# Rietveld refinement of the coronadite structure

## Jeffrey E. Post

Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.

## David L. Bish

Earth and Space Sciences Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, U.S.A.

## Abstract

Rietveld refinements using X-ray powder-diffraction data of coronadite samples from Morocco ($Pb_{1.06}Ba_{0.10}Mn_{7.7}V_{0.20}Al_{0.08}O_{16}$) and Australia ($Pb_{1.40}Mn_{7.9}Al_{0.05}Zn_{0.05}O_{16} \cdot 1.55H_2O$) in space group $I2/m$, $a = 9.938(2)$ Å, $b = 2.8678(5)$ Å, $c = 9.834(2)$ Å, $\beta = 90.39(2)°$ (Morocco) and $a = 9.913(1)$ Å, $b = 2.8652(4)$ Å, $c = 9.843(1)$ Å, $\beta = 90.20(1)°$ (Australia) confirm the basic hollandite structure. The Pb is displaced about 0.60 Å along the tunnels from the special position at (0, 0, 0). This displacement increases intercation distances in the tunnels, allowing up to two-thirds of the tunnel sites to be occupied by Pb cations.

## Introduction

The Rietveld refinement technique using X-ray powder-diffraction data provides a valuable approach for studying structures of minerals that do not form crystals suitable for single-crystal experiments (Rietveld, 1969). The method has been successfully used to refine structures for a variety of minerals and compounds (e.g., Hill and Madsen, 1984; Ercit et al., 1985; Post and Bish, 1988). In the present study we used the Rietveld method to refine for the first time the crystal structure of the lead manganese oxide mineral coronadite.

On the basis of X-ray powder-diffraction patterns, it has been assumed that coronadite is isostructural with the hollandite group minerals. The hollandite structure consists of double chains of edge-sharing Mn-O octahedra that corner-share with each other to form tunnels with square cross-sections, measuring two octahedra on a side (Fig. 1). The tunnels are partially filled with large univalent or divalent cations and, in some cases, water molecules. The different hollandite minerals correspond to the predominant tunnel cation species: hollandite (Ba), cryptomelane (K), manjiroite (Na), and coronadite (Pb). Typically, hollandite minerals with only divalent tunnel cations have their tunnel sites half filled. Coronadite, however, is somewhat anomalous in that chemical analyses show that the tunnel sites can apparently be up to about two-thirds filled.

Detailed structure refinements have been reported for hollandite and cryptomelane (Post et al., 1982); however, a crystal of coronadite has not yet been found that is suitable for single-crystal diffraction experiments.

## Data collection and refinement

The coronadite samples are from Broken Hill, Australia (University of Arizona, Tucson; no. 10217) and Bou Tazzoult, Morocco (AMNH; no. 23050). Electron-microprobe analyses give the following approximate chemical formulae, respectively: $Pb_{1.4}(Mn_{7.9}Al_{0.05}Zn_{0.05})O_{16} \cdot 1.55H_2O$ (water analysis by Dupont 903H Moisture Evolution Analyzer) and $Pb_{1.06}Ba_{0.10}(Mn_{7.7}V_{0.20}Al_{0.08})O_{16}$ (no water analysis was performed).

The samples were ground in a Brinkmann Microrapid Mill under acetone to particle sizes smaller than about 10 $\mu$m and were loosely packed into cavity mounts and their surfaces roughened with the edge of a razor blade (to minimize preferred orientation of the sample particles). The data were collected with $CuK\alpha$ radiation using a Scintag automated powder diffractometer equipped with Soller slits and an intrinsic-Ge solid-state detector. The incident- and diffracted-beam slits used were 1.0 and 0.3 mm, respectively, and data were collected for 16 and 50 s per 0.03° step (Table 1). For all of the refinements, the data for $2\theta < 30°$ were excluded because in this region, not all of the incident X-ray beam is striking the sample and therefore relative observed intensities are too low.

The starting model for the Rietveld refinements was the hollandite structure determined by Post et al. (1982), except with all of the Ba and/or Pb placed on the special position at (0, 0, 0). Space group $I2/m$ was assumed, on the basis of electron-diffraction evidence and its isostructural relationship with hollandite.

