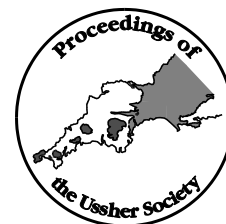


ASPECTS OF THE LITHOGEOCHEMISTRY OF ARSENIC, ANTIMONY AND BISMUTH IN SOUTH WEST ENGLAND

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Ball, T.K., Fortey, N.J. and Beer, K.E. 2002. Aspects of the lithogeochemistry of arsenic, antimony and bismuth in south west England. *Geoscience in south-west England*, 10, 352-357.

As, Sb and Bi are enriched in both sedimentary and intrusive igneous rocks of the south-west peninsula, with higher values for argillaceous compared with arenaceous rocks. All elements are particularly enriched close to mineralisation and it is often difficult to determine an effective background level resulting from widespread low level mineralisation. The granites are also enriched in these elements compared to crustal averages, with two orders of magnitude enrichment of Bi and one order for both As and Sb. As is a relatively mobile element and tends to form broad primary haloes near mineral deposits irrespective of the composition and style of the lodes. It is concluded that high As and Bi are ultimately derived from late stage granite derived mineralising fluids. Sb is enriched in association with volcanic basic rocks.

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INTRODUCTION

There is considerable interest in the distribution of arsenic (As), antimony (Sb) and bismuth (Bi) within soils, groundwater and rocks due to their potential for environmental contamination. Many recent studies concentrate upon the anthropogenic processes that have concentrated or redistributed these elements. However, the natural variability of these elements in rocks and soils in the region is not well recorded and they have not commonly been analysed for during previous geochemical studies. Reasons for this include their limited value for classification or petrogenetic studies and the susceptibility to weathering, particularly in inland exposures.

Nevertheless, analyses for these elements have been more widely undertaken during research into, and exploration for, mineralisation. Much of the data presented in this paper are from previously unpublished drilling investigations carried out by BGS in the 1980s. Although this means that these data are necessarily somewhat areally biased, they do provide a preliminary insight into the likely variability of these elements in a variety of environments. Unfortunately, the same samples were not always analysed for As, Sb or Bi and usually the additional analysed elements were restricted, limiting conclusions which may be drawn from element inter-relationships. Most of the samples were analysed by X-ray Fluorescence Spectrometry, with fairly high limits of detection. The use of such techniques as ICPMS would nowadays improve the detection limits considerably.

Studies of the regional distributions in secondary media have been undertaken using stream sediment data for As (Webb, 1978), panning concentrates for Sb (Jones, 1981), and soils for As, Sb and Bi (various Mineral Reconnaissance Programme publications cited herein; Camm and Moon, 2001).

There has been considerable production of As, Sb and Bi from the mines of the south-west peninsula (Dines, 1956). Dines (1956) observed zonation in the distribution of these elements within the mineralisation sequence and attributed this (partly) to variation according to distance from "emanative centres" that were often related to granites. The modern consensus is somewhat different in that whilst the high temperature mineralisation (Sn, W and Cu) is still regarded as granite controlled, being either within or close to granites, the more distant Pb, Zn and Sb bearing lodes, as well as some enriched in Cu, owe their existence to the presence of sedimentary concentrations which have been remobilised into the lodes (see for example Edwards, 1976; Alderton, 1993; Scrivener and Shepherd, 1998; Clayton *et al.*, 1990).

SUMMARY OF AS, SB AND BI GEOCHEMISTRY

Overview of basic geochemistry of As, Sb and Bi

Arsenic is one of the group V elements of the Periodic Table along with Sb and Bi (and N and P). It is a chalcophile element being usually found in sulphide minerals. They exhibit similar or identical atomic radii (As, 1.5 Å; Sb, 1.6 Å and Bi 1.7 Å), electronegativity (2, 1.9, 1.9) but dissimilar ionic radii (0.47, 0.62, 0.77 Å) (data from Heydemann, 1969).

In a very comprehensive review of the geochemistry of arsenic, Boyle and Jonasson (1973) point out that As is widespread in nature and accompanies deposits of some twenty elements of commercial importance. Taking their information mostly from Canadian sources, they gave a terrestrial abundance of about 3 ppm for As and about 0.7 ppm for Sb, with As/Sb of about 4.3. Amongst igneous rocks they noted little difference between the various classes (see also Onishi, 1969). Granites ranged between 0.18 ppm to 15 ppm As and intrusive basic rocks 0.06 ppm to 28 ppm. Elsewhere granites and other igneous rock series exhibit levels of As consistently about 1-2 ppm (Esson *et al.*, 1965).

