

A STUDY IN MORPHOLOGY BY ELECTRON DIFFRACTION

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ABSTRACT

A stabilized halloysite-glycerol complex was studied by electron microscope and electron diffraction techniques. The basal reflection was found to be 10.7 Å by both electron diffraction and X-ray diffraction analyses. Electron micrographs of the expanded lattice (halloysite-glycerol complex) were not different from those of the collapsed lattice (halloysite). On the basis of the tubes evident in the micrographs and the fact that the basal reflection was present in the transmission electron diffraction pattern, it was established that the halloysite-glycerol complex is tubular. Since this complex has an expanded lattice 0.6 Å greater than hydrated halloysite, it is believed that hydrated halloysite (endellite) is tubular as postulated by Bates, Hildebrand and Swineford.

INTRODUCTION

Hydrated halloysite (endellite), $(\text{OH})_4\text{Al}_2\text{Si}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, occurs in clays resulting from both weathering and hydrothermal processes. Hydrated halloysite dehydrates irreversibly very easily, by loss of its interlayer water, to halloysite, $(\text{OH})_4\text{Al}_2\text{Si}_2\text{O}_5$, (Alexander, *et al.*, 1943, p. 10). The phase boundary curve delineating the stability field of hydrated halloysite lies very close to the vapor pressure curve of water (Sand, 1952, p. 38). As a result, under conditions other than those of high vapor pressure dehydration occurs. Because of this instability, hydrated halloysite has never been observed in the electron microscope. Its dehydrated product, halloysite, had been reported by earlier workers as having a lath or rod morphology. The tubular morphology of halloysite was first ascertained by Bates, Hildebrand and Swineford (1950, p. 467) on the basis of their electron microscope studies. Extrapolating from the halloysite morphology, Bates *et al.* postulated that hydrated halloysite has a tubular structure on the basis of the misfit of the alumina octahedral layer and the silica tetrahedral layer and that the sheets in hydrated halloysite were allowed to curve by weakening of the constraining bonds due to separation by the interlayer water. Collapsing of the structure on dehydration resulted in splitting and unrolling due to the strain incurred.

That halloysite is tubular is now accepted generally. There has been some question whether hydrated halloysite particles are tubular, and whether the morphology of halloysite is pseudomorphous, or if hydrated halloysite

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consists of thin plates which curl into tubes upon subsequent treatment. The preshadowed replicas of halloysite (Comer and Turley, 1954) suggest that hydrated halloysite is also tubular. It is unlikely that curling of plates would result in the close packing of tubes shown by their replicas.

Bradley (1946, p. 706) and MacEwan (1948, p. 352) have shown how organic liquids reversibly replace the loosely held interlayer water. It was thought that these halloysite-organic complexes, because of their lower vapor pressure, might be suitable for electron microscope and diffraction examination of the expanded lattice. Glycerol was selected to form the complex with Wendover, Utah endellite, and formed an expanded lattice with the basal spacing of 11.0 Å as given by MacEwan.

RESULTS

The glycerol complex formed at room temperature was found to be unsuitable for examination. Excess glycerol on the clay interfered with preparation and the complex collapsed in a vacuum.

By heat treatment, the glycerol was firmly bonded in the interlayer position. This complex was unaffected when washed in boiling water to remove excess organic. The complex also was stable in a high vacuum during an hour's test.

By X-ray diffraction analysis the basal spacing was found to be 10.7 Å, a decrease of 0.3 Å from the loosely bonded complex, but still 0.6 Å more expanded than natural hydrated halloysite. This complex had the desired characteristics for the study of an expanded halloysite lattice: hydrophobic for easy sample preparation and stable in a vacuum and at the temperature to which it would be subjected in the electron beam.

Examination of the particles in the electron microscope revealed no differences in morphology from that of the Wendover halloysite particles. The tubes were uniform and well-formed as seen in the electron micrograph (Fig. 1). Split tubes are present which indicates the splitting might not be a function of dehydration.

The transmission electron diffraction pattern of the Wendover halloysite is shown in Figure 2, left half, and of the Wendover halloysite-glycerol complex in Figure 2, right half. The patterns are identical except for the basal spacings which measured 7.2 Å for the halloysite and 10.7 Å for the halloysite-glycerol complex. These were the same values as those obtained by X-ray diffraction; no structural change had occurred while being examined in the diffraction unit.

DISCUSSION

The firmly bonded halloysite-glycerol complex had a tubular morphology. This is evident on the basis of the electron micrographs and the fact that the basal reflection was present and unchanged in magnitude in the transmission electron diffraction pattern. The tubular morphology of this ex-



FIGURE 1. — Electron micrograph of Wendover halloysite-glycerol complex.

