

# Kintoreite, $\text{PbFe}_3(\text{PO}_4)_2(\text{OH},\text{H}_2\text{O})_6$ , a new mineral of the jarosite–alunite family, and lusungite discredited

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## Abstract

Kintoreite is a new lead iron phosphate mineral in the alunite–jarosite family, from Broken Hill, New South Wales, Australia. It is the phosphate analogue of segnitite and the iron analogue of plumbogummite. Kintoreite occurs as clusters and coatings of cream to yellowish green rhombohedral crystals up to 2 mm high and with the principal form {112}. The mineral also forms waxy, yellowish green globular crusts and hemispheres on other phosphate minerals. These associated species include pyromorphite, libethenite, rockbridgeite/dufrenite, apatite and goethite. Kintoreite formed during oxidation of primary ore rich in galena, in the presence of solutions with high P/(As + S) ratios. The mineral is named for the locality, the Kintore opencut, in which it is most common. A mineral closely resembling kintoreite in composition has also been found at several mines in Germany. Type material is preserved in the Museum of Victoria and the South Australian Museum.

Electron microprobe analysis showed a nearly complete spread of compositions across the P-dominant portion of the segnitite-kintoreite series. The selected type specimen has an empirical formula of

$\text{Pb}_{0.97}(\text{Fe}_{2.95}\text{Zn}_{0.13}\text{Cu}_{0.02})_{\Sigma 3.10}[(\text{PO}_4)_{1.30}(\text{AsO}_4)_{0.39}(\text{SO}_4)_{0.18}(\text{CO}_3)_{0.11}]_{\Sigma 1.98}(\text{OH})_{5.45} \cdot 0.74\text{H}_2\text{O}$ , calculated on the basis of 14 oxygens and with all Fe trivalent. The simplified formula is  $\text{PbFe}_3(\text{PO}_4)_2(\text{OH},\text{H}_2\text{O})_6$ . Kintoreite crystals are translucent with a vitreous to adamantine lustre, with globules appearing waxy. The streak is pale yellowish green and the Mohs hardness is  $\sim 4$ . Crystals show good cleavage on {001} and are brittle with a rough fracture. The calculated density is  $4.34 \text{ g cm}^{-3}$ . Kintoreite crystals are uniaxial negative with RIs between 1.935 and 1.955 and show light yellowish green to medium yellow pleochroism.

The strongest lines in the X-ray powder pattern are ( $d_{\text{obs}}$ ,  $I_{\text{obs}}$ ,  $hkl$ ) 3.07(100)113; 5.96(90)101; 3.67(60)110; 2.538(50)024; 2.257(50)107; 1.979(50)303; 1.831(40)220. The X-ray data were indexed on a hexagonal unit cell by analogy with beudantite, giving  $a = 7.325(1) \text{ \AA}$ ,  $c = 16.900(3) \text{ \AA}$ ,  $V = 785.3(5) \text{ \AA}^3$  and  $Z = 3$ . The probable space group is  $R\bar{3}m$ , by analogy with beudantite and other members of the alunite–jarosite family. Powder X-ray diffraction data for several intermediate members suggest that the segnitite–kintoreite series may not represent ideal solid solution.

During the study of kintoreite, part of the type specimen of lusungite from Zaïre was obtained and shown to be goyazite. The IMA's Commission on New Minerals and Mineral Names has voted to discredit lusungite as a species, and has approved the renaming of the 'lusungite' group as the segnitite group. However, as relationships between crystal structure, order–disorder and solid solution in the Pb-rich minerals of the alunite–jarosite family are not well documented, the nomenclatural changes resulting from this study should be seen as interim only.

KEYWORDS: kintoreite, new mineral, jarosite–alunite, lead-iron phosphate, Broken Hill (NSW).

### Introduction

In the oxidized zone of the Pb–Zn orebodies at Broken Hill, New South Wales, Pb-rich minerals in the alunite–jarosite family are especially well developed. A ready source of Pb, Fe, Al, P, As and S during a prolonged period of oxidation has resulted in crystallization of minerals whose compositions can be defined in terms of components of 'end-member' species such as beudantite, corkite, philipsbornite, plumbogummite, hinsdalite, hidalgoite and segnitite (Birch *et al.*, 1992).

