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Manganese minerals in geodes from Chihuahua, Mexico[1]

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SUMMARY. Seven manganese minerals have been observed in geodes from Chihuahua, Mexico. Ramsdellite occurs in a number of different habits, but the morphology and precession X-ray patterns suggest that it is pseudomorphous after groutite. Pyrolusite is found only in association with ramsdellite and is believed to be an alteration product of that mineral. Todorokite generally occurs as a late-stage fibrous overgrowth in many of the geodes. Ranciéite, birnessite, hollandite, and cryptomelane are present in trace amounts. This assemblage of manganese minerals is typical of supergene mineralization.

IN a previous article describing the mineralogy of geodes from North Central Chihuahua, Mexico, Finkelman *et al.* (1972) observed fifteen minerals. Among these were six manganese oxides: birnessite, cryptomelane, pyrolusite, ramsdellite, ranciéite, and todorokite. We have since confirmed the presence of hollandite, the seventh manganese mineral, as well as beidellite and mordenite. The only manganese oxide previously reported in geodes was pyrolusite (Sinotte, 1969).[2] There has been considerable interest in the genesis of this complex group of minerals, and many questions are still unanswered (Fleischer and Richmond, 1943; Bricker, 1965; McKenzie, 1971). We therefore felt that this unusual association deserved further mention and are now presenting additional descriptive and analytical data on all seven manganese minerals.

The state of Chihuahua is a noted manganese mining district (Wilson and Rocha, 1948; Trask and Cabo, 1948). The manganese is found primarily as fissure deposits in rhyolite (Trask and Cabo, 1948) and consists of psilomelane, cryptomelane, hollandite, and coronadite (Wilson and Rocha, 1948). It should be kept in mind that this previous work was done prior to the recognition of birnessite and ramsdellite and prior to the discovery of todorokite outside of Japan. The associated minerals are calcite, chalcedony, quartz, gypsum, hematite, and other iron oxides (Wilson and Rocha, 1948). All these minerals are also found associated with the manganese oxides in the geodes.

The geodes were reported (Jack Young, personal commun. 1971) to come from a rhyolite about 65 miles north of Chihuahua City; they were purchased from a dealer, and nothing further is known of their provenance.

The interior of the Chihuahua geodes consists of a zone of chalcedony of variable thickness, almost always overgrown by quartz crystals having their apices pointing to the centre of the geode. It is usually on or in the zone of quartz that the manganese

[1] Publication authorized by the Director, U.S. Geological Survey.

[2] Avaliani (1971) mentioned that bementite had developed in geodes in Russia.

minerals are found. Most of these minerals form grains that do not exceed 500 μm in length; the largest single crystal does not exceed 1 mm.

Most of the several hundred geodes examined contained at least one manganese mineral; a few had as many as four. In all but three geodes the manganese minerals were no more than trace constituents. Two of these three geodes contained large calcite crystals in which birnessite had formed in fractures. The dark birnessite on the light-grey calcite gave the impression that the birnessite was present in significant amounts, but in fact it constituted less than 1 % by volume of the crystals in the cavity of these geodes. The third geode (USNM no. B2906) was unique in that there was no quartz zone. The interior of this geode was simply a smooth shiny white surface of chalcedony, 80 % of which was covered by a 1-mm thick black layer consisting of a mixture of manganese oxides (birnessite, cryptomelane, and todorokite). Even the solid geodes (see Finkelman *et al.*, 1972, for comments on the definition of a geode) contained trace amounts of manganese oxides as dendrites embedded in the interior. In many instances the dendrites were curved parallel to the circumference of the geode, suggesting that the manganese had formed on the surface of a chalcedony layer and was then covered by subsequent precipitation of chalcedony.

