

THE CRYSTAL STRUCTURE OF MANNARDITE, A NEW HYDRATED CRYPTOMELANE-GROUP (HOLLANDITE) MINERAL WITH A DOUBLED SHORT AXIS

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ABSTRACT

The crystal structure of mannardite, $[\text{Ba}_x(\text{H}_2\text{O})_{2-x}][\text{Ti}_{8-2x}(\text{V},\text{Cr})_{2x}]\text{O}_{16}$, $x \approx 1$, has been solved and refined to $R = 2.68\%$ (weighted $R = 2.45\%$) from the 2210 observed reflections, out of a total of 3219 unique reflections averaged from a hemisphere of data collected with $\text{MoK}\alpha$ radiation to $2\theta = 100^\circ$. Mannardite is a hydrated cryptomelane-group (hollandite) mineral, with a tetragonal unit-cell, a 14.357(2), c 5.908(1) Å, space group $I4_1/a$. Its cell is four times larger than the basic hollandite cell (Byström & Byström 1950), with c and a multiplied by 2 and $\sim\sqrt{2}$, respectively. The doubling of the c axis is indicated by weak but sharp reflections with l odd, and is accompanied by sheets of weak diffuse scattering in the l -odd layers. The cell contains $Z = 4$ formula units. Two different positions for barium occur within the cation tunnels, with 81% and 11% occupancy. There are additional barium positions (2.8% occupancy) on either side of these, and separated from the main sites by 0.43(2) and 0.46(2) Å, respectively. The sum of barium is near one atom per formula unit; the remainder of the tunnel sites are filled with water. The newly redefined mineral redledgeite, $[\text{Ba}_x(\text{H}_2\text{O})_{2-x}][\text{Ti}_{8-2x}\text{Cr}_{2x}]\text{O}_{16}$, $x \approx 1$, has been found to have a unit cell very comparable to that of mannardite, and from the Bragg reflections, the same space-group. On X-ray-diffraction photos of redledgeite, additional very diffuse reflections are observed, and these occur close to, but displaced from those that violate the body-centring condition in the l -odd levels. Mannardite and redledgeite are isostructural, the differences being in the chemistry and degree of order in the cation tunnels.

Keywords: mannardite, hydrated cryptomelane-group (hollandite) mineral, doubled c -axis, mannardite structure refined to 2.68%, redledgeite-mannardite relationship.

SOMMAIRE

La structure cristalline de la mannardite $[\text{Ba}_x(\text{H}_2\text{O})_{2-x}][\text{Ti}_{8-2x}(\text{V},\text{Cr})_{2x}]\text{O}_{16}$, $x \approx 1$, a été résolue et affinée jusqu'au résidu $R = 2.68\%$ ($R_{\text{pondéré}} = 2.45\%$) sur les 2210 réflexions observées parmi les 3219 réflexions uniques (moyenne calculée sur hémisphère de données recueillies en radiation $\text{MoK}\alpha$ jusqu'à $2\theta = 100^\circ$). La mannardite est un minéral hydraté du groupe de la cryptomélane (hollandite), à maille tétragonale, a 14.357(2), c 5.908(1) Å, de groupe spatial $I4_1/a$. Le volume de la maille est quadruple de celui de la hollandite (Byström & Byström 1950), le c et le a étant, respectivement, multiplié par 2 et $\sim\sqrt{2}$. Le c doublé est étayé par les réflexions à l impair, faibles mais nettes, avec nappes de diffusion faible dans les cou-

ches à l impair. La maille élémentaire contient 4 unités formulaires. Deux positions différentes du baryum sont situées dans les tunnels à cations, occupées l'une à 81%, l'autre à 11%. Deux autres positions du baryum, occupées à 2.8%, ont leurs sites de part et d'autre des sites précédents, dont ils sont distants de 0.43(2) et 0.46(2) Å, respectivement. En tout, on compte près d'un atome de baryum par unité formulaire; les sites restants du tunnel sont occupés par l'eau. La redledgeite, espèce récemment redéfinie, $[\text{Ba}_x(\text{H}_2\text{O})_{2-x}][\text{Ti}_{8-2x}\text{Cr}_{2x}]\text{O}_{16}$, $x \approx 1$, se trouve avoir une maille très proche en dimensions de celle de la mannardite, minéral de même groupe spatial (d'après les réflexions de Bragg). La redledgeite montre, sur ses photos de diffraction, des réflexions supplémentaires, très diffuses et légèrement déplacées par rapport à celles qui violent la condition de centrage de maille dans les couches à l impair. Mannardite et redledgeite sont isotypiques; leurs différences résident dans leur chimisme et le degré d'ordre dans les tunnels cationiques.

Mots-clés: mannardite, minéral hydraté du groupe de la cryptomélane (hollandite), axe c doublé, structure affinée ($R = 2.68\%$) de la mannardite, relation entre mannardite et redledgeite.

INTRODUCTION

In the preceding paper (Scott & Peatfield 1986), the new mineral *mannardite* $[\text{Ba}_x(\text{H}_2\text{O})_{2-x}][\text{Ti}(\text{V},\text{Cr})_{2x}]\Sigma=8\text{O}_{16}$, $x \approx 1$ is described. In this paper, the crystal structure of mannardite is presented, and by implication, the gross structure of the redefined mineral *redledgeite* is given.

In a description of hollandite and related mineral phases (Byström & Byström 1950), the general formula of this family of compounds was given as $A_{2-y}B_{8-z}C_{2-u}X_{16}$, where A is a large cation, normally K^+ , Ba^{2+} or Pb^{2+} , B is a tetravalent transition-metal ion, partly substituted by divalent and trivalent ions, and C is a small cation that can fit into tetrahedral holes between oxygen atoms. In the formula, X is $[\text{O},\text{OH}]$, but predominantly oxygen, y is approximately unity, and z is small, 0.1 to 0.5. Hitherto, no structures have been reported which contain the proposed C metal ions. In view of the fact that preliminary flame-photometric examination of mannardite revealed the presence of lithium, and Li^+ is small enough to behave as a type- C cation described above, a structure determination was

undertaken to confirm the proposed model of filling of tetrahedral holes. At the start of the work, the proportion of lithium was unknown. It was only after X-ray-diffraction data had been collected that the results of an analysis by Secondary Ion Mass Spectrometry (SIMS) were obtained; these indicated that the lithium content is of the order of 0.02 – 0.06%, and that Li^+ could not be structurally significant. However, in view of the apparent similarity of the powder patterns of mannardite and redledgeite (Strunz 1961, 1963), and the fact that the latter had been reported as a cryptomelane-type phase with a doubled c -axis, structural work proceeded in order to define mannardite and its relationship to redledgeite (Scott & Peatfield 1986).

In the recent literature on minerals and synthetic phases of this family, the descriptive term "hollandite", "hollandite type" or "hollandite family" is used extensively, even for materials that contain no manganese. However, Strunz has consistently used the descriptive term "Kryptomelan" in reference to the group, thus: ". . . analog Kryptomelan" (Strunz 1963); "Kryptomelan-Reihe" (Strunz 1970); "Kryptomelan-Psilomelan-Gruppe" (Ramdohr & Strunz 1980). Fleischer (1983) used the term "cryptomelane group" for all such oxide minerals, whether they contain Mn^{4+} or Ti^{4+} as the tetravalent ion. In this group, he included hollandite itself, explaining (Fleischer, pers. comm.) that groups should be named . . . "for the member of the group that is most abundant and/or best studied. Cryptomelane is by far the most widely distributed member of the group." The term *hollandite* has acquired common usage today by virtue of the fact that this was the first structure to be solved in this group (Byström & Byström 1950), though it is not the most common mineral of the group. Structural crystallographers have perpetuated this misnomer by describing new structures of this family as *hollandites*. However, the term *cryptomelane group* shall be used throughout this paper as a more appropriate mineralogical description.

