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GLOBULAR CLUSTER MICROSTRUCTURE OF ENDELLITE (HYDRATED HALLOYSITE) FROM BEDFORD, INDIANA

SIDNEY DIAMOND

School of Civil Engineering, Purdue University, Lafayette, Indiana 47907, U.S.A.

and

JAMES W. BLOOR

Department of Civil Engineering, The University of Calgary, Calgary, Alberta, Canada

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Abstract—Scanning electron microscope observation of endellite from Bedford, Indiana, discloses the existence of globular clusters of quasi-tubular endellite particles radiating from common centers. Individual clusters are of the order of 10 μ in overall diameter. The individual quasi-tubular particles are irregularly flattened in cross section, and some may be plugged at the ends. Conventional oven drying at 105°C results in partial unrolling and incomplete flattening of the quasi-tubular particles of some of the clusters. The globular cluster microstructure is taken to represent the result of *in-situ* crystallization from solution. If this is so, these hollow tubes cannot have arisen by the mechanism of repeated extrusion of concentric zonal crystallites as postulated by Chukhrov and Zvyagin.

PREVIOUS DETERMINATIONS OF THE MORPHOLOGY OF ENDELLITE

THE MORPHOLOGY of endellite (hydrated halloysite) and metahalloysite particles and the relationship of morphology to hydration state have been somewhat controversial. Endellite starts to dehydrate irreversibly (if incompletely) at room temperature under less than 100% r.h., and does so quite rapidly *in vacuo*. It is in consequence an extremely difficult material to study without alteration. Bates, Hildebrand, and Swineford (1950) described dispersed metahalloysite as tubular, and hypothesized that a tubular morphology was inherited from an endellite precursor, which was thought to have assumed tubular form in its original growth process. Comer and Turley (1955) and Bates and Comer (1955) examined several kinds of surface replicas prepared from undispersed endellite masses, and confirmed that the endellite particles, in fact, were tubular. While the use of replicas permitted electron microscopic observation of the surface of the mass, it must be pointed out that preparation of the replicas involves evacuation of the sample as the initial step, and endellite does dehydrate under vacuum. Sand and Comer (1955) prepared an endellite–glycerol complex with glycerol replacing the water in interlayer positions. This complex was both stable under evacuation and tubular in morphology when examined by electron microscopy.

Davis *et al.* (1950), Taggart *et al.* (1955), Bates and Comer (1959), and other workers have reported studies of dehydrated endellite preparations and in general concur that the particles observed are generally tubular. No particular mutual orientation of particles has been reported, although some flattening of the tubes was observed in a number of cases.

In contrast to these observations, Pundsack (1956) proposed, on the basis of density determinations of endellite before and after drying, that the endellite and the dehydrated form derived from it (metahalloysite) must have radically different morphologies. He inferred that the hydrated form likely consists of laths rather than tubes; on dehydration the laths were pictured as undergoing shrinkage and distortion to generate the tubular particles observed in the electron microscope.

More recently, Chukhrov and Zvyagin (1966) proposed a model somewhat similar to that inferred by Pundsack, and presented electron micrographs of replicas substantiating it. They suggested that endellite crystallized as elongated polygonal solid particles with a complex internal structure. The particles were said to consist of radial zones and of separate polygonal ring zones, the latter usually coaxial. The long axis of the polygonal solid was usually the "*b*" axis, and the external prismatic faces were considered to be (001) faces. The polygonal solid particles were not considered to be completely solid, but to have spaces between individual zones which permit rapid dehydration on evacuation or heating. On dispersion, particularly ultrasonic dispersion, coaxial crystallite zones were said to be repeatedly extruded to form the hollow tubular morphology normally associated with endellite. Thus the tubular morphology was said to arise entirely from secondary processes associated with sample preparation or other disturbance.

