

MORPHOLOGY AND CHEMICAL STRUCTURE OF ALLOPHANE

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Abstract

Morphology and chemical structure of allophane which was found in soils developed from volcanic ash soils or pumice, has been established. High resolution electron micrographs have shown that the allophane consists of hollow spheres or polyhedra 3.5-5.0 nm in diameter with a wall thickness estimated to be about 0.7 nm. The wall of the hollow sphere, nano-ball, has some holes (defects) with diameter of 0.3-0.5 nm. Chemical structure of allophane is characterized by short-range order and the predominance of Si-O-Al bondings. Chemical composition of allophane varies ranging in the Si/Al atomic ratio from about 0.5 to 1. Allophane with Si/Al ratio of 0.5 is a fundamental structure which is composed of gibbsite $[Al(OH)_3]$ sheet with SiO_4 tetrahedra attaching on it, and has hollow spherical morphology to locate the SiO_4 tetrahedra inside of the sphere. Allophane with the Si/Al ratio more than 0.5 has some condensed SiO_4 tetrahedra weakly bonded to its structure.

Introduction

The mineral components of organo-mineral complexes in soils are generally better known than the organic components. For example, much is known of the structure, surface properties, and abundance of clay minerals (Brown et al., 1978). Less is known, however, of the nature, properties and abundance of amorphous, inorganic soil constituents, which are particularly reactive with organic matter. Occurrence of amorphous (such as imogolite, and allophane) to cryptocrystalline Al-Si complexes in some spodosols or in andisol were recognized only few years ago.

Allophane could be defined as a group of short-range ordered clay minerals that contain silica, alumina, and water in chemical combination (Parfitt and Childs, 1988). Allophane has been found in a wide range of soils including those formed in volcanic ash (Andepts), Spodosols, and podzolized soils (Lowe, 1986; Wada, 1987), and shallow stony brown soils (Ochrepts) (Parfitt and Webb, 1984). Occurrence of allophane was also identified by Wells et al. (1977), as a deposit in the streambed below the outlet of Silica Spring on Mt Ruapehu, New Zealand. Henmi (1979) also found it in a stream-deposit from Ehime Prefecture and from Shishigana at the northern foot of Mt. Chokai (Inoue et al., 1980), Japan. Genesis and characteristics of

allophane may have been influenced by an environmental condition where it exists.

Morphology and chemical structure of allophane

Morphology and chemical structure of allophane which was found in soils developed from volcanic ash soils or pumice, has been established (Henmi, 1980; Henmi and Wada, 1976; Shimizu et al., 1988). High resolution electron micrographs have shown that the allophane consists of hollow spheres or polyhedra 3.5-5.0 nm in diameter (Henmi and Wada, 1976) with a wall thickness estimated to be about 0.7 nm (Wada, 1979). The wall of the hollow sphere, nano-ball, has some holes (defects) with diameter of 0.3-0.5 nm (Paterson, 1977; Wada and Wada, 1977). Chemical structure of allophane is characterized by short-range order and the predominance of Si-O-Al bondings (van Olphen, 1971; Wada, 1977). Chemical composition of allophane varies ranging in the Si/Al atomic ratio from about 0.5 to 1 (Henmi and Wada, 1976). Allophane with Si/Al ratio of 0.5 is a fundamental structure which is composed of gibbsite $[Al(OH)_3]$ sheet with SiO_4 tetrahedra attaching on it, and has hollow spherical morphology to locate the SiO_4 tetrahedra inside of the sphere (Henmi, 1985; Parfitt and Henmi, 1980). Allophane with the Si/Al ratio more than 0.5 has some condensed

SiO_4 tetrahedra weakly bonded to its structure (Parfitt et al., 1980). The chemical structure of allophane is schematized at Fig. 1-2. The figure depicts some pores or defect part on allophane structure where resulting in Al-OH and Al-OH₂ groups exposed, whereas inside part of allophane shows silanol groups (Si-OH). The two functional groups play an important role in governing physico-chemical chemical characteristics on allophane. Base on the morphology (ball shape) and the size (nano level) of allophane, we introduce a new term, *nano-ball (shaped) allophane*. So, in this paper, the term allophane always refers to nano-ball shaped allophane.