TABLE I. *Semiquantitative electron microprobe analyses*

	Ramsdellite	Ranciéite	Todorokite	Birnessite
MnO_2	92·3	71·5	41·0	79·1
MgO	0	0	0·5	0·4
ZnO	0	0	0	0
BaO	0	0	0·3	0·5
CaO	0	11·9	1·5	2·9
Na_2O	0	0·2	1·3	1·2
K_2O	0	0·2	1·3	0·4
Al_2O_3	0·1	0	0·7–3·2	0·1
Fe_2O_3	0	0	2·0	0
SiO_2	0	0	0·7	0·2
TiO_2	0	0	0	0
P_2O_5	0	0	0·1	0
Sr_2O_3	0	0	0·3	0·1
SO_3	0·1	0	1·0	0

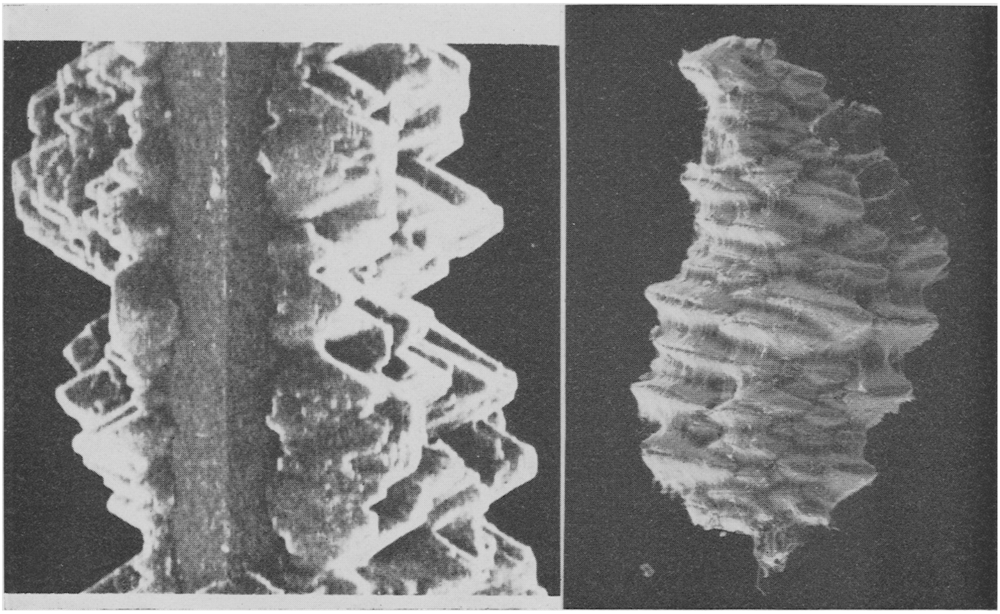
Most of the manganese minerals occur as individual crystals or as small monomineralic clusters of crystals. In addition to the mixture of birnessite, cryptomelane, and todorokite noted above, the only intergrowths observed between manganese minerals were ramsdellite with pyrolusite in three geodes and birnessite with todorokite in two geodes.

The soft friable nature of the minerals precluded quantitative microprobe analysis. The values given in Table I for ramsdellite, ranciéite, and birnessite should be within 15 % of the actual values, those for the spongy fibrous todorokite are essentially qualitative. Insufficient material was present for the determination of valence state;

therefore all the manganese is reported as MnO_2 and the iron as Fe_2O_3. Descriptions of each of the seven manganese minerals follow.

Ramsdellite (MnO_2)

Ramsdellite, an orthorhombic dimorph of pyrolusite, has been described from Mexico in only one location (Gavilan mine, Baja California, by Fleischer *et al.*, 1962). It occurs in about one-fourth of the Chihuahua geodes examined as small (*c.* 100 μm diameter) soft fibrous black masses on quartz or, more commonly, as black euhedral to subhedral crystals on blades of goethite. Although all the crystals studied were well developed, the optical goniometer signals were fair to very poor, permitting identification of forms but no accurate angular measurements. Four different crystal habits have been observed.



FIGS. 1 and 2: FIG. 1 (left). Scanning electron photomicrograph of lenticular ramsdellite (Habit A) developed perpendicular to the C-axis of a goethite blade. ×250. FIG. 2 (right). Scanning electron photomicrograph of lenticular ramsdellite (Habit A) covered by strands of todorokite. ×100.

