SOIL COLLOIDS CHARACTERISTICS AND PROPERTIES

Dr. V. K. Venugopal
Former Professor & Head
Department of Soil Science and Agricultural Chemistry
College of Agriculture, Vellayani
Consultant, Digital University, Kerala

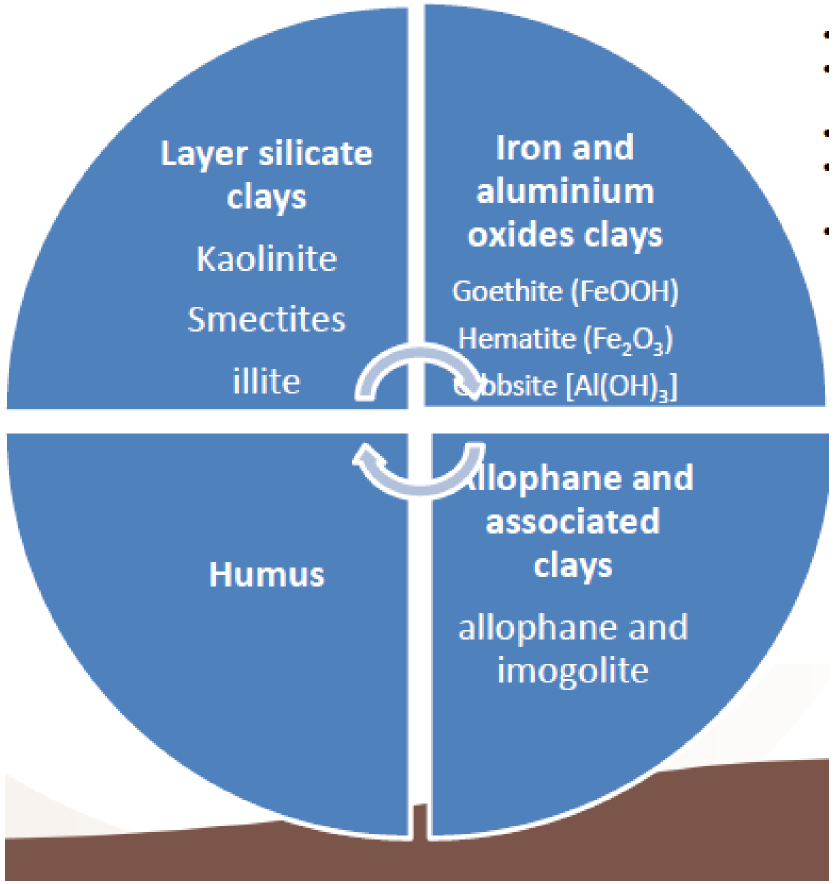
Soil Colloids

- **Present in clay fraction along with other particle size fractions sand and silt**
- **Forms the most active portion of the soil while other size fractions are inert**
- **Occur as clay minerals representing the inorganic colloids**
- **All clay minerals are not colloids since some have diameters of 0.002 mm**
- **Organic colloids are the highly decomposed organic matter called humus**

