

Manganoan ilvaite from Broken Hill, N.S.W. and Ban Ban, Queensland, Australia

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SUMMARY. Manganoan ilvaite forms as an early retrograde metamorphic phase from calcic rhodonite in the polymetamorphosed Pb-Zn sulphide/manganese silicate rocks at Broken Hill and from grossular-andradite in a skarn at Ban Ban. Ilvaite exists as a probable metastable phase into which Mn is apparently strongly partitioned. The manganoan ilvaites analysed contain up to 13.5% MnO substituting for FeO and this substitution shifts the 020 peak.

THE metamorphosed middle Proterozoic stratiform lead-zinc sulphide rocks at Broken Hill N.S.W. (fig. 1) are within a thick sequence of pelitic and psammitic gneisses. Units of felsic gneiss, garnet-plagioclase gneiss, amphibolite, and quartz-gahnite rocks are within the metasediments beneath the sulphide rocks. Quartz-gahnite rocks are commonly strike extensions of the sulphide rocks and banded iron formations commonly overlie the sulphide and quartz-gahnite rocks. A thick monotonous sequence of pelitic gneiss overlies the iron formations and sulphide rocks. The sequence has undergone two coeval events of deformation and granulite facies metamorphism at about 1700 Ma and later deformation and retrograde metamorphism to lower amphibolite facies. Five principal sulphide orebodies are present at Broken Hill and these are zoned from relatively sphalerite (\pm chalcopyrite \pm quartz)-rich at the base to galena + argentian-tetrahedrite + Mn silicates + fluorite (\pm plumbian orthoclase \pm quartz)-rich at the top. The Broken Hill orebodies are characterized by abundant galena, iron-rich sphalerite, and manganese-iron-calcium silicates. Ramdohr (1950) identified wedge-shaped fillings of ilvaite in manganese silicates from the Pinnacles Mine, Broken Hill and Lawrence (1968) records its presence in rhodonite-rich rocks from the New Broken Hill Consolidated Mine. The ilvaite described here is from the uppermost orebody (No. 3 lens) from the 18 level, Zinc Corporation Mine.

The Ban Ban zinc prospect in south-eastern Queensland (fig. 1) occurs in the early Permian Biggenden Beds within 1-2 km of the middle Triassic Mungore Adamellite intrusives. The prospect is in a narrow, elongate, subvertically dipping,

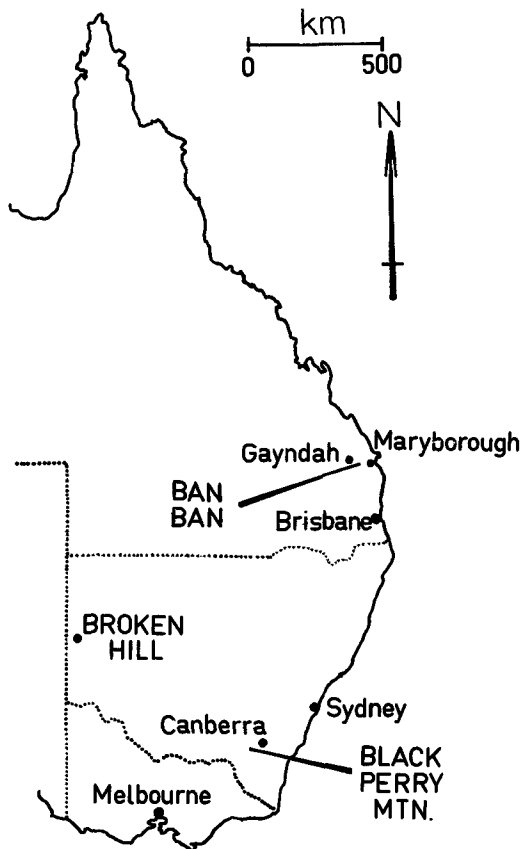


FIG. 1. Locality map.

stratabound skarn lens up to 17 m wide and 1370 m long. The skarn lenses are enclosed in fine-grained silica-rich shaly, cherty, and carbonaceous meta-sediments associated with metabasaltic lavas, pyroclastics, and volcanoclastic metasediments. Small stocks of microdiorite and adamellite occur 200–500 m from the skarn lenses. The skarn consists largely of grossular-andradite garnet + pyrite + sphalerite ± magnetite ± pyrrhotine in a central zone, locally grading into garnet + pyrite ± magnetite ± traces of chalcopyrite, and garnet-rich and clinopyroxene-rich rocks with a low sulphide content. Retrogression to chlorite and calcite (with or without quartz and epidote) is locally extensive.