In their description of hollandite and related minerals, Byström & Byström (1950) stated: "The minerals contain 0–5% non-essential water." However, in the further section entitled "General formula of the minerals", they discussed the proposal of Gruner (1943) that . . . "the number of water molecules + the number of Ba, Pb, K, Na ions is two, thus indicating that the water molecules (the H_2O^+ in the analyses) and the large cations together occupy a twofold position." Byström & Byström were not convinced of the structural nature of the water, preferring to consider it as "adsorbed". Although many synthetic cryptomelane-type phases and a number of cryptomelane-group minerals have been examined crystallographically since this was published, Gruner's description of the role of water

in these minerals has been largely ignored. The one exception to this is the description of the crystal structure of psilomelane $(\text{Ba}, \text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$ (Wadsley 1953). The latter mineral differs from cryptomelane and hollandite in that it has wider oxygen-walled tunnels in which the cations are located (cation tunnels), formed by the presence of two metal-oxygen octahedra along c and three octahedra along a of a monoclinic cell with β close to 90° . There are two sites per formula unit for the $(\text{Ba}, \text{H}_2\text{O})$ entity, with the proportion $\text{Ba}:\text{H}_2\text{O}$ being 1:2 in each site. Synthetic phases of this group are not likely to contain water, as they are formed by high-temperature fusion of the oxides, but cation refinement of hollandite, cryptomelane and priderite (Post *et al.* 1982, Sinclair & McLaughlin 1982) did not reveal the presence of water, despite the fact that early chemical analyses had usually shown water to be present. Analysis of manjiroite (Nambu & Tanida 1967) has shown it to be a hydrated Na-analog of cryptomelane, and infrared absorption spectroscopy (Potter & Rossman 1979) has identified structural water as being present in many manganese minerals of this group.

Although the majority of cryptomelane-group structures are based on a short (3 Å) axis (either c -tetragonal or b -monoclinic), a doubling of this has been proposed (Byström & Byström 1951), and observed (Mukherjee 1960). Strunz's redefinition of redledgeite (1961, 1963) is based on a $a = 20.23$, $c = 5.88$ Å tetragonal cell. Recently, Cadée & Prodan (1979) have observed a tripling of the short axis in certain synthetic phases, and the presence of layers of diffuse X-ray scattering perpendicular to the short axis of $\text{K}_{1.54}(\text{Mg}_{0.77}\text{Ti}_{7.23})\text{O}_{16}$ has been shown to arise from a quadrupling of the short axis (Beyeler 1976). In the latter case, there is virtually no periodicity within these layers, indicating that the disorder in occupancy and position of cations is one-dimensional. The present structure shows a radical departure from this, in that mannardite gives weak but sharp X-ray reflections for the layers that indicate a doubling of the 3 Å axis (see below). This is the first report of a structure determination of a cryptomelane-group mineral with a doubled short axis.

EXPERIMENTAL

An irregularly shaped fragment of mannardite, approximately $0.2 \times 0.15 \times 0.12$ mm, was extensively examined with precession photography. This showed a body-centred tetragonal cell, space group $I4_1/a$, with $a = 14.357$, $c = 5.908$ Å. No evidence was found of distortion to a monoclinic cell, as is known to occur with some phases of this group. The levels $h0l$ to $h6l$ and $hk0$ to $hk3$ were collected and examined for evidence of incommensurate lattice-ordering (Bursill & Grzanic 1980, Pring & Jefferson

1983). In addition, rotation photographs were taken about the a and c axes. The latter clearly show that reflections in the reciprocal levels having l odd are very much weaker than those with l even, suggesting a $c/2$ subcell. Furthermore, the l -odd levels show continuous sheets of diffuse scattering, with weak but sharp spots superimposed upon them. No such diffuse scattering was observed for the l -even levels, or anywhere in between; also, no vestige of incommensurate superlattice-ordering was observed in mannardite.

The crystal was mounted on a four-circle X-ray diffractometer, and precise cell-dimensions were obtained from the fitted values of 2θ , χ and ω of 138 reflections in the range $46 < 2\theta < 66^\circ$ (Busing 1970) for $\lambda(\text{MoK}\alpha_1) = 0.70930 \text{ \AA}$. A hemisphere of intensity data with l positive was collected to a limit of $2\theta = 100^\circ$ using monochromated $\text{MoK}\alpha$ radiation. A scan rate of $2^\circ/\text{min}$ in 2θ was used, with a peak base-width of 2° , increasing with α_1 - α_2 dispersion ($0.69 \tan\theta$). Background counts were measured for 40 seconds on either side of the peak. The collection of the hemisphere of data resulted in the measurement of a total of four equivalents of each reflection, with the exception of the $00l$ reflections. To improve the statistics on these, the $00\bar{l}$ reflections were measured and added to the data set. The crystal shape was measured in terms of 9 irregular "faces", and a Gaussian integration procedure (Gabe & O'Byrne 1970) was used to calculate the absorption corrections using a grid of $10 \times 10 \times 10$ points. The correction factors varied between 2.21 and 3.34. The intensity data were averaged among the equivalent reflections and reduced to a single octant containing 3219 unique reflections, of which 2210 were considered "observed" on the criterion that $I_{\text{obs}} > 1.65\sigma(I)$. The agreement factor, $\Sigma(I - \bar{I})/\Sigma I$, is 2.5% for the observed data and 2.7% overall. Further relevant details concerning the crystals are given in Table 1.

STRUCTURE DETERMINATION AND REFINEMENT

In view of the extreme weakness of the l -odd intensities, indicating a $c = 2.95 \text{ \AA}$ subcell, the structure was solved initially in the $hk0$ projection by Patterson and heavy-atom Fourier methods. The latter were then used to extend the projection information to a complete structure-determination. The (Ti, V, Cr) metals and all oxygen atoms were found in general (16f) positions, whereas the two barium atoms were found in the $4a$ and $4b$ sites. Least-squares refinement of positional and isotropic thermal parameters soon showed that there is a very significant difference between the occupancies of the two barium sites in the tunnels. Refinement of all metal occupancies, the positional and anisotropic thermal parameters, as well as an overall extinction-parameter (Larson 1970), lowered the Residual to 3.61% if scattering factors for the neutral species were used, and 3.57% if charged species were considered. In the latter case, the population parameters at both transition-metal sites refined to 1.00 to within a small fraction of a standard deviation. It appeared that the stoichiometry of mannardite, as shown by the least-squares refinement, is approximately $\text{Ba}^{2+}_x[\text{Ti}^{4+}_{8-2x}(\text{V}, \text{Cr})^{3+}_{2-x}]\text{O}^{2-}_{16}$, with $x \approx 1$. The scattering curves used at this stage of refinement were: for the transition metal, a composite of the Ti^{4+} , V^{3+} , Cr^{3+} curves (Cromer & Mann 1968) based on the average composition from several microprobe analyses of mannardite crystals; for Ba^{2+} , the curve was taken from the same source, and for O^{2-} the curve of Suzuki (1960) was used. The anomalous-dispersion corrections were taken from Cromer & Liberman (1970). At the end of this stage of refinement, the difference map was examined for evidence of residual electron-density in the tetrahedral holes between oxygen atoms, indicating that the lithium present in the analysis might be structurally important in the mineral. No evidence of any residual electron-density

TABLE 1. CRYSTAL DATA

Mannardite: $[\text{Ba}^{2+}_x(\text{H}_2\text{O})_{2-x}][\text{Ti}^{4+}_{8-2x}(\text{V}, \text{Cr})^{3+}_{2x}]_{16}$, $x = 1.01(2)$ from microprobe analysis, $x = 1.03(2)$ from structure determination.
Source: Rough Claims, Sifton Pass area, Kechika River, Northern British Columbia ($126^\circ 05' \text{W}$, $58^\circ 10' \text{N}$).
Crystal System: tetragonal, $Z = 4$.
Systematic Absences: hkl ; $h + k + l = 2n+1$ $hk0$; $h, (k) = 2n+1$ $00l$; $l \neq 4n$
Space group: $I4_1/a$, (#88).
Cell dimensions: $a = 14.357(2)$, $c = 5.908(1) \text{ \AA}$.
Density: $D_{\text{calc}} = 4.28 \text{ Mg m}^{-3}$, $D_{\text{obs}} = 4.12 \text{ Mg m}^{-3}$.
Absorption: $\mu(\text{MoK}\alpha) = 80.3 \text{ cm}^{-1}$.
Intensity data: Hemisphere of data collected with $\text{MoK}\alpha$ radiation to $2\theta = 100^\circ$, averaged to give 3219 unique reflections, of which 2210 were considered as "observed", [$I > 1.65\sigma(I)$].

was found in either tetrahedral position in the structure. The only significant features in the difference synthesis were near the Ba positions. On either side in z of both Ba sites, there was found a sharp peak, with a negative hole at the Ba site. This is in agreement with the results of the detailed analysis of the positional disorder and occupancy disorder within the cation tunnels in priderite (Post *et al.* 1982).

