Soil colloids: Properties, nature, types and significance. Layer silicates clays: Genesis and sources of charges

Soil Colloids

The clay fraction of the soil contains particles less than 0.002 mm in size. Particles less than 0.001 mm size possess colloidal properties and are known as **soil colloids.** The word colloid is derived from Greek word colla meaning glue, and eidos meaning like.

General Properties of Soil Colloids
1. Size:
2. Surface area:
3. Surface charges:

The negative electrical charge on clays comes from
  i) Ionizable hydrogen ions:
  ii) Isomorphous substitution:
  iii) Broken bonds

4. Adsorption of cations:
5. Adsorption of water:
6. Cohesion
7. Adhesion:.
8. Swelling and shrinkage:
9. Dispersion and flocculation:
10. Brownian movement:.
11. Non permeability

General Properties of Soil Colloids

1. Size: The most important common property of inorganic and organic colloids is their extremely small size. They are too small to be seen with an ordinary light microscope. Only with an electron microscope they can be seen. Most are smaller than 2 micrometers in diameter.

2. Surface area: Because of their small size, all soil colloids expose a large external surface per unit mass. The external surface area of 1 g of colloidal clay is at least 1000 times that of 1 g of coarse sand. Some colloids, especially certain silicate clays have extensive internal surfaces as well. These internal surfaces occur between plate like crystal units that make up each particle and often greatly exceed the external surface area. The total surface area of soil colloids ranges from 10 m2/g for clays with only external surfaces to more than 800 m2/g for clays with extensive internal surfaces. The colloid surface area in the upper 15 cm of a hectare of a clay soil could be as high 700,000 km2/g

3. Surface charges: Soil colloidal surfaces, both external and internal characteristically carry negative and/or positive charges. For most soil colloids, electro negative charges predominate. Soil colloids both organic and inorganic when suspended in water, carry a negative electric charge. When an electric current is passed through a suspension of soil colloidal particles they migrate to anode, the positive electrode indicating that they carry a negative charge. The magnitude of the charge is known as zeta potential. The presence and intensity of the particle

charge influence the attraction and repulsion of the particles towards each other, there by influencing both physical and chemical properties.

The negative electrical charge on clays comes from
i) Ionizable hydrogen ions and
ii) Isomorphism substitution.

i) Ionizable hydrogen ions: Ionizable hydrogen ions are hydrogen from hydroxyl ions on clay surfaces. The -Al-OH or -Si-OH portion of the clay ionizes the H and leaves an unneutralized negative charge on the oxygen (-Al-O- or - Si-O). The extent of ionized hydrogen depends on solution pH; more ionization occurs in more alkaline (basic) solutions.

ii) Isomorphous substitution: The second source of charge on clay particles is due to the substitution of one ion for another of similar size and often with lower positive valence. In clay structures, certain ions fit into certain mineral lattice sites because of their convenient size and charge. Dominantly, clays have Si^{4+} in tetrahedral sites and Al^{3+} in octahedral sites. Other ions present in large amounts during clay crystallization can replace some of the Al^{3+} and Si^{4+} cations. Substitutions that are common are the Si^{4+} replaced by Al^{3+}, and even more extensive replacement of Al^{3+} by one or more of these: Fe^{3+}, Fe^{2+}, Mg^{2+} or Zn^{2+} Since the total negative charge from the anions (the oxygen) remains unchanged, the lower positive charge because of substitution results in an excess negative charge at that location in the structure.

4. Adsorption of cations: As soil colloids possess negative charge they attract the ions of an opposite charge to the colloidal surfaces. They attract hundreds of positively charged ions or cation such as H^+, Al^{3+} Ca^{2+} , and Mg^{2+}. This gives rise to an ionic double layer.

The process, called Isomorphous substitution and the colloidal particle constitutes the inner ionic layer, being essentially huge anions; with both, external and internal layers that are negative in charge. The outer layer is made up of a swarm of rather loosely held (adsorbed) cations attracted to the negatively charged surfaces. Thus a colloidal particle is accompanied by a swarm of cations that are adsorbed or held on the particle surfaces.

