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SURFACE TENSION AND THE MORPHOLOGY OF HALLOYSITE[1]

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ABSTRACT

Electron micrographs of freeze-dried specimens indicate the existence of a tabular halloysite that forms tube-like shapes when subjected to normal drying. A similar phenomenon was observed with kaolin-like layers prepared by the nitrobenzene treatment of kaolinite. Thus, halloysite morphology can be tabular or tube-like, depending upon whether or not the material has been subjected to surface tension.

INTRODUCTION

The morphology of halloysite, based on electron microscope observations, has most frequently been described as tube-like. In recent years, theoretical considerations (Tamura and Jackson, 1953) and experimental observations (Fieldes, 1955; Bates and Comer, 1959) have resulted in a broadening of the tubular concept to include other variously curved forms that seem to suggest a morphological series from allophane to halloysite to kaolinite. An understanding of these minerals and their relationship to each other depends to a considerable extent upon understanding how they acquire their curved or tubular form.

The most widely accepted explanation for the tubular morphology of halloysite has been proposed by Bates *et al.* (1950). Their explanation is based upon curling engendered by a misfit in dimensions between the tetrahedral and octahedral layers. When the kaolin-like layers of hydrated halloysite are separated by water, the strain is thought to be relieved through intercellular slippage causing curling and subsequent tube formation. Other forms of halloysite presumably owe their curved shape to a similar process.

If strain is inherent in the halloysite structure and the tubular morphology of hydrated halloysite is exclusively the result of such strain, only curved or tubular shapes would ever be seen. However, if the tubular morphology also depended upon some additional operant not inherent in the structure, then non-curled hydrated halloysite particles should exist prior to the application of that operant.

Dehydration has been considered by many as such an operant, since the morphology of hydrated halloysite can be inferred only from the dehydrated form (as observed within the high-vacuum system of the electron microscope). Although replica work (Bates and Comer, 1959) has

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shown that the tubular shape of halloysite can exist prior to dehydration in the electron microscope, the observed tubes could have resulted from prior dehydration in nature. The pre-dehydration morphology of halloysite may not be tubular at all.

Surface tension is inherent in the ordinary drying process. The present investigation was undertaken in order to evaluate surface tension as a factor in halloysite morphology. The general approach in this investigation was to seek very thin, non-curled, fully-hydrated kaolin-like layers, and then to compare their morphology subsequent to regular drying and freeze drying. The absence of surface tension can be observed in samples that are freeze-dried, since the surface tension of liquid water is avoided through its removal by sublimation.

EXPERIMENTAL

It is anticipated that a supply of thin, non-curled, fully-hydrated, kaolin-like platelets is needed to investigate the effect of surface tension upon the curling of hydrated halloysite. One might perhaps expect to find them in a halloysite sample that had been subjected to a minimum amount of drying in recent years, or one might produce them from kaolinite.

Kaolin-like layers from halloysite. A search was made for thin kaolin-like layers in naturally occurring hydrated halloysite. An ideal sample for this purpose was obtained from M. L. Jackson. The sample has been kept under water since, 1941, when S. B. Hendricks obtained it from the Dragon Cone Mining Co., Eureka, Utah.[1] It is a hard porcelain-like material that has three different-appearing phases: (1) a large gravel-size particle, (2) some fine material, probably broken from the large particle, and (3) a colloidal phase. The bulk material and the colloidal phase both give fairly typical halloysite *x*-ray diffraction patterns (Fig. 1). All three phases were examined for kaolin-like layers with the electron microscope.

Grids for the electron microscope were prepared from the three phases. Single drops of sample were applied alternately to a grid to be air-dried, and a grid to be freeze-dried. It was anticipated that comparable grids would be made by alternating drops from a single dropper. The frozen samples were placed on the cold platform of the freeze-dry apparatus within fifteen minutes after preparation (see Kittrick, 1958, for general freeze-dry procedure). One-half of the air-dried grids were dried at room temperature outside the apparatus; the other half were dried under vacuum at room temperature. All samples were kept in a desiccator over $CaCl_2$ until placed in the electron microscope, to minimize rehydration.

