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MORPHOLOGY AND STRUCTURE OF HALLOYSITE IN NEW ZEALAND TEPHRAS

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Abstract—As shown by scanning and transmission electron microscopy, halloysite in three rhyolitic tephras occurs as squat and elongate ellipsoids. Both morphologies are presumed to result from a similar lattice building mechanism. The squat ellipsoids form from allophane; the elongate ellipsoids form from feldspars. The squat ellipsoids do not possess flattened faces or spaces between books of layers at field moisture levels. Outgrowths from the squat ellipsoids are possibly due to inclusions of allophane, glass, ferrihydrite, or feldspar crystallites. Possible spiral growth of halloysite, giving curved surfaces, may be due to a continuous distribution of crystal dislocations.

Key Words—Crystal dislocations, Electron microscopy, Growth mechanisms, Halloysite, Morphology.

INTRODUCTION

Since the electron optical studies by Bates *et al.* (1950), a tubular morphology has been associated with halloysite. Numerous workers, e.g., Birrell *et al.* (1955), Askenasy *et al.* (1973), Wada *et al.* (1977), and Kirkman (1975, 1977, 1980) showed that particles of halloysite with a circular outline when viewed by transmission electron microscopy are commonly the dominant and, in many samples, the only crystalline component of the clay fractions of tephras and volcanic ash-derived soils. Birrell *et al.* (1955) described such particles as distorted cylindrical shells or apparently incomplete toroids, whereas Askenasy *et al.* (1973) regarded them as oblate spheroids or stubby cylinders with rounded edges containing inclusions of noncrystalline material. Wada *et al.* (1977) suggested that the particles are composed of concentric and discontinuous stackings of kandite unit layers and that they do not contain noncrystalline material. From the morphology of unusual disks sandwiched between silica flakes and other electron optical data, Kirkman (1977) concluded that halloysite particles with circular cross sections may have formed by a spiral mechanism resulting from crystal dislocations. He observed that such particles have many flattened faces.

Building on the report of Kirkman (1977), this paper attempts to determine the cause of the flattened faces and investigates further the possibility of the spiral growth of halloysite. Additional electron optical information is presented on the morphology and possible structure of halloysite, and the theory of continuous dislocations in crystals (Nabarro, 1967) is offered as a possible explanation of such spiral growth. Kirkman (1977) suggested that particles of halloysite with circular cross section should be regarded as chunky cylinders, rather than spheres, since they have a well-defined axis. However, because such particles are in fact squat and barrel-shaped and do not possess parallel sides, they should be described, *sensu strictu,* as squat ellipsoids, and this term is used throughout this report. Long tubes, if formed by the same mechanism as the squat ellipsoids, are thus elongate ellipsoids, but to facilitate recognition and description of such particles, the terms tube or tubular are used below.

MATERIALS AND METHODS

The rhyolitic tephras containing the clays investigated include Woodstock 15 and Woodstock 16 (Kirkman, 1980), and a halloysite-rich rhyolitic tephra from the Hamilton Ash Formation. The <1.0-μm fractions were separated by centrifugation after ultrasonic dispersion of the tephras suspended in water made alkaline to pH 10.2 with ammonia (Kirkman and Pullar, 1978). After dilution, one drop of the clay suspension was placed on a copper grid coated with Formvar and carbon and dried at 50°C for 10 min prior to examination in the transmission electron microscope (TEM). Replicas were prepared from suspensions in distilled water in a Balzers BA 600 freeze-etch unit (Moore and Muhlethaler, 1963). Specimens were fractured at -100°C, and ice was permitted to sublime from the fracture faces for 2 min to achieve partial exposure of undamaged clay particles. The resulting surfaces were replicated by deposition of platinum/carbon shadow and a carbon backing film. After thawing, adherent clay particles were removed by floating the replicas on a bath consisting of equal parts of water, 40% HF, and concentrated HCl.

Scanning electron microscopy (SEM) studies were made on the fracture surfaces of small aggregates mounted directly on aluminum stubs with conducting paint and coated with gold. The aggregates had been stored at field moisture levels in polythene bags and received no pretreatment.

RESULTS

Freeze-etching was undertaken in an attempt to preserve the natural morphology of the halloysite parti-

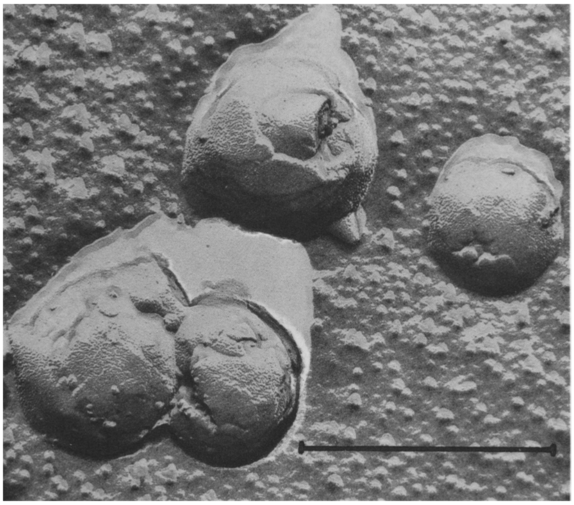

Figure 1. Transmission electron micrograph of replica of freeze-etched clay of Woodstock 16 tephra showing outgrowths and absence of flattened faces. Bar = 0.5 μm.

