

The crystal structure of kintoreite, $\text{PbFe}_3(\text{PO}_4)_2(\text{OH},\text{H}_2\text{O})_6$

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Abstract

The crystal structure of kintoreite, $\text{PbFe}_3(\text{PO}_4)_2(\text{OH},\text{H}_2\text{O})_6$, has been refined. The mineral is rhombohedral, $R\bar{3}m$ with $a = 7.3310(7)$, $c = 16.885(2)$ Å, $Z = 3$; the structure has been refined to $R = 3.0\%$ and $R_w = 3.0\%$ using 183 observed reflections [$I > 2\sigma(I)$]. Kintoreite has the alunite-type structure which consists of sheets of corner-sharing $\text{Fe}(\text{O},\text{OH})_6$ octahedra parallel to (001). The sheets are composed of clusters of three corner-linked octahedra which are tilted so that the three apical O atoms form the base of the XO_4 tetrahedra. The clusters of octahedra are linked to similar groups by corner-sharing to form six membered rings. The Pb cations occupy the cavities between pairs of octahedral sheets and are surrounded by six oxygen atoms from the tetrahedra and six oxygen atoms from the octahedra to form a very distorted icosahedron. The mean bond lengths for the various coordination polyhedra are $X-\text{O}$ 1.55 Å, ($X = \text{P}, \text{As}, \text{S}$); $\text{Fe}-(\text{O}, \text{OH})$ 2.01 Å; $\text{Pb}-\text{O}$ 2.84 Å. The composition of the crystal used in the refinement was $\text{PbFe}_3(\text{PO}_4)_{1.3}(\text{AsO}_4)_{0.4}(\text{SO}_4)_{0.3}(\text{OH},\text{H}_2\text{O})_6$. The XO_4 anions are disordered, as in beudantite, rather than being ordered, as they are claimed to be in corkite.

KEYWORDS: kintoreite, beudantite, corkite, crystal structure, Kintore opencut, New South Wales.

Introduction

KINTOREITE, ideally $\text{PbFe}_3(\text{PO}_4)_2(\text{OH},\text{H}_2\text{O})_6$, was described by Pring *et al.* (1995) from the Kintore opencut, Broken Hill, New South Wales, and is closely related to beudantite, corkite, plumbojarosite and segnitite. All of these minerals have the alunite-jarosite structure-type, $AB_3(\text{XO}_4)_2(\text{OH},\text{H}_2\text{O})_6$, where A is a large cation, such as Pb^{2+} , B is Fe^{3+} or Al^{3+} and (XO_4) is an anion such as AsO_4^{3-} , PO_4^{3-} or SO_4^{2-} . A wide range of substitutions has been noted on both the cation and the anion sites in these minerals. The cation substitutions appear to be disordered and

extensive solid-solution fields have been reported (Scott, 1987; Rattray *et al.*, 1996). The nature of the anion substitutions is less clear; in some of the members of the group, the anions are ordered, while in others they are disordered and have wide solid solution fields. The crystal structures of several members of the beudantite group have been reported. Giuseppetti and Tadini (1987) reported that SO_4^{2-} and PO_4^{3-} in corkite, $\text{PbFe}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$, are ordered and thus the space group is $R\bar{3}m$; on the other hand structure determinations of beudantite, $\text{PbFe}_3(\text{AsO}_4,\text{SO}_4)_2(\text{OH})_6$, (Szymánski, 1988, and Giuseppetti and Tadini, 1989) showed that the AsO_4^{3-} and SO_4^{2-} anions are disordered and that the space group is $R\bar{3}m$. That is, there are two crystallographically independent XO_4 sites in $R\bar{3}m$, while in $R3m$, the sites are related by the centre of symmetry.

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In order to establish the crystal chemistry of kintoreite and also to further explore the nature of anion order/disorder in the beudantite group we have completed an *ab initio* solution and a refinement of the kintoreite structure using single crystal X-ray diffraction methods. The crystal selected for this study had the composition $\text{PbFe}_3(\text{PO}_4)_{1.3}(\text{AsO}_4)_{0.4}(\text{SO}_4)_{0.3}(\text{OH},\text{H}_2\text{O})_6$, which is some way away from ideal end-member composition and allowed the nature of order/disorder on the anion sites to be explored.

