates. Their basic unit of structure consists of tetrahedral and octahedral sheets in which the anions at the exposed surface of the octahedral sheet are hydroxyls (see Figure 4). The general structural formula may be expressed by $Y_{2-3}Z_2O_5(OH)_4$, where Y are cations in the octahedral sheet such as Al^{3+} and Fe^{3+} for dioctahedral species and Mg^{2+}, Fe^{2+}, Mn^{2+}, and Ni^{2+} for trioctahedral species, and Z are cations in the tetrahedral sheet, largely Si and, to a lesser extent, Al and Fe^{3+}. A typical dioctahedral species of this group is kaolinite, with an ideal structural formula of $Al_2Si_2O_5(OH)_4$. Kaolinite is electrostatically neutral and has triclinic symmetry. Oxygen atoms and hydroxyl ions between the layers are paired with hydrogen bonding. Because of this weak bonding, random displacements between the layers are quite common and result in kaolinite minerals of lower crystallinity than that of the triclinic kaolinite. Dickite and nacrite are polytypic varieties of kaolinite. Both of them consist of a double 1:1 layer and have monoclinic symmetry, but they distinguish themselves by different stacking sequences of the two 1:1 silicate layers.

Halloysite also has a composition close to that of kaolinite and is characterized by its tubular nature in contrast to the platy nature of kaolinite particles. Although tubular forms are the most common, other morphological varieties are also known: prismatic, rolled, pseudospherical, and platy forms. The structure of halloysite is believed to be similar to that of kaolinite, but no precise structure has been revealed yet. Halloysite has a hydrated form with a composition of $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$. This hydrated form irreversibly changes to a dehydrated variety at relatively low temperatures (60° C) or upon being exposed to conditions of low relative humidity. The dehydrated form has a basal spacing about the thickness of a kaolinite layer (approximately 7.2 Å), and the hydrated form has a basal spacing of about 10.1 Å. The difference of 2.9 Å is approximately the thickness of a sheet of water one molecule thick. Consequently, the layers of halloysite in the hydrated form are separated by monomolecular water layers that are lost during dehydration.

In trioctahedral magnesium species, chrysotile, antigorite, and lizardite are commonly known; the formula of these three clay minerals is $Mg_3Si_2O_5(OH)_4$. Chrysotile crystals have a cylindrical roll morphology, while antigorite crystals exhibit an alternating wave structure. These morphological characteristics may be attributed to the degree of fit between the lateral dimensions of the tetrahedral and octahedral sheets. On the other hand, lizardite crystals are platy and often have a small amount of substitution of aluminum or ferric iron for both silicon and magnesium. This substitution appears to be the main reason for the platy nature of lizardite. Planar polytypes of the trioctahedral species are far more complicated than those of dioctahedral ones, owing to the fact that the trioctahedral silicate layer has a higher symmetry because all octahedral cationic sites are occupied. In addition, recent detailed structural investigations have shown that there are considerable numbers of hydrous-layer silicates whose structures are periodically perturbed by inversion or revision of SiO_4 tetrahedrons. Modulated structures therefore produce two characteristic

linkage configurations: strips and islands. Antigorite is an example of the strip configuration in the modulated 1:1 layer silicates. Greenalite, a species rich in ferrous iron, also has a modulated layer structure containing an island configuration.

Pyrophyllite-talc group

Minerals of this group have the simplest form of the 2:1 layer with a unit thickness of approximately 9.2 to 9.6 Å—i.e., the structure consists of an octahedral sheet sandwiched by two tetrahedral sheets (Figure 5B). Pyrophyllite and talc represent the dioctahedral and trioctahedral members, respectively, of the group. In the ideal case, the structural formula is expressed by $Al_2Si_4O_{10}(OH)_2$ for pyrophyllite and by $Mg_3Si_4O_{10}(OH)_2$ for talc. Therefore, the 2:1 layers of these minerals are electrostatically neutral and are held together with van der Waals bonding. One-layer triclinic and two-layer monoclinic forms are known for polytypes of pyrophyllite and talc. The ferric iron analogue of pyrophyllite is called ferripyrophyllite.

