

# Wolfeite and barbosalite from Thackaringa, Australia

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**SUMMARY.** Wolfeite  $(\text{Fe,Mn})_2\text{PO}_4(\text{OH})$  and barbosalite  $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2(\text{PO}_4)_2(\text{OH})_2$  are the principal phases in phosphate pods from the core of a zoned altered granitic pegmatite at Thackaringa. Chemical analyses of the wolfeite show it to be Fe-rich and extends the triploidite-wolfeite isomorphous series (Fron del, 1949) from  $\Sigma\text{Fe}/\text{Mn} = 3.39$  (this study) to greater than 100 (Clark and Couper, 1979).

THE Thackaringa district, 40 km southwest of Broken Hill ( $31^\circ 39' \text{S}$ ,  $141^\circ 29' \text{E}$ ) is well known for its quartz-alkali-feldspar-beryl pegmatites. The pegmatite at Thackaringa transgresses high-grade metamorphic pelitic, psammitic, and quartzofeldspathic sediments of the Middle Proterozoic Willyama Complex. The Complex underwent two events of synchronous deformation and high-grade metamorphism at about 1700 Ma (Shaw, 1968; Rutland and Etheridge, 1975). Lensoidal and planar intrusive masses of pegmatite are undeformed and are probably related to a tectonic event dated at 530 Ma by Richards and Pidgeon (1963) and Binns and Miller (1963). The unnamed pegmatite mass examined is mined for feldspar by R. K. Wilson. It is internally texturally and mineralogically zoned with a narrow border zone of muscovite-quartz which has grown normal to the pegmatite wall. An inner coarse-grained blocky feldspar-rich zone comprises perthitic and graphic orthoclase partially replaced by albite, quartz, celadonic muscovite, and tourmaline; minor sericitized biotite and rare sodic beryl. The core of the pegmatite comprises fractured milky quartz, with minor massive phosphate pods comprising wolfeite, barbosalite, triplite, and apatite, and rare arsenopyrite, scorodite (possibly secondary) pyrite, and beryl.

**Properties.** Wolfeite occurs as coarse grained resinous dark reddish-brown masses intimately associated with minor triplite and apatite. The wolfeite contains inclusions of quartz and acicular apatite and is transgressed by narrow veinlets comprising quartz, chlorite, wolfeite, and gypsum. It has

a Moh's hardness of  $6\frac{1}{2}$ , SG of 4.06, displays a poor (100) cleavage and, in thin section, is pleochroic from  $\alpha$  = pale yellowish-brown,  $\beta$  = deep yellowish-brown and  $\gamma$  = brown. Interference colours are masked by the strong body colour of wolfeite and vary from deep greenish blue to brown with  $\alpha_x = 1.72$  to  $1.74$ ,  $\beta_\beta = 1.72$  to  $1.73$  and  $\gamma_\gamma = 1.72$  to  $1.74$ . Wolfeite is biaxial positive with a  $2V_\alpha$  of  $65^\circ$ .

The masses of wolfeite are transgressed by fracture- and cleavage-controlled manganese oxides and are partially replaced by massive barbosalite. The barbosalite contains minor transgressive veinlets and inclusions of quartz. It is dull, dark green, has a Moh's hardness of 6, an SG of 3.62 and displays no prominent cleavage. In thin section, barbosalite is almost opaque with  $\alpha = \beta =$  dark blue-green,  $\gamma =$  dark green,  $\alpha_x = 1.76$  to  $1.78$ ,  $\beta_\beta = 1.77$  to  $1.81$  and  $\gamma_\gamma = 1.84$ . The interference colours are indeterminate because of the relative opacity of barbosalite.

**Mineral chemistry.** Mineral phases were analysed using an energy dispersive TMP microprobe with a Si(Li) detector. Synthetic and natural oxide standards and the methods and correction procedures of Reed and Ware (1975) were used. FeO was determined by metavanadate titration and water by gravimetric techniques. Infra-red absorption spectra in the range  $400\text{--}4000 \text{ cm}^{-1}$  were determined from a nujol mull on a Perkin-Elmer 337 IR spectrometer.