SCANNING ELECTRON MICROSCOPE OBSERVATIONS ON THE MORPHOLOGY OF ENDELLITE

Samples of apparently massive bluish-white endellite were collected by one of us (S.D.) from the source cave at Gardner Mine Ridge near Bedford, Indiana. The samples were kept immersed in water in sealed containers until immediately prior to sample preparation. The locality and geological origin of this deposit have been described several times (Callaghan, 1948; Kerr *et al.*, 1950; Keller *et al.*, 1966). Callaghan concluded that the bluish-whiteendellite found within the sandstone cavities was deposited directly from solution by circulating groundwater.

Samples of this material were prepared for scanning electron microscope examination by cutting small cubical blocks of the order of 0·5 cm on a side from the wet massive sample. Additional material was dried at 105°C and fractured into blocks of similar size. Samples of both kinds were mounted to sample stubs with cement, evacuated, and coated with a two-layer coating consisting of a nominally 50 Å thick coating of carbon and a nominally 250 Å thick coating of gold-platinum alloy. The results of observations conducted using a Cambridge Stereoscan scanning electron microscope are displayed in the following figures.

Figure 1 represents a low-magnification view of the surface of a sample cut in the wet state and subsequently evacuated at room temperature. Two distinct regions are observed: comparatively featureless zones such as those present around the perimeter of Fig. 1, and "open areas" such as that comprising the central portion of Fig. 1. The open areas reveal that the particles of this evacuated endellite are arranged in a basic microstructure consisting of globular clusters of the order of 10 μ in diameter, whose existence has been previously unsuspected. Some of the clusters are packed tightly against their neighbors, but others are separate and leave some space between themselves.

On examination at higher magnification (Fig. 2) the featureless areas turn out to consist largely of tubes that are flattened, deformed, and in some cases apparently unrolled. Tubes appear to be present in all possible orientations, but a general tendency toward preferential orientation in the plane of the surface of the sample is evident. The morphology of these areas possibly represents the results of severe local disturbance due to the sample cutting operations.

Each of the globular clusters visible in Fig. 1 is seen at higher magnification to consist of straight rod or tube shaped particles of halloysite extending radially from a common center (Fig. 3). The individual particles are of the order of 3000 Å in diameter and several microns long. Examination of the ends of exposed particles suggests that they are not, in fact, circular in cross-section, but rather tend to be straight-sided, with pentagonal or hexagonal cross-sections, in accord with the appearance of the replica electron micrographs of Chukhrov and Zvyagin (1966). The globular clusters are inherently different from the rounded grains reported by Sudo and Takahashi (1955) in certain volcanic clays of Japan. The latter were of the order of 0·2 μ in diameter, and according to these workers, were derived from coagulated fine particles of amorphous allophane which weathered to endellite and then to metahalloysite without change in the outline of the grains. The present clusters are of the order 10–20 μ in diameter and appear to represent an original growth habit from the solution phase.

Examination of surfaces of samples that were dried at 105°C before fracture revealed analagous regions of disturbed areas and of "open" areas displaying globular clusters of halloysite particles such as previously observed. However, as shown in Fig. 4, the clusters seen are now of two distinct morphologies. A significant fraction of them consist entirely of sheets that seem to be the formerly quasi-tubular particles in various stages of unrolling. The remaining clusters consist of apparently unchanged flattened tubular particles. Clusters seem to have behaved as individual units with regard to unrolling; either essentially all of the individual particles in a cluster have unrolled or else essentially none of them have. Adjacent clusters are as likely to be opposite in behavior as they are to be similar in behavior.

Figure 5 shows a high-magnification view of an area across the boundary between a pair of unlike clusters seen in Fig. 4. The particles belonging to the cluster on the left are very thin sheets of the order of several hundred Å in thickness. The sheets terminate in somewhat ragged edges. The quasi-tubular particles on the right show split ends, apparently preliminary to unrolling. The impression is inescapable that these particles are not completely

