

Incommensurate superlattice ordering in priderite

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ABSTRACT. The mineral priderite has been examined by electron microprobe analysis and electron diffraction. The composition was approximately $(K_{0.97}Ba_{0.33})(Fe_{1.17}Ti_{6.60}Mg_{0.23})O_{16}$, which is in line with the observed superlattice periodicity of $m = 5.88$, there being intergrowths of $m = 5$ and $m = 6$ superstructures. A surprisingly high degree of lateral correlation between tunnel cations was noted.

RECENTLY considerable interest has been shown in the crystal chemistry of compounds with the hollandite structure. One of the reasons for the interest is the proposal by Ringwood *et al.* (1979) to employ a synthetic rock, 'synroc', in the disposal of radioactive waste, one of the key components of this being the hollandite phase $BaAl_2Ti_6O_{16}$, which is intended as a host material for radioactive barium and cesium. The chemistry and structure of this phase is very similar to that of the mineral priderite, $(Ba,K)_{1.33}(Fe,Ti)_8O_{16}$, which was discovered in the leucite-bearing rocks of the West Kimberley region of Western Australia and first described by Norrish (1951).

The essential details of the hollandite structure are quite simple and were described originally by Bystrom and Bystrom (1950) for the mineral hollandite, of composition $BaMn_8O_{16}$. Subsequent structural refinements have now been completed on a wide variety of chemically distinct hollandite phases, including that of the synroc hollandite structure (Sinclair *et al.*, 1980) and of the mineral priderite (Sinclair and McLaughlin, 1982; Post *et al.*, 1982). The hollandite structure, depicted schematically in fig. 1, consists of an oxide framework, which is not close-packed, with Fe and Ti in octahedral co-ordination. Octahedra are linked by edge-sharing to form double strings parallel to the c -axis. These strings of octahedra share corners with each other to form a three-dimensional framework containing tunnels of approximately square cross-section running parallel to the c -axis. Ideally the crystal symmetry is tetragonal, but a monoclinic distortion has been observed in some hollandites (Cadée and Verschoor, 1978). The large cations (Ba and K in the case of priderite) are accommodated in sites within the tunnels, these

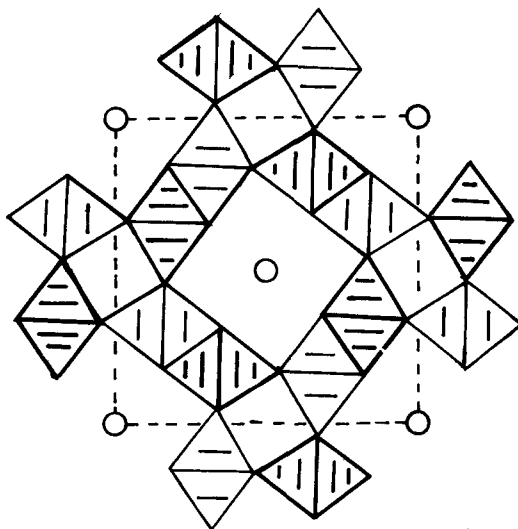


FIG. 1. [001] projection of the hollandite structure. $[MO_6]$ octahedra share edges along the c -axis, forming strings which are linked by corner-sharing and edge-sharing to form square tunnels which contain the large cations (Ba^{2+}, K^+).

sites being eightfold co-ordinated in a nominally cubic geometry.

Diffuse superlattice reflections indicating cationic ordering within the tunnels was first reported by Dryden and Wadsley (1958) for the compound $Ba_xMg_xTi_{8-x}O_{16}$, with x in the range $0.67 < x < 1.14$. They proposed a structural model based upon sequences of alternating Ba cations and vacant tunnel sites. More detailed measurement of these diffuse reflections, which generally have irrational repeats in reciprocal space (Bursill and Grzanic, 1980) has shown that this picture is an oversimplification of the situation. These latter workers established that incommensurate superlattice ordering occurred in this compound, and that the exact positions of the diffuse reflections was a function of composition. They therefore proposed a structural model based upon complex intergrowths of phases with doubled, tripled, and

quintupled *c*-axis repeats, involving considerable short-range order.

The possible importance of 'synroc' and hence of the 'synroc' hollandite has made a full understanding of this and related phases of vital importance in optimizing the stability of the material. Priderite, being a natural analogue of this synroc hollandite, provides a means of investigating the structure of a stable hollandite containing a mixture of cations within the tunnel sites. An examination of the superlattice ordering in priderite also proves a useful test for the Bursill and Grzanic model under geological conditions of crystallization.

Experimental

A specimen of priderite-bearing lamproite from the West Kimberley region of Western Australia, was obtained from Dr W. D. Birch of the National Museum of Victoria. The priderite grains (up to 3 mm in size) were concentrated from the matrix by crushing and separating in di-iodomethane ($\rho = 3.31 \text{ gm cm}^{-3}$). Separated material was initially examined by X-ray powder diffraction, and some grains were embedded in resin and examined in an energy dispersive electron microprobe designed and housed in the Department of Earth Sciences, University of Cambridge. Oxidation states of iron were monitored using ^{57}Fe Mossbauer spectroscopy.