Within the alunite–jarosite family, the 'lusungite' group (Scott, 1987) is a Pb–Fe<sup>3+</sup> series with a general formula  $\text{PbFe}_3[(\text{As},\text{P},\text{S})\text{O}_4]_2(\text{OH},\text{H}_2\text{O})_6$ , where  $S < 0.5$  in the molecular formula. It extends from the As end-member, segnitite, to the Pt end-member, currently called lusungite (Fig. 1). However, the existing nomenclatures is inappropriate, as lusungite was described originally as having Sr dominant over Pb (van Wambeke, 1958). Up until recently, no Pb-dominant mineral had been fully characterized. Pb-rich 'aluminian lusungite' was reported from Pegmont, Queensland, by Scott (1987), but was intimately intergrown with plumbogummite and its properties could not be determined. Crystals of 'sulphur-free corkite' were recently described from the Clara Mine near Oberwolfach and the Igelschlatt Mine near Grafenhausen in Germany (Walenta, 1993).

Distinct crystals of the Pb-rich, P-dominant analogue of segnitite have been found in the Kintore opencut at Broken Hill, NSW. The mineral has been approved by the Commission on New Minerals and Mineral Names (CNMMN) as a new

species, kintoreite, named for the locality. Type material has been preserved in the collections of the South Australian Museum and the Museum of Victoria.

### Occurrence

The most important of the secondary minerals in the Kintore and Block 14 opencuts have formed by oxidation of the primary ore of 3 Lens, the main Pb-bearing lode at Broken Hill. Structural control of the secondary mineralization has tended to maintain segregation of an As-rich suite from a P-rich suite, with As derived from arsenopyrite–loellingite and P from fluorapatite (Birch and van der Heyden, 1988). However, in some parts of the secondary zone, As and P-bearing fluids were present, leading to intermediate compositions in solid solution series such as pyromorphite–mimetite, olivenite–libethenite and Pb-rich alunite–jarosite minerals.

The Pb-rich minerals in the alunite–jarosite family are widespread, occurring as fine-grained aggregates, pseudomorphs, endomorphs, drusy crusts and, less frequently, well formed crystals. In the Kintore opencut, minerals in the segnitite–kintoreite series generally occur as crusts lining cavities in concretionary or stalactitic goethite, and are occasionally accompanied by pyromorphite or mimetite. In the northern part of the Block 14 Opencut, at the 290 m RL (i.e. about 25–30 m below the surface), kintoreite occurs late in a sequence of P-rich minerals which encrust quartz and garnet-rich lode rocks. The suite includes white pyromorphite, yellowish coatings of hinsdalite, green libethenite crystals, a dark green iron phosphate resembling