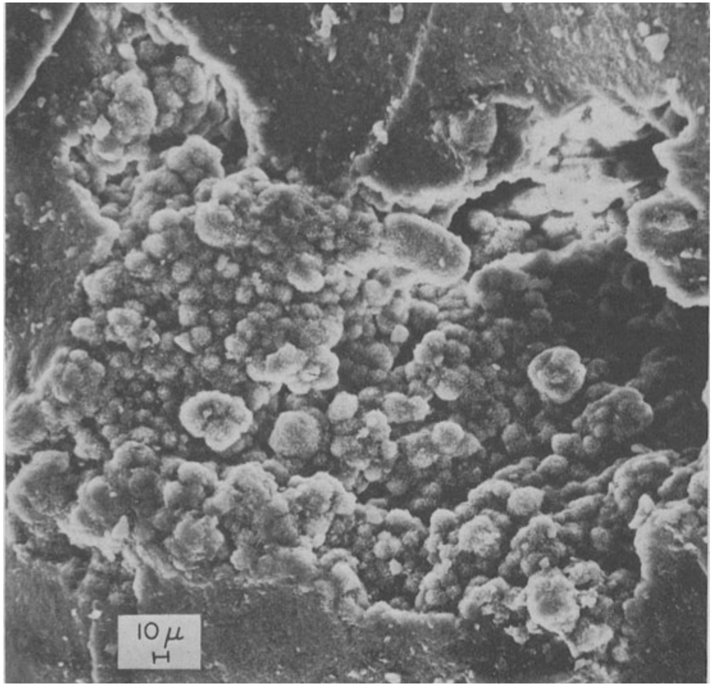

Fig. 1. General view of fracture surface of vacuum-evaporated sample of Bedford endellite, showing peripheral featureless area and central "open" areas containing globular clusters.

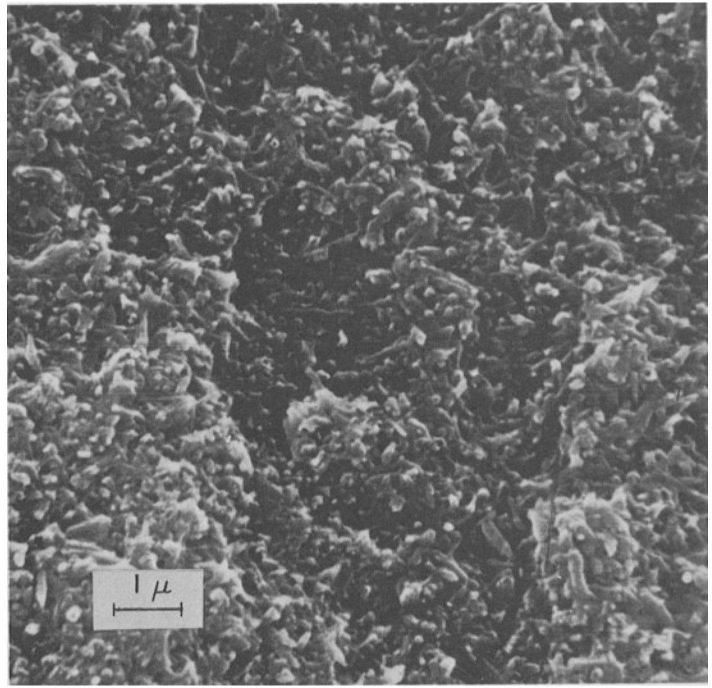

Fig. 2. High-magnification detail of typical peripheral area as seen in Fig. 1.

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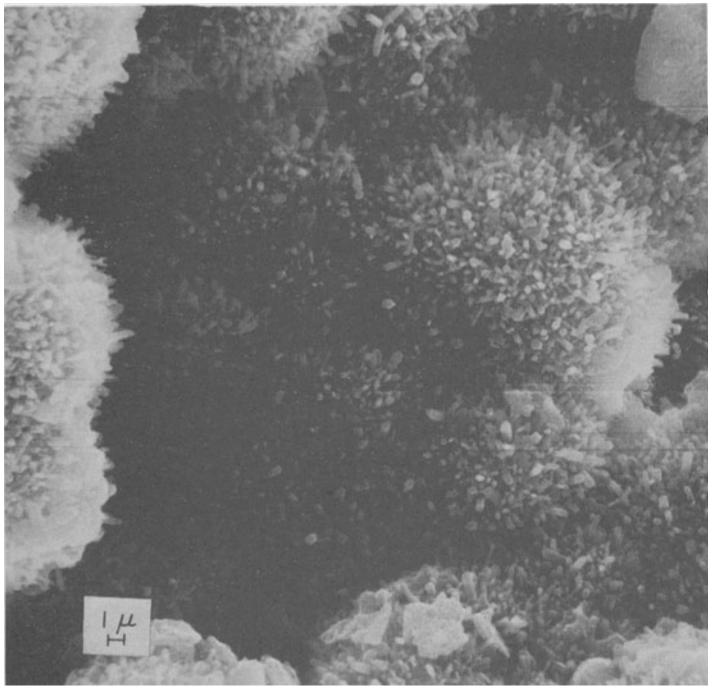