Some fragments of the priderite were ground under acetone in an agate mortar and pestle, and deposited from suspension on to holey carbon support films. Samples prepared in this way were examined by electron diffraction in order to investigate the superlattice ordering in the material. A JEOL 200 CX electron microscope was used, fitted with a side-entry double-tilt goniometer. Electron diffraction patterns were recorded with the electron beam parallel to [100] and [110] axes.

Results and discussion

Analytical. The X-ray powder diffraction pattern of the priderite was found to be in good agreement with that given by Norrish (1951). The material proved to be tetragonal, with cell parameters deduced from a least-squares fitting of the observed profile of $a = 10.12(1)$ and $c = 2.97(1) \text{ \AA}$.

Accurate chemical data were obtained by using the Link Systems ZAF4 program to deconvolute the energy-dispersive X-ray emission spectrum obtained in the electron microprobe. The program used the least squares peak stripping technique, with a counting lifetime of 80 sec, and accelerating voltage of 20 kV and the sample current nominally set at 45 nA. The normalized and averaged data, from twenty separate analyses, is presented, together with the analysis of Norrish (1951) for comparison, in Table I.

A check of the accuracy of the analyses came from consideration of the restraints implied by the

TABLE I. Analyses of priderite

	This work		Norrish (1951)		
	wt. %	Unit cell contents	wt. %	Unit cell contents	
K ₂ O	6.28	0.97	5.6	0.87	1.33
CaO	0.01	0.02	trace	—	
BaO	7.01	0.33	6.7	0.32	
Na ₂ O	—	—	0.6	0.14	7.95
Fe ₂ O ₃	12.52	1.17	12.40	1.14	
TiO ₂	72.75	6.60	70.6	6.48	
MgO	1.28	0.23	—	—	
Al ₂ O ₃	—	—	2.3	0.33	
Total	99.85		98.2		

nature of the structure. On the basis of sixteen oxygen atoms per unit cell, Fe, Ti, and Mg total eight atoms, and are assigned to octahedral sites. The structure imposes a maximum of two large cations (e.g. K⁺, Ca²⁺, and Ba²⁺) per unit cell, and substitution of Ti by Mg and Fe is consistent with the structure, the maximum number of large cations required being 1.32. From the maximum number of octahedral cations the Fe was assumed to be in the +3 oxidation state, this being confirmed by ^{57}Fe Mossbauer spectroscopy, the spectrum containing only a single doublet with parameters $\delta = 0.1777 \text{ mm sec}^{-1}$, $\Delta = 0.4552 \text{ mm sec}^{-1}$ and $\Gamma = 0.333 \text{ mm sec}^{-1}$ relative to $\alpha\text{-Fe}$, these being characteristic of ferric iron in octahedral coordination by oxygen (Bancroft, 1973).

Only minor differences exist between the analysis described above and that of Norrish (1951). The original material contained Al but no Mg, whereas the situation was reversed in the present study. Similarly, the original sample was found to contain Na, but none could be detected in the present study. The present analysis, however, is constrained by the detection limits of the energy dispersive analysis, which are of the order of 1000 ppm.

Structural. A typical electron diffraction pattern of priderite, viewed down the [100] axis, is shown in fig. 2. The superlattice reflections are relatively diffuse, but are clearly recognizable as diffraction maxima, rather than continuous streaks of intensity. Their centres lie approximately 0.17 reciprocal lattice units from the rows of principle reflections, corresponding to a multiplicity of 5.88 d_{002} (m). Owing to the likelihood of multiple scattering effects, no attempt was made to infer domain sizes from the half-widths of these reflections. In terms of the Bursill and Grzanic model, these reflections correspond to a situation having a disordered intergrowth of principally $m = 5$ and $m = 6$ structures. The $m = 5$ structure (fig. 3a) has all tunnels

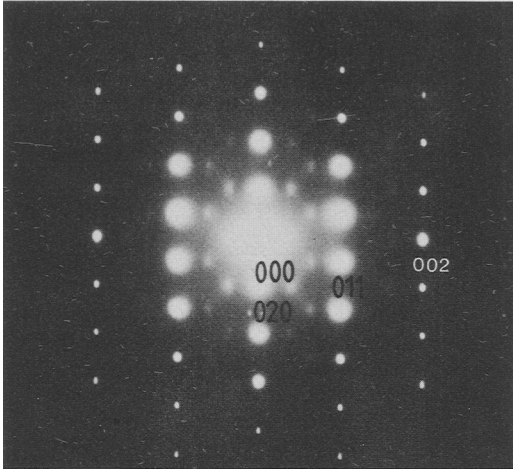


FIG. 2. [100] zone diffraction pattern of priderite. Note the superlattice reflections 0.17 reciprocal lattice units from the principal reflections.

