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NOTE

THE FORMATION OF HALLOYSITE TUBES FROM SPHERULITIC HALLOYSITE

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One of the writers (T.S.) and his collaborators has reported that some kaolin clays are composed of spherules as revealed by electron micrographs (Sudo, 1953; Sudo *et al.*, 1951; Sudo and Takahashi, 1956; Sudo *et al.*, 1964). These clays are largely halloysite (10 Å) and occur as weathering crusts on rhyolitic tuffs or tuffaceous sediments. The spherules usually are composed of a central spherule and some fine fibrous particles projecting radially from the central spherules. Since then similar materials have been reported by other authors: e.g. Alietti (1959), Chen (1959), Siefferman and Millot (1969), Trichet (1969), Minato and Utada (1969).

Sudo and Takahashi (1956) studied the morphology of the spherules in more detail and pointed out several morphological characteristics:

(a) The central spherulitic bodies and the fibrous particles are usually nearly uniform in size and shape in samples collected from one locality, but they tend to be slightly different from locality to locality.

(b) The fibrous particles, which are associated with the central spherulitic bodies of relatively small sizes, are usually extremely fine, like "curled hair".

(c) The length and width of the fibrous particles tend to increase with increasing sizes of the central spherules. When the spherules are large enough, the shape of the fibrous particles often appears like a "horn". This shape probably results from the peeling of a thin surface layer of the central spherule and then the partial rolling of the layer into a tubular particle. A horn-shaped particle appears to have rolled into a tubular form to the greatest extent at its top, whereas its bottom is spread over the surface of a central spherulitic body. The fibrous particles are also found as isolated particles distributed in interspaces between spherules. The isolated particles are usually better defined in shape than the "curled-hair"-type, but still commonly have part-tubular shapes and undulated edges. They are ill defined in shape as compared with usual halloysite (10 Å).

(d) In samples composed of large spherulitic bodies, isolated fibrous particles tend to have well-defined tubular forms like halloysite (10 Å). The relative amount of the spherulitic bodies with their attached elongated particles tends to decrease as compared with the amount of the isolated particles.

(e) The spherulitic bodies in (a)–(d) above show concentric textures, and occasionally polyhedral outlines.

Sudo and Takahashi (1956) named these particles "chestnut-shell-like particles", and proposed that the variation of the shapes of the particles as stated in (a)–(d) might be due to advancing crystallization of allophane into halloysite (10 Å).

Kurabayashi and Tsuchiya studied the geology and mineralogy of the volcanic ash beds in Japan, concentrating on the Kanto volcanic ash beds (so-called Kanto loam) which are widely distributed in the Kanto plane (Sudo *et al.*, 1964). The Kanto volcanic ash beds are divided into the following horizons: Tachikawa, Musashino, Shimosueyoshi, and Tama reading progressively from the upper horizon downward. The many profiles studied have extended from the uppermost layer of Tachikawa to the lowermost layer of Tama, the depth of which is less than about 40 m. X-ray powder diffraction patterns, electron micrographs, and DTA curves revealed that the uppermost horizon (Tachikawa) is composed entirely of allophane, and the amount of halloysite (10 Å) tends to increase downward. The following trends were confirmed:

(1) Generally speaking, the variation in morphology of the particles with burial depth is in accord with (a) toward (d) above.

(2) The uppermost horizon is composed entirely of allophane which is found as aggregates of extremely fine particles of 0.05 μm in mean size. In some instances, on going downward, the aggregates are found to have been coagulated into larger particles which are roundish in shape but not yet completely spherical. At this stage, the fibrous particles are absent, and X-ray powder diffraction peaks of halloysite (10 Å) are not discernible.

(3) On going toward lower horizons, "chestnut-shell-like-particles" appear and X-ray powder diffraction peaks of halloysite (10 Å) are discernible.

(4) Even farther downward, the following general tendencies are confirmed: X-ray intensities of halloysite (10 Å) increase; sizes of both the fibrous particles and central spherulitic bodies increase; shapes of the fibrous particles become better-defined, approaching those of halloysite (10 Å); the amount of the isolated fibrous particles relatively increase, and the amount of the spherulitic bodies relatively decrease; and finally, the pattern of the particle aggregates is observed to be entirely composed of tubular particles of halloysite (10 Å).

