Chemical properties of soils

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Why do we have to know the chemical properties of soils?

- **History of soil itself.**
- **Holding and supply of nutrients.**
- **Acidification, alkalization, salinization of soils.**
- **Soil pollution (organic, heavy metal pollutions)**
- **Soil improving methods.**

Understanding the soil chemical properties is necessary for the above matter.

Soil mineral components

Their change with soil formation

Igneous rocks

Plutonic rocks

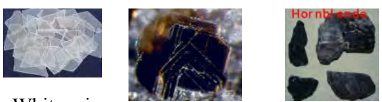
Granites Diorite Gabbro

Volcanic rocks

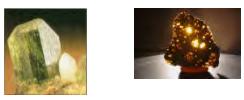
Rhyolite Dacite Andesite Basalt

Rock forming minerals

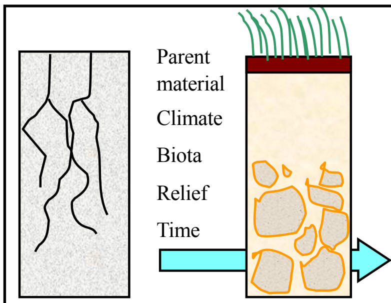
Quarts Orthoclase Microcline Plagioclase



White mica Biotite Amphibole



Pyroxene Olivine



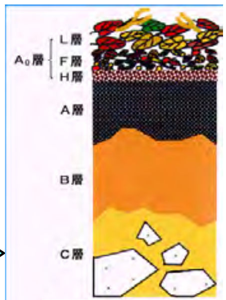


Diagram of soil profile

Weathering of rocks **Tens of thousands years**

Soil formation **Several thousands years**

Formation of soil layers

Formation of clay minera

Accumulation of soil orga matter

Process of soil formation

Formation of clay minerals

Formed through the reaction of rock and water near the surface of earth crust.

- **Diagenesis (deep underground, at high temperature and high pressure)**
- **Hydrothermal activity**

  (Reaction with water at high temperature)
- **Weathering (at normal temperature and pressure)**

Surface area of soil particles and clay

	Maximum radius	Surface area (when packed in 1 m^3)
Gravel	10 mm	157 m^2
Coarse sand	1 mm	1570 m^2
Fine sand	0.1 mm	1.57 ha
Silt	0.01 mm	15.7 ha
Clay	0.001 mm	1.57 km^2
Kaolinite	0.05 – 0.5 μm	75 km^2
Montmorillonite	0.1 – 0.25 μm	1051 km^2
Allophane	< 0.0025 μm	1433 km^2

Specific surface area of soil particles and clay

	Maximum radius	Specific surface area (m^2/g)	CEC (cmol kg^{-1})
Gravel	10 mm	1.15 x 10^{-4}	
Coarse sand	1 mm	11.5 x 10^{-4}	
Fine sand	0.1 mm	115 x 10^{-4}	
Silt	0.01 mm	0.115	
Clay	0.001 mm	1.15	
Kaolinite	0.05 – 0.5 μm	55	2 - 10
Montmorillonite	0.1 – 0.25 μm	770	60 - 100
Allophane	< 0.0025 μm	1050	30 - 135

Colloid

Particles with diameter of 10^{-7} – 10^{-9} m dispersed in air, liquid and solid, and their dispersed state.
Molecular colloid is composed of macro molecules. Particle colloid is composed of solid or liquid fine particles. Micelle colloid is composed of many associated molecules.

0.1~0.001 μm, 100~ 1 nm , 1000~ 10 Å

Soil colloids

- **Clay minerals**
- **Humic substances**

Both are indigenous substances on the surface of earth.

Adsorb cations, anions and organic matter.

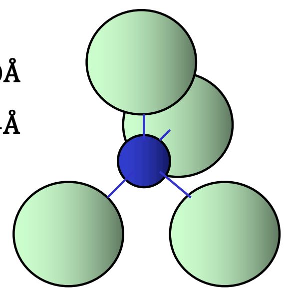
Indispensable for the soil environment suitable for life activity.