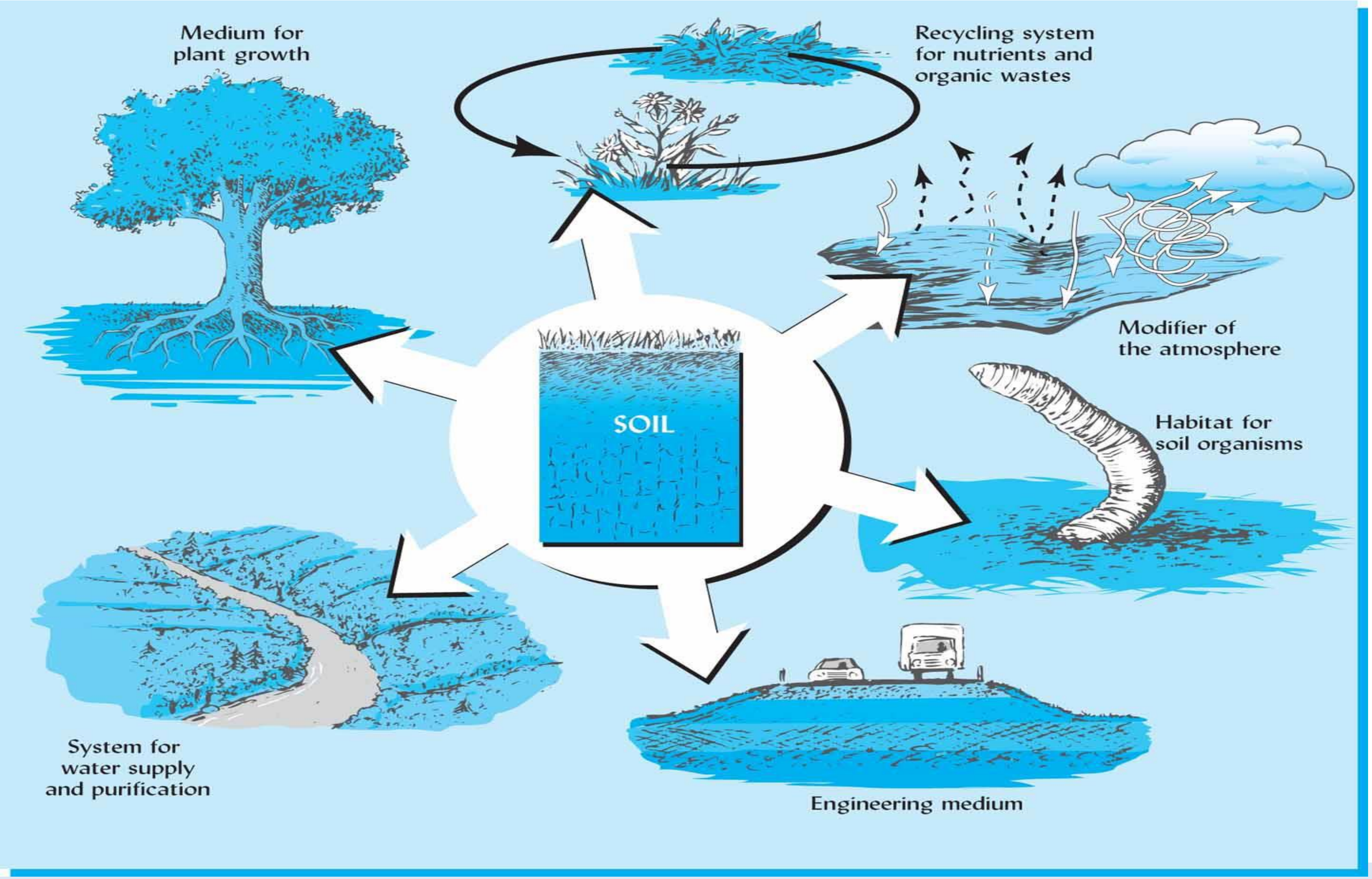
General properties of soil colloids

- **Extremely small in size cannot be seen by an ordinary microscope**
- **Large surface area 10 m^2 /g for clays with external surface area**
- **Minerals with both external and internal surface area have over 800 m^2/g**
- **Carry both negative and positive charges on the surface and interspaces**
- **Negative charges are often dominant in most soils**
- **Colloidal surfaces attract positive ions and are often referred as micelles or(micro cells)**

Classification soil colloids



Colloids –Ecological functions



Colloids play a significant role in three of the ecological functions of soil

1.Plant growth (direct)
2.Water purification (direct)
3.Engineering medium (direct)
4.Recycling of nutrients (Indirect)

Layer Silicates

- Eg kaolinite,montmorillonite,illite
- Dominant colloids in most soils
- Exhibit layer like crystalline structure
- Clay minerals are mostly negatively charged

Inorganic Oxide clays

- Found mostly in highly weathered tropical and semitropical soils
- Are amorphous or crystalline
- Mostly oxides of iron and aluminium
- Examples: Goethite, haematite, gibbsite
- Neither sticky or plastic
- Occur as coatings of crystalline clay minerals
- Carry a net positive charge in some soils (anion exchange)

Allophane and associated clays

- Inorganic, crystalline structure not well developed
- Not detected by XRD
- Common in soils from Volcanic ash material
- CEC varies with pH
- High phosphate adsorbing capacity

Organic colloids

- Formed as end product of organic matter decomposition
- Composed of complex ring structure consisting of C,H,O and N bonded together
- Have enolic (alcohol),Carboxyl (carboxylic acid) phenolic (aromatic alcohol) groups
- Prevailing charge depends on the soil pH condition

1:1 – Lattice structure - Kaolinite

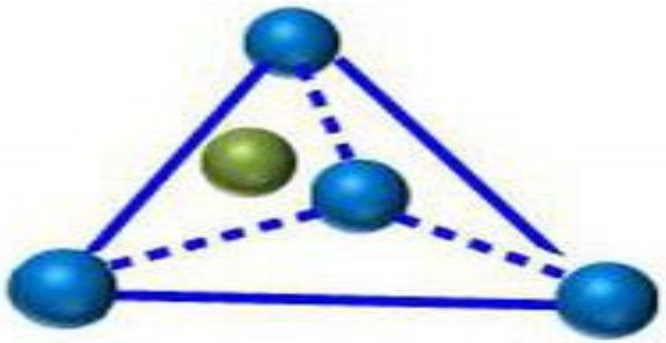
- **Sheets are held together by oxygen bonds**
- **Layers are held by hydrogen bonds**
- **Structure is fixed**
- **No expansion or contraction properties**
- **Water and cations do not enter into the structure**

2:1- lattice structure

- **Montmoillonite,Vermicullite, Illite**
- **Layers are held together by weak oxygen to oxygen or oxygen cation bonds**
- **Cations and water molecules enter between layers and cause expansion and contraction**
- **Has high internal surface area**
- **Has high cation exchange capacity**

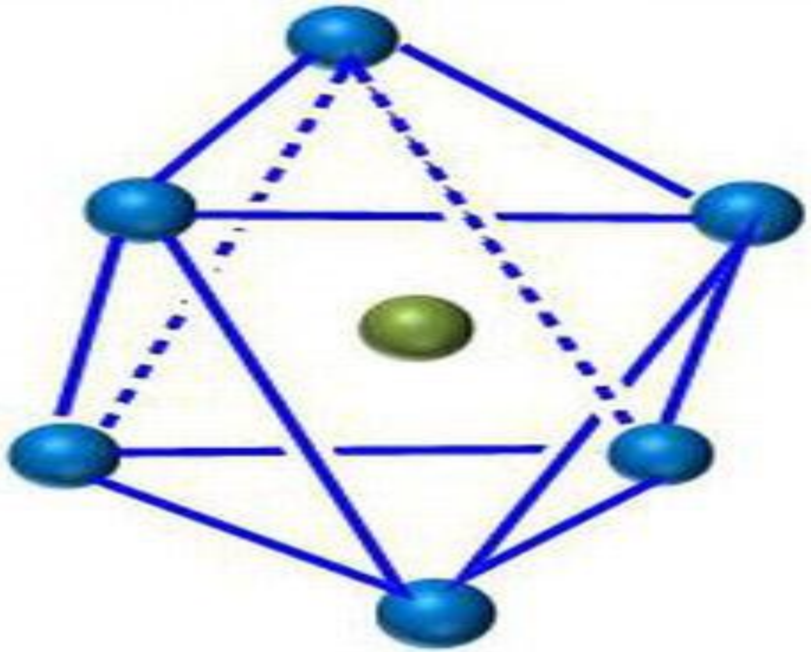
Clay mineral structure – Building blocks

