ONE

SILICATE STRUCTURES

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Technologists charged with using industrial minerals typically draw their expertise from disciplines other than mineralogy. They may have a strong practical understanding of chemical raw materials but often lack an appreciation of minerals beyond their obvious effects on product properties and cost. A mineral's name and chemical formula are admittedly seldom enlightening. A grasp of mineral crystal architecture can therefore provide at least a foundation for using industrial minerals as constituents in many products. Conjuring up images of mineral structures will perhaps unleash long-suppressed memories of space groups, unit cells, and planes of symmetry. These topics of Inorganic Chemistry 101 seem of little relevance when the job at hand is to improve the heat deflection temperature of polypropylene or to ensure the durability of a bridge coating. Picturing the structures of common industrial silicate minerals can, nevertheless, at least provide insight into their common features and subtle differences and how these are reflected in the properties and uses described in the following chapter.

In simplest terms, the silicate minerals can be considered inorganic polymers based on two basic "monomer" structures. These are the tetrahedron of Figure 1 and the octahedron of Figure 2. Many of the silicates can be pictured as the configurations made by joining of such tetrahedra and octahedra to themselves and to each other in three dimensions. These involve the sharing of corners, edges, and faces in numerous conformations. The possible geometric permutations are further modified by chemical substitutions within the structure, which usually depend on how well a metal ion will fit among close-packed oxygen ions. This is largely a matter of relative ionic radii. Given an O^{2-} ionic radius of 1.40 angstroms, the preferred (most stable) coordination of cations common in industrial silicate minerals has been calculated and expressed in terms of ionic radius ratio.

Figure 2. Tetrahedron

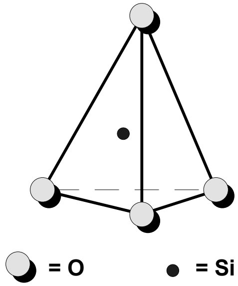
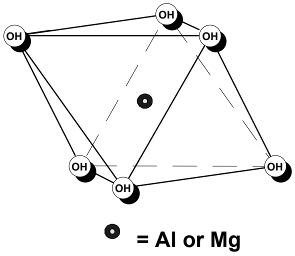


Figure 1. Octahedron



Tetrahedral, four-fold coordination is theoretically preferred when the radius ratio of metal cation to oxygen ion is in the range 0.225 to 0.414; for octahedral, six-fold coordination, this range is 0.414 to 0.732; for cubic, eight-fold coordination, it is 0.732 to 1.000. In nature, these ranges overlap to some extent, and the mineral lattice will distort to a limited degree to accommodate ions that are not a perfect fit. Aluminum, for example, is found in both tetrahedral and octahedral coordination. The following table lists the atomic radii of common metals found in silicate minerals, along with their ratio compared to O^{2-} and their coordination number.

Ion	**Radius, A**	**R_M:R_O**	**Coordination No.**
Si^{4+}	0.39	0.278	4
Al^{3+}	0.51	0.364	4
Al^{3+}	0.51	0.364	6
Fe^{3+}	0.64	0.475	6
Mg^{2+}	0.66	0.471	6
Li^{+}	0.68	0.486	6
Fe^{2+}	0.74	0.529	6
Na^{+}	0.97	0.693	8
Ca^{2+}	0.99	0.707	8
K^{+}	1.33	0.950	8-12

A mineral's unit cell formula or structural representation will usually reflect the theoretical composition or one with the most common substitutions. As the table above suggests, however, like-size cations can and do substitute for the theoretical components in nature. Chemical purity of industrial minerals is a concern when it adversely affects color or when the mineral is being used at least in part for its chemical constituents, as in ceramics.