cles. Hopefully the surfaces of the particles were replicated while retaining the support of the internal water, thus avoiding any modification of shape due to dehydration. Earlier studies of replicas (Kirkman, 1977) revealed many flattened faces on the particles which imparted a polygonal appearance. The particles in Figures 1 and 2 do not show this effect, which supports the idea that the flattened faces were caused by loss of internal water from the particles.

Figure 1 shows that two or more ellipsoids can grow together and that outgrowths can occur. A small conical protuberance together with a scar where an outgrowth has broken away (either in the field or during laboratory preparation) can be clearly discerned on one of the particles. Commonly the outgrowths from ellipsoids are elongate and well developed (Figure 2a), and scars on the ellipsoids were observed frequently. Two or more outgrowths from one ellipsoid are common (Figure 2b), and some outgrowths tend to taper (Figure 2c), a tendency also observed for a number of discrete particles (Figure 2d). The outgrowth shown in Figure 2d contains lines suggestive of a spirally wound or tightly rolled sheet. Discrete particles, interpreted as tubes within tubes, were also observed (Figure 2e). Although outgrowths from ellipsoids are common, small, distorted masses protruding from otherwise well-developed elongate particles were also observed (Figure 2f). Some ellipsoids display numerous protuberances, many of which appear as cones, bumps, or irregularities in the surface layer of the ellipsoids (Figure 2g), or as short, twisted and distorted outgrowths (Figure 2h). Flattened faces are absent from all of the ellipsoids shown in Figure 2, and on most the outline of the exterior layers is clearly evident.

The scanning electron micrograph of a fracture surface of Woodstock 15 (Figure 3) indicates that much of the sample consists of tightly packed ellipsoids of halloysite of varying size. Figure 4a shows halloysite (arrowed) in close proximity to sheets of a primary mineral in the same sample. Higher magnification (Figure 4b) reveals that the halloysite forms spherules and that each spherule is composed largely of a mass of particles, many of which have a tapered appearance (Figure 4c). The scanning electron micrographs show that the tapered particles invariably have what appear to be solid, rounded ends indicative of rods, but transmission electron microscope studies (Figure 5) indicate a tubular morphology. Interpretation of particles showing solid, rounded ends must be made with caution because: (1) coating particles with gold to a thickness of 100 Å is not easily controlled, and a non-uniform coating may give the particle a rounded appearance; (2) the resolution of the SEM is poorer than that of the TEM; (3) high secondary electron emission from all surfaces of projecting thin-walled tubes may swamp out contrast between their various parts, resulting in a featureless, general luminosity. In addition, the halloysite particles could be tubes packed with allophane, which is less electron dense to the TEM than halloysite but of equal response in the SEM. This possibility appears unlikely, because treatment with hot, dilute alkali failed to dissolve material from the particles (Kirkman, 1977). A hollow, tubular morphology therefore appears most probable, not only because of the TEM evidence and the problems of interpretation of the SEM evidence, but also because a similar particle observed in another specimen at higher magnification (Figure 2d) shows striations around the circumference suggestive of a spirally wound tape or a rolled up sheet. Indeed, TEM investigation failed to reveal solid rods in any of the samples investigated; the elongate particles always appeared tubular.

The growth of tubular halloysite is not confined to spherules associated with platy primary minerals. Tubes at the edges of possible feldspathic minerals are either parallel with (Figure 6a), or extend upwards from (Figure 6b), the surface of the parent grain. Like the particles shown in Figure 4c, those in Figure 6b have solid looking, rounded ends. Similar particles of halloysite (Figure 7a) grow inside small holes (arrowed Figure 7b) in the planar surfaces of probable feldspar minerals.

The surface of a platy primary mineral, probably feldspar (Figure 8a), apart from two relatively clean areas, is covered with numerous particles of two different, but probably closely related types of halloysite (Figure 8b). The presence of feldspar and halloysite and the absence of other crystalline minerals was confirmed by X-ray powder diffraction. One type of halloysite lies parallel to the surface, while the other extends upwards

