

Symmetry and Cation Displacements in Hollandites: Structure Refinements of Hollandite, Cryptomelane and Priderite

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Abstract

Precise single-crystal X-ray structure refinements of three hollandite-type minerals have allowed a detailed study of the hollandite structure to be made. The minerals hollandite $[(\text{Ba}_{0.75}\text{Pb}_{0.16}\text{Na}_{0.10}\text{K}_{0.04})(\text{Mn,Fe,Al})_8(\text{O,OH})_{16}]$, cryptomelane $[(\text{K}_{0.94}\text{Na}_{0.25}\text{Sr}_{0.13}\text{Ba}_{0.10})(\text{Mn,Fe,Al})_8(\text{O,OH})_{16}]$, and priderite $[(\text{K}_{0.90}\text{Ba}_{0.35})(\text{Ti,Fe,Mg})_8\text{O}_{16}]$ were refined to residuals of $R = 0.0165$ (599 observations, 48 parameters), $R = 0.0299$ (623 observations, 53 parameters), and $R = 0.0096$ (316 observations, 29 parameters) respectively. The first two structures are monoclinic ($I2/m$) and priderite is tetragonal ($I4/m$). The symmetry of hollandite compounds depends on the ratio of the average ionic radius of the octahedral cations to that of the tunnel cations. Structures in which this ratio is >0.48 distort, reducing the tunnel volume, and thereby lowering the symmetry from tetragonal to monoclinic. The position occupied by a tunnel cation is determined primarily by the size of the cation. Relatively small cations, such as Ba^{2+} in priderite and Pb^{2+} in hollandite, displace from the special position, $2(a)$, to more stable sites that are at the sum of the ionic radii from the nearest O atoms. This study also indicates that the reduced form of Mn in hollandite and cryptomelane is Mn^{3+} ; bond lengths calculated from the refinements suggest that Mn^{3+} is more easily accommodated in the structures than the larger Mn^{2+} .

Introduction

Considerable work has been done in recent years to unravel the complex mineralogical problems associated with manganese oxides; of special interest have been those minerals having hollandite or related structures. It has been found that feldspars transform into the hollandite structure when subjected to very high pressures (Ringwood & Reid, 1967); thus, hollandite-type feldspars may be a major phase of the earth's mantle. Recently, it has been proposed that a synthetic

rock (SYNROC) containing a hollandite compound as a major phase be used for storage of radioactive wastes (Ringwood, Kesson, Ware, Hibberson & Major, 1979). In spite of the great interest in hollandites, there is a limited amount of precise X-ray structural data for these compounds, especially for the minerals. We have, therefore, undertaken a detailed study of several natural hollandite minerals; this paper presents the results for three of these: hollandite, cryptomelane and priderite.

Hollandite and cryptomelane are two members of a group of manganese oxide minerals with the general formula $A_{0-2}(\text{Mn}^{4+}, \text{Mn}^{3+})_8(\text{O,OH})_{16}$, where A is primarily Ba^{2+} in hollandite and K^+ in cryptomelane. Other members of this group are coronadite and manjiroite where A is Pb^{2+} and Na^+ respectively. Byström & Byström (1950) originally solved the crystal structure for hollandite from Weissenberg film data, refining the structure in the space group $I4/m$ to a residual of $R = 0.19$. Structure refinements for the other manganese hollandites have not been reported.

Priderite is a relatively rare mineral having the chemical formula $(\text{K,Ba})_{0-2}(\text{Ti}^{4+}, \text{Fe}^{3+})_8\text{O}_{16}$. It was described by Norrish (1951) from the West Kimberley area of Western Australia and since then has been found at Leucite Hills, Wyoming (Carmichael, 1967), the Kola Peninsula (Zhuravleva, Yurkina & Ryabeva, 1978), and on Corsica (Velde, 1968). Despite its rarity, priderite is an interesting mineral because its composition is similar to that of the synthetic hollandite phase in SYNROC. To date, no single-crystal X-ray studies of priderite have been reported.†

The high residual value reported by Byström & Byström (1950) for the refinement of hollandite and the lack of precise structural data for other hollandite minerals have prevented detailed studies of their structures. X-ray refinements have been reported for several synthetic hollandite compounds (Dryden & Wadsley, 1958; Endo, Kume, Kinomura & Koizumi, 1976; Cadée & Verschoor, 1978; Sinclair, McLaughlin & Ringwood, 1980), but minerals generally present a

† However, after this paper was accepted for publication a paper on the structure of priderite by Sinclair & McLaughlin (1982) appeared. See note added in proof.

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more complex problem than compounds synthesized under controlled laboratory conditions.

The previous studies of compounds having the hollandite structure have posed some intriguing questions. Most hollandites have tetragonal symmetry, but some, including hollandite and cryptomelane, are monoclinic. The nature of the distortions that cause the lowering of symmetry is not well understood. Also, the tunnel cations in the ideal hollandite structure are located at the special position $2(a)$; however, in several hollandite compounds, some or all of the tunnel cations are displaced from that position. The systematics of these displacements have not been explored, nor is it known why displacements only occur in some of the hollandites and not in others. The high precision of our refinements permits us to make a considerably more detailed examination of the structures of these minerals than has previously been possible and provide at least some of the answers to these problems.

Experimental

Specimens of manganese hollandite minerals from several localities were searched for crystals suitable for single-crystal X-ray study. Most samples were poorly crystalline, giving extremely streaked diffraction patterns. Specimens of hollandite and cryptomelane yielded the most promising diffraction patterns, although all crystals of these minerals exhibited twinning to varying degrees. Twinning occurs readily because the a and c axes are of only slightly different lengths, forming a pseudo-tetragonal unit cell. The twinning was observed to take place on the (101) or $(10\bar{1})$ planes. This twinning has also been observed in electron-microscope images and diffraction patterns of hollandite and cryptomelane (Turner, 1978). After an extensive search, relatively untwinned crystals suitable for detailed X-ray study were found in hollandite from Stuor Njuoskes, Sweden (USNM #127118) and in cryptomelane from Chindwara, India (USNM #89104).

Microprobe analyses of the selected crystals (Table 1) confirm them to be hollandite and cryptomelane (because of the difficulty in identifying many manganese oxide minerals, we have encountered numerous mislabeled specimens). The analyses varied slightly from place to place on the samples; therefore, the numbers in Table 1 are averages of several analyses.

