Chapter 8: Soil Colloidal Fraction
Main Objectives:

1. Understand basic types of soil colloids and their properties.

2. Comprehend the basic mechanisms responsible for soil cation and anion exchange and their importance.
Key terms and Concepts:

1. 1:1 lattice clay, 2:1 lattice clay
2. Isomorphous substitution
3. Cation and anion exchange
4. Cation exchange capacity
1. **Colloidal fraction**

A. **General Statement:** Most clay fraction and humus are referred to collectively as the colloidal fraction, because of their small size and colloid-like properties. Some of the important functional properties of these colloids may include high specific surface area, electrostatic charges (cations and anions); adsorption of water, thereby the overall chemical and physical properties of the soil.

B. **Origins:** Mineral colloids came from various stages of weathering of primary materials or inherited from sediments of old clay formation; whereas humus came from various stages of organic residue decomposition.
Figure 8.1  Simplified representation of a silicate clay crystal (micelle), its complement of adsorbed cations, and ions in the surrounding soil solution. The enlarged view (right) shows that the clay comprises sheetlike layers with both external and internal negatively charged surfaces. The negatively charged micelle acts as a huge anion and a swarm of positively charged cations is adsorbed to the micelle because of attraction between charges of opposite sign. Cation concentration decreases with distance from the clay. Anions (such as Cl\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, and SO\textsubscript{4}\textsuperscript{2−}), which are repulsed by the negative charges, can be found in the bulk soil solution farthest from the clay (far right). Some clays (not shown) also exhibit positive charges that can attract anions.
C. Types of Colloids (See Table 8.1):

**Amorphous** such as allophane and humus

**Crystalline:**

(1) **1:1 lattice** such as kaolinite and serpentine (no expansion, low CEC);

(2) **2:1 lattice**, the smectite group such as montmorillonite (large expansion, high CEC), illite (or hydrous mica, K+ holding, moderate expansion and CEC), vermiculite (mg+ holding illite, moderate swelling, high CEC);

(3) **2:2 lattice**, the chlorites (tight holding of magnesium hydroxide layer, no expansion, low CEC);

(4) **Sesquioxides**, dominant clay for Oxisols, no expansion, low CEC, often form stable aggregates like sands, "fix" more P.
Figure 8.2 Crystals of three silicate clay minerals and a photomicrograph of humic acid found in soils, (a) kaolinite from Illinois (note hexagonal crystal at upper right), (b) a fine-grained mica from Wisconsin, (c) montmorillonite (a smectite group mineral) from Wyoming, and (d) fulvic acid (a humic acid) from Georgia. [(a)–(c) Courtesy of Dr. Bruce F. Bohor, Illinois State Geological Survey; (d) from Dr. Kim H. Tan, University of Georgia; used with permission of Soil Science Society of America]
## Table 8.1
**Major Properties of Selected Soil Colloids**

