5.2 Phyllosilicates

5. PHYLLOSILICATES (leaf, sheet) three O are shared Si2O⁵ , Si/O=2.5,

- **- Low specific density,**
- **- One prominent cleavage,**
- **- Contains OH group,**
- **- Important part of soil clays.**

(a) single silica tetrahedron; (b) silica tetrahedron arranged in a hexagonal network; (c) three hexagons joined into double chain and extends in all directions in this plane forming a tetrahedron sheet. Silicon and apical oxygens are projected onto the plane of the base of tetrahedron.

(d) A single octahedral unit; (e) Several octahedral units joined into the octahedral sheet structure, (H) and (I) combination of tetrahedron and octahedron combinations.

The atomic radii of a number of ions common in clays.

BASIC STRUCTURE OF CLAY MINERALS

Sheets of Tetrahedron and Octahedron

Sketch of kaolinite, 1:1 dioctahedral phyllosilicate. (From Grim, 1968, Fig. 4.4).

Sketch of muscovite, a 2:1 dioctahedral phyllosilicate. (From Grim 1968, Fig. 4.16).

etrahedral sheet.

ate 1-7. Structural scheme of soil minerals based on octahedral and tetrahedral sheets.

Plate 1-8. Structural models of representatives of three other aluminosilicate mineral groups that occur frequently in soils. All three are drawn to the same scale.

Apical oxygens OH group

G. 18.29 Undistorted, hexagonal ring in an $Si₂O₅$ sheet owing the location of apical oxygens and (OH) group. In an ideal eet structure the size of the triangles (outlined by shading) is the me as the size of triangular faces of XO_6 octahedra.

Plate 1-9. Structural details of phyllosilicates as illustrated by the octahedral and tetrahedral sheets of muscovite. Figures were prepared from the single-crystal structural refinement data of Rothbauer (1971).

Plate 1–6. (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 edges of octahedra in the octahedral sheet. Arrows 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. (c) An alternate edge view that arises when the 2:1 structure above is rotated normal to the plane of the layer.

>Talc Layer

Diagrammatic sketch of the structure of chlorite (after Grim)

Diagrammatic sketch of the vermiculite structure, showing layers of water molecules (after Grim)

Average structure of tetramethylammonium-exchanged vermiculite.

Mixed-layer illite/smectite

Triangular diagrams describing 2:1 layer silicates as three-way solid solutions with layer charge and location of layer charge as variables.

Triangular diagrams describing 2:1 layer silicates as three-way solid solutions with layer charge and location of layer charge as variables.

Dioctahedral 2:1 layer silicates: some ideal end-member compositions for the $O_{20}(OH)_4$ formula unit, and the compositional **ranges for some micas, illites, illite-smectites and smectites.**

Kaolinite structure showing probable breaking plane and mechanism for edge charge by picking up H or OH from solution to give positive charge at low pH and negative charge at higher pH.

XRD treatments of the common silicate clay minerals.

Classification and generalized structural formulae of phyllosilicates

X represents a monovalent cation except in brittle micas where X is a divalent cation.

For kaolinites $n=0$; for the halloysite (7 Å and 10 Å) minerals *n* ranges from about 0.6 to about 4.

Following Bradley (1940); according to Gard and Follett (1968) the anions are $O_{20}(OH)_{3}(OH)_{2}$.

Nature of octahedral sheet and negative charge of phyllosilicates.

† Negative charge per formula unit is twice that given by Bailey et al. (1980a) because the formula unit used here applies to the contents of a volume defined by the *a b* unit cell base area that is one layer thick. For example for chlorites this volume is approximately $5 \times 9 \times 14$ Å³, for palygorskite $18 \times 5 \times 6.5$ Å³.

Atoms per structural unit for clintonite

 \dagger A obtained using scaling factor $f = 48/5.64717 = 8.499833$ for 24(O, OH, F, Cl). B obtained using scaling factor $f' = 44/5.20717 = 8.449887$ for 44 equivalents.

