SHORT COMMUNICATIONS

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Calc–silicate minerals from the Dartmoor granite

DURING a study of the tin and tungsten contents of granites from south-west England (Alderton and Moore, 1981) it was noted that, whilst the typical biotite granites contained < 20 ppm Sn, one sample from Dartmoor contained 54 ppm Sn. At the time it was thought that much of the excess tin in this anomalous sample resided in accessory epidote, but further study has indicated that the mineralogy is more complex than previously thought.

The sample in question is a biotite-muscovite granite which was collected in the vicinity of the Birch Tor and Vitifer Sn–Fe mines in central Dartmoor (grid reference SX680810). In thin section the sample appears unaltered; the biotite is only slightly chloritized and the feldspar slightly sericitized. However epidote, garnet, and titanite are relatively common, typically included within the biotite, occurring as lenses along its cleavage (Fig. 1). Other accessory minerals include apatite, zircon, tourmaline, fluorite, and allanite.

Chemical analyses of the accessory calc-silicate minerals were obtained by energy-dispersive electron microprobe analysis, and are presented in Table 1. Many of the analyses exhibit low analytical totals and therefore preclude precise mineralogical recalculations. Although the low totals could represent poor analyses they could also be explained by the presence of additional, unanalysed components, such as OH and F (as found in other garnets and epidotes from S.W. England by Marcke de Lummen, 1986*a*, *b*) or by a physical problem as suggested for garnets by Coombs *et al.* (1977).

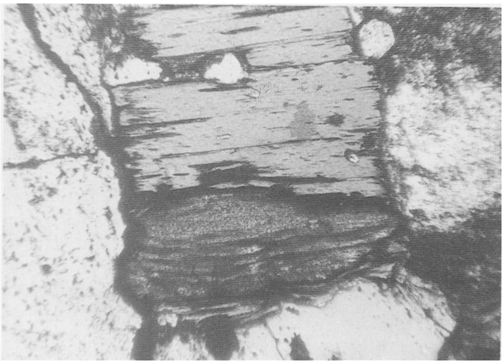

FIG. 1. Lensoid garnet replacing biotite along its cleavage (Birch Tor, Dartmoor). Biotite is surrounded by quartz and feldspar. Length of plate is 1.2 mm.

The garnet is a grandite with a composition close to And 64%-Gr 35%. The epidote has a formula close to $Ca_{2.0}Fe^{3+}_{1.1}Al_{1.8}Si_{3.1}O_{12}(OH)$ and a Ps content of *c*. 38%. Although the Ps content of most natural epidotes is less than 33% (Deer *et al.*, 1982) the experimental evidence (Holdaway, 1972) would support an association of epidote (Ps = *c*. 38%) and garnet (And = *c*. 64%) at temperatures around 600 °C. No tin was detected in either the garnet or the epidote.

The titanite ('grothite') has high Al and Fe contents, and contains appreciable tin. However the Sn content shows considerable variation, from < 0.01 up to a maximum of 4.61 wt.% SnO. It is not immediately clear how the tin substitutes in the titanite structure. Although there is a Sn-analogue of titanite (malayite, $CaSnSiO_5$) and a complete solid solution ($Ti \rightleftharpoons Sn$) exists between the two minerals (Takenouchi, 1971), no correlation between Sn and Ti was observed in the samples analysed here. However a negative correlation between Sn and (Al + Fe) was observed, suggesting that the mode of substitution could be similar to that proposed by Marcke de Lummen (1986*a*) for epidote:

$$Sn^{4+} + Fe^{2+} \rightleftharpoons 2(Fe^{3+},Al^{3+}).$$

The mineralogy and chemistry (barring the high tin contents) of these samples bear a striking resemblance to those described by Tulloch (1979) for regionally metamorphosed granites from South Island, New Zealand. Tulloch (1979) concluded that the calc-silicate minerals mostly had a secondary ('deuteric') origin and formed at temperatures of less than 300–350 °C. It is suggested, particularly from textural evidence, that the Dartmoor calc–silicate minerals also have a secondary,

Table 1: Chemical analyses of calc-silicate minerals from the Dartmoor granite

	1	2	3	4	5	6
SiO_2	34.88	0.47	36.84	0.40	30.48	0.42
TiO_2	1.83	1.46	0.37	0.16	29.78	1.02
Al_2O_3	6.59	0.26	17.90	3.42	5.06	0.81
Fe_2O_3	18.09	1.40	17.06	3.85	1.28	0.26
MnO	0.19	0.06	0.09	0.13	0.04	0.04
MgO	0.15	0.19	0.07	0.10	0.10	0.07
CaO	34.48	0.52	22.88	0.11	28.17	0.53
Na_2O	0.13	0.10	0.19	0.16	0.11	0.09
K_2O	<0.01	0.01	n.d.	-	0.05	0.09
SnO_2	n.d.	-	n.d.	-	1.05	1.29
Total	96.34	-	95.40	-	96.12	-