Fig. 3. Typical globular clusters of vacuum-dehydrated endellite seen in central "open" areas of Fig. 1.

Fig. 4. View of typical globular clusters of oven-dried preparation showing clusters of quasi-tubular and of unrolled particles adjacent to each other.

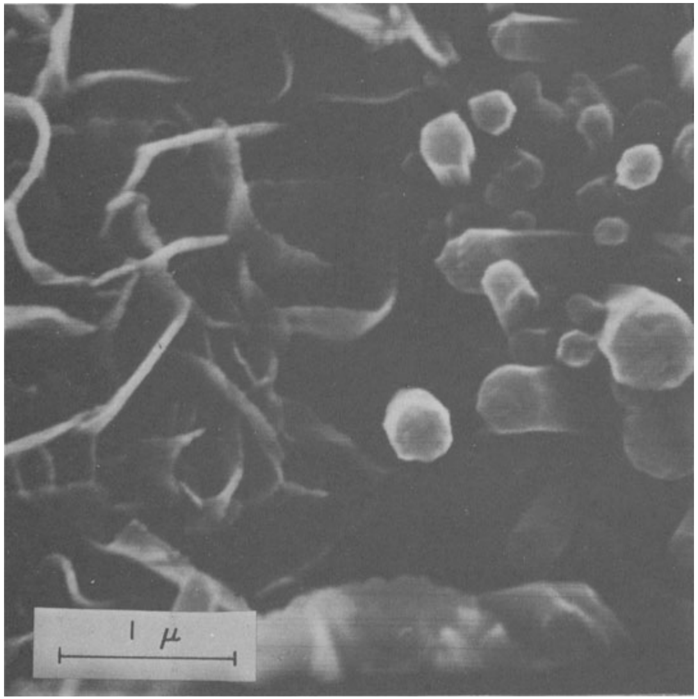

Fig. 5. High-magnification view of portions of adjacent clusters of unrolled and of intact quasi-tubular particles of Fig. 4.

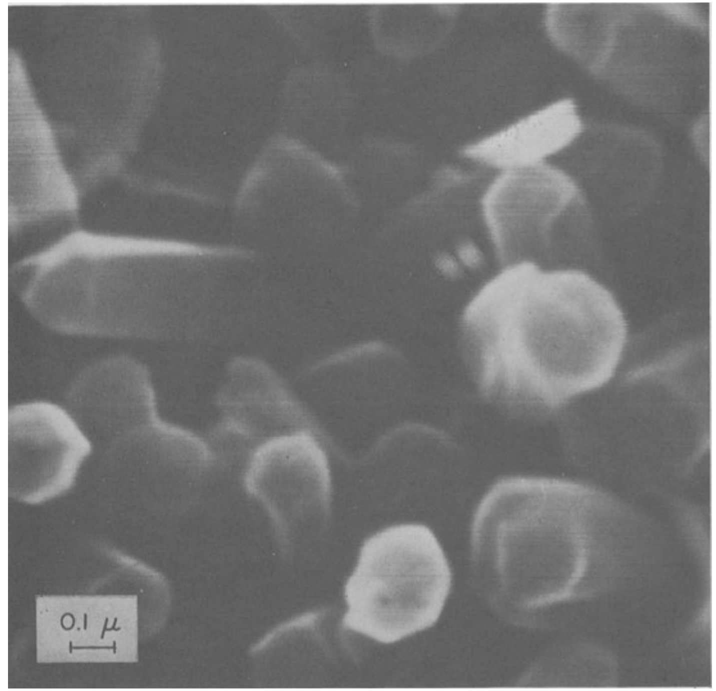

Fig. 6. Very high-magnification end view of portion of cluster of intact quasi-tubular particles.

hollow but rather seem to be either solid or to terminate in solid ends. Nevertheless, the impression may be in part at least an artifact associated with enhancement of secondary electron emission from the ends of the particles.

