Segnitite, PbFe₃H(AsO₄)₂(OH)₆, a new mineral in the lusungite group from Broken Hill, New South Wales, Australia

W. D. Birch
Department of Mineralogy, Museum of Victoria, 285 Russell Street, Melbourne, Victoria 3000, Australia

A. Pring
Department of Mineralogy, South Australian Museum, North Terrace, Adelaide, South Australia 5000, Australia

B. M. Gatehouse
Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia

Abstract

Segnitite is a new lead iron arsenate mineral in the alunite-jarosite family, from Broken Hill, New South Wales, Australia. The new species occurs as greenish brown to yellowish brown, pseudo-octahedral crystals up to 1 mm across, and as aggregates, crusts and clusters of yellowish brown rhombohedral crystals up to 5 mm high. The principal forms present are {112} and {001}. Associated species include beudantite, carminite, mimetite, bayldonite, agardite-(Y), goethite, and coronadite. Segnitite is the new As end-member of the lusungite group and the Fe^{3+} analogue of philipsbornite; it has formed by oxidation of primary ore rich in galena and arsenopyrite-loellingite. Segnitite is named after E. R. Segnit, and type material is preserved in the Museum of Victoria.

Electron microprobe analysis yielded an empirical formula of $(Pb_{1.05}Ba_{0.03})_{\Sigma 1.08}$-$(Fe_{2.76}Zn_{0.22}Al_{0.17}Cu_{0.01})_{\Sigma 3.16}[(AsO_4)_{1.85}(PO_4)_{0.05}(SO_4)_{0.04}]_{\Sigma 1.94}(OH,H_2O)_{6.24}$, calculated on the basis of 14 O atoms and with all Fe trivalent. The simplified formula is $PbFe_3H(AsO_4)_2(OH)_6$. The mineral is translucent to transparent, with an adamantine luster, rough fracture, good cleavage on {001}, and a pale yellow streak. The estimated Mohs hardness is 4, and d_{calc} = 4.77 gm/cm³. Segnitite crystals are uniaxial negative, ω = 1.975, ϵ = 1.955, and show pleochroism from pale to moderate yellow.

The strongest lines in the X-ray powder pattern are (d_{obs}, I_{obs}, hkl) 3.092(100)(113); 5.966(50)(101); 3.678(40)(110); 2.283(30)(107); 1.992(30)(303); and 1.840(25)(220). The X-ray data were indexed on a hexagonal unit cell by analogy with beudantite, giving a = 7.359(3) Å, c = 17.113(8) Å, V = 802.6(6) Å³; and Z = 3. The probable space group is $R\bar{3}m$, also by analogy with beudantite. There is a close resemblance between the powder data and unit-cell parameters for segnitite and "S-poor beudantite."

Introduction

Minerals of the alunite-jarosite family with the general formula $AB_3(XO_4)_2(OH)_6$ are widespread in gossans formed over lead sulfide–rich mineralization in arid regions. Scott (1987) discussed the wide range of substitutions that occur in these minerals and proposed a classification scheme that has been formally adopted by the International Mineralogical Association. The chemical complexity of the family has spawned a profusion of species names, but this paper is restricted to those species with general formulae defined by A = Pb^{2+}, B = Fe^{3+} or Al^{3+}, and X = P, As, and S.

Segnitite, a member of the lusungite group of alunite-jarosite minerals, is the Fe^{3+} analogue of philipsbornite. It occurs in the oxidized zone of the lead zinc sulfide ore bodies at Broken Hill, New South Wales, where it forms the As end-member of a suite of S-poor beudantite–like minerals in the lusungite group (Scott, 1987).

The mineral is named for E. Ralph Segnit (1923–) in recognition of his contribution to Australian mineralogy. The data and name were approved by the IMA Commission on New Minerals and Mineral Names prior to publication. Type material is preserved in the collections of the Museum of Victoria, as specimen no. M30044.

Occurrence

The wide variety of alunite-jarosite minerals occurring in the oxidized zone at Broken Hill has only recently been recognized. The minerals have been recovered during extensive mining operations by Minerals Mining and Metallurgy Ltd. in the Kintore and Block 14 opencuts since 1984. Most of the minerals can be defined as solid solutions involving end-member species hidalgoite, hinsdalite, plumbogummite, beudantite, and corkite. They occur as massive aggregates, pseudomorphs or endomorphs after pyromorphite or mimetite and as drusy crusts, single

crystals, or groups of attractive, well-formed crystals. Colors range from cream to shades of green, yellow, and brown. They are generally early-formed minerals in complex associations of arsenates or phosphates (Birch and van der Heyden, 1988) but may also occur as late-crystallizing minerals in cavernous iron and manganese oxide hydroxides.