Silicon tetrahedra



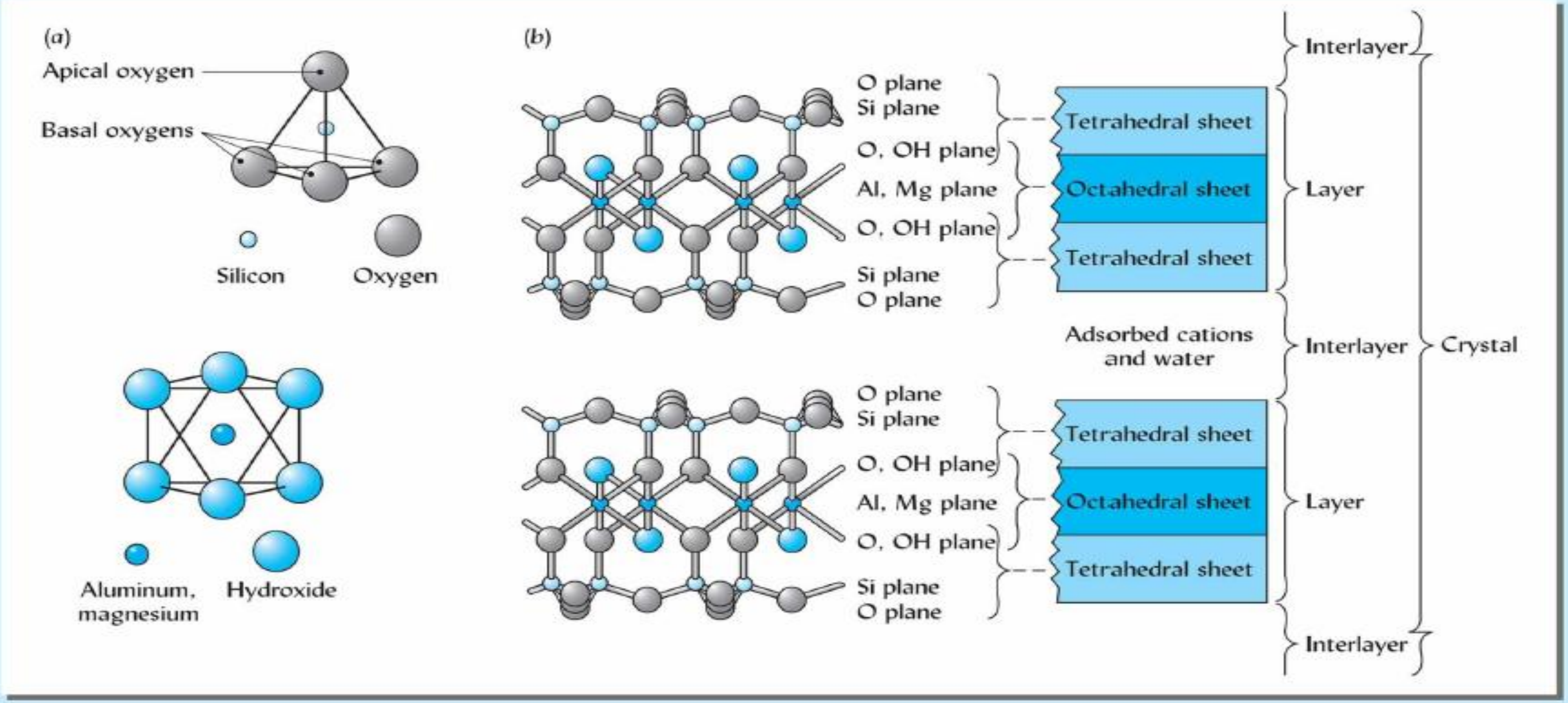
Tetrahedral unit

Aluminum/Magnesium Octahedra



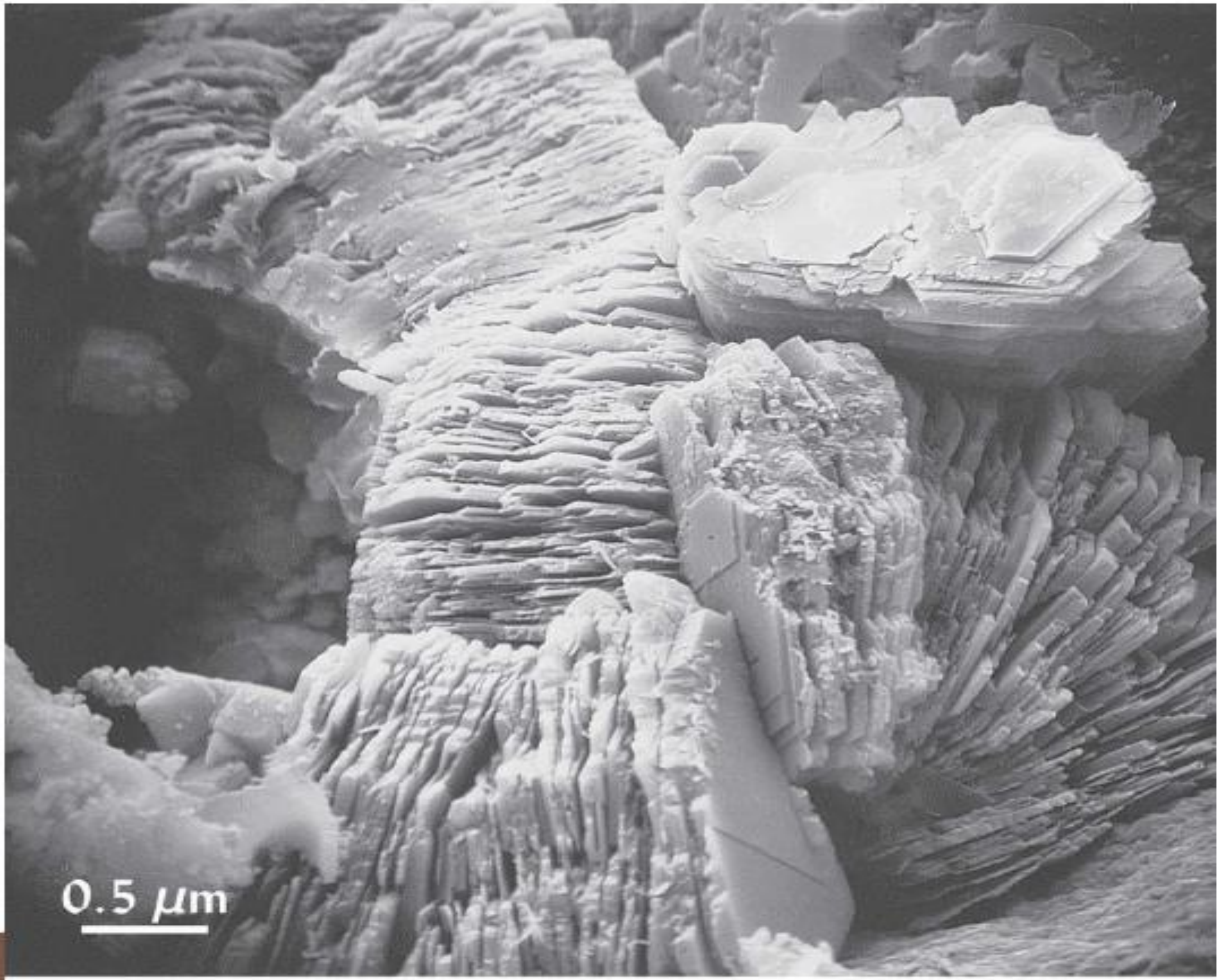
Octahedral unit