Based on the above trend, these authors suggested the chemical reactions which might result in the transformation: volcanic glass (rhyolitic) $\rightarrow$ allophane $\rightarrow$ "chestnut-shell-like-particles" $\rightarrow$ halloysite (10 Å) broadly with increasing burial depth.

Successive studies by several authors of the alteration of pumice beds in other localities have revealed that the transformation of allophane into halloysite in the beds is not necessarily due to a crystallization expressed simply as a function of time and increasing burial depth. It has been suggested that the degree of the transformation may also vary depending upon chemical, lithological, and sedimentological features of the profiles intercalating pumice beds.

Recent electron microscope with a high resolution power has revealed inner and outer textures of the particles in more detail than ever before. Figures 1–3 show micrographs of white clays altered from pumice beds occurring in the Naegi district, Nakatsugawa City, Gifu Prefecture. The white clays, intercalated with kaolin clay beds are weathering products from pumice fragments. The kaolin clay beds occur as detrital sediments derived from weathered granitic basement rocks and are composed largely of the usual kaolinite and tubular halloysite.

Figure 1(a) shows the concentric textures of the spherulitic bodies of the white clays which seemingly transform into a part-spiral pattern. Occasionally, aggregates of extremely fine particles (as marked with a cross), which seem to be a colloidal material like allophane, are found in association with the spherulitic bodies. Figure 1(b) shows an interestingly shaped particle (as marked with a cross) which seems to have resulted from the peeling and partial rolling of a thin surface layer of the spherulitic body. In Figures 1(a) and (b), the shape of elongated particles of halloysite having part-tubular forms and undulated edges is not so well defined as that of the usual halloysite (10 Å). Figures 2(a)–(c) are scanning micrographs. Figure 2(a) shows uneven surfaces of spherulitic bodies that look as though they had been piled up with curved tiles, and Figures 2(b) and (c) show inner textures of spherulitic bodies; the particle in Figure 2(c) seems to be hollow in its central part. Figures 3(a) and (b) show 7 Å lattice images which are certainly due to halloysite (7 Å)—a dehydration product of halloysite (10 Å) under vacuum conditions. The image is observed limitedly within dark colored bands in Figure 3(a) and as nearly concentric circles in Figure 3(b). Figure 3(c) shows an electron diffraction pattern of a domain including five or six spherulitic bodies. Seven Å and 3.5 Å diffraction patterns are observed as powder rings because some randomly oriented halloysite crystal lattices are involved in the domain. Figure 3(d) shows a pattern of a domain of about 200 Å across nearly corresponding to the domain as shown in Figure 3(b). Seven Å diffraction occurs here as two diffraction spots because the domain involves a nearly single crystal lattice of halloysite (7 Å).

From the data to date for the particles now under consideration, it is difficult to call them by a unique name because of their complicated variations in shape and mineralogical property. The name "chestnut-shell-like-particle" has been used to illustrate the morphology. Spherulitic bodies dominantly composed of halloysite may be called spherulitic halloysite. The name allophane–halloysite-spherules has been used in a sense stressing its genetic relation to allophane on one side and to halloysite on the other, and regarding particularly its occurrence, in some instances, as an incorporated body of allophane and halloysite, as suggested by the occurrence of weak X-ray peaks of halloysite.