<table>
<thead>
<tr>
<th>Colloid</th>
<th>Type</th>
<th>Size, μm</th>
<th>Shape</th>
<th>Surface area, m²/g</th>
<th>Interlayer spacing, nm</th>
<th>Net charge, cmol_c/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>External</td>
<td>Internal</td>
<td></td>
</tr>
<tr>
<td>Smectite</td>
<td>2:1 silicate</td>
<td>0.01–1.0</td>
<td>Flakes</td>
<td>80–150</td>
<td>550–650</td>
<td>1.0–2.0</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>2:1 silicate</td>
<td>0.1–0.5</td>
<td>Plates, flakes</td>
<td>70–120</td>
<td>600–700</td>
<td>1.0–1.5</td>
</tr>
<tr>
<td>Fine mica</td>
<td>2:1 silicate</td>
<td>0.2–2.0</td>
<td>Flakes</td>
<td>70–175</td>
<td>—</td>
<td>1.0</td>
</tr>
<tr>
<td>Chlorite</td>
<td>2:1 silicate</td>
<td>0.1–2.0</td>
<td>Variable</td>
<td>70–100</td>
<td>—</td>
<td>1.41</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1:1 silicate</td>
<td>0.1–5.0</td>
<td>Hexagonal crystals</td>
<td>5–30</td>
<td>—</td>
<td>0.72</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>Al-oxide</td>
<td>&lt;0.1</td>
<td>Hexagonal crystals</td>
<td>80–200</td>
<td>—</td>
<td>0.48</td>
</tr>
<tr>
<td>Goethite</td>
<td>Fe-oxide</td>
<td>&lt;0.1</td>
<td>Variable</td>
<td>100–300</td>
<td>—</td>
<td>0.42</td>
</tr>
<tr>
<td>Allophane &amp;</td>
<td>Noncrystalline</td>
<td>&lt;0.1</td>
<td>Hollow spheres or</td>
<td>100–1000</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Imogolite</td>
<td>silicates</td>
<td></td>
<td>tubes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Humus</td>
<td>Organic</td>
<td>0.1–1.0</td>
<td>Amorphous</td>
<td>Variable</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

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*a* From the top of one layer to the next similar layer, 1 nm = 10⁻⁹ m = 10 Å.

*b* Centimoles of unbalanced or net charge per kilogram of colloid (cmol_c/kg), a measure of ion exchange capacity (see Section 8.9).

*c* It is very difficult to determine the surface area of organic matter. Different procedures give values ranging from 20 to 800 m²/g.
Kaolinite (1:1)
Nonexpanding (no swelling)

Sillimanite (2:1)
Expanding (max. swelling)

Water molecules, Mg$^{2+}$ and other ions

Vermiculite (2:1)
Expanding (some swelling)

Fine-grained mica (2:1)
Nonexpanding (min. swelling)

Chlorite (2:1)
Nonexpanding (min. swelling)
2. Electrostatic Charges on Soil Colloids

Two major sources of charges on soil colloids:
1. hydroxyls and other functional groups;
2. the charge imbalance caused by the **isomorphous substitution** in some clay crystal structures.

In mineralogy, the process by which one element fills a structural position “usually” filled by another of similar size is called **isomorphous substitution**.
Figure 8.4  Simplified diagrams of octahedral sheets in a silicate mineral illustrating the effect of isomorphous substitution on the net charge. Note that for each oxygen atom, one of the two 2 charges is balanced by a + charge from either a H+ (making a hydroxyl group) or a Si atom in the tetrahedral sheet (not shown, but represented by a +). During the crystallization of the octahedral sheet shown on the right, a Mg2+ atom occupied one of the positions normally occupied by an Al3+ atom, thus leaving a 21 net charge on the sheet. Such net negative charges in the crystal can be balanced by cations from the soil solution adsorbed to the crystal surface.
How pH-dependent charges develop at the broken edge of a kaolinite crystal. Three sources of net negative surface charge at a high pH are illustrated (left): (A) One (21) charge from octahedral oxygen that has lost its H+ ion by dissociation (the H broke away from the surface hydroxyl group and escaped into the soil solution). Note that such dissociation can generate negative charges all along the surface hydroxyl plane, not just at a broken edge. (B) One half (2 1⁄2) charge from each octahedral oxygen that would normally be sharing its electrons with a second aluminum. (C) One (2:1) charge from a tetrahedral oxygen atom that would normally be balanced by bonding to another silicon if it were not at the broken edge. The middle and right diagrams show the effect of acidification (lowering the pH), which increases the activity of H+ ions in the soil solution. As more H+ ions bond to the oxygen atoms at the clay surface, the 1+ charge of each H+ ion either just balances a 21 charge on a tetrahedral oxygen or more than balances a 2 1⁄2 charge on an octahedral oxygen (middle). At the lowest pH shown (right), all of the edge oxygens have an associated H+ ion, giving rise to a net positive charge on the crystal. These mechanisms of charge generation are similar to those illustrated for humus in Figure 8.9.
3. Soil Cation and Anion Exchange

Surfaces of clay minerals and humus usually have negative charges due to either isomorphous substitution, or weak organic acids (COOH groups). These charges attract or hold positively charged ions (CATIONS) in equilibrium with other cations in solution. The replacement of adsorbed cations by other cations in solution is called cation exchange.