Petrology of the ilvaite-bearing rocks. Ilvaite is an uncommon mineral at Broken Hill, but in some areas of the No. 3 lens occurs as resinous black masses up to 10 cm across. In thin section it is commonly opaque, but on thinner edges is red-brown to yellowish-brown. Pleochroism is strong from α red-brown to yellowish-brown, β opaque (rarely dark red-brown), and γ opaque to deep yellowish-brown and the interference colours are indeterminate because of the relative opacity of the mineral. In polished section, the ilvaite has a low reflectivity, strong bireflectance from grey to blue, strong anisotropy from pale pink to blue, and deep-internal reflections.

The mineral occurs in a coarse grained mio-litic rhodonite-hydrogrossular (hibschite var.) - sphalerite - galena - chalcopyrite - calcite - zincian-ilmenite rock and is in contact with all of these phases. The ilvaite is intergrown with and interstitial to the abundant reticulated pale-pink rhodonite and, in places, cavities in the rock are lined with rhodonite crystals up to 0.5 cm in length. The rhodonite is calcic with 5.8–12.2 cations % Fe, 20.7–25.0 cations % Ca and 66.5–69.6 cations % Mn and contains exsolved manganian hedenbergite with 36.0–37.6 cations % Fe, 53.3–55.3 cations % Ca and 8.7–9.0 cations % Mn and rare exsolved calcian clinoferrosilite with 79.4 cations % Fe and 20.6 cations % Ca (fig. 2). Lamellar twinning and undulose extinction in rhodonite are common. Associated sphalerite contains 24.6 mole % FeS (determined by the X-ray technique of Skinner *et al.*, 1959).

At Broken Hill ilvaite appears to have crystallized interstitially to rhodonite and, in places, encloses remnants of replaced rhodonite grains. Rhodonite is also partly replaced by hydro-grossular; where the latter and ilvaite are in direct contact they appear to be in equilibrium.

Ilvaite from Ban Ban is sparsely disseminated (< 0.5 vol. % but locally up to 2 vol. %) in two samples and forms anhedral grains (up to 1.5 mm

across). In thin section it ranges from almost opaque deep orange-brown to yellowish-brown and deep olive-brown (on thinner edges). It is strongly pleochroic with α yellowish-brown to orange-brown, β deep brown to opaque, and γ deep greenish-brown to opaque. Interference colours are masked by the strong body colours of the mineral. A weak rectangular cleavage (probably {001} and {010}) is developed. In polished section, the ilvaite has a low reflectivity (< sphalerite), grey colour, strong bireflectance from grey to blue, and strong anisotropy from pale pink to bluish grey.

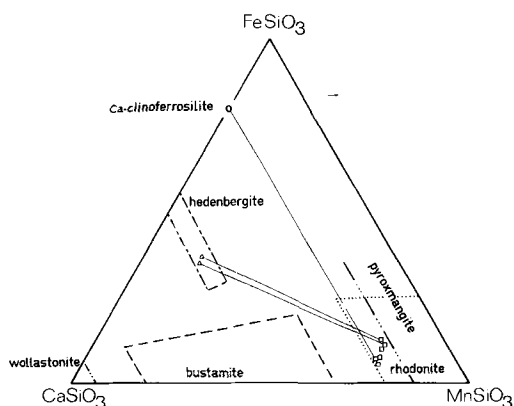


FIG. 2. Composition of silicate phases coexisting with manganian ilvaite from Broken Hill, N.S.W.

The mineral occurs in a medium- to coarse-grained rock rich in sphalerite, garnet, calcite, and quartz, with minor pyrite, magnetite, and tremolitic amphibole. Garnet is pale brownish-yellow in thin section, is commonly zoned, shows anomalous first-order interference colours and is a grossular-andradite with 55–99 mole % andradite and 0.68–4.29 % MnO. Sphalerite is deep orange-brown in thin section and contains sparse tiny exsolved pyrrhotine and chalcopyrite blebs. It contains 16.5 mole % FeS. Garnet and amphibole are partly replaced by calcite ± chlorite ± quartz, and locally the former is apparently replaced by ilvaite with or without magnetite. Elsewhere, ilvaite has crystallized interstitially to sphalerite, commonly with associated granular, anhedral to sub-radiating magnetite, enclosed in calcite and quartz.