5. Adsorption of water: In addition to the adsorbed cations, a large number of water molecules are associated with soil colloidal particles. Some are attracted to the adsorbed cations, each of which is hydrated; others are held in the internal surfaces of the colloidal particles. These water molecules play a critical role in determining both the physical and chemical properties of soil.

5. Cohesion: Cohesion is the phenomenon of sticking together of colloidal particles that are of similar nature. Cohesion indicates the tendency of clay particles to stick together. This tendency is primarily due to the attraction of the clay particles for the water molecules held between them. When colloidal substances are wetted, water first adheres to the particles and then brings about cohesion between two or more adjacent colloidal particles.

6. Adhesion: Adhesion refers to the phenomenon of colloidal particles sticking to other substances. It is the sticking of colloidal materials to the surface of any other body or substance with which it comes in contact.

7. Swelling and shrinkage: Some clay (soil colloids) such as smectites swell when wet and shrink when dry. After a prolonged dry spell, soils high in smectites (e.g. Vertisols) often are

crises-crossed by wide, deep cracks, which at first allow rain to penetrate rapidly. Later, because of swelling, such soil is likely to close up and become much more impervious than one dominated by kaolinite, chlorite, or fine grained micas. Vermiculite is intermediate in its swelling and shrinking characteristics.

8. Dispersion and flocculation: As long as the colloidal particles remain charged, they repel each other and the suspension remains stable. If on any account they loose their charge, or if the magnitude of the charge is reduced, the particles coalesce, form flocs or loose aggregates, and settle out. This phenomenon of coalescence and formation of flocs is known as flocculation. The reverse process of the breaking up of flocs into individual particles is known as deflocculation or dispersion.

9. Brownian movement: When a suspension of colloidal particles is examined under a microscope the particles seem to oscillate. The oscillation is due to the collision of colloidal particles or molecules with those of the liquid in which they are suspended. Soil colloidal particles with those of water in which they are suspended are always in a constant state of motion. The smaller the particle, the more rapid is its movement.

10. Non permeability: Colloids, as opposed to crystalloid, are unable to pass through a semi-permeable membrane. Even though the colloidal particles are extremely small, they are bigger than molecules of crystalloid dissolved in water. The membrane allows the passage of water and of the dissolved substance through its pores, but retains the colloidal particles.

Types of Soil Colloids
   There are four major types of colloids present in soil
1. Layer silicate clays
2. Iron and aluminum oxide clays (sesquioxide clays)
3. Allophane and associated amorphous clays
4. Humus.
        Layer silicate clays, iron and aluminum oxide clays, allophane and associated amorphous clays are *inorganic colloids* while humus is an *organic colloid*.
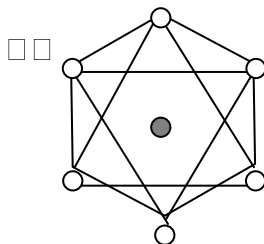
1.   Layer silicate clays

        Phyllosilicates (Gr. Phyllon, leaf) are comprised of two kinds of horizontal sheets, one dominated by silicon and other by aluminum and/or magnesium. The basic structure of silica tretrahedron and aluminum octahedran is explained below.
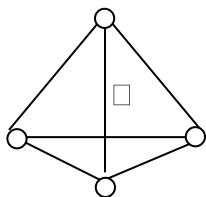
1.Silica Tretrahedron   2. Alumina-Magnesia Octahedron


□ Silicon◯   oxygen   ⬤Aluminium or magnesium

Both inorganic and organic colloids are intimately mixed with other soil solids. Thus, the bulk of the soil solids are essentially inert and the majority of the soil's physical and chemical character is a result of the colloids present.