Figure 6 is a very high magnification micrograph of a portion of a cluster of quasi-tubular particles. One of the flat-sided tubes in the lower right-hand portion of the figure is clearly a hollow particle in the early stage of unrolling. Another particle, in the upper right-hand portion of the figure, is seen as an open three-sided tube, presumably also starting to unroll or relax. It seems reasonable to conclude that the other particles are also, in fact, hollow. The possibility of thin plugs at the ends of all or some of them remains, however, and the bright object immediately above the three-sided open tube in Fig. 6 could be such a plug released from the tube end.

One of us has recently reported mercury pore-size distribution curves for air-dried and oven-dried Bedford halloysite (Diamond, 1970). These curves show a large increase in the volume of pores intruded by mercury after ovendrying. The increased pore volume occurs in the nominal diameter range of 1–10 μ, and it was hypothesize that the increase was likely due to partial unrolling of the tubes accompanying ovendrying. Figure 5 would appear to provide considerable support for this hypothesis, especially when coupled with the possibility that some or all of the "tubes" are sealed against fluid penetration by end plugs prior to oven drying.

COMPARISON BETWEEN SCANNING ELECTRON MICROGRAPHS AND PREVIOUSLY-PUBLISHED INDICATIONS OF MORPHOLOGY

Scanning electron micrographs reveal that apparently massive Bedford, Indiana endellite (examined after vacuum evaporation) consists to a large extent of globular clusters of radially-oriented quasi-tubular particles. The cross sections are roughly polygonal, in accord with the observations of Chukhrov and Zvyagin, but the endellite seems to be present as hollow particles, (perhaps with end plugs), rather than as solid prismatic particles. Oven drying results in unrolling and incomplete flattening of the tubes of some clusters, while leaving adjacent ones seemingly unaffected.

If, as is presumed, the globular cluster habit represents in-situ crystallization from solution, the mechanism of extrusion of concentric zonal crystallites that Chukhrov and Zvyagin postulate to account for the existence of hollow tubular particles could not have been operative here. It is not possible to say whether this particular endellite represents a specific exception to the general mechanism thought to have been observed for endellite by these workers, or whether their conclusions are in error. It does seem clear that Pundsack's suppositions are incorrect in that the tubes of endellite unroll, rather than form, as a result of rigorous dehydration.

REFERENCES

Bates, T. F., Hildebrand, F. A. and Swineford, A. (1950) Morphology and structure of endellite and halloysite: *Am. Mineralogist* **35**, 463–484.

Bates, T. F. and Comer, J. J. (1955) Electron microscopy of clay surfaces: *Clays and Clay Minerals* **3**, 1–25.

Bates, T. F. and Comer, J. J. (1959) Further observations on the morphology of chrysotile and halloysite: *Clays and Clay Minerals* **6**, 237–248.

Callaghan, E. (1948) *Endellite deposits in Gardner Mine Ridge, Lawrence Co., Indiana*: Indiana Dept. Cons. Div. Geol., Bull. 1.

Chukhrov, F. V. and Zvyagin, B. B. (1966) Halloysite, a crystallochemically and mineralogically distinct species: *Proc. Intern. Clay Conf. 1966, Jerusalem*, Vol. 1, 11–25. Pergamon Press, Oxford.

Comer, J. J. and Turley, J. W. (1955) Replica studies of bulk clays: *J. Appl. Phys.* **26**, 346–350.

Davis, D. W., Rochow, T. C., Rowe, F. G., Fuller, M. L., Kerr, P. F. and Hamilton, P. K. (1950) Electron micrographs of reference clay minerals: Preliminary Report No. 6, API Project 49, Columbia Univ. N.Y. 1–17.