Experimental

Several single crystals of kintoreite were removed from one of the co-type specimens held in the collection of the South Australian Museum (SAM G14354). The crystals were examined by optical microscopy and a suitable single crystal was selected and photographed by the precession method. The trigonal symmetry of the mineral was confirmed and the systematic absences indicated that the space group was either $R\bar{3}m$ or $R3m$.

Intensity data were collected on the Enraf-Nonius CAD4 turbo diffractometer at the Research School of Chemistry, The Australian National University, using graphite-monochromated Mo- $K\alpha$ radiation and a $\theta/2\theta$ scan. The faces developed on the tetrahedrally shaped data crystal were : (0 0 1) , (0 1 $\bar{1}$) , ($\bar{1}$ 0 $\bar{1}$) , and (1 $\bar{1}$ $\bar{1}$). The intensity data were corrected for absorption using this morphological information and upon merging gave $R = 0.03$.

The XTAL program system 3.2 (Hall *et al.*, 1992) was used to perform all crystallographic calculations in the structure solution and refinement. The kintoreite structure was solved using the heavy atom method and the atomic positions were found to be very similar to those of the beudantite structure (Szymanski, 1988; Giuseppetti and Tadini, 1989). Refinement of the structure with isotropic displacement parameters gave the R value of 0.32 and further refinement with anisotropic displacement parameters for the heavy atoms (Pb, As and Fe) converged to $R = 0.19$. A further cycle of refinement by refining the extinction parameter gave $R = 0.19$. At this point the site occupancy of the 6c site containing P/As/S was refined and this reduced R to 0.075 and resulted in a P/As/S ratio of 73/16/11. However, the difference map showed that there was still a large peak very close to the origin, indicating that Pb is disordered around the origin, similar to the situation in the beudantite structure.

Moving the assumed position of Pb off the origin, with an imposed site occupancy of 1/12 gave $R = 0.28$. Attempts to refine the coordinates of Pb in this position were not successful. Pb was then fixed at the origin and its position was not refined until the

refinement of all other atoms were stable. The Pb position was then adjusted by trial and error until a minimum R value was obtained. Refinement of all atoms isotropically gave $R = 0.10$ and refinement anisotropically gave $R = 0.047$. The final refinement included applying a dispersion correction and refining an extinction correction and gave $R = 0.030$.

The matter of whether the space group was centrosymmetric or noncentrosymmetric ($R\bar{3}m$ or $R3m$) was tested by refining the structure again this time in noncentrosymmetric $R3m$. In this refinement, P was assigned to one site and As/S to the other site; the distribution of cations being based on electron probe microanalysis which gave $P = 0.65$, $As = 0.2$ and $S = 0.15$. The first refinement with Pb at the origin converged with $R = 0.07$. When Pb was shifted off the origin (site occupancy of 1/12) an $R = 0.047$ was obtained. It is concluded, on the basis of the lower R , that the true structure of kintoreite is centrosymmetric and the space group is $R\bar{3}m$; and thus the XO_4 anions are disordered. Details of the crystallographic data of kintoreite in space group $R\bar{3}m$ can be seen in Table 1.

Results and discussion

The final atomic coordinates and displacement parameters for the structure refinement are listed in Tables 2 and 3 and selected interatomic distances and bond angles are provided in Table 4. A summary of the bond valence calculations for the structure is given in Table 5, while a full list of observed and calculated structure factors for the final refinement are given in Table 6¹.

