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STUDIES OF THE MANGANESE OXIDES. V. RAMSDELLITE, MnO_2, AN ORTHORHOMBIC DIMORPH OF PYROLUSITE[1]

Michael Fleischer,[2] W. E. Richmond,[3] and
Howard T. Evans, Jr.[2]

Abstract

Ramsdellite is an orthorhombic dimorph of pyrolusite; the composition is close to MnO_2 with no certain deviation from that composition. It inverts to pyrolusite at about 300°; the inversion is presumed to be monotropic. Examination of crystals from the Gavilan Mine, Mexico, shows them to be pseudomorphs after groutite; a secondary lattice is probably that of an intermediate stage of oxidation. Chemical analyses and x-ray data are given, and the physical properties are summarized.

Introduction

Early in 1941, in the course of an extensive study of manganese oxide minerals, a sample collected by S. C. Creasey of the U. S. Geological Survey from Lake Valley, New Mexico, was found to give a distinctive x-ray pattern. Analysis showed that the composition was close to MnO_2; at our request Mr. Creasey collected a large suite of samples. Through the courtesy of Professor L. S. Ramsdell of the University of Michigan, we obtained his specimen, from an unknown locality, of a dimorphous form of MnO_2 (Ramsdell, 1932); it proved to be the same mineral as that from Lake Valley. It was named ramsdellite and a preliminary report, in which this name was used, was published in 1943 (Fleischer and Richmond, 1943). At that time, chemical analyses had been made, the inversion to pyrolusite had been noted, and a preliminary determination of the unit cell had been completed.

Shortly thereafter, Dr. Richmond left the U. S. Geological Survey, and Fleischer was assigned to more urgent work for the Manhattan Project; various circumstances have unfortunately prevented the publication of the data on which the new mineral name was based. We have, however, supplied many investigators the world over with samples from Lake Valley, and some twenty papers dealing with the mineral have appeared; all the data on Lake Valley samples cited were obtained on samples supplied by the U. S. Geological Survey. This paper gives our data and summarizes the published information.

Chemistry

All available chemical analyses of ramsdellite are assembled in Table 1. The composition is close to MnO_2, but the ratio of total cations to oxygen

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

[2] U.S. Geological Survey, Washington, D. C.

[3] R.F.D. No. 2, Hillsboro, N. H.

TABLE 1. CHEMICAL ANALYSES OF RAMSDELLITE

	1	2	3	4	5	6
MnO_2	97.14[a]	95.02[a]	—	—		
MnO	none	none	—	—		
MgO	0.12	none	—	—		
ZnO	n.d.[b]	0.25[c]	—	0.96	0.68	0.28
BaO	none	none	—	0.16	tr.	tr.
CaO	none	1.12	0.2	—	—	—
Na_2O	0.31	present, n.d.	—	—	—	—
K_2O	0.41	present, n.d.	—	—	—	—
H_2O^-	1.24	0.05	1.3	0.62	0.96	—
H_2O^+		1.39				
Al_2O_3	0.48	0.72	0.8	—	—	—
Fe_2O_3	0.34	0.22	1.2	—	high	low
SiO_2	0.42	0.36	0.8	—	—	—
TiO_2	none	none	0.2	—	—	—
P_2O_5	none	n.d.	—	—	—	—
	100.46	99.13				
Active O[a]	17.88	17.49	—			
Total Mn	61.00	59.62	—	61.28	60.17	—
Active O/Mn	1.006	1.007	—	—	—	
G.	4.73	4.65	4.83	—		

[a] Calculated from active O; determination by the method of Fleischer (1943). Active O = oxygen reactive with oxalic acid, that is, oxygen above the requirements for MnO.

[b] Shown by K. J. Murata spectrographically to contain about as much Zn as No. 2.

[c] Determined by C. M. Warshaw on a separate portion of the same sample.