The Rietveld refinements were carried out using the computer program DBW3.2 (Wiles and Young, 1981) as modified by S. Howard (personal communication). During the early stages of the refinements, only scale factors and background coefficients were allowed to vary, and then gradually in successive least-squares cycles, additional parameters were included, i.e., unit-cell parameters, full-width parameters, sample displacement error, and peak asymmetry ($<50°$ $2\theta$). The backgrounds were fit using a third-order polynomial, and the observed peak shapes were approximated with a pseudo-Voigt profile function, limited to six full-widths on each side of the peak maxima. After convergence with the above parameters, atom positions and occupancy factors were includ-
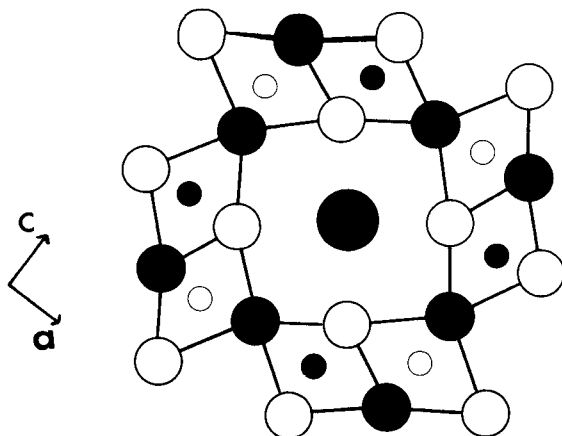
Fig. 1. Projection of the hollandite structure down the tunnels. The Mn atoms are represented by small circles, the oxygen atoms by medium circles, and the tunnel cations by large circles. The open circles indicate atoms at $y = 0$, and the filled circles at $y = \frac{1}{2}$.

**Table 1.** Final Rietveld refinement parameters

|  | Morocco | Broken Hill |
|---|---|---|
| $a$ (Å) | 9.938(2) | 9.913(1) |
| $b$ (Å) | 2.8678(5) | 2.8652(4) |
| $c$ (Å) | 9.834(2) | 9.843(1) |
| $\beta$ (°) | 90.39(2) | 90.20(1) |
| Pseudo-Voigt coefficient | 0.79(3) | 1.21(3) |
| Overall $B$ | −1.26(13) | −1.75(7) |
| Parameters | 30 | 30 |
| Bragg reflections | 160 | 205 |
| $2\theta$ range (°) | 30–100 | 33–110 |
| Time/step (s) | 16 | 50 |
| $R_p$ | 0.086 | 0.060 |
| $R_{wp}$ | 0.109 | 0.074 |
| $R_{wp}$ (expected) | 0.077 | 0.046 |
| $R_{Bragg}$ | 0.093 | 0.069 |

ed in the refinements. In general, isotropic temperature factors were held fixed to reasonable values for framework cations ($B = 0.6$) and oxygen atoms ($B = 0.8$), and overall temperature factors were refined. We attempted to refine isotropic thermal parameters for the Pb cations. The final refinement parameters are summarized in Table 1, and atom positions are listed in Table 2, along with the previously reported single-crystal values for hollandite. Selected bond distances for hollandite and coronadite are compared in Table 3. Final observed, calculated, and difference X-ray powder-diffraction patterns are plotted in Figure 2.

## RESULTS AND DISCUSSION

Our Rietveld refinements of coronadite confirm that it is isostructural with hollandite and cryptomelane. Our results also indicate that the coronadite structure is monoclinic, not tetragonal as has been previously reported. The unit-cell parameters refined for the two coronadite samples (Table 1) indicate that the sample from Broken Hill has a slightly smaller $\beta$ angle than that from Morocco, probably reflecting the difference in the amount of Pb in the tunnels in the two structures. The greater proportion of filled tunnel sites in the Broken Hill material allows less collapse of the octahedral framework, and consequently there is less monoclinic distortion (Post et al., 1982).