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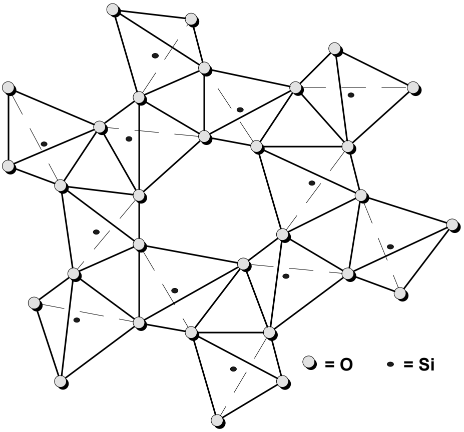
Mineralogical purity of industrial minerals is a factor distinct from chemical purity for some end uses. Commercially exploitable ore deposits are rarely monomineralic. A substantial component of the value-added cost of many industrial mineral products is the expense incurred by the producer in reducing mineral impurities by screening, air classification, washing, flotation, centrifuging, magnetic separation, heavy media separation, electrostatic separation, or various combinations of these. Conversely, some rocks such as nepheline syenite derive commercial value from their component mineral properties. The reasons why certain minerals coexist in ore deposits are beyond the intent of this chapter. An understanding of the structural relationships among these minerals, however, can help to explain this coexistence. Perhaps more interesting to those who use industrial minerals are the structural features common to minerals that are otherwise mutually exclusive in use.

Quartz

The fundamental structural unit of industrial silicate minerals is the silica tetrahedron. Quartz is just a densely packed arrangement of these tetrahedra, as depicted in Figure 3.

Figure 3. Quartz



Extended in three dimensions, this structure provides the characteristic hardness and inertness of quartz. The different forms of crystalline silica – most commonly quartz, cristobalite, and tridymite – differ mainly in the relative orientation of adjacent tetrahedra and the shape of voids created within a given plane.

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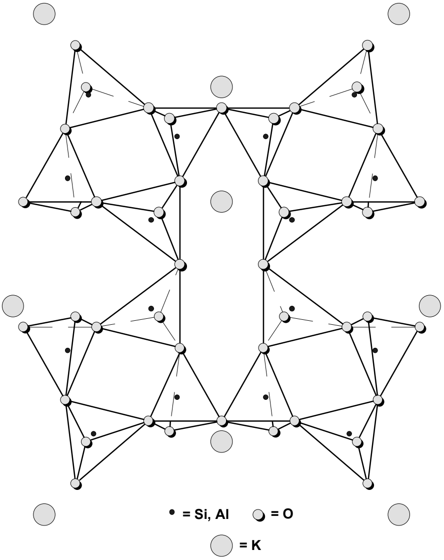
Feldspar

Similar dense-packed tetrahedra characterize the crystal framework of feldspar minerals, as depicted in Figure 4.

Figure 4. Feldspar



This figure shows a single layer viewed perpendicular to its plane. The framework is extended by rotating each successive layer 90°. Feldspars usually have one of every four Si^{4+} substituted with Al^{3+}. The resulting charge imbalance is compensated by sodium, and/or potassium ions. Some feldspars have half their silicon replaced by aluminum with calcium balancing the framework charge. Feldspars are nearly as hard as quartz and are exploited for their chemistry in glassmaking and ceramics, since the aluminum content improves chemical and physical stability while its alkali content provides fluxing action.

Wollastonite

Among the industrial minerals high terahedra density and consequent hardness are also found in chain silicates. Wollastonite is characterized by the repeating, twisted, three-tetrahedra unit depicted in Figure 5.

The chains formed by these silica tetrahedra are connected by calcium in octahedral coordination. Because of this chain structure wollastonite can occur as acicular crystals, in some cases of macroscopic dimensions. This acicular particle shape is important in certain uses as a functional mineral filler.

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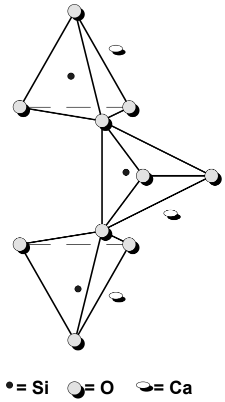
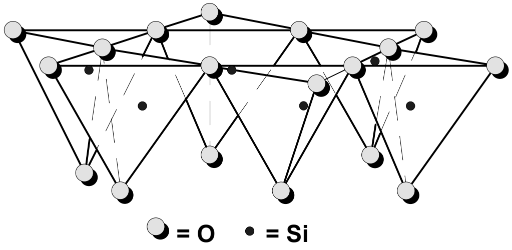
Figure 5. Wollastonite



Phyllosilicates

Silica tetrahedra also can join into rings, as depicted in Figure 6.