The basic molecular and structural components of silicate clays



Layerlike structure

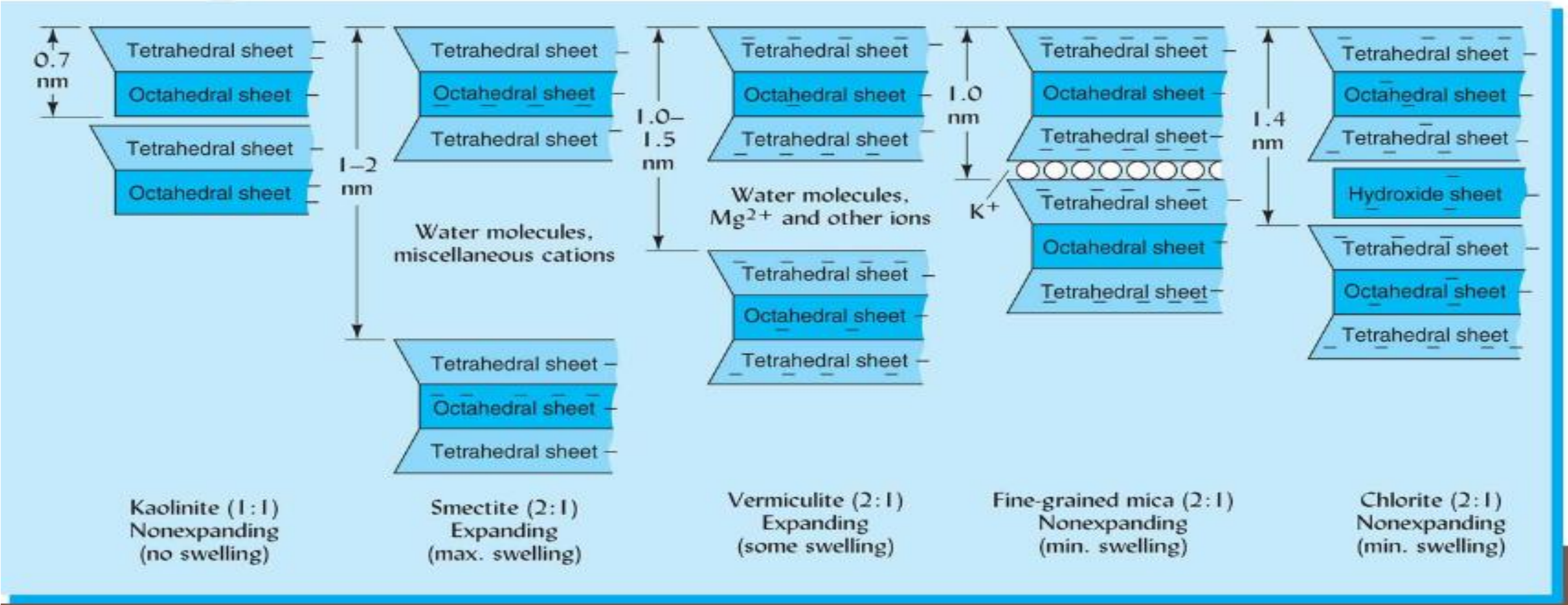
Electron micrograph



(a)

