TIN-BEARING EPIDOTE FROM SKARN IN THE LAND'S END AUREOLE, CORNWALL, ENGLAND

GUY VAN MARCKE DE LUMMEN

*Laboratoire de Minéralogie et Géologie appliquée, Université Catholique de Louvain, 3, place Louis-Pasteur,
B-1348 Louvain-la-Neuve, Belgique*

ABSTRACT

Skarn assemblages in the aureole developed around the Land's End granite (Cornwall, England) contain tin as cassiterite, malayaite and tin-bearing epidote (up to 2.84% SnO_2), titanite (up to 7.0% SnO_2), and amphibole (up to 0.7% SnO_2). X-ray-diffraction data and microprobe analyses indicate that tin occurs in solid solution in the epidote, probably by coupled substitution according to the scheme: $Sn^{4+} + Fe^{2+} = 2 (Fe^{3+}, Al^{3+})$. The introduction of tin into the epidote structure increases the volume of the cell.

Keywords: epidote, tin, coupled substitution, skarn, Cornwall, England.

SOMMAIRE

Des skarns minéralisés en étain affleurent dans l'auréole du granite de Land's End (Cornouailles, Angleterre). Outre la cassitérite, on trouve des silicates stannifères: épidote (jusqu'à 2.84% en poids SnO_2), titanite (jusqu'à 7.0% en poids SnO_2), malayaïte et amphibole (jusqu'à 0.7% en poids SnO_2). Les données de diffraction X et les analyses par microsonde électronique montrent que l'étain se trouve dans l'épidote en remplacement de Al ou Fe suivant le schéma de substitution couplée: $Sn^{4+} + Fe^{2+} = 2 (Fe^{3+}, Al^{3+})$. L'introduction d'étain entraîne un accroissement de la maille.

Mots-clés: épidote, substitution de Fe, Al par Sn, skarn, Cornouailles, Angleterre.

INTRODUCTION

Tin-bearing epidote is rare; it is known from a few localities only (Myer 1965, Mulligan & Jambor 1968, Alderton & Jackson (1978) (Table 1). Epidote that contains up to 2.84% SnO_2 occurs in a skarn at The Crowns near Botallack, Cornwall, England. It has been studied to establish the mode of the substitution of tin in the structure.

GEOLOGICAL SETTING

The St. Just mining district is located on the northwestern flank of the Land's End granite. The metamorphic aureole forms a narrow coastal strip about 0.5 km wide and 5 km long (Fig. 1). Hornfelsic rocks consist of pelites (Mylor Slates) interbedded with basalts that occur as massive or pillow lava and intrusive sheets (Jackson 1976). Thermal contact metamorphism produced cordierite-spotted slates in pelites and amphibolites (greenstones) in some basalts. Next, an intense metasomatism produced the skarns by transformation of hornfelses. Finally, fluids circulating through a fracture system deposited the tin-bearing mineral assemblage (Jackson *et al.* 1982).

Mineralogical and paragenetic studies of skarns (Alderton & Jackson 1978, van Marcke de Lummen 1985) have led to the recognition of two main stages in the process of skarn formation. The first stage is marked by the crystallization of a garnet (grossular-andradite) zone surrounded by an amphibole zone. Locally, the two are separated by a narrow zone of pyroxene. The second stage produced two main mineralogical facies by transformation of the minerals of the first stage. One of these is a vesuvianite facies with or without magnetite; the other is a chlorite – amphibole – tourmaline (or axinite) facies that also locally contains tin-bearing minerals in quantities of economic significance. Besides malayaite $CaSnSiO_5$ and cassiterite, the other tin-bearing minerals are titanite, epidote, amphibole and axinite (van Marcke de Lummen 1985).

EPIDOTE PARAGENESIS

The tin-bearing epidote is associated with cassiterite, malayaite, titanite and amphibole. Titanite contains up to 7.0% SnO_2, *i.e.*, 10 mole % $CaSnSiO_5$. The amphibole is a ferroan pargasite with up to 0.7% SnO_2 (Table 2). Titanite and malayaite are closely associated with cassiterite in a dark brown mixture surrounded by Sn-bearing epidote, Sn-bearing amphibole and a chlorite (Fe-ripidolite) that does not contain tin.

Epidote as well as chlorite and amphibole are considered to have been formed by alteration of garnet during the second stage of skarn formation.