Si-O 1.62Å

Ion radius

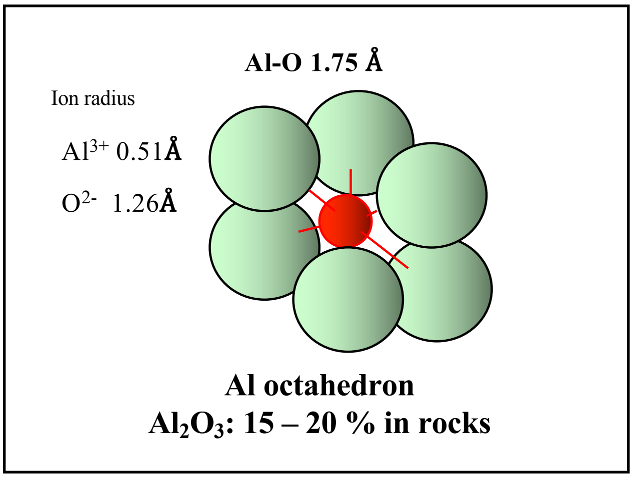
Si^{4+} 0.40Å

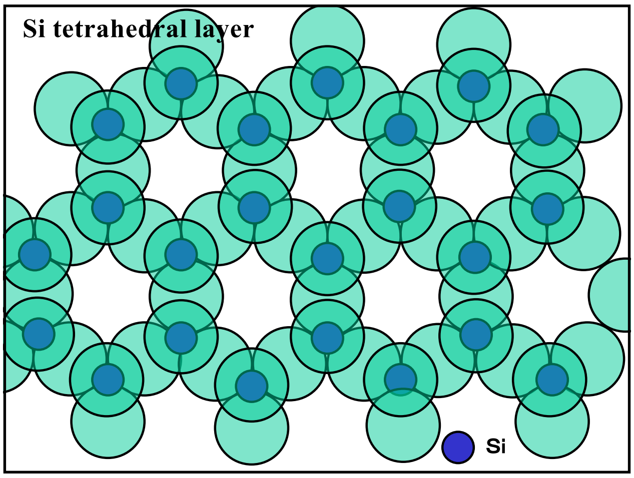
O^{2-} 1.24Å

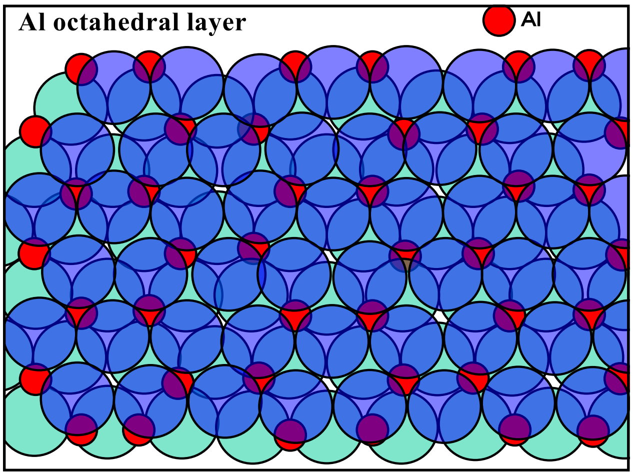


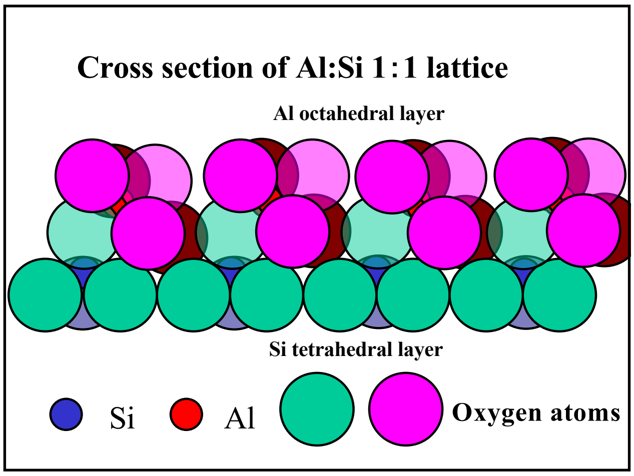
Si tetrahedron

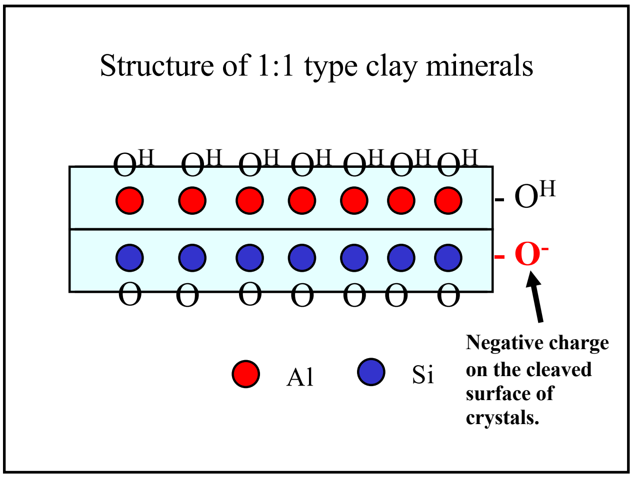