IDEAL}
TOTAL cations 44 **[** $\text{Si}_{2.74}$ Al_{5.26}] $\text{[Al}_{1.36}$ $\text{Fe}_{0.04}^{3+}$ $\text{Fe}_{0.18}^{2+}$ $\text{Mg}_{4.43}$] $\Sigma1.93$ **Ca is divalent 1.93 x 2 = 3.86 Total cations ideal 8 Si x 4 = 32 4 Al or 6 Mg = 12** $36 \text{ Fe}_{0.04} \text{ Fe}_{0.18} \text{ Fig. 34.4}$
 13 x 2 = 3.86
 al 8 Si x 4 = 32
 4 Al or 6 Mg = 12
 L}
 TOTAL cations 44
 rge deficit - 5.26 **Tetrahedral charge deficit - 5.26 Octahedral charge excess + 1.40 Overall charge deficit** - 3.86 $(2.74 \times 4) + (5.26 \times 3) + (1.36 \times 3) (0.04 \times 3) + (0.18 \times 2) + (4.43 \times 2) =$ **10.96 + 15.78 + 4.08 + 0.12 + 0.36 + 8.86 = 40.16 Actual total + 40.14; Charge Deficit - 3.86**

$C_i = 1000 \zeta/M$

- **Ci= potential interlamellar cation exchange capacity (meq/g)**
- ζ = cation density, equivalent /mol for half **or one unit cell.**

 M = Mean molecular mass (without exchangeable cations) calculated for typical composition, or the mineral with known chemical composition .

pH dependence of surface charge on allophane and montmorillonite, measured from the adsorption of cations and anions in 0.1 *M* **CsCl, respectively. (Data taken from Greenland, 1974; Clark & McBride, 1984a).**

¹
Without exchang
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Formula weight.
(See A. R. Merm

¹ Without exchangeable cations and calculated for typical composition

(Lagaly, 1994, corrected).

² Formula weight.

(See A. R. M ermut.1994. Layer charge characteristics of 2:1 silicate

caly minerals. CMS Workshop l ¹ Without exchangeable cations and calculated for typical con

² Eormula weight.

² Formula weight.

(See A. R. Mermut.1994. Layer charge characteristics of 2:1

caly minerals. CMS Workshop lectures vol. 6 CMS Societ

the elemental composition of source clay mineral

<u>KGa-1 **KGa-2** SWy-2 SAz-1 Syn-1</u> **Summary of the elemental composition of the source clay mineral**

(Mermut and Faz-Cano, 2001; Clays and Clay Minerals); SE standard error

 (Mermut and Faz-Cano, 2001; Clays and Clay Minerals)

Influence of exchangeable cations on permeability of different clays.

Edge-view sketches to show relative size and shape of clay particles; dimension not shown is equal to length.

HIGH RESOLUTION TEM MICROGRAPHS OF

Palygorskite

Diffraction patterns of ethylene glycol treated samples of montmorillonite, and randomly interstratified illite/montmorillonite. Percentages of montmorillonite layers: A, 100; B, 70; C, 50; and D, 40 (Reynolds and Hower, 1970).

rable 12–1. Mineral species and formulas for some common 1.1 phynosineale species. More common examples are highlighted in bold fonts.

† Ideal formulas are from Bailey (1980, 1988), Brown (1984), and Guggenheim and Eggleton (1988).

‡ Observed formulas are from the JCPDS files (1983), Bailey (1988), Compagnoni et al. (1985), and Guggenheim and Eggleton (1988).

§ represents empty octahedral sites.

Fig. 12-1. Kaolinite and halloysite morphology. (a) Kaolinite from a Cretaceous limestone of Central Texas with a spiral growth step (arrow). (b) Thin, hexagonal kaolinite plates from a Katy Alfisol of southeast Texas. (c) Commercial grade kaolinite from Central Georgia composed of large vermiforms and smaller, complex aggregates. (d) Kaolinite vermiform (right) forming using muscovite (left) as a template from a Florida Spodosol (White & Dixon, 1997). (e) Tubular halloysite from saprolite beneath an Ultisol of the Alabama Piedmont. (f) An unusually uniform tubular halloysite from Australia with thin walls and fibers; aspect ratio 1:1200.

Plate 12-1. Structural diagram for kaolinite generated from the data of Young and Hewat (1988) with the edge sites predicted by White and Zelazny (1988).

Plate 12-2. Effects of pH on the charge of the kaolinite edge that is affected by pH (modified from White and Zelazny, 1988). Color code for model is same as for Plates 12-1 and 12-3.

Plate 12-3. Calculated serpentine subgroup minerals structural schemes. (a) Lizardite - 1T from the data of Mellini and Viti (1994). (b) Amesite from the models of Hall and Bailey (1979) and Giese (1980). (c) Ball-and-stick model of the modulated trioctahedral 1:1 phyllosilicate, bementite, from the Heinrich et al. (1994) model. (d) Polyhedral model of bementite showing the wave pattern of the octahedral sheet.