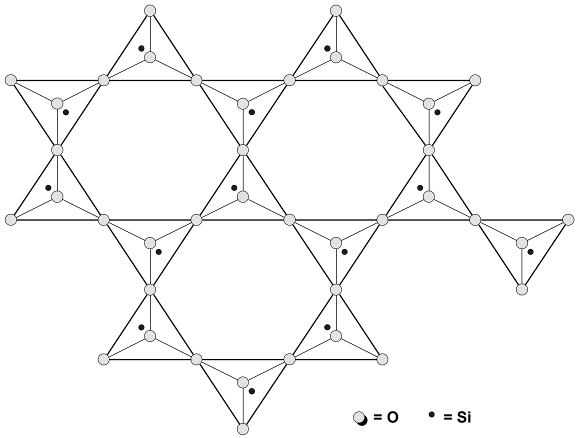
Figure 6. Silica Ring



Phyllosilicates are characterized in part by an indefinitely extended sheet of rings, with three of the tetrahedral oxygens shared and the fourth (apical) oxygen in each case pointing in the same direction, as illustrated in Figure 7.

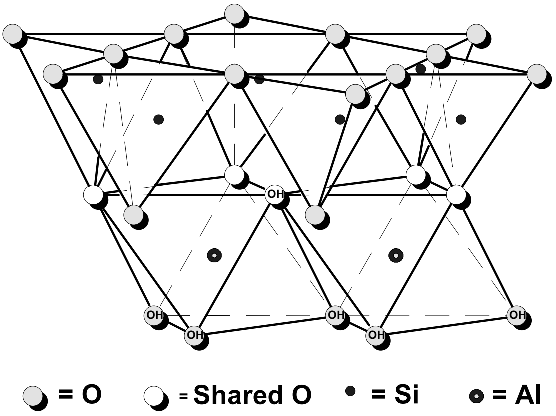
Another characteristic of most phyllosilicate minerals is the presence of an hydroxyl group central to the apical oxygens. This configuration is achieved through bonding of the silica sheet to a continuous sheet of octahedra, with each octahedron tilted onto one of its triangular sides. These octahedra, shown in Figure 2, most often contain either Mg^{2+} or Al^{3+}. When the metal cation is trivalent, as with aluminum, charge balancing requires only two of every three octahedral positions to be filled. This structure, that of the mineral gibbsite, is called dioctahedral. For divalent cations such as magnesium, all octahedral positions must be filled for charge balancing. This structure, that of the mineral brucite, is called trioctahedral. Phyllosilicates accordingly are often differentiated as dioctahedral or trioctahedral based on octahedral occupancy.

Figure 7. The Silica Sheet



Kaolinite – When a layer of silica rings is joined to a layer of alumina octahedra through shared oxygens, as shown in Figure 8, the mineral kaolinite is formed. Kaolinite is the sole or dominant constituent of what is known as kaolin clay or simply kaolin.

Figure 8. Kaolinite



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Kaolin may be considered the prototypical phyllosilicate in that its sheet structure results in platy or flake-shaped particles that occur as overlapping, separable layers. Because an individual kaolin particle has an oxygen surface on one side and an hydroxyl surface on the other, it is strongly hydrogen bonded to the laminae above and below it. These particles stack together in such a way that under magnification they look like sheaves of paper and are often called "books". It is difficult to delaminate kaolin books into individual platelets, although this is done commercially. Compared to the silica, feldspar, and chain silicate structures, kaolin, and phyllosilicates in general, are relatively soft and lower in specific gravity.

Pyrophyllite – If the kaolin structure is bound through shared oxygens to a layer of silica rings on its alumina side, the pyrophyllite structure of Figure 9 results. Because both faces of a pyrophyllite platelet are composed of silica oxygens, interlaminar bonding is by relatively weak van der Waals forces. Pure pyrophyllite is therefore soft with talc-like slipperiness, because its laminae will slide past each other or separate fairly easily.