1. From Lake Valley, New Mexico, analysis by Michael Fleischer in 1942; X-ray study showed that the sample contained considerable pyrolusite.
2. Locality unknown, Ramsdell's type specimen; analysis by Michael Fleischer in 1942; X-ray study showed a very small amount of pyrolusite.
3. From Lake Valley, Byström (1949).

4–6. Three different samples from Lake Valley, analyses by Charlotte M. Warshaw in 1951; X-ray study showed very small amounts of pyrolusite.

is not known because of the uncertainty as to the role of zinc (present in all the Lake Valley samples), calcium, alkalies, and H_2O. The SiO_2, Fe_2O_3, and Al_2O_3 present are assumed to be due to impurities (chert and iron oxide are known to have been present). Spectrographic analyses by K. J. Murata showed that beryllium, cobalt, nickel, thallium, and vanadium were absent in samples 1 and 2 of Table 1 and showed traces of lead and 0.0X per cent Zn in ramsdellite from the Gavilan Mine, Lower California, Mexico. A semiquantitative spectrographic analysis was made by Nancy M. Conklin in 1959 of another sample from Lake Valley; she found (weight per cent) Mg 3, Ca 0.15, Fe 0.015, Zn 0.7, Ag 0.015, Cu 0.003, Mo 0.03, V 0.015, W 0.003, Pb 0.3, Ba 0.07, S 0.007, and Y 0.003.

As discussed later in this paper, ramsdellite is related structurally to gamma-MnO_2 (or Nsuta MnO_2, Sorem and Cameron, 1960), which is generally believed to be a defect structure with Mn:O less than 2. Wadsley and Walkley (1951) state, "A specimen (of ramsdellite from Lake Valley) has been analyzed by the authors, and in common with all the manganese dioxides shows a departure from true stoichiometric proportions. The cell dimensions and the thermodynamic properties should therefore be capable of some variation." The analysis unfortunately is lost (A. D. Wadsley, priv. comm. to Fleischer, 1960). The published *x*-ray data on ramsdellite (Table 3) show no indication of compositional variation.

BEHAVIOR WHEN HEATED

Ramsdell (1932) reported, "After heating to a low dull red heat, a normal pyrolusite pattern was secured. This heating was accompanied by a loss of water of only 1 per cent and the total loss in weight was less than 2 per cent. This would seem to eliminate either dehydration or a change from some other oxide as a cause of the change in pattern. A possible explanation is that this specimen represents an unstable form of MnO_2, which is converted to the normal form by heating."

We confirmed Ramsdell's observations in studies of Lake Valley material. Samples heated in air at 200°[1] for 4 days and at 240° for 7 days showed no change in *x*-ray pattern, but a sample heated at 310° for 5 days had been converted almost entirely to pyrolusite (*x*-ray data by J. M. Axelrod). Klingsberg and Roy (1959) found that ramsdellite from Chisholm, Minnesota, was unchanged when heated in air at 316° for 4 days, but gave a trace of pyrolusite when heated at 313° for 14 days. They also reported that groutite, MnO(OH), changed slowly to ramsdellite above 130°, changed in a few hours at 300°, but above 300° it went directly to pyrolusite.

Differential thermal analysis curves for ramsdellite have been published by McMurdie and Golovato (1948) (Lake Valley), Kulp and Perfetti (1950) (Idorado Mine, Colorado), and by Caillère and Kraut (1954) (locality not stated). Kulp and Perfetti found a small endothermic peak at 120° (capillary water) and an exothermic break at 500° corresponding to the inversion to pyrolusite. Caillère and Kraut found a break at 450°. McMurdie and Golovato report that "below the first break at 670° heat

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[1] This and all other temperatures are °C.

was being absorbed and *x*-rays indicated a change to pyrolusite. This change from ramsdellite to pyrolusite does not appear to occur sharply or to be accompanied by a large energy effect, and is not reversible." After the inversion to pyrolusite, the D.T.A. curves, as might be expected, are essentially identical with those given by pyrolusite, except that Caillère and Kraut report an extra endothermal break at 850°.