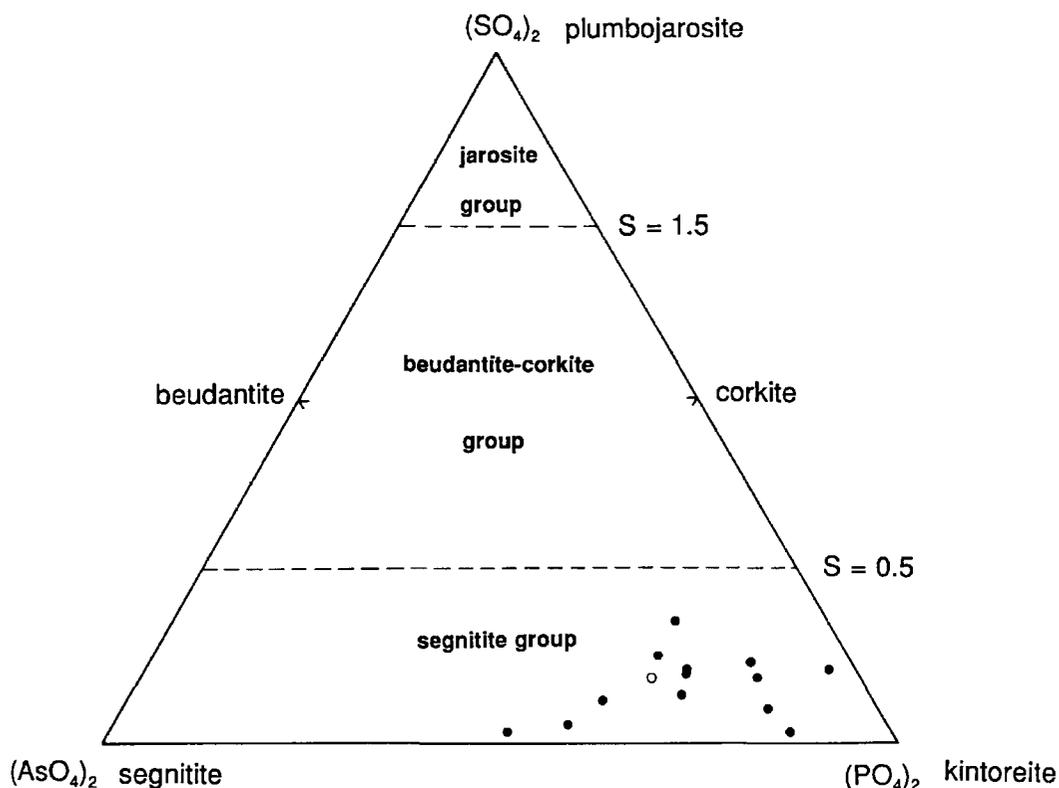


FIG. 1. Triangular plot showing microprobe analyses for kintoreite. Type specimen shown by open circle. The nomenclature for the diagram is based on the classification scheme of Scott (1987), but with the lusungite group renamed the segnitite group and with lusungite replaced by kintoreite.

rockbridgeite or dufrenite and hemispheres of fibrous white apatite.

#### Appearance

In the Kintore Opencut, members of the segnitite–kintoreite series form clusters and coatings of cream to yellowish green and brownish yellow ‘dog-tooth’ crystals up to several mm high. The dominant form is the rhombohedron {112} and crystals are usually sharply defined. It is difficult to distinguish between phosphorus and arsenic-dominant intermediate members of the series solely by appearance, although the former tend to more yellowish green shades. For example, in the Block 14 Opencut, kintoreite with the highest P-content detected forms waxy, yellowish green globular crusts and hemispheres on the other phosphate minerals.

#### Physical and optical properties

Kintoreite crystals are translucent with a vitreous to adamantine lustre, while globules are transparent to translucent, with a greasy or waxy lustre. The streak is pale yellowish green and Mohs hardness is  $\sim 4$ . Crystals show good cleavage on {001} and are brittle with a rough fracture. The measured density exceeds  $4.2 \text{ g cm}^{-3}$  — crystals sink in Clerici solution.

Crystals selected as the type material are uniaxial negative, with refractive indices between 1.955(5) and 1.935(5). Pleochroism is from light yellowish green to medium yellow.

#### Chemical composition

Minerals in the segnitite–kintoreite series were analysed using two microprobes, a JEOL and a

Cameca SX50. The standards (hematite, Fe; sphalerite, Zn, S; galena, Pb; corundum, Al; fluorapatite, P; arsenopyrite, As; metallic copper, Cu; strontianite, Sr; and benitoite, Ba) and the operating conditions (15 kV and specimen current of 0.02  $\mu$ A) were the same for both instruments. The water content was determined on a 3 mg sample of well formed crystals using a Perkin-Elmer CHN analyser.

Nineteen microprobe analyses, including six on crystal fragments from the type specimen, were obtained from ten samples from within the series (Table 1). The analyses show a virtually complete spread across the P-dominant portion of the series (Fig. 1). The type specimen for kintoreite is not the most P-rich, but was selected on the basis of superior X-ray diffraction properties, crystal size and amount of material available for H<sub>2</sub>O determination.

The empirical formula for the type material, calculated on the basis of 14 oxygen atoms and with all iron assumed to be Fe<sup>3+</sup>, is Pb<sub>0.97</sub>(Fe<sub>2.95</sub>Zn<sub>0.13</sub>Cu<sub>0.02</sub>)<sub>3.10</sub>[(PO<sub>4</sub>)<sub>1.30</sub>(AsO<sub>4</sub>)<sub>0.39</sub>(SO<sub>4</sub>)<sub>0.18</sub>(CO<sub>3</sub>)<sub>0.11</sub>] $\Sigma$ 1.98(OH)<sub>5.45</sub>·0.74H<sub>2</sub>O. The simplified formula applies to the pure end-member composition and the preferred formula is PbFe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(OH,H<sub>2</sub>O)<sub>6</sub>, which accommodates the uncertainties about the amount of structural water and the presence or absence of ordering in the P sites.

