

Halloysite (10 \AA) occurs as cylindrical tubes of overlapping sheets of the kaolinite type (Fig. 3.21). The c axis at any point nearly coincides with the tube radius. The formation of tubes has been attributed to a misfit in the b direction of the silica and gibbsite sheets (Bates et al., 1950). The b dimension in kaolinite is 8.93 \AA ; in gibbsite it is only 8.62 \AA . This means that the (OH) spacing in gibbsite sheets is stretched in order to obtain a fit with the silica sheet. Evidently, in halloysite (10 \AA), the reduced interlayer bond, caused by the intervening layer of water molecules, enables the (OH) layer to revert to 8.62 \AA , resulting in a curvature with the hydroxyls on the inside and the bases of the silica tetrahedra on the outside. The outside diameters of the tubular particles range from about 0.05 to 0.20 \mu m , with a median value of 0.07 \mu m . The wall thickness is about 0.02 \mu m . The tubes range in length from a fraction of a micrometer to several micrometers. Drying of halloysite (10 \AA) may result in splitting or unrolling of the tubes. The specific surface area of kaolinite is about 10 to $20 \text{ m}^2/\text{g}$ of dry clay; that of halloysite (10 \AA) is 35 to $70 \text{ m}^2/\text{g}$.

3.17 SMECTITE MINERALS

Structure

The minerals of the *smectite* group have a prototype structure similar to that of pyrophyllite, consisting of an octahedral sheet sandwiched between two silica sheets, as shown schematically in Fig. 3.22 and diagrammatically in three dimensions in Fig. 3.23. All the tips of the tetrahedra point toward the center of the unit cell. The oxygens forming the tips of the tetrahedra are common to the octahedral sheet as well. The anions in the octahedral sheet that fall directly above

and below the hexagonal holes formed by the bases of the silica tetrahedra are hydroxyls.

The layers formed in this way are continuous in the a and b directions and stacked one above the other in the c direction. Bonding between successive layers is by van der Waals forces and by cations that balance charge deficiencies in the structure. These bonds are weak and easily separated by cleavage or adsorption of water or other polar liquids. The basal spacing in the c direction, $d_{(001)}$, is variable, ranging from about 9.6 \AA to complete separation.

The theoretical composition in the absence of isomorphous substitutions is $(\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20} \cdot n(\text{interlayer})\text{H}_2\text{O}$. The structural configuration and corresponding charge distribution are shown in Fig. 3.24. The structure shown is electrically neutral, and the atomic configuration is essentially the same as that in the nonclay mineral pyrophyllite.

Isomorphous Substitution in the Smectite Minerals

Smectite minerals differ from pyrophyllite in that there is extensive isomorphous substitution for silicon and aluminum by other cations. Aluminum in the octahedral sheet may be replaced by magnesium, iron, zinc, nickel, lithium, or other cations. Aluminum may replace up to 15 percent of the silicon ions in the tetrahedral sheet. Possibly some of the silicon positions can be occupied by phosphorous (Grim, 1968).

Substitutions for aluminum in the octahedral sheet may be one-for-one or three-for-two (aluminum occupies only two-thirds of the available octahedral sites) in any combination from a few to complete replacement. The resulting structure, however, is either almost exactly dioctahedral (*montmorillonite* subgroup) or trioctahedral (*saponite* subgroup). The charge deficiency resulting from these substitutions ranges from 0.5 to 1.2 per unit cell. Usually, it is close to 0.66 per unit cell. A charge deficiency of this amount would result from replacement of every sixth aluminum by a magnesium ion. Montmorillonite, the most common mineral of the group, has this composition. Charge deficiencies that result from isomorphous substitution are balanced by exchangeable cations located between the unit cell layers and on the surfaces of particles.

Some minerals of the smectite group and their compositions are listed in Table 3.5. An arrow indicates the source of the charge deficiency, which has been assumed to be 0.66 per unit cell in each case. Sodium is indicated as the balancing cation. The formulas should be considered indicative of the general character of the mineral, but not as absolute, because a variety of compositions can exist within the same basic crystal structure. Because of the large amount of unbalanced

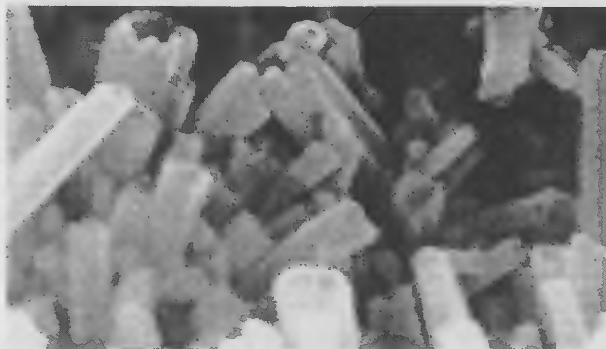


Figure 3.21 Electron photomicrograph of halloysite from Bedford, Indiana. Picture width is 2 \mu m (Tovey, 1971).

