Soil Colloids

General Properties

Soil colloids are minute and, therefore, have a large surface area per unit mass. Soil colloids also carry electrostatic charges (- and +) that are balanced by adsorbed cations and anions.

Four general types

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.

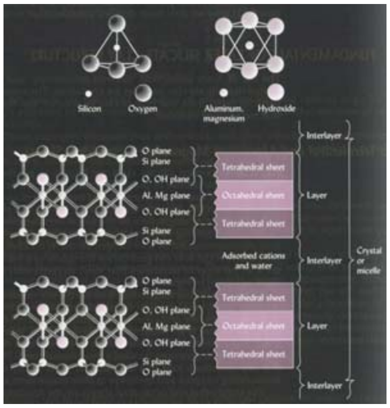
Al and Fe oxides which may be crystalline or amorphous. These are common in subtropical and tropical regions.

Organic (humus) which are 3D non-crystalline polymers present in all soils.

Layer Silicates

General structure

Composed of alternating sheets of Si tetrahedra and Al (or Mg) octahedra. The octahedral sheet is called *dioctahedral* if Al is the central metal atom or *trioctahedral* if it is Mg. The Si tetrahedral sheet is chemically bonded to the one or two adjacent Al (or Mg) octahedral sheet(s) via shared oxygen atoms.



Basic units are the Si tetrahedron and the Al (or Mg) octahedron. Many tetrahedra are linked together to form a Si tetrahedral sheet and many octahedra are similarly linked to form an octahedral sheet. In turn, these different sheets are bonded together to form crystalline units.

Source of electrostatic charge

Isomorphic substitution

Al^{3+} for Si^{4+} in the tetrahedral sheet and Mg^{2+} for Al^{3+} in the *di*octahedral sheet.

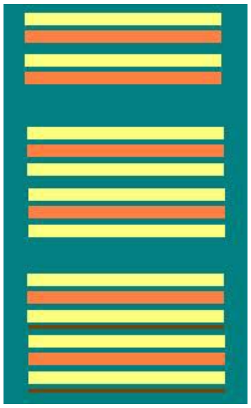
These substitutions occur during formation of the clay mineral and are permanent to the structure. Both lead to net negative charge within the crystal lattice that is balanced by adsorbed cations.

pH-dependent charge

Loss of ionizable H^+ from certain sites on mineral colloids or from certain functional groups in humus leads to negatively charged sites. Protonation of other sites leads to positively charged sites. pH-dependent negative charge increases with increasing pH but pH-dependent positive charge increases with decreasing pH.

Types of layer silicates

1:1
2:1
2:1:1

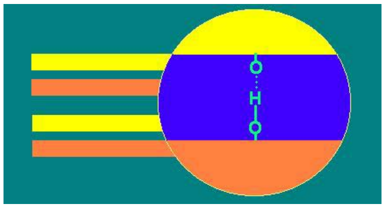


Orientation of tetrahedral and octahedral sheets in 1:1, 2:1 and 2:1:1layer silicates.

1:1 layer silicates

These have one Si tetrahedral and one Al octahedral sheet per crystalline unit.

Adjacent layers (units) are H-bonded together via sharing of H from octahedral -OH with O of the tetrahedral sheet of adjacent layer.



1:1 layer silicates do not expand.

Since adjacent layers are H-bonded together, these minerals are nonexpanding and exhibit only an external surface area. These exhibit little plasticity, cohesion or swelling. Also, there is little isomorphic substitution and the capacity to adsorb cations (cation exchange capacity, CEC) is low.

Kaolinite, halloysite and dickite are 1:1 layer silicates.

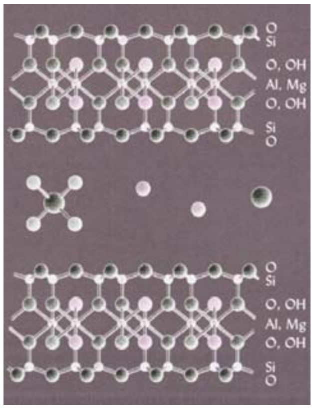
2:1 layer silicates

These have the Al (or Mg) octahedral sheet bonded to Si tetrahedral sheets on top and bottom. Unlike the 1:1 type minerals, certain 2:1 types of minerals may expand by adsorption of water between adjacent 2:1 units. There are three types of 2:1 minerals

Smectite
Vermiculite
Illite

Smectite

The octahedral sheet in smectites is dioctahedral. Adjacent 2:1 units are weakly held together by cations mutually adsorbed by each layer. Accordingly, smectites expand upon adsorption of water between layers and, therefore, exhibit a large total (external + internal) surface area. These minerals are highly plastic, cohesive and swelling. The CEC is large due to a high extent of isomorphic substitution, especially in the dioctahedral sheet.