A roughly prismatic hollandite crystal fragment measuring $0.12 \times 0.17 \times 0.14$ mm and an irregularly shaped cryptomelane crystal fragment $0.5 \times 0.3 \times 0.2$ mm were mounted on glass fibers. A complete series of precession and Weissenberg photographs was taken using Mo $K\alpha$ radiation. The diffraction patterns show $2/m$ Laue symmetry with all reflections having $h + k + l = 2n + 1$ extinct, indicating the space group to be

Table 1. Average oxide weight percent and unit-cell contents from microprobe analyses

	Cryptomelane (Chindwara, India)	Hollandite (Stuor Njuoskes, Sweden)	Priderite (West Kimberley, Australia)
Na ₂ O	1.02	0.58	0.27
MgO	0.15	0	1.44
Al ₂ O ₃	0.99	1.45	0.05
SiO ₂	0	0.58	0
K ₂ O	5.78	0.23	5.94
TiO ₂	0	0	74.75
Mn ₂ O ₃ } a	84.41	67.48	0
MnO ₂ }			
Fe ₂ O ₃	3.03	12.63	11.57
SrO	1.75	0	0
BaO	1.97	13.81	7.54
PbO	0	4.45	0
	99.18	101.21	101.57
Na ⁺	0.25	0.10	0.06
Mg ²⁺	0.03	0	0.25
Al ³⁺	0.15	0.23	0.01
Si ⁴⁺	0	0.08	0
K ⁺	0.94	0.04	0.90
Ti ⁴⁺	0	0	6.68
Mn ³⁺	1.20	0.50	0
Mn ⁴⁺	6.33	6.08	0
Fe ³⁺	0.30	1.32	1.03
Sr ²⁺	0.13	0	0
Ba ²⁺	0.10	0.75	0.35
Pb ²⁺	0	0.16	0
O ²⁻ , OH ⁻	16	16	16

(a) The Mn³⁺/Mn⁴⁺ ratios for cryptomelane and hollandite were assumed to be 0.19 and 0.08 respectively. These values most closely satisfied charge-balance considerations while at the same time giving summations for the analyses near 100%.

$I2/m$, $I2$ or Im . The structure was assumed to be centrosymmetric and the fitting parameters of the final structure indicate that this assumption is probably correct. The nonstandard space group $I2/m$ was used in preference to the standard space group $C2/m$ because the former gives an angle for β of very nearly 90° and facilitates comparison of our structure with previously reported work.

The priderite crystal used in this study was from the West Kimberley area of Western Australia. The sample is crystalline and shows a pronounced basal and prismatic cleavage. The specimen from which the crystal was taken also contains perovskite (CaTiO₃) and a mineral having the formula (K,Ba)₂(Ti,Fe)₆O₁₃, which to our knowledge has been described but not named (Bagshaw, Doran, White & Willis, 1977). Table 1 shows the microprobe analysis of the priderite crystal selected for study; it agrees well with that given by Norrish (1951). The analysis reported for priderite from Wyoming (Carmichael, 1967) shows a higher Ba:K ratio, implying the possibility of a chemical series with pure K and Ba priderites as end members. This

would be analogous to a cryptomelane and hollandite chemical series.

A prismatic cleavage fragment of priderite measuring $0.4 \times 0.3 \times 0.1$ mm was mounted on a glass fiber. Precession and Weissenberg photographs gave diffraction patterns having $4/m$ Laue symmetry with all reflections having $h + k + l = 2n$ extinct, indicating the space group $I4/m$. Careful comparison of the lengths of the a and b axes on zero-layer Weissenberg photographs showed no evidence of a monoclinic distortion.

Data collection

The hollandite crystal was mounted on a Syntex $P1$ autodiffractometer, and refinement of setting angles obtained at 295 K for 15 reflections ($11.5^\circ \leq 2\theta \leq 27.0^\circ$) gave the lattice parameters listed in Table 2. Examination of ω scans across each of the 15 reflections suggested that the crystal was acceptable for data collection.

Intensity data for 1503 reflections from one half of the reflection sphere were collected using graphite-monochromated Mo $K\alpha$ radiation for $4^\circ \leq 2\theta \leq 71^\circ$. θ - 2θ scans were made at 1° min^{-1} over a scan range of 0.7° above and below the $K\alpha_1 K\alpha_2$ doublet; background counts were collected for 0.25 of the scan time at each end. A set of four check reflections was examined periodically and showed little variation throughout the data collection. The intensities were corrected for Lorentz and polarization effects for monochromated radiation (Azaroff, 1955). The crystal dimensions were measured on an optical goniometer and analytical absorption corrections applied (de Meulenaer & Tompa, 1965) for $\mu = 151 \text{ cm}^{-1}$ (*International Tables for X-ray Crystallography*, 1974). Transmission factors ranged from 0.6344 to 0.7473.

Data collection and treatment for cryptomelane followed procedures similar to those used for hollandite. Refinement of setting angles from 15 reflections

($5.5^\circ \leq 2\theta \leq 19.0^\circ$) gave lattice parameters listed in Table 2. Intensity measurements were made for 1486 reflections from one half of the reflection sphere. The linear mass absorption coefficient used in the absorption correction for cryptomelane was 98 cm^{-1} (*International Tables for X-ray Crystallography*, 1974) and transmission factors ranged from 0.1839 to 0.4466.

Refinement of setting angles from 15 reflections ($5.68^\circ \leq 2\theta \leq 21.64^\circ$) for priderite yielded the lattice parameters in Table 2. Intensity data were collected for 1595 reflections from one half the reflection sphere. Analytical absorption corrections using a mass absorption coefficient of 69.17 cm^{-1} (*International Tables for X-ray Crystallography*, 1974) resulted in transmission factors of 0.2701 to 0.4839.