The inversion of ramsdellite to pyrolusite is presumably irreversible and monotropic, although there is no direct evidence of this; very likely the inversion would occur at temperatures below 300° if sufficient time were allowed. It should be noted that neither ramsdellite nor groutite has ever been synthesized (Moore, Ellis, and Selwood, 1950) although they are readily converted into one another hydrothermally (Klingsberg and Roy, 1959).

CRYSTALLOGRAPHIC AND *X*-RAY STUDIES

The first work on the crystal structure of ramsdellite was by Richmond (quoted by Fleischer, 1944), who determined the orthorhombic symmetry and the approximate cell constants on cleavage fragments from Lake Valley, and who recognized the similarity to diaspore. The structure was worked out by Byström (1949) on Lake Valley material. She found it to be orthorhombic, space group D_{2h}^{16}, with the cell constants given in Table 2, $Z=4$, sp. gr. calculated 4.84, determined 4.83. Cell constants given by Kedesdy *et al.* (1957) (locality not stated), Klingsberg and Roy (1959) (Chisholm, Minn.), and Evans (this paper) (Lower California) agree closely with Byström's. The only discordant values are those on a sample from Gözörem, Ereğli region, Turkey, published in an abstract by Schröder (1952), who stated that he obtained them from powder data that agreed closely with those published by Fleischer and Richmond (1943). Schröder's unit-cell constants, given in Table 2, show no apparent relation to those of other investigators and give a calculated density of 4.346, in good agreement with his own determined value, 4.370. More detailed data have not been published. We are unable to explain these results.

Crystals of ramsdellite have not previously been described, although Klingsberg and Roy (1957) mention crystals as much as 6 mm long from Chisholm, Minnesota. What appeared to be single crystals of ramsdellite were found on samples from the Gavilan Mine, Lower California, Mexico, kindly given to us by James A. Noble. The samples consist of massive plumboan hollandite, with the surface incrusted by crystals of ramsdellite and with apparently excellent single crystals, a few tenths to two mm in size, in fissures and cavities. When examined by Evans in 1958, these crystals proved to be pseudomorphs of ramsdellite after groutite. Fig. 1,

Table 2. Cell Constants (in Å) of Ramsdellite and Related Phases

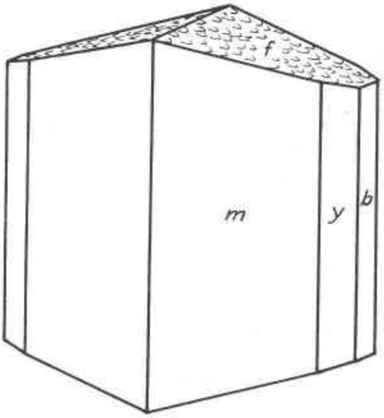
Material	*a*	*b*	*c*	Reference
Ramsdellite	4.5	9.2	2.83	Richmond (in Fleischer, 1944)
Ramsdellite	4.533	9.27	2.866	Byström (1949)
Ramsdellite	6.374	10.126	4.092	Schröder (1952)
Ramsdellite	4.528	9.285	2.866	Kedesdy *et al.* (1957)
Ramsdellite	4.52	9.27	2.87	Klingsberg and Roy (1959)
Ramsdellite (strong phase)	4.53	9.28	2.86	Evans, this paper
Ramsdellite (weak phase)	4.61	9.54	2.88	Evans, this paper
Groutellite	4.71	9.52	—	Klingsberg and Roy (1959)
Groutite	4.58	10.76	2.89	Collin and Lipscomb (1949)
Groutite	4.56	10.70	2.85	Gruner (1947)
Groutite	4.56	10.00	3.03	Klingsberg and Roy (1959)
Gamma-MnO$_2$	4.46	9.32	2.850	Kondrashev and Zaslavskii (1951)
Gamma-MnO$_2$	4.418	9.51	2.811	Kedesdy *et al.* (1957)
Gamma-MnO$_2$	4.450	9.305	2.850	de Wolff (1959)
Gamma-MnO$_2$	4.470	9.336	2.848	de Wolff (1959)
Gamma-MnO$_2$	4.489	9.391	2.848	de Wolff (1959)
Gamma-MnO$_{1.96}$(OH)$_{0.04}$	4.42	9.70	2.79_0	Feitknecht *et al.* (1960)
Gamma-MnO$_{1.92}$(OH)$_{0.08}$	4.43	9.70	2.79_3	Feitknecht *et al.* (1960)
Gamma-MnO$_{1.74}$(OH)$_{0.26}$	4.49	9.79	2.82_0	Feitknecht *et al.* (1960)
Gamma-MnO$_{1.64}$(OH)$_{0.36}$	4.51	9.93	2.84_0	Feitknecht *et al.* (1960)
Gamma-MnO$_{1.46}$(OH)$_{0.54}$	4.54	10.20	2.85_6	Feitknecht *et al.* (1960)
Rho-MnO$_2$	4.453	9.396	2.827	Kedesdy *et al.* (1957)

