6.3 Clay Crystals

Definitions

Tetrahedron: A polyhedron with four triangular faces. In a regular tetrahedron, all four triangles are congruent equilateral triangles. It constitutes a regular triangular pyramid.

Tetrahedral compound: A compound in which four atoms or groups situated at the corners of a tetrahedron are linked by covalent bonds to an atom at the centre of the tetrahedron. For example, silicon is covalently linked to four oxygen atoms in a tetrahedral silicon.

Tetrahedral sheet: Sheet of horizontally linked, tetrahedral-shaped units that serve as one of the basic structural components of silicate clay minerals. Each unit consists of a central four-coordinated atom (e.g. Si, Al, or Fe) surrounded by four oxygen atoms which, in turn, are linked with other nearby atoms (e.g. Si, Al, or Fe), thereby serving as inter-unit linkages to hold the sheet together.

Octahedron: A polyhedron with eight triangular faces. In a regular octahedron all eight triangles are congruent equilateral triangles.

Octahedral compound: A compound in which six atoms or groups situated at the corners of a octahedron are linked by covalent bonds to an atom at the center of the tetrahedron. For example, aluminum is covalently linked to six oxygen or hydroxyl ions in octahedral aluminum.

Octahedral sheet: Sheet of horizontally linked, octahedral-shaped units that serve as one of the basic structural components of silicate clay minerals. Each unit consists of a central six-coordinated metallic atom (e.g. Al, Mg, or Fe) surrounded by six hydroxyl groups which, in turn, are linked with other nearby metal atoms (e.g. Al, Mg, or Fe), thereby serving as inter-unit linkages to hold the sheet together.

Phyllosilicates: Phyllosilicate minerals have layer structures composed of shared octahedral and tetrahedral sheets.

Plane (of atoms): A flat (planar) array of atoms of one atomic thickness. Example: plane of basal oxygen atoms within a tetrahedral sheet.

Sheet (of polyhedra): Flat array of more than one atomic thickness and composed of one level of linked polyhedra. A sheet is thicker than a plane and thinner than a layer. Example: tetrahedral sheet, octahedral sheet.

Layer: A combination of sheets in a 1:1 or 2:1 assemblage.

Interlayer: Materials between structural layers of minerals, including cations, hydrated cations, organic molecules, and hydroxide octahedral groups and sheets.

Unit structure: The total assembly of a layer plus interlayer material.

Basal spacing: Distance between similar faces of adjacent layers.

Concepts

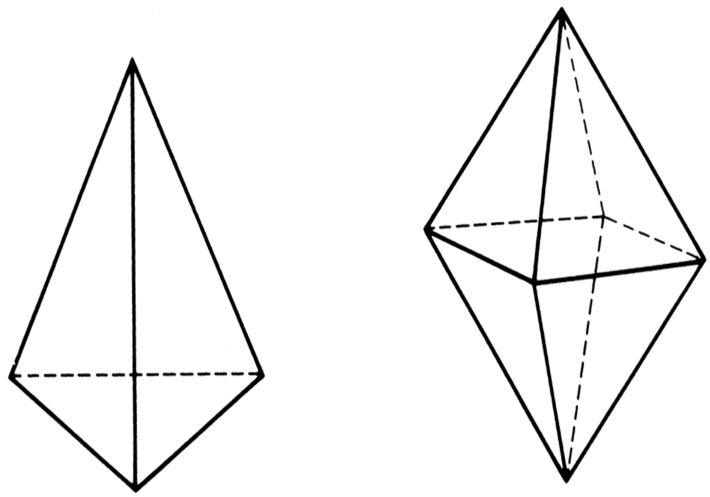

Fig. 6.4. Shape of silicon tetrahedron and aluminum octahedron (Kohnke, 1968). Reproduced with permission from McGraw-Hill, New York.

The tetrahedral sheet is composed of silicon bounded to four oxygen atoms. Each unit consists of a central four-coordinated atom (e.g. Si) surrounded by four oxygen atoms which, in turn, are linked with other nearby atoms (e.g. Si), thereby serving as inter-unit linkages to hold the sheet together. The aluminum octahedral sheet is composed of aluminum bounded to six oxygen or hydroxyl ions. Each unit consists of a central six-coordinated metallic atom (e.g. Al) surrounded by six hydroxyl groups which, in turn, are linked with other nearby metal atoms (e.g. Al), thereby serving as inter-unit linkages to hold the sheet together.