Mica mineral group

Mica minerals have a basic structural unit of the 2:1 layer type like pyrophyllite and talc, but some of the silicon atoms (ideally one-fourth) are always replaced by those of aluminum. This results in a charge deficiency that is balanced by potassium ions between the unit layers. The sheet thickness (basal spacing or dimension along the direction normal to the basal plane) is fixed at about 10 Å. Typical examples are muscovite, $KAl_2(Si_3Al)O_{10}(OH)_2$, for dioctahedral species, and phlogopite, $KMg_3(Si_3Al)O_{10}(OH)_2$, and biotite, $K(Mg, Fe)_3(Si_3Al)O_{10}(OH)_2$, for trioctahedral species. (Formulas rendered may vary slightly due to possible substitution within certain structural sites.) Various polytypes of the micas are known to occur. Among them, one-layer monoclinic (1M), two-layer monoclinic (2M, including 2M$_1$ and 2M$_2$), and three-layer trigonal (3T) polytypes are most common. The majority of clay-size micas are dioctahedral aluminous species; those similar to muscovite are called illite and generally occur in sediments. The illites are different from muscovite in that the amount of substitution of aluminum for silicon is less; sometimes only one-sixth of the silicon ions are replaced. This reduces a net unbalanced-charge deficiency from 1 to about 0.65 per unit chemical formula. As a result, the illites have a lower potassium content than the muscovites. To some extent, octahedral aluminum ions are replaced by magnesium (Mg^{2+}) and iron ions (Fe^{2+}, Fe^{3+}). In the illites, stacking disorders of the layers are common, but their polytypes are often unidentifiable.

Celadonite and glauconite are ferric iron-rich species of dioctahedral micas. The ideal composition of celadonite may be expressed by $K(Mg, Fe^{3+})(Si_{4-x}Alx)O_{10}(OH)_2$, where $x = 0$–0.2. Glauconite is a dioctahedral mica species with tetrahedral Al substitution greater than 0.2 and octahedral Fe^{3+} or R^{3+} (total trivalent cations) greater than 1.2. Unlike illite, a layer charge deficiency of celadonite and glauconite arises largely from the unbalanced charge due to ionic substitution in the octahedral sheets.

Vermiculite

The vermiculite unit structure consists of sheets of trioctahedral mica or talc separated by layers of water molecules; these layers occupy a space about two water molecules thick (approximately 4.8 Å). Substitutions of aluminum cations (Al^{3+}) for silicon cations (Si^{4+}) constitute the chief imbalance, but the net charge deficiency may be partially balanced by other substitutions within the mica layer; there is always a residual net charge deficiency commonly in the range from 0.6 to 0.8 per $O_{10}(OH)_2$. This charge deficiency is satisfied with interlayer cations that are closely associated with the water molecules between the mica layers. In the natural mineral, the balancing cation is magnesium (Mg^{2+}). The interlayer cation, however, is readily replaced by other inorganic and organic cations. A number of water molecules are related to the hydration state of cations located at the interlayer sites. Therefore, the basal spacing of vermiculite changes from about 10.5 to 15.7 Å, depending on relative humidity and the kind of interlayer cation. Heating vermiculite to temperatures (depending on its crystal size) as high as 500° C drives the water out from between the mica layers, but the mineral quickly rehydrates at room temperature to maintain its normal basal spacing of approximately 14 to 15 Å if potassium or ammonium ions are not present in the interlayer sites. It has been reported that some dioctahedral analogues of vermiculite occur in soils.

Smectite

The structural units of smectite can be derived from the structures of pyrophyllite and talc. Unlike pyrophyllite and talc, the 2:1 silicate layers of smectite have a slight negative charge owing to ionic substitutions in the octahedral and tetrahedral sheets. The net charge deficiency is normally smaller than that of vermiculite—from 0.2 to 0.6 per $O_{10}(OH)_2$—and is balanced by the interlayer cations as in vermiculite. This weak bond offers excellent cleavage between the layers. The distinguishing feature of the smectite structure is that water and other polar molecules (in the form of certain organic substances) can, by entering between the unit layers, cause the structure to expand in the direction normal to the basal plane. Thus this dimension may vary from about 9.6 Å, when there are no polar molecules between the unit layers, to nearly complete separation of the individual layers.