Among sedimentary rocks mudstones contain the most As, especially those pyritic and phosphorus rich variants (Boyle and Jonasson, 1973). For a suite of Carboniferous sedimentary rocks from Nova Scotia these authors observed that the carbonaceous shales had the highest range: 1 to 45 ppm, whilst arenaceous and carbonate-rich rocks contain much lower levels. Tourtelot (1964) noted an average for shales of about 13 ppm in offshore marine samples, with a reasonable correlation between increasing C and As.

In minerals antimony occurs most commonly as the Sb³⁺ form having geochemical properties very close to As. Its average crustal abundance is about 0.2 ppm (Boyle and Jonasson, 1984). It can substitute for iron in early -formed igneous minerals and, like As, tends not to be enriched with igneous differentiation such that basic igneous rocks contain similar levels of Sb to acid rocks (0.1 - 0.2 ppm). Strongly chalcophilic, Sb is usually found associated with sulphide minerals (Boyle and Jonasson, 1984) and is often dispersed around hydrothermal galena and sphalerite deposits.

The general geochemistry and behaviour of Bi, with special reference to the south-west peninsula, has been described by Ball *et al.* (1982). Isomorphic replacement of As by Bi is unknown and of Sb by Bi is possible but rare.

Previous work in SW England

Although we do not claim a rigorous study, the only As primary minerals we have found in the rocks studied here are arsenopyrite (FeAsS) and löllingite (FeAs₂), although scorodite (Fe(AsO₄)₂·2H₂O) has been noted near surface at the Hemerdon open pit. Dines (1956) noted that arsenic was produced as a by-product to Sn and Cu extraction. It occurs "in the sulphide zone mainly associated with chalcopyrite and pyrite, but occasionally with cassiterite in the upper part of the tin zone. Though generally found in lodes of E-W trend it is known to occur in cross courses ... and is present in the sulphide impregnation deposits".

The main locality for antimony mineralisation is in the Wadebridge area (Figure 1). The main minerals are stibnite (Sb₂S₃), jamesonite (Pb₄FeSb₆S₁₄) and bournonite (CuPbSbS₃) as well as tetrahedrite ((Cu,Fe)₁₂Sb₃S₁₃). They occur "in N-S cross courses, usually scattered on the fringes of the mineralised areas beyond the lead and zinc deposits and are in places associated with galena, occasionally in workable quantities" (Dines, 1956; Edwards, 1976; Clayton *et al.*, 1990). These lodes contain relatively small concentrations of arsenopyrite.

The main Bi minerals are native bismuth and bismuthinite (Bi₂S₃). Small quantities occur frequently in the early high temperature lodes, but they appear to be much more common in the much later, lower temperature cross courses. Complex mesothermal cross course mineralisation (Beer, 1978) commonly carries substantial quantities (sometimes mineable amounts) usually in association with Ni, Co and U ores. In contrast, the cross course mineralisation of simple type (Ba and F) has no reported Bi minerals. Altered granite shows the highest rock concentrations of Bi. Of the types of alteration studied, only tourmalinisation is associated with enhanced Bi, and this in the late blue tourmalines rather than the earlier (magmatic?) brown tourmalines.

MAIN MINERAL OCCURRENCES

It is generally agreed that the granite intrusions provided the main impetus for mineralisation in Devon and Cornwall. The granites are variably specialised but those enriched in Sn and W seem to be situated close to or at the emanative centres of Dewey (1923) and Dines (1956) and to be characterised by Sn and W rich lode systems. These two authors proposed a general zonation of mineralisation with Sn and W close to the granites and with progressive replacement by Cu, Pb, Zn and finally Sb with distance. However, Scrivener and Shepherd (1998) consider that the Sb, Fe lodes spatially related to Devonian basic volcanic and volcanoclastic rocks were earlier than the granite intrusions.