Comparison between the hollandite single-crystal atom coordinates and the coronadite positions (Table 2) reveals slight differences. Powder patterns collected from several repacked mounts for the same coronadite samples indicate evidence for a small degree of preferred orientation. Also, the relatively broad powder-diffraction peaks indicate some structural disorder [probably chain-width disorder similar to that observed in hollandite and romanechite (Turner and Buseck, 1979)]. Consequently, it

is impossible to assess accurately the errors in the coronadite refinements, and the apparent differences between the coronadite and hollandite structures might not be real. Even assuming, however, the level of accuracy of Rietveld refinements on hollandite and romanechite (unpublished results), there seems to be significant deviations of the coronadite structure from that of hollandite. This is reinforced by the fact that similar shifts (e.g., for O1 and O3) are reflected in refinement results for both coronadite samples.

Because of the uncertainties of the errors, it is not possible to analyze bond lengths in coronadite in detail. The fact, however, that the average Rietveld-refined Mn–O distances for individual octahedra in hollandite and romanechite compare well with those determined by single-crystal studies (unpublished results) suggest that the comparable values resulting from refinements of coronadite also might be reasonably correct. On the basis of the chemical analyses, the coronadite from Morocco has 1.07 $Pb^{2+}$ and 0.07 $Ba^{2+}$ cations per cell, therefore requiring approximately 2.28 $Mn^{3+}$ (out of eight) on the octahedral sites to balance the charges of the tunnel cations. The material from Broken Hill has approximately 1.40 $Pb^{2+}$ per cell, thus mandating 2.80 $Mn^{3+}$. The ideal average Mn–O bond lengths should be about 1.93 Å (Morocco) and 1.94 Å (Broken Hill) (Shannon, 1976), which compare reasonably well with the values given in Table 3, especially for the Moroccan sample.

The refined Pb position is displaced approximately 0.60 Å along the tunnels from the special position at (0, 0, 0), which is consistent with observed displacements of a portion or all of the tunnel cations in other hollandite phases. For example, Post et al. (1982) reported tunnel cation sites at (0, 0, 0) and at (0, 0.20, 0) in the hollandite from Sweden, and they assigned the Ba to the special position and the Pb to the subsidiary site. Sinclair et al. (1980) reported that the Ba in $BaTi_7AlO_{16}$ is located 0.38 Å along the tunnel from the special position. A couple of explanations have been proposed for these displacements: (1) that they minimize Coulombic repulsions between cations in neighboring unit cells along a given tunnel (Sinclair et al., 1980) and (2) that they enable tunnel cations
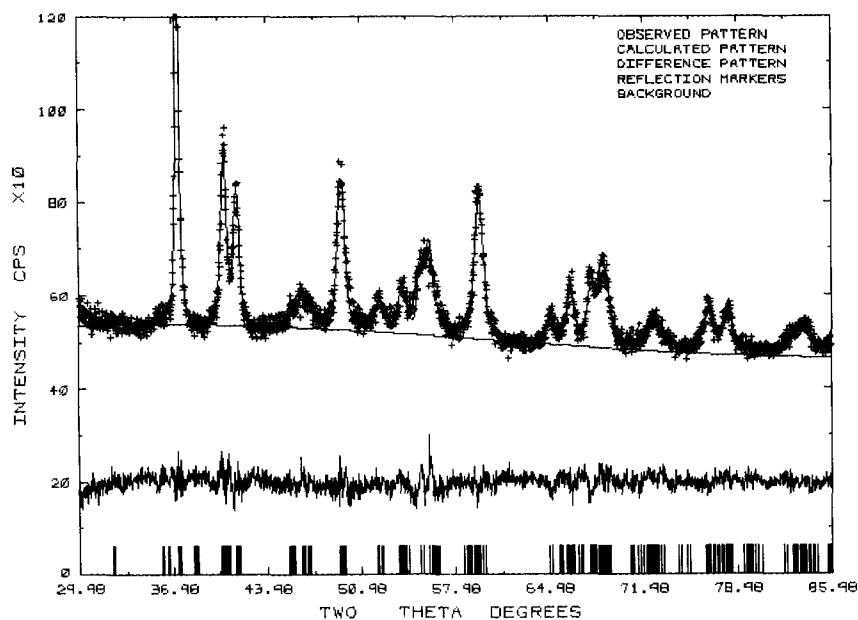
Fig. 2. Observed and calculated X-ray powder-diffraction patterns for coronadite from Morocco. The crosses are the observed data, and the solid lines are the calculated profiles. The smooth line beneath each set of patterns is the calculated background. The patterns have been offset by two major divisions along the $y$ axis. The difference between the observed and calculated profiles is plotted below each set of patterns. The vertical bars mark all possible Bragg reflections ($K\alpha_1$ and $K\alpha_2$).

