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Wada, Shin-Ichiro
Department of Agro-environmental Sciences, Faculty of Agriculture, Kyushu University

Wada, Koji
Department of Bioscience and Biotechnology, Faculty of Agriculture, University of the Ryukyus

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Visualization of the Hollowness in Unit Particles of Allophane and Imogolite

Shin–Ichiro WADA* and Koji WADA

Laboratory of Environmental Geochemistry, Division of Bioproduction Environmental Sciences,
Department of Agro–environmental Sciences, Faculty of Agriculture,
Kyushu University, Fukuoka 812–8581, Japan
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Allophane and imogolite were negatively stained with $LaCl_3$ and examined in an electron microscope. Many white spots having a diameter of 20 to 25 Å and white striations having a width of 8 to 10 Å appeared against dark background in the micrographs of allophane and imogolite, respectively. This is taken as an evidence of the presence of the hollow in the unit particles of allophane and fibrous structural units of imogolite. In some micrographs unit particles of allophane appeared to have thicker and electron denser wall. This is interpreted in terms of positive staining through simultaneous adsorption of La^{3+} and Cl^- ions.

Key words: allophane, electron microscopy, imogolite, negative staining

INTRODUCTION

There is a widespread recognition that allophane in weathered volcanic ash and pumices consists of hollow spherical unit particles having an external diameter of 35 to 50 Å. This picture of allophane was first proposed by Kitagawa (1971) based on the high–resolution electron microscopic observation. Henmi and Wada (1976) also examined allophanic clays of different origins and compositions in a similar manner and reached the above–mentioned recognition. There are other supporting experimental evidences with regard to the fine particulate nature of allophane. Small angle X–ray diffraction data for allophanes at relative humidities of 0 to 100% (Van der Gasst *et al*., 1985) and small angle neutron scattering data from aqueous suspensions of allophanes (Hall *et al*., 1985) indicated that allophane consists of particles having diameters of 40 to 60 Å.

In addition to the images from the transmission electron microscopy, Wada and Wada (1977) indicated the presence of the hollow in allophane particles based on the density measurement in organic liquids. However, no further information has been obtained by any other methods. In published electron micrographs, allophane particles mostly exist as large porous aggregates, which may indicate difficulty in dispersion to a single particle. Karube *et al*. (1996) examined a dilute suspension of allophane separated from a weathered pumice by means of viscometry, light scattering and ultra filtration and concluded that unit particles associate like strings of beads forming domains of about 1000 Å. However, they considered that these domains are not observable by electron microscopy because of aggregation during drying in preparation of the sample.

The purpose of the present electron microscopic study is to verify the presence of the hollow in the allophane unit particles by its negative staining with $LaCl_3$. In this study, a nanometer tube unit of imogolite (Cradwick *et al*., 1972) is also examined for comparison.

MATERIALS AND METHODS

The samples of allophane and imogolite were separated from the weathered pumice from Kitakami pumice bed, Iwate, Japan following the method described by Wada and Wada (1977) but without dithionite–citrate–bicarbonate and Na_2CO_3 treatments. The collected suspension of allophane was dialyzed against distilled water to remove NaCl and its pH was readjusted to about 4.5 with 0.1 mol L^{-1} HCl followed by sonication. A fifty mL portion of the suspension was centrifuged at $10^5 \times G$ for 1 h to remove the large aggregates and the slightly opalescent brown supernatant was used for electron microscopy after diluting to a concentration of about 100 mg L^{-1}.

The imogolite sample was prepared in a similar manner from gelatinous film from Kitakami pumice bed.

To minimize aggregation of allophane particles during drying process, the surface of supporting carbon membrane placed on specimen grids was turned hydrophilic by glow discharge method (Adachi *et al*., 1975). A drop of the diluted suspension was placed on the specimen grid and the most part of it was blotted by a pointed end of a small piece of filter paper. With this technique, the suspension spread on the specimen grid dried within five seconds. A specimen was prepared also from a freshly prepared ferrihydrite sol and examined in the same way.

For negative staining, $LaCl_3$ was dissolved in the diluted suspensions of allophane and imogolite to make $LaCl_3$ concentrations 5 g L^{-1} and the drops of these suspensions were dried on the specimen grid in the same way. Imogolite prepared from gelatinous film was also treated in the same way and examined for comparison.