Modern studies of the paragenesis of veins in part supports this general scheme with lode systems showing successive stages of mineralisation corresponding to decreasing fluid temperatures. Shepherd *et al.* (1985), Scrivener and Shepherd (1998) and Clayton and Spiro (2000) indicated that there were two main processes which involved separating the hydrous saline phases directly from the crystallising magma and later induction and circulation of external crustal fluids partly of meteoric origin. They consider that these partly result from the separation of a parent magmatic fluid into a denser fraction (the tourmaline association) and a lighter CO₂ rich fraction (the greisen event). Early greisenisation was accompanied by tourmaline, cassiterite, wolframite, bismuthinite, löllingite, arsenopyrite and stannite. Then followed sulphides associated with fluorite and Mg-rich chlorite in turn followed by low temperature iron-rich mineralisation. Notably, Sn (and W, As) mineralisation was associated with the early introduction of B whilst fluorite was deposited later.

The main economic mineralisations of Sn, Cu and As are later than, but develop from, the tourmaline and greisen bordered vein complexes noted above. The infillings are multi-episodic and mineralogically complex. Beer (1978) and Beer and Scrivener (1982) recognised four major phases of lode mineralisation: (1)

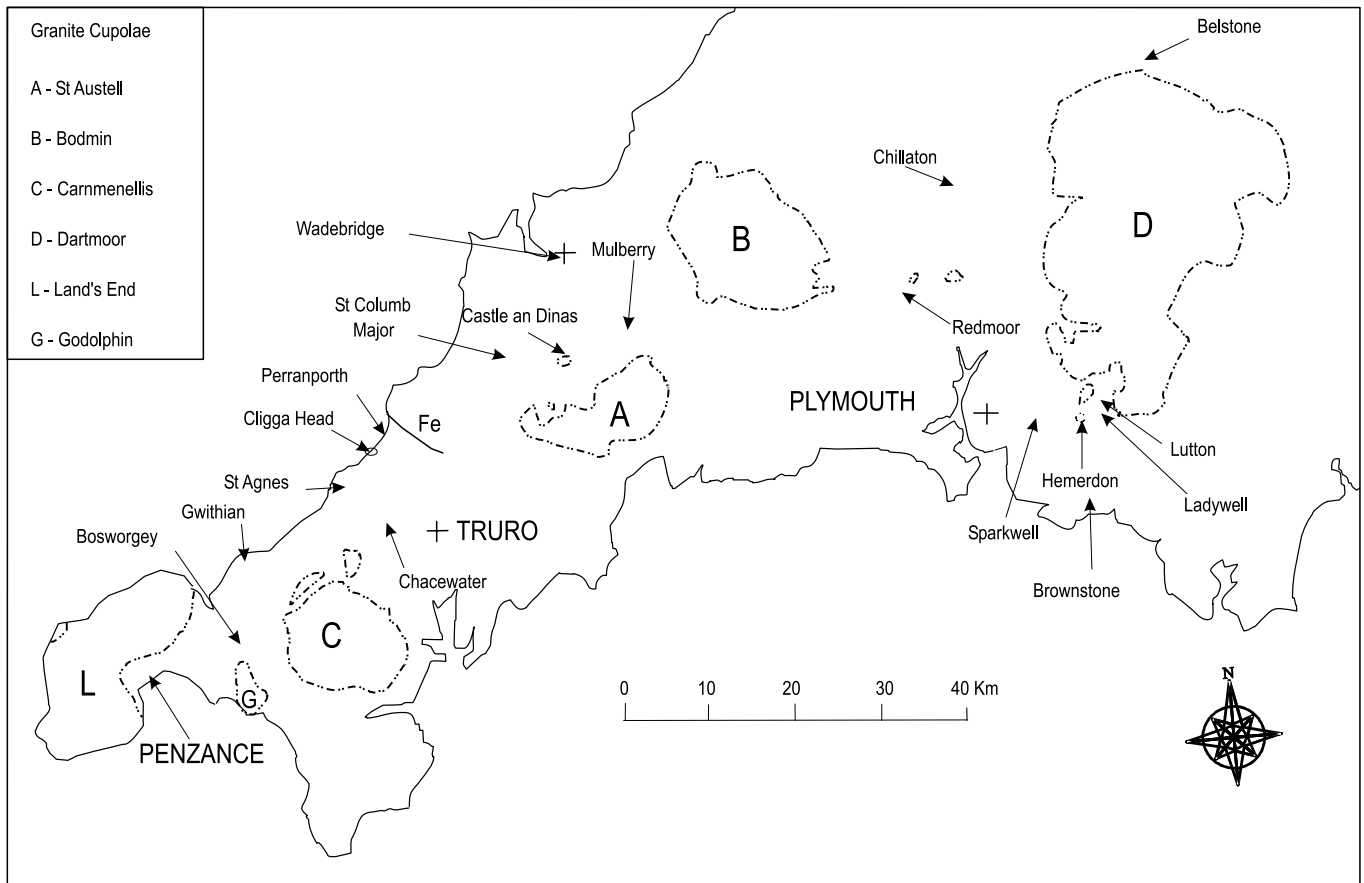


Figure 1. Diagram showing the location of areas discussed. Fe - Perran iron lode.

	Hemerdon area						Background rocks			
	Redmoor	Castle an Dinas	Cligga	Greenstones	Slates	St Agnes	Bosworgey	Cornwall	St Columb	Sparkwell
Number	26	9	8	9	10	9	23	11	7	9
SiO ₂	-0.03	-0.68	0.13	-0.15	0.28	-0.81	0.20	-0.51	0.21	-0.55
Al ₂ O ₃	0.01	0.60	-0.20	0.18	-0.60	0.81	-0.14	0.57	-0.08	0.21
TiO ₂	0.04	0.85	-0.01	0.40	-0.07	0.82	-0.13	0.44	0.05	-0.50
Fe ₂ O ₃	0.01	0.23	0.05	-0.22	0.52	0.60	-0.20	-0.03	-0.53	0.01
MgO	0.05	-0.24	0.58	0.36	-0.67	0.52	-0.67	-0.51	-0.35	0.71
CaO	-0.08	0.13	0.05	0.09	-0.44	0.85	-0.30	-0.34	0.50	0.07
Na ₂ O	-0.16	0.16	0.26	-0.37	-0.78	0.64	-0.14	-0.03	0.29	-0.32
K ₂ O	0.24	-0.47	-0.33	-0.02	-0.39	0.72	0.52	0.71	0.21	0.66
MnO	-0.15	-0.25	-0.18	0.41	-0.83	-0.17	-0.39	-0.05	-0.27	-0.16