SiO_2: 50 – 60 % in rocks





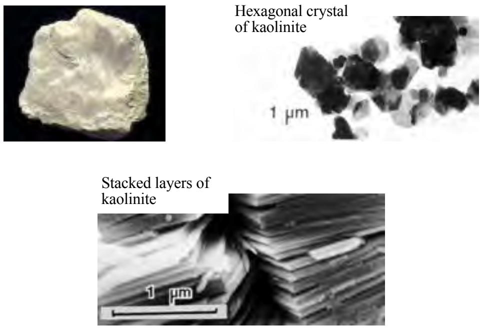






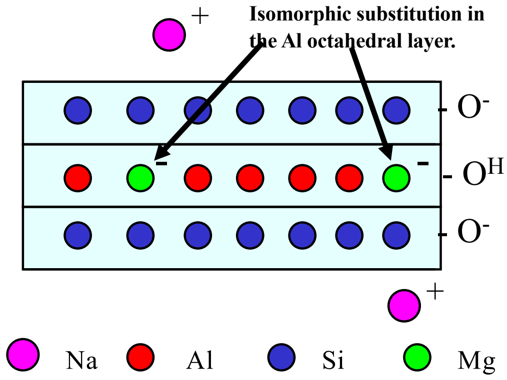
Cause of negative charge in kaolinite

SiO^- on the cleaved surface of crystals.

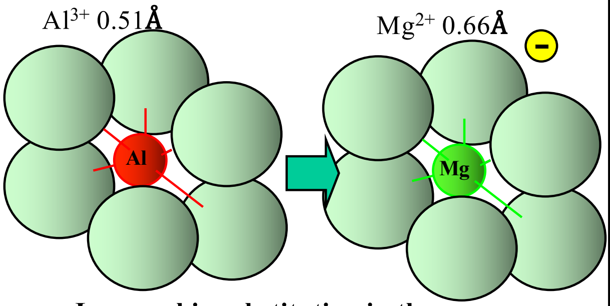


Kaolinite

2:1 type clay minerals (eg. Montmorillonite)