ANALYTICAL METHOD

Analyses were done by using a CAMEBAX electron microprobe (wavelength-dispersion spectro-

TABLE 1. REPORTED OCCURENCES OF TIN-BEARING EPIDOTE

locality	occurrence	paragenesis	% SnO₂ in epidote (number of analyses)	reference
Baja California Mexico	hydrothermal vein	?	0.38 (1)	Myer 1965
Cassiar district northern British Columbia	massive skarn	cpx,am,gr(0.9), qtz,cc	0.80 (1)	Mulligan & Jambor 1968
Chycornish Carn Botallack, Cornwall, England	vein	ax,am(0.1),to	0.16 (1)	Alderton & Jackson 1978
The Crowns, Botallack, Cornwall, England	massive skarn	am(0.7),cas, ti(7.0),chl,mal	up to 2.84 (8)	this study

cpx clinopyroxene, am amphibole, gr garnet, qtz quartz, cc calcite, ax axinite, to tourmaline, cas cassiterite, ti titanite, chl chlorite, mal malayaite. Tin-bearing minerals are underlined (with weight % SnO₂).

meter). Acceleration voltage was 15 kV and probe current (Faraday cage current) was 20 nA. A counting time of 10 s was used. Natural and synthetic silicates and oxides were used as standards: fayalite for Si, wollastonite for Ca, hematite for Fe, corundum for Al, rhodonite for Mn, and malayaite for Sn. Cations other than these were not detected in epidote. The raw data were reduced using a ZAF model correction-program from CAMECA.

COMPOSITION OF THE EPIDOTE

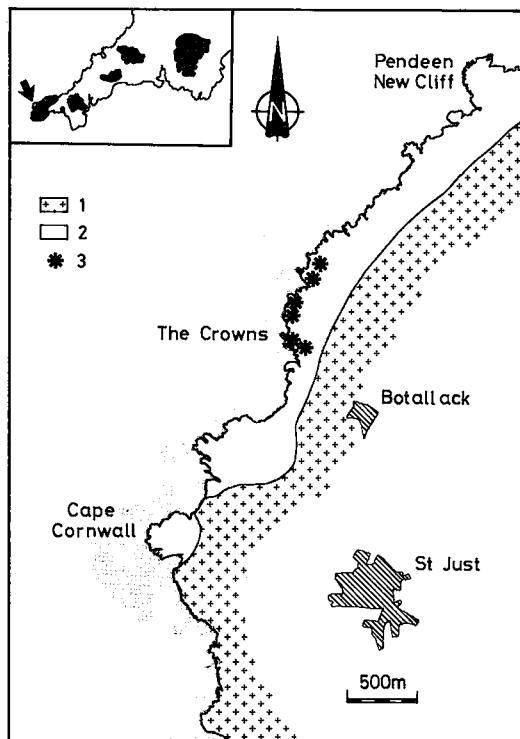Calculation of the mineral formula was made on

TABLE 2. COMPOSITION OF TIN-BEARING MINERALS ASSOCIATED WITH EPIDOTE

	1	2	3	4
SiO₂	36.56	22.87	29.07	0.00
TiO₂	0.14	0.00	31.51	0.54
Al₂O₃	15.59	0.00	3.34	0.00
FeO¹	22.37	0.48	1.02	1.02
Fe₂O₃	6.55	–	–	–
MnO	0.30	0.00	0.00	0.05
MgO	1.34	0.00	0.00	0.00
CaO	11.13	21.91	28.09	0.00
Na₂O	0.64	0.00	0.00	0.00
K₂O	2.18	0.00	0.00	0.00
SnO₂	0.70	55.39	6.71	98.81
F	0.00	–	1.22	–
Cl	0.17	–	0.00	–
H₂O¹	1.87	–	–	–
Total	99.54	100.65	100.96	100.42
O=F,Cl	0.04		0.61	

ATOMIC PROPORTIONS:

O + OH	24	5	5	2
Si	5.90	1.00	0.98	
Al	2.10			
	8.00			
Al	0.87		0.13	
Fe	0.80			
Ti	0.02	0.00	0.80	0.01
Sn		0.97	0.09	0.97
Fe	3.02	0.02	0.03	0.02
Mg	0.32			
	5.03	0.99	1.05	1.00
Ca	1.93	1.03	1.02	
K	0.22			
Na	0.10			
	2.25			
OH	2.00			
F			0.13	

1. amphibole, 2. malayaite, 3. titanite, 4. cassiterite.¹ FeO/Fe₂O₃ and H₂O based on ion proportions. – not determined.

