

Structure Refinement of Priderite

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Abstract. $(K_{1.2}Ba_{0.4})(Ti_{6.7}Mg_{0.2}Fe_{1.1})O_{16}$, tetragonal, $I4/m$, $Z = 1$, $a = 10.140$ (1), $c = 2.965$ (1) Å, $D_c = 4.0$ Mg m⁻³, $\mu = 7.28$ mm⁻¹. Priderite is isostructural with hollandite. The conventional R factor converged to 0.052 for 987 observed intensities. The large cations (K, Ba) occupy a range of positions within the tunnels of the structure. K predominantly occupies the central site at $(0,0,\frac{1}{2})$ and Ba occupies the off-centred site 4(e) $(0,0,\pm z)$, with $z = 0.327$ (6).

Introduction. In a previous study of the hollandite-type phase $BaAl_2Ti_6O_{16}$ (Sinclair, McLaughlin & Ringwood, 1980), it was found that the large A cation, Ba, was displaced off its ideal site of $(0,0,\frac{1}{2})$ within the tunnels of the structure. This effect was attributed to the size and charge of the Ba atoms. The analysis also demonstrated the ability of the structure to immobilize large radioactive waste elements when used as a constituent phase of a synthetic rock (SYNROC) (Ringwood, Kesson, Ware, Hibberson & Major, 1979). Recently, Bursill & Grzanic (1980) reported similar conclusions after electron-microscope examination of the hollandite-type phase $Ba_xTi_{8-x}Mg_xO_{16}$. Post, Buseck & Von Dreele (1980) have also reported, in abstract form, a displacement of Ba of 0.6 Å from the ideal site in the mineral hollandite, $Ba_xMn_8O_{16}$, from a single-crystal X-ray structure analysis. The position of K in cryptomelane, however, did not show a similar displacement.

The mineral priderite occurs in the leucite-lamproites from the west Kimberley area of Western Australia (Norrish, 1951; Prider, 1960; Gupta & Yagi, 1980). The mineral is a close natural analogue to the synthetic Ba hollandite-type phase, and contains both K and Ba in the tunnel sites. The present study has been undertaken in order to gain further information on the location and environment of the large A cations in natural specimens. The information so obtained will have a direct bearing on the ability of synthetic 'hollandite' to immobilize large elements of varying size and charge.

A small crystal, of approximately rectangular shape with dimensions of $0.04 [\perp(001)] \times 0.04 [\perp(1\bar{1}0)] \times 0.12 [\perp(110)]$ mm, was chosen for intensity data collection. Intensities for 1356 reflections having 2θ values between 3 and 120° were collected by the θ - 2θ scan technique using Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) reflected from a graphite-crystal monochromator. The data were corrected for absorption, sorted and averaged and reduced to structure amplitudes in the usual way. Reflections for which $I/\sigma(I) < 3.0$ were discarded as being unobserved. A total of 987 (78%) unique reflections remained. Transmission factors for I_{obs} varied from 0.583 to 0.772.

Scattering factors for neutral atoms as well as corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). Initially, a three-dimensional difference Fourier map was calculated using only phases derived from the Ti/Fe and the two O positions. This showed a region of residual electron density centred about $(0,0,\frac{1}{2})$ and elongated parallel to the c axis by ~ 1.5 Å. This suggested that some of the large cations (K, Ba) reside on $(0,0,\frac{1}{2})$ while the rest occupy a range of positions on either side. Refinement proceeded using three models. First, K and Ba were placed on site 4(e) at $(0,0,\pm z)$. Secondly, these atoms were placed on 2(b) at $(0,0,\frac{1}{2})$ and thirdly, K (A) was placed on $(0,0,\frac{1}{2})$ and Ba [$A(1)$] on $(0,0,\pm z)$. Table 1 summarizes the final residual values for these models. The decrease in the value of R of model 3, compared to model 1, is highly significant (Hamilton, 1965). Atomic parameters for model 3 are

Table 1. Residual values for priderite

Model	K	Ba	R	R_w^a
1	$0,0,\pm z^b$	$0,0,\pm z^b$	0.061	0.079
2	$0,0,\frac{1}{2}$	$0,0,\frac{1}{2}$	0.061	0.079
3 ^c	$0,0,\frac{1}{2}$	$0,0,\pm z^d$	0.052	0.068

(a) The weight of an observation $w(hkl) = 1/\sigma_2^2$ where $\sigma_2 = \{\sigma_1^2 + 0.25[0.04(F_o)]^2\}^{1/2}$. (b) $z = 0.49$ (2). (c) Secondary extinction = 1.6 (5) $\times 10^{-4}$. (d) $z = 0.327$ (6).