The basic crystal structure of kintoreite is the same as those of corkite (Giuseppetti and Tadini, 1987) and beudantite (Szymanski, 1988; Giuseppetti and Tadini, 1989), being derived from the alunite-type structure (Mencetti and Sabelli, 1976). This structure consists of sheets of corner-sharing $\text{Fe}(\text{O},\text{OH})_6$ octahedra lying parallel to (001) plane (Fig. 1). These sheets have clusters of three octahedra with the three apical Fe-O bonds tilted towards the three-fold axis and form the base of the XO_4 tetrahedron. The octahedral groups are linked to similar groups by corner-sharing to form six membered rings. The one remaining vertex of each tetrahedron points alternatively up and down the c axis towards the centre of six membered rings of the octahedral sheets above and below (Fig. 2). The O atom at the vertex of the tetrahedron forms a hydrogen bond with the hydroxyl group of the $\text{Fe}(\text{O},\text{OH})_6$ octahedra. The Pb^{2+} cations occupy the cavities between pairs of octahedral sheets and are surrounded by six O from the

¹ A copy of this Table is available from the editor.

TABLE 1. Crystal data, data collection information, and refinement details for kintoreite

Crystal data:	
Formula	[PbFe ₃ (PO ₄) _{1.3} (AsO ₄) _{0.4} (SO ₄) _{0.3} (OH) ₆]
Mr	684.6
Crystal system	Rhombohedral
Space group	<i>R</i> $\bar{3}m$
<i>a</i> (Å)	7.3310(7)
<i>c</i> (Å)	16.885(2)
<i>V</i> (Å ³)	785.9(2)
D _c (g/cm ⁻³)	4.34
Z	3
μ (cm ⁻¹)	215.33
λ(Mo-Kα) (Å)	0.71073
Crystal dimension (mm)	0.15 × 0.15 × 0.15
Shape	tetrahedral
Colour	yellowish brown
Data Collection :	
Diffractometer	CAD4
Temperature (°K)	293
θ _{max} (°)	25
<i>h</i>	0 → 4
<i>k</i>	-8 → 7
<i>l</i>	-19 → 19
Total reflections measured	313
Number after averaging	199
R for averaging	0.03
Refinement :	
Refinement on	F
Weight	1/σ ² _(F)
R	0.03
R _w	0.03
Reflections used in refinement (I > 2σ(I))	183
Number of parameter refined	31
H atoms not located	
Goodness of fit S	3.437
Sigma goodness of fit	0.197
(Δ/σ) _{max}	0.026
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.303, -0.815
Extinction factor	13(4) × 10 ⁻³

tetrahedra and six O from the octahedra with very distorted icosahedral stereochemistry.

The Pb²⁺ ion in kintoreite is displaced from the origin and disordered on a 12i general position with 1/12 occupancy. The Pb coordination in kintoreite is similar to that found in beudantite, with Pb displaced from the origin in both structures by similar amounts along the *a*, *b*, *c* axis, i.e. 0.132, 0.279, 0.008 Å in kintoreite, and 0.091, 0.237, 0.012 Å in beudantite. The average bond Pb–O distance is slightly longer in

beudantite, 2.858 Å, (Szymanski, 1988) than in kintoreite 2.842 Å. In corkite Pb is located at the origin which is at the intersection of the 3-fold axis and the minor planes and the average distance of Pb–O is smaller, 2.823 Å (Giuseppetti and Tadini, 1987). The displacement of Pb²⁺ from the origin in beudantite and kintoreite could be attributed to Pb²⁺ 6s² lone-pair interaction with neighbouring bond-pairs. However, the fact that Pb is localised at the origin in corkite suggests that the size and shape of