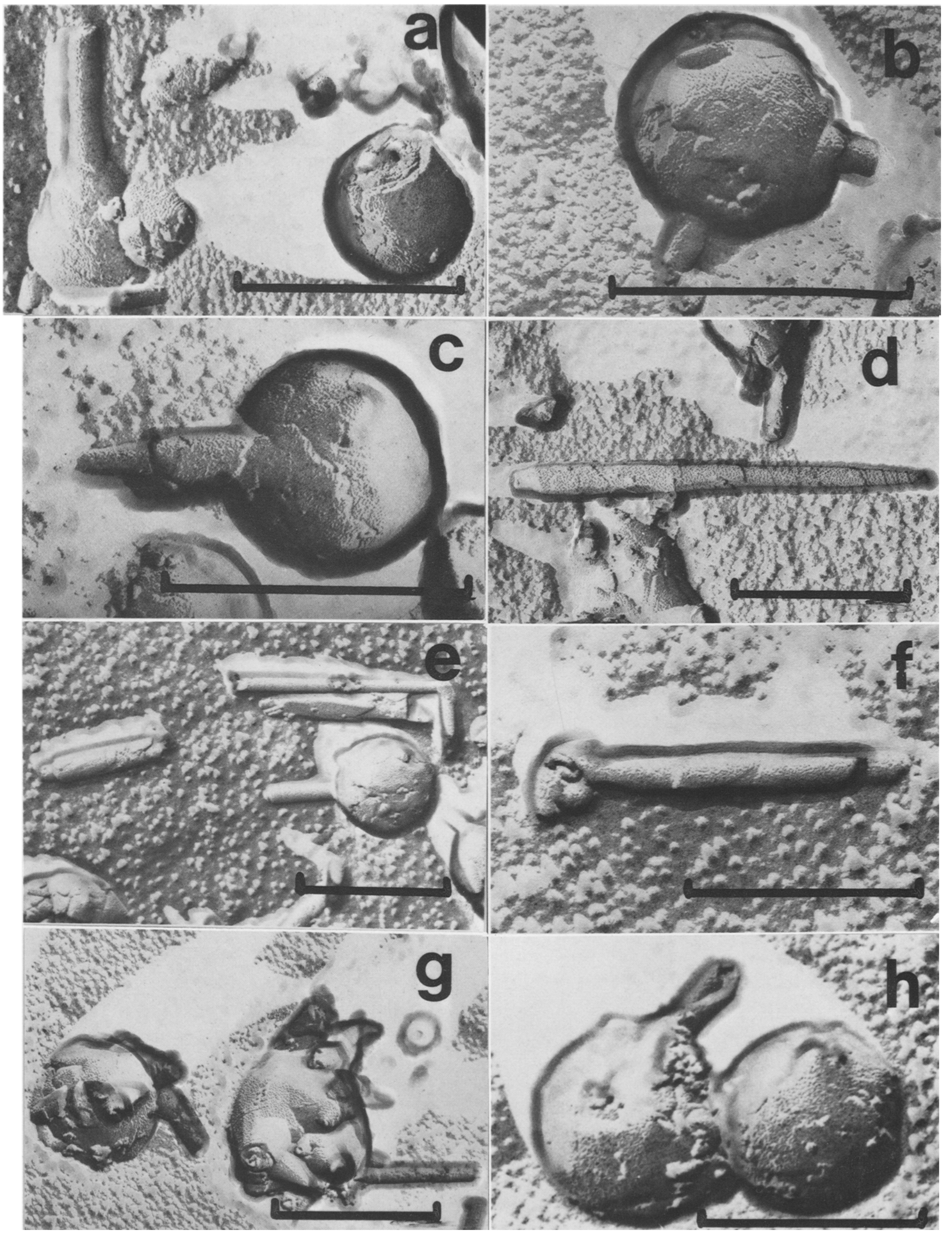

Figure 2. Transmission electron micrographs of replica of freeze-etched clay of Woodstock 16 tephra showing (a) elongate tubular outgrowth from a squat ellipsoid, and a scarred ellipsoid; (b) two tubular outgrowths from one ellipsoid; (c) a tapered tubular outgrowth from an ellipsoid; (d) single tapered tube with surface striations; (e) tubes within tubes; (f) small distorted outgrowth from a long tube; (g) numerous outgrowths and distorted outer layers of ellipsoids; (h) twisted tubular outgrowth from two linked ellipsoids. Bar = 0.5 μm.

(Figure 8c). The upward extending particles are generally shorter and thicker than those lying parallel to the surface. Those parallel to the surface have a length:width ratio of approximately 9.0, and are commonly tapered, and some, although supine, appear to be extending out from the surface, or are partially buried in it. The size of both types of particle is variable; the upward extending particles are approximately 0.5 μm long and 0.2 μm wide, and the largest supine particles are as much as 1.5 μm long and 0.2 μm wide.