P ₂ O ₅	-0.18	0.47	0.44	0.05	0.76	0.61	-0.37	-0.18	0.19	-0.01
LOI	-0.02	0.81	-0.47	-0.08	0.78	0.75		0.21	-0.26	0.20
B	-0.05	0.34	0.58	-0.60	-0.05	0.70	0.79	0.69	0.45	0.67
Ba	0.10	-0.17	-0.52	-0.39	0.23	0.63	0.68	0.48	0.04	0.17
Be	-0.06	0.85	0.68	0.70	0.55	0.73	-0.35	0.51	0.23	0.12
Bi	0.92	0.80	0.64	0.43	0.39	0.17		-0.12	-0.13	-0.28
Ce	0.49	-0.06	0.54	-0.24	-0.10	0.79	-0.28	0.44	0.07	0.25
Cl	-0.10	0.86	-0.27			0.32		0.11	0.16	0.82
Co	0.24	0.70	0.10	0.41	0.01	0.49	-0.41	-0.62	-0.35	-0.43
Cr	0.02	-0.51	0.10	0.60	-0.05	0.84	0.38	0.35	0.28	0.66
Cs	-0.06	0.14	0.24	-0.53	-0.10	0.44	0.22	-0.13	0.87	0.86
Cu	0.48	0.91	0.87	0.67	0.08	0.62	0.14	-0.05	0.25	0.95
F				0.35			-0.05			
Ga	0.23	0.41	0.29	0.34	-0.32	0.77	0.42	0.56	0.07	-0.19
Hf		0.66					0.21			0.62
La	0.12	0.04	0.15	-0.34	-0.08	0.77	0.06	0.36	0.33	0.66
Li	-0.07	-0.11	0.68			0.62	-0.24	0.04	-0.37	0.80
Mo				0.71						0.86
Nb	-0.05	0.84	-0.26	-0.01	-0.03	0.82	0.08	0.57	0.10	-0.50
Ni	-0.16	0.46	0.13	0.77	-0.03	0.65	-0.01	-0.17	-0.59	-0.49
Pb	-0.00	0.12	0.87	0.71	-0.25	0.36	0.37	0.45	-0.43	0.16
Rb	0.08	-0.12	0.34	-0.42	-0.07	0.51	0.59	0.78	0.97	0.92
S	0.43		0.37	0.47		0.61	-0.37	0.34	-0.33	
Sb				-0.34	-0.53		0.63			
Sc		0.77		0.87			0.39			-0.26
Sn	0.16	0.89	0.31	0.03	0.04	0.29	0.58	0.85	-0.17	0.85
Sr	-0.05	0.65	0.60	-0.16	-0.32	0.86		0.38	0.30	-0.03
Ta							-0.53			
Th	0.19	-0.10	0.75	-0.61	-0.02	0.81	0.28	0.72	0.20	0.04
U	-0.18	-0.12	0.77	-0.41	0.54	0.17	-0.04	-0.12	0.33	0.41
V	-0.01	0.89	0.55	0.75	-0.33	0.72	-0.00	0.17	-0.04	-0.20
W	0.58	0.58	-0.01	0.17	0.82	0.34	0.93	0.84	-0.14	-0.10
Y	0.03	0.77	-0.01	0.72	-0.45	0.59	-0.13	0.32	0.15	0.62
Zn	0.10	0.62	0.66	0.29	0.07	0.56	-0.03	0.20	-0.41	0.02
Zr	-0.05	0.49	-0.10	0.07	-0.30	-0.04	-0.30	0.05	0.37	-0.26
As										
Mean	111	61	130	580	379	63	222	17	16	98
Median	45	24	45		318	44	71	14	14	34
Min	2	4	13	2	159	5	14	6	7	7
Max	1352	223	585	2132	628	193	1900	37	318	501
Sb										
Mean		No Data		19	18	No Data		3	No Data	
Median				12	16			2		
Max				51	32			9		
Min				3	7			1		
Bi										
Mean	5	6	6	32	27	5		2	2	<1
Median	3	2	5	27	33	4		2	2	<1
Max	41	29	14	62	65	12		3	3	1
Min	<1	<1	<1	4	3	2		<1	<1	<1
As/Sb										
Mean				58	3		50			
Max				236	6		235			
Min				0.90	0.30		4.90			