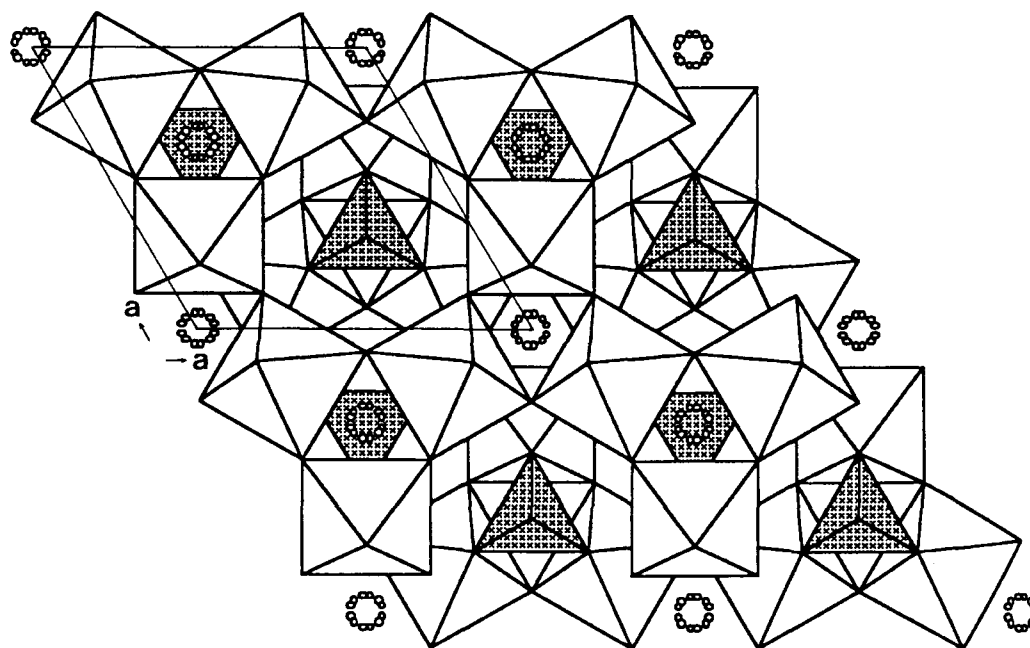


FIG. 1. The kintoreite structure projected down [001]. Only two octahedral layers are shown. The positions of the Pb sites are indicated by small circles, each site has 1/12 occupancy.

the Pb site is largely determined by the octahedral and tetrahedral framework around the site. The unit cell volume of corkite is approximately 4% smaller than those of kintoreite and beudantite. The larger average size of the XO_4 groups in kintoreite and beudantite leads to the site being slightly too large for Pb to be located at the centre of the icosahedral coordination polyhedron and have optimal contact

with all the O atoms. It is therefore closer to some and further away from others.

The $Fe(O,OH)_6$ octahedra coordination is regular; the Fe–O distances range from 2.002 to 2.030 Å with a mean of 2.011 Å. The internal angles confirm that there is only a slight distortion of the octahedra in the kintoreite structure with O–Fe–O angles deviating a maximum of $\pm 3.49^\circ$ from 90° (see

TABLE 2. Fractional atomic coordinates and isotropic displacement parameters for kintoreite. E.s.d.'s in parenthesis

Atom	X	Y	Z	U_{eq}	PP
Pb	-0.0180*	0.0380*	0.0005*	0.03(1)	0.0833
Fe	1/2	0	1/2	0.0118(7)	
As	0	0	0.3146(2)	0.008(1)	0.73(1)
P					0.16(1)
S					0.11*
O(1)	0	0	0.5946(5)	0.019(3)	
O(2)	0.2181(5)	-0.2181(5)	-0.0528(3)	0.019(2)	
O(3)	0.1283(5)	-0.1283(5)	0.1331(3)	0.010(2)	

* Refinement of S occupancy and Pb coordinates was done by trial and error. No e.s.d.'s were obtained.