FIG. 1. Schematic geological map of the St. Just mining district. 1: Land's End granite, 2: hornfels, 3: main skarn outcrops.

TABLE 3. COMPOSITION OF TIN-BEARING EPIDOTE

SiO_2	36.69	37.07	36.39	36.36	36.81	36.91	36.91	37.27
Al_2O_3	22.88	23.63	21.86	21.68	22.74	23.17	23.01	23.67
Fe_2O_3[1]	13.60	13.40	14.51	14.25	13.80	12.91	12.60	12.37
MnO	0.44	0.00	0.26	0.38	0.00	0.11	0.41	0.14
CaO	22.51	23.55	22.66	22.33	23.16	23.07	21.91	22.86
SnO_2	1.91	0.63	2.00	2.47	1.64	1.71	2.84	0.47
H_2O[2]	1.84	1.88	1.82	1.82	1.86	1.86	1.87	1.86
Total	99.87	100.16	99.50	99.29	100.01	99.74	99.55	98.64

ATOMIC PROPORTIONS:(13 O + OH):

Si	2.96	2.96	2.99	3.00	2.96	2.97	2.98	3.00
Al	0.04	0.04	0.01		0.04	0.03	0.02	
	3.00	3.00	3.00		3.00	3.00	3.00	
Al	2.14	2.18	2.11	2.10	2.11	2.16	2.17	2.25
ΣFe	0.82	0.81	0.81	0.80	0.84	0.78	0.77	0.75
Sn	0.06	0.02	0.06	0.08	0.05	0.05	0.09	0.02
	3.02	3.01	2.98	2.98	3.00	2.99	3.03	3.02
Ca	1.94	2.01	1.99	1.97	2.00	1.99	1.90	1.97
Mn	0.03		0.02	0.03			0.03	
	1.97		2.01	2.01			1.93	
OH	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Fe_2O_3[3]	11.61	12.40	12.72	12.15	12.16	11.59	9.82	11.71
FeO[3]	1.79	0.91	1.61	1.90	1.48	1.19	2.50	0.59

[1] total iron as Fe_2O_3, [2] calculated after ion proportions, [3] calculated FeO and Fe_2O_3 weight percent (see text for explanation). ΣFe total number of iron cations.

the basis of 13 O,OH per formula (Table 3). The variations in the chemical formula of the clinozoisite – epidote minerals are restricted to the range between $Ca_2Al_3Si_3O_{12}(OH)$ and $Ca_2Al_2Fe^{3+}Si_3O_{12}(OH)$. As shown in Table 3, the epidote composition is clinozoisite$_{10-20}$ – epidote$_{90-80}$.

TABLE 4. X-RAY-DIFFRACTION DATA FOR Sn-BEARING EPIDOTE

hkl	$d(A)_{mes}$	I	$d(A)_{calc}$
2 0 0	4.03	50	4.027
2 1 1̄	3.51	40	3.496
2 0 1	3.21	10	3.201
1 1 3̄	2.91	100	2.912
3 0 0	2.68	70	2.672
3 1 1̄	2.61	50	2.606
1 0 3] 2 0 2]	2.54	25	2.530
1 2 1]	2.46	10	2.462
3 1 3̄	2.41	40	2.401
2 2 0	2.31	15	2.306
1 2 2	2.17	30	2.172
2 2 1	2.12	25	2.115
4 1 2̄	2.08	10	2.075
4 0 0	2.014	10	2.014
2 1 3	1.930	10	1.930
1 2 3] 1 1 4] 2 2 2]	1.881	10	1.881
1 3 2	1.646	40	1.645
4 2 0	1.635	40	1.635
1 1 5	1.582	10	1.581

a 8.936, *b* 5.635, *c* 10.225 Å, β 115.62°, V 464.3 Å³. Standard errors are unknown. Intensities I are estimated visually.

Up to 0.44% MnO is present and is assumed to be Mn^{2+} in substitution for Ca. A Mn^{3+} content as low as 0.20% Mn_2O_3 would produce a strong pink pleochroism (not observed in our samples); the (Fe,Mn)O content can range up to 5% without affecting the optical properties of epidote (Strens 1966).

Although most of the iron presumably occurs as Fe^{3+}, Fe^{2+} is likely to be present in small amount and enters the epidote structure as a substitution for Al as well as Ca (Deer *et al.* 1962). The Sn content in the sample analyzed reaches 2.84% SnO_2.

