

## Chapter 4: The Solid Phase

The solid phase of soils consists of both inorganic and organic components. Inorganic components range in size from tiny colloids ( $< 2\mu\text{m}$ ) to large gravels ( $>2\text{mm}$ ) and rocks, and include many soil minerals, both primary and secondary. Inorganic components usually control soil properties and its suitability as a plant growth medium.

Organic components include plant and animal residues at various steps of decomposition, cells, and tissues of soil organisms (0.5 – 5% of the solid phase). Yet, they can significantly alter soil properties even though their quantities may be small relative to the inorganic component.

**I. Inorganic components:** mainly consist of 2 types of minerals.

### a. Primary minerals

Which were formed at high temperatures and usually derived from igneous and metamorphic rocks. The most abundant primary minerals in soils are quartz ( $\text{SiO}_2$ ), the feldspars ( $\text{MAlSi}_3\text{O}_8$ ) where M is a combination of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$ . Mica [ $\text{K}(\text{Al}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ )] is also a primary mineral.

### b. Secondary minerals

Which were formed at low temp and either inherited from sedimentary rocks or formed directly by weathering. Common secondary minerals in soils include the carbonates, sulfur minerals, larger silicates, and various oxides such as Al, Fe, Mn and Ti oxides.

The most abundant carbonate mineral in soils is calcite ( $\text{CaCO}_3$ ), especially in arid and semi arid regions, also in sub-soils of the humid regions, which were derived from calcareous parent materials (e.g., marbles).

Sulfur minerals are gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) which occurs in many semi arid and arid region soils. Pyrite ( $\text{FeS}_2$ ) is frequently associated with shale and coal, and may form in soils under reducing conditions.

Layer silicates are the most important minerals found in clay fractions of soils, which include kaolinite, smectites, and vermiculite.

Oxide minerals such as hydrous oxides of Al, Fe, Mn and Ti are also important in modifying chemical properties of soils. These oxides range from amorphous to crystalline.

## II. Crystal Chemistry of Silicates

### a. Ionic (electrostatic) bonds

This kind of bonding occurs between ions of opposite charge such as  $\text{Na}^+$  and  $\text{Cl}^-$ . Such ions are formed by a complete loss or gain of electrons to form positive or negative ions having an electronic structure of an inert gas (octet rule).

Ex:  $\text{Cl} + e^- \rightarrow \text{Cl}^-$  (argon structure)

$\text{Na} \rightarrow \text{Na}^+ + e^-$  (neon structure)

Ionic bonding forces are :

- strong ex: NaCl melting point  $\sim 900^\circ\text{C}$
- undirected, that is, they are exerted (present) uniformly in all directions.

### b. Covalent bonds

Covalent bonding is the sharing of  $e^-$  pairs between the combining atoms so that each atom attains the electronic structure of an inert gas.

Ex:  $\text{H}_2\text{O} \equiv \text{e}^-$

$\text{CH}_4 \equiv \text{e}^-$

$\text{PO}_4 \equiv \text{e}^-$

Covalent bonding is also **strong**, but it is **directional**. The difference between ionic and covalent bonds is that a molecule with ionic bonding tends to ionize easily in H<sub>2</sub>O. Meanwhile, a molecule with covalent bonding can hardly ionize.

c. Hydrogen bonds

Occur between hydrogen and two atoms of high electronegativity, such as F, O, and N. The H-bond is a weak electrostatic bond but sometimes is important in crystal structures of oxy-compounds, such as layer silicates.

d. Van der Waals bonds

Very weak. This kind of bonding is the result of weak electronic attraction force between residual charges on polar molecules.

Bonding in most crystals is not clear-cut. For example, the Si-O bond in layer silicates is intermediate between purely ionic and purely covalent. If more than one type of bond occurs in a crystal, the physical properties such as hardness, mechanical strength and melting point are generally determined by the weakest bond. Therefore, the physical properties of layer silicate structures are determined by the strength of interlayer bonds.

e. Ionic bonds in silicates

Internal bonding in silicates is predominantly ionic. Therefore forces are undirected and ionic size plays an important part in determining crystal structure.