with every third site and every fifth site vacant, such that vacancies in adjacent tunnels are as far apart as possible. The $m = 6$ structure (fig. 3b) is simpler, with all tunnels having every third site vacant. A simple arrangement of an $m = 5$ and $m = 6$ intergrowth is indicated in fig. 3c. To simulate the observed $m = 5.88$ periodicity the simplest intergrowth is one containing seven $m = 6$ regions to every one $m = 5$ area. The stoichiometry implied by this arrangement requires, on average, 1.31 large cations per unit cell, which is in very good agreement with the determined chemical analysis. The

slight discrepancy is almost certainly due to inaccuracies in the measurement of the superlattice periodicity arising from the diffuseness of the extra reflections. It should be emphasized that the arrangement proposed above does not preclude the existence of other *local* periodicities in the crystals, but the two listed must predominate.

It has been assumed in this study that there is no ordering of different cations within the tunnels, as no experimental evidence for this was obtained. In terms of cation size, such ordering would appear unlikely, as the ionic radii for K and Ba are similar. Post *et al.* (1982) and Sinclair and McLaughlin (1982) in their refinements of the priderite structure found that the slightly smaller Ba ions occupied an off-centre tunnel site such that these ions were closer to one face of the cubic site. They, however, did not find any evidence for supercell ordering of Ba and K ions in their refinements. In terms of charge, there might be a tendency to order, with Ba-Ba pairs being avoided. This tendency, if it exists, was not, however, detected in the electron diffraction study, even though multiple diffraction effects invariably observed in such studies could readily enhance the weak superlattice reflections which would be generated in such ordering.

As regards lateral correlation between adjacent tunnels, the observed superlattice reflections indicated that this was relatively well developed. Beyeler and Schuler (1980) found planar sheets of diffuse scattering parallel to [100] in their studies of alkali magnesium titanium hollandites, demonstrating the complete absence of any lateral correlations. However, in the case of barium magnesium titanium hollandites, the same authors found rela-

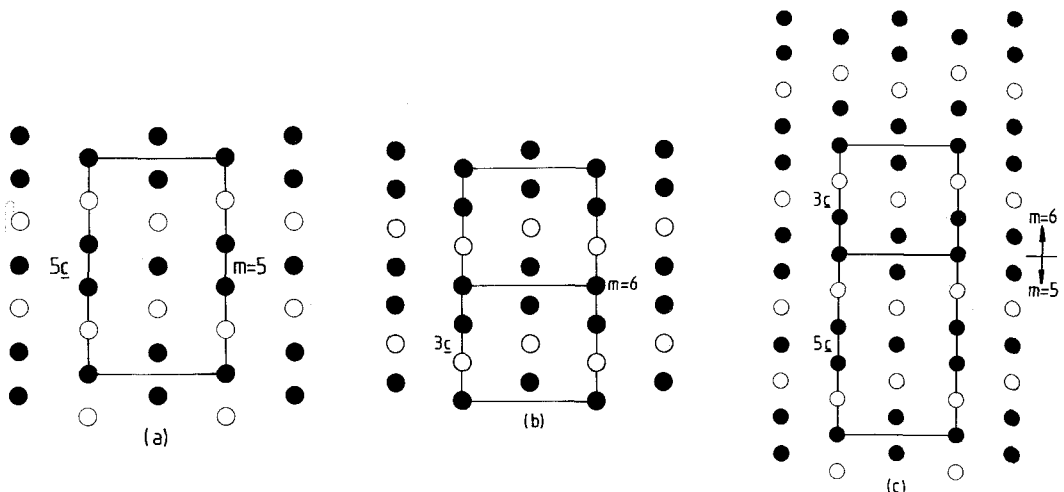


FIG. 3. Schematic diagram of the hollandite structure projected down [100], showing only the positions of the tunnel cation sites. (a) and (b) patterns of filled and empty large cation sites with $m = 5$ and $m = 6$ repeats respectively (c) intergrowth of $m = 6$ and $m = 5$ structures.

tively sharp superlattice maxima, indicative of strong inter-tunnel interactions. These findings were confirmed by Bursill and Grzinic (1980) and attributed to the difference in the cation charge, the electrostatic interactions between Ba^{2+} ions being strong enough to enforce inter-tunnel ordering, whereas those from the singly charged alkali cations were not of sufficient strength to overcome the dielectric shielding between channels due to the highly polarized TiO_6 octahedra.

As priderite contains predominantly potassium little correlation between cation ordering in adjacent tunnels might have been expected. However, it appears that the interaction between Ba^{2+} and K^+ is sufficiently strong to impose this ordering. Consequently, a relatively small proportion of divalent cations in the tunnels are capable of forcing the structure into a relatively rigid honeycomb arrangement. This in turn, imposes an unexpected activation energy barrier opposing diffusion along the tunnels, and hence may be one of the reasons why priderite is such a stable mineral, extremely resistant to leaching. By analogy, the synroc hollandite $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ with up to 10% of Cs substituted for Ba may be expected to behave similarly, making it a very stable repository for radioactive waste.

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