2, (from Lake Valley), and 3 show three typical forms. The wheel-shaped crystal (Fig. 3) is very similar to a crystal of groutite figured by Gruner (1947). Professor Paul Ramdohr has kindly called our attention to the similarity of Fig. 1 to a drawing of a crystal figured as "pyrolusite" in Dana's System of Mineralogy, 5th Ed., 1868, p. 165.

The faces gave poor signals on the goniometer and were not measured accurately; *m*{110} was prominently developed on most crystals and other faces identified were *b*{010}, *a*{100}, *c*{001}, *f*{011}, *y*{120}, *k*{130}, *e*{021}, *Q*{241}.

Buerger precession patterns gave a unit cell identical with that of Byström (1949), but a second, less prominent lattice was also present, similar to that of ramsdellite, but with a slightly larger unit cell. The measured lattice constants are (in Å):

	a	*b*	*c*
Strong phase (Gavilan Mine)	4.53 ±0.02	9.28±0.03	2.86 ±0.02
Lake Valley (Byström, 1949)	4.533±0.005	9.27±0.01	2.866±0.005
Weak phase (Gavilan Mine)	4.61 ±0.04	9.54±0.05	2.88 ±0.03



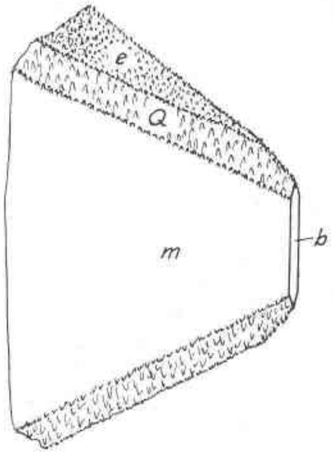
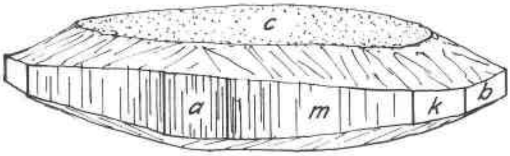


FIG. 1. (Left) Ramsdellite after groutite, Gavilan Mine, Lower California, Mexico. *b* {010}, *m* {110}, *y* {120}, *f* {011}. Drawing by Evans.

FIG. 2. (Right) Ramsdellite after groutite, Lake Valley, New Mexico. *b* {010}, *m* {110}, *e* {021}, *Q* {241}. Drawing by Evans.

The patterns were somewhat diffuse for both the strong and weak phases. Traces of a pattern due to a pyrolusite lattice in parallel orientation were also present on the photographs; this lattice is oriented so that the tetragonal a, $b=a$, and c axes of pyrolusite are parallel to the orthorhombic a, b, and c axes, respectively, of ramsdellite.