DISCUSSION

The results of the freeze drying procedure support the idea that the flattened faces of squat ellipsoids found

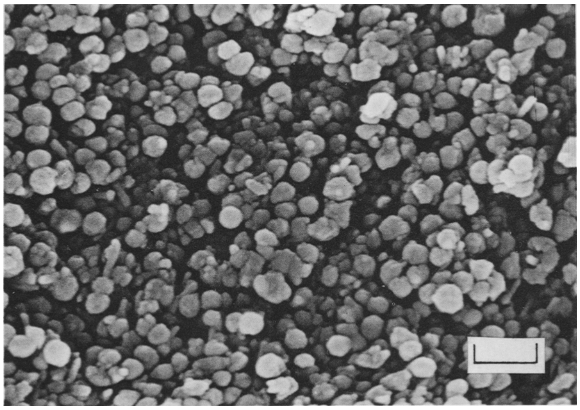

Figure 3. Scanning electron micrograph of squat ellipsoids of halloysite at a fracture surface of an aggregate of Woodstock 15 tephra. Bar = 1 μm.

earlier by Kirkman (1977) are caused by loss of internal water. Layer separation, a characteristic of halloysite disks (Kirkman, 1977), which gives rise to the "core and crust" appearance common to squat ellipsoids is believed to be due to dehydration, although direct evidence for this effect was not obtained in the present study. Water molecules between crystal layers of the fully hydrated mineral suppress hydrogen bonding between layers, but after dehydration such bonding becomes more effective. The stress induced by contraction of the interlayer space resulting from increased hydrogen bonding after dehydration is possibly relieved by gaps between books of crystal layers, hence the "core and crust" appearance which is well illustrated in Figure 9a of Kirkman (1977). This suggestion is supported by the observation of Saigusa *et al.* (1978) that halloysite particles subjected to glycerol saturation do not show layer separation, whereas marked separation results from dehydration in the absence of glycerol. These observations imply that contrary to the claim of Askenasy *et al.* (1973), Wada *et al.* (1977) were correct in suggesting that the spaces observed between books of layers in squat ellipsoids do not contain noncrystalline material.

This study, together with that of Kirkman (1977), shows that halloysite occurs in two different forms, tubes and squat ellipsoids, and that the ellipsoids display a variety of outgrowths. The outgrowths probably result from minor disturbances of the fundamental growth mechanism. Despite obvious differences in the appearance of the tubes and ellipsoids, the mechanism of formation is probably the same, a conclusion suggested by the fact that the literature reveals no significant differences resulting from differential thermal analysis, infrared spectroscopy, X-ray diffraction, and intercalation studies. Furthermore, it is unlikely that different crystallization mechanisms produce identical unit cells, and it follows that the tubes and ellipsoids were formed by the same mechanism.

It has been shown that interlayer water preserves the curvature of crystal layers, but clearly such curvature is not necessarily caused by the intercalating water. The fact that curved surfaces, be they curled flakes, tubes, or ellipsoids, are invariably characteristic of halloysite, indicates that crystal growth was not symmetric. Curvature in halloysite has been ascribed to the misfit between tetrahedral and octahedral sheets which are inherently of different dimensions (Bates *et al.*, 1950), but such a mechanism should produce a circular section rather than a spiral, yet the present electron optical evidence and that of Kirkman (1977) suggests a spiral. Undoubtedly, curvature is "locked" into the structure of halloysite, because dehydration and the consequent increase in the effectiveness of hydrogen bonding between layers do not cause tubes to revert to flat plates. A system of continuous dislocations may be inherent in the growth of halloysite crystals; such dislocations could cause spiral growth.

Nabarro's theory of a continuous distribution of dislocations (1967) suggests that a single crystal can exist in several states (Figure 9). Figure 9a shows the unstressed state which, if elastically bent (Figure 9b) is regained when the applied stresses are released. This situation would result if stress were applied to a kaolinite flake. In state (c) the crystal is plastically bent and contains a random distribution of dislocations all of the same kind. It retains its form when the applied stresses are released. State (d) is the polygonized state which contains the same number of dislocations as state (c), but now arranged in tilt boundaries separating regions of the crystal which are almost perfect. States (c) and (d) may apply to hydrated and dehydrated halloysite, respectively, the dislocations being inherent in the crystallization process and not induced by external stress. According to Nabarro (1967) a continuum of such dislocations would produce lattice rotations but not long range lattice strain. Thus, this type of rotation may contribute to the a- and b-axis disorder characteristic of halloysites.

If continuous dislocations are the cause of spiral growth in halloysites, the mechanism of growth may be either Archimedean or equiangular, or a combination of features of both. An end-on view of a sheet of paper of constant thickness rolled into a multi-walled tube is an example of an Archimedean spiral, whereas an equiangular spiral develops if the thickness of the paper instead of remaining constant, increases steadily to give a wedge section. If halloysite tubes form by simple rolling up of kandite layers of constant thickness the result would be an Archimedean spiral. The electron optical evidence (Kirkman, 1977) does not support this mechanism.