The exact source within the Broken Hill oxidized zone of the type specimen of segnitite is unknown. The specimen was initially described as beudantite and illustrated by Birch et al. (1982). It consists of segnitite crystals overgrowing beudantite on a matrix of goethite encrusting bluish gray quartz and small spessartine crystals. Subsequently, segnitite specimens have been found in the Kintore opencut along with a diverse range of previously unrecorded secondary species (Pring et al., 1989; Birch, 1990). These occur as drusy crusts on fractures in a spessartine-quartz rock known as garnet sandstone and in cavities lined with concretionary coronadite and goethite in massive siliceous rocks.

Segnitite belongs to an As-rich paragenetic sequence (Birch, 1990), occurring with mimetite, carminite, bayldonite, and agardite-(Y), exposed at 240-m relative level (RL) in the Kintore opencut, about 60–70 m below the present surface. It also occurs with mawbyite and mimetite on concretionary goethite at 250-m RL (Pring et al., 1989). The arsenate suite has crystallized from solutions rich in Pb, Fe, and As derived from the breakdown of the primary ore of 3 Lens, one of the lead lodes at Broken Hill. This primary ore consists mainly of galena and sphalerite, with minor chalcopyrite and arsenopyrite-loellingite in a quartz-rich gangue (van der Heyden and Edgecombe, 1990).

APPEARANCE

On the type specimen, segnitite forms lustrous pseudooctahedral, greenish brown to yellowish brown crystals up to 1 mm across. Many crystals have cores of brown beudantite. On specimens from the Kintore opencut, segnitite occurs as drusy crusts and spongy aggregates of yellow-brown acute rhombohedral crystals, usually less than 1 mm high. In one exceptional specimen, clusters of dark yellow-brown segnitite rhombs up to 5 mm high occur with aggregates of bladed carminite crystals in a cavity in massive mimetite coronadite quartz.

Segnitite crystals show two main forms, the rhombohedron $\{112\}$ and the pinacoid $\{001\}$. The most common habit is as hemispherical clusters; twinning on specific laws is not observed.

PHYSICAL AND OPTICAL PROPERTIES

Segnitite crystals are generally greenish brown to yellowish brown or dark brown, and translucent to transparent, and have a vitreous to adamantine luster. The streak is pale yellow and the Mohs hardness is approximately 4; the crystals show one good cleavage, $\{001\}$, and are brittle with a rough fracture. The measured density exceeds 4.2 g/cm^3 (crystals sink in Clerici solution).

TABLE 1. Electron microprobe analysis of segnitite

Wt%	1	2	3
CuO	0.14	0.01	
ZnO	1.87	0.22	
BaO	0.49	0.03	
PbO	30.58	1.05	29.54
Al$_2$O$_3$	1.13	0.17	
Fe$_2$O$_3$	28.91	2.76	31.69
P$_2$O$_5$	0.37	0.05	
As$_2$O$_5$	27.89	1.85	30.42
SO$_3$	0.57	0.04	
H$_2$O*	8.01	6.79	8.35
Total	99.96		100.00

Note: 1. Segnitite, average of 10 (Museum of Victoria M30044). 2. Empirical formula for 1 (element proportions, based on 14 O atoms). 3. PbFe$_3$H(AsO$_4$)$_2$(OH)$_6$.
* H$_2$O by CHN analyzer.

The mineral is uniaxial negative, with refractive indices between 1.955(5) (ω) and 1.975(5) (ϵ). Pleochroism is from pale to moderate yellow. Fluorescence in UV light was not observed.

CHEMICAL COMPOSITION

Segnitite and other members of the low-S lusungite series from Broken Hill were analyzed using two microprobes, a JEOL and a Cameca. Operating conditions (15 kV and specimen current of 0.02 μA) and standards (hematite, Fe; sphalerite, Zn and S; galena, Pb; arsenopyrite, As; fluorapatite, P; corundum, Al; metallic copper, Cu; benitoite, Ba) were the same for both instruments. H$_2$O content was determined on a 3.4-mg sample from the type specimen using a CHN analyzer.