The structural formula of smectites of the dioctahedral aluminous species may be represented by $(Al_{2-y}Mg^{2+}/y)(Si_{4-x}Al_x)O_{10}(OH)_2M^+/_{x+y} \cdot nH_2O$, where M^+ is the interlayer exchangeable cation expressed as a monovalent cation and where x and y are the amounts of tetrahedral and octahedral substitutions, respectively ($0.2 \leq x + y \leq 0.6$). The smectites with $y > x$ are called montmorillonite and those with $x > y$ are known as beidellite. In the latter type of smectites, those in which ferric iron is a dominant cation in the octahedral sheet instead of aluminum and magnesium, are called nontronite. Although less frequent, chromium (Cr^{3+}) and vanadium (V^{3+}) also are found as dominant cations in the octahedral sheets of the beidellite structure, and chromium species are called volkonskoite. The ideal structural formula of trioctahedral ferromagnesian smectites, the series saponite through iron saponite, is given by $(Mg, Fe^{2+})_3(Si_4$

$_-xAl_x)O_{10}(OH)_2M^+/x \cdot nH_2O$. The tetrahedral substitution is responsible for the net charge deficiency in the smectite minerals of this series. Besides magnesium and ferrous iron, zinc, cobalt, and manganese are known to be dominant cations in the octahedral sheet. Zinc dominant species are called sauconite. There are other types of trioctahedral smectites in which the net charge deficiency arises largely from the imbalanced charge due to ionic substitution or a small number of cation vacancies in the octahedral sheets or both conditions. Ideally x is zero, but most often it is less than 0.15.

Chlorite

The structure of the chlorite minerals consists of alternate micalike layers and brucitelike hydroxide sheets about 14 Å thick. Structural formulas of most trioctahedral chlorites may be expressed by four end-member compositions:

$(Mg_5Al)(Si_3Al)O_{10}(OH)_8$	(clinochlore)
$(Fe_5^{2+} Al)(Si_3Al)O_{10}(OH)_8$	(chamosite)
$(Mn_5Al)(Si_3Al)O_{10}(OH)_8$	(pennantite)
$(Ni_5Al)(Si_3Al)O_{10}(OH)_8$	(nimite)

The unbalanced charge of the micalike layer is compensated by an excess charge of the hydroxide sheet that is caused by the substitution of trivalent cations (Al^{3+}, Fe^{3+}, etc.) for divalent cations (Mg^{2+}, Fe^{2+}, etc.). Chlorites with a muscovite-like silicate layer and an aluminum hydroxide sheet are called donbassite and have the ideal formula of $Al_{4.33}(Si_3Al)O_{10}(OH)_8$ as an end-member for the dioctahedral chlorite. In many cases, the octahedral aluminum ions are partially replaced by magnesium, as in magnesium-rich aluminum dioctahedral chlorites called sudoite. Cookeite is another type of dioctahedral chlorite, in which lithium substitutes for aluminum in the octahedral sheets. Chlorite structures are relatively thermally stable compared to kaolinite, vermiculite, and smectite minerals and are thus resistant to high temperatures. Because of this, after heat treatment at 500°–700° C, the presence of a characteristic X-ray diffraction peak at 14 Å is widely used to identify chlorite minerals.

Interstratified clay minerals

Many clay materials are mixtures of more than one clay mineral. One such mixture involves the interstratification of the layer clay minerals where the individual component layers of two or more kinds are stacked in various ways to make up a new structure different from those of its constituents. These interstratified structures result from the strong similarity that exists between the layers of the different clay

minerals, all of which are composed of tetrahedral and octahedral sheets of hexagonal arrays of atoms, and from the distinct difference in the heights (thicknesses) of clay mineral layers.