Table 1. Product moment correlation coefficients between As and other elements, and summary statistics for As, Sb and Bi, in the contact metamorphic aureoles surrounding named granite cusps and in background rocks. All concentrations are ppm.

An early phase of extensive tourmalinisation of slates surrounding the lode fractures and with the introduction of disseminated fine cassiterite. (2) Fracture infilling of quartz and a little chlorite with cassiterite, wolframite, pyrite and much arsenopyrite. (3) Further quartz and chlorite introduction with pyrite, chalcocopyrite, more arsenopyrite and a little galena, sphalerite and siderite. (4) Filling of fractures with fluorite and siderite with minor pyrite and chalcocopyrite.

N-S trending cross course veins are thought to be later than the granites and are of two types (Beer, 1978): (1) complex Pb-Zn-Ag-Ni-Co bearing types can carry Bi and sometimes substantial As concentrations; (2) the simple type dominated by barite or fluorite is generally free of Bi and arsenopyrite but can contain tetrahedrite (e.g. the Teign valley lodes: Beer *et al.*, 1992). Some of the mines that formerly worked simple cross-courses however, did produce substantial quantities of As, although it is uncertain what the structural relations are (e.g. Wheal Fortune; Dines, 1956).

Skarns developed near the contacts with granite bodies are usually hosted within basic igneous or calcareous sedimentary rocks with the presumption that the deposits require the energy and chemical input from a granite intrusion to mobilise mineralisation (Beer and Scrivener, 1982; Scrivener and Shepherd, 1998). They invariably contain arsenopyrite along with cassiterite, magnetite, and copper minerals (Dines, 1956). Bi minerals are often reported but there is a paucity of Sb minerals. However, the enigmatic Great Perran Iron Lode is remote from granites and drilling into calc-silicate rocks of skarn-type in the vicinity revealed both Sn and Sb enrichment (9 samples Sn: mean 1590, range 4-3390 ppm, Sb: mean 62, range 6-98 ppm).