The presence of striations on the walls of tubes (Fig-

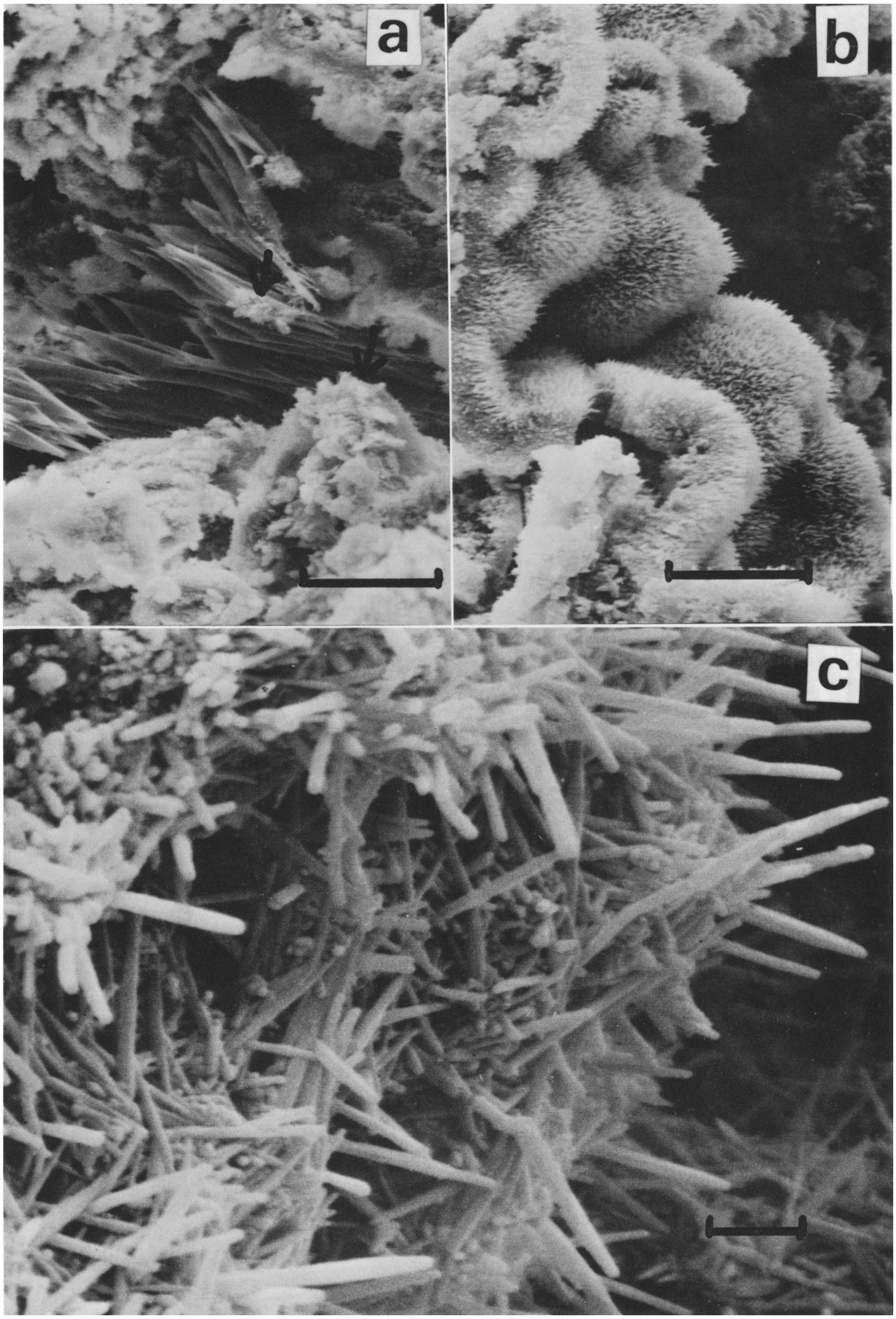

Figure 4. Scanning electron micrograph of fracture surface of aggregate of Woodstock 15 tephra showing (a) spherules of halloysite among platy primary minerals (arrowed). Bar = 40 μm; (b) spherules at higher magnification. Bar = 10 μm; (c) tapered particles composing the spherules. Bar = 1 μm.

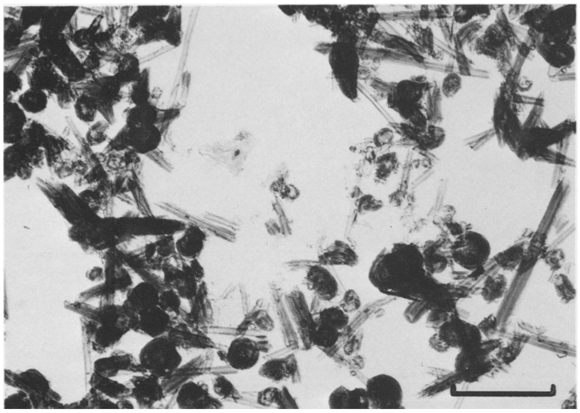

Figure 5. Transmission electron micrograph of <1.0-μm size clay of Woodstock 15 tephra showing tubes and squat ellipsoids (round particles) of halloysite. Bar = 0.5 μm.