X-RAY-DIFFRACTION DATA

A single-crystal fragment was examined. A Gandolfi camera was used with Ni-filtered CuKα radiation. The parameters of the monoclinic cell were computed using a FORTRAN program written by J. Gvildys, Argonne National Laboratory, U.S.A. The cell parameters *a, b, c, β* and *V* (unit-cell volume) were calculated using nineteen reflections. The results are listed in Table 4.

Seki (1959) and Myer (1965) demonstrated that the lattice constants of epidote increase with increasing Fe/(Fe + Al) ratio. Using Myer's (1965) determinative curves, the cell parameters of the analyzed Land's End epidote (X_{Fe} = 0.27) should be: *a* 8.898, *b* 5.637, *c* 10.162 Å, *V* = 460.7 Å³. Except for *b*, these calculated values are smaller than the measured ones. The large values of *a, c* and *V* of
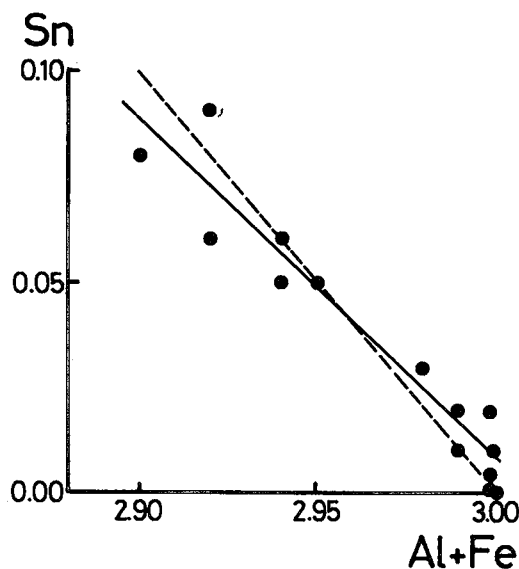
FIG. 2. Plot of Sn *versus* ΣFe + Al. Number of cations calculated on the basis of 13 O,OH per formula. Dashed line: theoretical (Fe + Al): Sn correlation in the case of a replacement of 1 Al^{3+},Fe^{3+} by 1 Sn^{4+}. Solid line: measured correlation ($R^2 = 0.864$).
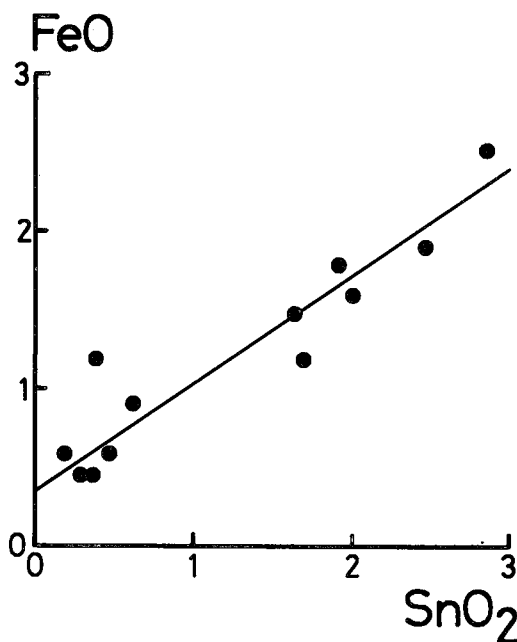

FIG. 3. Plot of calculated FeO (weight %) *versus* measured SnO_2 ($R^2 = 0.94$). See text for explanation of the method of calculation.

the Land's End epidote are most probably due to the presence of tin in its structure. Unfortunately, it was not possible to relate this feature to an exact tin content because the analyzed fragment was zoned (0 – 1.0% SnO_2).

DISCUSSION

Tin in epidote could be accommodated by substitution of $(SnO_4)^{4-}$ for $(SiO_4)^{4-}$, by substitution for calcium (ionic radius 1.20 Å: Whittaker & Muntus 1970) as Sn^{2+} (0.93 Å), or by substitution of Sn^{4+} (0.77 Å) for Fe^{3+} (0.73 Å).

No inverse correlation is shown between Ca or Si and Sn. In the calculated formula, Si is always close to 3.0, and Ca + Mn is close to 2.0. Thus the substitution of Ca or Si by Sn seems to be unlikely. On the contrary, an inverse correlation occurs between Sn and Al + Fe (Fig. 2), indicating that the substitution of Al + Fe by Sn^{4+} is most likely. As no univalent cations such as Na or K are present, charge balance is assumed to be achieved by the presence of Fe^{2+} instead of Fe^{3+}.