to optimize bond distances with coordinating oxygen atoms (Post et al., 1982). Most likely a combination of factors is at play. The Pb cation is at a mean distance of 2.61 Å from the four nearest oxygen atoms, which is consistent with the predicted Pb–O distance of 2.67 Å (Shannon, 1976), and 3.19 Å from four other oxygen atoms.

In order to understand better the nature of the Pb site in coronadite, a Fourier difference map was calculated for the tunnel region of the Broken Hill structure. A Rietveld refinement was carried out using the hollandite Mn–O

octahedral framework as the structure model, and only the unit-cell, background, full-width, and profile parameters were refined along with the scale factor. The observed Bragg intensities determined by the Rietveld procedure were corrected for Lorentz-polarization and multiplicity effects and then were converted into structure factors. The difference map was calculated using the same model Mn–O framework used for the Rietveld refinement. The contoured difference map in Figure 3 shows a smeared-out Pb site centered at about (0, 0.22, 0), which is consistent with the refined position. There is no indication of electron density at the special position at (0, 0, 0). The height of the Pb peak is small compared to what might be expected on a comparable Fourier difference map calculated using single-crystal data. Typically, the

**TABLE 2.** Atom parameters for hollandite and coronadite

| | | Hollandite single-crystal* | Coronadite | |
|---|---|---|---|---|
| | | | Morocco | Broken Hill |
| Mn1 | x | 0.85180(3) | 0.852(1) | 0.837(1) |
| | z | 0.33266(4) | 0.333(1) | 0.327(1) |
| Mn | x | 0.33670(3) | 0.333(1) | 0.338(1) |
| | z | 0.15345(3) | 0.156(1) | 0.138(1) |
| O1 | x | 0.6583(2) | 0.637(3) | 0.639(2) |
| | z | 0.3022(2) | 0.294(3) | 0.311(2) |
| O2 | x | 0.6552(2) | 0.657(3) | 0.636(2) |
| | z | 0.0414(2) | 0.051(3) | 0.042(2) |
| O3 | x | 0.2940(2) | 0.284(3) | 0.286(2) |
| | z | 0.3502(2) | 0.327(3) | 0.336(2) |
| O4 | x | 0.0415(2) | 0.034(3) | 0.045(2) |
| | z | 0.3222(2) | 0.329(3) | 0.323(2) |
| Ba | occ | 0.74 | | |
| Pb | y | 0.20(1) | 0.214(2) | 0.214(2) |
| | occ** | 0.30(1) | 1.07(2) | 1.34(2) |

Note: (1) y parameters for Mn and O are fixed to 0 by symmetry. (2) occupancies are cations per unit cell.
* Post et al. (1982).
** Site also contains some water.

**TABLE 3.** Mn–O bond lengths (Å) for hollandite and coronadite

| | Hollandite single-crystal* | Coronadite | |
|---|---|---|---|
| | | Morocco | Broken Hill |
| Mn1–O1 | 1.958(2) | 2.14(2) | 1.97(2) |
| –O1 (×2) | 1.949(2) | 1.94(1) | 1.99(1) |
| –O2 (×2) | 1.892(2) | 1.88(1) | 1.94(1) |
| –O4 | 1.907(2) | 1.85(2) | 2.06(2) |
| Mean | 1.925 | 1.94 | 1.98 |
| Mn2–O2 | 1.899(2) | 1.97(2) | 1.79(2) |
| –O3 | 1.969(2) | 1.93(2) | 2.02(2) |
| –O3 (×2) | 1.946(2) | 1.91(1) | 1.90(1) |
| –O4 (×2) | 1.899(2) | 1.94(1) | 1.88(1) |
| Mean | 1.926 | 1.93 | 1.90 |

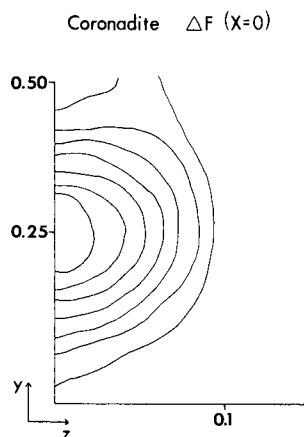* Post et al. (1982).