Types of clay minerals

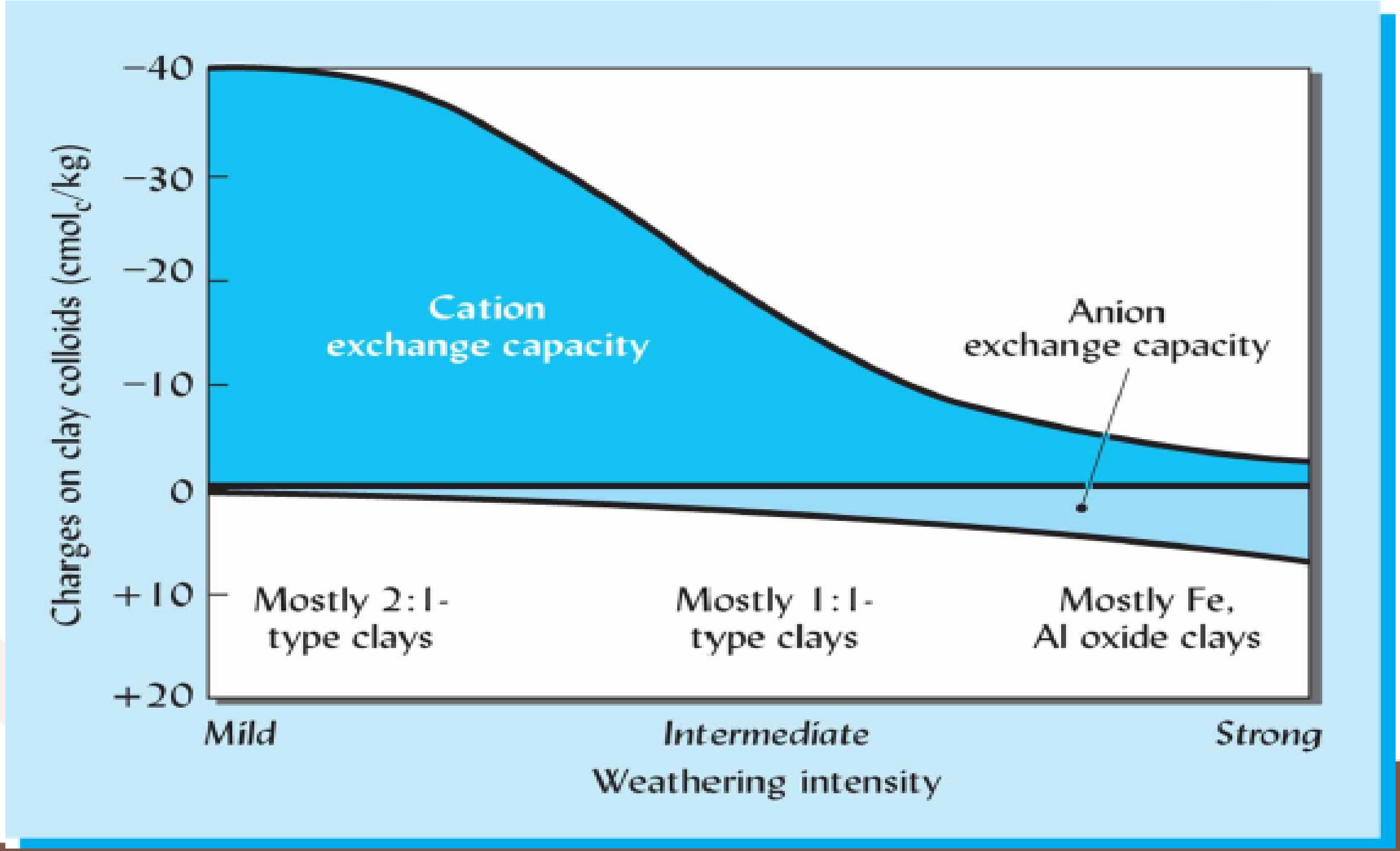
- Two main types; 2:1 and 1:1 based on their lattice structure



Occurrence of layer clay minerals and sesqui oxides in soils

Stage of Weathering	Minerals	Typical Soil groups
Early	Gypsum,Calcite,Olivine,Hornblende, Biotite,Albite	Soils with these minerals in the fine silt and clay fraction, occur in the desert regions where limited moisture keeps weathering reactions to the minimun
Intermediate	Quartz, Muscovite, Montmorillonite, Vermiculite, Illite	Mostly found in temperate regions in grasslands or tree vegetation.
Advanced	Kaolinite, Sesquioxides Goethite,Haematite,Gibbsite,Anatase	Intensely weathered regions of the warm and tropical high rainfall regions with infertile soils

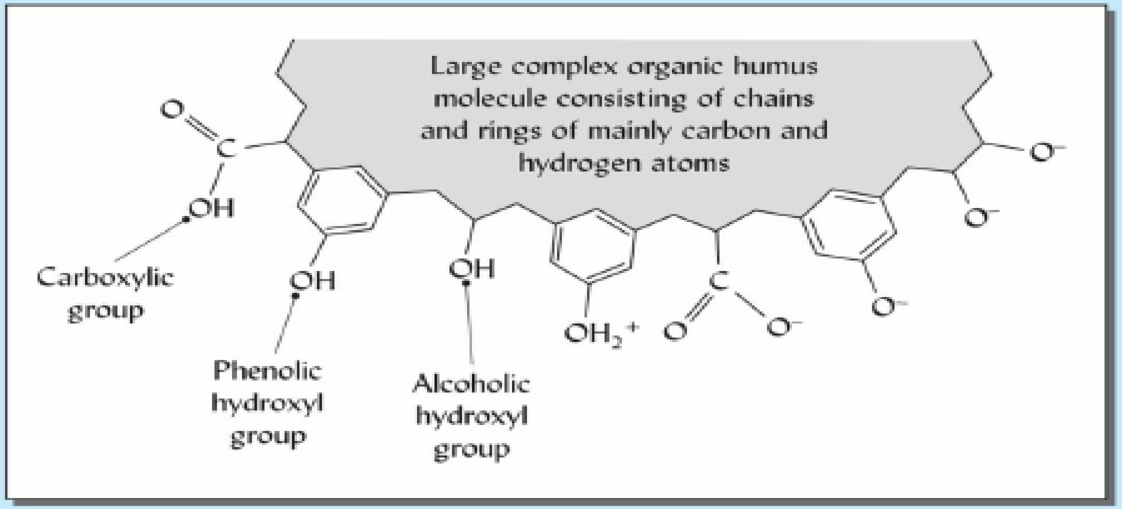
The effect of weathering intensity on the charges on clay minerals and, in turn, on their cation and anion exchange capacities (CECs and AECs).