Mineral chemistry and X-ray data. Minerals were analysed using an energy dispersive TMP micro-probe with a Si(Li) detector. Synthetic and natural oxides and the methods and correction procedures of Reed and Ware (1975) were used. FeO was determined by metavanadate titration and water by gravimetric techniques. A 114.59 mm diameter

TABLE I. Chemical analyses of ilvaite

	1		2	3
	\bar{x}	σ		
SiO ₂	30.54	0.35	30.21	29.54
TiO ₂	0.00	0.00	0.21	0.01
Al ₂ O ₃	0.00	0.00	0.70	0.38
Cr ₂ O ₃	0.05	0.06	0.08	n.d.
Fe ₂ O ₃	17.10	0.71	n.d.	18.71
FeO	23.41	1.02	38.43*	31.30
MnO	13.55	0.26	12.42	2.32
MgO	0.29	0.07	0.94	0.73
CaO	14.39	0.13	14.49	13.91
K ₂ O	0.00	0.00	0.05	0.00
ΣH ₂ O	1.40	0.11	n.d.	1.99
Total	100.73	—	97.53	98.89
Structural formulae on the basis of nine oxygens				
Si	2.026		2.235	2.013
Ti	0.000		0.012	0.000
Al	0.000		0.061	0.031
Cr	0.003		0.005	—
Fe ³⁺	0.853		0.931*	0.960
Fe ²⁺	1.299		0.966*	1.784
Mn	0.761		0.778	0.134
Mg	0.029		0.104	0.074
Ca	1.023		1.148	1.016
K	0.000		0.004	0.000
OH	0.328		—	0.480
Total	6.322		6.244	6.492

1. Ilvaite from Broken Hill, mean (\bar{x}) and standard deviation (σ) of nine analyses. Analyst: I. R. Plimer.

2. Ilvaite from Ban Ban, mean of two analyses. Analyst: P. M. Ashley.

3. Ilvaite from Black Perry Mountain, N.S.W., mean of three analyses from Gole (1972). Analyst: M. J. Gole.
n.d. = not determined.

* Total iron analysed as FeO and Fe³⁺ and Fe²⁺ calculated from structural formula.

camera and Mn-filtered Fe radiation were used for the powder diffraction photographs.

The Broken Hill and Ban Ban ilvaites are characterized by MnO contents of 13.55% and 12.42% respectively (Table I). Ilvaite from iron calc-silicate rocks at Black Perry Mountain, N.S.W., contains 2.32% MnO (Gole, 1972) whereas ilvaite from a magnetite + andradite + ilvaite skarn assemblage in the Mackay district, Idaho, contains 6.4% MnO (Leonard *et al.*, 1962), TiO₂, Al₂O₃, Cr₂O₃, MgO, and K₂O are low or below the limit of detection in Broken Hill ilvaite and are minor in Ban Ban ilvaite.

Many low intensity X-ray diffraction peaks of ilvaite from Broken Hill, Ban Ban, and Black Perry Mountain were not detected, but all diagnostic

peaks are present. It appears that with increasing substitution of MnO in ilvaite, there is a linear increase in d of the low-angle moderately intense 020 peak (fig. 3).

Manganese most probably substitutes for Fe²⁺ in the ilvaite structure and, from the chemical and X-ray diffraction data, a miscibility range of 7–35 wt% CaMn₂Fe³⁺Si₂O₈(OH) in CaFe₂²⁺Fe³⁺Si₂O₈(OH) has been observed in this study. The Broken Hill and Ban Ban ilvaites have 35% and 33% CaMn₂Fe³⁺Si₂O₈(OH) but no characteristic X-ray peaks have been determined, indicating a direct solid solution.

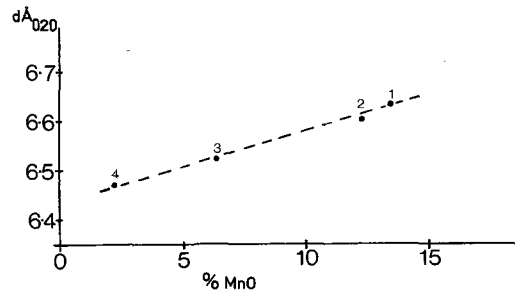
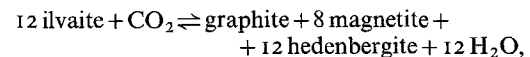


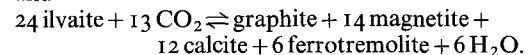
FIG. 3. Plot of d_{020} (Å) versus wt% MnO for ilvaite. 1, Broken Hill; 2, Ban Ban; 3, A.S.T.M. Index; 4, Black Perry Mountain.