The prepared samples were examined in a JEM 100–B transmission electron microscope at an accelerating voltage of 80 kV. Exposure to the electron beam was kept minimized to avoid collapse by beam heating.

[1] Present address: Aoba 7–48–2, Higashi–ku, Fukuoka 813–0025

* Corresponding Author (E–mail: wadasi@agr.kyushu–u.ac.jp)

RESULTS AND DISCUSSION

In Fig. 1, allophane particles appear mostly as porous aggregates of various sizes and shapes and infrequently as isolated unit particles (arrows). There is no particular indication that unit particles of allophane associate and form domains of definite sizes and shapes. Since freshly prepared synthetic ferrihydrite mounted and dried in the same way appeared as near isolated particles having diameter around 30 Å as shown by Murphy *et al*. (1976), the aggregates of allophane seen in Figure 1 is not likely to be the artifacts formed during drying.

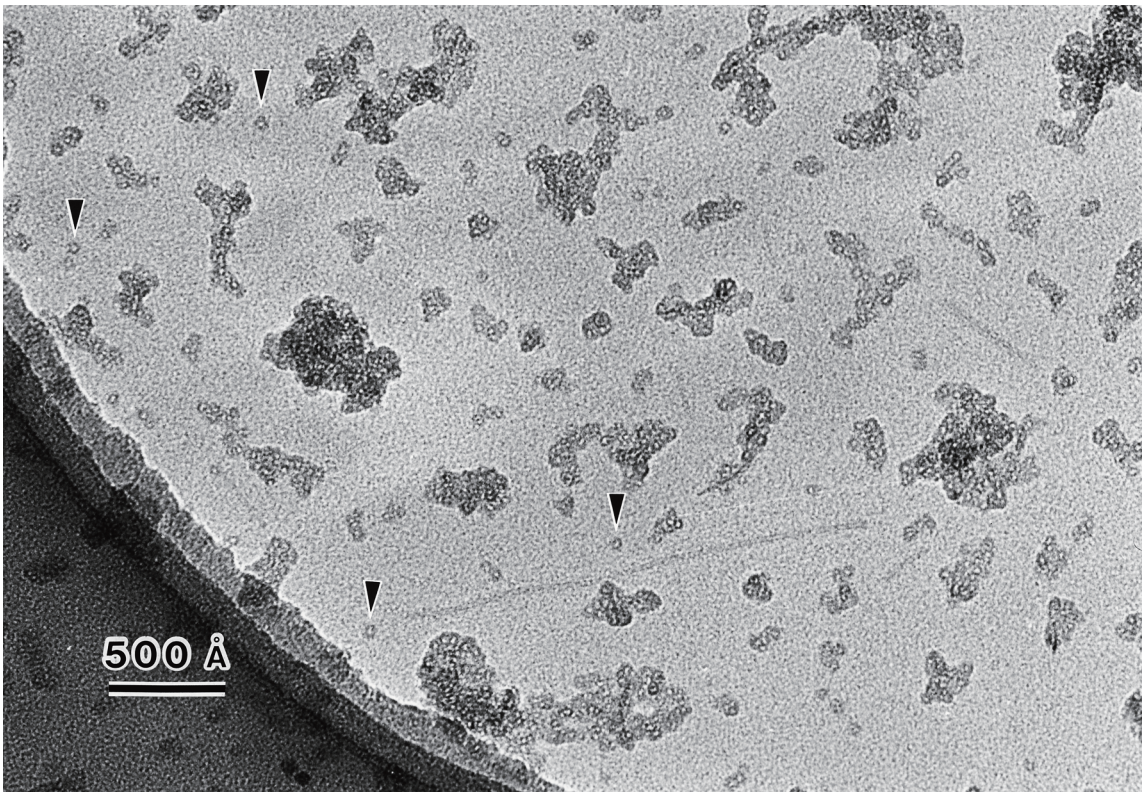

Fig. 1. Electron micrograph of allophane mounted on hydrophilic carbon film. Arrows indicate isolated unit particles.