Mulligan & Jambor (1968) described an unusually high Fe^{2+} content (1.5 % FeO) in their tin-bearing epidote. Unfortunately, the Fe^{2+}/Fe^{3+} ratio cannot be determined by electron-microprobe analysis. However, the amount of Fe^{2+} and Fe^{3+} in the epidote structure can be estimated with the aid of the stoichiometry of the mineral formula and charge-balance considerations. Assuming that there are 3 Si in the formula, the other cations Ca, Mn, Al, Fe^{2+}, Fe^{3+} and Sn^{4+} are calculated to total 5 cations:

$$x \text{ Ca} + y \text{ Mn} + z \text{ Al} + u \text{ Fe}^{2+} + v \text{ Fe}^{3+} + w \text{ Sn}^{4+} = 5 \qquad (1)$$

and u Fe^{2+} + v Fe^{3+} = ΣFe   (2)
where x Ca, y Mn, z Al, u Fe^{2+}, v Fe^{3+} and w Sn^{4+} are the atom proportions in the formula. As these 5 cations must give 13 positive charges:

$$2x \text{ Ca} + 2y \text{ Mn} + 3z \text{ Al} + 2u \text{ Fe}^{2+} + 3v \text{ Fe}^{3+} + 4w \text{ Sn}^{4+} = 13 \qquad (3)$$

where the coefficient 2, 3 and 4 refer to the number of positive charges assigned to each cation. By subtraction of (1) and (3),

$$v \text{ Fe}^{3+} = 3 - 2w \text{ Sn}^{4+} - z \text{ Al} \qquad (4)$$

Knowing ΣFe, z Al and w Sn from the calculated mineral formula, the proportions of Fe^{2+} and Fe^{3+} can then be estimated from (2) and (4). The results are presented in Table 3.
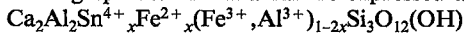
The number of Fe^{2+} ions is systematically higher than the number of Sn^{4+} ions. In the calculation of the epidote formula, Fe^{2+} is first allocated to the 6-fold co-ordination site with Sn in substitution for Al and Fe^{3+}, and the excess is then allocated to the 8-fold co-ordination site with Ca and Mn. The calculated Fe^{2+} increases and (Fe^{3+} + Al^{3+}) decreases

with increasing Sn^{4+} (Fig. 3) following the coupled substitution:

$$Sn^{4+} + Fe^{2+} = 2 (Al^{3+}, Fe^{3+})$$
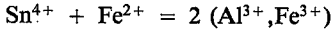
This type of substitution was previously proposed by Mulligan & Jambor (1968) for the introduction of tin in andradite. In allanite, substitution of Fe^{3+} and Al^{3+} by Fe^{2+} is similarly used to correct the charge imbalance arising from the replacement of Ca^{2+} by trivalent rare-earth elements (Deer *et al.* 1962). Substitution of the larger cations Sn^{4+} (r 0.77 Å) and Fe^{2+} (r 0.73 Å) for Fe^{3+} (r 0.64 Å) and Al^{3+} (r 0.61 Å) is responsible for the increase of the lattice constants.

Assuming that the total amount of tin and iron does not exceed one atom per formula, the tin-bearing epidote formula can be expressed as:
$Ca_2Al_2Sn^{4+}_xFe^{2+}_x(Fe^{3+},Al^{3+})_{1-2x}Si_3O_{12}(OH)$
with a maximum of 0.5 for x. In our samples, x reaches 0.09 *i.e.*, 18% of the maximum substitution.

CONCLUSIONS

Tin probably is present in epidote in substitution for Fe^{3+} and Al^{3+}; charge balance is considered to be achieved by the presence of Fe^{2+} according to the coupled substitution:

$$Sn^{4+} + Fe^{2+} = 2 (Fe^{3+}, Al^{3+})$$
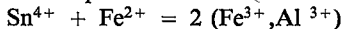
However, owing to the relatively small amount of tin in our samples, this interpretation must be regarded with caution. Our understanding of the mechanism of tin substitution in epidote could be greatly improved using Mössbauer spectroscopy. Unfortunately, the samples available for this study are quite small and not sufficiently plentiful for the use of such a spectroscopic approach.

ACKNOWLEDGEMENTS

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