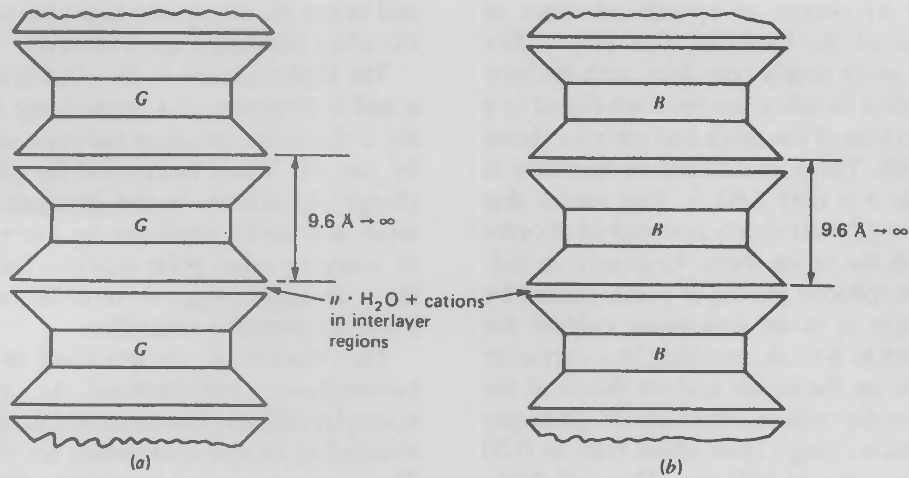


Figure 3.22 Schematic diagrams of the structures of the smectite minerals: (a) montmorillonite and (b) saponite.

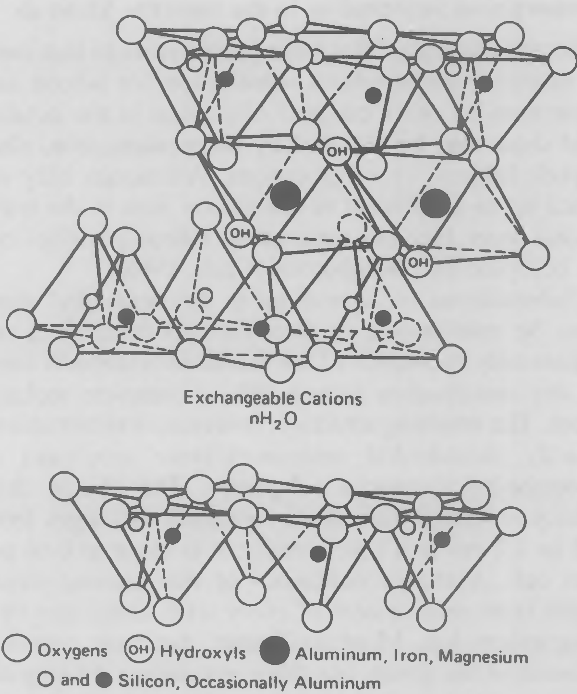


Figure 3.23 Diagrammatic sketch of the montmorillonite structure.

substitution in the smectite minerals, they have high cation exchange capacities, generally in the range of 80 to 150 meq/100 g.

Morphology and Surface Area

Montmorillonite may occur as equidimensional flakes that are so thin as to appear more like films, as shown

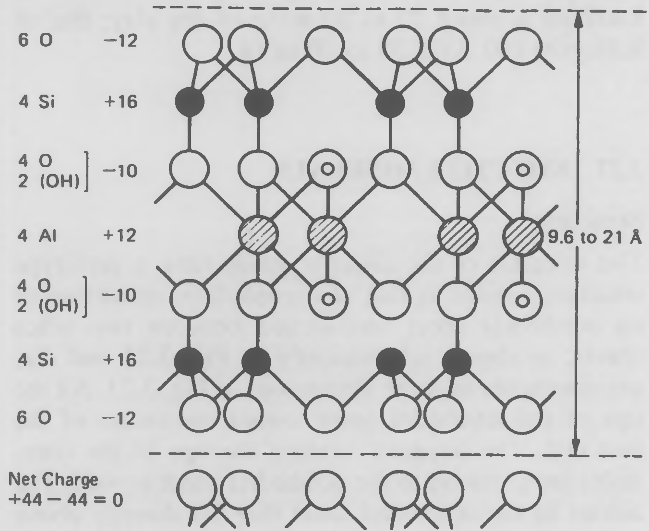


Figure 3.24 Charge distribution in pyrophyllite (type structure for montmorillonite).