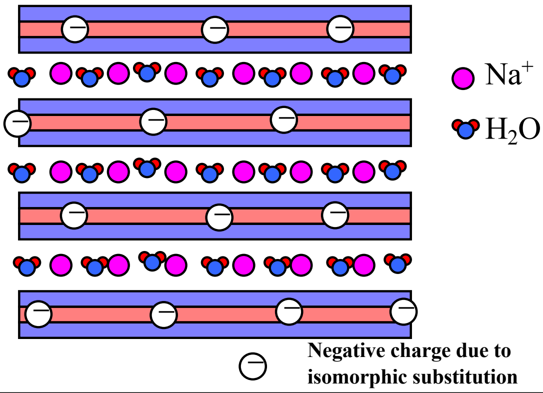


Cause of negative charge in montmorillonite

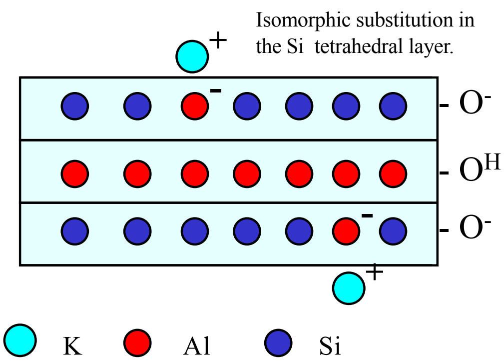


Isomorphic substitution in the Al octahedral layer.

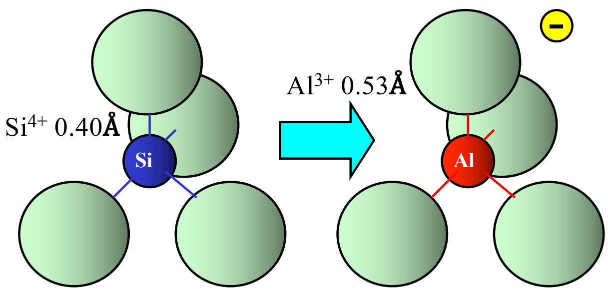
Structure of montmorillonite



2:1 type clay minerals (Illite, Vermiculite)

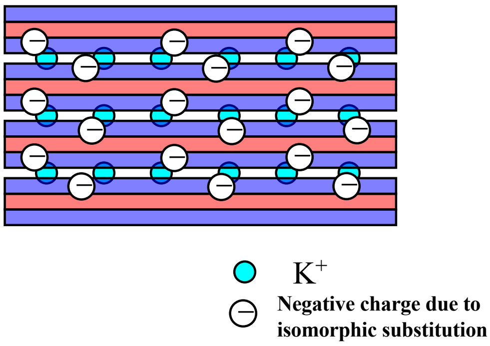


Cause of negative charge in illite.

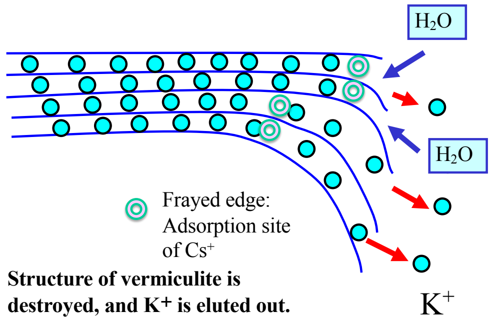


Isomorphic substitution in the Si tetrahedral layer.

Structure of illite (mica type clay minerals)