The e.s.d. for each reflection was calculated using a modification of the method of McCandlish, Stout & Andrews (1975) where $\sigma(F_o) = [(\sigma_c^2 + P^2 I^2)/4ILpA]^{1/2}$. Counting statistics gave $\sigma_c = R(C + k^2 B)^{1/2}$, where C is the total count on a scan at rate R , and k ($= 2$) is the ratio of scan time to background count (B) time. The instrument instability factor, P ($= 0.011$ for hollandite, 0.005 for cryptomelane, and 0.0035 for priderite), was evaluated from deviations of the intensities of the check reflections from a smooth curve. Each reflection was assigned a weight $w = 1/\sigma_c^2$. Equivalent reflections were merged to give a final data set of 750 unique reflections for hollandite, 741 for cryptomelane, and 393 reflections for priderite.

Refinement

The ionic scattering factors for Ba^{2+} , K^+ , Mn^{4+} , Sr^{2+} , Na^+ , Pb^{2+} , Ti^{4+} and O^{2-} used during the refinement were taken from *International Tables for X-ray Crystallography* (1974) with anomalous-dispersion corrections applied to Ba, Mn, Pb, K, Fe and Ti. The function minimized during all least-squares refinement processes was $\sum w(F_o - F_c)^2$, where $w = 1/\sigma_c^2$.

Initial atom positions used in the structure refinement for hollandite, cryptomelane and priderite were those determined by Byström & Byström (1950), but shifted by one-half along the unique axis. Starting occupancies for the tunnel cations were calculated from the microprobe analyses listed in Table 1. During the early stages of the refinements, all of the A cations in hollandite were considered to be Ba^{2+} and Pb^{2+} ; in cryptomelane, K^+ ; and in priderite, K^+ and Ba^{2+} .

For all three minerals, the final cycles of least-squares refinement used only reflections with $\sin \theta/\lambda \geq 0.30 \text{ \AA}^{-1}$; the low-angle reflections were omitted because they are subject to absorption, secondary extinction and valency effects. Also, in the final cycles of refinement all variable parameters, including the tunnel-cation occupancies, were refined.

Table 2. Unit-cell parameters and final refinement data (e.s.d.'s are shown in parentheses)

	Cryptomelane	Hollandite	Priderite
a (Å)	9.956 (3)	10.026 (3)	10.139 (2)
b (Å)	2.8705 (9)	2.8782 (7)	—
c (Å)	9.706 (4)	9.729 (3)	2.9664 (9)
β ($^\circ$)	90.95 (3)	91.03 (2)	—
V (Å ³)	277.35 (17)	280.72 (13)	304.94 (14)
Space group	$I2/m$	$I2/m$	$I4/m$
No. of reflections	623	599	316
No. of parameters	53	48	29
R	0.0299	0.0165	0.0096
R_w	0.0394	0.0215	0.0117

Hollandite

Full-matrix least-squares refinement* of hollandite with anisotropic temperature factors for all atoms yielded a residual of $R = 0.0613$ ($R_w = 0.0763$). A difference Fourier synthesis based on least-squares results showed an area of electron density in the tunnel between the cation sites (0,0,0) and (0,1,0). A plot of the observed electron density along the tunnel, as determined by a Fourier synthesis, revealed a subsidiary cation site at about (0,0.21,0). Approximately 20% of the Ba^{2+} and Pb^{2+} was shifted from (0,0,0) to the subsidiary site; using this model, the refinement converged to a residual of $R = 0.0189$ ($R_w = 0.0244$). At this point, for reasons discussed below, all of the Ba^{2+} was placed at (0,0,0) and the Pb^{2+} was placed at the subsidiary site. Also, Fe^{3+} was put at the octahedral sites in the amount indicated by the microprobe analyses. A final least-squares refinement converged at $R = 0.0165$ ($R_w = 0.0215$), and a difference Fourier map using these final parameters showed a maximum peak of $0.20 \text{ e } \text{Å}^{-3}$ at (0.520, 0.003, 0.661).

Cryptomelane

Full-matrix least-squares refinement of all atom positions and anisotropic temperature factors for cryptomelane converged to a residual of $R = 0.0329$ ($R_w = 0.0446$). A difference Fourier synthesis revealed a small peak ($\approx 2 \text{ e } \text{Å}^{-3}$) at (0,0.5,0); placement of 0.25 of an Na^+ ion, indicated by the microprobe analysis, at this position and subsequent refinement lowered the residual to $R = 0.0313$ ($R_w = 0.0412$).

The temperature factor refined for the K^+ was large in the tunnel direction ($U_{22} = 0.128 \text{ Å}^2$) indicating some positional disorder. The probe analysis showed 0.13 Sr^{2+} per unit cell, which was placed at (0,0.19,0), and the refinement was continued with 0.2 general shifts. The refinement was stabilized by introducing soft constraints (Waser, 1963) on some of the parameters. The y parameter and U_{22} temperature factor for Sr^{2+} were constrained to 0.19 (± 0.05) and 0.08 (± 0.05) Å^2 respectively. The refinement converged to $R = 0.0312$ ($R_w = 0.0410$). Although the residuals were not significantly reduced, the U_{22} temperature factor for K^+ decreased to a more reasonable value of 0.072 (14) Å^2 . A final cycle of refinement with the constraints removed showed little change and converged to $R = 0.0299$ ($R_w = 0.0394$). A final difference Fourier map showed 0.83 $\text{e } \text{Å}^{-3}$ peaks near the octahedral cation positions. It is likely that these peaks are due to errors in the absorption correction resulting from the irregular shape and large size of the crystal used (transmission factors of 0.1839 to 0.4466).

* Calculations were performed with the *CRYSTALS* package of computer programs adapted for the Univac 1110 and Amdahl 470V/7B (Rollett & Carruthers, 1974).