Inorganic soil colloids:

- Layer aluminosilicates which consist of thin layers of repeated structural units. These are the dominant clay minerals in temperate regions.
- Amorphous aluminosilicates that form from volcanic ash
- Al and Fe oxides which may be crystalline or amorphous. These are common in subtropical and tropical regions.
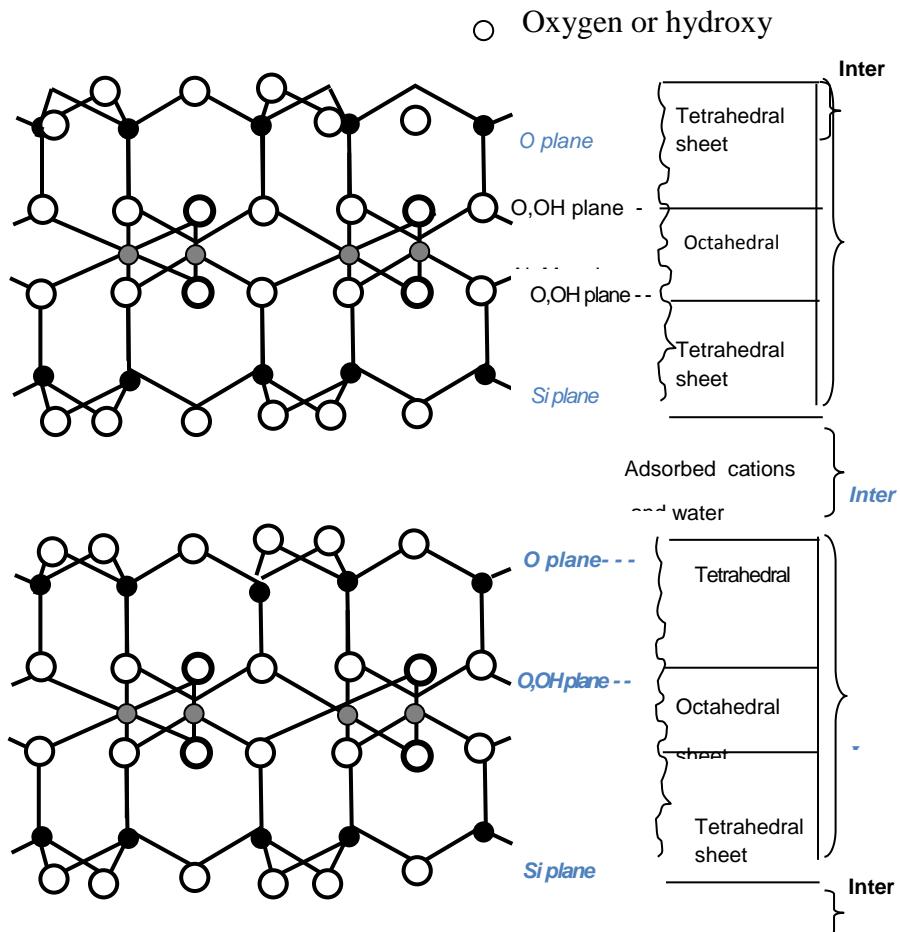
Basic molecular and structural components of silicate clays (crystal or micelle).

Organic colloids:

- Include highly decomposed organic matter generally called humus.
- Organic colloids are more reactive chemically and generally have a greater influence on soil properties per unit weight than the inorganic colloids.
- The negative charges of humus are associated with partially dissociated enolic (-OH), carboxyl (-COOH), and phenolic groups; these groups in turn are associated with central units of varying size and complexity.
- The complex humus colloid is composed of C,H and O rather than Al, Si and O like the silicate clays.

- Humus is amorphous and its chemical and physical characteristics are not well defined. The organic colloidal particles vary in size, but they may be at least as small as the silicate clay particles.
- They are not stable as clay and thus more dynamic, being formed and destroyed more rapidly than clay.

Layer Aluminosilicates: The most important silicate clays are known as phyllosilicate (Gr. Phullon, leaf) because of their leaf or plate like structure.
- Two types of structural units are basic in the layer lattice structure of most clay minerals that are tetrahedral and octahedral unit.

Silica tetrahedron:

- The tetrahedral unit is SiO^{4-} in which silicon ion is equidistant from the four oxygen anions. It is called silica tetrahedron because of its four sided configuration.
- Many tetrahedra are linked together horizontally by shared oxygen anions gives a tetrahedral sheet.

