

Malayaite and tin-bearing garnet from a skarn at Gumble, NSW, Australia

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ABSTRACT. Malayaite and tin-bearing garnet occur within a skarn assemblage at Gumble, NSW. A metasomatic origin is proposed for these minerals under conditions of $T = 300\text{--}500^\circ\text{C}$, $X_{\text{CO}_2} < 0.30$ and $f_{\text{O}_2} = 10^{-18}$ to 10^{-30} bars. Malayaite has formed as a result of reaction between a metasomatic fluid rich in Sn, F, H_2O and silica, and tin-bearing andradite and wollastonite. The main requirements for tin-bearing skarn formation appear to be an F-Sn-rich granite, an iron-rich skarn assemblage, and a relatively long cooling history.

THE Gumble area (long. $148^\circ 40'$ E, lat. $33^\circ 05'$ S) is situated 225 km west of Sydney, NSW. The object of this paper is to report and present data on the occurrence of Malayaite and tin-bearing garnet which are found in two lenticular limestone horizons within a contact metamorphosed sequence of Silurian-age calcareous and pelitic shelfal facies sediments. The two limestone horizons host calc-silicate mineralization typical of skarns within the hornblende hornfels facies. The intrusive Devonian-age Gumble Granite has many of the characteristics of an A-type (Beams, 1980), containing high Th, U, Zr, Nb, Y, Ce, V, Sn, Mo, F, and high Fe/Mg (Table I). The occurrence of malayaite and tin-bearing garnets at Gumble is one of the first reported in Australia.

Metamorphism. This occurred under peak conditions of $T = 500\text{--}600^\circ\text{C}$, $X_{\text{CO}_2} < 0.30$ and $f_{\text{O}_2} > 10^{-18}$ bars (Mulholland, 1979). The primary calc-silicate minerals grossular, andradite, wollastonite, hedenbergite, and diopside formed early, whereas tin-bearing andradite, epidote, vesuvianite, magnetite, sphene, and tremolite/actinolite probably formed late in this primary stage.

A secondary stage occurred associated with the introduction of large amounts of silica, tin, and fluorine. During this metasomatic stage, fluorite, malayaite, more tin-bearing andradite, opaline silica, cristobalite, and amphibole formed. Conditions at this time were deduced as $T = 300\text{--}500^\circ\text{C}$,

$X_{\text{CO}_2} < 0.30$ and $f_{\text{O}_2} = 10^{-18}$ to 10^{-30} bars (Mulholland, 1979).

Chalcopyrite, cassiterite, marcasite, and nontronite were formed during the last mineral-forming stage under conditions of $T = 200\text{--}300^\circ\text{C}$, $f_{\text{O}_2} = 10^{-30}$ to 10^{-42} bars, pH about 5, and higher f_{S_2} than had earlier prevailed (Mulholland, 1979). No greisenization is found at the granite contact, but an aplite dyke swarm extends up to 2 km out from the granite contact. Malachite, azurite, and chrysocolla were formed as supergene weathering products.

TABLE I - WHOLE ROCK ANALYSES

	GG1	GG2	GG3	GG4	GG5	GG6	GG7
SiO_2	74.50	45.10	11.33	32.16	40.01	48.52	44.21
TiO_2	0.16	0.16	0.16	0.20	0.13	0.15	0.20
Al_2O_3	13.50	4.52	2.13	4.36	3.43	2.44	4.46
Fe*	11.36	18.85	1.18	15.74	10.32	1.53	15.38
MnO	0.01	0.41	0.07	0.66	0.25	0.13	0.21
MgO	0.05	0.16	0.95	1.06	0.93	0.88	1.20
CaO	0.38	29.85	51.57	33.56	38.11	46.29	29.49
Na_2O	3.67	0.08	0.07	0.11	0.04	0.16	0.04
K_2O	4.28	0.13	0.13	<0.01	<0.01	0.09	<0.01
P_2O_5	<0.01	0.02	0.05	<0.01	0.04	0.06	<0.01
L.O.I.	0.72	0.43	32.37	0.46	0.74	0.41	1.33
TOTAL	98.63	99.71	100.01	87.39	94.00	100.66	96.72
Trace elements (ppm)							
Ba	216	64	<20	27	38	<20	53
Rb	319	8	<5	8	7	<5	7
Sr	27	14	883	4	25	201	10
Bi	<2	5	<2	560	555	14	485
Pb	20	14	22	46	19	12	34
W	<10	<10	<10	<10	<10	<10	<10
Th	20	55	97	68	68	77	56
U	15	<1	<1	<1	<1	<1	19
Zr	101	58	29	66	34	19	33
Ta	<5	<5	15	11	10	12	<5
Sn	20	8950	10	1.46%	1.56%	255	1.67%
Ag	<1	<1	<1	23	53	<1	<1
Mo	10	<5	<5	<5	<5	<5	<5
Nb	25	<5	11	8	<5	10	<5
Y	100	15	14	13	18	14	22
La	27	101	163	111	117	142	113
Ce	137	96	234	91	95	95	105
Sm	6	12	7	11	9	6	11
Eu	<1	13	3	11	8	2	16
Tb	<2	<2	<2	<2	<2	<2	<2
Yb	1	<1	<1	<1	<1	<1	<1
Sc	5	5	4	10	6	4	10
V	10	67	30	62	42	30	58
Co	5	23	13	23	15	10	17
Ni	5	29	20	39	31	20	28
Cu	8	11	3	8375	1.43%	58	5630
Zn	35	58	59	94	116	63	105
As	<2	<2	9	<2	<2	11	4
F	1285	650	133	10.25%	3.30%	495	1.08%
B	<5	<5	<5	<5	<5	<5	<5
TOTAL	98.84	100.69	100.14	100.01	100.37	100.78	100.11