The variability of both shape and size of allophane particles probably arises from aggregation of the spherules with themselves

and with other soil constituents. An X-ray fluorescence spectroscopy showed that allophanic clays contain Al in both 4- and 6-fold coordination and that the content of Al in 4-fold coordination increases from 20 to 50 % of total Al as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio increase (Henmi and Wada, 1976; Campbell et al., 1977). Parfitt and Henmi (1980) found that the Al in allophanes with low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was almost entirely in 6-fold coordination. Study by using ^{27}Al nuclear magnetic resonance (NMR), Childs et al. (1999) observed 5-coordination Al in Silica Spring allophane. It was supposed that the 5-coordination Al is associated with the edges of fragments of incomplete octahedral sheets that are bonded to disordered, though more complete, curved tetrahedral sheet in the primary particles of this allophane.

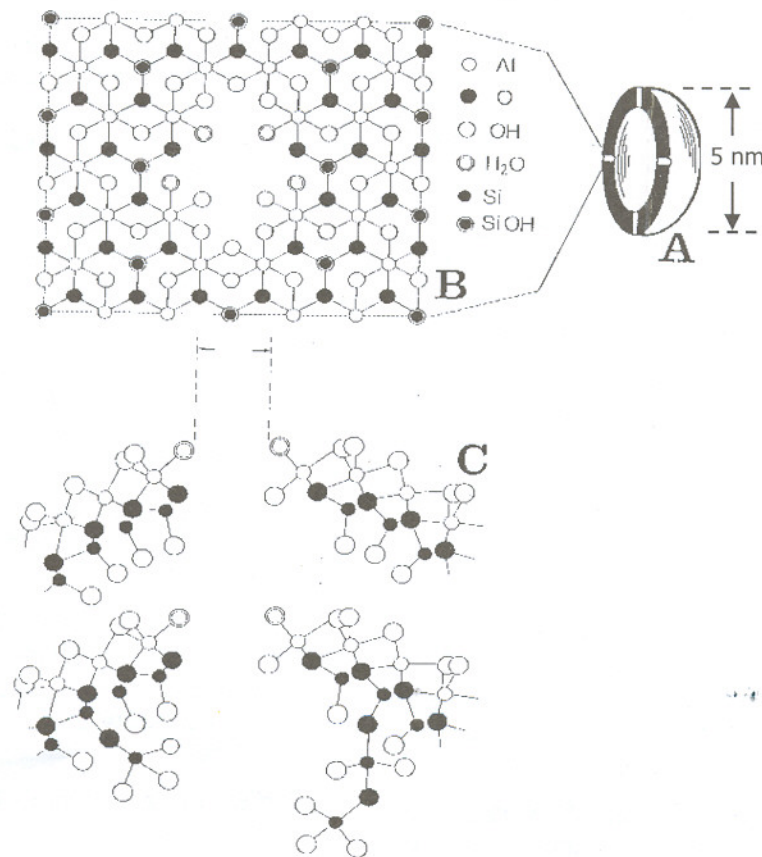


Fig. 1-2 Scheme of chemical structure of a unit particle of nano-ball shaped allophane (A: molecular morphology in section; B: atomic arrangement near the hole of hollow particle; C: atomic arrangement in the cross section of allophane particles) (Parfitt and Henmi, 1980).

As noncrystalline mineral, allophane gives an amorphous features in X-ray diffraction pattern, with the maximum band

vary from 1.23 to 1.45 nm, depending on its Si/Al ratio (Wada, 1989). For thermal characteristics, allophane generally shows a

broad endothermic peak between 50 and 300°C and an exothermic peak between 800–1000°C due to continuous dehydration and dehydroxylation, and to the formation or nucleation of mullite and/or gamma-alumina, respectively (Mitchell et al., 1964; Wada and Harward, 1974; Fieldes and Claridge, 1975; Wada, 1989). Infrared spectra of allophane appear in three regions; 2700–3700, 1400–1800, and 650–1200 cm^{-1} . The absorption bands in the first and second regions are due to the OH stretching and bending vibrations of SiOH, AlOH, and/or adsorbed water. The HOH deformation vibration of adsorbed water appears at 1630–1640 cm^{-1} (Inoue et al., 1980). The absorption bands in the third region are attributed mainly to SiO (AlO) stretching vibrations and partly to SiOH (AlOH) deformation vibrations (Wada, 1989).

Conclusion

High resolution electron micrographs have shown that the allophane consists of hollow spheres or polyhedra 3.5-5.0 nm in diameter with a wall thickness estimated to be about 0.7 nm. The wall of the hollow sphere, nano-ball, has some holes (defects) with diameter of 0.3–0.5 nm. Chemical structure of allophane is characterized by short-range order and the predominance of Si–O–Al bondings. Chemical composition of allophane varies ranging in the Si/Al atomic ratio from about 0.5 to 1.