Cation exchange is controlled by (1) type of cations, and (2) their concentration relative to concentrations of other cations in the solution and on the exchangeable surfaces. All cation exchange processes are reversible reactions, and take place following the principle of charge equivalence.
Figure 8.9 A simplified diagram showing the principal chemical groups responsible for the high amount of negative charge on humus colloids. The three groups highlighted all include—OH that can lose its hydrogen ion by dissociation and thus become negatively charged. Note that the alcoholic, phenolic, and carboxylic groups on the right side of the diagram are shown in their disassociated state, while those on the left side still have their associated hydrogen ions. Note also that association with a second hydrogen ion causes a site to exhibit a net positive charge.
Types of Cations:

The strength of cation adsorption increases as (1) the charge of the cation increases; and as (2) the radius of the hydrated cation decreases:

\[ \text{Na}^+ < \text{NH}_4^+ = \text{K}^+ < \text{Cs}^+ < \text{Fe}^{2+} < \text{Zn}^{2+} < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Fe}^{3+} < \text{Al}^{3+} \]

**Cation Exchange Capacity (CEC)** is the total quantity of exchangeable cation sites (mole of charge) per unit weight of dry soil, often expressed in cmolc/kg

(1 cmolc/kg = 1 milliequivalent /100g).

Importance of CEC:

- Nutrients (\(\text{NH}_4^+, \text{K}^+, \text{Ca}^{2+}\), etc)
- Acidity/alkalinity
- Purifying water by cation exchange (e.g., removal of \(\text{Pb}^{2+}\), \(\text{Zn}^{2+}\), \(\text{Ni}^{+2}\), etc)
<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius, nm ($10^{-9}$ m)</th>
<th>Found in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$^{4+}$</td>
<td>0.042</td>
<td></td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>0.051</td>
<td>Tetrahedral sheet</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.064</td>
<td></td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.066</td>
<td>Octahedral sheet</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>0.074</td>
<td></td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.076</td>
<td>Exchange or interlayer sites</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.095</td>
<td></td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.099</td>
<td></td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.133</td>
<td></td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>0.140</td>
<td>Both sheets</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>0.155</td>
<td></td>
</tr>
</tbody>
</table>
Figure 8.14 Ranges in the cation exchange capacities (at pH 7) that are typical of a variety of soils and soil materials. The high CEC of humus shows why this colloid plays such a prominent role in most soils, and especially those high in kaolinite and Fe, Al oxides, clays that have low CECs. Ranges in the cation exchange capacities (at pH 7) that are typical of a variety of soils and soil materials. The high CEC of humus shows why this colloid plays such a prominent role in most soils, and especially those high in kaolinite and Fe, Al oxides, clays that have low CECs.
Anion Exchange:

Anion (SO$_4^{2-}$, H$_2$PO$_4^{2-}$, MoO$_4^{2-}$, etc.) exchange sites are (1) positively charged particles (such as iron oxides), or (2) organic ligands. Anion exchange capacities for most soils are usually low, often in the range of a fraction of one cmolc/kg of soil.

