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New determinations of tin and tungsten in granites from south-west England

RECENT studies on the development of Sn-W mineralization in south-west England (Sheppard, 1977; Simpson *et al.*, 1979; Jackson *et al.*, 1979) indicate that the hydrothermal fluids dominantly consisted of local meteoric waters. These waters were heated up and drawn into the granite in a convective hydrothermal system. It is proposed that the fluids leached Sn and W from minerals such as the dark micas, during their passage through the granite. These metals were then deposited in veins at higher levels in the system.

This model could be substantiated if the precise concentration and distribution of Sn and W in the granites were known. Several Sn and W analyses of granites from south-west England have previously been published and the values range from 1 ppm to more than 50 ppm for both elements (Butler, 1953; Hosking, 1964, 1965; Bradshaw, 1967; Hall, 1971; Wilson, 1972; Edwards, 1976). However, these workers used a variety of analytical techniques, which could not always be expected to produce accurate results (see, for example, the recent discussion on the analytical problems by Hall, 1980). Because of this uncertainty, several granites and their constituent minerals from south-west England were accurately analysed for Sn and W.

Petrology of the samples. Typical granites were selected from the suite of specimens used in recent regional studies (Alderton, 1976; Moore; 1980). The granites from Cligga Head and St. Michael's Mount are examples of the more evolved protolithionite-muscovite granites whilst the others are examples of the normal coarse, porphyritic, biotite-muscovite granites (Exley and Stone, 1964). All the granites can be considered unaltered, except for minor chloritization of biotite and sericitization of plagioclase feldspar. The texture of the granites is largely a result of metasomatism and recrystallization during the final stages of emplacement and consolidation (Exley and Stone, 1964). These changes caused the growth of K-feldspar, muscovite, tourmaline, topaz, and fluorite in the granite. Petrographic evidence for replacement by these mineral phases is common and it is clear that their growth represents a later phase of crystallization. Muscovite in particular has commonly replaced biotite and protolithionite. As this fabric is cut by the microgranite (elvan) dykes it seems probable that these metasomatic fluids were truly magmatic (i.e. the volatile-rich residuum from the crystallizing granite). This is supported by the isotopic data. Firstly, the granitic muscovites plot in the 'magmatic' field (Sheppard, 1977), and secondly, their growth precedes the earliest mineralization, which has magmatic characteristics (Jackson *et al.*, 1979).

Analysis for Sn and W. Neutron activation is an accurate method for the determination of both Sn (e.g. Hamaguchi *et al.*, 1964) and W (e.g. Atkins and Smales, 1960) down to levels of less than 1 ppm, so this technique was used for the present study. W analysis is straightforward as this element can be measured instrumentally. The analysis for Sn takes longer as a radiochemical separation is involved. The experimental details are as follows:

The Sn analyses were performed under the supervision of Dr G. Gilmore at the University of Manchester Reactor Centre, Risley. A powdered sample (0.5 to 1 g) was first irradiated in an epithermal neutron flux. After decay of ^{24}Na the sample was fused with Na_2O_2 and 10 mg Sn carrier for 10 minutes at 850 °C. After cooling, the cake was dissolved in water and made 2N in H_2SO_4. SnS_2 was precipitated with thioacetamide, washed, dried, and the isotope ^{117m}Sn measured on a high-resolution γ-spectrometer. The chemical yield was determined by re-irradiation for a few minutes and measuring the isotopes ^{123m}Sn and ^{125m}Sn. Analysis of the standard diabase W1 gave 2.9 ppm Sn, with a standard deviation of 0.3 ppm. This is in good agreement with the recommended value of 3.2 ppm (Flanagan, 1973). Standard deviations based on counting uncertainty were generally less than 1 ppm.

The W analyses were obtained by Dr F. Moore at the University of London Reactor Centre, Ascot. A sample (0.1 g) was irradiated in an epithermal neutron flux using a cadmium tube. The γ-ray energies of the radioisotope ^{187}W were measured using a Ge-Li multichannel analyser. Analysis of W1 gave 0.39 ppm W, which is similar to the accepted value of 0.5 ppm (Flanagan, 1973).

The micas were separated by electromagnetic and heavy-liquid techniques. No impurities were visible under 400 × microscopic examination.

Tin. The results of the analyses for Sn are presented in Table I. The Sn content of the granites lies between 12 and 54 ppm. These values are much higher than the world average for granites (2-3 ppm, Hamaguchi and Kuroda, 1969) and seem typical for granites which are associated with Sn mineralization (see Flinter, 1971). The sample with 54 ppm Sn is probably anomalous, and it seems likely that values of 10–20 ppm are typical for the normal biotite-muscovite granites, whilst higher values of 30–40 ppm may be typical for the more differentiated protolithionite-bearing granites (Cligga, St. Michael's Mount).