Habit A. In this frequently observed form, the ramsdellite crystals have an irregular, lenticular shape, similar to that observed by Fleischer *et al.* (1962) for crystals from Lake Valley, New Mexico (their fig. 3). They are found clinging to the edges of and projecting from lath-shaped goethite crystals (fig. 1). These crystals are sometimes found stacked one on top of another, giving the appearance of a pagoda, or, when covered by strands of todorokite, the aggregate is reminiscent of a cocoon (fig. 2). This habit is very similar to the common lenticular habit described by Gruner (1947) for groutite from Minnesota.

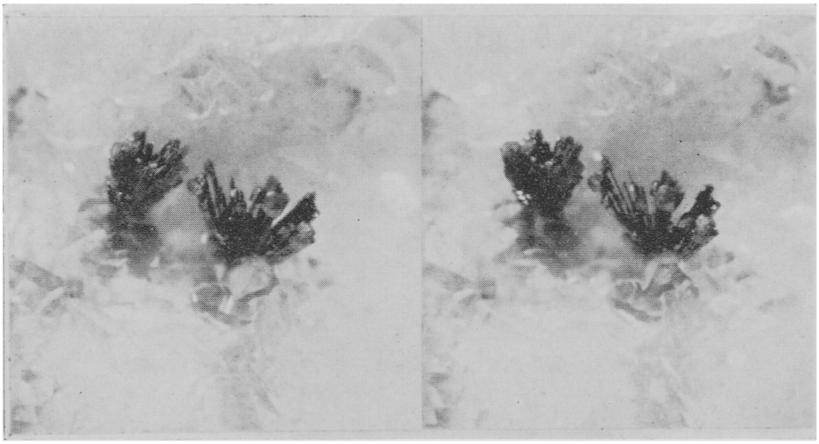


FIG. 3. Stereo pair of two groups of goethite laths with ramsdellite crystals (Habit B) implanted on them. The goethite laths projecting from the quartz matrix are 2–3 mm in length.

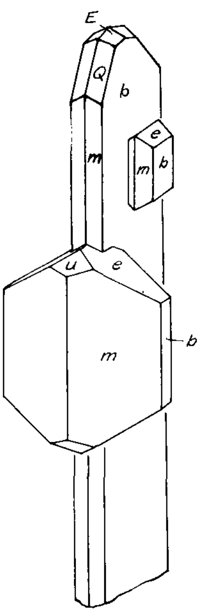


FIG. 4. Ramsdellite crystals (Habit B) implanted on a lath-like crystal of goethite. Forms are: *b*{010}, *m*{110}, *u*{110}, *Q*{241}, *E*{184}, *e*{021}.

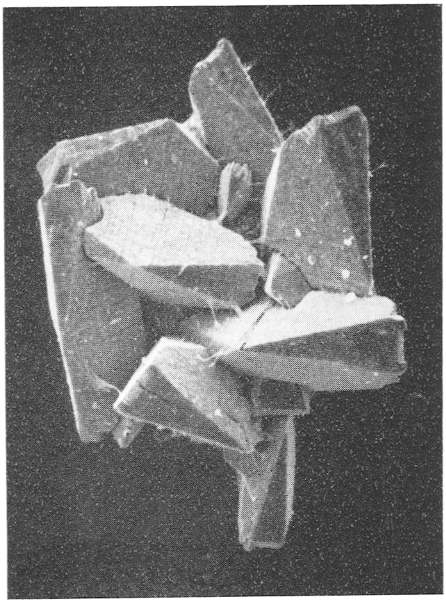
Habit B. Sometimes both the goethite and ramsdellite are developed in sharper, more euhedral forms (figs. 3, 4, and fig. 11a of Finkelman *et al.*, 1972). In this case it is easy to verify that the analogous orthorhombic axes of the two crystals are parallel. The ramsdellite tends to be elongated parallel to the *c*-axis, and the chief forms are *b*{010}, *m*{110}, *e*{021}, and *u*{101}. The goethite blades are bounded by *b*{010} and *m*{110} and terminated by *Q*{241} and *e*{021}. Sometimes *e* is replaced by vicinal forms such as *E*{184}, as shown in fig. 4.

