Halloysite is a kaolin-group clay mineral which is characterized by a diversity of morphology. Generally it occurs with a tubular morphology, but spheroidal halloysite particles are also common in weathered volcanic ashes and pumices. In addition, 'tabular' halloysite was found in Texas soils by Kunze and Bradley (1964) and Carson and Kunze (1970). Carson and Kunze (1970) also reported similar material in soils of Florida and Guatemala. Recently, platy halloysites with rolled edges were reported by Nagasawa and Miyazaki (1976) and Wilke et al. (1978). The present paper reports a morphologically new type of halloysite that displays a unique crumpled, lamellar morphology.

MATERIALS AND METHODS

Samples were collected from the weathered Tarumae d3 pumice bed at Uenae, Tomakomai basin, Hokkaido, Japan, at a depth of 120–150 cm from the present surface. The samples were stored at a field moisture content in a stopped polyethylene bottle. The pumice was derived from the Tarumae volcano and is augite-hypersthene andesitic in composition (Ishii and Kondo, 1962). The C14 age of a charred wood fragment at the bottom of the bed was estimated to be 8490 ± 50 years B.P. (Sato, 1971). The halloysite occurs as yellowish brown clayey patches, nearly at the bottom of the pumice bed. The surrounding pumice grains are relatively hard and apparently less weathered. The pumice structure remains in the weathered portion, indicating that the halloysite formed by differential weathering of the pumice.

The undried bulk clay was gently pulverized in water, and the pH of the resulting suspension was adjusted to 10 with NaOH. The clay (<2-μm fraction) was dispersed with the aid of an ultrasonic treatment and collected by sedimentation. Part of the clay separate was stored as such for electron microscopy and cation-exchange capacity (CEC) determination, and the remainder was successively treated with dithionite-citrate and 2% Na2CO3 solutions to remove free iron oxides and the adsorbed citrate, respectively. Part of the treated clay was kept as a suspension for X-ray powder diffraction (XRD) analysis and electron microscopy. The remainder was successively washed with a water-methanol solution, methanol and acetone, and then air-dried.

Total elemental analysis of the air-dried clay was carried out according to the procedure described by Aomine and Harada (1971). Ferrous ion was not determined separately, and the iron content is therefore expressed as percent Fe₂O₃. XRD patterns were obtained from K- and Mg-saturated samples of the clay oriented on glass slides using CuKα radiation. Infrared (IR) absorption spectra were recorded with KBr pellets. Differential thermal analysis (DTA) was carried out on a 30-mg sample at a heating rate of 20°C/min. Electron micrographs were obtained from specimens prepared by air-drying a drop of the clay suspension on a collodion film or on a plastic microgrid. CEC was determined on the clay without any treat-
Figure 3. Transmission electron micrographs of halloysite. (a) Halloysite, Japan, (a) halloysite particles with crumpled lamellar morphology; (b) very thin flakes containing a particle; (c) lattice images observed on a protruding edge; (d) a particle with sharp edges replaced with the halloysite.
RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the clay. The basal spacing of air-dried specimens (10.0 Å) expanded to 11.3 Å on glycerol solvation and collapsed to 7.4 Å on heating the sample at 300°C. The b₀ parameter calculated from the (006) spacing (1.49 Å) is 8.94 Å, indicating that the mineral is dioctahedral. These features are typical of halloysites.

The present halloysite is characterized by relatively low Al content and high Fe content compared with the data summarized by Weaver and Pollard (1973) (Table 1). Because the clay was treated with dithionite-citrate and 2% Na₂CO₃ solutions, the remaining Fe is probably located in the silicate structure. The calculated SiO₂/(Al₂O₃ + Fe₂O₃) molar ratio of 2.09 indicates that most of Fe is in the octahedral position. The CEC of the clay without dithionite and 2% Na₂CO₃ treatments is 58.1 meq/100 g. This high CEC can be accounted for by assuming the substitution of ferrous ion for aluminum ions, providing layer charge.

Figure 2 shows the IR spectrum of the air-dried clay. An OH-stretching absorption band appears in the range 3700 to 3200 cm⁻¹. The absorption bands of structural OH groups of tabular halloysite can be accounted for in a similar manner. The incorporation of iron in the octahedral sheet is a likely cause for an increase in its lateral dimensions and results in a decrease in the misfit between the tetrahedral and octahedral sheets. The invariably high iron content of tabular halloysites (Kunze and Bradley, 1964; Carson and Kunze, 1970) supports this view.

Allophane and imogolite, clays commonly derived from volcanic ejecta, were not detected in the present sample. On the other hand, the fine-sand fraction of the bulk sample contained abundant volcanic glass fragments with sharp edges. Many particles with similar sharp edges were also found in the silt and clay fractions. Most of these particles were found to be noncrystalline by electron diffraction. Some of these particles in the clay fraction were almost replaced with the aggregates of the lamellae (Figure 3d). The above observations suggest that this halloysite forms directly from volcanic glass.

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REFERENCES


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