**\* Coordination number of cations**

An ion in a crystal surrounds itself with ions of opposite charge. The number of anions that can be packed around a central cation depends on the ratio of radii of the two ions and is called the coordination number of the central cation.

Remember: the number of anions around each cation is called the coordination number and is determined by the radius ratio of the cations to anions, and not by the charge of the cation.

For example, the number of Oxygen anions associated with Si<sup>4+</sup>, Al<sup>3+</sup>, and Mg<sup>2+</sup> in layer silicates:

Ion	Ionic Radius (A)	cation/anion	coordinate # of cation
O <sup>2-</sup>	1.32	--	--
Si <sup>4+</sup>	0.42	0.32	4
Al <sup>3+</sup>	0.51	0.39	4, 6
Mg <sup>2+</sup>	0.66	0.50	6

The arrangement of four oxygens around Si<sup>4+</sup> forms a tetrahedral structure (4 faces), and the hole between the four O<sub>2</sub><sup>-</sup> ions has theoretically a radius of :  $0.223 \times 1.32 = 0.29 \text{ A}$ . Although this hole can accommodate cations with a radius ranging from 0.29 to 0.52 A, Si<sup>4+</sup> with an ionic radius of 0.42 A would probably fit in this tetrahedral structure hole, but some distortion must have occurred. The **electrostatic bond strength**, which is defined as the ratio of cationic charge to the coordination number of the ion, is  $4/4 = 1$  for SiO<sub>4</sub><sup>4-</sup>.

For Al<sup>3+</sup> with 4 fold coordination, the electrostatic bond strength is:  $\frac{3}{4} e^-$  charge. Six-fold coordination yields an eight-faced structure or octahedral structure. The hole between O<sub>2</sub><sup>-</sup> ligands in this configuration has a theoretical radius of about 0.61 A. Ions commonly found in octahedral coordination in layer silicates include Al<sup>3+</sup> (r=0.51 A), Mg<sup>2+</sup> (0.66 A), and Fe<sup>2+</sup> (0.74 A) and the electrostatic bond strength is either:

$$\text{Al}^{3+} = \frac{3}{6} = 0.5 e^- \text{ charge}$$

$$\text{or Mg}^{2+}, \text{Fe}^{2+} = \frac{2}{6} = \frac{1}{3} e^- \text{ charge}$$

#### f. Isomorphic substitution

Is the replacement of one element by another in a crystal without changing the structure of the crystal. Isomorphic substitution usually occurs at **time of crystallization**, and is controlled by the **size** of the ions rather than the charge. The substitution generally takes place between ions differing by less than about 10 to 15% in crystal ionic radii. And generally, a larger ion substitutes for a smaller one. For example, Al<sup>3+</sup> (r = 0.51A) for Si<sup>4+</sup> (r = 0.42A) in tetrahedral coordination, and Mg<sup>2+</sup> (r = 0.66A), Fe<sup>2+</sup> (0.74A) or Fe<sup>3+</sup> (r = 0.64A) for Al<sup>3+</sup> (r = 0.51A) in octahedral coordination. Substitutions between ions of unequal charge leave excess

negative or positive charges within the crystal. In soils, substitutions commonly produce a net negative charge and contribute to the cation exchange capacity (known as CEC) of soils.

**Unit cell** - the smallest repeating three dimensional array of a crystal. A unit cell is usually defined in terms of its repeating dimensions along the horizontal a, b, and vertical c axis. However, the chemical formula of layer silicate minerals is conventionally expressed as one-half of a unit cell.