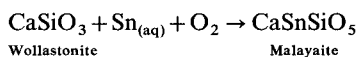
Sample Details

*Total Fe as FeO
 GG1 - Gumble Granite
 GG2 - And-Hd Skarn
 GG3 - Limestone
 GG4 - Flu-Mly-Ccp-And-Hd-Woll Skarn
 GG5 - And-Hd-Woll Skarn
 GG6 - Woll-Gr Hornfels
 GG7 - Mly-Op Sil-Flu-And Skarn
 Analyst: Pilbara Laboratories Pty Ltd., Perth, W.A.
 Most elements analysed by ICP, but with Sn, Cu, Pb, Zn, Ag, Mo, Bi, As and Rb by AAS, F by specific ion electrode, U by fluorimetry and Lu1 by gravimetry.

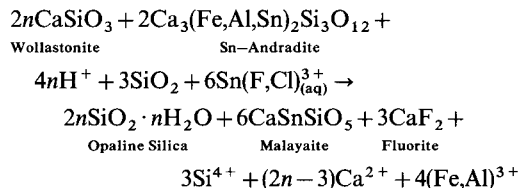
* Now at: Esso Australia Ltd., Minerals Department, 127 Kent Street, Sydney, NSW 2000, Australia.

Malayaite. This tin analogue of sphene (Hosking, 1970, Takenouchi, 1971; Higgins and Ribbe, 1977; Burt, 1978) occurs as disseminated subhedral grains, within tin-bearing garnet-opaline silica-fluorite rock. Optical data were: RI; $\alpha = 1.764$, $\beta = 1.783$, $\gamma = 1.798$ all ± 0.005 , $2V_{\alpha} = 86^{\circ} \pm 5^{\circ}$. X-ray diffraction data correspond with those reported by Takenouchi, 1971; Miyahisa *et al.*, 1975. Electron microprobe analysis gave $\text{SiO}_2 = 22.49 \pm 0.87\%$, $\text{SnO}_2 = 56.38 \pm 0.57\%$, $\Sigma\text{Fe} = 0.15 \pm 0.10\%$, $\text{CaO} = 20.94 \pm 0.43\%$, total = 99.96 to give $\text{Ca}_{0.997}\text{Sn}_{0.999}\text{Fe}_{0.006}\text{Si}_{1.000}\text{O}_5$.

A simple reaction for the formation of malayaite is favoured by many writers:



However, there is evidence that tin-bearing andradite has been involved in the formation of malayaite at Gumble. Malayaite appears to have formed as a result of reaction between a metasomatic fluid rich in Sn, F, H₂O and silica, and tin-bearing andradite and wollastonite. Transport of Sn^{4+} may have been in the form of a fluoride (or chloride), (Eadington and Giblin, 1979). Thus a possible reaction might have been:



Tin-bearing garnets. These range in composition from $\text{And}_{59}\text{Gr}_{41}$ to $\text{And}_{79}\text{Gr}_{21}$ and contain up to 2.87% SnO_2 . Some garnets are zoned both optically and chemically, and in addition to Sn, contain a minor amount of Mg. Tin is found in Fe-rich garnets and is concentrated in Fe-rich zones (Table II). Al-rich garnets and idocrase contain much lower tin (Table II).