Priderite

Full-matrix least-squares refinement of positions and anisotropic temperature factors for all atoms in priderite converged to a residual of $R = 0.0263$ ($R_w = 0.0313$). Fe^{3+} was placed at the octahedral cation position in the amount determined by the microprobe analysis. Subsequent refinement of occupancies and temperature factors for Fe^{3+} and Ti^{4+} lowered the residual to $R = 0.0238$ ($R_w = 0.0291$). A Fourier map of observed electron density along the tunnels revealed a broad, tailing peak at the special position at (0,0,0). The temperature factor in the tunnel direction refined for this position was $U_{33} = 0.12$ (4) Å^2 . The Ba^{2+} was moved to (0,0,0.18) and further least-squares refinement resulted in a residual of $R = 0.0120$. A second Fourier synthesis of observed electron density indicated that the K^+ also was slightly displaced from the special position. Refinements of the temperature factors, occupancies, and positions for Ba^{2+} and K^+ using 0.2 general shifts placed the K^+ at [0, 0, 0.03 (2)]. Both the Ba^{2+} and K^+ show large e.s.d.'s for their refined parameters. This is not surprising when considering the large number of parameters that were refined for these atoms. Also, the large size of the temperature factor refined for Ba^{2+} [$U_{33} = 0.11$ (3) Å^2] probably indicates additional positional disorder within the tunnels. As with cryptomelane, soft constraints were placed on some of the parameters for the tunnel cations to stabilize the refinement. The z parameters for K^+ and Ba^{2+} were constrained to 0.03 (± 0.03) and 0.17 (± 0.03) respectively, and the U_{33} temperature factor for Ba^{2+} was constrained to 0.08 Å^2 (± 0.03). Least-squares refinement using these constraints lowered the residual to $R = 0.0099$ ($R_w = 0.0122$). An additional cycle of refinement with the constraints removed

Table 3. Atom positions and equivalent isotropic thermal parameters (e.s.d.'s are shown in parentheses)

		x	y	z	U_{eq}^a (Å^2)	
Hollandite	Mn(1)	0.85183 (3)	0	0.33266 (4)	0.0049 (1)	
	Mn(2)	0.33670 (3)	0	0.15345 (3)	0.0050 (1)	
	O(1)	0.6583 (2)	0	0.3022 (2)	0.0088 (7)	
	O(2)	0.6552 (2)	0	0.0414 (2)	0.0084 (7)	
	O(3)	0.2940 (2)	0	0.3502 (2)	0.0088 (7)	
	O(4)	0.0415 (2)	0	0.3222 (2)	0.0079 (6)	
	Ba	0	0	0	0.014 (2)	
	Pb	0	0.202 (11)	0	0.036 (4)	
	Cryptomelane	Mn(1)	0.85145 (4)	0	0.33185 (4)	0.0044 (2)
		Mn(2)	0.33546 (4)	0	0.15305 (4)	0.0043 (2)
O(1)		0.6572 (2)	0	0.3019 (2)	0.0068 (8)	
O(2)		0.6561 (2)	0	0.0420 (2)	0.0070 (9)	
O(3)		0.2947 (2)	0	0.3499 (2)	0.0068 (8)	
O(4)		0.0423 (2)	0	0.3249 (2)	0.0072 (8)	
K,Ba		0	0	0	0.026 (5)	
Sr		0	0.185 (14)	0	0.02 (1)	
Na		0	$\frac{1}{2}$	0	0.03 (3)	
Priderite		Ti,Fe	0.85138 (1)	0.33235 (1)	0	0.0076 (1)
	O(1)	0.65498 (6)	0.29604 (6)	0	0.0062 (3)	
	O(2)	0.04076 (6)	0.33441 (6)	0	0.0068 (3)	
	K	0	0	0.03 (2)	0.026 (9)	
	Ba	0	0	0.18 (2)	0.024 (6)	
	Na	0	0	$\frac{1}{2}$	0.01 ^b	

(a) $U_{eq} = (U_{11} U_{22} U_{33})^{1/3}$. (b) U_{iso} set equal to 0.01.

showed no significant changes. A difference Fourier synthesis showed a 0.6 e \AA^{-3} peak at $(0,0,0.5)$. Placement of 0.05 of an Na^+ ion, indicated by the microprobe analysis, at this site and subsequent refinement of the occupancy for Na^+ and of all parameters for the other atoms resulted in a residual of $R = 0.0096$ ($R_w = 0.0117$). A final difference Fourier map showed no peaks greater than 0.22 e \AA^{-3} .

Atom positions determined for hollandite, cryptomelane and priderite are listed in Table 3.*

Discussion

The refined structures for hollandite, cryptomelane and priderite are similar to that determined for hollandite by Byström & Byström (1950). In general, the hollandite structure consists of double chains of edge-sharing $B\text{--O}$ octahedra that corner share with other double chains to form a framework structure containing large tunnels (Fig. 1). The octahedral (B) cations and coordinating O atoms occupy special positions on the mirror planes located at 0 and 0.5 along the two- or fourfold axes. Byström & Byström (1950) placed the tunnel (A) cations at the special position, $2(b)$, defined by the intersection of a mirror plane and rotation axis. Byström & Byström's structure was solved in the tetragonal space group $I4/m$; subsequent work by Byström & Byström (1950) and others (Mathieson & Wadsley, 1950; Mukherjee, 1960) revealed a slight monoclinic distortion in the hollandite unit cell. In the present work, hollandite and cryptomelane were refined in the monoclinic space group $I2/m$; priderite, however, shows no monoclinic distortion from a tetragonal unit cell.

Octahedral sites

The octahedral sites can accommodate a large variety of cations that range greatly in size. In addition to the Mn^{4+} in hollandite and cryptomelane and the Ti^{4+} in priderite, the octahedral sites contain Mn^{3+} , Fe^{3+} , Al^{3+} , Si^{4+} and Mg^{2+} . The lower-valence cations in the octahedra are essential to offset the positive charges of the tunnel cations.

Several synthetic hollandite compounds with different octahedral cations have been described in the literature (e.g. Bayer & Hoffman, 1966; Endo *et al.*, 1976; Cadée & Verschoor, 1978; Sinclair *et al.*, 1980). The unit-cell volumes vary linearly with the sizes of the octahedral cations; they are smallest for cations such

* Tables of structure factors, bond lengths, anisotropic thermal parameters and the compounds and data used in preparing Figs. 2 and 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36390 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

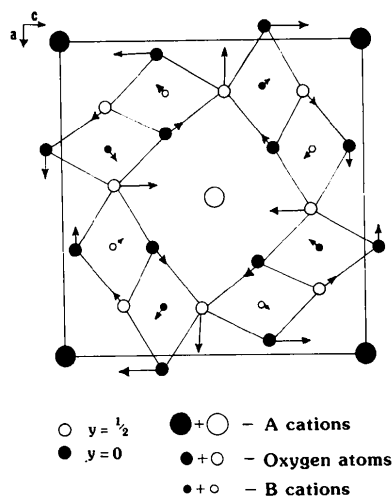


Fig. 1. Projection of the hollandite unit cell down the monoclinic b axis. Arrows indicate the direction of displacement of atom positions from those in an ideal tetragonal hollandite unit cell; the lengths of the arrows are proportional to the magnitude of displacement.

as Mn^{4+} and Si^{4+} and largest for cations having large ionic radii, e.g. Zn^{2+} and In^{4+} . This is shown graphically in Fig. 2, which plots the average octahedral cation radii (Shannon, 1976) against the unit-cell volumes for several natural and synthetic hollandite compounds.* The size of the A cation also has a slight effect on the cell volume, as can be seen from the vertical spread of the points.