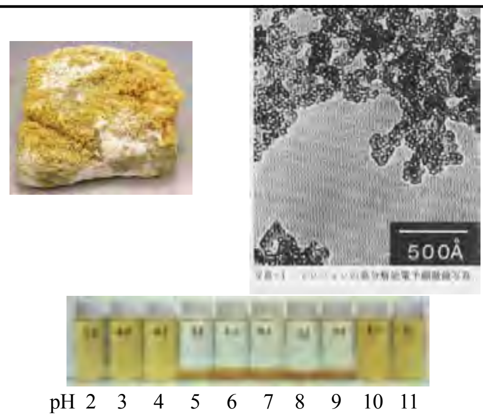


Structure of vermiculite



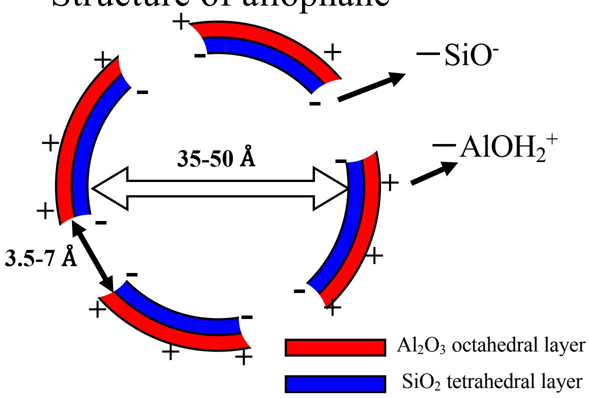
Adsorption of Cs^+ at the frayed edge

- Wedge like site in the loosened part of the stacked layers of vermiculite is called "frayed edge".
- Hydrated cations can not enter this site.
- Unhydrated Cs+ ion just fit this opening (niche).
- Dr. Nakao Atsushi http://www.kpu.ac.jp/cmsfiles/contents/0000002/2873/nakao.pdf



Allophane
(dispersed at both acidic and alkaline pH)

Structure of allophane



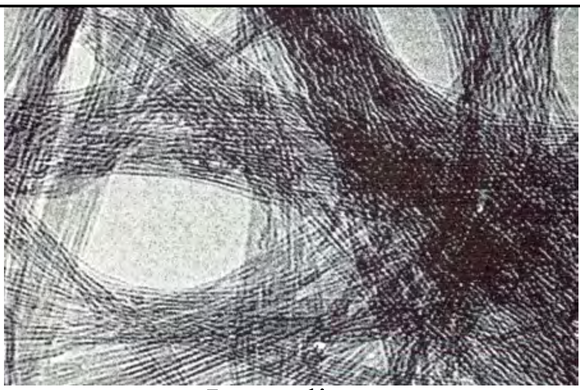
Unit: Ångstrom

- 1 Å = 10^{-10} m = 10^{-1} nm = 10^{-4} µm
- Size of allophane particle:
  35 - 50 Å is 3.5-5.0 / 1000 of 1 µm .
  = 3.5 – 5.0 nm

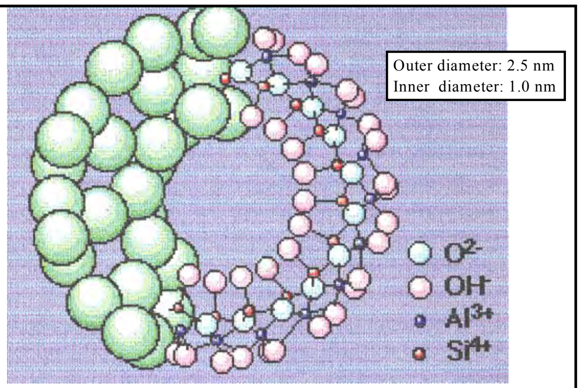
Functions of allophane

- Source of negative and positive charges.
- Adsorption of cations and anions.
- Fixation of phosphate.
- Absorption of moisture.
- Contribution to good physical property of soil.

Allophane and Imogolite
Prof. Yoshinaga, Ehime Univ., Japan



Imogolite
Prof. Yoshinaga, Ehime Univ., Japan



Structural model of Imogolite
(Cracdwick et al. 1972)

Imogolite

Form

Tubular alumino-silicate
Outer diameter: 2.5 nm,
Inner diameter: 1.0 nm
Length: Tens ～ thousands nm