Ex: Kaolinite is written as  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

its unit cell is  $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$

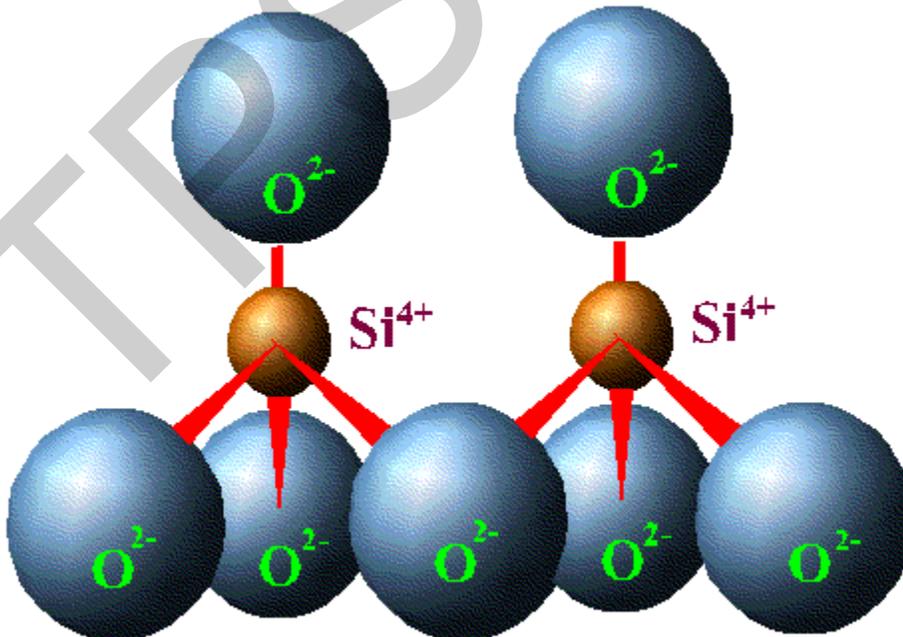
### III. Structural Classification of Silicates

#### a. Layer silicate structures (clay minerals)

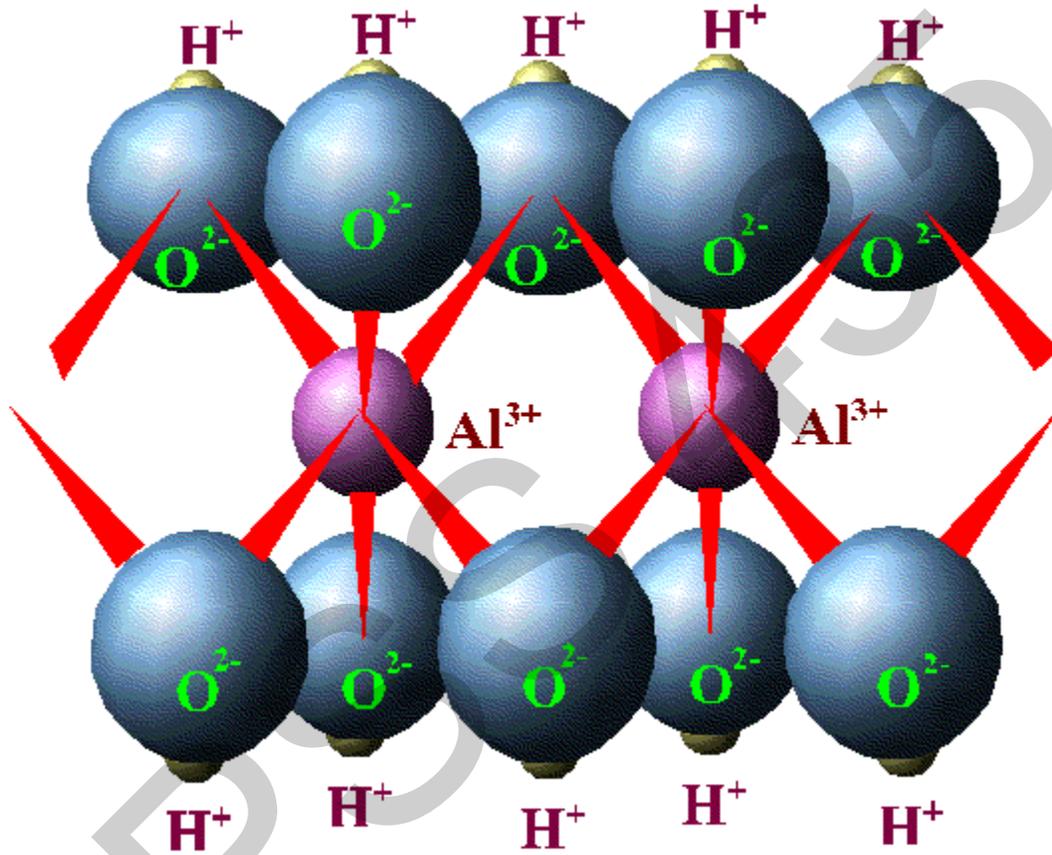
They are called clay minerals because (1) their crystal size is less than  $2\mu\text{m}$  and (2) they are layer silicates, which are also called phyllosilicates or leaf-like structures.