The successive attempts in the refinement of the Ba positions and occupancies were as follows:

1. An attempt was made to resolve the disordered Ba positions in terms of two sites for each: $z = \frac{1}{8} \pm \Delta_1$, $\frac{3}{8} \pm \Delta_2$. Hitherto, in the structure determination and refinement, the XRAY-76 system of programs had been used (Stewart *et al.* 1976). All attempts to refine this model in the least-squares program CRYLSQ resulted in matrix singularity, owing to the very high correlation of parameters. Finally the 1978 version of XFLS-4 (Busing *et al.* 1978), based on ORFLS (Busing *et al.* 1962), was used. This includes a parameter to damp ill-conditioned variables by multiplying the diagonal elements of the least-squares matrix by a factor greater than 1 (a "slack constraint constant"). A value of 1.4 was initially used, and was slowly decreased to 1.0 (Rae 1973). From the starting values of $z = \frac{1}{8} \pm 0.4 \text{ \AA}$, $\frac{3}{8} \pm 0.4 \text{ \AA}$, after 26 cycles of full-matrix least-squares, the positions of both Ba sites had refined back to within one standard deviation of the $4a$ and $4b$ sites, and the thermal parameters and occupancies were found to be close to where they had been before. There was no improvement in the Residual.

2. An attempt was made to describe the thermal motion of the barium atoms as a third-order (gamma) tensor. This can be viewed as a representation of the motion not as a simple oscillator, but as having a potential well near the extremity of motion along z . There was a marginal improvement in the Residual to 3.55%, but the difference synthesis still indicated that this was not the correct model, and that there was still a significant density of electrons away from the special positions along z .

3. In view of the fact that cation ordering in priderite (Sinclair & McLaughlin 1982, Post *et al.* 1982) was described in terms of a K^+ ion at or very near the special position, and a Ba^{2+} ion significantly further away on either side of the K^+ ion, an attempt was made to describe mannardite in terms of comparable multiple sites for each of the Ba^{2+} positions. The sites proposed were $z = \frac{1}{8}$ and $\frac{1}{8} \pm 0.4 \text{ \AA}$ for one tunnel position, and $z = \frac{3}{8}$ and $\frac{3}{8} \pm 0.4 \text{ \AA}$ for the other. The following restrictions were placed on the anisotropic thermal parameters of the barium atoms: the thermal ellipsoids of the atoms at the $8e$ position were made equal to that of the neighboring atom at the special ($4a$, $4b$) position, the latter being a spheroid with principal axis parallel to c ($U_{22} = U_{11}$, $U_{12} = U_{13} = U_{23} = 0$). The occupancy

parameters were unrestricted. Slack constraints were again used, gradually being relaxed as the refinement converged, until the final cycles were completely unconstrained and showed no indicated shifts. The refinement confirmed the presence of minor satellite sites about the Ba position: Ba($1b$) at $0.46(2) \text{ \AA}$ from Ba($1a$) [$0, \frac{1}{4}, \frac{3}{8}$], and Ba($2b$) at $0.42(2) \text{ \AA}$ from Ba [$0, \frac{1}{4}, \frac{3}{8}$]. At convergence, the Residual had dropped to 2.87% for the 2210 observed data. However, there were still significant peaks present near the Ba sites in the difference synthesis calculated at this stage, though these peaks were now smaller than before the introduction of satellite Ba positions. A totally unsatisfactory aspect of this structural model is that the sum total of the Ba occupancies was such that it indicated 1.14 barium atoms per formula unit, a value far in excess of 1.01(2), as found by microprobe analysis for Ba or for $(V + Cr)/2$. The correlation of parameters in this model was very severe: for the 66 parameters varied in the final cycle, there were 21 elements in the correlation matrix greater than 0.7, 9 were greater than 0.89, and 3 were greater than 0.95 (maximum 0.978).

4. At this stage, the crystal used in the structure determination was mounted in a polished section and microprobed extensively to determine its composition. Three different analysts probed it on three different instruments: some 18 analyses were done, and these results are summarized in Table 2. Optically, the crystal appears homogeneous with no apparent zoning, but significant variation was observed from spot to spot in any given series of microprobe analyses. Thus, the crystal is *not* homogeneous on a micro scale, and its bulk composition must be obtained from an average of the microprobe results. The mean of the average compositions from the three sets of analyses was taken as a fair estimate of the crystal's composition. The sums of the analytical results (with the elements expressed as oxides: BaO, TiO₂, V₂O₃, Cr₂O₃), were invariably low, the range being 96.8 – 97.8%. No trace was found of other elements such as Na and K, frequently encountered in cryptomelane-group

TABLE 2. MICROPROBE DATA ON MANNARDITE CRYSTAL USED FOR X-RAY STRUCTURE DETERMINATION

	Elemental Weight %			Mean	Composition on (Ti+V+Cr)=8
	1.	2.	3.		
Ba	17.44	16.70	17.44	17.20	1.01
Ti	36.01	35.87	35.07	35.65	5.97
V	11.11	10.73	11.16	11.00	1.76
Cr	1.94	2.10	1.23	1.76	0.27
O (by difference)	33.50	34.60	35.07	34.39	17.24

1. Average of 3 analyses, M.A.C. Model 400 microprobe, D.R. Owens analyst, CANMET.
2. Average of 10 analyses, CAMECA CAMEBAX Microprobe, John Wiffl analyst, CAMECA Demonstration Laboratories, San Diego, Calif.
3. Average of 5 analyses, M.A.C. Model 400 microprobe, D.C. Harris analyst, Geological Survey of Canada.

minerals. With the exception of Li, which is known to be present, but not in significant quantity, the only other possibility to make the compositional total up to 100% is to include a water molecule into the cation-tunnel site, in the way originally proposed by Gruner (1943) and discussed at some length by Byström & Byström (1950). This is analogous to the situation in psilomelane (Wadsley 1953), where $\frac{1}{2}$ Ba and $\frac{2}{3}$ water are disordered in each site of the larger cation-tunnels. One water molecule per formula unit in mannardite accounts for some 2.3%, and makes the total sum close to 100%.

In view of the already very high correlation between parameters, no attempt was made to refine any of the parameters of the water molecules included. Water(1) was introduced at the Ba(1a) site (0, $\frac{1}{4}$, $\frac{3}{8}$), with an occupancy parameter reset to $1 - [\text{occupancy of Ba}(1a) + 2 \times \text{occupancy of Ba}(1b)]$. Similar restrictions were made on the occupancy parameters of Water(2) at (0, $\frac{1}{4}$, $\frac{1}{8}$). The thermal parameters of the water oxygen atoms were reset to those of the barium atoms at the same sites. No provision was made for possible movement of the water molecules from the 4a and 4b sites toward the 8e (satellite) sites found for Ba(1b) and Ba(2b), or for movement anywhere within the cation tunnels. Such positional disorder is quite likely, as the water molecules would undoubtedly co-ordinate to the barium atoms at the expected distance of 2.7 - 2.8 Å, which is shorter than the c/2 separation of 2.954 Å.

The refinement converged to 2.71% for the charged species as described before, and to 2.68% (weighted: 2.45%) for the neutral species Ba, the composite transitional metal M (= Ti, V, Cr) and O. For the 1509 reflections with F_{obs} greater than an arbitrary value of $4 * F_{\text{min}}$ (= 16.0), the Residual was 1.64%. With the maximum F_{obs} near 720, this is an indication that the high proportion of weak reflections (a common feature of subcell-supercell structures) is the dominant factor in the Residual. For all elements, the neutral atomic scattering-factors of Cromer & Mann (1968) were used, with the compo-

sition of M (defined above) being taken from the average of the microprobe determinations for this crystal. For the water molecule, the neutral oxygen curve was used, with no attempt to locate or refine the hydrogen atoms.