TABLE 1. Electron microprobe analyses for kintoreite and type lusungite (= goyazite)

	1	2	3	4
CuO	0.25	—	Cu 0.02	—
ZnO	1.58	—	Zn 0.13	—
PbO	31.37	0.04	Pb 0.97	—
CaO	—	0.45	Ca —	0.04
SrO	—	18.65	Sr —	0.93
BaO	0.09	0.26	Ba —	0.01
Al <sub>2</sub> O <sub>3</sub>	0.02	31.58	Al —	3.19
Fe <sub>2</sub> O <sub>3</sub>	34.01	0.82	Fe <sup>3+</sup> 2.95	0.05
P <sub>2</sub> O <sub>5</sub>	13.30	27.57	P 1.30	2.00
As <sub>2</sub> O <sub>5</sub>	6.43	—	As 0.39	—
SO <sub>3</sub>	2.02	—	S 0.17	—
CO <sub>2</sub>	0.73	—	C 0.11	—
H <sub>2</sub> O	9.0	*20.63	H 7.02	11.8
Total	98.90	100.00		

1. Kintoreite, average of six analyses, H<sub>2</sub>O, CO<sub>2</sub> by CHN microanalysis
2. 'Lusungite', average of six analyses, \*H<sub>2</sub>O by difference
3. Formula for kintoreite based on 14 oxygen atoms
4. Formula for 'lusungite' (= goyazite) based on P + As + S = 2. Note low analytical total due to nature of grains.

### X-ray crystallography

Powder X-ray diffraction data (Table 2) for the type specimen of kintoreite were obtained using a Guinier-Hagg camera with 100 mm diameter, Cu-K $\alpha$  radiation and Si as an internal standard. The data were indexed by analogy with the rhombohedral cell of beudantite (Giuseppetti and Tadini, 1989) and segnitite. Unit cell parameters of  $a = 7.325(1)$ ,  $c = 16.900(3)$  Å,  $V = 785.3(5)$  Å<sup>3</sup> were refined from the powder data, using 28 reflections with  $2\theta < 78^\circ$ . The cell parameters are slightly smaller than those of segnitite, in line with the relative size of the P and As ions. The space group  $R\bar{3}m$  is proposed for kintoreite, again by analogy with beudantite. For  $Z = 3$ , the calculated density is 4.34 g cm<sup>-3</sup>.

Single crystal studies were attempted on five samples roughly in the compositional range from As<sub>90</sub>P<sub>2</sub>S<sub>8</sub> to As<sub>20</sub>P<sub>65</sub>S<sub>15</sub>. None proved suitable, due to the effects of twinning revealed on precession

TABLE 2. X-ray powder diffraction data for kintoreite

$l/l_0$	$d_{\text{obs}}(\text{Å})$	$d_{\text{calc}}(\text{Å})$	$hkl$
90	5.96	5.94	101
2	5.66	5.63	003
5	5.09	5.07	012
60	3.67	3.66	110
20	3.52	3.52	104
5	3.12	3.12	021
100	3.07	3.07	113
2	2.985	2.983	015
40	2.971	2.970	202
40	2.818	2.817	006
50	2.538	2.537	024
20	2.374	2.374	211
20	2.306	2.313	205
50	2.257	2.256	107
10	2.232	2.233	116
2	2.086	2.085	214
50	1.979	1.980	303
5	1.955	1.956	125
40	1.831	1.831	220
5	1.758	1.758	208
5	1.701	1.701	217
10	1.671	1.671	119
5	1.560	1.561	315
10	1.535	1.535	226
20	1.492	1.493	01,11
1	1.485	1.491	02,10
2	1.404	1.404	039
5	1.240	1.246	327