A typical layer silicate mineral consists of 2 types of structural units.

1.) One is a two dimensional array of Si-O tetrahedral (the tetrahedral sheet)



2.) The second is a two dimensional array of cations (generally  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ) in octahedral coordination with oxygen and OH (hydroxyl) ions (the octahedral sheet). The tetrahedral and octahedral sheets are bonded together by a layer of shared oxygens. As a matter of fact, the apical oxygen of tetrahedron replaces OH of the octahedral structure.

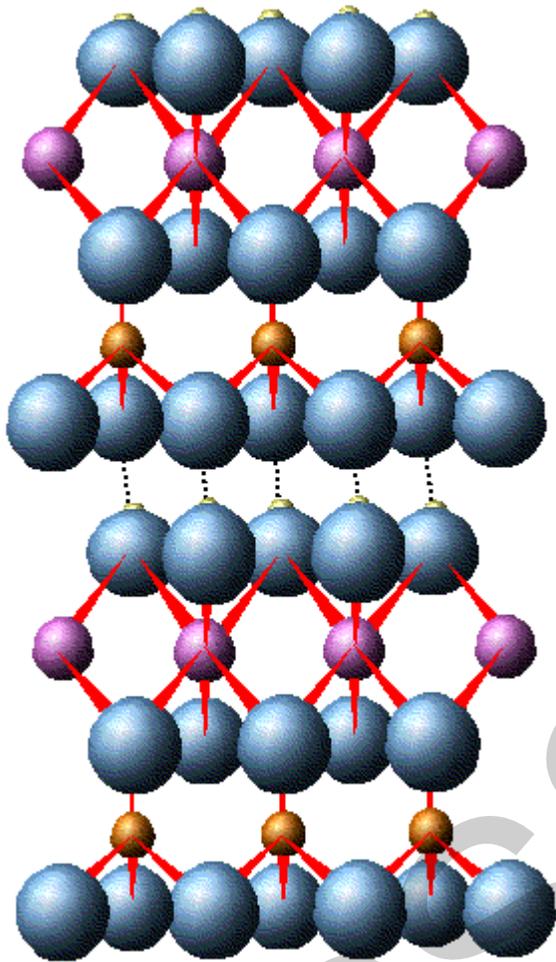


So as a rule: O is bonded with both Si and Al

OH is bonded with Al only.

Layer silicate minerals are differentiated by 4 criteria:

1. the number and sequence of tetrahedral and octahedral sheets. (1:1, 2:1, 2:1:1)
2. the layer charge/unit cell (0, 0.5, 1)
3. the type of interlayer bonds and interlayer cations.
4. the nature of cations in the octahedral sheet, whether it is Al, Mg or Fe.



1.) Kaolin group or 1:1 layer silicates. The mineral structure consists of 1 tetrahedral sheet overlapped by 1 octahedral sheet.

Kaolinite is the typical mineral of 1:1 layer silicates. Its half cell formula is  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . Its structural configuration is

Net charge of kaolinite is zero.

<u>Charge</u>	<u>positive</u>	<u>negative</u>
6 OH <sup>-</sup>		6
4 Al <sup>3+</sup>	12	
4 O <sup>2-</sup> , 2OH <sup>-</sup>		10
4 Si <sup>4+</sup>	16	
6 O <sup>2-</sup>	—	<u>12</u>
	28	28

In kaolinite and the kaolin group, the basal planes (which are planes between adjacent unit cells parallel to the a-b plane) are held together by H bonding between O ions from the tetrahedral sheet of a unit cell and OH ions from the octahedral sheet of another unit cell.