Discussion. Ilvaite [Ca(Fe²⁺, Mn)₂Fe³⁺Si₂O₈(OH)] is a relatively rare mineral in nature and most typically occurs as a late stage mineral in Ca-Fe-Si skarns (Burt, 1971). If babingtonite (Ca₂Fe²⁺Fe³⁺Si₅O₁₄(OH)), a chemically similar phase to ilvaite, forms a stable assemblage with magnetite, then the isobaric, isothermal, invariant point magnetite-hematite-calcite-quartz-ilvaite-andradite proposed by Bartholomé and Dimanche (1967) is metastable (Burt, 1971). No babingtonite was observed at Broken Hill or Ban Ban and the data of Burt (1971) shows that the conditions that favour the formation of ilvaite rather than babingtonite are higher-temperature reducing conditions in which CO₂ is enriched and H₂O is depleted.

The following reactions of ilvaite involving CO₂ possibly control its stability:

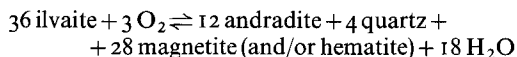


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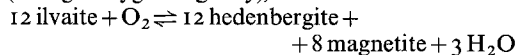


Gustafson (1974) showed that in a CO₂-free system, Mn-free synthetic ilvaite is stable below 470 °C ± 25 °C over a wide f_{O_2} range, but only at high fluid pressures. It was also reported by

Gustafson (1974) that the equilibria governing the upper stability limit of ilvaite are:

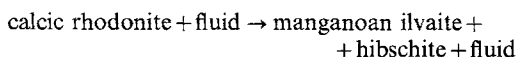


(at high oxygen fugacity), and



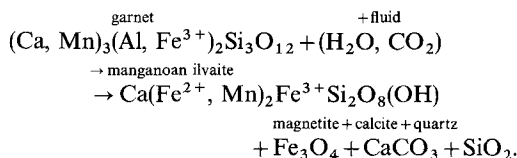
(at low and moderate oxygen fugacities).

The mineralogy of portions of the Broken Hill orebodies is rather similar to some manganiferous skarns (e.g. Chichibu and Nakatatsu Mines, Japan; Burt, 1971) and other metamorphosed stratiform manganiferous Zn deposits (e.g. Franklin Furnace; Frondel and Baum, 1974). Phases such as calcite, quartz, bustamite, rhodonite, manganian wollastonite, vesuvianite, manganian hedenbergite, pyroxmangite, johannsenite, tephroite, knebelite, spessartine-grossular, spessartine-andradite, sulphides, manganian fluorite, and apatite are present in the upper sulphide lenses at Broken Hill. Minor local metasomatic activity and element and mineral redistribution are associated with the high-grade metamorphism and later retrogression of the Broken Hill orebodies. The formation of ilvaite and associated hydrogrossular at Broken Hill appears to be a retrograde metamorphic breakdown of calcic rhodonite in the presence of sulphides, prograde calcite, and ilmenite. A possible reaction for the formation of ilvaite at Broken Hill is:



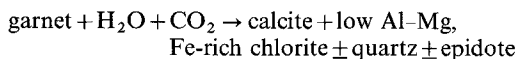
Mn would be lost and Al gained in the above rhodonite retrogression reaction.

At Ban Ban, ilvaite is in direct contact with garnet, sphalerite, magnetite, quartz, and calcite and is probably in equilibrium with all except garnet, as evidenced by patchy granular and spongy ilvaite on and penetrating garnet grain margins. A possible idealized reaction for the formation of manganian ilvaite at Ban Ban is:



In the reaction, Mn and Fe could be redistributed from garnet into the small volume of ilvaite present. Al is lost from the system (possibly into subaluminous Mg-poor Fe-rich chlorite). The ilvaite- and magnetite-forming reaction from gar-

net appears to have preceded the common retrograde reaction:



The petrographic data suggest that ilvaite is an early retrograde phase and the mineral assemblages indicate that Mn is preferentially partitioned into ilvaite.

If temperature, pressure, and chemical potentials of H₂O, CO₂, and O₂ are independently controlled variables then, in general, no more than three minerals in the system Ca-Fe-Si-C-O-H can stably exist in a given volume of μ_{O_2} - $\mu_{\text{H}_2\text{O}}$ - μ_{CO_2} space (Burt, 1971) and hence assemblages containing ilvaite from Broken Hill and Ban Ban are probably metastable as a result of partial retrogression.

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