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[1] Personal communication from Dr. Jackson.

Electron microscope observations were made within two days after grid preparation.

In all the electron micrographs showing air-dried Dragon Mine halloysite, regardless of the phase from which it was taken, almost all particles appear to be entirely or partially tubular. Further, the air-dried and freeze-dried material from the large particle and the fine material were essentially identical. However, a striking morphological difference can be seen between the freeze-dried and the air-dried halloysite taken from the colloidal suspension (Fig. 2).

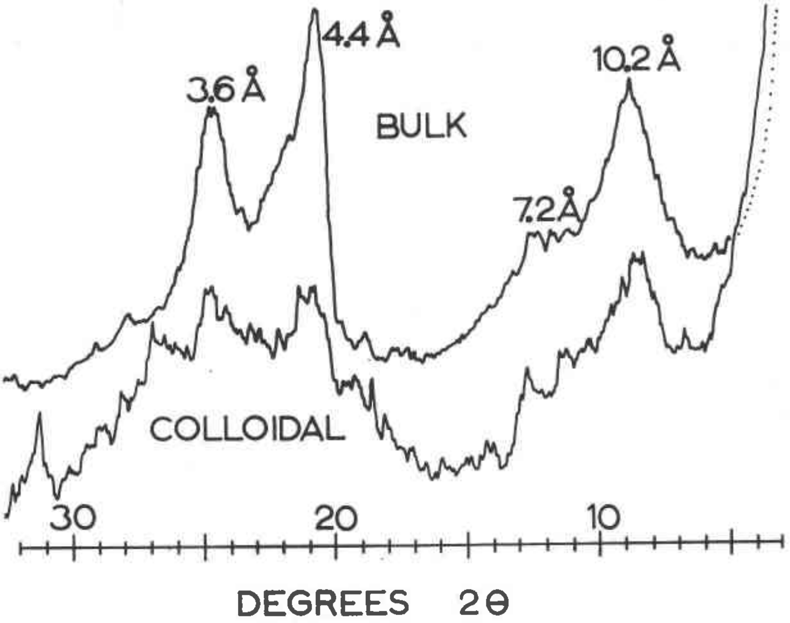

FIG. 1. Dragon Mine halloysite. The position of the 10.2 Å peak depended upon hydration. When heated to 400° C. for 2 hrs., a broad peak between 7 and 8 Å was obtained, with no peaks indicating longer d spacings. An oriented slide of the glycerated material was x-rayed using 1° divergence and scatter slits, a 0.003-inch receiving slit, 2° 2θ/min., time constant 8, Cu$k\alpha$, Ni filter, 40 KV. The bulk material was run at 20 MA, 200 counts/sec. full scale. The colloidal material (apparently less crystalline) was run at 30 MA, 100 counts/sec. full scale.

The freeze-dried colloidal phase, though it varied somewhat with different grids, was dominantly tabular. Similar results were obtained 4 other times over a period of 5 years. Six to twelve grids of each material were examined each time. Although the freeze-dried material shown in Fig. 2 resembles montmorillonite, no montmorillonite was indicated in the x-

ray diffraction patterns of either the solid or colloidal suspension. Further, no montmorillonite-like particles were observed in the air-dried colloidal phase.

The general arrangement of freeze-dried particles is probably inherited from the original suspension or possibly the result of the freeze-drying process. The important feature of the freeze-dried material is that it does not display the strongly tubular character of the air-dried material. The gross difference between the air-dried and freeze-dried preparations of the colloidal suspension indicates that surface tension is essential to curling and subsequent tube formation.