Is cation or anion exchange capacity of a given soil always the same? The answer is ???, depending on???
Figure 8.17

Charges on clay colloids (cmolc/kg)

Cation exchange capacity

Anion exchange capacity

Mostly 2:1 type clays

Mostly 1:1 type clays

Mostly Fe, Al oxide clays

Mild
Intermediate
Strong

Weathering intensity
Figure 8.16 Effect of complementary ions on the availability of a particular exchangeable nutrient cation. The half spheres represent the zones in which the ion oscillates, the more loosely held ions moving within larger zones of oscillation. For simplicity, the water molecules that hydrate each ion are not shown. (Left) H+ ions from the root are more likely to encounter and exchange with loosely held Na+ ions rather than the more tightly held K+ ion. (Right) The likelihood that H+ ions from the root will encounter and exchange with a K+ ion is increased by the inaccessibility of the neighboring tightly held Al3+ ions. The K+ ion on the right colloid is comparatively more vulnerable to being replaced and sent into the soil solution, and is therefore more available for plant uptake or leaching than the K+ ion on the left colloid.
Figure 8.13  Adsorption of ions on a colloid by the formation of outer-sphere and inner-sphere complexes. (1) Water molecules surround diffuse cations and anions (such as the Mg$^{2+}$, Cl$^{-}$, and HPO$_4^{2-}$ shown) in the soil solution. (2) In an outer-sphere complex (such as the adsorbed Ca$^{2+}$ ion shown), water molecules form a bridge between the adsorbed cation and the charged colloid surface. (3) In the case of an inner-sphere complex (such as the adsorbed H$_2$PO$_4^{2-}$ anion shown), no water molecules intervene and the cation or anion binds directly with the metal atom (aluminum in this case) in the colloid structure. Outer-sphere complexes typify easily exchangeable ions that satisfy, in a general way, the net charge on the colloid surface. Inner-sphere complexes, on the other hand, are not easily replaced from the colloid surface, as they represent strong bonding of specific ions to specific sites on the colloid. In this example, all the charges originate with the dissociation of H$^+$ ions from surface hydroxyl groups. Although not shown in this example, permanent charges from isomorphous substitution in the interior structure of a colloid could also cause adsorption of outer-sphere complexes.
Figure 8.18  Adsorption of a toxin called Bt, the insecticidal protein produced by the soil bacteria, Bacillus thuringiensis, and used to protect some crop plants. Highly active clay minerals such as montmorillonite (a member of the smectite group of 2:1 clays) adsorb and bind much larger amounts of these biomolecules than do low-activity clays such as kaolinite (a 1:1 mineral). In both cases, the adsorption reaction was completed in 30 minutes or less. Since only 500 µg of either clay mineral was used in the experiment, it appears that the clays adsorbed an amount of the toxin equal to 30 to 80% of their mass. [Redrawn from Stotzky (2000)]
Discussion:

1. If a farmer is about to apply fertilizers in two different ways, one big dose vs. several small doses, what would you recommend if you know that the CEC of the top soil in the farmer’s field is very low?

2. If you are to choose a kind of nitrogen fertilizer for a flooded rice paddy between sodium nitrate and ammonium sulfate, what will be your choice? Why?

3. If a pollutant is spilled onto three kind of soils by accident, (1) clay loam with kaolinite clay, (2) clay loam with smectite clay, and (3) loamy sand without any measurable clay, which soil will be most likely to have the least possibility for leaching of the pollutant to the ground water?

4. If you want to increase the CEC of your garden soil, what would you do first, second, and last?

5. Given the known high level of CEC in smectite clays, why hasn’t they been used much in potting mix?

6. If a soil consists of sand and organic materials only, does it have much pH-independent charge in its colloidal fraction?

7. If a technician wants to get all exchangeable cations off the soil exchange sites into a solution, what kind of chemical solution will the person use to do the extraction?
Figure 8.10 General conditions for the formation of the various layer silicate clays and oxides of iron and aluminum. Fine-grained micas, chlorite, and vermiculite are formed through rather mild weathering of primary aluminosilicate minerals, whereas kaolinite and oxides of iron and aluminum are products of much more intense weathering. Conditions of intermediate weathering intensity encourage the formation of smectite. In each case silicate clay genesis is accompanied by the removal in solution of such elements as K, Na, Ca, and Mg.