Although there are additional constraints to a refinement using this model in preference to the anhydrous model (#3 above), there is no increase in the number of parameters refined, and the improvement in Residual is certainly significant. The sum total of the population parameters of barium refined to 1.034(20) Ba atoms per formula unit, a value in good agreement with the microprobe results. The refined occupancies, positional and anisotropic thermal parameters are given in Table 3. The observed and calculated structure-factors are given in Table 4, available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DESCRIPTION OF THE STRUCTURE

The structure of mannardite as projected on (001) is illustrated in Figure 1. There is virtual overlap in all aspects of the structure between the two 3 Å sub-cells. The differences between the projected positions of $M(1)$ and $M(2)$, O(1) and O(4) and O(2) and O(3) are 0.059, 0.018 and 0.030 Å, respectively. The barium/water positional overlap is exact. The relationship of the hollandite cell (Byström & Byström 1950) to the mannardite cell is also shown in the diagram, and involves a 45° rotation and an increase in cell edge by $\sqrt{2}$. Thus the mannardite cell is larger than the hollandite cell by a factor of four.

There are two independent transition-metal ions in the structure, $M(1)$ and $M(2)$, where M represents ($\text{Ti}_{0.746}^{4+} \text{V}_{0.220}^{3+} \text{Cr}_{0.034}^{3+}$). There is no apparent metal-ordering between the sites occupied by the transition metals, as both refine to full site-occupancy. There are four independent oxygen atoms, which form local close-packed columns in z . The M atoms

TABLE 3. ATOMIC OCCUPANCIES, POSITIONAL AND THERMAL PARAMETERS

Atom posit.	Occupancy	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1a)	4b 0.1143(47)	0	1/4	5/8	2.13(4)	2.13	2.92(20)	0	0	0
Ba(1b)	8e 0.0279(19)	0	1/4	0.5474(27)	2.13	2.13	2.92	0	0	0
Ba(2a)	4a 0.8081(60)	0	1/4	1/8	1.91(1)	1.91	1.89(4)	0	0	0
Ba(2b)	8e 0.0280(26)	0	1/4	0.0525(32)	1.91	1.91	1.89	0	0	0
M(1)	16f 1.0	0.24452(2)	0.34237(2)	0.12453(7)	0.79(1)	0.62(1)	0.52(1)	0.02(1)	-0.06(1)	-0.20(1)
M(2)	16f 1.0	0.59098(2)	0.50933(2)	0.12613(7)	0.61(1)	0.92(1)	0.54(1)	-0.08(1)	0.22(1)	-0.08(1)
O(1)	16f 1.0	0.32088(6)	0.22580(6)	0.12611(33)	0.62(3)	0.61(3)	0.67(3)	0.01(2)	0.17(4)	0.04(4)
O(2)	16f 1.0	0.35252(7)	0.56283(7)	0.12194(29)	0.82(3)	0.77(3)	0.63(3)	0.32(2)	0.25(5)	0.39(4)
O(3)	16f 1.0	0.18545(7)	0.10368(7)	0.12477(29)	0.82(3)	0.85(3)	0.64(3)	0.32(2)	0.41(4)	-0.27(5)
O(4)	16f 1.0	0.47578(6)	0.43039(6)	0.12928(31)	0.57(3)	0.67(3)	0.58(3)	0.02(2)	0.00(4)	0.13(4)
Water1	4b 0.8299	0	1/4	5/8	2.13	2.13	2.92	0	0	0
Water2	4a 0.1360	0	1/4	1/8	1.91	1.91	1.89	0	0	0

The anisotropic thermal parameters are expressed in the form: $T = \exp[-2\pi^2\{U_{11}a^2h^2 + 2U_{12}a*b*hk\}]$, and the values quoted are $\times 100$. The unit-cell content of an atom is given by the occupancy factor times the positional-multiplicity factor. The co-ordinates refer to the space-group setting with origin at $\bar{1}$.

occupy the octahedral holes between oxygen atoms, with $M-O$ bond lengths between 1.923(1) and 2.005(1) Å (Fig. 2). The octahedra share edges and corners, such that each oxygen atom is bonded to three M metals, and of course, each M metal to six oxygen atoms.

The distribution of barium in the oxygen tunnels of the structure is illustrated in Figure 3. As explained above, the $4a$ ($0, \frac{1}{4}, \frac{1}{2}$) and $4b$ ($0, \frac{1}{4}, \frac{3}{4}$) sites have satellite positions on either side in z . The total population of barium within one tunnel is $[0.8081 + 2 \times 0.0279 + 0.1143 + 2 \times 0.0280] = 1.03(2)$, a value in excellent agreement with the microprobe result of 1.01(2). In addition to barium within the cation tunnels, there is water at the $4a$ and $4b$ sites, supplementing the barium population to full occupancy. The Ba-O bond lengths are $4 \times 2.990(1)$ and $4 \times 3.014(1)$ Å for Ba(1a) and $4 \times 2.983(1)$ and $4 \times 2.989(1)$ Å for Ba(2a). In addition to this, each

barium has two water molecules at $c/2$, *i.e.*, 2.954 Å, but with partial occupancy. Full details of bond lengths and angles for both the mean and satellite positions of barium and for the transition-metal octahedra are given in Table 5.

EVIDENCE FOR THE PRESENCE OF WATER

If enough material were available, the presence of water might be shown by DTA or infrared absorption techniques. However, with the few crystals of mannardite at hand, this is not possible. The presence of water must be deduced from information already available. From the following, it must be assumed that this is likely.

Gruner (1943) reported that "... psilomelane . . . contains . . . 1-2% H₂O. Most of this is not lost below 300°C." Wadsley (1953) solved the crystal structure of psilomelane, and showed that it

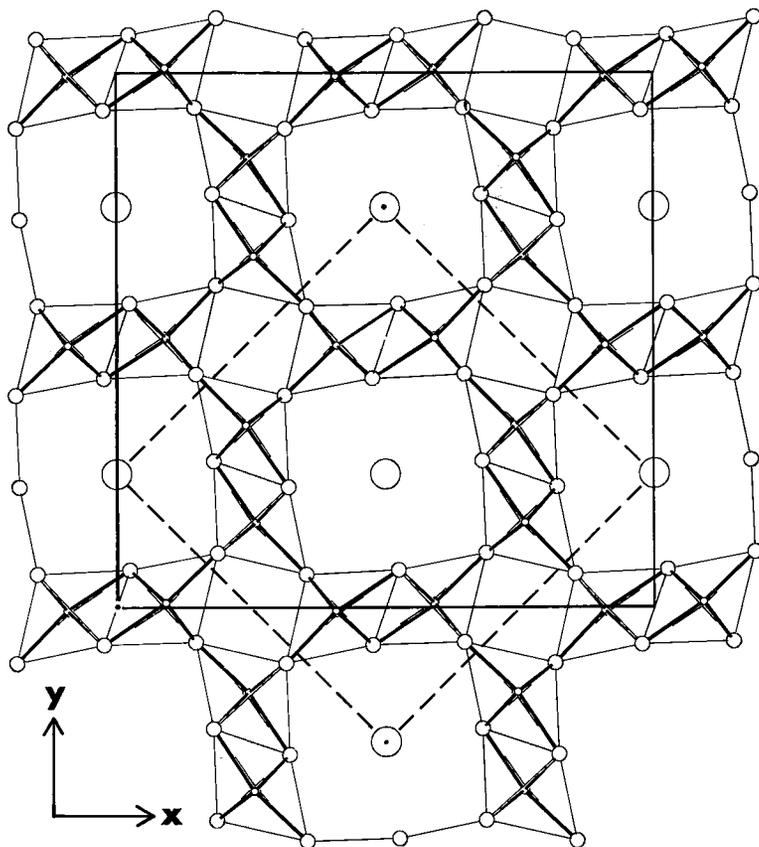


FIG. 1. The structure of mannardite projected on (001). The unit cell is bounded by the solid lines, with the origin in the lower-left corner. The cell of the related mineral hollandite (Byström & Byström 1950) is indicated by the broken-line square. There is virtual overlap in the transition-metal and oxygen positions, and exact overlap in the barium positions between the two 3-Å subcells.