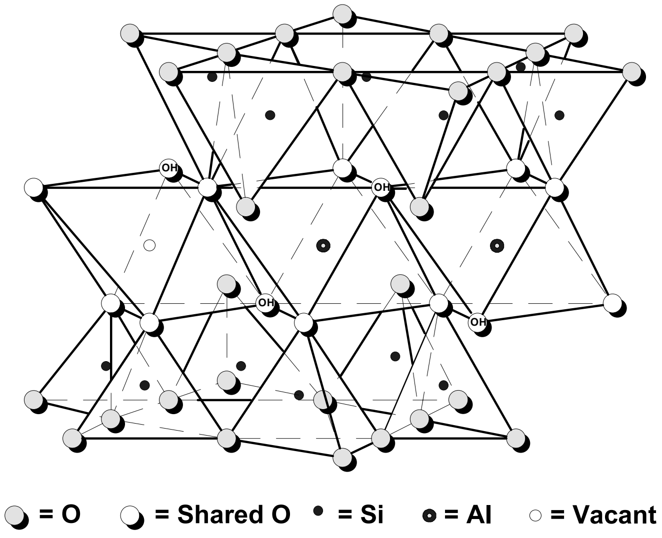
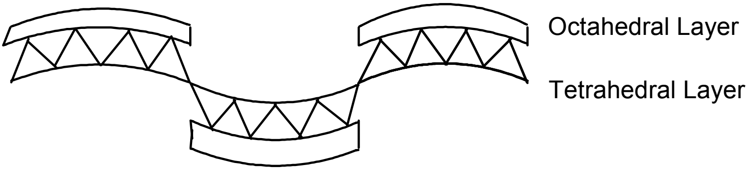


Figure 9. Pyrophyllite

Serpentines – If a magnesia octahedral layer rather than an alumina layer is joined to one sheet of silica rings, two minerals of the serpentine group result. These differ markedly from each other and from the analogous aluminum-based kaolinite. One is the mineral antigorite, whose sheet structure does not directly correspond to that of kaolinite. This is because brucite does not fit quite as well to the silica sheet as does gibbsite. This minor mismatch is compensated by a slight stretching of the apical silica oxygens so that they can form a common oxygen link with the magnesium-based octahedral layer. This stretching results in a bending of the entire structure. Antigorite is laminar because its tetrahedral silica layer is continuous, although it periodically rotates 180°, preventing continuity of the octahedral layer. The face of an antigorite platelet is therefore corrugated, as pictured schematically in Figure 10.

Figure 10. Antigorite Corrugation



When both the octahedral and tetrahedral sheets are continuous (no rotation of the silica layer), the brucite-silica mismatch causes a continuous bending into long tubes. This results in the asbestos mineral chrysotile. Chemically, kaolinite and chrysotile differ only in their octahedral cation. This relative subtlety, however, explains the difference between their respective microscopically laminar and macroscopically fibrous morphologies.

Talc – If a sheet of silica rings is attached to the magnesia side of chrysotile, the bending tendencies on either side of the octahedral layer negate each other. The mineral structure remains planar, and the laminar trioctahedral analogue of pyrophyllite results. This is the talc structure shown in Figure 11.

As with pyrophyllite, individual talc laminae are held together by weak van der Waals forces. Sliding and delamination are relatively easy, giving talc its characteristic soft, slippery feel.

Tremolitic talc is a related industrial mineral that, despite its classification as a talc product, is actually a natural mineral blend with tremolite as the major component and talc as a minor component. As such, tremolitic talc has properties and uses that depend primarily on its tremolite content. The hardness and prismatic shape of tremolite crystals are derived from a structure analagous to that of wollastonite. While wollastonite is comprised of single chains of silica tetrahedra, tremolite is comprised of double chains, as depicted in Figure 12.

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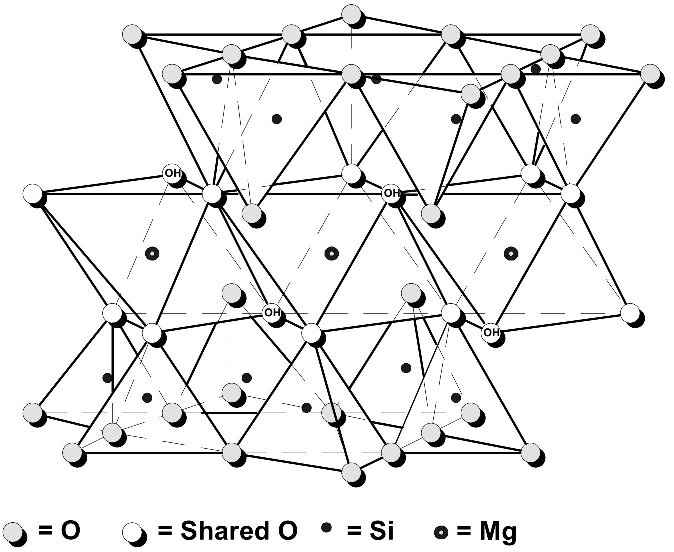
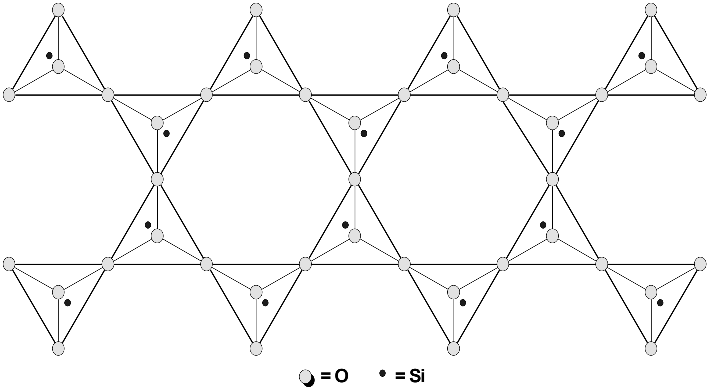
Figure 11. Talc