Table 2. Final atomic and thermal parameters for priderite with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{8}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq} (Å ²)
A	0.0	0.0	0.5	2.1 (2)
A(1)	0.0	0.0	0.327 (6)	6.7 (5)
B	0.3514 (1)	0.1677 (1)	0.0	0.6 (1)
O(1)	0.1553 (2)	0.2040 (2)	0.0	0.5 (1)
O(2)	0.5407 (2)	0.1652 (2)	0.0	0.6 (1)

Table 3. Interatomic distances (Å) and angles (°) of priderite with e.s.d.'s in parentheses

A—O(1)	2.992 (1)	8×	O(1)—A—O(1)	59.39 (4), 75.79 (2), 120.60 (4), 104.21 (2), 180.00
A—O(2)	3.420 (2)	4×		
A(1)—O(1)	2.775 (7)	4×	O(1)—A(1)—O(1)	139.1 (7), 82.9 (3), 57.9 (1), 163.0 (6), 102.3 (2), 105.0 (5), 68.3 (3)
A(1)—O(1)	3.28 (1)	4×		
A(1)—O(2)	3.457 (3)	4×		
B—O(2)	1.920 (2)	1×	O(2)—B—O(2)	94.4 (1) 97.5 (1)
B—O(2)	1.971 (2)	2×		
B—O(1)	1.974 (1)	2×	O(2)—B—O(1)	92.5 (1) 170.3 (1)
B—O(1)	2.023 (2)	1×		
B—B	2.965 (1)			82.1 (1) 173.1 (1) 92.0 (1) 97.4 (1) 81.2 (1)
			O(1)—B—O(1)	

given in Table 2 and bond lengths and angles are given in Table 3.*

Several other refinements, varying the type and composition of the A and A(1) site, were also attempted. An improvement in the R factor did not result for any of these arrangements, although when Ba was placed on (0,0, $\frac{1}{2}$) and K on (0,0, $\pm z$) the values for the residuals were close to the values obtained in model 3. This was expected, since the composition of priderite is such that the scattering power of 1.2 × K and 0.4 × Ba is similar (~11 e). The results of previous investigations suggested that this model was highly improbable and was subsequently discarded.

A long-exposure oscillation photograph, with c as rotation axis, produced extra diffuse spectra between the Bragg layer lines. The location of these extra planes is very similar to those found by Sinclair *et al.* (1980),

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36309 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and is indicative of positional disorder of the large cations within the tunnels.

Discussion. The structure of priderite is essentially that reported by Sinclair *et al.* (1980). In priderite, however, K has been found to occupy the ideal site (0,0, $\frac{1}{2}$) and the Ba atoms occupy the off-centred site at (0,0, $\pm z$). Although this model gave the best agreement factor (R) in the least-squares refinement, some mixing of K and Ba on either site cannot be ruled out. K has been found to be displaced from (0,0, $\frac{1}{2}$) in $\text{K}_{1.54}\text{Mg}_{0.77}\text{Ti}_{7.23}\text{O}_{16}$ (Beyeler, 1976) and the large U_{33} (0.26 Å²) parameter reported for $\text{K}_{1.8}\text{V}_8\text{O}_{16}$ (Abriel, Rau & Range, 1979) with K on (0,0, $\frac{1}{2}$) also suggests an off-centred site. The high value of U_{33} [0.17 (2) Å²] for the Ba atom indicates additional positional disorder and is similar to that found for Ba in the synthetic Ba hollandite-type phase.

The cage of O atoms which surrounded the A and A(1) (K,Ba) atoms has expanded slightly in comparison to the synthetic Ba hollandite-type phase. The diagonal distance across the square-planar arrangement of O(1) atoms has now increased by 0.11 Å to 5.208 Å. This value is small in comparison to the sum of the A cations' and O radii, and should act as an effective barrier to the movement of the large 'radwaste' elements.

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