Unit cell: hexagonal  $a = 7.325(1)$  Å,  $c = 16.900(3)$  Å,  $V = 785.3(5)$  Å<sup>3</sup>

photographs. Powder X-ray diffraction patterns for two of the intermediate composition samples showed the presence of a two-phase intergrowth, rather than solid solution, suggesting that the mid-member composition ( $As_{50}P_{50}$ ) may exist as a distinct ordered phase. These results suggest that the segnitite–kintoreite series may not represent ideal solid solution, despite the theoretical considerations which suggest that P–As substitution should be close to ideal (Williams, 1990). However, more detailed investigation of compositional zonation, intergrowths and overgrowths, and twinning is required before firm conclusions can be drawn.

### Nomenclatural implications

*Status of lusungite and kintoreite.* Prior to the approval of kintoreite, its position in the compositional spectrum of alunite–jarosite minerals had been occupied by lusungite. This mineral had been described from Kobokobo in the Belgian Congo by van Wambeke (1958). A formula of  $(Sr,Pb)Fe_3(PO_4)_2(OH)_5 \cdot H_2O$  was assigned to the species. In Scott's (1987) classification scheme, lusungite was applied as a group name for the Pb-dominant species in which  $S < 0.5$  in the molecular formula. In their description of segnitite, Birch *et al.* (1992) continued to use 'lusungite' as a group name and to imply a Pb-dominant, rather than Sr-dominant mineral.

*Discreditation procedure for lusungite.* Type material of lusungite was obtained from the collections of the Museum of Central Africa, in Tervuren, Belgium. The sample which constituted about one third of the available material, consisted of earthy pale to dark brown grains up to  $\sim 0.1$  mm across. With both reflected and transmitted light, the grains appeared inhomogeneous, being mixtures of opaque, dark brown iron oxide, quartz and a soft, near colourless mineral. This mineral decomposed slowly under the beam during analysis with a Cameca SX50 microprobe, using the same standards and conditions as for the kintoreite analysis. Six grains gave consistent analyses (Table 1) which yielded a simplified formula  $SrAl_3(PO_4)_2(OH,H_2O)_{12}$ . This is close to the formula for goyazite, allowing for lower analytical totals, and hence greater apparent OH and  $H_2O$  contents, due to the behaviour of the mineral under the microprobe beam. Only minor amounts of Pb were obtained in the analyses. Because of the paucity of material, the inhomogeneity of the grains and the impossibility of separating a pure 'lusungite' fraction, X-ray powder diffraction was not undertaken.

The discreditation of type lusungite was approved by a vote of the Commission on New Minerals and Mineral Names. The specific recommendations flowing from this vote are that material from the

original type locality be referred to as goyazite and that the 'lusungite' group as defined by Scott (1987) be renamed the segnitite group.

*Current nomenclature.* Existing nomenclature schemes for alunite–jarosite minerals are inadequate to cope with the complexity of the solid solution and order–disorder relations. The IMA-approved scheme proposed by Scott (1987) and subsequent variations (Birch *et al.*, 1992; and this paper) are essentially compositionally based but, because of lack of data, do not take into account possible limits on order–disorder and solid solution in parts of the compositional spectrum. Simple group names such as 'beudantite' or 'crandallite' (Fleischer and Mandarino, 1991) are inconsistent with Scott's scheme.

There is contradictory evidence for order–disorder involving  $PO_4^{3-}/SO_4^{2-}$  and  $AsO_4^{3-}/SO_4^{2-}$  in some minerals; for example beudantite shows anion disorder (Szymanski, 1988; Giuseppetti and Tadini, 1989) but corkite may be anion-ordered (Giuseppetti and Tadini, 1987).

In view of the likelihood of new evidence being produced on the relationships between crystal structure, order–disorder and solid solution in these minerals, the nomenclatural changes resulting from this study should be seen as interim only.

### Summary

Kintoreite is the new Pb–Fe<sup>3+</sup>–P analogue of segnitite in the alunite–jarosite family. The type locality is the Kintore Opencut at Broken Hill, New South Wales, Australia. Kintoreite replaces lusungite, type material of which has been shown to be goyazite, and is therefore discredited. The former 'lusungite' group within the alunite–jarosite family is to be renamed the segnitite group.

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