These double silica chains form the hexagonal rings common to phyllosilicates, but they extend in one direction instead of two. While the single wollastonite chains are joined by octahedrally coordinated calcium, the double chains of tremolite are joined by octahedrally coordinated magnesium between apical oxygens and by calcium on the opposite side. The schematic view of this structure shown in Figure 13 also suggests why hard prismatic tremolite can coexist with soft laminar talc in the same ore body.

Figure 12. Silica Double Chain



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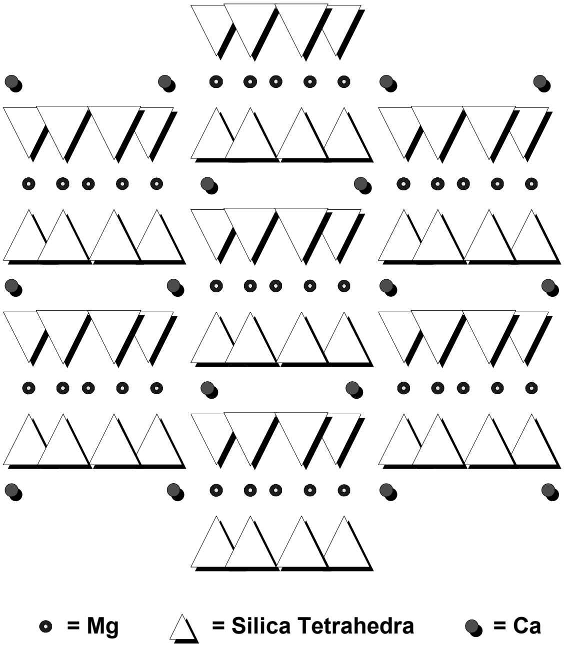
This is because tremolite can be viewed as offset strips of talc strongly linked back-to-back by calcium ions. A simple analogy would be to compare the tremolite structure to a brick wall, with the talc strips represented by the bricks and the calcium ions by the mortar. The structure is dense, rigid, and of high structural integrity. Talc, on the other hand, might be viewed as a stack of ceramic tiles. With little effort, one tile can be pushed across or removed from an adjacent tile in the stack.

Figure 13. Tremolite



Hormite clay – Hormite clays are trioctahedral chain silicate minerals having certain structural features in common with both tremolite and antigorite, although their properties are quite unlike either. As in the case of antigorite, silica sheets are continuous but periodically inverted. Since hormites have a silica layer on both sides of the octahedral layer, silica sheet inversions limit the width of the octahedral sheet, leaving it to grow in just one direction. The result is talc-like strips resembling tremolite. However, these strips are joined by shared tetrahedral oxygens at the lines of inversion. This creates channels that are filled with water, as depicted schematically in Figure 14. Removal of this water confers highly absorptive properties.