1 = Garnet. Mean of 7 analyses

2 = Standard deviation (1σ) of garnet analyses

3 = Epidote. Mean of 4 analyses

4 = Standard deviation (1σ) of epidote analyses

5 = Titanite. Mean of 22 analyses

6 = Standard deviation (1σ) of sphene analyses

Notes:

Chemical analyses were obtained, using a Cambridge Mark 5 'Microscan' electron microprobe and a Link systems energy dispersive detector, housed in the Dept of Geology, University College, London. All values as weight %. Total Fe expressed as Fe_2O_3; n.d. = not detected.

hydrothermal origin, although the absence of minerals such as prehnite and pumpellyite would indicate somewhat higher temperatures of formation. The fluid inclusion evidence has shown that these granites interacted with a high-temperature (often > 500 °C), saline fluid (Rankin and Alderton, 1985; Shepherd *et al.*, 1985) and this fluid could have been responsible for the development of the calc-silicate minerals. The main Dartmoor granite appears to have a significantly higher CaO content than the other S.W. England granites (e.g. Edmonds *et al.*, 1968; Darbyshire and Shepherd, 1985; Stone and Exley, 1985) and this may explain why this secondary mineral assemblage is not found in other granites of the province.

These samples provide further evidence of the complex nature of metasomatic activity in the granites and for the involvement of tin during the earliest stages of hydrothermal activity. Subsequent examination of granites from other localities on Dartmoor has revealed that epidote has a widespread occurrence. Definite secondary garnet (as opposed to that of xenolithic origin) has not been found at other localities although some of the widespread garnet recorded as an accessory phase by Brammall and Harwood (1923) could have a similar origin. This evidence, allied with the presence of appreciable Sn in some skarns (El Sharkawi and Dearman, 1966; Marcke de Lummen, 1986*a*) and pegmatites (e.g. Couper and Clark, 1977), and the presence of Sn-bearing phases in fluid inclusions in unaltered granites (Rankin and Alderton, 1982), tends to support current mineralization models (e.g. Simpson *et al.*, 1979; Jackson *et al.*, 1982) where tin is derived from a fluid which exsolved directly from a granite melt, whereas the majority of the hydrothermal fluid has a meteoric derivation.

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Philipsburgite from the Caldbeck Fells and kipushite from Montana, and their infrared spectra

THE material forming the main subject of this paper was collected in 1965 from the dumps around the then recently abandoned mine buildings of Potts Gill or Ghyll baryte mine, Caldbeck, Cumbria, which were situated at NY 320 367. No sign of these workings can be seen today, as the land has been completely reclaimed for agricultural use. All the material collected came from one small boulder of vein quartz and white cleavable massive baryte containing drusy cavities lined with quartz terminations about 2 mm across, partly coated with black wad and iron staining, and with minor pale green fibrous chrysocolla (identified by infrared spectroscopy), presumably pseudomorphous after a fibrous mineral. On the wad and quartz crystals in some of these cavities are sparse to rich coatings of green globular aggregates to about 2 mm in diameter. Many of these spherules are of dark green compact fibrous radiating malachite, in which only traces of zinc could be detected by a microchemical test using diammonium tetrathiocyanatomercurate(II) solution. Other spherules are more spiky than fibrous in appearance, more translucent, and of a paler green colour. These latter gave an infrared spectrum which did not match that of any material available to the authors at the time, and which indicated that the material contained hydroxide, phosphate and arsenate, and was distinct from phosphatian cornwallite, known from the same mine. Microchemical tests indicated the presence of Cu and Zn, and an energy dispersive SEM scan confirmed the presence of major Cu, Zn, As and P.

An X-ray powder diffraction photograph (X 12696) of a sample was taken by Miss E. E. Fejer at the British Museum (Natural History), and shown to match that of a sample submitted previously by Mr W. F. Davidson, but which was otherwise unknown at the time, though related to those of the adelite group.

The discovery of philipsburgite, $(Cu,Zn)_6(AsO_4,PO_4)_2(OH)_6 . H_2O$, from Montana by Peacor *et al.* (1985) suggested a possible comparison, and a sample of the type material in the Smithsonian Institution, off NMNH 161201, was sent to one of us (R.S.W.B.). The infrared spectrum of this sample