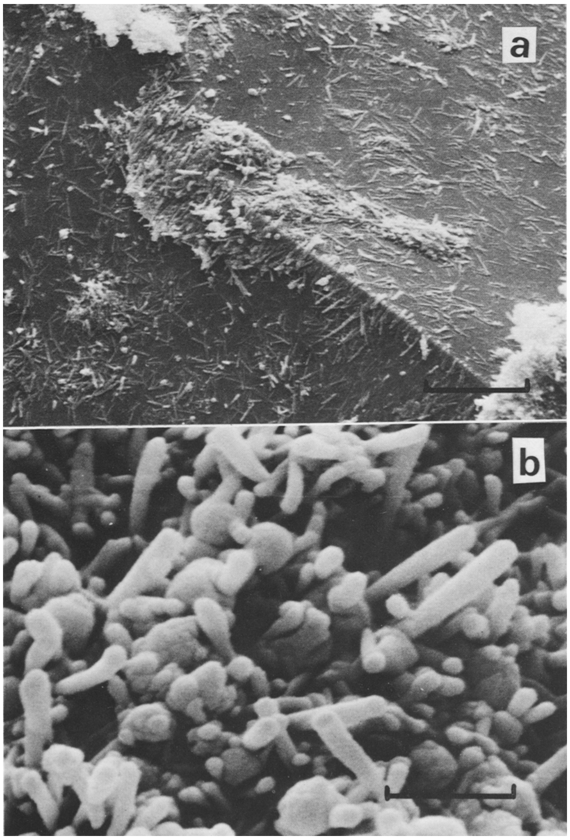

Figure 6. Scanning electron micrograph of fracture surface of aggregate of Hamilton tephra showing (a) primary mineral coated with tubular halloysite clustered at the edge. Bar = 10 μm; (b) higher magnification of halloysite clustered at the edge. Bar = 1 μm.

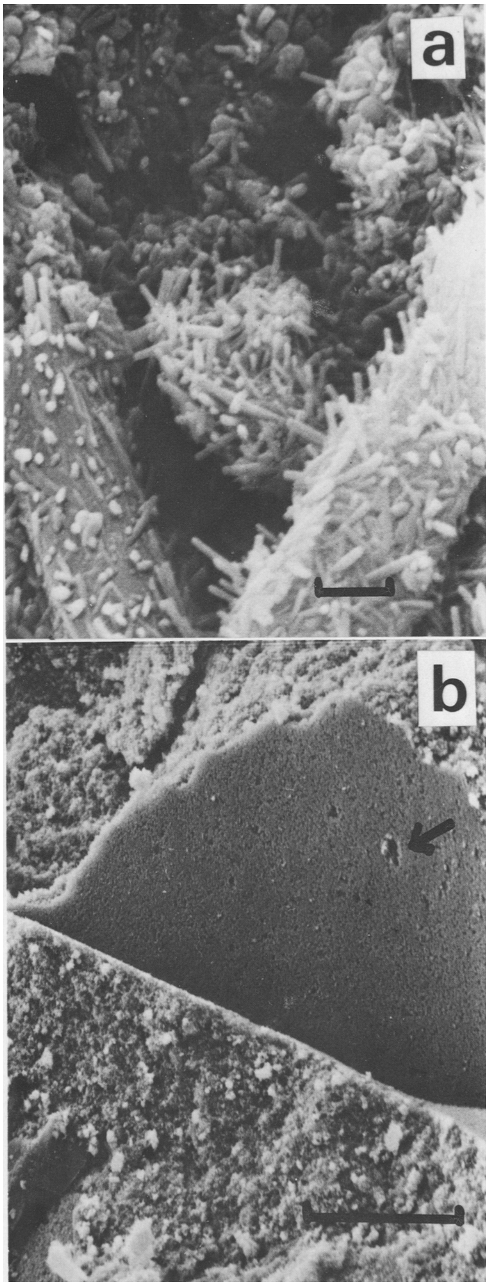

Figure 7. Scanning electron micrograph of fracture surface of aggregate of Hamilton tephra showing tubular halloysite (Figure 7a) in the hole arrowed on Figure 7b. Bar on Figure 7a = 1 μm; Figure 7b = 40 μm.

ure 2d) suggest a spirally wound tape; the tapered appearance of the tubes in Figures 2d and 8c implies that the tape thickens as it lengthens and spirals to form not a tube, but an elongate ellipsoid, or a long, thin cone. It follows that the spiral mechanism has features which are both Archimedean and equiangular. The spiral mechanism that produces the two types of particle—