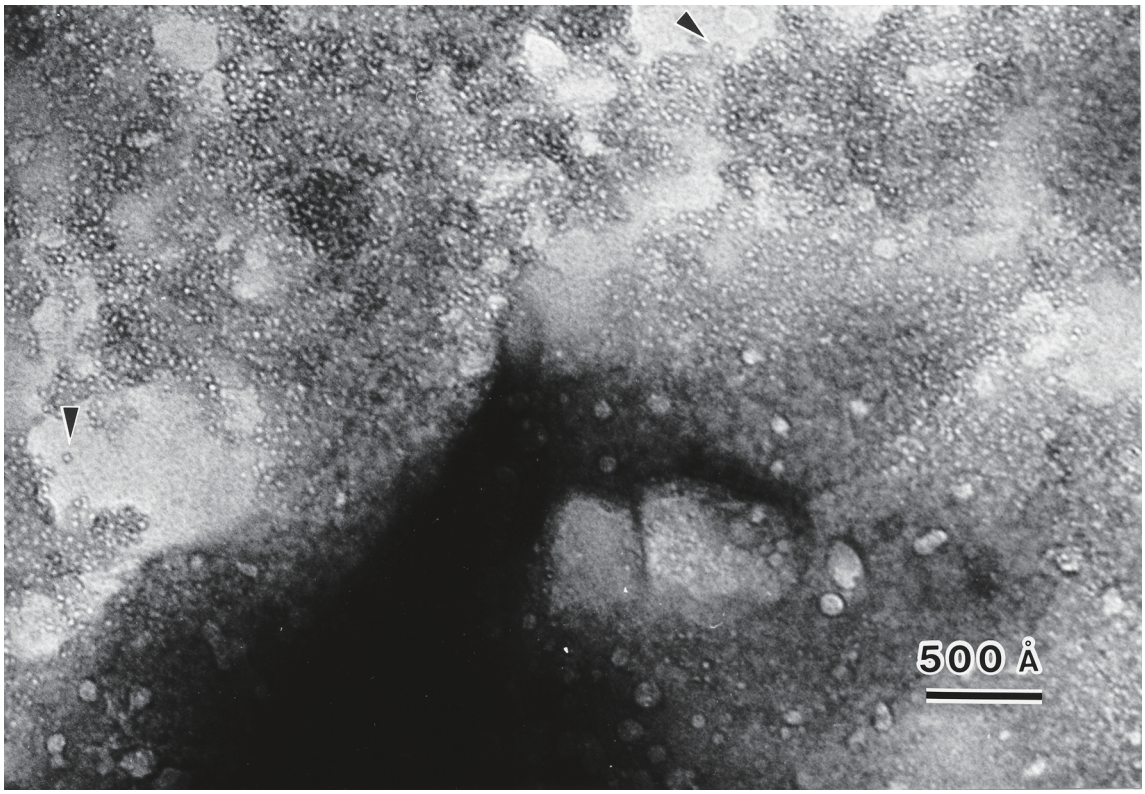

Fig. 2. Electron micrograph of allophane that was negatively stained with $LaCl_3$. Arrows indicate isolated unit particles.

These facts suggest the presence of some bonding among the unit particles, which is not broken by conventional treatments for dispersion.

Figs. 2 and 3 show the images of allophane and imogolite stained with $LaCl_3$. There appear many circular spots with well–defined black rims for allophane (Fig. 2) and white, smooth curvilinear striations for imogolite (Fig. 3), both against generally dark background with black smears. The diameter of the spot, 20 to 25 Å, and the width of the striation, 8 to 10 Å, are smaller than the diameters of allophane unit particle and imogolite tube. The dark background and smears are caused by the presence of $LaCl_3$. The white spots and the striations are, therefore, the spaces in which $LaCl_3$ is not present, and demonstrate "negative" staining of the hollows and hence their presence in the allophane unit particle and the imogolite tube. Since the negative staining with $LaCl_3$ is completed when the suspension has dried up on the specimen grids in the air, the images in Fig. 2 clearly shows that the observed hollow spherical morphology of the unit particles of allophane is not an artifact due to the beam heating in the electron microscope.