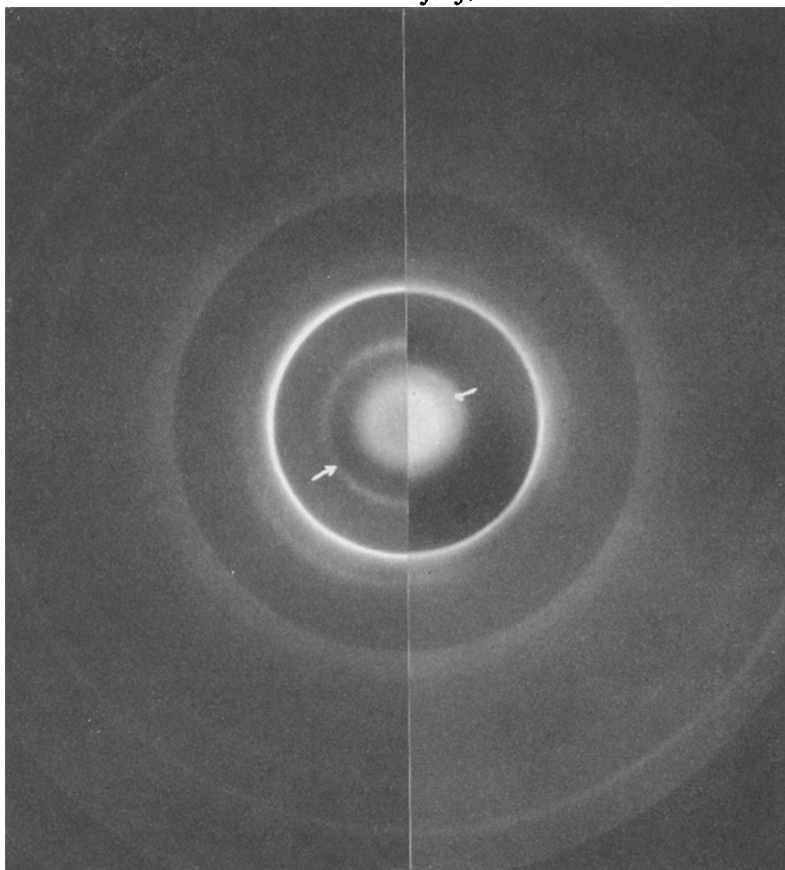


FIGURE 2. — Transmission electron diffraction patterns of Wendover halloysite (left half) and of the halloysite-glycerol complex (right half). The arrows indicate the basal reflections.

panded lattice gives support to Bates, Hildebrand and Swineford's theory that natural hydrated halloysite has this morphology and is the unstrained structure when interlayer water is present. If hydrated halloysite were platy, like kaolinite, expanding its lattice further by replacing the water with an organic liquid would not cause it to become tubular.

An alternative to consider is that hydrated halloysite might be formed under constraint as plates but when dispersed "peels off" in very thin layers and rolls into tubes. Bates is quoted by Grim (1953) as believing that "the rolling-up process is possible in very thin flakes where the number of silicate layers is so few that the strain produced by the misfit of the silicon-oxygen and alumina-hydroxyl sheets in each layer is not overcome by the cumulative effect of interlayer bonds between a large number of successive layers." If this were the case with hydrated halloysite, however, one should

expect inter-action in the process resulting in nonuniform particles. One also might expect this phenomenon to occur in the compact, porcelain-type halloysite, rather than in the porous residual halloysite. It generally holds, conversely, that the halloysites derived from the latter consist of particles of nonuniform length and thickness while the halloysites derived from porcelain halloysites consist, in general, of uniform and short tubes. Some relatively long (20μ) residual halloysite particles from North Carolina have been observed. That these should be the result of the curling of large plates is unlikely. These possibilities would still affirm that the unstrained lattice for hydrated halloysite is tubular.

The only other evident alternative is that halloysite is not tubular when formed upon dehydration of hydrated halloysite, but only becomes so upon exposure to heat such as from the electron beam. This heat energy also presumably would cause the tubular formation of the halloysite-glycerol complex. No disturbance of the sample screen substratum, which should occur, has ever been observed to support this possibility. Also, the replicas of halloysite by Comer and Turley conclusively rule out this possibility.

It appears evident that hydrated halloysite has a tubular structure, as proposed originally by Bates, Hildebrand and Swineford, and that their reasons are structurally valid.

At the Third International Crystallographic Congress, Correns (1954) presented photomicrographs taken with the phase contrast microscope of hydrated halloysite which showed its tubular morphology.

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