4. Organic soil colloids

- They are negatively charged as a result of the presence of dissociated enolic (alcohol) carboxyl (carboxylic acid) and phenolic groups (aromatic alcohol).
- Prevailing charge on organic colloids at any given time depends on soil pH condition

- Highly decomposed organic matter (plant residues and organic amendments
- Most active colloids
- Have greater influence on soil properties per unit weight than inorganic colloids



Major properties of selected soil colloids

Colloid	Type	Size, µm	Shape	Surface area, m^2/g External	Surface area, m^2/g Internal	Interlayer spacing[a], nm	Net charge[b], $cmol_c/kg$
Smectite	2:1 silicate	0.01–1.0	Flakes	80–150	550–650	1.0–2.0	−80 to −150
Vermiculite	2:1 silicate	0.1–0.5	Plates, flakes	70–120	600–700	1.0–1.5	−100 to −200
Fine mica	2:1 silicate	0.2–2.0	Flakes	70–175	—	1.0	−10 to −40
Chlorite	2:1 silicate	0.1–2.0	Variable	70–100	—	1.41	−10 to −40
Kaolinite	1:1 silicate	0.1–5.0	Hexagonal crystals	5–30	—	0.72	−1 to −15
Gibbsite	Al-oxide	<0.1	Hexagonal crystals	80–200	—	0.48	+10 to −5
Goethite	Fe-oxide	<0.1	Variable	100–300	—	0.42	+20 to −5
Allophane & Imogolite	Noncrystalline silicates	<0.1	Hollow spheres or tubes	100–1000	—	—	+20 to −150
Humus	Organic	0.1–1.0	Amorphous	Variable[c]	—	—	−100 to −500

Significance of soil colloids

- **Sites for most chemical reactions in soils including all ion exchange processes**

- **Sites within the soil where essential plant nutrients are held and protected from leaching by percolating rain or irrigation water**
  - In humid regions Ca^{2+} H^{+} and Al^{3+} dominate the exchange complex resulting in acid soils.
  - In arid and semi-arid regions Ca^{2+}

- **Influence soil structure formation and stability, soil fertility retention of water.**

- **Determine the fertility of soils.**

- **Factors influencing the type of colloids present in a soil have a direct impact on soil fertility**

Table 2. Representative values and common ranges of cation exchange capacities of clay minerals and humus.

Clay mineral or humus	Cation Exchange Capacity	
	Representative value	Common range
	meq/100 g or cmol (+) kg^{-1}	
Kaolinite†	8	3–15
Chlorite	30	15–40
Illite	30	15–40
Montmorillonite	80	60–100
Allophane†	100	50–200
Vermiculite	125	80–150
Humus†	200	100–300

Charges on Colloids

- Negative charges on colloids can be grouped into
- Permanent negative charge or constant charge due to Isomorphous substitution

pH dependent charge

Isomorphous substitution

- Substitution of one ion by another in the crystal structure
- Ions should have comparable ionic radii
- Substitution of lower charged ion in place of a higher charged ion causes charge imbalance
- Eg. Si with 4 positive charges is replaced by by Al with 3 positive charges
- Al with 3 positive charges is replaced by Mg with 2 charges
- Above substitutions result in one free negative charge

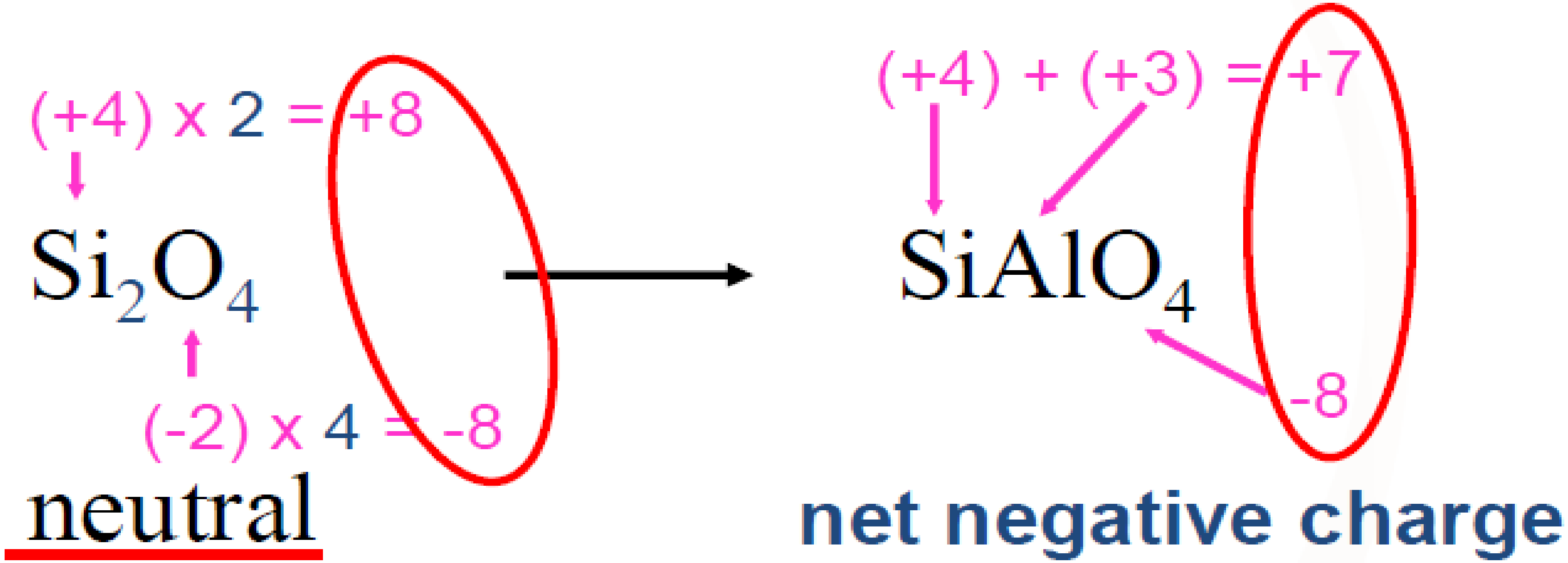
pH Dependent charge or Variable charge colloids

- Charges could develop from the exposed hydroxyl groups or other functional groups on the surface of the colloids based on prevailing pH conditions
- At high pH values the OH^- in the octahedral sheets dissociate from the colloidal surface resulting in a negative charge
- Positive charges on the colloids result from attachment of H^+ in acid conditions on the OH^- in the octahedral layer.
- The same site on colloid exhibit a negative charge at high pH, positive charge at very low pH and no charge at neutral pH (Zero point charge)
- These colloids are characteristic of highly weathered tropical soils – Ultisols, Oxisols and soils from volcanic areas –Andisols