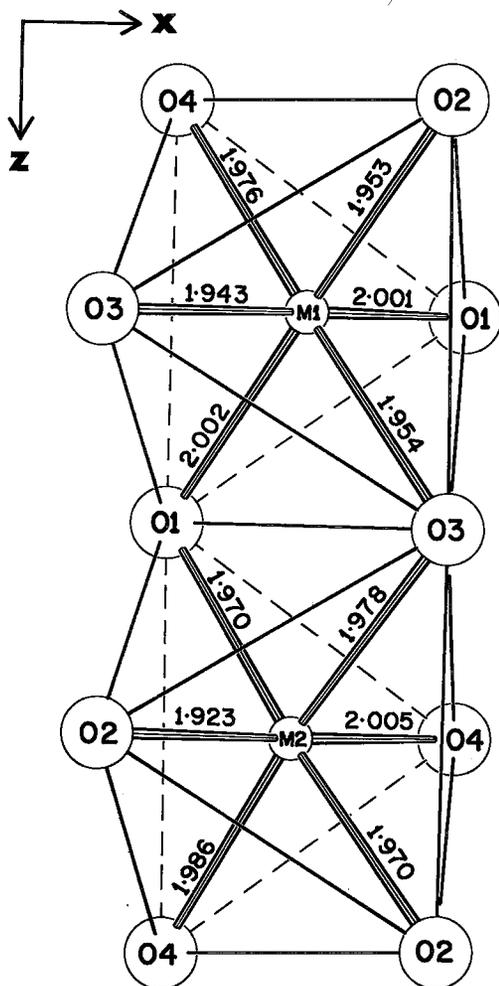


FIG. 2. The transition-metal - oxygen octahedra within one unit cell along z . The standard deviations of the bond lengths are 0.002 Å or less. Full details are given in Table 5. This diagram and Figure 1 were prepared using ORTEP-II (Johnson 1965).

contains $(\text{Ba}, \text{H}_2\text{O})$ in a ratio of 1:2 at the sites of cations in the tunnel. This water is removed by heating to 400°C, but returns if the specimen is left exposed to the atmosphere for a few days. At 550°C, structural conversion to hollandite occurs.

Post *et al.* (1982) found residual electron density at the cation site in a difference synthesis calculated after the refinement of hollandite, and evaluated this as corresponding to 0.5 H_2O molecules per formula unit, in good agreement with the reported chemical analysis of 0.5 - 0.65 molecules for hollandite from the same locality (Byström & Byström 1950).

Infrared-absorption spectroscopy (Potter & Rossman 1979) appears to have resolved the dilemma of the role of water in these mixed-oxide phases. Two different types of spectrum are observed in this family of minerals, and these authors classify the role of water by the one or other type of spectrum shown by the water component as follows:

1. *Hollandite*. "Most hollandite-group samples exhibit an extremely broad low-intensity absorption (. . . band . . .) covering approximately the 3500 cm^{-1} to 2500 cm^{-1} region and a rather broad, low-intensity H_2O bending band near 1600 cm^{-1} . There must be some water in most samples; however, the broadness and weakness of the bands suggest that little is present and that it does not occupy well-defined crystallographic sites."
2. *Romanechite (psilomelane)*. "Our work clearly resolves the uncertainty regarding the nature of the hydrous component of romanechite. (The) bands . . . in the IR spectrum . . . indicate a single, crystallographically ordered type of water. They resemble, in intensity and position, the (. . . bands corresponding to . . .) water found in channels of such minerals as beryl and cordierite."

The differences between the above two types of spectrum are attributed to the $2\text{o} \times 2\text{o}$ cation tunnel (o: octahedral block) in the hollandite (cryptomelane) group, and to the $3\text{o} \times 2\text{o}$ cation tunnel in psilomelane (romanechite). In the former, water is disordered crystallographically; in the latter, it appears to occupy fixed, ordered sites.

The Secondary Ion Mass Spectroscopy (SIMS) data clearly show the presence of peaks for the following atomic weights: 1, (H), strong; 2, (H_2), very minor; 17, (OH), very strong; 18, (H_2O), minor. An assessment of the proportion of water using lepidolite as a standard indicates $2.1 \pm 0.2\%$ water calculated from the hydrogen peak.

The inclusion of approximately one molecule of water per formula unit makes the microprobe totals very close to 100% in both mannardite and redlegite (see below). The presentation of totals (as oxides) that are 2½-3% low was not considered satisfactory.

Lastly, the introduction of water into the partly occupied barium sites improves the structural model on two counts:

1. The agreement factor decreases from 2.87 to 2.68%, *with no increase in the number of parameters refined*. This improvement, at that level of agreement, is certainly significant.
2. The sum total of the barium population, as obtained from the least-squares refinement, is now in agreement with the microprobe results. The equality of the distribution of barium within the satellite positions, [previously significantly different on the anhydrous model, and now each equal to 0.028(2)], is a much more reasonable result.

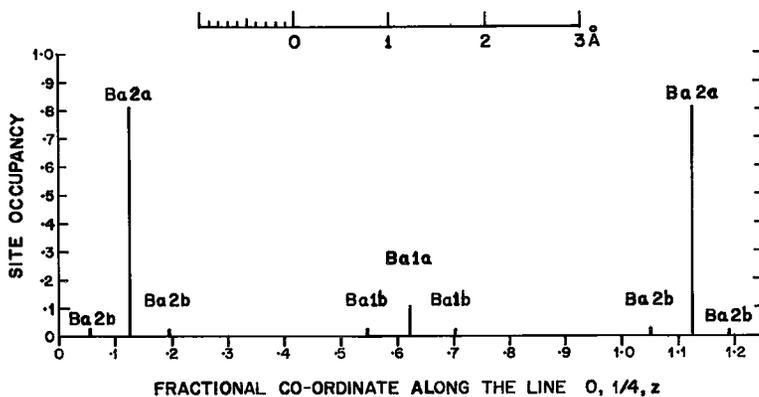


FIG. 3. Site occupancy of barium along the tunnel in the line, $0, \frac{1}{4}, z$, with $1\frac{1}{4}$ unit cells shown. The "mean" positions are Ba2a (at $z = \frac{1}{4}$) and Ba1a (at $z = \frac{3}{4}$). Satellite ("off-centre") positions are indicated as Ba2b and Ba1b.

DISCUSSION

The essential aspects of cryptomelane-group (hollandite) structures, such as the metal-oxygen octahedra and the large oxygen-tunnels, which contain disordered cations, are relatively invariant between the ever-increasing number of structures examined. There are two aspects in which these phases differ structurally, and both relate to cation ordering within the tunnels:

1. Incommensurate superlattice-ordering may occur, as in priderite ($K_{0.97}Ba_{0.33}(Fe_{1.17}Ti_{6.60}Mg_{0.23})O_{16}$ (Pring & Jefferson 1983). In this case, a disordered intergrowth of two types of superstructure ($m = 5$ and $m = 6$) results in the formation of additional reflections, which indicate a superlattice periodicity m of 5.88. An analysis of this condition was done by Bursill & Grznic (1980) for the phases $Ba_x(Ti_{8-x}Mg_x)O_{16}$ and $Ba_x(Ti_{8-2x}Ga_{2x})O_{16}$, where $0.80 < x < 1.33$. It has been found that redledgeite, which is structurally related to mannardite (very comparable cell-dimensions, same space-group) gives additional very diffuse reflections (Scott & Peatfield 1986), but these are not strictly "incommensurate" as the term normally implies (*i.e.*, located at nonintegral submultiples of the reciprocal lattice). In redledgeite, these additional reflections occur in the l -odd levels, based on a $c = 5.983$ Å cell, and are found near, *but displaced by a small constant amount from*, the Bragg positions that violate the body-centring condition (for l odd, $h + k = 2n + 1$).

2. Where only one type of supercell ordering occurs (usually as a result of a specific composition), a simple supercell results where additional reflections occur at the Bragg positions that are exact submultiples (in reciprocal-lattice units) of those corresponding to the 3-Å cell. Mannardite is in this latter

category: Bragg reflections, which are *weak but sharp*, clearly reveal a doubled c -axis, and no incommensurate or diffuse reflections are observed. The only evidence of cation disorder are the sheets of weak diffuse scattering in the l -odd levels of the reciprocal lattice.

The Bursill & Grznic (1980) analysis of incommensurate superlattice-ordering in "hollandites" (cryptomelane-like structures) was based on a $c = 3$ Å model, with one cation site per unit-cell translation. As mannardite and redledgeite have a doubled c -axis, they each have two crystallographically different sites within the 6 Å length of the cation tunnel, and the resolution of the problem of ordering of cations within this length is much more complicated. Rather than attempting to deal with this problem using a Beyeler (1976) model or a Bursill & Grznic (1980) model, the present paper treats the disorder as a static problem, an analysis analogous to that used by Sinclair *et al.* (1980), by Post *et al.* (1982) and by Sinclair & McLaughlin (1982).