Structural distortions

It has long been noted that, while the ideal hollandite unit cell is tetragonal ($I4/m$), many hollandites show a

* See deposition footnote.

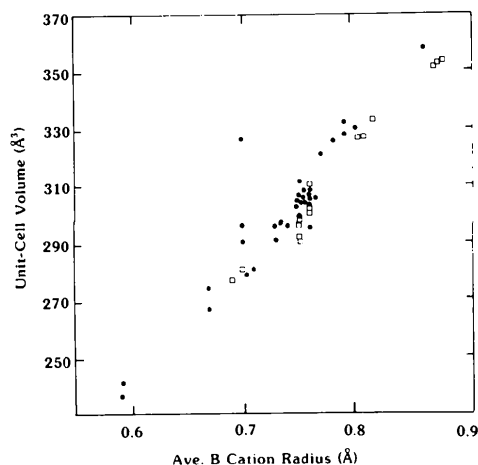


Fig. 2. Unit-cell volume *vs* \bar{r}_B for hollandite compounds reported in the literature; circles represent tetragonal structures and squares monoclinic structures.

small distortion that lowers the symmetry to the monoclinic space group $I2/m$ ($C2/m$). As mentioned above, the hollandite and cryptomelane used in this study are monoclinic, whereas the priderite is tetragonal. Sinclair *et al.* (1980) and others proposed that as the B cations get larger, the B -O octahedra must distort, causing a lowering of the symmetry. Thus, compounds with small B cations and, consequently, small unit cells should be tetragonal and ones with large unit cells should be monoclinic. They suggest that the symmetry change takes place at cell volumes between 290 and 300 Å³. Fig. 2 shows that while generally true, this is not the case for many hollandite compounds, e.g. hollandite ($V = 280.72$ Å³) and cryptomelane ($V = 277.35$ Å³) are monoclinic, and priderite ($V = 304.94$ Å³) is tetragonal.

Using the program *MOLFIT* (Dollase, 1974), we compared the octahedra in hollandite, cryptomelane and priderite to ideal B -O octahedra. In all cases the octahedra were found to be distorted. As expected, the shared octahedral edges were considerably shortened. Also, in all three minerals the octahedral cations are displaced from the centers of the octahedra. In hollandite and cryptomelane, the B cations (Mn^{4+} , Mn^{3+} , Fe^{3+}) have moved along an octahedral triad axis, thus forming three long and three short B -O bonds. In priderite, however, the Ti^{4+} and Fe^{3+} are displaced along a tetrad axis. In general, off-center displacements occur when the effective radius of the B cation is small relative to that of the O atoms (Megaw, 1968). A slight tetragonal distortion in the octahedra of hollandite and cryptomelane may be a Jahn-Teller effect from Mn^{3+} .

The average r.m.s. displacements, calculated using *MOLFIT*, of the atom positions in the observed octahedra in hollandite, cryptomelane and priderite from those of an ideal octahedron are 0.126, 0.125 and 0.141 Å respectively. If these displacements are considered to be a measure of the degree of distortion, then the octahedra of priderite are more distorted than those of hollandite or cryptomelane. As has already been pointed out, however, priderite has a tetragonal unit cell; therefore, it seems that the monoclinic distortion observed in some hollandites cannot result solely from the distortion of the B -O octahedra.

The arrows in Fig. 1 indicate the displacement of the refined atom positions for monoclinic hollandite from those for an ideal tetragonal unit cell. The lengths of the arrows are proportional to the magnitude of the displacement. This diagram demonstrates the nature of the monoclinic distortion to be a twisting of the columns of B -O octahedra about an axis halfway between $O(3)$ - $O(3')$ and $O(1)$ - $O(1')$, parallel to \mathbf{b} . The result of this twisting is that the volume of the tunnels is decreased slightly. This is similar to the situation encountered for compounds with the perovskite structure, where octahedra tilt or twist,

causing a lowering of symmetry. Such distortion generally occurs when the central cation is too small for the cavity formed by the octahedral framework. Megaw (1973a) reports that the amount of distortion in perovskites increases as the ionic radius of the central cation decreases relative to that of the octahedral cations.

In an attempt to determine if the nature of the twisting in hollandites is similar to that observed in perovskites, we plot in Fig. 3 the average A -cation radii versus the average B -cation radii for the hollandite compounds used in Fig. 2. In general, compounds with monoclinic symmetry plot in the lower right-hand portion of the figure. This corresponds to hollandites with small A cations and relatively large B cations. Thus, it appears that if the A cation is too small for the tunnel, the columns of B -O octahedra twist to decrease the volume of the tunnel and a monoclinic structure results, in agreement with what is observed in perovskite structures.