Ionic Radii of cations in the clay structural units

Ion	*Radius, nm (10^{-9} m)*	*Found in*
Si^{4+}	0.042	
Al^{3+}	0.051	Tetrahedral sheet
Fe^{3+}	0.064	
Mg^{2+}	0.066	Octahedral sheet
Zn^{2+}	0.074	Exchange or interlayer sites
Fe^{2+}	0.076	
Na^{+}	0.095	
Ca^{2+}	0.099	
K^{+}	0.133	
O^{2-}	0.140	Both sheets
OH^{-}	0.155	

Isomorphic Substitution in **tetrahedral** sheet



Al^{3+} for Si^{4+} as in vermiculite and the micas

Isomorphic Substitution in **octahedral** sheet

$(-1) \times 2 = -2$

$(-2) \times 2 = -4$

$= -6$

$(+3) \times 2 = +6$

$$(OH)_2Al_2O_2 \longrightarrow (OH)_2AlMgO_2$$

$(-2) + (-4) = -6$

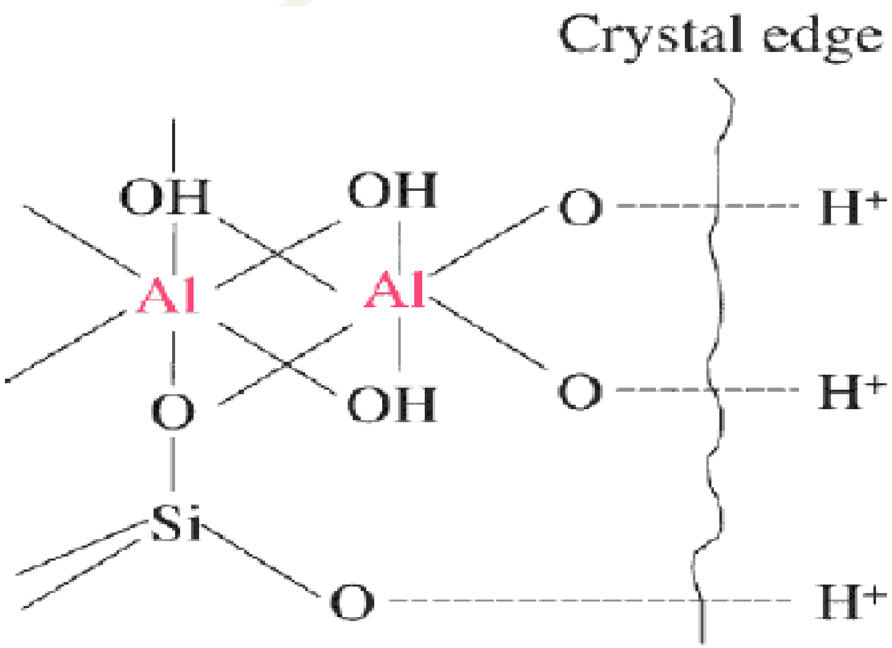
$(+3) + (+2) = +5$

neutral

net negative charge

Mg^{2+} for Al^{3+} in the octahedral sheet as in smectite, vermiculite, and chlorite

pH-dependent charge : on edges!!!