The ramsdellite crystals are therefore pseudomorphs after groutite, like those found by Klingsberg and Roy from Chisholm, Minnesota, and are formed by the oxidation reaction $4MnO(OH)+O_2 \rightarrow 4MnO_2+2H_2O$. Exactly the same reaction is involved in the conversion of manganite to pyrolusite. Pseudomorphs of pyrolusite after manganite ($MnO(OH)$) are well known. Another example, found at Lake Valley, New Mexico, is shown in Fig. 4. The x-ray pattern of the pyrolusite crystal shown exhibits the same kind of diffuseness as that of the ramsdellite pseudomorphs from Gavilan Mine. These conversions are readily understood on the basis of the crystal structures of the phases involved. The structure of ramsdellite is essentially similar to that of groutite, so that the latter can transform to the former by a diffusion of the hydrogen atoms to the surface of the structure, where they react with atmospheric oxygen, while only minor adjustments are required for the positions of the manganese and oxygen atoms. A similar controlling structural relationship exists between manganite and pyrolusite. Such an alteration process may be expected to disturb the periodicity within the large crystals sufficiently to account for the diffuseness of the x-ray photographs of the altered phases.



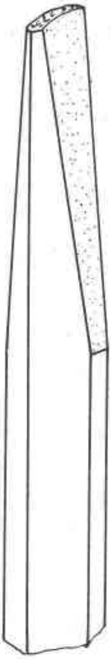


FIG. 3. (Left) Ramsdellite after groutite, Gavilan Mine, Lower California, Mèxico. *c* {001}, *b* {010}, *a* {100}, *m* {110}, *k* {130}. Drawing by Evans.

FIG. 4. (Right) Pyrolusite pseudomorph after manganite, Lake Valley, New Mexico. Drawing by Evans.

The hypothesis of alteration also parallels that proposed for the pair montroseite [VO(OH)]-paramontroseite (VO_2) by Evans and Mrose (1955). They also found one or more intermediate phases between montroseite and paramontroseite, similar to the weak phase referred to above, and suggested that the intermediate phase might be a partially dehydrogenated step between the two end phases. Klingsberg and Roy (1959) found an intermediate phase, which they named groutellite, to be formed in the reduction of ramsdellite to groutite, but not in the reverse reaction. Their cell constants are given in Table 2; they are closer to those of the weak phase of the ramsdellite from Gavilan Mine than to those of ramsdellite proper.

The published *x*-ray powder patterns of ramsdellite give spacings in good agreement,[1] except for one sample studied by Allsman (1955). The strongest lines are listed in Table 3, along with measurements for "Nsuta MnO_2" and groutellite. It will be noted that the spacings given

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[1] The patterns of 2 samples from Czechoslovakia given by Bernardova and Slansky (1960) also are in good agreement with Nos. 1–6 of Table 3.

TABLE 3. STRONGEST LINES OF RAMSDELLITE AND GROUTELLITE x-RAY PATTERNS (IN Å)

Indexed after Byström, 1949	1		2		3		4		5		6		7		8		9	
	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I
	—	—	—	—	—	—	—	—	4.641	49	—	—	—	—	4.58	W	—	—
110	4.08	10	4.04	VS	4.10	VS	4.03	VS	4.062	100	4.059	10	4.132	10	4.11	VS	4.219	100
130	2.53	8	2.54	S	2.535	VS	2.53	S	2.547	60	2.544	9	2.655	—	2.66	M	2.633	60
021	2.40	4	2.43	M	2.436	S	2.43	M	—	—	2.427	1	2.458	8	2.46	M	—	—
111	2.32	4	2.33	M	2.343	M	2.32	M	2.317	62	2.330	2	2.360	—	2.36	M	2.380	40
040	—	—	—	—	2.329	M	—	—	—	—	—	—	—	—	—	—	—	—
121	2.13	5	2.13	MS	2.143	S	2.13	M	—	—	2.130	—	2.163	—	2.17	S	—	—
131	1.88	5	1.90	M	1.903	S	1.89	M	1.870	7	1.904	3	—	—	1.88	VW	—	—
221	1.64	6	1.65	MS	1.656	S	1.65	S	1.658	3	1.658	6	1.672	6	1.67	S	—	—
240	1.60	7	1.61	MS	1.616	VS	1.61	S	1.619	11	1.617	8	—	—	—	—	—	—
151	1.46	5	1.47	M	1.479	VS	1.46	S	1.472	5	—	—	—	—	—	—	—	—
{330 {061	1.35	5	1.36	MS	1.357	VS	1.35	VS	—	—	—	—	—	—	1.36	VW	—	—

1–6. Ramsdellite.