Fron del (1949) shows that wolfeite forms an isomorphous series with triploidite extending from  $\text{Fe}/\text{Mn} = 0.30$  to  $\text{Fe}/\text{Mn} = 3.39$ . The chemical analyses of wolfeite from Wilson's Quarry, Thackaringa (Table I) show that this isomorphous series can be further extended to  $\text{Fe}/\text{Mn} = 9.35$ . Substitution of  $\text{Fe}^{2+}$  for  $\text{Mn}^{2+}$  in the triploidite-wolfeite series is accompanied by an increase in SG (Table I). The wolfeite and barbosalite from Thackaringa are associated with arsenopyrite and scorodite and hence it is possible that there is substitution of  $\text{AsO}_4^{3-}$  for  $\text{PO}_4^{3-}$ . Infra spectra of

wolfeite and barbosalite (fig. 1) show that there is limited substitution of  $\text{AsO}_4^{3-}$  for  $\text{PO}_4^{3-}$  in these phases from Thackaringa. Wolfeite from Thackaringa is chemically similar to the three wolfeite analyses presented by Frondel (1949).

The barbosalite analysed from Thackaringa has less FeO and more  $\text{Fe}_2\text{O}_3$  than barbosalite from the type locality (Table II) and there is minor substitution of Mn and Mg for  $\text{Fe}^{II}$ . A small but significant  $\text{TiO}_2$  and  $\text{Na}_2\text{O}$  content is present in the analysed barbosalite.

*X-ray data.* A Phillips P 1720 X-ray spectrometer with Mn-filtered Cu radiation was used for powder diffraction photographs and diffractometer scans. The X-ray diffraction patterns of wolfeite and barbosalite are very similar to those reported by Frondel (1949) and Lindberg and Pecora (1955) respectively.

*Discussion.* Wolfeite and barbosalite are uncommon iron hydroxy phosphate phases from granitic pegmatites, e.g. North Groton, New Hampshire; Cyrillhof, Czechoslovakia; Skrumptorp, Sweden; Hagendorf, FR Germany; Sapucaia, Brazil; and the Olary and Broken Hill districts, Australia.

Wolfeite was discovered in the famous Palermo granitic pegmatite, North Groton, New Hampshire by Frondel (1949). Phosphate mineral pods in the

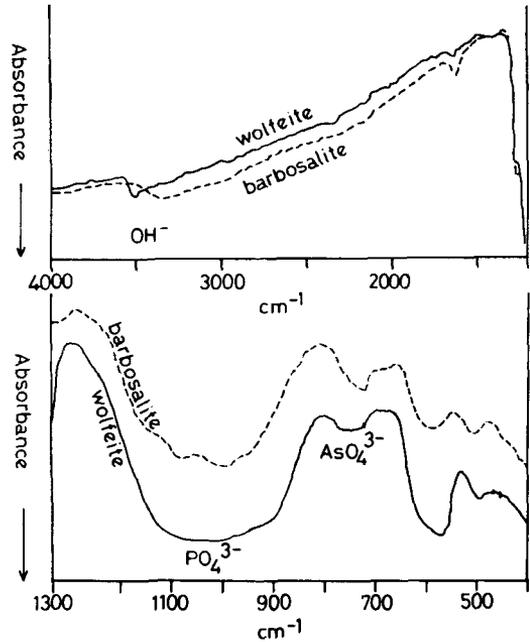


FIG. 1. Infra-red absorption spectra of wolfeite and barbosalite.

TABLE I. Chemical analyses of wolfeite and barbosalite

	1	2	3	4
$\text{SiO}_2$			0.24	0.00
$\text{TiO}_2$			0.76	0.43
$\text{Al}_2\text{O}_3$			0.00	0.23
$\text{V}_2\text{O}_3$			0.00	0.00
$\text{Cr}_2\text{O}_3$			0.00	0.00
$\text{Fe}_2\text{O}_3$			2.96	4.52
FeO		64.24	33.38	51.03
MnO	63.95		17.34	5.46
MgO			0.77	1.02
CaO			0.46	0.13
$\text{K}_2\text{O}$			0.24	0.00
$\text{Na}_2\text{O}$			1.08	0.86
$\text{H}_2\text{O}$	4.06	4.03	3.66	3.66
$\text{SO}_3$			0.00	0.00
Cl			0.13	0.00
$\text{P}_2\text{O}_5$	31.99	31.73	34.36	33.24
Total	100.00	100.00	95.09	100.68
SG			4.06	

1. Theoretical composition  $\text{Mn}_2(\text{PO}_4)(\text{OH})$ , tripliodite.

2. Theoretical composition  $\text{Fe}_2(\text{PO}_4)(\text{OH})$ , wolfeite.

3. and 4. Wolfeite, Thackaringa, NSW.