Ten microprobe analyses were obtained on the type specimen (Table 1). These showed variable but small Cu, Zn, Ba, Al, P, and S contents. The empirical formula, calculated on the basis of 14 O atoms is (Pb$_{1.05}$Ba$_{0.03}$)$_{\Sigma1.08}$(Fe$_{2.76}$Zn$_{0.22}$Al$_{0.17}$Cu$_{0.01}$)$_{\Sigma3.16}$[(AsO$_4$)$_{1.85}$(PO$_4$)$_{0.05}$(SO$_4$)$_{0.04}$]$_{\Sigma1.94}$(OH,H$_2$O)$_{6.24}$. All Fe was assumed to be trivalent by analogy with other members of the alunite-jarosite family and from species associated with segnitite, such as carminite. There are a number of options for the simplified formula: (1) PbFe$_3$(AsO$_4$)$_2$(OH)$_5$·H$_2$O, (2) PbFe$_3$(AsO$_4$)$_2$(OH,H$_2$O)$_6$, (3) PbFe$_3$(AsO$_4$)(AsO$_3$OH)(OH)$_5$, (4) PbFe$_3$H(AsO$_4$)$_2$(OH)$_6$. Structural evidence suggests that protonation of one of the XO_4 cations may occur in crandallite (Blount, 1974) and gorceixite (Radoslovich, 1982). On this basis, Scott (1987) recommended either formula 3 or 4 (in general form), for alunite-jarosite minerals. Szymanski (1988) referred to an undescribed compound with a formula in the form of option 1, but there is little evidence for structural H$_2$O in known, naturally occurring members of the family. The preferred formula for segnitite is option 4, PbFe$_3$H(AsO$_4$)$_2$(OH)$_6$, as, unlike option 3, it suggests that protonation of the AsO$_4$ anion is disordered. This choice is consistent with the suggested space group $R\bar{3}m$ for segnitite.

TABLE 2. Powder X-ray diffraction data for segnitite and sulfate-free beudantite

Segnitite				S-free beudantite		
I/I_0	d_{obs}	d_{calc}	hkl	I/I_0	d_{obs}
50	5.966	5.972	101	8	6.02
10	5.719	5.704	003	1	5.77
40	3.678	3.679	110	7	3.69
5	3.530	3.552	104	1	3.58
5	3.119	3.133	201	—	—
100	3.092	3.092	113	10	3.09
10	3.011	3.015	105	—	—
5	2.987	2.986	202	3	2.99
20	2.849	2.852	006	5	2.87
10	2.550	2.556	204	4	2.56
5	2.382	2.385	211	2	2.38
2	2.334	2.332	205	—	—
3	2.318	2.319	212	—	—
30	2.283	2.283	107	6	2.29
15	2.254	2.254	116	2	2.25
5	2.011	2.028	108	—	—
30	1.992	1.991	303	6	1.99
25	1.840	1.840	220	6	1.84
15	1.688	1.688	313	3	1.692
8	1.546	1.546	226	4	1.549
10	1.508	1.508	2, 0, 10	4	1.511
5	1.418	1.417	309	2	1.421

Note: Cell parameters for segnitite refined from the above data: $a = 7.359(3)$ Å, $c = 17.113(8)$ Å, $V = 802.6(5)$ Å³ (a Guinier-Hagg camera with a 100-mm diameter and CuKα radiation). Cell parameters for sulfate-poor beudantite from above data: $a = 7.36$ Å, $c = 17.21$ Å (from Walenta, 1966).

Fig. 1. Triangular $(AsO_4)_2$-$(PO_4)_2$-$(SO_4)_2$ diagram for Pb-Fe³⁺-dominant groups within the alunite-jarosite family. Subdivisions at S = 0.5 and 1.5 are based on the classification scheme of Scott (1987). Plotted are analyses of the type specimen (solid triangles) and intermediate compositions in the lusungite group from the Kintore opencut at Broken Hill (open triangles).

X-RAY CRYSTALLOGRAPHY

Powder X-ray diffraction data for segnitite were obtained using a Guinier-Hagg camera with a 100-mm diameter, CuKα radiation, and Si as an internal standard (Table 2). The data were indexed using the hexagonal setting of the rhombohedral cell with reference to beudantite (Giusepetti and Tadini, 1989). Parameters of the hexagonal unit cell, $a = 7.359(3)$ Å, $c = 17.113(8)$ Å, $V = 802.6(5)$ Å³ were refined from the powder data using 24 reflections with $2\theta < 66°$. The cell parameters are slightly larger than those reported by Giusepetti and Tadini (1989) for beudantite ($a = 7.339(1)$ Å, $c = 17.034(1)$ Å, $V = 794.55$ Å³) due to the replacement of SO_4^{2-} by AsO_4^{3-}. The space group $R\bar{3}m$ is tentatively proposed for segnitite, again by analogy with beudantite. With $Z = 3$, the calculated density is 4.77(1) g/cm³. The crystallographic and crystal chemical relations of segnitite and intermediate compositions along the segnitite-lusungite join are currently under detailed investigation (Pring et al., unpublished data).