The basis of the problem is as follows: on a $c = 3$ Å cell, the unit-cell translation is less than the preferred cation-cation separation. Consequently, partial occupancy of these cation sites is the rule, so that over the whole crystal, usually a little over half the sites are filled. Within a given cation tunnel, there is short-range ordering of the sites according to "filled - empty - filled - empty, *etc.*". On the average, cation-cation distances will be acceptable, except where the short-range order breaks down, and the disorder brings two cations into immediately adjacent sites, 3 Å apart. Repulsion then occurs, and the cations favor a position displaced from their normal special-position site. Earlier analyses of cation ordering in these phases (*e.g.*, Dryden & Wadsley 1958) had postulated that the occupancy of cation

TABLE 5. BOND LENGTHS (Å) AND INTERBOND ANGLES (°) WITH STANDARD DEVIATIONS

Barium-oxygen square prisms													
1. Co-ordination of Ba(1a)													
Atom	d(Å)	O(1) ³	O(1) ⁵	O(1) ⁹	O(4) ²	O(4) ³	O(4) ⁵	O(4) ⁹					
O(1) ²	2.990(1)	120.49(5)	104.26(3)	104.26(3)	75.72(3)	75.64(3)	179.86(5)	59.65(5)					
O(1) ³	2.990(1)	—	104.26(3)	104.26(3)	75.64(3)	75.72(3)	59.65(5)	179.86(3)					
O(1) ⁵	2.990(1)	—	—	120.49(5)	59.65(5)	179.86(3)	75.72(3)	75.64(3)					
O(1) ⁹	2.990(1)	—	—	—	179.86(4)	59.65(5)	75.64(3)	75.72(3)					
O(4) ²	3.014(1)	—	—	—	—	120.21(5)	104.38(3)	104.38(3)					
O(4) ³	3.014(1)	—	—	—	—	—	104.38(3)	104.38(3)					
O(4) ⁵	3.014(1)	—	—	—	—	—	—	120.21(5)					
O(4) ⁹	3.014(1)	—	—	—	—	—	—	—					
2. Co-ordination of Ba(1b), [0, ½, 0.5474(27)]; distance Ba(1a)-Ba(1b) = 0.46(2)Å													
Atom	d(Å)	O(1) ³	O(1) ⁵	O(1) ⁹	O(4) ²	O(4) ³	O(4) ⁵	O(4) ⁹					
O(1) ²	2.790(6)	136.9(6)	102.7(1)	102.7(1)	82.2(2)	82.1(2)	164.7(5)	58.4(1)					
O(1) ³	2.790(6)	—	102.7(1)	102.7(1)	82.1(2)	82.2(2)	58.4(1)	164.7(5)					
O(1) ⁵	3.241(9)	—	—	106.4(5)	58.6(1)	165.0(5)	69.0(2)	69.0(2)					
O(1) ⁹	3.241(9)	—	—	—	165.0(5)	58.6(1)	69.0(2)	69.0(2)					
O(4) ²	2.814(6)	—	—	—	—	136.4(6)	102.9(1)	102.9(1)					
O(4) ³	2.814(6)	—	—	—	—	—	102.9(1)	102.9(1)					
O(4) ⁵	3.267(9)	—	—	—	—	—	—	106.2(4)					
O(4) ⁹	3.267(9)	—	—	—	—	—	—	—					
3. Co-ordination of Ba(2a)													
Atom	d(Å)	O(1) ³	O(1) ⁵	O(1) ¹⁰	O(4) ²	O(4) ³	O(4) ⁵	O(4) ¹⁰					
O(1) ²	2.983(1)	120.93(5)	104.07(3)	104.07(3)	76.19(3)	76.11(3)	179.52(5)	58.59(5)					
O(1) ³	2.983(1)	—	104.07(3)	104.07(3)	76.11(3)	76.19(3)	58.59(5)	179.52(5)					
O(1) ⁵	2.983(1)	—	—	120.93(5)	58.59(5)	179.52(5)	76.19(3)	76.11(3)					
O(1) ¹⁰	2.983(1)	—	—	—	179.52(5)	58.59(5)	76.11(3)	76.19(3)					
O(4) ²	2.989(1)	—	—	—	—	121.89(5)	103.64(3)	103.64(3)					
O(4) ³	2.989(1)	—	—	—	—	—	103.64(3)	103.64(3)					
O(4) ⁵	2.989(1)	—	—	—	—	—	—	121.89(5)					
O(4) ¹⁰	2.989(1)	—	—	—	—	—	—	—					
4. Co-ordination of Ba(2b), [0, ½, 0.0525(32)]; distance Ba(2a)-Ba(2b) = 0.43(2)Å													
Atom	d(Å)	O(1) ³	O(1) ⁵	O(1) ¹⁰	O(4) ²	O(4) ³	O(4) ⁵	O(4) ¹⁰					
O(1) ²	3.216(11)	107.6(5)	102.7(1)	102.7(1)	69.9(3)	69.8(3)	165.2(6)	57.6(1)					
O(1) ³	3.216(11)	—	102.7(1)	102.7(1)	69.8(3)	69.9(3)	57.6(1)	165.2(6)					
O(1) ⁵	2.796(7)	—	—	136.3(7)	57.6(1)	166.1(6)	82.2(3)	82.2(3)					
O(1) ¹⁰	2.796(7)	—	—	—	166.1(6)	57.6(1)	82.2(3)	82.2(3)					
O(4) ²	3.219(11)	—	—	—	—	108.5(5)	102.3(1)	102.3(1)					
O(4) ³	3.219(11)	—	—	—	—	—	102.3(1)	102.3(1)					
O(4) ⁵	2.806(7)	—	—	—	—	—	—	137.2(7)					
O(4) ¹⁰	2.806(7)	—	—	—	—	—	—	—					
Transition-metal octahedra													
5. Co-ordination of M(1)					6. Co-ordination of M(2)								
Atom	d(Å)	O(1) ²	O(2) ¹⁰	O(3) ²	O(3) ¹¹	O(4) ¹⁰	Atom	d(Å)	O(2) ¹	O(2) ¹²	O(3) ⁴	O(4)	O(4) ¹
O(1)	2.301(1)	81.06(5)	93.86(6)	92.65(6)	166.69(4)	81.06(6)	O(1) ⁴	1.970(2)	173.82(4)	91.89(5)	83.07(6)	81.09(5)	98.30(6)
O(1) ²	2.302(2)	—	174.59(5)	82.94(6)	89.68(6)	94.53(6)	O(2) ¹	1.970(2)	—	94.28(5)	96.03(6)	92.83(5)	82.11(6)
O(2) ¹⁰	1.953(2)	—	—	99.23(6)	95.01(5)	82.78(6)	O(2) ¹²	1.923(1)	—	—	94.60(5)	170.29(4)	92.75(5)
O(3) ²	1.951(2)	—	—	—	95.70(5)	173.53(4)	O(3) ⁴	1.978(2)	—	—	—	91.22(5)	172.54(4)
O(3) ¹¹	1.943(1)	—	—	—	—	90.23(5)	O(4)	2.005(1)	—	—	—	—	81.68(5)
O(4) ¹⁰	1.976(2)	—	—	—	—	—	O(4) ¹	1.986(2)	—	—	—	—	—
Oxygen co-ordination [excluding Ba(1b), Ba(2b)]													
7. Co-ordination of O(1)					8. Co-ordination of O(2)								
Atom	d(Å)	Ba(1a) ²	Ba(2a) ²	M(1) ²	M(2) ¹⁰	Atom	d(Å)	M(1) ⁴	M(2) ⁷				
M(1)	2.001(1)	111.83(5)	112.17(5)	98.94(6)	99.08(6)	M(2) ¹	1.970(2)	97.90(9)	131.97(9)				
Ba(1a) ²	2.989(1)	—	59.29(2)	145.62(5)	94.04(6)	M(1) ⁴	1.953(2)	—	129.64(9)				
Ba(2a) ²	2.983(1)	—	—	95.66(6)	144.39(6)	M(2) ⁷	1.923(1)	—	—				
M(1) ²	2.302(2)	—	—	—	95.95(5)								
M(2) ¹⁰	1.970(2)	—	—	—	—								
10. Co-ordination of O(4)													
Atom	d(Å)	M(2) ¹	Ba(1a) ²	Ba(2a) ²	M(1) ⁴								
M(2)	2.005(1)	98.32(6)	112.70(5)	113.47(5)	98.74(6)								
M(2) ¹	1.986(2)	—	92.95(6)	143.38(5)	96.61(4)								
Ba(1a) ²	3.014(1)	—	—	58.95(2)	145.38(5)								
Ba(2a) ²	2.989(1)	—	—	—	96.04(6)								
M(1) ⁴	1.976(2)	—	—	—	—								

Superscripts refer to the following equivalent positions:

- 1 - x, 1 - y, - z
- ½ - x, ½ - y, ½ - z
- ½ + x, y, ½ - z
- ½ - y, ½ + x, ½ + z
- ½ - y, - ½ + x, ½ + z
- ½ - y, - ½ + x, - ½ + z
- ½ + y, ½ - x, ½ - z
- ½ + y, ½ - x, ½ - z
- ½ + y, ½ - x, ½ + z
- ½ + y, ½ - x, - ½ + z
- ½ - y, ½ + x, ½ - z
- ½ - y, ½ + x, ½ - z

sites in a given tunnel has no effect on the neighboring cation sites in adjacent tunnels. Bursill & Grzanic (1980) showed that this was an oversimplification, and that "in fact, there are very strong correlations between the ordering in adjacent tunnels."