Chemical composition

$SiO_2 \cdot Al_2O_3 \cdot 2H_2O$

Origin

Volcanic glass, amorphous hydrated-oxides

Characteristics of 1:1 type clay minerals

Clay minerals	Form of particles	Specific surface area (m^2/g)	CEC ($cmol\ kg^{-1}$)
Kaolinite	Plate, thin plate	10 - 55	2 - 10
Halloysite (10 Å)	Hollow tubular, spherical	60 - 1100	5 - 40
Halloysite (7 Å)	Hollow tubular	60 - 1100	5 - 15

Characteristics of 2:1 and 2:1:1 type clay minerals

Clay minerals	Form of particles	Specific surface area (m^2/g)	CEC ($cmol\ kg^{-1}$)
2:1 type			
Smectite	Thin film	770	60 - 100
Vermiculite	Plate, thin plate	770	100 - 150
Illite	Plate, thin plate	10 - 55	10 - 15
2:1:1 type			
Chlorite	Plate, thin plate	10 - 55	2 - 10

Characteristics of quasicrystal and amorphous clay minerals

Clay minerals	Form of particles	Specific surface area (m^2/g)	CEC ($cmol\ kg^{-1}$)
quasicrystal			
Imogolite	Hollow tubular	1025	20 - 30
amorphous			
Allophane	Hollow spherical	1050	30 - 135

Negative charges in soil

1) Isomorphic substitution in 2:1 type clay minerals

2) Broken bond SiO^- charges of 1:1 clay minerals and allophane

3) Acidic functional groups of humic substances: COO^-, phenolic O^-

Permanent negative charge

Isomorphic substitution in 2:1 type clay minerals.

Does not change with pH.

Behaves as strong acid.

pH dependent negative charge

1) Broken bond SiO^- in 1:1 clay minerals and allophane.

2) Acidic functional groups of humic substances: COO^-, phenolic O^-

Decreases with the decrease in pH.

Behaves as weak acid. Has pH buffering action.

Function of negative charges in soil.

Holding the cations NH_4^+, Ca^{2+}, Mg^{2+}, K^+, Na^+, etc.

Cation Exchange Capacity（CEC)

Positive charges in soil.

1) $AlOH^{+}$ in the surface of allophane and broken bond charge.

2) Nitrogen functional groups of humic substances.

R- NH_3^{+}, R- $N^{+}H_2CH_3$, etc.

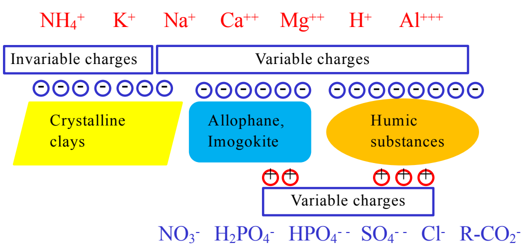
Increases with the decrease in pH.

Function of positive charges in soil.

Holding NO_3^{-}, SO_4^{2-}, PO_4^{3-},

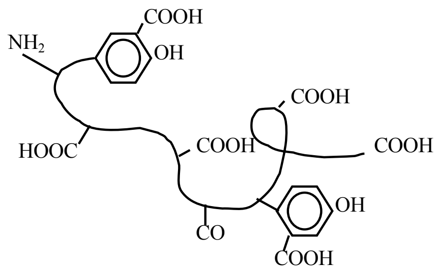
Organic anions, and humic substances.

Positive and negative charges in soil



Clay and humic substances load large amount of variable charges which attract ions in soil.

Simplified model of the structure of humic substances



Molecular weight: Tens of thousands – several million

Characteristics of organic colloids in soil (1)

- **Many charges per unit weight. ---- Becomes the dominant charge.**
- **Dissociation of carboxyl group. ---- Negative charge.**
- **Protonation of amino group. ---- Positive charge.**

Characteristics of organic colloids in soil (2)

- **Variable charge depending on pH.**
- **Keep negative charge even at low pH due to low isoelectric point.**
- **Easily decomposed and lost.**
- **Can be increased by organic matter application.**