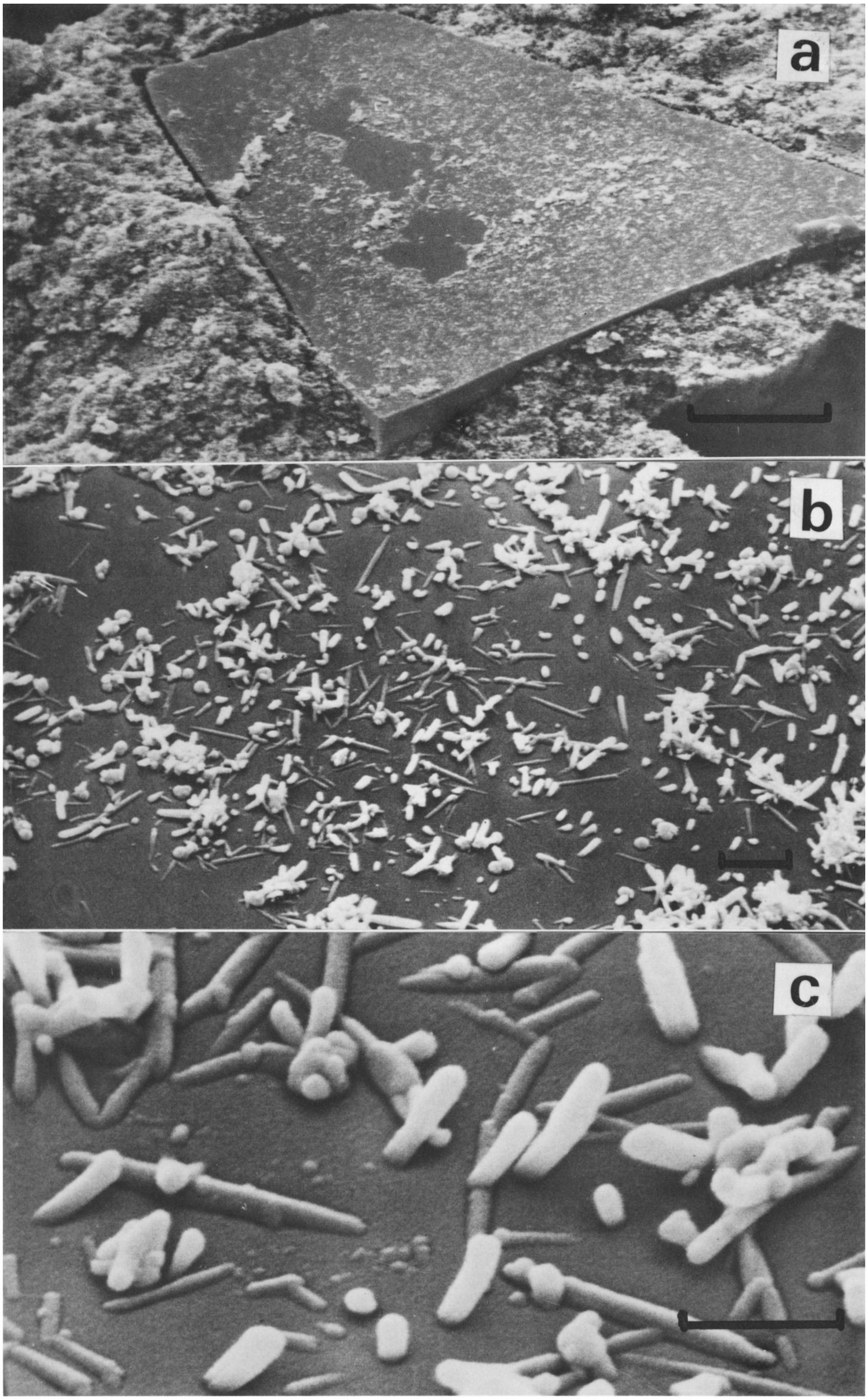

Figure 8. Scanning electron micrograph of fracture surface of aggregate of Hamilton tephra showing (a) trapezoid mineral. Bar = 40 μm; (b) halloysite particles coating the trapezoid. Bar = 2 μm; (c) two different forms of crystal, one of which is protruding upwards, the other is tapered and supine. Bar = 1 μm.

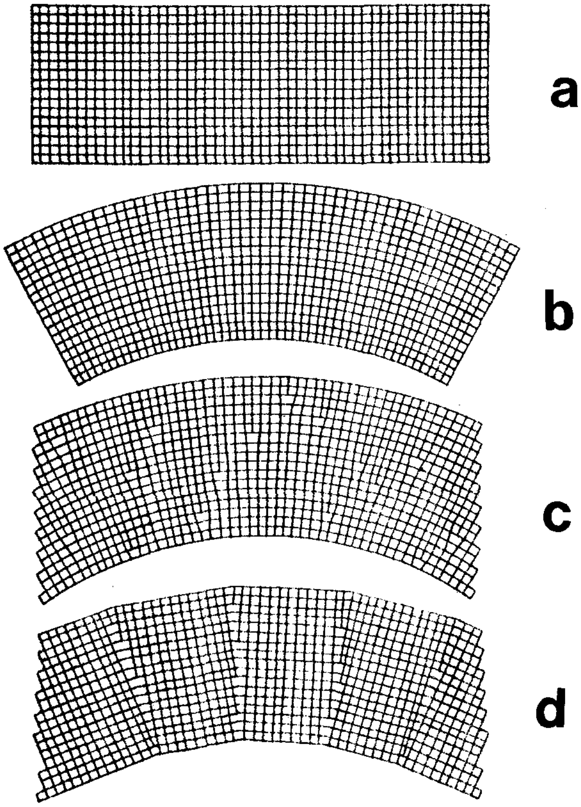

Figure 9. Four states of a single crystal (a) unstrained; (b) elastically bent; (c) plastically bent; (d) polygonized. Reproduced from F. R. N. Nabarro, Theory of crystal dislocations, © Oxford University Press, 1967.