$$U_{eq} = (1/3) \sum_i \sum_j \sum_{ij} a_i^* a_j^* a_i \cdot a_j$$

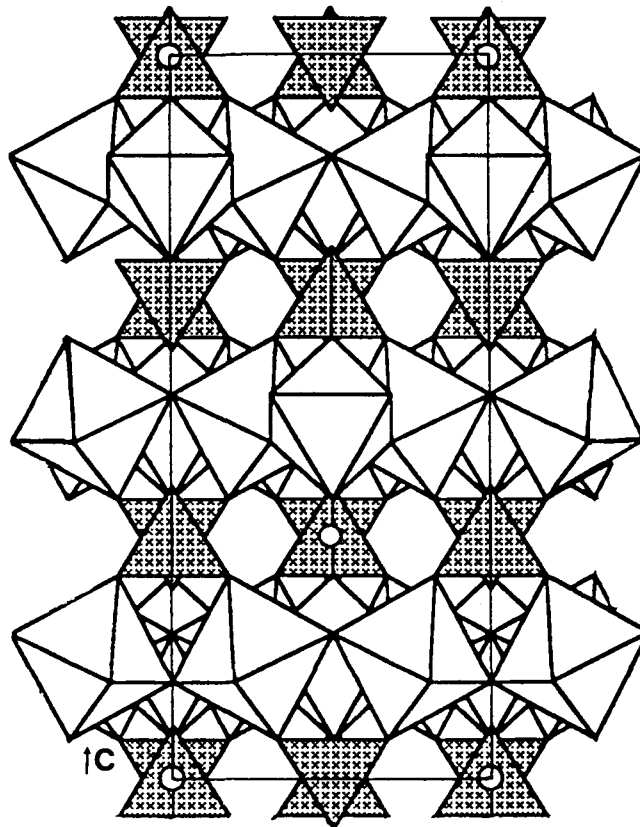


Fig. 2. View of the kintoreite structure down [100]. The c repeat corresponds to 3 layers of $\text{Fe}(\text{O},\text{OH})_6$ octahedra. For simplicity the Pb is represented by a large circle at the origin.

Table 4). The $\text{Fe}(\text{O},\text{OH})_6$ octahedra in beudantite and corkite are very similar (Szymánski, 1988; Giuseppetti and Tadini, 1987).

The central site in the XO_4 tetrahedron is fractionally occupied by P, As, S. The refinement suggested that the occupancy of this site was in the proportions $\text{P}_{0.73} + \text{As}_{0.16} + \text{S}_{0.11}$. This result is

similar to the average electron probe microanalysis ($\text{P}_{0.65} + \text{As}_{0.20} + \text{S}_{0.15}$). The small difference is with the limits of accuracy for the site occupancy. The relatively small displacement parameters for the site (Table 3) and the low bond valence sums for O(1) and O(2) suggest that the As content on the site may be slightly underestimated by the refinement. The

TABLE 3. Anisotropic displacement parameters for kintoreite

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	0.06(1)	0.03(2)	0.0138(76)	0.030(7)	0.00(2)	-0.00(3)
Fe	0.0120(8)	$2U_{12}$	0.0144(8)	0.0038(5)	0.0001(4)	$2U_{13}$
X	$2U_{12}$	$2U_{12}$	0.007(1)	0.0045(7)	0.0	0.0
O(1)	$2U_{12}$	$2U_{12}$	0.018(5)	0.010(2)	0.0	0.0
O(2)	0.026(3)	U_{11}	0.014(3)	0.019(3)	0.000(1)	$-U_{13}$
O(3)	0.006(2)	U_{11}	0.013(2)	-0.000(2)	0.001(1)	$-U_{13}$

TABLE 4. Interatomic distances (Å) and bond angles for the coordination polyhedra in kintoreite

Pb–O(2)	2.825(6)	2.571(5)	3.149(7)	3.035(7)	3.253(5)	2.697(6)
Pb–O(3)	2.591(6)	2.871(5)	2.942(5)	2.647(5)	2.724(5)	2.992(7)
Fe–O	O(2)	O(2)	O(3)	O(3)	O(3)	O(3)
	2.030(5)	2.028(4)	2.002(3)	2.002(9)	2.002(3)	2.002(9)
P/As/S	O(1)	O(2)	O(2)	O(2)		
	1.533(9)	1.573(5)	1.573(6)	1.573(6)		
Fe(O,OH) ₆ octahedron			XO ₄ tetrahedra			
O(2)–Fe–O(3)	93.4(2)°		O(1)–X–O(2)	111.5(2)°		
O(2)–Fe–O(3) × 2	93.4(2)°		O(1)–X–O(2)	111.5(2)°		
O(2)–Fe–O(3) × 4	86.6(2)°		O(1)–X–O(2)	115.5(2)°		
O(3)–Fe–O(3)	89.7(3)°		O(2)–X–O(2)	107.4(3)°		
O(3)–Fe–O(3)	90.4(2)°		O(2)–X–O(2)	107.4(2)°		
O(2)–Fe–O(3)	86.6(2)°		O(2)–X–O(2)	107.4(2)°		
O(3)–Fe–O(3)	90.4(3)°					
O(2)–Fe–O(3) × 2	93.4(2)°					
O(3)–Fe–O(3)	89.6(3)°					