There is a close resemblance between the powder diffraction data and unit-cell parameters for segnitite and the sulfate-free beudantite described from the Silberbrunnle mine, Schwarzwald, Germany, by Walenta (1966) (Table 2).

NOMENCLATURE IMPLICATIONS

The full extent of solid solution in the alunite-jarosite family, in particular involving the anion sites, is not well known, and there is a lack of reliable crystal str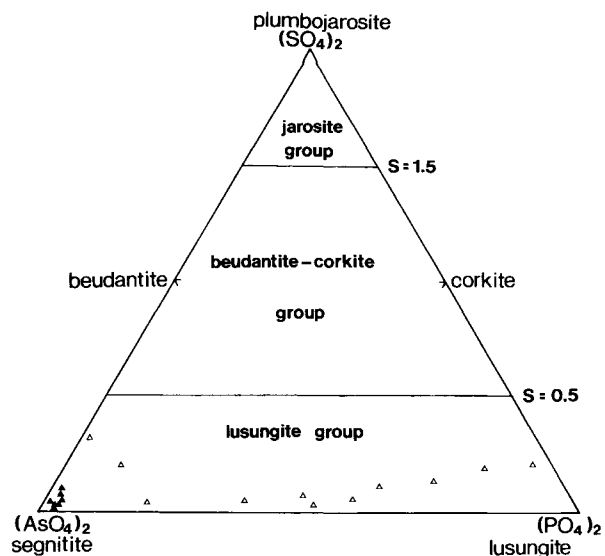ucture information on many members. Some evidence appears at odds: for example, beudantite shows anion disordering (AsO_4^{3-} and SO_4^{2-}) (Szymanski, 1988; Giusepetti and Tadini, 1989), whereas Giusepetti and Tadini (1987) suggest that corkite is anion ordered (PO_4^{3-} and SO_4^{2-}). On these grounds, beudantite could be considered as the midpoint of a binary solid-solution series and, on the basis of recent IMA nomenclature rules, should not have species status. Corkite however, although a compositional midpoint, may be entitled to retain species status on structural grounds. The existing nomenclature for jarosite-like minerals with Pb dominant in the A site and Fe > Al in the B site is shown in the triangular plot of Figure 1. On this diagram, lusungite, the Fe³⁺ analogue of plumbogummite, is considered to be Pb dominant, as proposed by Scott (1987), rather than as Sr dominant, as described originally by van Wambeke (1958). Segnitite is the new As end-member of the lusungite group. The type specimen has an average composition that plots very close to the As vertex. Data for minerals with intermediate compositions from Kintore, effectively defining the full lusungite series, are also plotted on Figure 1.

An equivalent Al-dominant triangular diagram can be constructed and linked to the Fe plot using Fe/(Fe + Al) as the vertical dimension (Fig. 2). Using these two diagrams, most compositions of Pb-dominant species in the alunite-jarosite family can be named using appropriate qualifiers, such as ferrian, arsenian, etc. (some segnitite analyses could be referred to as zincian). Note that whereas the diagrams are based on Pb-dominant members, they do not allow for variation in Pb from 1 atom per formula unit in the beudantite and lusungite groups (and in hins-
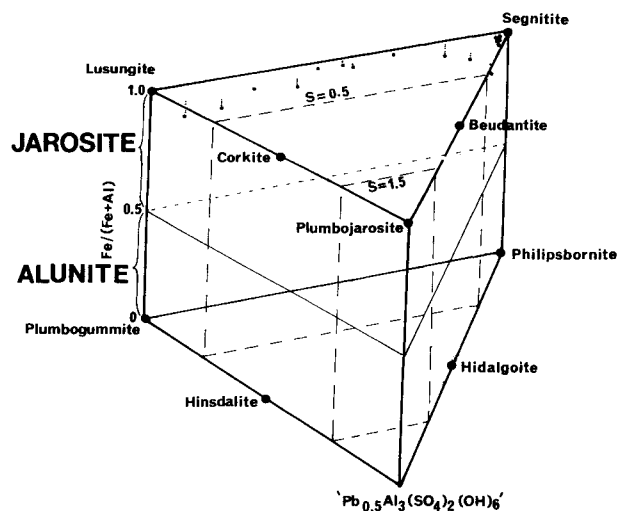
Fig. 2. Wedge diagram combining Pb-Fe^{3+} compositional field of Figure 1 (upper face) and the equivalent field for Pb-Al dominant compositions (lower face) in the alunite-jarosite family. $Fe^{3+}/(Fe^{3+} + Al)$ is the vertical dimension. Approved species are shown at vertices and midpoints of edges. Compositions in segnitite-lusungite series from Broken Hill are shown as solid circles (see text for discussion).