Sections of two units of a smectite. Water and cations may enter and leave the interlayer region.

Smectites shrink when dry and swell when wet.

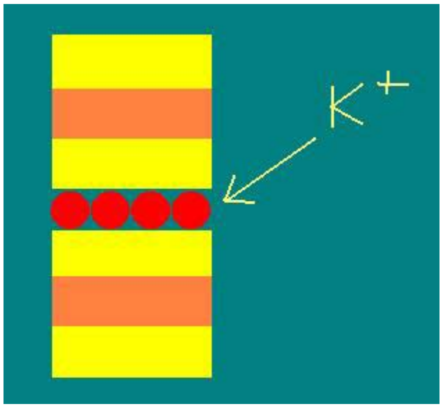
Smectites include montmorillonite, beidellite and nontronite.

Vermiculite

The octahedral sheet may be dioctahedral or trioctahedral. Extensive isomorphic substitution of Al^{3+} for Si^{4+} in the tetrahedral layers leads to an even larger CEC than in the smectites. There is strong affinity for cations (especially adsorbed Mg^{2+}) bridging tetrahedral sheets of adjacent 2:1 layers, leading to limited-expansion.

Illite (or fine-grained mica)

These are chemically altered micas. There is extensive isomorphic substitution in the Si tetrahedral sheet. Due to geometry of the substituted tetrahedral sheet, adsorption of K^+ at interlayer positions holds adjacent 2:1 units tightly together.



Interlayer K holds adjacent units of illite tightly together. It does not expand.

Therefore, illite is nonexpanding and exhibits a much smaller total surface area per unit mass than smectites or vermiculites. The CEC is much less than other 2:1 minerals.

2:1:1 layer silicates

These are also <u>2:1:1</u> type minerals that consist of a Mg octahedral sheet between adjacent 2:1 units. There is little Al in octahedral sheet, Fe and Mg instead. These minerals are nonexpanding and exhibit a fairly low CEC similar to illite.

Formation of Soil Colloids

Layer Silicate Clays

These may develop from chemical alterations of primary minerals such as micas or feldspars. Alternatively, these may precipitate from soil solution containing dissolved Al and SiO_2. The particular layer silicate that precipitates depends on relative stability in the prevailing soil chemical environment. In general, the 2:1 minerals are less stable under hot and wet conditions than are the 1:1 minerals.

Al and Fe oxides

In a general sequence, these minerals are the end products of a sequence leading from primary minerals to 2:1 clays to 1:1 clays. Therefore, the Al and Fe oxides are stable mineral colloids.

Examples include $Al(OH)_3$ (gibbsite), FeOOH (goethite) and Fe_2O_3 (hematite).

Amorphous colloids

Weathering of volcanic ash releases substantial quantities of dissolved Al and SiO_2 which precipitate as amorphous allophane.

Organic colloids

Complex organic molecules formed by microbial transformation of biomolecules.

Distribution of Clay Minerals

Varies within the profile as well as geographically depending upon climate (internal and external) and parent material. The different soil orders, therefore, tend to differ in clay mineralogy.

Order	*Dominant Clay Minerals*
Aridisols	2:1
Vertisols	2:1 smectites
Mollisols	2:1 > 1:1
Alfisols	2:1 = 1:1
Ultisols	1:1 > Al + Fe oxides > 2:1
Spodosols	Al + Fe oxides = 1:1
Oxisols	Al + Fe oxides > 1:1

Note that the mineralogy of the sequence of increasingly weathered soil orders, Alfisols, Ultisols and Oxisols, is reflected in the dominant clay mineralogy of these orders.

More on Electrostatic Charges

Permanent

Negative charges arise from isomorphic substitution in tetrahedral or octahedral layers. Limited positive charges may also arise from substitution of Al^{3+} for Mg^{2+} in trioctahedral sheet of chlorite and some vermiculites.

The difference between permanent negative and positive charges gives net permanent charge

pH-dependent

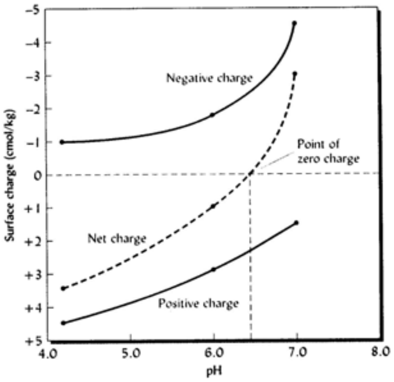
Negative charge

Other than permanent charge, the magnitude and sign of electrostatic charge on soil colloidal particles is pH-dependent. Negative pH-dependent charge arises from the ionization of H from -OH groups on surfaces or at edges of silicate clays and Al and Fe oxides. Ionization of H from -OH, -COOH and aromatic -OH of humic colloids also generates localized negative sites. Neutralization of positive charge associated with adsorbed Al^{3+} (or hydrolyzed species) also effectively increases CEC.