Alumina octahedron:

- Aluminium and/or magnesium ions are the key cations surrounded by six oxygen atoms or hydroxyl group giving an eight sided building block termed octahedron
- Many octahedra are linked horizontally to form an octahedral sheet. An aluminum-dominated sheet is known as a di-octahedral sheet, whereas one dominated by magnesium is called a tri-octahedral sheet.
- The distinction is due to the fact that two aluminum ions in a di-octahedral sheet satisfy the same negative charge from surrounding oxygen and hydroxyls as three magnesium ions in a tri-octahedral sheet.
- The tetrahedral and octahedral sheets are the fundamental structural units of silicate clays. These different sheets are bonded together to form crystalline units composed of alternating sheets of Si tetrahedra and Al (or Mg) octahedra.
- The Si tetrahedral sheet is chemically bonded to the one or two adjacent Al (or Mg) octahedral sheet(s) via shared oxygen atoms.
- The specific nature and combination of sheets, called layers, vary from one type of clay to another and control the physical and chemical properties of each clay.

Types of layer Silicates

- On the basis of the number and arrangement of tetrahedral (silica) and octahedral (alumina-magnesia) sheets contained in the crystal units or layers, silicate clays are classified into three different groups:

(a) 1 :1 Type clay minerals
(b) 2:1 Type clay minerals
(c) 2: 1: 1 (or) 2:2 Type clay minerals

a)1:1 layer Silicates:

- In soils, kaolinite group is the most prominent 1:1 clay mineral, which includes kaolinite, hallosite, nacrite and dickite.
- These have one Si tetrahedral and one Al octahedral sheet per crystalline unit
- The tetrahedral and octahedral sheets in a layer of a kaolinite crystal are held together tightly by oxygen anions, which are mutually shared by the silicon and aluminum cations in their respective sheets.
- These layers, in turn, are held together by hydrogen bonding. Consequently, the structure is fixed and no expansion ordinarily occurs between layers when the clay is wetted.
- Cations and water do not enter between the structural layers of a 1:1 type mineral particle. The effective surface of kaolinite is restricted to its outer faces or to its external surface area.
- Kaolinite crystals usually are hexagonal in shape.
- Because of the strong binding forces between their structural layers, kaolinite particles are not readily broken down into extremely thin plates.
- Kaolinite exhibits very little plasticity, cohesion, shrinkage, and swelling.

b) 2:1layer Silicates

- The crystal units (layers) of these minerals are characterized by an octahedral sheet sandwiched between two tetrahedral sheets. Three general groups have this basic crystal structure. Two of them, *smectite* and *vermiculite* are expanding type minerals, while the third *mica group* (*illite*), is non-expanding

Expanding Minerals:

- The smectite group of minerals includes *montmorillonite,beidellite,nontronite* and *saponite*
- This group of minerals are noted for their interlayer expansion and swelling when wetted. The water enters the interlayer space and forces the layers apart. Montmorillonite is the most prominent member of this group in soils.
- The flake-like crystals of smectite are composed of an expanding lattice 2:1 type clay mineral. Each layer is made up of an octahedral sheet sandwiched between two tetrahedral (silica) sheets.
- The layers are loosely held together by very weak oxygen – oxygen and cation-to-oxygen linkages.
- Exchangeable cations and associated water molecules are attracted between layers causing expansion of the crystal lattice.
- The internal surface exceeds the external surface of clay crystal. In montmorillonite, magnesium replaces replaced aluminum in some sites of octahedral sheet.
- Likewise, some silicon atoms in the tetrahedral sheet may be replaced by aluminum. These substitutions give rise to a negative charge.
- These minerals show high cation exchange capacity, swelling and shrinkage properties. Wide cracks commonly form in smectite dominated soils (e.g., Vertisols) when dried. The dry aggregates or clods are very hard, making such soils difficult to till.

Vermiculites: Vermiculites have structural characteristics similar to those of montmorillonite in that an octahedral sheet is found between two tetrahedral sheets.

- In the tetrahedral sheet of most vermiculite, aluminum is substituted by silicon in most of the sites. This accounts for most of the very high net negative charge associated with these minerals.
- Water molecules, along with magnesium and other ions, are strongly adsorbed in the interlayer space of vermiculites. They act primarily as bridges holding the units together rather than as wedges driving the units apart.
- The degree of swelling is less for vermiculites than for smectite. Therefore, vermiculites are considered *limited expansion* clay minerals, expanding more than kaolinite but much less than the smectite.
- The cation exchange capacity (CEC) of vermiculite is higher than all other silicate clays because of very high negative charge in the tetrahedral sheet. Vermiculite crystals are larger than those of the smectite but much smaller than those of kaolinite.