TABLE II. Chemical analyses of barbosalite

	1	2	3	4	5
$\text{SiO}_2$	0.15	0.00	0.26	0.24	
$\text{TiO}_2$	1.11	0.57	1.30	0.75	
$\text{Al}_2\text{O}_3$	0.19	0.00	0.18	0.16	
$\text{V}_2\text{O}_3$	0.14	0.00	0.00	0.12	
$\text{Fe}_2\text{O}_3$	49.41*	52.10*	50.21*	50.05*	41.65
FeO	1.35	1.42	1.37	1.37	13.10
MnO	2.22	1.36	1.30	1.15	
MgO	0.87	0.87	0.88	1.11	
CaO	0.12	0.00	0.36	0.17	
$\text{K}_2\text{O}$	0.00	0.00	0.07	0.00	
$\text{Na}_2\text{O}$	0.83	0.73	0.79	0.85	
$\text{H}_2\text{O}$	6.24†	6.24†	6.24†	6.24†	4.93
$\text{SO}_3$	0.18	0.00	0.23	0.00	
Cl	0.09	0.05	0.16	0.17	
$\text{P}_2\text{O}_5$	36.65	38.61	38.21	36.72	37.50
Total	99.55	101.95	101.56	97.99	97.18

\* = metavanadate titration on massive specimen.

† = gravimetric determination on massive specimen.

1-4 (inclusive). Electron microprobe/wet chemical analyses of barbosalite Thackaringa (this study).

5. Barbosalite, Sapucaia pegmatite mine, Minas Gerais, Brazil (from Lindberg and Pecora, 1955).

Palermo pegmatite comprising triphylite, ludlamite, and vivianite display alteration as a result of retrograde hydrothermal attack and wolfeite derives from alteration of triphylite (Fron del, 1949). Low temperature hydrothermal alteration, weathering, and oxidation have produced uncommon phosphate minerals such as arrojadite, childrenite, foggite, geodkenite, jahnsite, messelite, mitridatite, rockbridgeite, samuelsonite, schoonerite, whitmoreite and xanthoxenite (Fron del, 1949; Moore *et al.*, 1975; Moore and Araki, 1974, 1977; Moore and Kampf, 1977).

Unlike wolfeite from the Palermo pegmatite, the wolfeite at Thackaringa does not appear to be an alteration phase of a pre-existing phosphate and is a late stage phase in the core of the pegmatite. A number of generations of hydrothermal alteration are evident in the Thackaringa pegmatites such as the albitization of K-feldspar, sericitization of biotite and alteration of beryl to bertrandite. The wolfeite at Thackaringa has undergone oxidation during low temperature hydrothermal alteration or weathering to form barbosalite.

Barbosalite was first described by Lindberg and Pecora (1955) from the Sapucaia granitic pegmatite in Minas Gerais, Brazil. The quartz-muscovite-perthite-beryl pegmatite is texturally and mineralogically zoned with abundant phosphate minerals in the central part of the pegmatite. The principal phosphate mineral is triphylite which is commonly altered to heterosite. Other phosphate phases of diverse origin from the pegmatite are: frondelite, hurealite, vivianite, tavorite, faheyite, childrenite, apatite, roscherite, strengite, metastrengite, variscite, ferrisicklerite, montebrasite, and moraesite. At Sapucaia, barbosalite results from the alteration of triphylite and forms a dark blue-green layer between porous triphylite and heterosite.

Clark and Couper (1979) found end member triploidite from Wheal Owles, St. Just, Cornwall and Fe-rich wolfeite from Thackaringa shows that

the isomorphous triploidite-wolfeite isomorphous series of Fron del (1949) can be greatly extended from  $\Sigma\text{Fe}/\text{Mn} = 3.39$  (this study) to greater than 100 (Clark and Couper, 1979).

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