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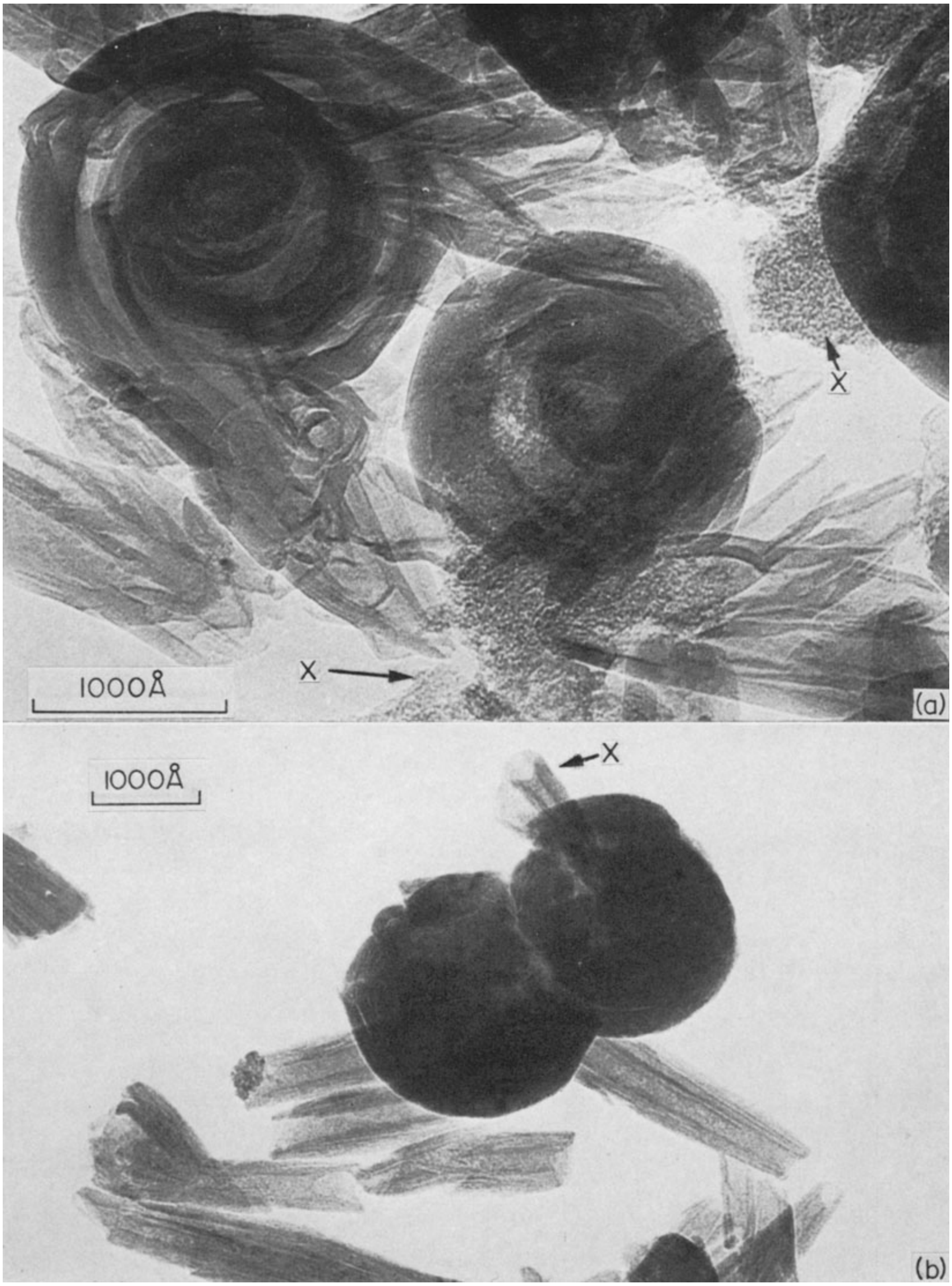

Figures 1–3. Transmission and scanning images, lattice images and electron diffraction patterns of halloysite particles in white clays derived from weathered pumice beds occurring at Yawata, Naegi district, Gifu Prefecture. Photographs: S. Aida, JEOL, Tokyo, Japan.

Figure 1. Transmission photographs: (a) showing a photograph suggestive of the relation among spherulitic bodies, elongated particles of halloysite, and aggregates of extremely fine particles (X) (probably of a colloidal material), and (b) showing a photograph suggestive of a relation between spherical and tubular halloysite; a particle (X) seems to have resulted from the peeling and partial rolling of a thin surface layer of a spherulitic body.