It is inferred that tin occurs as Sn^{4+} (0.069 nm ionic radius) in andradite rather than as Sn^{2+} , for two reasons. First, the ionic radius of Sn^{2+} (0.093 nm) is too large to occupy either an Fe^{3+} (0.64 nm) or Al^{3+} (0.053 nm) site. Secondly, from microprobe data, it appears that tin must occur in octahedral co-ordination, since all the dodecahedral positions are occupied by Ca^{2+} , Mn^{2+} , and Mg^{2+} . Charge imbalance caused by Sn^{4+} in Fe^{3+} sites may be balanced by substitution of Mg^{2+} in these Fe^{3+} sites. Amthauer *et al.* (1979) propose that Sn^{4+} and Fe^{2+} substitute for two Fe^{3+} ions. No data on ionic species of iron are available for the garnets at Gumble, but this conclusion appears reasonable.

Discussion of Sn substitution in garnets can be

found in Hosking (1965), McIver and Mihalik (1975), El Sharkawi and Dearman (1966). Dadak and Novak (1965), Mulligan and Jambor (1968).

TABLE II

No. Anal.	TABLE II		
	A	B	C
	7	3	3
SiO ₂	35.23	37.72	34.43
TiO ₂	-	0.53	0.72
SnO ₂	1.87	-	-
Al ₂ O ₃	4.22	17.88	16.06
Σ Fe	22.85*	7.02*	4.92*
MnO	0.09	0.05	0.20
MgO	0.42	0.11	2.04
CaO	33.36	35.96	36.49
TOTAL	98.12	99.27	96.88

Sample Details

A. Typical Sn-garnet with paragenesis: Sn-garnet-malayaite-fluorite-opaline silica.

No. Cations	8 oxygens	8 oxygens	37 oxygens
Si	4.98	2.93	8.56
Al	0.02	0.07	0.44
	5.00	3.00	9.00
Al	0.41	1.57	4.27
Ti	-	0.03	0.13
Sn	0.06	-	-
Fe ³⁺	1.45	0.41	1.62
Mg	0.05	-	0.57
	1.97	2.01	3.99
Mg	-	0.01	0.23
Mn	0.01	-	0.04
Ca	3.03	2.99	9.72
	3.04	3.00	9.99
TOTAL	8.01	8.01	24.98

B. Typical Sn-poor garnet with paragenesis: grossular-diopside-quartz-wollastonite.

C. Typical Vesuvianite with paragenesis: grossular-vesuvianite-wollastonite.

anal. I.R. Mulholland
*Total Fe assumed to be FeO
*Total Fe assumed to be Fe₂O₃

Zoned garnets. Optical and chemical zoning is exhibited by garnets at Gumble. Al and Fe vary antipathetically (fig. 1), and the chemical zones correspond to optical zones. Refractive indices vary correspondingly with the optical zoning, although limited quantitative data have been obtained. Zones range in width from about 0.002 mm to 0.05 mm and some zones (especially Fe-poor zones) are anisotropic. Difference in ionic radius between Fe^{3+} and Al^{3+} may account for the observed anisotropism (Lessing and Standish, 1973; Verkaeren, 1971) and substitution of Sn^{4+} for Fe^{3+} may further increase strain due to ionic size differences and thus be a contributing factor to the anisotropism.

Discussion. Large amounts of material have been introduced from the Gumble Granite to form the skarn rocks. Table I shows whole-rock analyses of some samples from the skarn. Sample GG3 is of unmetamorphosed limestone, containing up to 16% impurities (SiO_2 , Al_2O_3 , FeO , and MgO). Sample GG6 is of metamorphosed but relatively unmetasomatized hornfels. Samples GG4, 5, and 7 are of significantly metasomatized skarn and show enrichment in F, Sn, Zn, Ag, Bi, and Cu, while being relatively depleted in Ce and Sr. It appears that the Gumble Granite (Sample GG1) was the source of the enrichment elements, as it contains high F, Sn, Nb, Ce, Y, Rb, Th, Mo, and U. Zn, Ag, Bi, and Cu are probably late-stage enrichments not present in the unaltered granite, but concentrated at a late stage in the cooling history.

