





#### pH 2 3 4 5 6 7 8 9 10 11 Allophane (dispersed at both acidic and alkaline pH)



Unit: Ångstrom

•  $1 \text{ Å} = 10^{-10} \text{ m} = 10^{-1} \text{ nm} = 10^{-4} \text{ }\mu\text{m}$ 

• 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



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 (m²/g)	CEC (cmol kg <sup>-1</sup> )
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 (m²/g)	CEC (cmol kg <sup>-1</sup> )
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 <sup>2</sup> /g)	CEC (cmol kg <sup>-1</sup> )
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<sup>-</sup> charges of 1:1 clay minerals and allophane<sup>-</sup>

3) Acidic functional groups of humic substances: COO<sup>-</sup>, phenolic O<sup>-</sup>

Permanent negative charge

Isomorphic substitution in2:1 type clay minerals.Does not change with pH.Behaves as strong acid.

### pH dependent negative charge

1) Broken bond SiO<sup>-</sup> in 1:1 clay minerals and allophane.

2) Acidic functional groups of humic substances: COO<sup>-</sup>, phenolic O<sup>-</sup>

Decreases with the decrease in pH.

Behaves as weak acid. Has pH buffering action.

Function of negative charges in soil.

Holding the cations NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, etc.

Cation Exchange Capacity (CEC)

## Positive charges in soil.

1) AlOH<sup>+</sup> 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



 $NO_3^ H_2PO_4^ HPO_4^{--}$   $SO_4^{--}$   $Cl^ R-CO_2^-$ 

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

### Simplified model of the structure of humic substances



– 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.