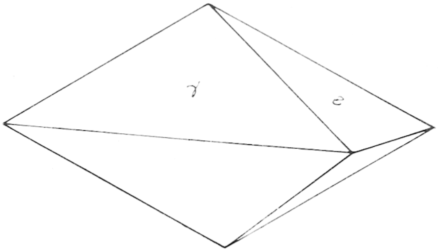
Habit C. This habit of ramsdellite was observed in only one geode, in which clusters of sharp wedge-shaped ramsdellite crystals (fig. 5) formed on small spherules of hematite, which had grown on quartz crystals. These ramsdellite crystals show two forms, *e*{021} and γ\{301\}, which are illustrated in ideal form in fig. 6, although the growth is frequently irregular.

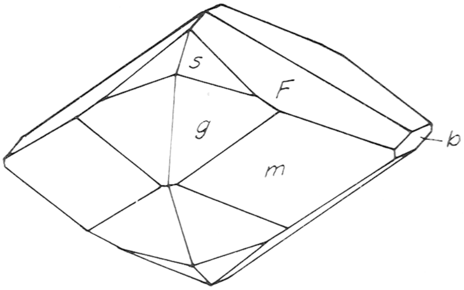
Habit D. One beautifully developed ramsdellite crystal, 0·5 mm in longest dimension, was found mounted sceptre-fashion on the end of a goethite lath. The habit, illustrated in fig. 7, is unique, showing *b*{010}, *m*{110}, *s*{111}, *g*{311}, and *F*{1.12.6}. The last two forms may be considered as vicinal forms replacing γ\{301\} and *e*{021}, respectively.

The X-ray powder data and single crystal data for the geode ramsdellite agree well with the literature values (Byström, 1949; Fleischer *et al.*, 1962). The precession patterns show the diffuse spot character observed by Fleischer *et al.* but unlike their patterns only the 'strong phase' was present.

Most of the ramsdellite crystal habits observed in the geodes are similar to habits reported for groutite (Gruner, 1947; Fleischer *et al.*, 1962, particularly their figs. 1 and 3). Although conclusive proof is lacking, it seems reasonable to suppose that the ramsdellite in the geodes from Chihuahua has all been derived by solid-state alteration from originally deposited groutite. The unique ramsdellite habits described in this report (habits C *and* D) would also be consistent with this origin. This view is also supported to some degree by the extreme friability of the ramsdellite crystals, and the appearance of numerous parting cracks parallel to (010) (easily visible in fig. 5), which may have resulted from the change in structure from groutite to ramsdellite ($HMnO_2 \rightarrow MnO_2$).