Coronadite  $\triangle F$  (X=0)



Fig. 3. Difference-Fourier map at $x = 0$ for the tunnel region of coronadite from Broken Hill. The map was calculated using the hollandite Mn-O framework and Rietveld-derived observed Bragg intensities. The contour interval is 1.0 e Å$^{-3}$.
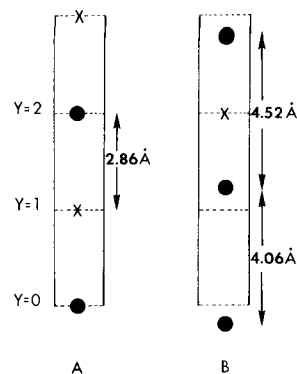


Fig. 4. Representation of three unit cells along a tunnel in coronadite showing distances between adjacent sites for tunnel cations (A) at the special position at (0, 0, 0) and (B) displaced 0.60 Å off the special position as determined by Rietveld refinements for coronadite. The increased intercation distance in B minimizes repulsion forces between adjacent tunnel cations and allows up to two-thirds of the tunnel sites to be filled, compared with only one-half of the sites in A.

observed intensities determined by Rietveld refinements are heavily biased by the model structure, and consequently the resulting Fourier maps show less detail than those derived from single-crystal experiments (Post and Bish, 1988).

The diffuse nature of the Pb site suggests the presence of positional disorder. Single-crystal studies have shown that temperature factors refined for tunnel cations in hollandite structures typically are anomalously large and anisotropic in the tunnel direction (e.g., Sinclair et al., 1980; Post et al., 1982). This large apparent thermal motion has been interpreted as positional disorder of the tunnel cations due to various arrangements of the lower-valence octahedral cations (e.g., $Mn^{3+}$ in coronadite) in different unit cells (Post and Burnham, 1986). Additionally, water molecules in the tunnels probably contribute to the disorder on the Pb site. Refinement of an isotropic temperature factor for Pb in coronadite yielded $B = 1.9$, which is comparable to single-crystal values for tunnel cations in hollandites (Post et al. 1982). The refined occupancies of 1.07 (Morocco) and 1.34 (Broken Hill) Pb cations per unit cell compare well with the microprobe-determined values of 1.12 (Ba included as Pb) and approximately 1.4 cations per unit cell, respectively.

One of the interesting aspects of the coronadite structure is that it is able to accomodate more tunnel cations than hollandite minerals that have $Ba^{2+}$ as the predominant tunnel cation. Coronadite analyses typically show 1.0 to 1.4 tunnel cations per unit cell, i.e., the tunnel sites are half to about two-thirds filled, whereas the mineral hollandite seldom has more than 1.0 tunnel cation per unit cell. If hollandite contains some univalent tunnel cations or $Pb^{2+}$, then the tunnel occupancy might reach 1.1–1.2 cations per unit cell. The maximum occupancy

of the tunnel sites is probably limited by the size and charge of the cations. Thus hollandites can accommodate more small than large and more univalent than divalent tunnel cations. This is supported by observations that $K^+$ and $Na^+$ hollandite phases commonly have 1.3–1.5 tunnel cations per unit cell. In the case of the mineral hollandite, charge repulsion prevents Ba cations from occupying neighboring unit cells along a given tunnel; thus only every other tunnel site is filled (Fig. 4). In coronadite, however, the smaller Pb cations can be displaced off the special position, thus increasing the distances between cation sites in a given tunnel (Fig. 4). The Pb cations are displaced toward vacant and away from filled sites in adjacent unit cells along a tunnel. As a result, Pb cations can fill two-thirds of the tunnel sites (1.33 cations per unit cell).

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