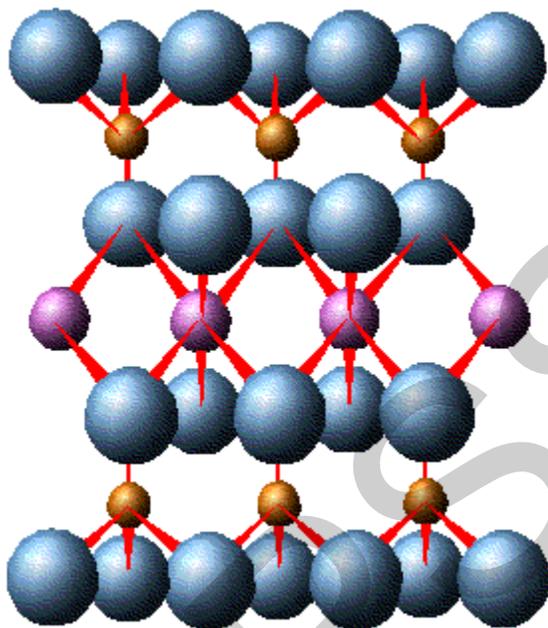
2.) 2:1 layer silicates. The unit cell consists of one octahedral sheet sandwiched between two tetrahedral sheets. You have: tetrahedral sheet

octahedral sheet

tetrahedral sheet

Pyrophyllite is an unsubstituted, therefore electrically neutral, 2:1 mineral.

$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$  **B** half-cell formula



	<u>positive</u>	<u>negative</u>
$6\text{O}^{2-}$		12
$4\text{Si}^{4+}$	16	
$4\text{O}^{2-}$		10
$4\text{Al}^{3+}$	12	
$4\text{O}^{2-}, 2\text{OH}^-$		10
$4\text{Si}^{4+}$	16	
$6\text{O}^{2-}$	—	<u>12</u>
	44	44

The bonding between basal planes is weak Van der Waals forces. Various 2:1 minerals do exist depending on kind and amount of isomorphic substitution in both the tetrahedral and octahedral sheets. This substitution leads to the presence of charge within the crystal. This charge must be balanced either internally or by cations outside the crystal structure. From this phenomenon, cation-exchange capacity of soil arises.

Depending upon the extent of charge per formula unit cell, 2:1 layer silicates can be expanding or essentially non expanding and have different names.

Ex: Smectites (2:1 minerals) where charge/formula is low (0.25- 0.60) the sheets are held together by a weak bond so polar molecules like  $\text{H}_2\text{O}$  can enter the

space between sheets (basal planes), therefore the minerals expand or swell drastically.

On the other hand, in case of mica where the charge is high, the bonds between sheets are electrostatic and very strong. H<sub>2</sub>O cannot enter between basal planes and the minerals are not expanding.

3.) 2:1:1 layer silicates. The unit cell consists of:

1 octahedral layer ... of a combination between  $Mg_3(OH)_6$  and  $Al_2(OH)_6$  so that

1 tetrahedral layer                      this layer has a positive charge  $[Mg_2Al(OH)_6]^+$

1 octahedral layer

1 tetrahedral layer

The chlorite minerals are nonexpanding and have low cation-exchange capacity.

b. Structure-related properties

1.) Bonding between adjacent layers determines crystal size.

The type of interlayer bond has a significant effect on physical and chemical properties of layer silicates. Bonding within the unit layers is much stronger than among unit layers. When the mineral is subjected to physical or thermal stress, fracture will first occur along the basal plane, that is, between the unit layers.

The stronger the interlayer bond, the greater the crystal growth in the c-dimension before breaking down. Therefore the size of layer silicate crystals is a direct function of their interlayer bond strength.

2.) Hardness and swelling are also dependent on interlayer bonds.