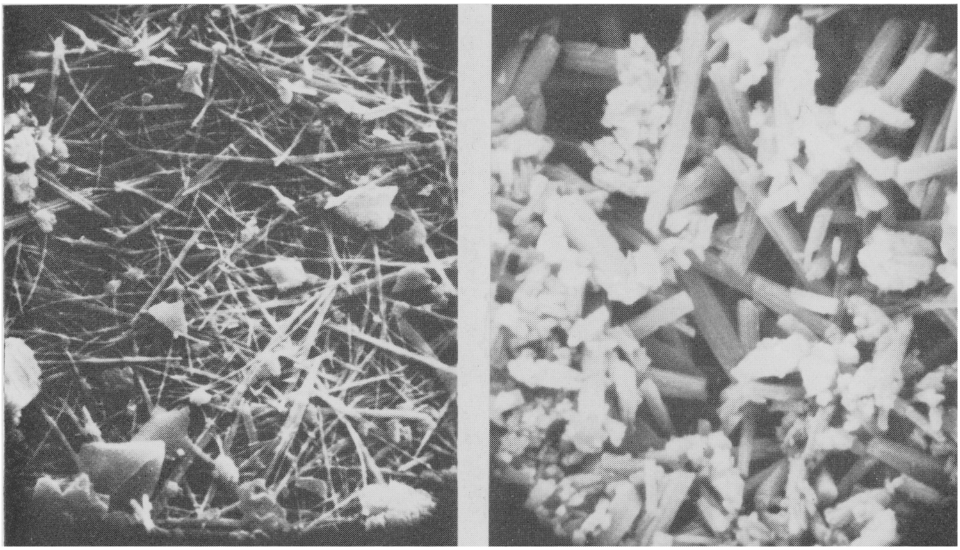




FIGS. 5 to 7: FIG. 5 (left). Scanning electron photomicrograph of a cluster of wedge-shaped ramsdellite crystals (Habit C). Note the partings. × 190. FIG. 6 (upper right). Ramsdellite crystal (Habit C), showing forms $e\{021\}$ and $\gamma\{301\}$. FIG. 7 (lower right). Crystal of ramsdellite (Habit D), showing $b\{010\}$, $m\{110\}$, $s\{111\}$, $g\{311\}$, $F\{1.12.6\}$.

The thermal behaviour of the geode ramsdellite differed somewhat from the behaviour reported in the literature. Fleischer *et al.* (1962) reported that the Lake Valley ramsdellite converted almost entirely to pyrolusite when heated at 310 °C for 5 days. Klingsberg and Roy (1959) found a trace of pyrolusite in ramsdellite from Chisholm, Minnesota, after heating at 313 °C for 14 days. When ramsdellite from our geodes was heated in air for 14 days, no change was noted at 350 °C but at 375 °C the ramsdellite was entirely converted to pyrolusite.

Fleischer *et al.* (1962) noted the universal presence of pyrolusite in ramsdellite and suggested that ramsdellite undergoes slow alteration to the more stable pyrolusite phase. Pyrolusite is very rare in the ramsdellite from the geodes (see below). This may indicate that the geode material was not heated to as high a temperature as the ramsdellite samples studied by Fleischer *et al.* (1962), but more likely it suggests that the geode material is fresher (younger or purer). This might also explain the discrepancy in the thermal behaviour. The fresher ramsdellite would have fewer pyrolusite nucleation sites and would tend to convert at somewhat higher temperatures than the older or less pure material. A microprobe analysis appears in Table I.



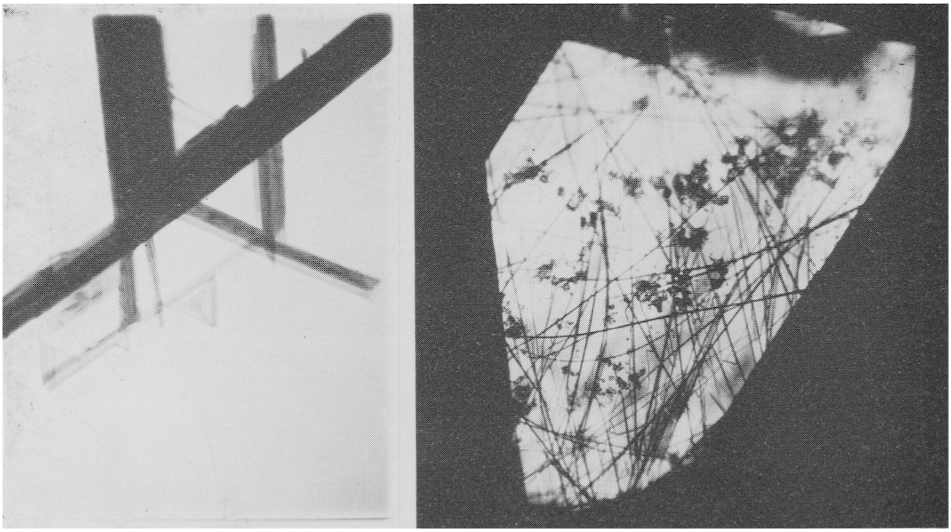
FIGS. 8 and 9: FIG. 8 (left). Scanning electron photomicrograph of fibrous todorokite. The irregular particles enmeshed in the fibres consist of kaolinite and unidentified crystalline and amorphous material. × 7500. FIG. 9 (right). Scanning electron photomicrograph of lathlike crystals of todorokite. No attempt was made to identify the small irregular particles dispersed over the todorokite laths. × 10 000.