in Fig. 3.25. Particles range in thickness from 1-nm unit layers upward to about 1/100 of the width. The long axis of the particle is usually less than 1 or 2 μm. When there is a large amount of substitution of iron and/or magnesium for aluminum, the particles may be lath or needle shaped because the larger Mg²⁺ and Fe³⁺ ions cause a directional strain in the structure.

The specific surface area of smectite can be very large. The primary surface area, that is, the surface area exclusive of interlayer zones, ranges from 50 to 120 m²/g. The secondary specific surface that is exposed

Table 3.5 Some Minerals of the Smectite Group

Mineral	Tetrahedral Sheet Substitutions	Octahedral Sheet Substitutions	Formula/Unit Cell ^a
Diocahedral, Smectites or Montmorillonites			
Montmorillonite	None	1Mg ²⁺ for every sixth Al ³⁺	(OH) ₄ Si ₈ (Al _{3.34} Mg _{0.66}) O ₂₀ ↓ Na _{0.66}
Beidellite	Al for Si	None	(OH) ₄ (Si _{6.34} Al _{1.66}) Al _{4.34} O ₂₀ ↓ Na _{0.66}
Nontronite	Al for Si	Fe ³⁺ for Al	(OH) ₄ (Si _{7.34} Al _{0.66}) Fe _{4.34} O ₂₀ ↓ Na _{0.66}
Triocahedral, Smectites, or Saponites			
Hectorite	None	Li for Mg	(OH) ₄ Si ₈ (Mg _{5.34} Li _{0.66}) O ₂₀ ↓ Na _{0.66}
Saponite	Al for Si	Fe ³⁺ for Mg	(OH) ₄ (Si _{7.34} Al _{0.66}) Mg ₆ O ₂₀ ↓ Na _{0.66}
Sauconite	Al for Si	Zn for Mg	(OH) ₄ (Si _{8-y} Al _y)(Zn _{6-x} Mg _x) O ₂₀ ↓ Na _{0.66}

^aTwo formula units are needed to give one unit cell.

After Ross and Hendricks (1945); Marshall (1964); and Warshaw and Roy (1961).

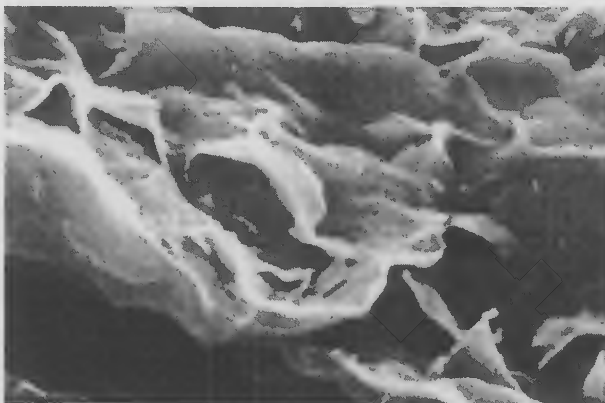


Figure 3.25 Electron photomicrograph of montmorillonite (bentonite) from Clay Spur, Wyoming. Picture width is 7.5 μm (Tovey, 1971).

by expanding the lattice so that polar molecules can penetrate between layers can be up to 840 m²/g.

Bentonite

A very highly plastic, swelling clay material known as *bentonite* is very widely used for a variety of purposes, ranging from drilling mud and slurry walls to clarification of beer and wine. The bentonite familiar to most geoenvironmental engineers is a highly colloidal, expansive alteration product of volcanic ash. It has a liquid limit of 500 percent or more. It is widely used as a backfill during the construction of slurry trench walls, as a soil admixture for construction of seepage barriers, as a grout material, as a sealant for piezometer installations, and for other special applications.

When present as a major constituent in soft shale or as a seam in rock formations, bentonite may be a cause of continuing slope stability problems. Slide problems at Portuguese Bend along the Pacific Ocean in southern California, in the Bearpaw shale in Saskatchewan, and in the Pierre shale in South Dakota are in large mea-