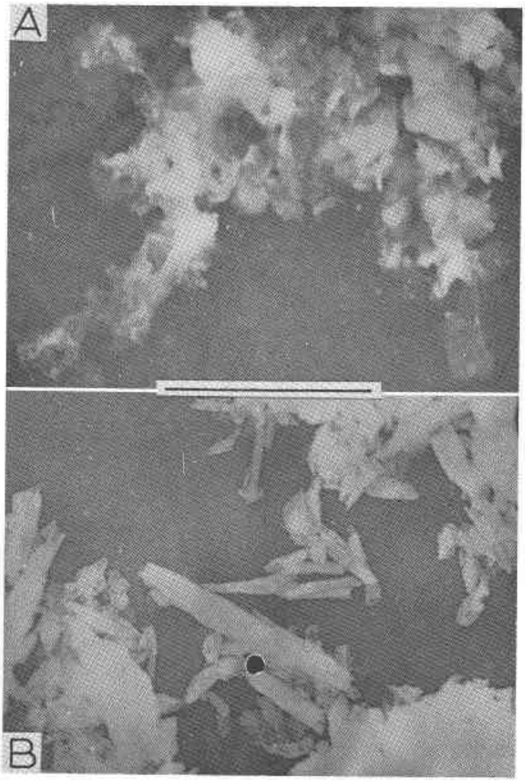

FIG. 2. Electron micrographs of colloidal Dragon Mine Halloysite: A. Freeze-dried; B. Nonfreeze-dried. Uranium shadow at approximately 40°. Line indicates 1 μ.

Kaolin-like layers from kaolinite. To produce thin kaolin-like layers from kaolinite, the hydrogen bonds between the layers must be broken. Using the chemical approach, Gastuche *et al.* (1954) subjected two types of kaolinite to boiling nitrobenzene (a proton accepting substance) for 305 hours. They reported that they had " . . . broken the hydrogen bonds of kaolinite," producing kaolin-like layers that rolled into tubes. Accordingly, the $< 2\,\mu$ fraction of four kaolinites[1] was treated with boiling nitrobenzene for two months. The clays were then given successive washes with benezene, acetone, and water, and suspended in water, avoiding drying at any time. Electron microscope specimens were taken from the entire $<2\,\mu$ fraction and prepared as described for the Dragon Mine Halloysite.

The kaolinite most altered by nitrobenzene was the English Colloidal (Fig. 3). None of the freeze-dried material was curled, though the nitrobenzene treatment appeared to break down the kaolinite into thinner, smaller, particles. After normal drying some curling was observed. The extent of curling ranged from turned-up edges to complete tubes. This variety of curled and tube-like shapes may be engendered by the variety of kaolinite fragments what exist prior to drying. In any event, surface tension appears to be essential to curling and tube formation in nitrobenzene-altered kaolin particles, as it was previously shown to be for curling and tube formation in halloysite.

It is not known if the curled and tube-like particles were internally hydrated prior to normal drying. *X*-ray diffraction analysis of the $<2\,\mu$ material did not indicate the formation of hydrated halloysite by the nitrobenzene treatment, although hydrated halloysite may have been present in amounts insufficient to produce a recognizable *x*-ray pattern.

DISCUSSION

Probable morphology of hydrated halloysite. It has been observed that hydrated halloysite exists as tube-like particles when dried normally, but exists as flat particles when freeze-dried. It appears reasonable to suppose that either the hydrated colloidal Dragon Mine halloysite was originally flat, then curled due to surface tension during drying, or that it was originally curled and then flattened due to freezing. The former seems more likely, since surface tension has been known to cause curling in the drying of macroscopic objects. It can also produce forces of sufficient magnitude to change shapes of microscopic particles. Bickerman (1948) states that capillary attraction, a function of surface tension, exerts considerable influence on the shape of moist bodies during the course of their drying. Anderson (1952) considered the distortion forces exerted by surface ten-

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[1] Kaolinites H-2, H-5, and H-17 were obtained from Wards Natural Science Establishment. English Colloidal kaolinite was obtained from Hammerill and Gillespie Inc., N. Y.

sion as water evaporates, and pointed out that a column 0.02 μ in diameter must be able to withstand a stress of 2,000 psi if it is not to collapse. He shows that a rod bridging a 2 μ gap is subject to a force of more than 600,000 psi, which is over twice the tensile strength of piano wire.