The dashed line in Fig. 3, corresponding to $\bar{r}_B/\bar{r}_A = 0.48$, approximately separates the tetragonal from the monoclinic hollandite structures. Therefore, in general, hollandite compounds with $\bar{r}_B/\bar{r}_A < 0.48$ are tetragonal and those with a larger ratio are monoclinic. The transition region from tetragonal to monoclinic symmetries, as seen in Fig. 3, does not form a sharp boundary. There are several possible explanations. The precision of the X-ray measurements reported for many of the hollandite compounds may not be sufficient to distinguish between a tetragonal and a slightly distorted monoclinic cell. The number and types of tunnel cations might affect the structure. Also,

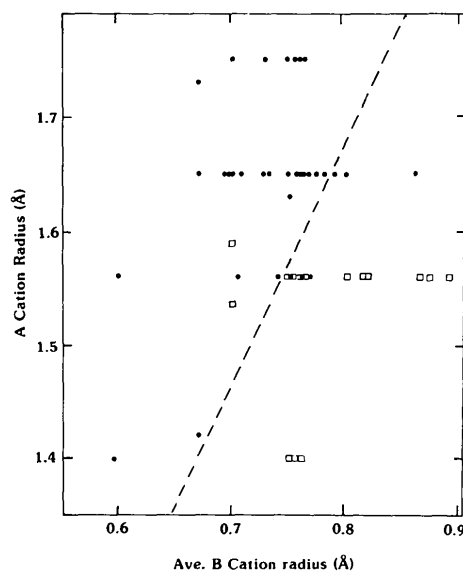


Fig. 3. \bar{r}_A vs \bar{r}_B for hollandite compounds reported in the literature; circles represent tetragonal structures and squares monoclinic structures.

the use in Fig. 3 of the average cation radii for minerals might not be valid, which may explain why hollandite and cryptomelane are monoclinic although Fig. 3 suggests that they should be tetragonal.

The β angles for the monoclinic hollandites plotted in Fig. 3 increase as \bar{r}_B/\bar{r}_A gets larger. Thus, as expected, the hollandite structure must increasingly distort as the tunnel cation decreases in size relative to the octahedral cation.

Manganese oxidation states

There has been some controversy in the literature as to whether the reduced form of Mn in hollandite and cryptomelane is Mn^{2+} or Mn^{3+} . For many years, it was assumed that Mn^{2+} was present based on oxidation-reduction potential arguments that Mn^{2+} and Mn^{4+} are more stable than Mn^{3+} (Burns, 1970). Several papers, mostly in the Eastern European literature, have presented detailed studies of oxidation states of Mn in manganese oxide minerals (e.g. Yanchuk, 1973, 1977; Yanchuk & Povarennykh, 1975). Based on chemical arguments and detailed X-ray spectroscopy studies, these authors generally conclude that the reduced Mn is Mn^{3+} .

The results of our refinements for hollandite and cryptomelane tend to support the conclusion that Mn^{3+} is the reduced form of Mn. Mn^{2+} in an oxygen octahedral framework would exist in the high-spin state; consequently, the calculated Mn^{2+} -O bond distance (Shannon, 1976) would be 2.20 Å. This is considerably longer than the observed average B-O bond distances of 1.917 (3) and 1.925 (3) Å in cryptomelane and hollandite respectively. The calculated Mn^{3+} -O bond distances of 2.01 Å is exactly the same as that for the Fe^{3+} found in both of these minerals; therefore, Mn^{3+} should also fit into the octahedral site. The largest octahedral cation reported in a synthetic hollandite is In^{3+} (Kinomura, 1973), which forms an In^{3+} -O bond of 2.17 Å, still shorter than that expected for Mn^{2+} . Thus, for steric reasons alone, the smaller Mn^{3+} should be accommodated into the structure more easily than Mn^{2+} .

Tunnel cations

Perhaps the most interesting aspect of the hollandite structure pertains to the positions and occupancies of the tunnel cations. Byström & Byström (1950) placed these cations at the special position 2(b) [corresponding to our special position 2(a)]. In our study, however, we have observed that some or all of the tunnel cations in hollandite, cryptomelane and priderite are displaced from the special position. Displacement of the tunnel cations has also been reported for several synthetic hollandite compounds (Sinclair *et al.*, 1980; Cadée & Verschoor, 1978; Beyeler, 1976).

The tunnel cations fit into cavities that are formed by eight O atoms at the corners of a distorted prism. A tunnel cavity contains one of the A cations, or H_2O , or it can be empty. The cation can occupy the special position at the center of the cavity or be displaced along the tunnel toward four of the surrounding O atoms. Table 4 summarizes the types of tunnel cations, the positions they occupy and the fraction of tunnel cavities filled by each cation for the three minerals studied here. In hollandite and cryptomelane, the Ba^{2+} and K^+ are at the special position, and the Pb^{2+} and Sr^{2+} are displaced; in priderite, however, both the Ba^{2+} and K^+ are displaced. These tunnel-cation displacements can be explained by considering the geometry of the tunnel cavity.

The K^+ in cryptomelane is at (0,0,0), at a distance of about 2.88 Å from the eight coordinating O atoms. This K^+ -O contact distance is nearly that predicted using the ionic radii of Shannon (1976). Therefore, the K^+ in cryptomelane is not displaced because it is best able to satisfy its ionic contact distances to the nearest O atoms by occupying a position at or near (0,0,0) (Fig. 4a). The Sr^{2+} and Na^+ (in cryptomelane), however, are smaller than K^+ and, thus, form shorter cation-oxygen contacts. Either of these cations at (0,0,0) will be farther than the ideal contact distance from the eight nearest O atoms. According to the Born-theory treatment presented by Megaw (1973b), the smaller cations are stabilized by displacing to either of two equivalent off-center positions. Therefore, in cryptomelane the Sr^{2+} and Na^+ are displaced along the tunnel from the special position (Fig. 4b). The Sr^{2+} must displace about 0.60 Å to be at the predicted

Table 4. Tunnel cations in hollandite, cryptomelane and priderite

Occupancies used for octahedral cations in the refinement model are those determined from the microprobe analyses.

	Tunnel cation	Cation location	Fraction of location occupied	
			Refinement	Analysis ^c
Hollandite	Ba^{2+}	(0,0,0)	0.34 (2)	0.37 (3)
	Pb^{2+}	[0, 0.20 (1), 0]	0.15 (1) ^a	0.08 (2)
	Na^+	(0,0.5,0)	0	0.05 (3)
	K^+	(0,0,0)	—	0.02 (1)
Cryptomelane	K^+	(0,0,0)	0.65 (5) ^b	0.47 (1)
	Na^+	(0,0.5,0)	0.11 (4)	0.12 (13)
	Sr^{2+}	[0, 0.18 (1), 0]	0.08 (3)	0.07 (1)
	Ba^{2+}	(0,0,0)	— ^b	0.05 (1)
Priderite	K^+	[0, 0.03 (2), 0]	0.66 (7)	0.45 (1)
	Ba^{2+}	[0, 0.18 (2), 0]	0.10 (2)	0.17 (1)
	Na^+	(0,0.5,0)	0.02 (1)	0.03 (1)

(a) This site also contains H_2O . (b) Occupancy refined for K^+ also includes Ba^{2+} . (c) The numbers in parentheses are the standard deviations in the average values based on 6, 5 and 7 analyses for hollandite, cryptomelane, and priderite respectively.