The analysis of mineral phases from the granite demonstrates that the Sn can be present in a variety of forms. The granites from Cligga and St. Michael's Mount both contain about 10% modal muscovite and 2% protolithionite. In the sample from Cligga almost all (>90%) of the Sn must be located in the micas. Slightly more Sn is found in the muscovite as compared to the protolithionite, and the muscovite plays the major role volumetrically. From similar results Hosking (1964) concluded that replacement of biotite by muscovite would not release Sn to the fluid phase. The granite from St. Michael's Mount has only about 20% of its total Sn in the micas, but this Sn is still relatively concentrated in the muscovite. Minor amounts of cassiterite were noted in this granite so the majority of the remaining Sn must be present at this phase.

TABLE I. *Sn content of granites and micas from SW England (in ppm)*

Sample	Sn content	Locality
Granite	13.1	Buttern Hill (Bodmin Moor)
Granite	53.9	Birch Tor (Dartmoor)
Granite	14.9	Eastern part of St. Austell mass
Granite	19.4	Merrivale (Dartmoor)
Granite	13.5	Holman's Quarry (Carnmenellis)
Granite	34	Cligga Head
Protolithionite	232	Cligga Head
Muscovite	301	Cligga Head
Granite	32	St. Michael's Mount
Protolithionite	36	St. Michael's Mount
Muscovite	66	St. Michael's Mount

The sample from Birch Tor contains small crystals of a Sn-bearing silicate. The exact nature of this phase is yet to be determined but it appears to be a Sn-bearing epidote.

Sn could also be concentrated in sphene, ilmenite (Hamaguchi and Kuroda, 1969), or feldspar (Bradshaw, 1967). However, the mean of 29 ppm Sn for Cornish feldspars quoted by Bradshaw seems rather high and needs confirmation.

The granites from Cligga and St. Michael's Mount have very similar chemical and modal compositions, and their protolithionites are chemically identical (Hall, 1971; Moore, 1980). Because these micas have very different Sn contents it seems that the previously suggested empirical relationships between Sn content of the granite, Sn content of the biotite, and various modal and chemical parameters (Hesp, 1971; Neiva, 1976) do not hold for these samples. The intense metasomatism which caused the recrystallization of the granites could have redistributed the Sn *prior* to the onset of hydrothermal ore mineralization. Variation in fluid composition would result in the formation of different Sn-bearing phases (e.g. Dmitriyev *et al.*, 1962). This could explain the general observation that cassiterite-bearing granites contain biotites with low Sn contents (e.g. Hesp, 1971). Fluorine-rich solutions seem to be more efficient at extracting Sn from biotite (Barsukov, 1967) so the abundance of topaz at St. Michael's Mount might explain why the micas are relatively depleted in Sn when

TABLE II. *W content of granites and micas from SW England (in ppm)*

Sample	No. analysed	Range	Mean	Standard deviation	Locality
Granite	8	12–28	20	5.1	Cligga Head
Muscovite	8	89–115	102	10.4	Cligga Head
Protolithionite	6	40–86	64	14.1	Cligga Head
Granite	16	9–23	14	5.5	St. Michael's Mount
Muscovite	11	78–112	92	11.5	St. Michael's Mount
Protolithionite	8	52–98	73	16.6	St. Michael's Mount
Granite	1	—	13	—	Pendarves (Carnmenellis)
Granite	1	—	17	—	Hawkswood (Bodmin Moor)
Granite	1	—	18	—	Pendarves (Carnmenellis)
Granite	1	—	21	—	Holman's Quarry (Carnmenellis)
Granite	1	—	9	—	Birch Tor (Dartmoor)
Granite	1	—	16	—	Pendarves (Carnmenellis)
Granite	1	—	24	—	Pendarves (Carnmenellis)

compared with those from Cligga. However, experiments to test the feasibility of extracting Sn from biotite under hydrothermal conditions have produced conflicting results (Barsukov, 1967; Hesp and Rigby, 1972; Hosking—quoted in Taylor, 1974).

Tungsten. The W analyses of rocks and minerals are presented in Table II. The rocks contain from 9 to 28 ppm W. These values are several orders of magnitude larger than the world average for granites (probably 1-2 ppm, Evans and Krauskopf, 1970). W does not always appear to be enriched in granites associated with W mineralization, unlike the situation with Sn (e.g. Ivanova and Butuzova, 1968; Shepherd *et al.*, 1976). Analysis of the micas reveals that they have high contents of W. This element, like Sn, tends to be preferentially concentrated in the muscovite. Simple calculations reveal that a large proportion of the W is located in the micas (at least 50% in the samples from Cligga and St. Michael's Mount). No other W-bearing phases have been found but it is possible that the remaining W is located in Fe- and Ti-bearing phases such as magnetite, sphene, and rutile (Evans and Krauskopf, 1970). A sample of K-feldspar from St. Michael's Mount was analysed for W but it contained less than 0.5 ppm.

Conclusions. This study has confirmed that the granites of south-west England are enriched in Sn and W when compared with 'average' granites. A large proportion of the Sn and W is fixed in the micas but Sn can be present in other forms. The exact nature of these Sn-bearing phases (biotite, muscovite, cassiterite, epidote) is controlled by the early, metasomatic recrystallization in the granites. This would control the resulting mineralogy and thus the ease with which the metals could be extracted by the later hydrothermal fluids. One factor influencing the development of Sn and W deposits could therefore be the extent of pre-mineralization, metasomatic activity in the granite.

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