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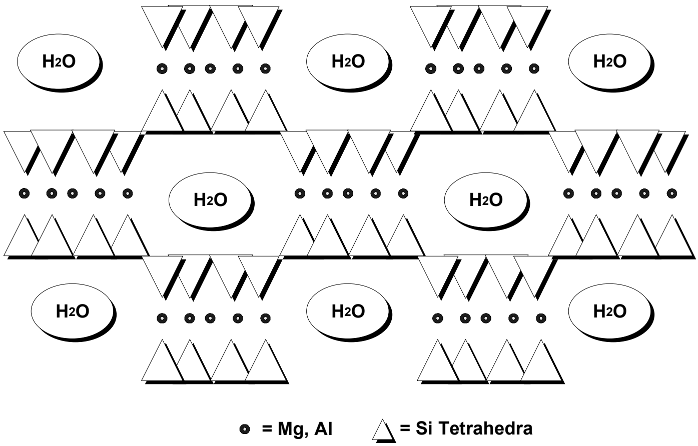
This structure accounts for the high surface area and acicular particle shape of the commercial hormites – palygorskite (attapulgite) and sepiolite. Sepiolite is the high-magnesia end member containing minor substitution of Al^{3+} and/or Fe^{3+} for octahedral Mg^{2+} and tetrahedral Si^{4+}. Palygorskite exhibits higher substitution, principally aluminum for magnesium. The charge imbalance arising from these substitutions is compensated by exchangeable alkaline and alkaline earth cations. Palygorskite and sepiolite differ in the number of octahedral sites per unit cell.

Figure 14. Hormite



In addition to their use as absorbents, hormite clays are used as rheological agents. When dispersed in water, their needle-like particles deagglomerate in proportion to the amount of energy applied and form a random colloidal lattice.

Chlorite – Chlorite is an accessory mineral in some talc ores. It is laminar and composed of alternating talc and brucite sheets. The chlorite structure depicted in Figure 15 includes the upper silica layer of an adjoining platelet. Unlike talc, chlorite accommodates appreciable substitution of both tetrahedral and octahedral cations. Up to half of the tetrahedral Si^{4+} and up to one third of the octahedral Mg^{2+} may be replaced by Al^{3+}. Fe^{2+} and Fe^{3+} both commonly substitute for part of the Mg^{2+} as well. The charge imbalance from tetrahedral substitution is generally balanced by octahedral substitution either in the talc structure or the brucite structure. Hydroxyl-bearing brucite sheets between the talc sheets allow for hydrogen bonding and a corresponding increase in delamination difficulty.

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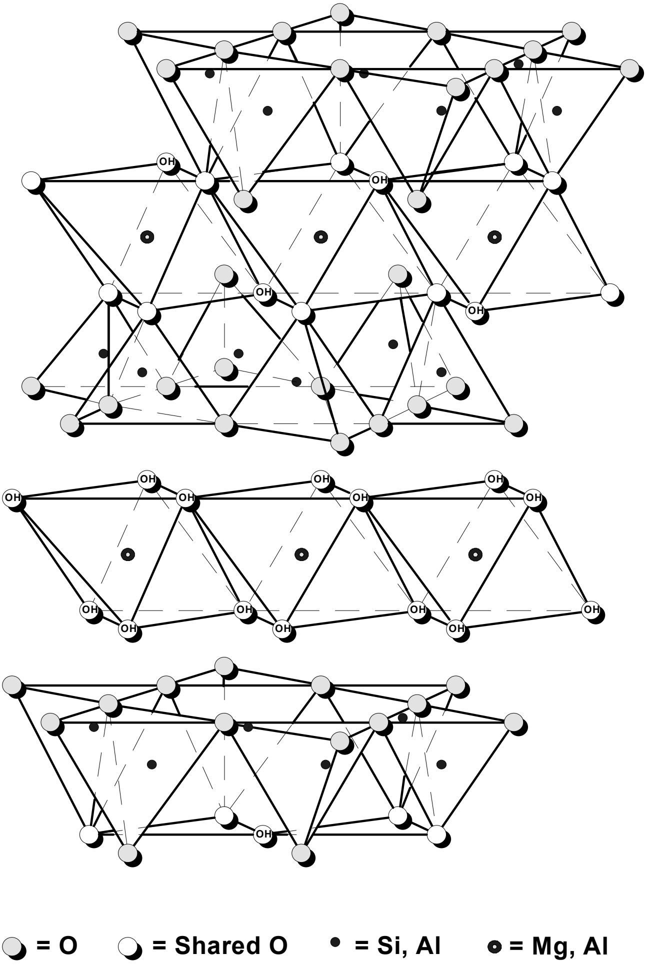
Figure 15. Chlorite



Vermiculite – The basic talc structure also typifies vermiculite, as illustrated in Figure 16. Vermiculite differs from talc primarily in its substitution of Al^{3+} for tetrahedral Si^{4+} and the presence of two oriented layers of water between individual laminae. Limited substitution of octahedral Mg^{2+} by Fe^{3+} and Al^{3+} also occurs. The charge imbalance arising primarily from tetrahedral substiutions is compensated by cations, usually Mg^{2+}, between interlaminar water layers. Because these cations are not structural components, they can be exchanged with other charge-balancing cations under the proper conditions.