Phyllosilicate minerals have layer structures composed of shared octahedral and tetrahedral sheets. The silicon and aluminum layers are held together by shared chemical bonds. Kaolinite has one layer of silicon atoms and one layer of aluminum layers in 1:1 structure (Fig. 6.5). It is a non-expanding clay mineral and different layers are held together by hydrogen bonding which occurs between the plane of basal oxygen atoms within a tetrahedral sheet and the plane of hydroxyl groups within the octahedral layer. The formula for kaolinite is $(Si_4)^{IV}(Al_4)^{VI}O_{10}(OH)_8$, which indicates that there is no substitution of Si^{4+} with Al^{3+} in the tetrahedral layer and no substitution of Al^{3+} with Mg^{2+}, Zn^{2+}, Fe^{2+}, Ca^{2+}, Na^{+}, or K^{+} in the octahedral layer. In order to calculate the net charge of kaolinite, one has to remember that the charge of Si is +4, Al is +3, oxygen is –2 and OH is –1. Thus, the net layer charge of kaolinite is:

= [4(+4)] + [4(+3)] + [10(-2)] + [8(-1)]

= 28 – 28 = 0

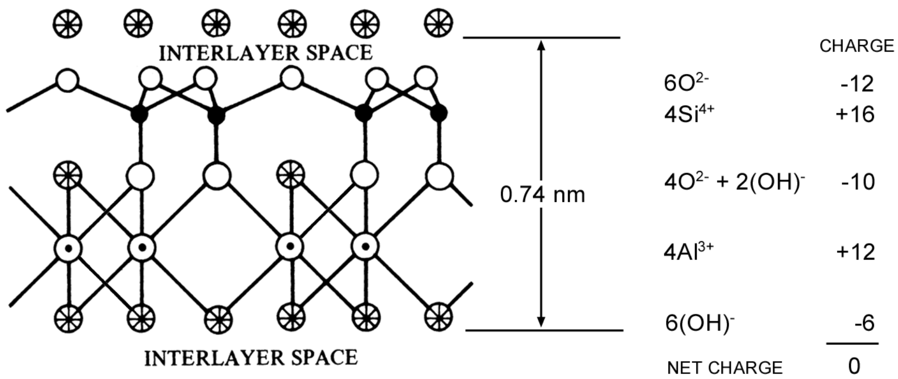

Fig. 6.5. The structure of kaolinite: sheets of silicon tetrahedra and aluminum octahedra are linked by shared oxygen atoms (Singer and Munns, 1996). Reproduced with permission from Prentice-Hall, Upper Saddle River.

In nature, kaolinite has a small net negative change because the clay crystals have broken edges (Fig. 6.6).

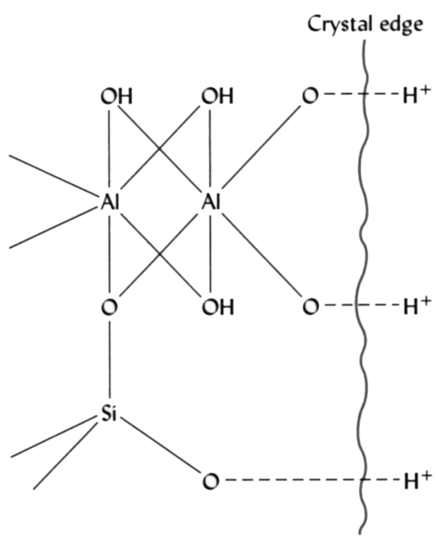

Fig 6.6. Broken edge of a kaolinite crystal showing oxygen atoms as the source of the negative charge (Brady and Weil, 1996). Reproduced with permission from Prentice-Hall, Upper Saddle River.

Smectite minerals have three layers with the aluminum sheets lying between two sheets of silicon atoms in a 2:1 structure, sharing the valencies of their oxygen atoms (Fig. 6.7). Montmorillonite, a type of smectite, has two sheets of silicon and one sheet of aluminum in 2:1 structure (Fig. 6.7). It is an expanding clay mineral and different layers are held together by bonding between divalent cations and water with the basal oxygen atoms of the tetrahedral sheets. A formula for montmorillonite is $(Si_{7.8}Al_{0.2})^{IV}(Al_{3.4}Mg_{0.6})^{VI}O_{20}(OH)_4$. The formula indicates that there is substitution for Si^{4+} by Al^{3+} in the tetrahedral layer and for Al^{3+} by Mg^{2+} in octahedral layer. In order to calculate the net charge of montmorillonite, one has to remember that the charge of Si is +4, Al is +3, Mg is +2, oxygen is –2 and OH is -1. Thus net layer charge of montmorillonite per unit cell is:

= [7.8(+4)] + [0.2(+3)] + [3.4(+3)]+[0.6(+2)] + [[20(-2)] + [4(-1)]
= 43.2 – 44.0
= 0.8 charge/unit cell

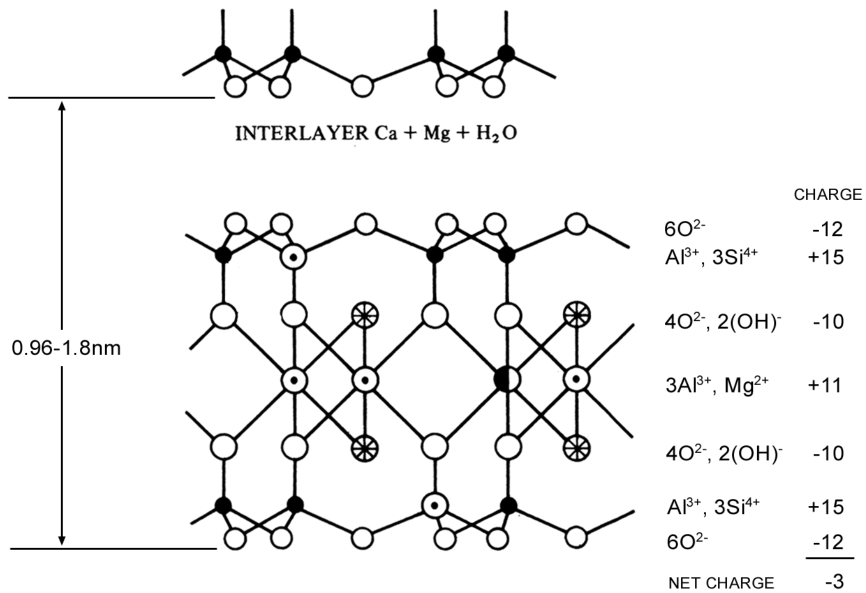

Fig. 6.7. Structure of montmorillonite (smectite): it is built of two sheets of silicon tetrahedra and one sheet of aluminum octahedra, linked by shared oxygen atoms. Smectite is a 2:1 mineral (Singer and Munns, 1996). Reproduced with permission from Prentice-Hall, Upper Saddle River.

Isomorphous substitution is the replacement of one atom by another of similar size in a crystal lattice without disrupting or changing crystal structure of the mineral. In Fig. 6.7, there are three isomorphous substitutions: two in the tetrahedral sheets and one in the octahedral sheet. The formula for smectite shows that there is greater isomorphous substitution in the octahedral sheet than in the tetrahedral sheet. Also, the amount of water present in the interlayer of montmorillonite results in swelling under wet conditions and shrinking in dry conditions. The net negative charge of montmorillonite has to be satisfied by cations which swarm around negatively charged mineral.

In contrast to montmorillonite, illite is a 2:1 clay mineral with potassium (K) as a main cation in the interlayer, which restricts shrinking and swelling (Fig. 6.8). Potassium ions bind the oxygen plane of the basal tetrahedral layers to adjacent units.