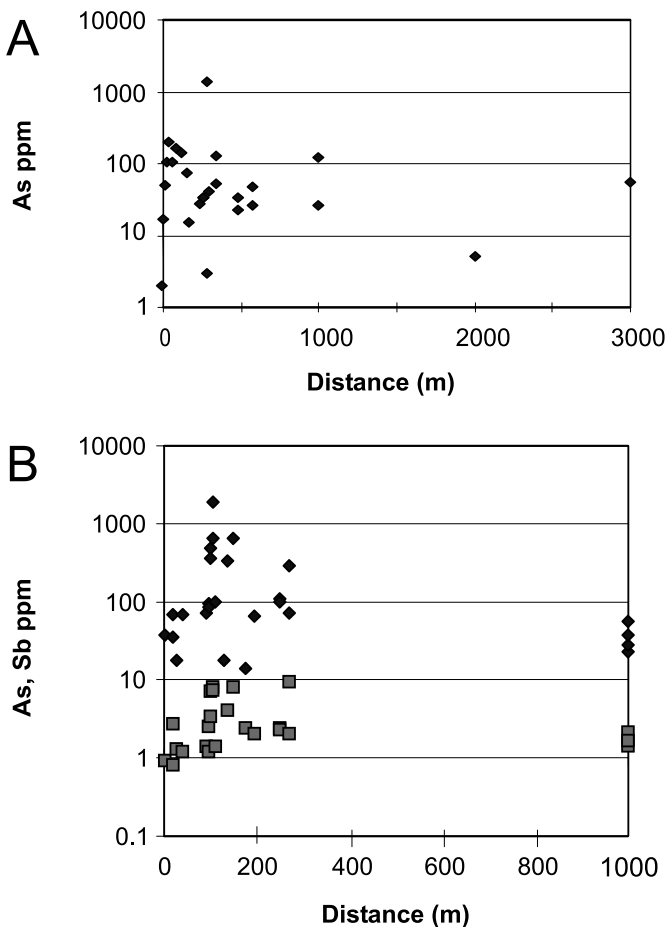


Figure 2. Distribution profiles for (A) As in the Redmoor aureole, and (B) for As and Sb in the Bosworgey aureole pelites. As data as diamonds and Sb as squares.

CONTACT METAMORPHISM AND METASOMATISM

Pervasive alteration of both granites and contact rocks is generally consistent with the mineralising sequences outlined above although it is likely that even earlier mineralising events occur. For example in the granites, chloritisation of biotites and sericitisation of plagioclase are accompanied by the introduction of fluorite, calcite, topaz, cassiterite and sulphides (pyrite, sphalerite and chalcocopyrite) whilst K-feldspars remain unaltered. With more intense alteration, greisens of two types develop: a quartzose variety with little fluorite, hydrothermal tourmaline or significant sulphides and a virtually quartz free variety rich in bundles of tourmaline prisms and angular pockets of fluorite along with arsenopyrite, bismuthinite and galena (e.g. Ball and Basham, 1984).

In the granite aureoles a rather simple thermal zonation is often overprinted by hydrothermal alteration. Zones of spotted slate with chlorite (>400 m), biotite (400 m-30 m) and then K-feldspars (<10-30 m) are observable. The relation with textural evolution is described by Ball *et al.* (1998). Four styles of subsequent hydrothermal alteration affect these rocks: (1) kaolinisation without noticeable arsenic minerals, (2) sericite-chlorite alteration with pyrite and sparse arsenopyrite, (3) fluorite introduction, a minor component of most of the granites investigated is most common out to about 50 m from the contact and is associated with white mica, quartz, pyrite, chalcocopyrite, sphalerite and arsenopyrite, (4) tourmalinisation, accompanied by pyrite, pyrrhotite, chalcocopyrite, arsenopyrite and sphalerite.

Table 1 summarises the statistical correlations between As and the other elements in the metamorphic aureoles around either mineralised cusps or emanative centres. As correlates with a number of granite-sourced elements of former economic value. For the Sn-associated Redmoor dyke the correlation is mostly with Bi and W. In the W-Sn specialised Bosworgey cusp with B and W; at Castle an Dinas (W) with Bi - Cu - Sn and V; at Cligga Head (W) with Cu and Pb; in slate at Hemerdon (W) with W. Where data allow, the correlation with Sb is inconclusive.