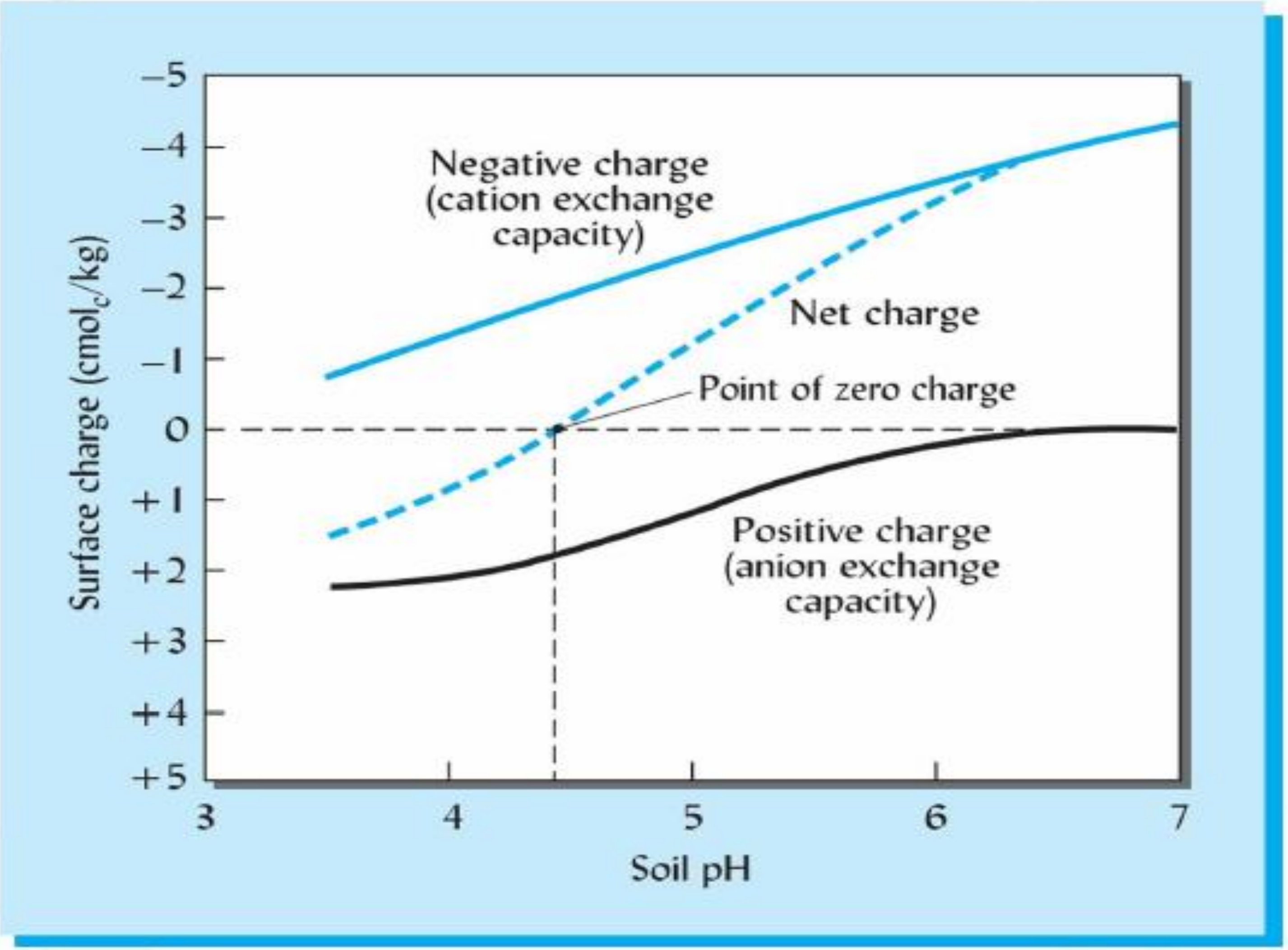


H^+ bound tightly, so the lower the pH, the less exchange there is (i.e., lower nutrient availability)

As the pH increases more OH- is available and therefore more CEC and conversely acid soils have a lower CEC from OM

Especially Important in kaolinite and humus, where no internal charge imbalance occurs (no isomorphous substitution)

Relationship between soil pH and positive and negative charges. The negative charges (cation exchange capacity) increase and the positive charges (anion exchange capacity) decrease with increasing soil pH.



Factors influencing CEC

- Concentration and number of ions
- Strength of Complementary ions held on the colloid

$Al^{+3} > Ca^{2+} = Mg^{2+} > K^{+} = NH_4^{+} > Na^{+} > H^{+}$
held tight ---------------------------> easily replaced

- Type of colloids (organic matter, 2:1 or 1:1 type clays; surface area)

  - **Kaolinite: 3 – 15**
  - **Montmorillonite: 100 – 150**
  - **Fe/ Al oxides: 3**
  - **Organic matter (humus) : 150 – 250**
  - **Amorphous minerals: 5 - 350**

- **Also influenced by soil pH because H^{+} is the most active ion in cation replacement**

Factors influencing Cation Exchange Capacity

Organic Amendments

- Organic matter

Excessive Irrigation

- Acidification

Burning of plant residue

- Change in mineralogy
- Organic matter content
- Fertilizer Application

Liming increases CEC

- Deprotonation of charged sites on oxides, hydroxides
- Carboxylic or phenolic OH groups

Significance of CEC in soil management

- Soils with high CEC have more of negative charge, adsorb, retain more cations, water and hence more fertile with lesser deficiencies of Mg, K and other nutrients
- High CEC soils require less frequent irrigations because of greater water adsorption/retention
- Split application of fertilizers and soil amendments required in low CEC soils to prevent leaching loss of nutrients
- Incorporation of fertilizers/amendments applied needed to prevent run off loss due to slow infiltration rate
- Sandy soils with low CEC tend to acidify faster due to leaching of base cations
- High CEC soils require more lime rates as compared to lower CEC to attain optimum pH
- Frequency of lime application more in low CEC soils

Selected cations and anions commonly adsorbed to soils colloids and importance in plant nutrition and environmental quality

Cation	*Formula*	*Comments*	*Anion*	*Formula*	*Comments*
Ammonium	NH_4^+	Plant nutrient	Arsenate	AsO_4^{3-}	Toxic to animals
Aluminum	Al^{3+} etc.[a]	Toxic to many plants	Borate	$B(OH)_4^-$	Plant nutrient, can be toxic
Calcium*	Ca^{2+}	Plant nutrient	Bicarbonate	HCO_3^-	Toxic in high-pH soils
Cadmium	Cd^{2+}	Toxic pollutant	Carbonate*	CO_3^{2-}	Forms weak acid
Cesium	Cs^+	Radioactive contaminant	Chromate	CrO_4^{2-}	Toxic pollutant
Copper	Cu^{2+}	Plant nutrient, toxic pollutant	Chloride*	Cl^-	Plant nutrient, toxic in large amounts
Hydrogen*	H^+	Causes acidity	Fluoride	Fl^-	Toxic, natural and pollutant
Iron	Fe^{2+}	Plant nutrient	Hydroxyl*	OH^-	Alkalinity factor
Lead	Pb^{2+}	Toxic to animals, plants	Nitrate*	NO_3^-	Plant nutrient, pollutant in water
Magnesium*	Mg^{2+}	Plant nutrient	Molybdate	MoO_4^{2-}	Plant nutrient, can be toxic
Manganese	Mn^{2+}	Plant nutrient	Phosphate	HPO_4^{2-}	Plant nutrient, water pollutant
Nickel	Ni^{2+}	Plant nutrient, toxic pollutant	Selenate	SeO_4^{2-}	Animal nutrient and toxic pollutant
Potassium*	K^+	Plant nutrient	Selenite	SeO_3^{2-}	Animal nutrient and toxic pollutant
Sodium*	Na^+	Used by animals, some plants, can damage soil	Silicate*	SiO_4^{4-}	Mineral weathering product, used by plants
Strontium	Sr^{2+}	Radioactive contaminant	Sulfate*	SO_4^{2-}	Plant nutrient
Zinc	Zn^{2+}	Plant nutrient, toxic pollutant	Sulfide	S^{2-}	In anaerobic soils, forms acid on oxidation

[a] Important aluminum cations include Al^{3+}, $AlOH^{2+}$, and $Al(OH)_2^+$.

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Anion Exchange

- Mostly observed in sesquioxide clays with a net positive charge
- Anion exchange is less common in soils and there is heavy loss of anions through leaching
- Anions Nitrate, chloride, carbonate, bicarbonates, sulphate etc are adsorbed and retained by anion exchange
- Anion exchange increases with decrease in pH

References

Fundamentals of Soil Science, Revised: February 2012, Indian Society of Soil Science

The Nature and Properties of Soils (2016), Nyle C. Brady, Ray R. Weil

Dreamstime .com

ScienceDirect.com

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