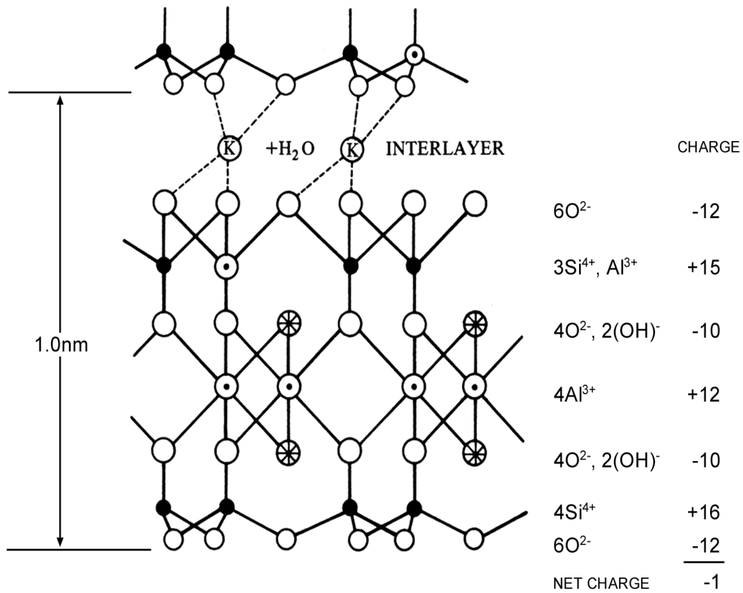

Fig. 6.8. Structure of fine mica, illite (Singer and Munns, 1996). Reproduced with permission from Prentice-Hall, Upper Saddle River.

The formula for illite is $(Si_{6.4}Al_{1.6})^{IV}(Al_4)^{VI}O_{20}(OH)_4K_{1.4}M_{0.2}{}^{+}$. There is no substitution for Al in the octahedral layer, but there is significant substitution in the tetrahedral layer. The potassium (K) and metal (M) ions are present to satisfy the negative charge and will not be used in the calculation of the negative charge. Thus, the net layer charge of illite per unit cell is:

= [6.4(+4)] + [1.6(+3)] + [4(+3)] + [[20(-2)] + [4(-1)]
= 42.2 – 44.0
= 1.6 charge/cell

The charge is satisfied by K ions in the interlayer space and by other cations on the exchange sites of this mineral.

In nature, 2:1 type of clay minerals without isomorphous substitutions are found. In case of pyrophyllite, there is no substitution of Si^{4+} with Al^{3+} in the tetrahedral layer and no substitution of Al^{3+} with Mg^{2+}, Zn^{2+}, Fe^{2+}, Ca^{2+}, Na^{+}, or K^{+} in the octahedral layer. The formula for pyrophyllite is $(Si_8)^{IV}(Al_4)^{VI}O_{20}(OH)_4$. The net layer charge is:

= [8 (+4)] + [4(+3)] + [20(-2)] + [4(-1)]
= 44 – 44 = 0

Similarly, the formula for talc is $(Si_8)^{IV}(Mg_6)^{VI}O_{20}(OH)_4$. The net layer charge is:

= [8(+4)] + [6(+2)] + [20(-2)] + [4(-1)]
= 44 – 44 = 0

Table 6.1. Nonhydrated ionic radii of elements common in silicate clays and their location in the crystal lattice (Brady and Weil, 1996). Reproduced with permission from Prentice-Hall, Upper Saddle River.

Location	Ion	Radius (nm or 10^{-9} m)
Silica tetrahedral layer	Si^{4+}	0.042
	Al^{3+}	0.051
	Fe^{3+}	0.064
Aluminum octahedral layer	Al^{3+}	0.051
	Fe^{3+}	0.064
	Mg^{2+}	0.066
	Zn^{2+}	0.074
	Fe^{2+}	0.070
Both Layers	O^{2-}	0.140
	OH^{-}	0.155

Isomorphous substitution occurs in the tetrahedral and octahedral layers (Table 6.1). For example, the substitution of Si^{4+} with Al^{3+} in the tetrahedral layer or the substitution of Al^{3+} with Zn^{2+} in the octahedral layer leads to a charge imbalance in silicate clays, which accounts for the permanent charge on clay particles and for the ability of clays to attract ions to particle surfaces. This chemical property determines the cation holding capacity of soil, which determines the nutrient supplying power of soil. The properties of common silicate clay minerals are summarized in Table 6.2.

Table 6.2. Comparative properties of common silicate clay minerals (Brady and Weil, 1996). Reproduced with permission from Prentice-Hall, Upper Saddle River.

Property	Montmorillonite	Illite	Kaolinite
Size (μm)	0.01-1.0	0.02-2.0	0.5-5.0
Shape	Flakes	Irregular flakes	Hexagonal crystals
External surface area (m^2/g)	70-120	70-100	10-30
Internal surface area (m^2/g)	550-650	-	-
Plasticity	High	Medium	Low
Cohesiveness	High	Medium	Low
Swelling capacity	High	Low to none	Low
Unit-layer charge	0.5-0.9	1.0-1.5	0
Interlayer spacing (nm)	1.0-2.0	1.0	0.7
Bonding	Van der Waal's bonds (weak attractive force)	Potassium ions	Hydrogen
Net negative charge ($cmol_c/kg$)	80-120	15-40	2-5