In the present case of mannardite, there are 1.03 barium atoms within a 6-Å length of tunnel, distributed between the 81% occupied site, the 11% occupied site and the two satellite sites adjacent to each of the above (Fig. 3). The correlation between

adjacent tunnels is such that these occupancies are related to those in adjacent tunnels by the space-group condition of body-centring, *i.e.*, the correlation between adjacent tunnels is exact. Within each tunnel, every time a Ba atom is found in a *4b* site [Ba(1*a*) in Fig. 3], it must of necessity repel the barium atoms on either side of it in the *4a* sites [Ba(2*a*) in Fig. 3] and tend to move them to the *8e* sites [Ba(2*b*)]. If both *4a* sites were filled, both barium atoms will tend to move *away* from the Ba(1*a*) position to the further out Ba(1*b*) positions. If only one adjacent Ba(1*a*) is occupied, it will be displaced and so will the cause of the displacement, namely Ba(2*a*) will go to Ba(2*b*). It is not unreasonable to expect that the populations of Ba(1*b*) and Ba(2*b*) should be the same, and indeed for the hydrated model of the structure, these refined to identical values of 0.028(2). Obviously, the positions refined in the X-ray analysis are *average* positions, based on all possible combinations of interactions, a time-and-space average over all the tunnels. The situation is complicated by the fact that the "off-centre" positions could be energetically more favorable than the special mean positions, as the mean positions give rise to bond lengths that are significantly longer than the optimum distances of 2.78 – 2.82 Å (Shannon 1976). Shifting the Ba positions to either of the satellite sites, where half of the Ba–O bonds are between 2.79 and 2.81 Å, increases the remaining four bonds to values of 3.22 to 3.27 Å (Table 5).

A true assessment of the co-ordination of cations within the tunnels is made much more difficult by the presence of water in the barium sites. Owing to the limited possibilities of least-squares refinement of such a complicated model as is here presented, no attempt could be made to refine the disordered positions of the water molecules, which coexist with barium in the cation tunnels. Yet it is evident that the *4a* and *4b* sites can only be approximate locations for the water molecules. The Ba^{2+} – O distance is less than $c/2$ (Shannon 1976), and this will tend to pull the water (*4a*) toward both barium atoms (*4b*) [at $\pm c/2$], the result being a disordered position for water, probably about 0.2 Å away from the *4a* position. Similarly, the small fraction of water at site *4b* will be pulled toward the barium atoms at site *4a*. However, where the barium satellite positions are occupied (0.43, 0.46 Å from *4a* and *4b*, respectively), these will tend to push the water molecules in the opposite direction. Furthermore, there is no reason why the oxygen atom of the water should be restricted to the line (0, $\frac{1}{4}$, z). Given the fact that the water molecule would be co-ordinated to the oxygen atoms in the tunnel walls *via* hydrogen bonding, it is unlikely that such co-ordination would restrict the oxygen atoms to stay on the line (0, $\frac{1}{4}$, z). What is postulated here is that the "sphere of confusion" (the limit of the possible disordered

sites) is somewhere near the *4a* and *4b* positions. Obviously, the result is a totally intractable model, and the present representation of it is little more than an approximation. In both the observed and calculated aspects of the structure, no account has been taken of the sheets of diffuse scattering in the *l*-odd levels of reciprocal space, and these are certainly related to the positional disorder within the cation tunnels. Bearing in mind the nature and extent of the proposed disorder in mannardite, it is not surprising that for the related hollandite and similar phases, the infrared absorption spectrum (Potter & Rossman 1979) does not show evidence of ordered structural water.

Sinclair *et al.* (1980) discussed the large thermal parameter observed for the cations in the tunnel direction (U_{33}) for a synthetic phase $(\text{Ba,Ca,Zr})(\text{Ti,Al,Ni})_8\text{O}_{16}$, and related it to positional disorder for the cation over a range of z . In the present structure, when only the *4a* and *4b* sites are considered, refinement of thermal parameters for these two atoms gives U_{11} and U_{33} for Ba(1) and Ba(2) as 0.0255(5), 0.0681(14) and 0.0192(1), 0.0227(2) Å², respectively. The parameters are reasonable for Ba(2), but U_{33} for Ba(1) is excessive. However, when split Ba atoms were introduced, [Ba(1*a*) + Ba(1*b*), *etc.* see Fig. 3], the thermal parameters became nearly isotropic for Ba(2*a*) (81% occupied): $U_{11} = 0.0190$, $U_{33} = 0.0187$ Å², and large but still reasonable for Ba(1*a*) (20% occupied): $U_{11} = 0.0250$, $U_{33} = 0.0308$ Å². With the introduction of the water molecules into these sites, the large parameters for Ba(1*a*) decreased still further to $U_{11} = 0.0213$, $U_{33} = 0.0292$ Å². It can be seen from Table 3 that these parameters are by far the greatest for all the atoms in the structure, but this is not unreasonable in view of the large holes that constitute the tunnels for Ba and water, and the octahedral cages that hold the transition metals and restrict their vibration.

In the refinement of the structure of priderite $(\text{K}_{1.2}\text{Ba}_{0.4})(\text{Ti}_{6.7}\text{Mg}_{0.2}\text{Fe}_{1.1})\text{O}_{16}$, Sinclair & McLaughlin (1982) found that potassium ions occupy the "ideal" sites in the tunnel, whereas barium atoms occupy the "off-centre" sites. These authors wisely gave a *caveat*, that "although this model gave the best factor (R) in the least-squares refinement, some mixing of K and Ba on either site cannot be ruled out". Indeed, in the present case of mannardite, there is only one cationic species (Ba^{2+}), and this is found both in the "ideal" and the "off-centre" sites, both for the highly populated position [Ba(2)] and the less-populated position [Ba(1)]. If barium can behave this way in mannardite, there seems no reason why potassium cannot do so in other structures of this type. There appears little justification now for separating the types of atom between the ordered and disordered sites in structures like priderite.

There remains the problem of the known but unaccounted presence of lithium, which was shown to occur in a number of mannardite specimens in the range 0.02 – 0.06 wt. %. This represents a range of 0.022 – 0.066 atoms per formula unit, and a maximum count of 0.066 electrons in the two possible tetrahedral sites. No evidence of this was found; both tetrahedral sites are completely featureless in the final difference-synthesis. Although the ionic radius of octahedrally co-ordinated lithium ${}^{\text{VI}}\text{Li}^+$ (0.76 Å) is significantly larger than that of ${}^{\text{VI}}\text{Ti}^{4+}$ (0.61) or of ${}^{\text{VI}}\text{V}^{3+}$ or ${}^{\text{VI}}\text{Cr}^{3+}$ (0.64, 0.62, respectively) [Shannon 1976], it is still possible that what little lithium is present substitutes for Ti in the octahedral sites. This would have the added effect of increasing the Ba^{2+} content in the tunnels in order to maintain electroneutrality, though with the very limited amount of lithium, the effect could be no larger than 0.013 Ba per formula unit.