Positive charge

Protonation of -OH to give $-OH_2^+$ leads to positive charges. Common for Al and Fe oxides and 1:1 silicate clays.

Electrostatic charge on the mixture of inorganic and organic colloids in soil includes negative and positive charges.



pH-dependent negative charge increases with increasing pH but pH-dependent positive charge decreases with increasing pH.

Cation Exchange

There is thermodynamic equilibrium between the concentration of cations in solution and adsorbed on soil colloids. The below example show stoichiometric exchange of solution phase K^+ for adsorbed Ca^{2+} (represented as, XCa^{2+}).

$XCa^{2+} + 2K^+ <=> Ca^{2+} + 2XK^+$

The distribution of Ca^{2+} and K^+ between solution and adsorbed phases depends on the exchange selectivity coefficient.

$K = [Ca^{2+}][XK^+]^2 / [XCa^{2+}][K^+]^2$

Note that if the concentration of K^+ in solution were increased, the concentration of adsorbed K^+ would increase such that equilibrium was maintained and visa versa. Also, the colloid typically exhibits greater preference for one of the pair of adsorbed cations. In general, the order of affinity for cation adsorption follows

$Al^{3+} = H^+ > Ca^{2+} > Mg^{2+} > K^+ > Na^+$

In soil there are many such binary cation pairs and binary equilibrium relations. The distribution of the various types of cations between solution and adsorbed phase depends on many different exchange equilibria (one for each different pair of cations) like the one above.

These include cation exchange with acidic cations

$3XCa^{2+} + 2Al^{3+} <=> 3Ca^{2+} + 2XAl^{3+}$

$XCa^{2+} + 2H^+ <=> Ca^{2+} + 2XH^+$

The natural source of solution and adsorbed basic cations is (chemical weathering of) primary minerals. The supply of these primary minerals is limited. On the other hand, there is a continuous supply of H^+ from H_2CO_3 and organic acids. Thus, if there is sufficient rainfall for leaching conditions to prevail, basic cations tend to be depleted and replaced by acidic cations. Therefore, the long-term tendency is toward soil acidification (loss of basic cations). This is aggravated by the fact that exchange equilibria involving H^+ and Al^{3+} favor replacement of basic with acidic cations. Also, coupled this with the weathering of clay minerals to those of lower and lower CECs, increased weathering leads to infertile, acidic soil.

Al^{3+}, Ca^{2+} and H^+ are the commonly adsorbed cations in humid regions. This reflects the long-term leaching loss of basic cations and their replacement by acidic cations. In contrast, Ca^{2+}, Mg^{2+}, K^+ and Na^+ are the commonly adsorbed cations in arid regions.

To raise or maintain fertility that otherwise is reduced by leaching losses of basic cations and the removal of basic cations in crop harvest, fertilizer and lime are added.

Cation Exchange Capacity

CEC is moles of positive charge adsorbed per unit mass of soil. It is expressed in $cmol_c$ / kg. It includes acidic and basic cations.

CEC varies with

Types of colloids present
Amounts of these colloids
pH

Charge at pH 7

Colloid	*Permanent*	*pH-dependent*	*Total*
	----------------- cmol$_c$ kg^{-1} ------------------		
Humus	20	180	200
Vermiculite	140	10	150
Smectite	95	5	100
Illite	24	6	30
Kaolinite	0.4	7.6	8
$Al(OH)_3$	0	4	4

Exchangeable Basic Cations

Sum of adsorbed charges due to Ca^{2+}, Mg^{2+}, K^+ and Na^+ per kg of soil divided by the CEC (cmol$_c$/kg) is called the *percentage base saturation (%BS).* The higher the soil pH, the higher the percentage base saturation and the lower the pH, the lower the percentage base saturation.

Anion Exchange

Analogous to cation exchange

$XSO_4^{2-} + 2Cl^- \ SO_4^{2-} + 2XCl^-$

Common with 1:1 type silicate clays and Al and Fe oxides at low pH.

The sum of exchangeable anions per unit mass of soil is called the *anion exchange capacity (AEC)*. It is expressed in units of cmol$_c$ / kg.

In addition to anion adsorption at positively charged exchange sites, certain anions may also be *specifically adsorbed*, i.e., bonded to the colloid surface rather than simply attracted by electrostatic force. This is common for phosphate, sulfate and molybdate anions.