squat ellipsoid and long ellipsoid—may be modified by inclusions such as fragments of glass, allophane, ferrihydrite, or feldspar crystallites. Such inclusions might impair crystal development and cause the protuberances, outgrowths, and twisted and malformed external layers visible on many particles (Figure 2).

Elongate ellipsoids (tubes) growing from squat ellipsoids emerge either from deep within a particle, or, more commonly, result from a modification of the external layer of squat ellipsoids. Both types have been observed and can be explained by changes in the direction of spiral growth induced by localized inclusions, as can the occasional end-swelling of long ellipsoids (Figure 2f). Elongate ellipsoids, unlike squat ellipsoids, generally do not show protuberances, or grow together in groups of two or more.

It is well documented that the squat ellipsoid form of halloysite is common in clays formed from volcanic glass; this form may indeed be the only form which develops from allophane, but such clays commonly contain tubes. Tubes grow from feldspar grains (Visconti *et al.*, 1956; Bates, 1962; Wolff, 1967; Parham, 1969), and it is assumed that the primary minerals supporting tubes or elongate ellipsoids (Figures 4, 5, 7, 8) are feldspars. Feldspars are a common precursor of halloysite in many tephras (Kirkman, 1980), but it is uncertain from the literature whether halloysite nucleates from a gel coating feldspar grains, or whether it grows from the feldspar surface using the array of weathering lattice ions as a template. Figure 8c suggests that halloysite is growing from within the primary grain and not from a gel coating. Such growth and the crystallization of halloysite from allophane indicate that the precursors of halloysite include both long-range and short-range ordered materials.

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Резюме—С помощью сканирующего и трансмиционного электронного микроскопа было показано, что галлоизит в трех реолитовых тефрах встречается в виде сплющенных и вытянутых эллипсоидов. Обе морфологии предположительно являются результатом подобного механизма построения решетки. Сплющенные эллипсоиды формируются из аллофана, вытянутые эллипсоиды—из фельдшпата. В условиях полевого уровня влажности сплющенные эллипсоиды не имеют ни плоских поверхностей, ни расстояний между «книгами» слоев. Отростки сплющенных эллипсоидов вываны, возможно, инклюзиями аллофана, стекла, ферригидрита, или кристаллитов фельдшпата. Возможный спиральный рост галлоизита, который приводит к искривлению поверхности, может быть вызван сплошным распределением кристаллических дислокаций. [E.C.]

Resümee—Raster- und transmissionselektronenmikroskopische Untersuchungen zeigten, daß Halloysit aus drei rhyolithischen vulkanischen Lockerprodukten als gedrungene oder längliche Ellipsoide auftritt. Es wird angenommen, daß beide Formen durch einen ähnlichen Gitterbildungsmechanismus entstehen. Die gedrungenen Ellipsoide bilden sich aus Allophan; die länglichen Ellipsoide entstehen aus Feldspäten. Die gedrungenen Ellipsoide haben bei Bergfeuchte keine glatten Flächen oder Zwischenräume zwischen Schichtpaketen. Auswüchse auf den gedrungenen Ellipsoiden sind wahrscheinlich durch Einschlüsse von Allophan, Glas, Ferrihydrit, oder Feldspatkristalliten bedingt. Ein mögliches Spiral—wachstum von Halloysit, das gebogene Oberflächen ergibt, könnte von einer kontinuierlichen Verteilung von Versetzungen im Kristall herrühren. [U.W.]

Résumé—La microscopie électronique balayante et à transmission montre que l'halloysite dans trois tephres est présente sous la forme d'ellipsoides trappus et élongés. On présume que les deux morphologies résultent d'un mécanisme semblable de construction de l'édifice cristallin. Les ellipsoides trappus sont formés à partir d'allophane, ceux qui sont élongés sont formés à partir de feldspars. Les ellipsoides trappus n'ont pas de faces aplaties ou d'espaces entre les livres de couches à des niveaux d'humidité naturels. Des protrusions des ellipsoides trappus sont possiblement dus à des inclusions d'allophane, de verre, de ferrihydrite, ou de cristallites de feldspars. La croissance en spirale possible d'halloysite, donnant des surfaces recourbées, peut être due à une distribution continuelle de dislocations de cristaux. [D.J.]