2.64 Å contact distance from four of the coordinating O atoms. This corresponds to the site we observed in cryptomelane at [0, 0.185 (14), 0], where the Sr²⁺ is 2.65 (1) Å from the nearest O atoms.

The difference Fourier synthesis for cryptomelane also showed an area of electron density in the tunnel at the center of the plane of four O atoms at $y = 0.5$. The only cation in cryptomelane small enough to fit into this site is Na⁺. The four observed Na⁺—O distances of 2.490 (2) Å are between the 2.56 and 2.37 Å values predicted for Na⁺ in eight- and fourfold coordination respectively.

In hollandite, the distance from the special position to the eight coordinating O atoms is 2.89 Å, about the same as in cryptomelane. This distance is only 0.1 Å longer than the theoretical Ba²⁺—O contact distance. The Ba²⁺ in hollandite occupies the site at (0,0,0). The smaller Pb²⁺, however, must displace 0.58 Å (to 0,0.20,0) to be at the theoretical 2.67 Å Pb²⁺—O contact distance. This agrees with our observation of a subsidiary tunnel site at [0, 0.202 (11), 0] in hollandite, where the Pb²⁺ is 2.65 (1) Å from four of the neighboring O atoms.

The ionic radius of Ti⁴⁺ is larger than that of Mn⁴⁺ (0.745 vs 0.67 Å); consequently, the framework structure for priderite is expanded relative to hollandite and cryptomelane. For the K⁺ in priderite to be at its predicted K⁺—O contact distance of 2.88 Å and the Ba²⁺ to be at the predicted Ba²⁺—O contact distance of 2.79 Å, they would have to occupy positions at about (0,0,0.065) and (0,0,0.17) respectively. The refined site for Ba²⁺, [0, 0, 0.18 (2)], is close to that predicted for Ba²⁺; however, the site refined for K⁺ at [0, 0, 0.03 (2)] is less displaced than predicted. The refined temperature factors for both of these cations are large in the tunnel direction, indicating additional positional disorder on these sites.

The tunnels in priderite are more than $\frac{2}{3}$ filled by cations; therefore, tunnel sites in adjacent unit cells will commonly be occupied. It would be expected that

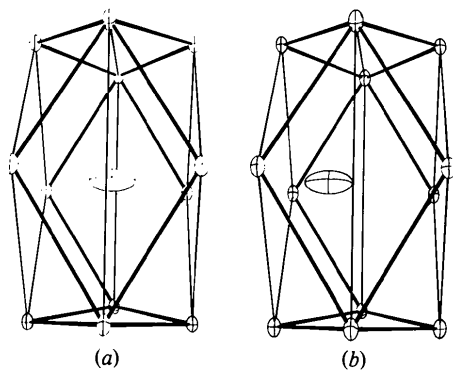


Fig. 4. View of the A cation coordination polyhedron along [101] in cryptomelane for (a) A = K⁺ and (b) A = Sr²⁺. The b axis is horizontal.

charge repulsion between cations in neighboring tunnel cavities would affect the magnitude of the displacements of the cations. A cation would occupy one of a series of closely spaced positions depending upon whether adjacent tunnel cavities contain Ba²⁺, K⁺, H₂O, or are unoccupied. This range of positions could account for the large apparent temperature factor refined for the Ba²⁺. The two tunnel sites determined by the structure refinement indicate the best average cation positions. Charge repulsion between tunnel cations might also cause positional disorder that contributes to the large temperature factors for the tunnel cations in hollandite and especially in cryptomelane where the tunnels are also about $\frac{2}{3}$ filled by cations.

The magnitudes of displacement of the tunnel cations in other hollandite compounds are also consistent with contact-distance considerations. Sinclair *et al.* (1980) observed the Ba²⁺ to be displaced 0.34 Å along the tunnel in (Ba_{0.98}Ca_{0.03}Zr_{0.02})Al_{1.1}Ni_{0.48}Ti_{6.4}O₁₆. The resulting Ba²⁺—O contacts to the four nearest O atoms are 2.79 Å, exactly as predicted from ionic radii. Similarly, Cadée & Verschoor (1978) report a displacement of 0.52 Å for Ba²⁺ in Ba_xSn_{4-2x}Cr_{2x}O₈, resulting in Ba²⁺—O distances of 2.79 Å. Also, Endo *et al.* (1976) did not observe a displacement for K⁺ in K₂Cr₈O₁₆, which has K⁺—O contact distances to the eight coordinating O atoms of 2.90 Å, very close to the predicted value of 2.88 Å.

Water in hollandite minerals

Water as molecular H₂O and OH⁻ has been reported in hollandite and cryptomelane (Gruner, 1943; Byström & Byström, 1950). They suggest that the H₂O molecules fill some of the tunnel sites not occupied by cations and that OH⁻ substitutes for O²⁻ in the framework structure. Our refinement of the occupancies of the tunnel cations in hollandite revealed more electron density than could be reconciled with the amounts of cations determined by microprobe analyses. This excess electron density was located at the site to which we assigned the Pb²⁺. When we subtract the number of electrons that should be contributed by 0.16 Pb²⁺ (see Table 1), an excess of four to five electrons remains. This corresponds to about 0.5 H₂O molecules per unit cell. Byström & Byström (1950) report an analysis for a hollandite from the same locality as the crystal used in this study that shows 0.5 to 0.65 H₂O molecules per unit cell. The H₂O molecules in the tunnels are probably hydrogen bonded to the O atoms at opposite corners of the square formed by O(1) and O(3) atoms at $y = 0.5$ (see Fig. 1). Assuming an average O—H...O bond of 2.80 Å, the H₂O would be at approximately (0,0.29,0). Water at this position may partly explain the large temperature factor refined for the Pb²⁺ tunnel site at [0, 0.202 (11), 0].