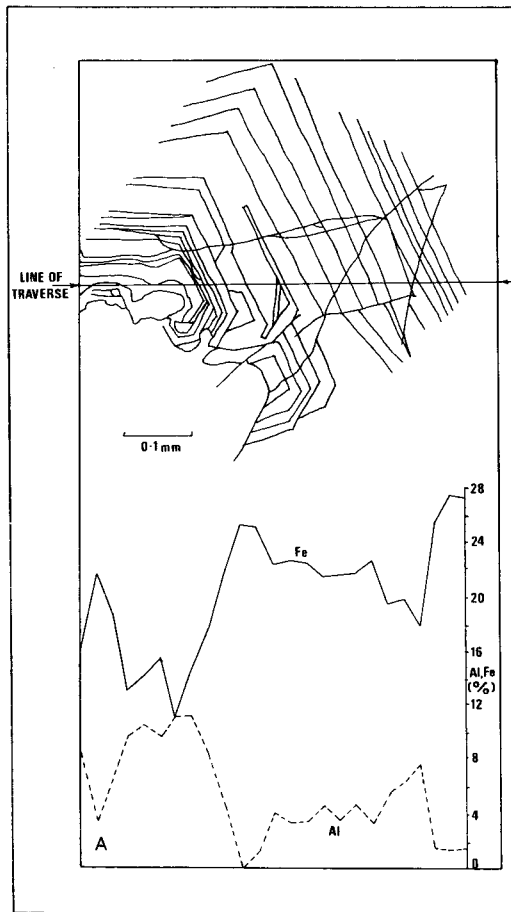


FIG. 1. The antipathetic variation of Fe and Al and correspondence of chemical and optical zones in garnet from Gumble, obtained from an electron microprobe traverse.

From an examination of the assemblages produced it is probable that F and Sn were available for mineral genesis from a time close to the thermal peak until late in the cooling history. The formation of cassiterite with chalcopyrite indicates that Sn was available for longer than F.

The formation of the skarn at Gumble appears to have followed the paths proposed by Atkinson and Einaudi (1978), and Verkaeren and Bartholome (1979), and to some extent, that described by Kwak and Tan (1981), and Ashley (1980). The primary stage involves the alteration of limestone to hedenbergite, andradite, grossular, epidote, idocrase, diopside, wollastonite, and magnetite. The later lower temperature hydrothermal stage produces pyrite (cf. marcasite at Gumble), chlorite, mont-

morillonite (cf. nontronite at Gumble), sericite, and talc from the earlier calc-silicates (Atkinson and Einaudi, 1978) or quartz, magnetite, ferrotremolite/actinolite, ilvaite, babingtonite, fluorite, calcite, and scheelite (Verkaeren and Bartholome, 1979), with additional late-stage Cu, Fe mineralization. The zoning pattern observed at Gumble closely follows that of Reid (1978). Malayaite and tin-bearing garnet were the first two tin-bearing phases to develop in the skarn.

Metasomatic genesis of malayaite at Gumble is favoured, and a three-stage process of tin enrichment is suggested:

1. Tin initially introduced into a zone undergoing skarnification is incorporated into garnet (particularly andradite) and vesuvianite (El Sharkawi and Dearman, 1966; Hosking, 1970).

2. Tin introduced at a later stage metasomatically would be likely to form a mineral with Ca and Si, if available, in which it was an essential component (Hosking, 1970; Takenouchi, 1971; Burt, 1978) especially since the matrix would now be depleted in Al_2O_3 and garnet formation no longer favoured (El Sharkawi and Dearman, 1966). Such a mineral might be malayaite, although other possibilities include stokesite and pabstite (Hosking, 1970).

3. Finally, during the hydrothermal stage, mineralizing agents rich in tin might form cassiterite, stannite, or some other Sn-bearing sulphide, or may be incorporated to a slight extent in lattices of other sulphides (e.g. galena or sphalerite).

At Gumble, the first two stages of metasomatic tin enrichment have occurred, while the third stage may have occurred to a limited extent. It is clear from this study, that the main requirements for a tin-bearing skarn to form are:

1. A granite with a high level of volatiles, rich in F and Sn. This provides the high levels of metasomatic fluid essential for incorporation of tin in silicates since the fluids evolved are rich in complexing agents (F, Cl) and carry metals in complexed form which may be deposited in suitable environments (e.g. a limestone contact) on temperature decrease, fluid dilution, and pH rise.

2. An iron-rich metasomatic environment produced during skarnification.

3. A relatively long cooling history to enable the silicate species (malayaite and tin-bearing garnet) to develop.

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