References

- Campbell, A.S., Young, A.W., Livingstone, L.G., Wilson, M.A., and Walker, T.W. (1977) Characterization of poorly-ordered aluminosilicates in a vitric Andosol from New Zealand. *Soil Sci.*, 123, 362-368.
- Childs, C.W., Hayasi, S., and Newman, R.H. (1999) Five-coordinate aluminium in allophane. *Clays and Clay Minerals*, 47, 64-69.
- Fieldes and Claridge, 1975; Fieldes, M., and Claridge, G.G.C. (1975) Allophane. p.351-393. In J.E. Gieseking (ed.) *Soil Components Vol. 2 Inorganic components*, Springer-Verlag, New York.
- Henmi, T. (1979) The occurrence of allophane in a stream-deposit from Ehime-Prefecture, Japan. *Clay Minerals*, 14, 333-338.
- Henmi, T and Wada, K. (1976) Morphology and Composition of Allophane. *American Mineralogist*, 61, 379 – 390
- Henmi, T. (1980) Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio on thermal reactions on allophane. *Clays Clay Miner.*, 28, 92-96.
- Henmi, T. (1985) Importance of chemical composition ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio) as factor affecting physico-chemical properties of allophanes from weathered volcanic ash and pumice. In: J. Konta (Ed.) 5th Meeting of European Clay Groups, 459-464.
- Inoue, K., Yoshida, M., and Henmi, T. (1980) The occurrence of allophane in stream-deposits from Shishigana at the northern foot of Mt. Chokai, Japan. *Clay Science*, 5, 267-276.
- Lowe, D.J. (1986) Controls on the rate of weathering and clay mineral genesis in airfall tephra: A review and New Zealand case study. p. 265-330. In S.M. Colman and D.P. Dethier (ed.) *Rates of chemical weathering of rocks and minerals*. Academic Press, New York.
- Mitchell, B.D., Farmer, V.C., and McHardy, W.J. (1964) Amorphous inorganic material in soils. *Adv. Agron.*, 16, 327-383.
- Parfitt, R.L., and Childs, C.W. (1988) Estimation of forms of Fe and Al: A review, and analysis of contrasting soils using dissolution and Moessbauer methods. *Aust. J. Soil Res.*, 26, 121-144.
- Parfitt, R.L. and Henmi, T. (1980) Structure of some allophane from New Zealand: *Clay and Clay Minerals*, 28, 285-294
- Parfitt, R.L., and Webb, T.W. (1984) Allophane in some South Island yellow-brown shallow and stony soils and high country and upland yellow-brown earths. *N.Z. J. Sci.*, 27, 37-40.
- Parfitt, R.L. and Henmi, T. (1980) Structure of some allophane from New Zealand: *Clay and Clay Minerals*, 28, 285-294
- Paterson, E. (1977) Specific surface area and pore structure of allophanic soil clays. *Clay Miner.*, 12, 1-9 Shimizu et al., 1988).
- Van Olphen, H. (1971) Amorphous clay minerals: *Science*, 171, 90-91
- Wada, K. and Harward, M.E. (1974) Amorphous clay constituents of soils. *Adv. Agron.*, 26, 211-260.

Wada, S. and Wada, K. (1977) Density and structure of allophane. *Clay Miner.*, 12, 289-298

Wada, K. (1977) Allophane and imogolite. p.603-638. In J.B. Dixon and S.B. Weed (eds.) *Minerals in Soil Environments* (1st ed.). Soil Sci. Soc. Am., Madison.

Wada, K. (1979) Structural formulas of allophane. p.537-545. In VI International Clay Conference 1978, Oxford, M.M. Mortland and V.C. Farmer (eds.) Elsevier, Amsterdam

Wada, K. (1987) Minerals formed and mineral

formations from volcanic ash by weathering. *Chem. Geol.*, 60, 17-28.

Wada, K. (1989) Allophane and imogolite. p. 1051-1087. In J.B. Dixon and S.B. Weed (eds.) *Minerals in soil environments* 2nd ed. SSSA, Madison, WI.

Wells, N., Childs, C.W., and Downes, C.J. (1977) Silica springs, Tongariro National Park, New Zealand: Analyses of springwater and characterisation of the alumino-silicate deposit. *Geochim. Cosmochim. Acta*, 41, 1497-1506.