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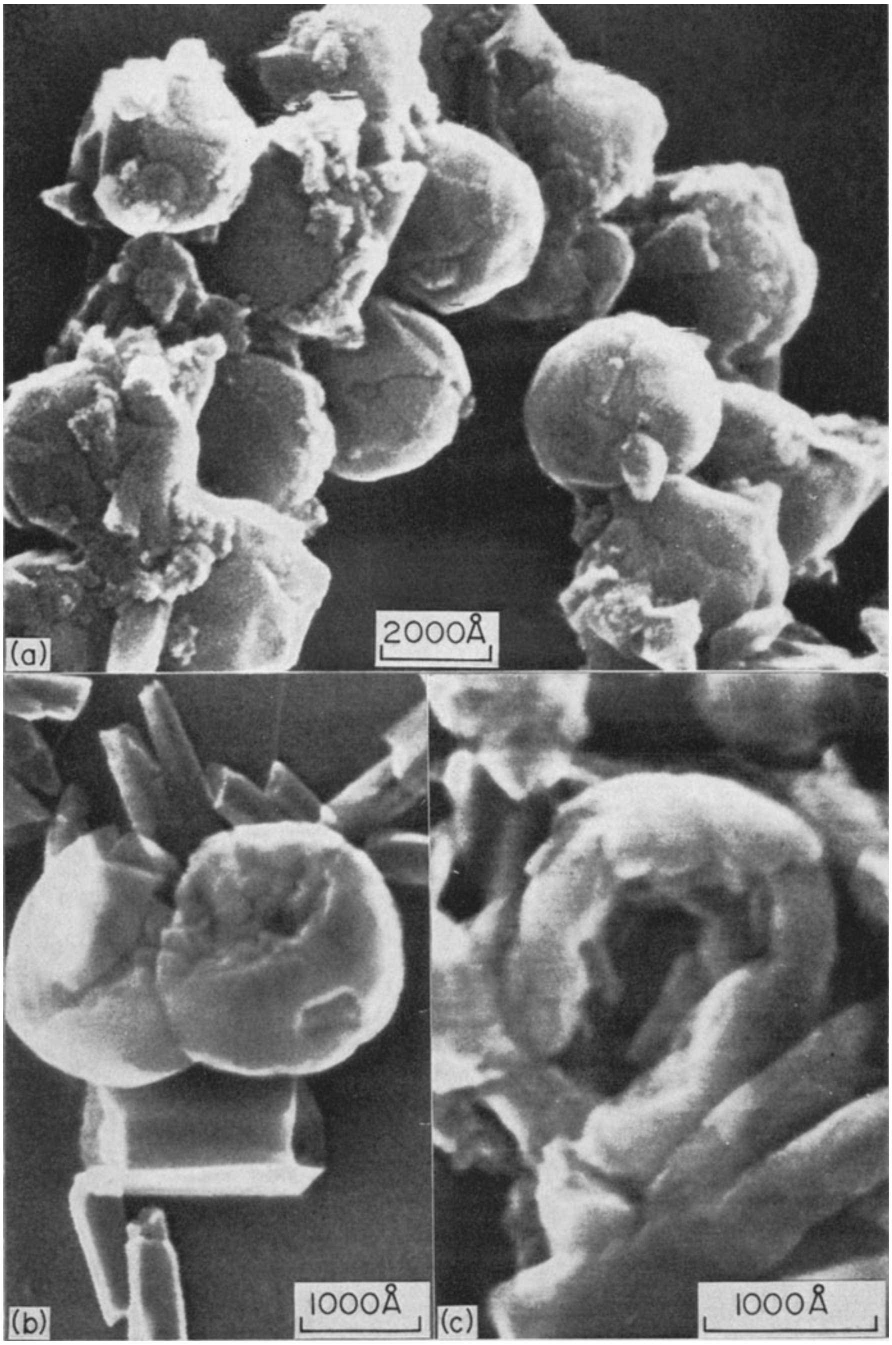

Figure 2. Scanning micrographs. (a) Surface textures of spherulitic bodies. (b) and (c) Inner textures.