The striations in Figure 3 have no noticeable breaks. Some of them can be traced over several μm on micrographs at lower magnifications (not shown). These results serve as additional evidence that the structural unit of imogolite is a seamless hollow fiber and support the proposed structural model (Cradwick *et al*., 1972).

The wall of the isolated unit particles seen in Fig. 2 (arrows) seems to show higher contrast than those in Fig. 1. This may be due to the "positive" staining of the wall with La^{3+} and Cl^- ions. The diameter of La^{3+} is 2.28 Å and that of Cl^- is 3.60 Å (Marcus, 1988). Since the wall of allophane particles have defects to allow free access of water molecules (Wada and Wada, 1977), it is probable that some La^{3+} was adsorbed on Si–OH groups exposed on the internal surface of the particles and Cl^- was adsorbed on Al–OH groups exposed at the defects of the wall through the following reactions (Wada, 1984)

$$3Si–OH + La^{3+} = (Si–O)_3La + 3H^+ \quad (1)$$

$$3Al–OH + 3H^+ = 3Al–OH_2Cl \quad (2)$$

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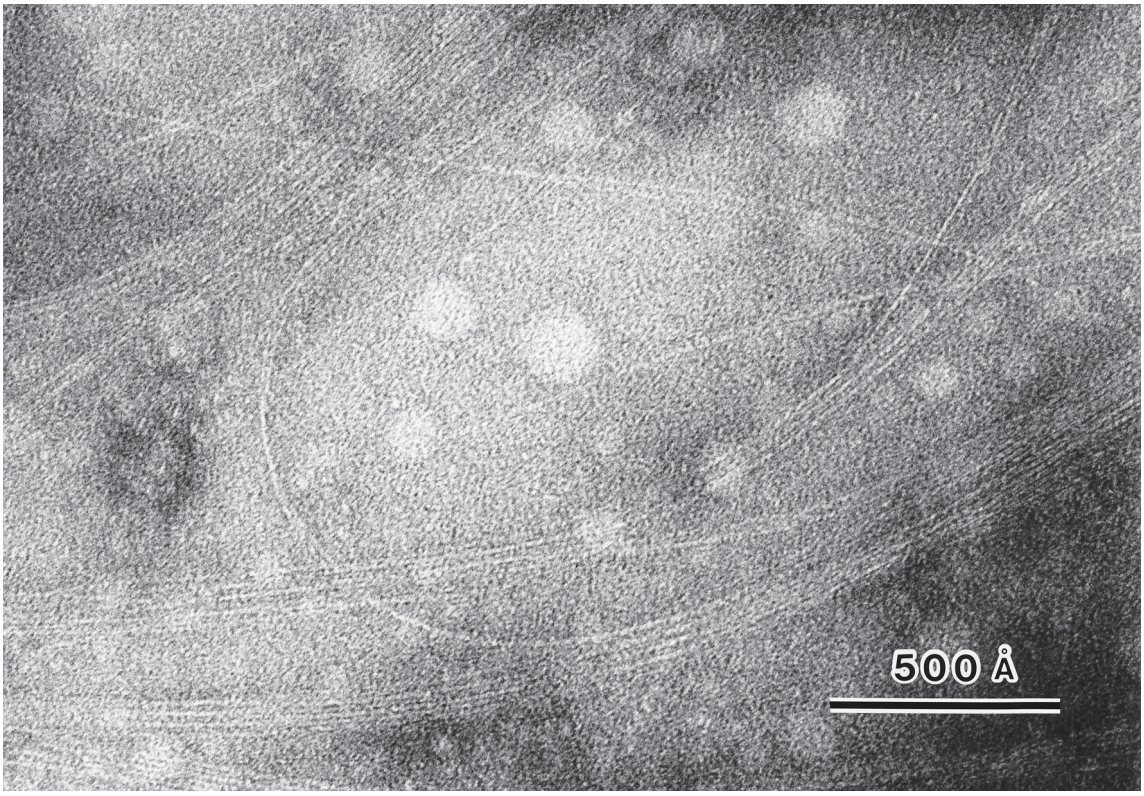

Fig. 3. Electron micrograph of imogolite that was negatively stained with $LaCl_3$.

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