bond length distribution in the XO₄ tetrahedra are one short, 1.525 Å, and three long, 1.576 Å, with the average bond length of 1.56 Å. This average bond length is equal to the weighted average sums of ionic radii of As–O, P–O and S–O, i.e. 1.70, 1.53 and 1.48 Å respectively (Shannon, 1976).

The fractional occupancy of the Pb site and the multiple occupancy of the XO₄ site complicates the calculation of bond valence sums (BVSs) for the kintoreite structure. In the calculation of bond valence sums of O(2) and O(3), which are bonded to Pb, the average Pb–O(2) and Pb–O(3) valence strengths were used. Because of the disordered nature of the Pb site there is a range of Pb–O(2) and Pb–O(3) distances and valence contributions. The BVS of X was calculated by assuming 100% occupancy of the XO₄ site by each of the cations in turn. Then the BVS in kintoreite was taken to be the weighted mean of those values based on the refined composition (see Table 5).

Calculation of the BVSs for the structure suggests that the O(3) atom is the OH group, because it has the lowest BVS of the oxygen atoms. This assignment is confirmed by stereochemical considerations as O(3) is the only oxygen coordinated to Fe and Pb but not As, and the Fe–O(3) distances are the shortest metal–oxygen distances in the co-ordination sphere (2.00 Å). The OH group is probably hydrogen bonded to O(1), since O(1) has the second lowest of bond valence total (1.32 *vu*). The O(3)–O(1) distance is 2.80 Å which is a reasonable hydrogen bond distance. By assuming an O(3)–H bond length 1.05 Å and O(1) ... H contact of 1.75 Å the bond

valence contributions for O(3) and O(1) are 0.64 *vu* and 0.18 *vu*, respectively (Brown and Altermatt, 1985). This brings the BVS for O(1) and O(3) to 1.50 *vu* and 1.85 *vu*. The BVS for O(1) is still low

TABLE 5. Empirical bond-valence calculations for kintoreite

	Pb	Fe	P/As/S	Sum
O(1)			1.32	1.32*(1.50)
O(2)	(0.14)# 0.29 0.21 0.15 0.08 0.06 0.05	0.48 (×2)	1.20 (×3)	1.82
O(3)	(0.17)# 0.09 0.27 0.23 0.19 0.13 0.11	0.52 × 2 (×4)		1.21*(1.85)
Sum	1.86	3.04	4.92	

* excluding the hydrogen bond, the value in parentheses is obtained after adding the H bond contribution and includes the mean of Pb–O bond valence values.

Mean of 6 values

probably because O(1) is only bonded to X. As noted above, it seems that the As content on the X site is underestimated and this would result in the lowering the BVS for O(1).

It is clear that the anion site in kintoreite, like that in beudantite, is disordered. Such a finding is not unexpected, given the extended nature of the compositional fields for the kintoreite–segnitite–beudantite minerals found at Broken Hill, New South Wales (Birch *et al.*, 1992; Pring *et al.*, 1995). On this basis there does not appear to be an ordered mid-member in the segnitite–kintoreite series, but rather a continuous solid solution between the end-members. The reason why the tetrahedral anions in corkite should be ordered, given that SO_4^{2-} and PO_4^{3-} are isoelectronic while AsO_4^{3-} and SO_4^{2-} in beudantite or AsO_4^{3-} and PO_4^{3-} in kintoreite are disordered is difficult to explain. The structure of corkite is clearly worthy of a detailed re-investigation in order to clarify this anomaly.

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