The degree of swelling is inversely related to the interlayer bonding energy, and the surface area of larger silicates is related to their expanding properties. External surface refers to the faces and edges of the whole crystal. Internal surface refers to the area of basal plane surfaces only. Non expanding minerals exhibit only external surface, but expanding minerals have both internal and external surfaces.

3.) Relative surface area: kaolinite vs. smectite

Internal surface area is normally much larger than external surface. For example, total surface area of smectite, which is an expanding 2:1 layer silicate

mineral, is about  $800\text{m}^2/\text{g}$ , but the surface area of Kaolinite, a 1:1 non expanding mineral, is only 10 to  $20\text{m}^2/\text{g}$ .

#### 4.) C-spacings

The c-spacing of layer silicates is determined by:

- \* the number of tetrahedral and octahedral sheets per unit structure
- \* the presence of ion or polar molecules in the basal plane

##### a. 2:1 minerals

1. Pyrophyllite- has two tetrahedral and 1 octahedral layer- no layer charge therefore there's no interlayer cations.  $C = 9.3\text{ \AA}$
2. Mica- layer charge is high =  $1\text{ e}^-/\text{formula unit}$ . Interlayer cations =  $\text{K}^+$   
More space is needed to accommodate  $\text{K}^+$ . C-spacing =  $10\text{ \AA}$
3. Smectite- fairly weak layer charge, which is  $0.25\text{-}0.60\text{ e}^-/\text{formula unit}$ .  
Cations, water and other polar molecules can enter the basal plane.  
C-spacing can vary from  $10\text{ \AA}$  to over  $18\text{ \AA}$  depending upon exchangeable cations and degrees of interlayer solvation.

##### b. 1:1 minerals

In kaolinite which is non expanding, there's no interlayer cations or molecules, therefore C-spacing is fixed at  $7.2\text{ \AA}$ .

##### c. 2:1:1 minerals

similar to kaolinite, chlorite has a fixed c-spacing =  $14\text{ \AA}$

### IV. Important properties of layer silicates

#### a. Kaolins (1:1)

Unit formula is:  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

- the ratio of  $\text{Si}/\text{Al} = 1$  which means no detectable isomorphic substitution.

Therefore,

- CEC is low ( $1\text{ to }10\text{ cmol}_c\text{ kg}^{-1}$ ), but highly pH dependent.

- non expanding minerals, c-sp. =  $7.2\text{ \AA}$  (kaolinite)

=  $10\text{ \AA}$  (halloysite)

Since they're non expanding, surface area is small and limited to external surface, ranges from 10-20 m<sup>2</sup>/g

#### b. Smectites (2:1)

Unit formula (with no substitution) is Al<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>

- relatively low layer charge = 0.25 – 0.60 mole of e<sup>-</sup>/ formula unit
- because of low layer charge, smectites are freely expanding.

c-spacing = 10-18 Å

- CEC = 80-120 cmol<sub>c</sub> kg<sup>-1</sup>, slightly pH dependent (0.25 eq/360g = 69 cmol<sub>c</sub> kg<sup>-1</sup>)
- and because they're freely expanding, surface area is large 600-800 m<sup>2</sup>/g

montmorillonite is the most important clay mineral of the smectite group. In montmorillonite, Al<sup>3+</sup> is the major and Mg<sup>2+</sup> is the minor cation in the octahedral structure. A typical unit formula is: Na<sub>x</sub>[(Al<sub>2-x</sub>Mg<sub>x</sub>)Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>]

Smectites, and especially montmorillonite, are usually fine clays, their effective diameter is from 0.01 to 1 µm. They have high colloidal activity, high plasticity and cohesion.

#### c. Vermiculites

A product of mica weathering. 2:1 layer silicates- unit formula is Al<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>

- Al<sup>3+</sup> is substituted for Si<sup>4+</sup> in tetrahedral layers; Mg<sup>2+</sup>, Fe<sup>2+</sup>
- layer charge = 0.6 – 0.9 eq/unit formula
- because the layer charge is relatively high, vermiculites have limited expansion.
- c-spacing = 14Å because exchangeable cation is usually Mg<sup>2+</sup>
- CEC = 120 – 150 cmol<sub>c</sub> kg<sup>-1</sup> - because of its high layer charge, vermiculites can fix K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> and collapse (c-spacing = 10 Å)
- total surface area (when not K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> saturated) is about 600 – 800 m<sup>2</sup>/g

#### d. Micaceous Chlorites

Micas are the precursors for other 2:1 clay minerals, especially vermiculites.