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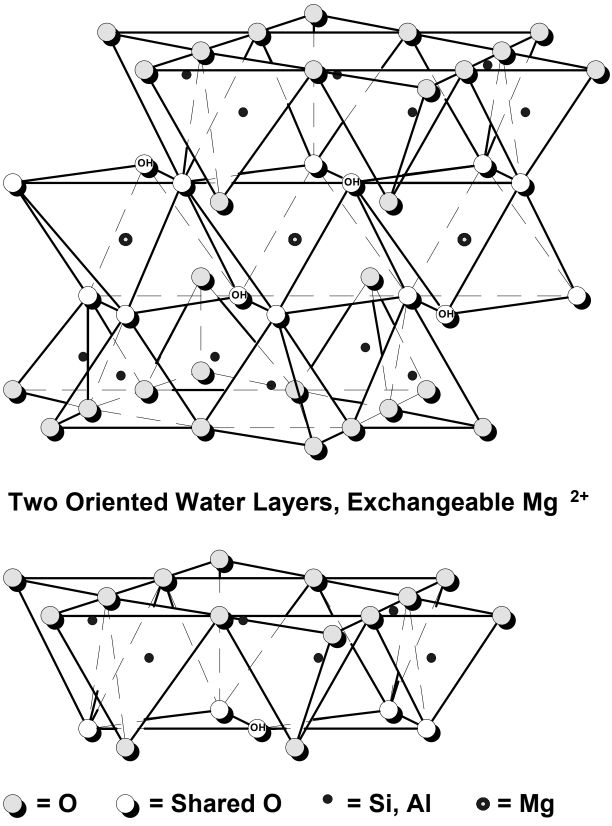
As a consequence, vermiculite has the greatest cation exchange capacity among all of the phyllosilicates, at 100 to 260 meq/100 g.

The water-Mg^{2+}-water structure has nearly the same height, at approximately 5 angstoms, as does a brucite sheet. The talc-like laminae of chlorite and vermiculite are therefore separated by about the same distance, although the interlaminar structure of vermiculite is less rigid and usually less regular. Vermiculite is nearly as soft as talc, but delamination is prevented by the attraction of opposing laminae to exchangeable cations plus the simultaneous hydrogen bonding of oriented water to laminae faces while forming hydration shells around these cations. When heated rapidly to high temperature, however, interlaminar water volatilizes and pushes the talc-like layers apart. The result is low-density, high-porosity, concertina-shaped particles.

Figure 16. Vermiculite



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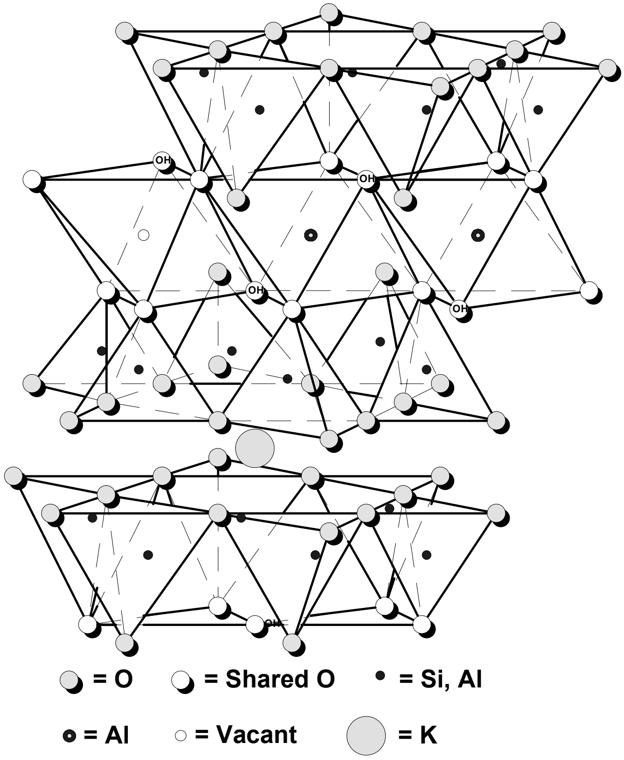
Mica – Most vermiculite has been altered from biotite, a trioctahedral mica containing substantial substitution of Fe^{2+} for octahedral Mg^{2+}. Biotite itself is not produced as a commercial industrial mineral. Phlogopite, a trioctahedral mica with less octahedral substitution, is available commercially, but dioctahedral muscovite is the most commonly used mica. All micas have either a talc or pyrophyllite structure and accordingly are characterized by platy or flake-shaped particles. For both phlogopite and muscovite there is some replacement of OH^- with F^-, and about one of four tetrahedral Si^{4+} is replaced by Al^{3+}. The resulting charge imbalance is compensated most often by K^+ located central to the opposing hexagonal openings in the silica sheets of adjacent platelets. There is usually little or no water between mica plates. Mica is well known for its ready delamination, even in the form of large sheets. This is due to the relatively weak bonding effect of the univalent counterion. The muscovite structure is depicted in Figure 17.