dalite and plumbogummite) to ≈ 0.5 atoms in plumbojarosite (or its unknown Al analogue). They also do not take into account other minor elements such as Cr or V, which may substitute in the X site.

In terms of ternary solid solution involving As, P, and S, the proposed classification scheme departs from the recent IMA guidelines. This is due in part to the existence of accepted species (such as beudantite and corkite) at midpoints of binary series and also to the adoption of Scott's (1987) proposal, which did not distinguish between As and P for nomenclature purposes. The classification scheme proposed in this paper may therefore be considered an interim one until further data on solid-solution limits and crystal structure in the alunite-jarosite family are obtained.

REFERENCES CITED

Birch, W.D. (1990) Minerals from the Kintore and Block 14 Opencuts, Broken Hill, N.S.W.; a review of recent discoveries, including tsumebite, kipushite and otavite. Australian Mineralogist, 5 (4), 125–141.

Birch, W.D., and van der Heyden, A. (1988) Minerals from the Kintore Opencut, Broken Hill, New South Wales. Mineralogical Record, 19, 425–436.

Birch, W.D., Chapman, A., and Pecover, S. (1982) The minerals. In H.K. Worner and R.W. Mitchell, Eds., Minerals of Broken Hill, p. 68–195. Australian Mining and Smelting Ltd., Melbourne.

Blount, A.M. (1974) The crystal structure of crandallite. American Mineralogist, 59, 41–47.

Giusepetti, G., and Tadini, C. (1987) Corkite, $PbFe_3(SO_4)(PO_4)(OH)_6$, its crystal structure and ordered arrangement of the tetrahedral cations. Neues Jahrbuch für Mineralogie Monatshefte, 19, 71–81.

———(1989) Beudantite: $PbFe_3(SO_4)(AsO_4)(OH)_6$, its crystal structure, tetrahedral site disordering and scattered Pb distribution. Neues Jahrbuch für Mineralogie Monatshefte, 1989(1), 27–33.

Pring, A., McBriar, E.M., and Birch, W.D. (1989) Mawbyite, a new arsenate of lead and iron related to tsumcorite and carminite, from Broken Hill, New South Wales. American Mineralogist, 74, 1377–1381.

Radoslovich, E.W. (1982) Refinement of gorceixite structure in Cm. Neues Jahrbuch für Mineralogie Monatshefte, 446–464.

Scott, K.M. (1987) Solid solution in, and classification of, gossan-derived members of the alunite-jarosite family, northwest Queensland, Australia. American Mineralogist, 72, 178–187.

Szymanski, J.T. (1988) The crystal structure of beudantite, $Pb(Fe,Al)_3[(As,S)O_4]_2(OH)_6$. Canadian Mineralogist, 26, 923–932.

van der Heyden, A., and Edgecombe, D.R. (1990) Silver-lead-zinc deposit at South Mine, Broken Hill. In F.E. Hughes, Ed., Geology of the mineral deposits of Australia and Papua New Guinea, p. 1073–1077. Australasian Institute of Mining and Metallurgy, Melbourne.

van Wambeke, L. (1958) Une nouvelle espece minerale: La lusungite en provenance de la pegmatite de Kobokobo (Kivu-Congo Belge). Société Belge de Geologie, de Paleontologie, et d'Hydrologie, Bulletin, 67, 162–169 (not seen; extracted from American Mineralogist, 44, 906, 1959).

Walenta, K. (1966) Beitrage zur Kentniß seltener Arsenatmineralien unter besonderer Berucksichtigung von Vorkommen des Schwarzwaldes. Tschermaks mineralogische und petrographische Mitteilungen, 11, 121–164 (not seen; extracted from American Mineralogist, 52, 1585, 1967).