Even though the force created by surface tension can be large, it alone does not appear to be enough to cause the formation of tubular halloysite. If it were, one might expect montmorillonite to curl, since it appears similar to uncurled halloysite in electron micrographs. The essential difference may be that in montmorillonite two tetrahedral layers distribute stress evenly, whereas in halloysite unevenly distributed stress could account for some of the tube-forming force (as suggested by Bates,

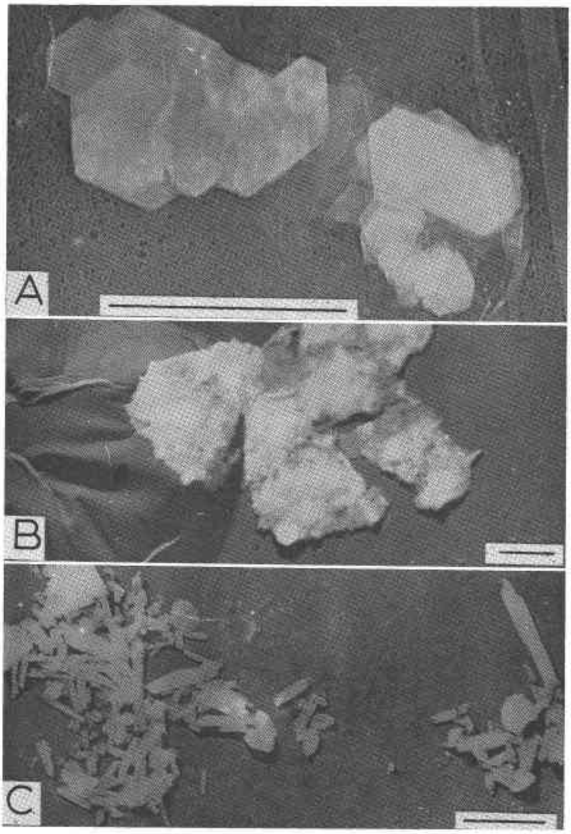

FIG. 3. Electron micrographs of kaolinite: A. Untreated; B. Nitrobenzene-treated, freeze-dried; C. Nitrobenzene-treated, nonfreeze-dried. Uranium shadow at approximately 40°. Line indicates 1 μ.

Hildebrand, and Swineford, 1950), though not all of it (in agreement with Radoslovich, 1963). It would appear that neither lattice stress nor surface tension alone is sufficient.

Electron microscope examination of the Dragon Mine halloysite sample showed most of it to be tubular even when freeze-dried (only the colloidal phase was tabular under these conditions). Since *x*-ray diffraction analysis of the bulk sample showed it to be predominantly hydrated halloysite, it is relatively certain that tubular halloysite can also be internally hydrated. However, the tabular (when freeze-dried) colloidal phase of the Dragon Mine sample also gave a hydrated halloysite *x*-ray diffraction pattern. Therefore, it appears that some (perhaps all) internally hydrated halloysite is flat prior to dehydration. Repeated drying of halloysite deposits in the past could account for the present abundance of curled or tubular forms.

Halloysite-kaolinite relationship. One might have expected kaolin-like layers (present in both halloysite and nitrobenzene-treated kaolinite) to form flat hydrogen-bonded pseudokaolinite as the water evaporated and the plates came together. Instead, they formed curled tube-like particles when dried. If kaolinite weathers to halloysite in nature, many of the different forms of halloysite can be explained. When a kaolinite crystal breaks apart during weathering, the shape of a resultant halloysite particle would be largely determined by the shape of the kaolinite fragment prior to drying. Typical tubes would form only where platelets were uniformly thin enough to be completely curled by surface tension; other shapes would result in only partial curling or twisting. This would be in agreement with the wetting and drying experiments of Oberlin and Tchoubar (1959) and the observation by Bates and Comer (1959) of kaolinite-like shapes on the edges of partially rolled halloysite.

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