Figure 17. Muscovite



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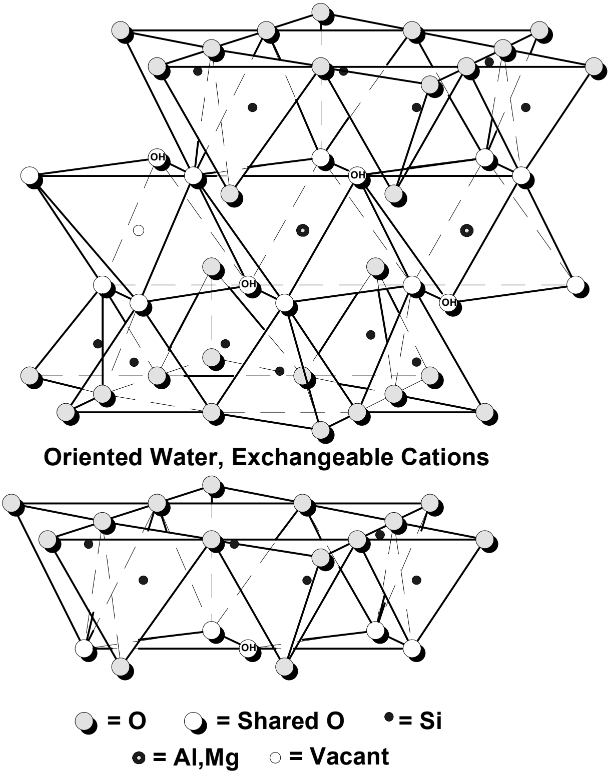
Smectite clay – Like mica, smectite clay (commonly called bentonite) has either a pyrophyllite or talc structure. Montmorillonite, a common high-aluminum smectite, can be characterized by the pyrophyllite crystal structure with a small amount of octahedral Al^{3+} replaced by Mg^{2+}. The resulting charge imbalance is compensated by exchangeable cations, usually Na^{+} or Ca^{2+}, between the laminae. In addition to these counterions, oriented water, similar to that in vermiculite, occupies the interlaminar space. When Ca^{2+} is the exchangeable cation, there are two water layers, as in vermiculite; when Na^{+} is the counterion, there is usually just one water layer. Figure 18 shows the montmorillonite structure.

Figure 17. Montmorillonite



Unlike vermiculite, the smectite crystal structure accommodates additional interlaminar water layers, due at least in part to its lower counterion density. This allows for hydraulic delamination. On immersion in water, sodium smectites incorporate enough additional water layers to overcome weak lamina-lamina attractions so that particles ultimately separate. Sodium smectites are therefore used as rheology control agents because of the colloidal structure their delaminated particles form in water. Calcium smectites also swell through interlaminar water absorption, but will not proceed to complete delamination due to the greater bonding effect of their divalent cations. Smectites can also absorb polar liquids other than water and will accomodate organic cations in exchange for their native counterions. This enables them to be used as absorbents and as rheological agents in nonaqueous systems.

Saponite, a high magnesium smectite, is similar in structure to talc but with limited substitution of tetrahedral Si^{4+} by Al^{3+}, while hectorite has the talc structure but with limited substitution of Li^{+} for octahedral Mg^{2+} and F^{-} for OH^{-}. As with montmorillonite, the resulting charge imbalance is compensated by Na^{+} or Ca^{2+} residing with oriented water in the interlaminar spaces. Saponite and hectorite have swelling, ion exchange, and absorbent properties similar to those of montmorillonite.

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