Todorokite [(Mn,Ca,Mg)$Mn_3O_7 . H_2O$]

Todorokite has been described (Straczek *et al.*, 1960) from one Mexican locality and has also been cited as a major constituent of marine manganese nodules (Cronan and Tooms, 1969). Todorokite, like ramsdellite, occurs in about one-fourth of the Chihuahua geodes, but volumetrically it is the most abundant manganese mineral in these samples. It is almost exclusively a late-stage mineral occurring as brown or black fibrous overgrowths on the other geode minerals (fig. 2). It is also commonly found as dense mats generally composed of long fibres (fig. 8) and less commonly of lathlike crystals (fig. 9). These mats often include clay minerals and unidentified amorphous material.

The todorokite generally gave weak X-ray powder patterns. The initial identification of this material was made from electron-diffraction patterns. In the transmission electron microscope the material appears as long flat blades elongated in the *b* direction. The cell dimensions, *a* 9·80 Å, *b* 2·84 Å, agree well with the data of Straczek *et al.* (1960). The blades intersect at angles of about 60°, forming equilateral triangles (fig. 10).

Todorokite and late-stage quartz precipitated simultaneously as the last crystals in some geodes, thus forming quartz crystals impregnated with dispersed strands of fine todorokite fibres (fig. 11). We have also observed quartz grains enclosing euhedral brown hexagonal prisms. Apparently the todorokite had completely enclosed earlier quartz crystals and subsequent growth of the quartz along the same crystallographic directions resulted in these brown phantom crystals. A microprobe analysis appears in Table I.



FIGS. 10 and 11: FIG. 10 (left). Transmission electron photomicrograph of fibrous todorokite. ×27 000. FIG. 11 (right). Quartz impregnated with todorokite fibres. Crossed polarizers. ×450.

Birnessite [(Na,Ca)Mn$_7$O$_{14}$·3H$_2$O]

Birnessite was first described by Jones and Milne (1956) and has since been shown to be one of the most common forms of manganese oxide in both soils (McKenzie, 1971) and in manganese nodules (Cronan and Tooms, 1969).

In the only reported occurrence of birnessite in Mexico, Levinson (1962) noted that it was a major constituent in a shipment of manganese ore from a source about 475 miles south of Chihuahua.

We found birnessite in only four of the geodes examined. Three of the occurrences were described in the introduction. In all three the finely granular birnessite was thoroughly intermixed with other minerals, and all three geodes contained substantial amounts of calcite. In the fourth geode the birnessite occurred as small hard black masses covered by a tan mat of fibrous todorokite. These masses always occurred at the bases of intersecting quartz crystals. There was no calcite in this geode. In all four cases the birnessite gave four-line X-ray diffraction patterns very similar to those obtained by Brown *et al.* (1971). A microprobe analysis appears in Table I.

Pyrolusite (MnO_2)

Although pyrolusite is one of the most common manganese oxides and is the only one previously reported in geodes (Sinotte, 1969), it is uncommon in the Chihuahua samples. No individual grains of pyrolusite were observed. It was only detected in four powder patterns of ramsdellite grains taken from three different geodes. In only one pattern did the intensity of the pyrolusite lines exceed those of ramsdellite. In view of the intimate association with ramsdellite, it is likely that all the pyrolusite observed is an alteration product of ramsdellite (see section on ramsdellite and Fleischer *et al.*, 1962).

Ranciéite [$(Ca,Mn)Mn_4O_9.3H_2O$]

Ranciéite, a soft black vitreous material, was observed in only three geodes. Richmond *et al.* (1969) noted that it often occurred in association with todorokite, but in our samples the ranciéite was not associated with any other manganese mineral. It occurred as irregular growths in a calcite crystal and as delicate dendritic growths, often containing hexagonal plates (fig. 12), on the surface of quartz and calcite. The X-ray data agree well with those given by Richmond *et al.* (1969). A microprobe analysis appears in Table I.