Diamond, S. (1970) Pore-size distribution in clays: *Clays and Clay Minerals* **18**, 7–23.

Keller, W. D., McGrain, P., Reesman, A. L. and Saum, N. M. (1966) Observations on the origin of endellite in Kentucky, and their extension to "Indianaite": *Clays and Clay Minerals* **13**, 107–120.

Kerr, P. F., Main, M. S. and Hamilton, P. K. (1950) Occurrence and microscopic examination of reference clay mineral specimens, Part 1, Occurrence: Preliminary Report No. 5, API Project 49, Columbia Univ., N.Y. 1–14.

Pundsack, Fred L. (1956) Density and structure of endellite: *Clays and Clay Minerals* **5**, 129–135.

Sand, L. B. and Comer, J. J. (1955) A study in morphology by electron diffraction: *Clays and Clay Minerals* **3**, 26–30.

Sudo, T. and Takahashi, H. (1955) Shapes of halloysite particles in Japanese clays: *Clays and Clay Minerals* **4**, 67–79.

Taggart, M. S., Milligan, W. O. and Studer, H. P. (1955) Electron micrographic studies of clays: *Clays and Clay Minerals* **3**, 31–64.

Résumé—L'observation d'endellite de Bedford, Indiana, par exploration au microscope électronique, a mis à jour l'existence de groupes globulaires de particules d'endellite quasi tubulaires partant de centres communs. Ces groupes individuels ont un diamètre hors-tout de l'ordre de 10μ. Les particules individuelles quasi tubulaires sont irrégulièrement applaties par le travers et certaines peuvent être enfoncées aux bouts. Le séchage à 105°C dans un four traditionnel donne pour résultat un déroulement partiel et un applatissement incomplet des particules quasi tubulaires de certain des groupes. La microstructure globulaire des groupes est considérée comme étant le résultat de la cristallisation insitu de la solution. Si cela est, ces tubes creux ne peuvent s'être dèveloppés par le mécanisme de l'extrusion répétée de cristallites à zone concentrique comme il a été postulé par Chukhrov et Zvyagin.

Kurzreferat – Die genaue Prüfung im Elektronenmikroskop von Endellit aus Bedford, Indiana, zeigt die Anwesenheit kugelförmiger Büschel von quasi-röhrenförmigen Endellit Teilchen, die aus gemeinsamen Mittelpunkten ausstrahlen. Einzelbüschel haben einen Gesamtdurchmesser in der Grössenordnung von 10 Mikron. Die einzelnen quasi-röhrenförmigen Teilchen sind im Querschnitt unregelmässig abgeflacht, und manche können an den Enden verstöpselt sein. Die übliche Trocknung im Ofen bei 105°C ergibt teilweises Aufrollen und unvollständige Abflachung der quasi-röhrenförmigen Teilchen einiger der Büschel. Es wird angenommen, dass das Mikrogefüge von kugelförmigen Büscheln das Ergebnis örtlicher Kristallisation aus der Lösung darstellt. Wenn das zutrifft, so können diese Hohlröhren nicht, wie von Chukhrov und Zvyagin postuliert, durch den Mechanismus Wiederholter Extrusion konzentrischer Kristalliten zonen entstanden sien.

Резюме — Исследование в сканирующем электронном микроскопе образцов энделлита из Бедфорда (шт. Индиана) обнаружило наличие в них шаровых агрегатов, образованных из квази-трубчатых частиц энделлита, радиально расходящихся из общего центра. Поперечник отдельных агрегатов — порядка 10 мк. Отдельные квази-трубчатые частицы неправильно сплющены в поперечном сечении, а некоторые закупорены на концах. Высушивание в печи при температуре 105° вызывало частичное разворачивание и неполное выравнивание квази-трубчатых частиц некоторых агрегатов. Микроструктура из шаровых агрегатов принимается как следствие их кристаллизации *in situ* из раствора. Если это так, то эти полые трубки не могут возникать в результате повторного выпадения концентрических зональных кристаллитов, на которое указывали Чухров и Звягин.