Non-expanding minerals:

- Micas are the type of minerals in this group-*muscovite* and *biotite.*
- Weathered minerals similar in structure to these micas are found in the clay fraction of soils.They are called *fine-grained micas* or *illite*.
- The basic structure of illite or micaceous mineral is similar to that of montmorillonite. However, the particles are much larger than those of the smectite.
- Some of the silicon ions are replaced by aluminium ions in the tetrahedral sheet (20%). This results in a net negative charge in the tetrahedral sheet which is compensated by potassium ions
- The potassium as a binding agent, preventing expansion of the crystal. Hence, fine-grained micas are quite non-expanding.
- The properties such as hydration, cation adsorption, swelling, shrinkage and plasticity are less intense in fine grained micas.The specific surface area varies from 70 to 100 $m^2 g^{-1}$, about one eighth that for the smectite.

c) 2:1:1 layer Silicates :

- This silicate group is represented by **chlorites**. Chlorites are basically iron magnesium silicates with some aluminum present.
- The crystal unit is composed of one 2:1unit like mica or montmorillonite and one octahedral unit, Brucite, $Mg_3(OH)_6$ layer.
- Mg dominates the octahedral sheet in the 2:1 unit.
- There is no water adsorption between the chlorite crystal units, which accounts for the non expanding nature of this mineral.

Mixed and interstratified layers:

- Specific groups of clay minerals do not occur independently of one another. In a given soil, it is common to find several clay minerals in an intimate mixture.
- Furthermore, some mineral colloids have properties and composition intermediate between those of any two minerals.

- Such minerals are termed *mixed layer* or *interstratified* because the individual layers within a given crystal may be of more than one type.
- Terms such as "chlorite-vermiculite" and "mica - smectite" are used to describe mixed layer minerals.

Comparative properties of silicate clay minerals

Property	Kaolinite	Monotmorillonite	Vermiculite	Mica or Illite
Structure size (microns)	1:1 lattice 0.5 to 5.0	2:1 0.01 to 1.0	2:1 0.1to5.0	2:1 0.1 to 2.0
Shape	Hexagonal crystals	Irregular flakes	Plates; flakes	Flakes
Specific surface (m^2/g)	5-20	700-800	500-600	100-200
External and internal surface	Low	Very High	High	Medium
Cohesion and plasticity swelling capacity	Low	High	High	Medium
Cation exchange capacity (cmol (P^+) kg^{-1})	3-15	80-120	100-180	15-40
Anion exchange capacity	High	Low	Low	Medium

Oxides and hydroxides of Iron and Aluminum (sesquioxide clays):

- The most common examples of iron and aluminum oxides are gibbsite ($Al_2O_3.3H_2O$) and geothite ($Fe_2O_3.H_2O$). Less is known about these clays than about the layer silicates.
- Under conditions of extensive leaching by rainfall and long time intensive weathering of minerals in humid warm climates, most of the silica and alumina in primary minerals are dissolved and slowly leached away. The remnant materials, which have lower solubility are called sesquioxides.
- Sesquioxides (metal oxides) are mixtures of aluminum hydroxide, Al $(OH)_3$, and iron oxide, Fe_2O_3, or iron hydroxide, $Fe(OH)_3$.
- Some of these clays have crystalline structure.
- They carry a small negative charge at high pH values which attract cations. However, their capacity to adsorb cations is less than kaolinite.
- These clays do not swell, not sticky and have high phosphorus adsorption capacity.

Allophane and other amorphous minerals:

- These are amorphous, hydrated alumino-silicate. Typically, these clays occur where large amount of weathered products existed. These clays are common in soils forming from volcanic ash (e.g. Allophane). Its approximate general composition is $Al_2O_3.2SiO_2.H_2O$.

These clays have high anion exchange capacity or even high cation exchange capacity.