The most striking examples of interstratified structures are those having a regular *ABAB* . . . -type structure, where *A* and *B* represent two component layers. The following interstratifications of two components are found in these modes in addition to those given above: illite/smectite, glauconite/smectite, dioctahedral mica/chlorite, dioctahedral mica/vermiculite, and kaolinite/smectite.

Sepiolite and palygorskite

Sepiolite and palygorskite are papyrus-like or fibrous hydrated magnesium silicate minerals and are included in the phyllosilicate group because they contain a continuous two-dimensional tetrahedral sheet of composition Si_2O_5. They differ, however, from the other layer silicates because they lack continuous octahedral sheets. The structures of sepiolite and palygorskite are alike and can be regarded as consisting of narrow strips or ribbons of 2:1 layers that are linked stepwise at the corners. One ribbon is linked to the next by inversion of the direction of the apical oxygen atoms of SiO_4 tetrahedrons; in other words, an elongated rectangular box consisting of continuous 2:1 layers is attached to the nearest boxes at their elongated corner edges. Therefore, channels or tunnels due to the absence of the silicate layers occur on the elongated sides of the boxes. The elongation of the structural element is related to the fibrous morphology of the minerals and is parallel to the *a* axis. Since the octahedral sheet is discontinuous, some octahedral magnesium ions are exposed at the edges and hold bound water molecules (OH_2). In addition to the bound water, variable amounts of zeolitic (i.e., free) water (H_2O) are contained in the rectangular channels. The major difference between the structures of sepiolite and palygorskite is the width of the ribbons, which is greater in sepiolite than in palygorskite. Thus, sepiolite and palygorskite have the ideal compositions $Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4(H_2O)_8$ and $(Mg, AlO3)_5Si_8O_{20}(OH)_2(OH_2)_4(H_2O)_4$, respectively.

Imogolite and allophane

Imogolite is an aluminosilicate with an approximate composition of $SiO_2 \cdot Al_2O_3 \cdot 2.5H_2O$. This mineral was discovered in 1962 in a soil derived from glassy volcanic ash known as "imogo." Electron-optical observations indicate that imogolite has a unique morphological feature of smooth and curved threadlike tubes varying in diameter from 10 to 30 nanometres (3.9×10^{-7} to 1.2×10^{-6} inches) and extending several micrometres in length. The structure of imogolite is cylindrical and consists of a modified gibbsite sheet in which the hydroxyls of one side of a gibbsite octahedral sheet lose protons and bond to silicon atoms that are located at vacant octahedral cation sites of gibbsite. Thus, three oxygen atoms and one hydroxyl as the fourth anion around one silicon atom make up an isolated SiO_4 tetrahedron as in orthosilicates, and such tetrahedrons make a planar array on the side of a gibbsite sheet. Because silicon-oxygen bonds are shorter than aluminum-oxygen bonds, this effect causes that sheet to curve. As a result, the curved sheet ideally

forms a tubelike structure with inner and outer diameters of about 6.4 Å and 21.4 Å, respectively, and with all hydroxyls exposed at the surface. The number of modified gibbsite units therefore determines the diameter of the threadlike tubes.

Allophane can be regarded as a group of naturally occurring hydrous aluminosilicate minerals that are not totally amorphous but are short-range (partially) ordered. Allophane structures are characterized by the dominance of Si-O-Al bonds—i.e., the majority of aluminum atoms are tetrahedrally coordinated. Unlike imogolite, the morphology of allophane varies from fine, rounded particles through ring-shaped particles to irregular aggregates. There is a good indication that the ring-shaped particles may be hollow spherules or polyhedrons. Sizes of the small individual allophane particles are on the order of 30–50 Å in diameter. In spite of their indefinable structure, their chemical compositions surprisingly fall in a relatively narrow range, as the $SiO_2:Al_2O_3$ ratios are mostly between 1.0 and 2.0. In general, the $SiO_2:Al_2O_3$ ratio of allophane is higher than that of imogolite.