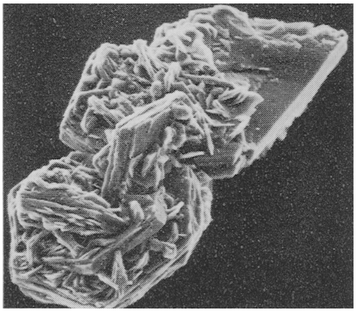


FIG. 12. Scanning electron photomicrograph of a composite of ranciéite crystals. ×560.

Cryptomelane [$K(Mn^{2+},Mn^{4+})_8O_{16}$]

Cryptomelane, a relatively common manganese mineral, was observed in only two of the Chihuahua geodes. It occurred as tufts of fine black fibres in one geode and was also detected in an X-ray powder pattern from the complex mixture described in the introduction (USNM geode no. B2906).

Hollandite [$BaMn_8O_{16}$]

Hollandite was observed in one geode, where it occurred as clusters of small shiny black needles. The powder patterns of cryptomelane and hollandite are virtually identical. The presence of hollandite was confirmed by a qualitative microprobe scan which indicated the presence of major barium.

Discussion

Since the geodes were not collected in the field, valuable information for determining the parageneses of the mineral assemblage is lacking. Nevertheless some pertinent observations can be made.

It appears that the temperature of the mineralizing solutions did not exceed about 400 °C and may have been considerably lower. Our heating experiments indicated that ramsdellite would be converted to pyrolusite at 375 °C and that goethite would be converted to hematite at 350 °C. Data presented by Deer *et al.* (1962) on thermal effects on mordenite and beidellite suggest that these minerals would not form above 400 °C.

The assemblage of manganese minerals in the geodes is characteristic of supergene mineralization. Bricker (1965) noted several similar assemblages created by the oxidation of manganese proto-ores. In his study of manganese oxides in the system $MnO–O_2–H_2O$ he stated that the degree of oxidation is the principal factor in controlling the mineralogy. McKenzie (1971), studying more complex systems, stated that the concentration of alkali and alkali-earth ions in the mineralizing solutions is also critical in determining the mineralogy.

Although there is insufficient evidence to indicate which factors determined the manganese mineralogy within the geodes, it is interesting to note that todorokite, a ubiquitous late-stage mineral in the geodes, contains substantial amounts (*c.* 10 wt. % MnO) of divalent manganese (Straczek *et al.*, 1960; our samples contained insufficient material for analysis of valence state). This would seem to argue against a progressive oxidation of the assemblage.

Some of the manganese minerals may be alteration products of previous manganese minerals (as with ramsdellite and pyrolusite). Cryptomelane has been derived from birnessite by heating (Jones and Milne, 1956; McKenzie, 1971) but in two of the three geode occurrences, cryptomelane appears to be a primary mineral. The third occurrence was in the unique geode (USNM no. B2906) with at least two other manganese oxides; the complex nature of this material precludes the determination of the paragenesis of the minerals. Glasby (1972) cited the conversion of todorokite to birnessite by heating at 225 °C for 1 hour. This combination of minerals was noted in two geodes. In one (USNM no. B2906), the difficulty of determining the paragenesis has already been mentioned; in the other, fibrous todorokite is found on hard black masses of birnessite. The structure of those masses suggests that the birnessite acted as nucleation sites for the todorokite, but conversion of one to the other cannot be ruled out. Finally, Bricker (1965) noted the common oxidation and ageing sequence of birnessite (δ-MnO_2) → nsutite (α-MnO_2) → pyrolusite (β-MnO_2). As the only pyrolusite found in the geodes is associated with, and probably genetically related to, ramsdellite, the above sequence probably has not taken place in the geodes. The presence of birnessite but not of nsutite in the geodes is possibly another indication of the relative freshness of the geode minerals.

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