- typical unit formula, K[Al<sub>2</sub>(Si<sub>3</sub>Al)O<sub>10</sub>(OH)<sub>2</sub>]. It has 1 negative charge/formula unit

- it is abundant in soils, but not very chemically active
- since  $K^+$  is fixed, CEC of micas is low:  $20-40 \text{ cmol}_c \text{ kg}^{-1}$
- and because it is not expanding, total surface area of mica is also low:  $70-120 \text{ m}^2/\text{g}$

#### e. Soil clays

Soil clays often differ significantly in properties from those of pure minerals. Soil clays are usually a mixture of various layer silicates and often coated with iron and Al oxides, and organic matter. Such coatings can drastically alter mineral properties by decreasing CEC and surface area, and by increasing anion exchange capacity and other properties associated with positively charged surface.

### V. Accessory soil minerals

As soils weather, they become enriched in oxides, hydroxides, hydroxy-oxides of Al, Fe, and Ti, relative to Si. These materials can be either amorphous or crystalline or somewhere in between.

#### a. Allophane

Allophane is a general name for amorphous aluminosilicate gel. It is predominant in soils derived from volcanic ash. Allophane has a relatively high CEC (up to  $150 \text{ cmol}_c \text{ kg}^{-1}$ ) but this CEC depends heavily on pH and degree of hydration. Allophane also has a fairly high surface area ( $70-300 \text{ m}^2/\text{g}$ ), but this property also varies widely with pH and degree of crystallinity.

#### b. Al minerals

Gibbsite,  $\text{Al}(\text{OH})_3$ , is the most abundant Al hydroxide in soils. The sheets of gibbsite are held together by H bonding. Boehmite,  $\text{AlOOH}$ , is an aluminum hydroxyoxide. Both gibbsite and boehmite are present in large quantity in highly weathered soils which can be formed by heating gibbsite at  $130^\circ\text{C}$ .

#### c. Fe minerals

The most common Fe oxides are hematite ( $\text{Fe}_2\text{O}_3$ ) and goethite ( $\text{FeOOH}$ ). They have a red color that gives the characteristic of highly weathered soils.

- d. To a lesser extent, in highly weathered solids, we can also find  $\text{TiO}_2$  (anatase) or  $\text{MnO}_2$  (pyrolusite) .

## **VI. Charge development in solids.**

(Read Dr. El-Swaify's paper: *Charges associated with mineral soil components and their implications for the behavior of soils of the tropics*).

Reactivity of soils is due to 2 factors:

- 1.) Surface area: which is a function of particle size and shape
- 2.) surface charge: which is a result of isomorphic substitution and ionization of functional groups. These 2 mechanisms give rise to the permanent and pH dependent charge in soils.

### a. Permanent charge

Isomorphic substitution is the substitution of one ion for another of similar size within a crystal lattice. If a cation of lower charge substitutes for one of higher charge (such as  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$  or  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$ ), then the mineral will have a net negative charge. Isomorphic substitution need not result only in net negative charge, but negative charge development is far more common in most soil minerals. Once formed, usually during the crystallization, such charge is essentially independent of the environment. Therefore, it is called the permanent charge.

### b. pH dependent charge

In contrast to the permanent charge, which is independent of the environment, the total charge of soil particles varies with pH at which the charge is measured. The positive charge developed at low pH, and the excess negative charge developed at high pH, are known as pH dependent charge.

Most soils have a net negative charge because of the negative charges in clay minerals and organic matter, but some highly weathered soils dominated by allophone and hydrous oxides may have a net positive charge at low pH as discussed by Dr. El-Swaify in his paper.

The zero point charge (ZPC) has been used to characterize the relative abundance of positive and negative charge. The zero point of charge is defined as the pH at which – and + charges are equal.