(1) Frondel quoted by Fleischer and Richmond (1943), Lake Valley, pyrolusite lines omitted. (2) Cole, Wadsley, and Walkley (1947), Lake Valley; (3) Byström (1949), Lake Valley; (4) Ramdohr and Frenzel (1956), Lake Valley; (5) Klingsberg and Roy (1957), Chisholm, Minn.; (6) Allsman (1955), Bannock Co., Idaho, excellent crystallized specimen; (7) "Ramsdellite," Allsman (1955), Norwich Mine, Butte, Mont., black, massive ore; (8) Nsuta MnO_2, type 1.67, Sorem and Cameron (1960), Nsuta Mine, Ghana; (9) Groutellite, synthetic, Klingsberg and Roy (1959).

for sample No. 7 differ distinctly from all the others and are very close to those of the "Nsuta MnO_2" of Sorem and Cameron (1960); the material is probably not ramsdellite.

The relation of ramsdellite to the synthetic compounds called gamma-MnO_2 and rho-MnO_2 and to the naturally occurring material called Nsuta MnO_2 is a very important problem because of their extensive use in dry cell batteries. It is evident from the cell constants for these materials, listed in Table 2, that they are closely related, but the various investigators have disagreed markedly on the nature of the relationship and the details of the structure of gamma-MnO_2. No further discussion is given here; the problem is discussed with many references by Sorem and Cameron (1960), and new data are also given by de Wolff (1959), Nye *et al.* (1959), and Feitknecht *et al.* (1960). The Swiss workers formulate gamma-MnO_2, not as a defect structure, but as $MnO_{2-n}(OH)_n$, with n ranging from nearly zero to a maximum of 0.54, and find a straight line increase of total cell volume from nearly anhydrous gamma-MnO_2 with increasing n, which when extrapolated, falls close to the value for groutite ($n=1$).

Physical Properties

Ramsdellite is steel-gray to iron-black in color. The streak is given as black by Fleischer and Richmond (1943) and by Klingsberg and Roy (1957), but Ramdohr and Franzel (1956) state emphatically that the streak is reddish. New trials on material from Lake Valley and Gavilan Mine showed that nearly all samples free of iron oxide gave a dull black streak; a few gave black streaks with a slightly brownish tint. The hardness is variable, 2–4, mostly about 3. Specific gravities measured are 4.73, 4.65, 4.83 (Lake Valley), 4.37 (Gözörem, Turkey, Schröder, 1952); calculated from Byström's x-ray data *assuming the composition* MnO_2, 4.84. Cleavages on three pinacoids and a prism (Ramdohr and Frenzel, 1956) commonly give the mineral the appearance in hand specimen of overlapping platelets; in polished section it commonly appears to be finely fibrous. Optical data in reflecting light are given by Ramdohr and Frenzel (1956) and by El Shazly and Saleeb (1959).