RELATIONSHIP OF REDLEGEITE TO MANNARDITE

Owing to the previously described limitation of not having more than about one Ba atom per 6-Å length of cation tunnel, there is a charge-balance limitation of about two trivalent transition-metal atoms substituting for Ti in the octahedral 16f sites in the structure of mannardite. Ti^{4+} will always be the major occupant of these sites, with Cr^{3+} in redledgeite and V^{3+} in mannardite providing the minor component. Although there is minor replacement of V^{3+} by Cr^{3+} and Fe^{3+} in the mannardite examined, the mannardite end-member is close to $\text{Ba}(\text{H}_2\text{O})(\text{Ti}_6\text{V}_2)\text{O}_{16}$ and the corresponding redledgeite end-member is close to $\text{Ba}(\text{H}_2\text{O})(\text{Ti}_6\text{Cr}_2)\text{O}_{16}$.

The very similar cell-dimensions of redledgeite (Scott & Peatfield 1986) and mannardite and the additional diffuse reflections observed in the diffraction data of redledgeite lead to speculation about the structure of this enigmatic mineral. The presence of these reflections close to positions that are forbidden by the body-centring condition, and that occur only in the *l*-odd levels, leads to the following conclusions:

1. The sharp Bragg reflections indicate a cell and a structure very comparable to those of mannardite, as indicated by cell dimensions, space group and intensities of reflections.
2. The partial ordering of cations within the tunnels is no longer strictly governed by the body-centring condition, *i.e.*, there may be interchange of the 81% site and the 11% Ba site between tunnels in a way opposed to the space-group condition of body-centring. This still does not affect the structural similarity of the two minerals, which are virtually indistinguishable by powder pattern [minor differences are discussed by Scott & Peatfield (1986)]. Chemical analysis can, of course, lead to an iden-

tification of the minerals, and single-crystal work can differentiate between them by means of the above-mentioned diffuse reflections shown by redledgeite but not by mannardite.

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REFERENCES

- BEYELER, H.U. (1976): Cationic short-range order in the hollandite $\text{K}_{1.54}\text{Mg}_{0.77}\text{Ti}_{7.23}\text{O}_{16}$: evidence for the importance of ion-ion interactions in superionic conductors. *Phys. Rev. Lett.* **37**, 1557-1560.
- BURSILL, L.A. & GRZINIC, G. (1980): Incommensurate superlattice ordering in the hollandites $\text{Ba}_x\text{Ti}_{8-x}\text{Mg}_x\text{O}_{16}$ and $\text{Ba}_x\text{Ti}_{8-2x}\text{Ga}_{2x}\text{O}_{16}$. *Acta Cryst.* **B36**, 2902-2913.
- BUSING, W.R. (1970): Least-squares refinement of lattice and orientation parameters for use in automatic diffractometry. In *Crystallographic Computing* (F.R. Ahmed, ed.). Munksgaard, Copenhagen.
- , BROWN, G.M., ELLISON, R.D., HAMILTON, W.C., IBERS, J.A., JOHNSON, C.K. & THIESSEN, W.E. (1978): XFLS4, based on ORFLS. *Oak Ridge Nat. Lab., Oak Ridge, Tennessee*.
- , MARTIN, K.O. & LEVY, H.A. (1962): ORFLS. *Oak Ridge Nat. Lab., Rep.* **ORNL-TM-305**.
- BYSTRÖM, A. & BYSTRÖM, A.M. (1950): The crystal structure of hollandite, the related manganese oxide minerals, and $\alpha\text{-MnO}_2$. *Acta Cryst.* **3**, 146-154.
- & —— (1951): The positions of the barium atoms in hollandite. *Acta Cryst.* **4**, 469.
- CADÉE, M.C. & PRODAN, A. (1979): Tripling of the short axis in the hollandite structure. *Mat. Res. Bull.* **14**, 613-618.
- CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X-rays. *J. Chem. Phys.* **53**, 1891-1898.
- & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Cryst.* **A24**, 321-324.

- DRYDEN, J.S. & WADSLEY, A.D. (1958): The structure and dielectric properties of the compounds with the formula $Ba_x(Ti_{8-x}Mg_x)O_{16}$. *Trans. Faraday Soc.* **54**, 1574-1580.
- FLEISCHER, M. (1983): *A Glossary of Mineral Species*. The Mineralogical Record, Tucson, Arizona.
- GABE, E.J. & O'BYRNE, T. (1970): An absorption correction program for the PDP-8. *Amer. Cryst. Assoc., Summer Meet. Abstr.* **A4** (translated into FORTRAN IV and adapted to CDC computers by Gabe & Szymański).
- GRUNER, J.W. (1943): The chemical relationship of cryptomelane (psilomelane), hollandite, and coronadite. *Amer. Mineral.* **28**, 497-506.
- JOHNSON, C.K. (1965): ORTEP: A FORTRAN thermal ellipsoid plot program for crystal structure illustrations. *Oak Ridge Nat. Lab., Rep. ORNL-3794* [2nd Rev. ORTEP-II addition 1971; modified for use in the Stewart X-RAY system by J.F. Guédon, S.R. Hall, P. Richard & S. Whitlow (1974)].
- LARSON, A.C. (1970): The inclusion of secondary extinction in least-squares refinement of crystal structures. In *Crystallographic Computing* (F.R. Ahmed, ed.). Munksgaard, Copenhagen.
- MUKHERJEE, B. (1960): Space group and cell dimensions of a specimen of hollandite. *Acta Cryst.* **13**, 164-165.
- NAMBU, M. & TANIDA, K. (1967): Manjiroite, a new manganese dioxide mineral from Kohare mine, Iwate Prefecture, Japan. *J. Jap. Assoc. Mineral., Petrol., Econ. Geol.* **58**, 39-54 [*Amer. Mineral.* **53**, 2103 (abstr.)].
- POST, J.E., VON DREELE, R.B. & BUSECK, P.R. (1982): Symmetry and cation displacements in hollandites: structure refinements of hollandite, cryptomelane and priderite. *Acta Cryst.* **B38**, 1056-1065.
- POTTER, R.M. & ROSSMAN, G.R. (1979): The tetravalent manganese oxides: identification, hydration, and structural relationships by infrared spectroscopy. *Amer. Mineral.* **64**, 1199-1218.
- PRING, A. & JEFFERSON, D.A. (1983): Incommensurate superlattice ordering in priderite. *Mineral. Mag.* **47**, 65-68.
- RAE, A.D. (1973): A new approach to the least-squares refinement of highly covariant parameters in crystal structure determinations. *Acta Cryst.* **A29**, 74-77.
- RAMDOHR, P. & STRUNZ, H. (1980): *Klockmanns Lehrbuch der Mineralogie (16th edition)*. Ferdinand Enke Verlag, Stuttgart, Germany.
- SCOTT, J.D. & PEATFIELD, G.R. (1986): Mannardite, $[Ba.H_2O][Ti_6 V_3^{3+}]O_{16}$, a new mineral, and new data on redledgeite. *Can. Mineral.* **24**, 55-66.
- SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.* **A32**, 751-767.
- SINCLAIR, W. & MCLAUGHLIN, G.M. (1982): Structure refinement of priderite. *Acta Cryst.* **B38**, 245-246.
- _____, _____ & RINGWOOD, A.E. (1980): The structure and chemistry of a barium titanate hollandite-type phase. *Acta Cryst.* **B36**, 2913-2918.
- STEWART, J.M., MACHIN, P.A., DICKINSON, C.W., AMMON, H.L., HECK, H. & FLACK, H. (1976): The X-RAY system of crystallographic programs. *Univ. Maryland Comp. Sci. Ctr. Tech. Rep. TR-446*.
- STRUNZ, H. (1961): "Chromrutil" von der Red Ledge Mine ist kein Rutil. Redledgeit. *Neues Jahrb. Mineral. Monatsh.*, 107-111.
- _____, (1963): Redledgeit, eine TiO_2 -Einlagerungsstruktur analog Kryptomelan. *Neues Jahrb. Mineral. Monatsh.*, 116-119.
- _____, (1970): *Mineralogische Tabellen (5th edition)*. Akademische Verlagsgesellschaft Geest & Portig K.-G., Leipzig, Germany.
- SUZUKI, T. (1960): Atomic scattering factor for O^{2-} . *Acta Cryst.* **13**, 279.
- WADSLEY, A.D. (1953): The crystal structure of psilomelane, $(Ba, H_2O)Mn_2O_{10}$. *Acta Cryst.* **6**, 433-438.

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