### Nature of pH dependent charge

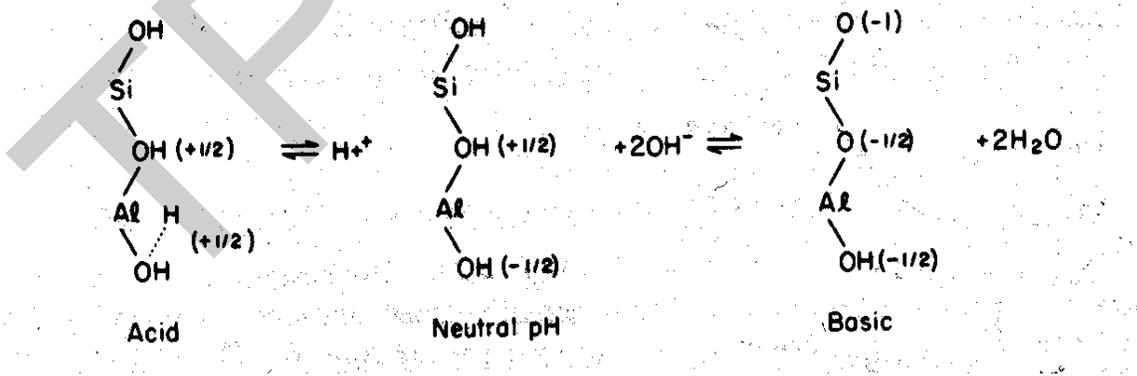
The source of pH dependent charge is usually the gain or loss of H<sup>+</sup> from functional groups on the surface of soil colloids.

#### 1.) From clay mineral edge

Electrostatic bond strength: charge of cation/coord. #

Ex. Si<sup>4+</sup> in coord. 4 = +1

Al<sup>3+</sup> in coord 6 = +1/2



#### 2.) From organic matter



Dissociation of ionization constant

$$K = \frac{(R-COO^-)(H^+)}{(RCOOH)} = 10^{-2} \text{ to } 10^{-7}$$

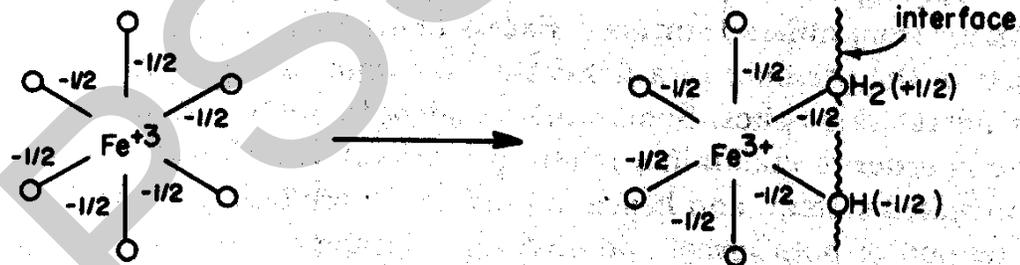
At pH = pK half of R-COOH is ionized to R-COO<sup>-</sup>, as pH increases (greater than pK), this reaction moves toward the right, and more R-COO<sup>-</sup> will be present. More negative charge resulting in a greater CEC.

### 3.) From hydrous oxides of Al and Fe

In highly weathered soils, Fe and Al oxides are abundant and they may play a major role in the development of pH dependent charge.

For example, the Fe<sup>3+</sup> ion in an Fe<sub>2</sub>O<sub>3</sub> crystal is in 6 coordination with oxygen ions. Each valence bond of an O supplies -1/2 charge to satisfy the +3 charge of Fe. The remaining negative charge of each oxygen (-1.5) is balanced by 3 adjacent (Fe 3+) ions in the crystal.

At the crystal-liquid interface, however, all crystal bonding terminates. Crystal neutrality is maintained by interaction with H<sup>+</sup>, OH<sup>-</sup> and water molecules.



The end result is that the surface of the oxide mineral is covered by hydroxyl or water molecules, which may result in a net positive charge at low pH, and negative charge at high pH.