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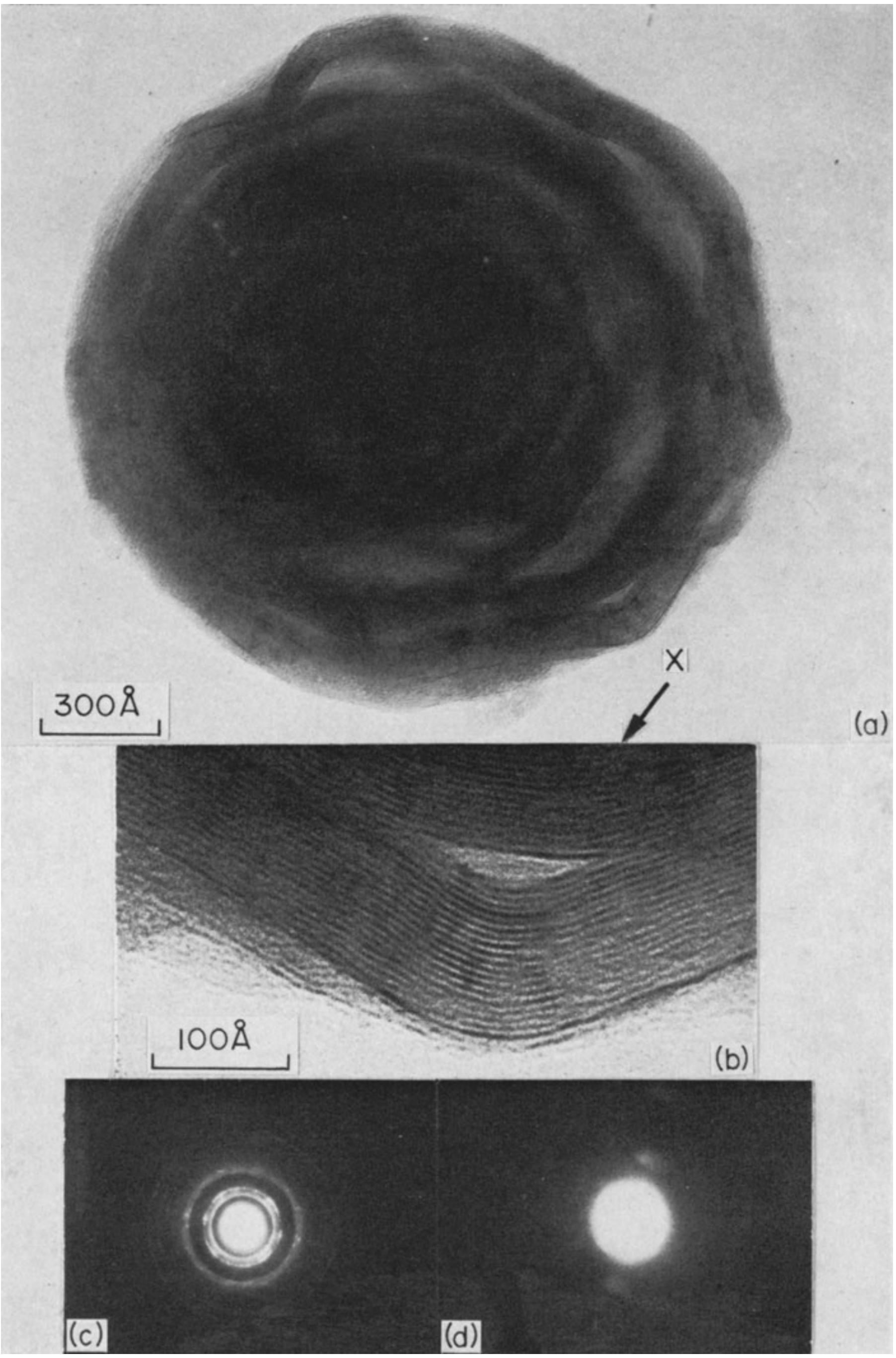

Figure 3. (a) and (b) 7-Å lattice image. (c) and (d) Electron diffraction patterns.