Fig. 12-2. X-ray powder diffraction curves for two specimen kaolinites, the kaolinitic clay from the Katy soil (Fig. 12-1b), and halloysite showing the range in expression of the prismatic peaks in the 0.45to 0.35-nm region. The two truncated peaks on the soil kaolinite pattern represent quartz.

3. Morphology

Serpentines occur in three principal forms: platy, lath-like, and fibrous (Sudo et al., 1981). The edges are either irregular or bound by an apparent cleavage plane. Plates and laths are the principal morphologies for all members of the sub-

Fig. 12-3. Morphologies of serpentine subgroup minerals. (a) Modulated serpentine group mineral from the coarse clay fraction of a Honduran Inceptisol. (b) Higher magnification view of a portion of the modulated mineral grain outlined by the square in (a) showing the lattice fringes measuring 3.8 nm. (c) Serpentine lath containing Mg, Fe, and Cr from the Nipe Oxisol from Puerto Rico (White & Dixon, 1997). (d) Antigorite laths with characteristic rectangular terminations. (Source: Antigorio Valley, Italy; USNM # R-4648 provided by S. Guggenheim, Chicago, IL). (e) Serpentine occluded by Fe oxides from the Nipe soil clay. (f) Higher magnification view of the area of the particle in (e) outlined by the rectangle showing lattice fringes of serpentine.

Table 13-1. Theoretical and representative observed formulas for members of the pyrophyllite-talc group.

† References for observed formulas: (1) Koster (1982), (2) Coey et al. (1984), (3) De Waal (1970), and (4) derived from observed formulas in Brindley et al. (1979).

Discrepancy in 22 charge basis of observed formulas for pyrophyllite, talc, willemseite, and minnesotaite maybe due to rounding errors or presence of impurities. $\S M$ = metal cation of valency given.

If Minnesotaite is included here but may be placed more appropriately with modulated layer structures (Martin et al., 1991).

Location of H₂O in all kerolite and pimelite structures is likely on external surfaces as well as within interlayer. $x =$ value ranging from 0.8 to 1.2 (Brindley et al., 1979).

Fig. 13-1. Worldwide distribution of reported pyrophyllite and tale in geologic and soil settings.

Fig. 13-2. X-ray powder diffraction patterns (modified from Harris et al., 1984): (a) for oriented mounts of clay, silt, and ground sand fractions from different depths of a Virginia Piedmont Ultisol. Talc is identified by peaks at 0.94 (001) and 0.267 (003) nm; (b) for the Bt1 silt fraction of a random and oriented mount at room temperature and for an oriented mount after heating to 550°C for 9 h. In a random mount, talc can also be identified by the 0.153- (060) nm peak. Also observe that the 0.94and 0.267-nm peaks for talc are stable after heating to 550°C, whereas kaolinite (0.72 nm) is destroyed.

Fig. 13-3. Characterization of the Bt1 silt fraction (modified from Harris et al., 1984) by: (a) Thermal gravimetric analysis. Observe weight loss from 840 to 1000°C, which is equivalent to 14% talc. The large weight loss from 400 to 700°C is equivalent to 56% kaolinite. (b) Infrared analysis at room temperature and after heating to 550°C for 9 h. Observe talc peak at 3679 cm⁻¹, which is small at room temperature, but persists after heating to 550°C. The kaolinite peaks at 3696 and 3623 cm⁻¹ are large at room temperature but are lost after heating to 550°C.

Criteria for Classification

- *1. Type of tetrahedra octahedra sheet combination,*
- *2. Types and amounts of cations in octehedral sheets dioktahedral, trioktahedral,*
- *3. Layer Charge,*
- *4. Type of interlayer cations,*
- *5. Overall chemical composition,*

6. Polytypes (layer stacking) and nature of stacking.

Origin and Distribution

- • **They are found in the outer layer of of earth,**
- • **Results of the mineral alteration with hydrosphere,**
- • **Occurs in < 500^oC environment,**
- • **Soils, sedimentary rocks are the most abundant, shales is the most common**

Mermut, A. R and H. Kodama. 1999. Clay Mineralogy of Canadian soils. Proceed. 11th International Clay conference, Ottawa. Published ICC 97 Org. Com.