Occurrences

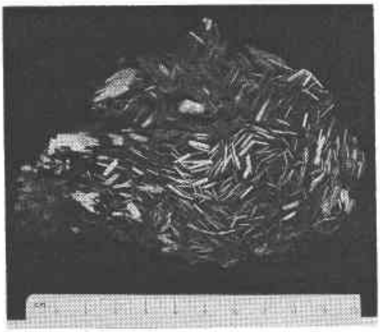
Verified occurrences of ramsdellite are. U.S.A.: Lake Valley, Sierra County, New Mexico; Monroe-Tener Mine near Chisholm, Minnesota (Klingsberg and Roy, 1957); Idorado Mine, Colorado (Kulp and Perfetti, 1950); Bannock County, Idaho (Allsman, 1955); Blythe, California; Canada, East River, Pictou County, Nova Scotia; Mexico, Gavilan Mine, Lower California; Czechoslovakia, Horni Blatna (Platten) and

Přebuz, Bohemia (Bernardova and Slansky, 1960); Turkey, Kodjas Karil Mine, Roumelia, (Fleischer and Richmond, 1943), and perhaps at Gözörem (Schröder, 1952); Egypt, Yoider, Gebel To Yu, and Um Bogna (El Shazly and Saleeb, 1959); India, Dongri Buzurg and Sandur (Mukherjee, 1959). No doubt many more occurrences will be found.

The manganese deposits at Lake Valley have been described by Creasey and Granger (1953). Ramsdellite occurs in fissures and faults in limestone; most of the samples came from a few pockets in the Stone Cabin fissure, which is marked on their map. Most commonly it occurs as groups of crystals (Fig. 5) on highly ferruginous chert; less commonly as "nail-head ore" (Fig. 6). Much of the ramsdellite has inverted to pyrolusite; portions of a single crystal may give the x-ray pattern of ramsdellite or of pyrolusite or of a mixture of the two.

Ramsdell's type specimen, from an unknown locality, is mostly massive, but partly platy; it occurs on a light brown chert distinctly different from that at Lake Valley. The specimen from East River, Nova Scotia (U. S. National Museum C1724) consists of fine platelets of ramsdellite, entirely surrounded by coarse blades of pyrolusite. The specimen from Blythe, California, is an irregular nodule approximately 3 by 2 inches, with an outer rim 1/16 to $\frac{1}{4}$ inch wide of fine-grained psilomelane, the interior consisting of a mixture of finely crystalline ramsdellite and pyrolusite.

The origin of ramsdellite and pyrolusite as weathering products of groutite and manganite, respectively, can be explained on a crystal chemical basis as described above. Pyrolusite is recognized as the stable form of MnO_2 and presumably can also be formed as a primary mineral but it is possible that ramsdellite, like paramontroseite (see Evans and Mrose, 1955), is actually metastable and can be formed only by the oxida-



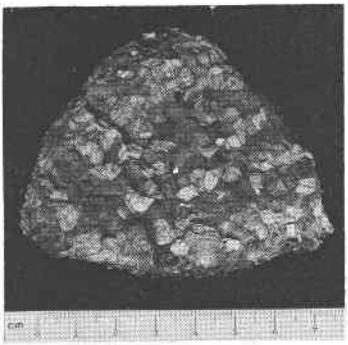


FIG. 5. (Left) Ramsdellite, group of crystals, Lake Valley, New Mexico.
FIG. 6. (Right) Ramsdellite, "nail-head spar," Lake Valley, New Mexico.

tion of groutite. The apparently universal presence of pyrolusite in varying amounts disseminated in ramsdellite in oriented position suggests that ramsdellite undergoes further, slower (reconstructive) alteration to pyrolusite as the more stable phase. Ramsdellite has not so far been observed in a mineral association that would suggest it to be of primary occurrence, that is, deposited directly from mineralizing solutions. There is as yet no evident clue in the observed occurrences as to the specific conditions that cause the formation of manganite rather than groutite and vice versa. Further attempts to synthesize these compounds are desirable.

ACKNOWLEDGMENTS

We are indebted to our colleagues S. C. Creasey, who collected the samples from Lake Valley and gave us data on the occurrence, K. J. Murata and Nancy M. Conklin for spectrographic, Charlotte M. Warshaw for chemical, and J. M. Axelrod for *x*-ray analyses; to L. S. Ramsdell who loaned us his type specimen, and to J. A. Noble for the gift of the samples from the Gavilan Mine. The photographs were made by Anthony M. Denson.

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