Cryptomelane has fewer unoccupied tunnel sites than hollandite; therefore it should contain less molecular H₂O. Gruner (1943) reported the presence of 0 to 1.3 H₂O molecules per unit cell; our refinement, however, does not indicate the presence of H₂O.

Difference Fourier maps for hollandite and cryptomelane revealed 0.2 to 0.3 e Å⁻³ peaks located in the tunnels about 1 Å from O(1) and O(3). It is possible that these are H positions, suggesting that a portion of the O(1) and O(3) atoms are OH⁻.

Cation ordering in tunnels

Long-exposure Weissenberg zero-layer and oscillation photographs of hollandite show diffuse streaks between the reciprocal-lattice planes perpendicular to **b***. Similar streaking has been observed in hollandite and hollandite compounds by other investigators (Dryden & Wadsley, 1958; Mukherjee, 1964; Beyeler, 1976; Sinclair *et al.*, 1980; Turner & Buseck, 1982). Beyeler (1976) showed that these streaks arise from the tunnel cations and attributed them to one-dimensional cation ordering along the tunnels. The occupancy of the tunnel-cation sites in hollandite is about 50%; this is consistent with streaking resulting from short-range ordering, where the cations occupy every other tunnel cavity along **b** with no correlation between tunnels. Cadée & Prodone (1979) and Bursill & Grzinic (1980) have made detailed electron diffraction and high-resolution electron microscopy studies of the ordering of tunnel cations in some synthetic hollandites. Streaking was not observed in X-ray diffraction patterns for cryptomelane or priderite but has been observed in electron diffraction patterns for cryptomelane from this and other localities (Turner, 1978; Turner & Buseck, 1979, 1982).

Conclusions

The high quality of the structure refinements presented here for hollandite, cryptomelane and priderite have enabled us to answer many of the questions that have been raised about the hollandite structure. (1) The distortion responsible for lowering the symmetry from tetragonal to monoclinic in some hollandites occurs when the ratio of the radius of the octahedral cation to that of the tunnel cation is greater than about 0.48. (2) The nature of the distortion is a twisting of the columns of octahedra about an axis parallel to **b**, reducing the volume of the tunnel cavities. (3) The position that a tunnel cation occupies depends primarily on the size and to a lesser degree on the charge of the cation. Relatively small cations are displaced from the center of the tunnel cavity to positions that are at the sum of the ionic radii from the nearest O atoms. (4) The reduced form of Mn in

hollandite and cryptomelane is probably Mn³⁺ rather than Mn²⁺. Bond-length calculations from the X-ray refinements indicated that Mn²⁺ is too large to be accommodated into the structures.

We are continuing our study of the hollandite structure. In addition to investigating several synthetic hollandites, we are searching for suitable crystals of manjiroite and coronadite. Also, we are looking for possible ordering of Mn and Fe on the octahedral sites in hollandite using neutron powder diffraction.

The authors are grateful to Shirley Turner, Dr David Veblen and Dr Michael O'Keeffe for helpful discussions. The microprobe analyses of priderite were completed by James Clark using the Chemistry Department microprobe facility. The samples of hollandite and cryptomelane were supplied by John White, Smithsonian Institution, and the priderite sample was supplied by Dr Martin Prinz, American Museum of Natural History. We wish to thank Arizona State University for a generous allocation of computer time for calculations. Financial support was provided by grant EAR-7926375 (to PRB) from the Earth Sciences Division of the National Science Foundation.

Note added in proof: A recent structure refinement of a priderite also from the West Kimberley area of Western Australia has appeared (Sinclair & McLaughlin, 1982). The refined values of the atomic coordinates, with one exception, from that work are essentially identical with ours and have been determined with only slightly less precision. However, they failed to detect any shift of the *A* cation (K⁺ in our work) from the special position. They also obtained the same equivalent isotropic temperature factors for all atoms except for the displaced *A*(1) cation (Ba²⁺ in our work).

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Acta Cryst. (1982). **B38**, 1065–1070

The Structure of Silver Fluoride Iodide Hydrate $\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2.5\text{H}_2\text{O}$

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Abstract

$\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2.5\text{H}_2\text{O}$ is monoclinic, space group $P2_1/n$, with $a = 7.4061$ (6), $b = 17.8298$ (32), $c = 9.3618$ (9) Å, $\beta = 91.278$ (8)°, $Z = 4$, and $D_m = 5.9$, $D_x = 6.17$ Mg m⁻³. The structure was determined from single-crystal X-ray diffractometer data. The refinement based on 2961 reflexions and anisotropic thermal parameters converged to a final R value of 0.039. Layers built up by Ag, I and F atoms are joined by a hydrogen-bond system containing four-membered $(\text{H}_2\text{O} \cdots \text{F})_2$ rings. The I atoms are rather unsymmetrically surrounded by seven or eight Ag atoms. Five of these describe a pentagon. These pentagons share edges to form layers, two per unit cell, also containing F atoms. Every Ag atom has six neighbours (two I, three F, and one F or one O atom), creating a distorted octahedron. Every F atom in the layer is surrounded by six Ag atoms in octahedral coordination. Two of the Ag–Ag distances are remarkably short – 2.92 and 2.98 Å respectively. The F atoms in the hydro-

gen-bond system have a tetrahedral environment of three Ag atoms and one O atom. The O–H \cdots F distances are short – 2.52, 2.55, 2.57 and 2.59 Å.

Introduction

This work is part of a systematic structural investigation of compounds $\text{Ag}_n\text{X}_x\text{A}_y$ ($n > x$) with various counterions A and $X = \text{Cl}, \text{Br}, \text{or I}$. The investigations aim at a clarification of the coordination of the Ag atoms to the halide in these compounds where Ag is in excess over halide. Until now the detailed crystal structure is known only for a few compounds meeting these stoichiometric requirements. These compounds are Ag_2ClNO_3 (Persson, 1979a), Ag_2BrNO_3 (Persson & Holmberg, 1977), Ag_2INO_3 (Persson, 1979b), $\text{Ag}_3\text{I}(\text{NO}_3)_2$ (Birnstock & Britton, 1970), and $\text{Ag}_{13}\text{I}_9(\text{WO}_4)_2$ (Chan & Geller, 1977).

From the early work by Hayek (1936) and Lieser (1960) it should be possible to prepare an analogous