The distribution profiles for As for the Redmoor aureole, and As and Sb for the Bosworgey aureole are shown in Figure 2. Stone and Awad (1988) note that in the Mylor Slate Formation, the As values decline with distance from the contact of the Tregonning Granite, in concert with a range of other elements including the alkalis and tin. However, for the smaller Porthmeor cusp, there was no enrichment with proximity to the contact. Henley (1970) gives a median value of 30 ppm for As for 96 samples of the sedimentary rocks of the Perranporth area, with medians of 42, 21 and 35 ppm respectively for slates, sandstones and chert-banded slates of the Gramscatho Formation, whilst the Penhale and Ligger Slates gave a median of 33 ppm. Using discriminant analysis, Henley (1970) observed a perceptible but irregular increase in As towards the granite but concluded that it was "probably due to local wall rock enrichment near hydrothermal veins".

Calc-silicate rocks at Belstone (Figure 1) lie within the aureole of the Dartmoor Granite. The Belstone Mine worked chalcocopyrite with arsenopyrite and pyrite within richly garnetiferous beds (Dines, 1956). Drilling (Beer *et al.*, 1989) penetrated Carboniferous mudstones of the Crackington and Meldon Chert formations, which exhibited slightly enhanced values of both As and Bi (medians for As are 23 and 18 ppm respectively for 21 and 12 samples respectively, whilst for Bi medians for both formations are 3 ppm).

Log probability plot analysis (e.g. Sinclair, 1975) for the calc-silicates reveals a single lognormally distributed population of As values (Table 2) but a bimodal distribution for Bi. The largest population (92%) of the Bi values (Table 2) is no more than slightly high for sedimentary rocks whilst the remainder are definitely anomalous. The calc-silicate rocks contain large amounts of the boron mineral axinite (Beer *et al.*, 1989) which indicates pervasive introduction of fluids from the nearby granite and suggesting that any original As signature within these rocks has been entirely overprinted by the granitic metasomatism. It is

Rock type	Element	Samples	Mean (ppm)	-1 SD value (ppm)	+1 SD value (ppm)
All calc silicate samples	As - all samples	320	302	78	1300
	Bi - main population	294	5.5	2	14
	Bi - second population	26	190	78	280
Meldon Chert Formation	As- main population	204	130	66	932
	As - second population	36	1260	590	2800
	Bi- main population	204	2.3	0.8	5.6
	Bi - second population	36	28	10	74

Table 2. Summary of analyses of As and Bi from sedimentary rocks in the Belstone area. Probability analyses may be used to test whether a data-set is normally or lognormally distributed, and also whether the distribution is polymodal and if so, to indicate the statistics of the different sub-populations.

possible that much of the Bi content is original, the higher population only reflecting the later mineralization

The Meldon Chert Formation exhibits bimodality for both As and Bi (Table 2). If the lower populations represent the original sedimentary compositions then the values are high but not exceptional.

IGNEOUS ROCKS

Granites

The data are insufficient to characterise each type of granite according to the various classes (e.g. Exley and Stone, 1966; Hawkes and Dangerfield, 1978). However, our pooled As data for all granites identify two lognormally distributed populations, the lower, describing 60% of the data gives a mean of 12 ppm (-1 S.D. of 4.5, +1 S.D. of 32 ppm) whilst the higher, mostly tourmaline bearing, gives a mean of 205 ppm (50, 950).

Data for Sb are sparse. In the Bosworgey Granite 5 samples ranged from 3 to 6 ppm, the highest values being in those samples with the highest B content (Ball and Basham, 1984). There are Sb but no As data for the Godolphin Granite and these ranged between <1-5 ppm (mean 1.5, S.D. 1.17) for 97 samples (Beer *et al.*, 1986a). Sb showed no significant correlations with any of the other elements analysed (Ce, Ba, Sn, Pb, Zn, Cu, Ca, Ni, Fe, Mn, and Ti).

Data for Bi has already been published (Ball *et al.*, 1982). In the Bosworgey Granite cusp high values of Bi were noted in the marginal zones of the granite. An intergrowth of native bismuth and bismuthinite was recognised as the most important host for Bi, the two minerals being common as inclusions within arsenopyrite. Altered granite shows the highest concentrations. Increase in Bi was associated with rocks containing late blue tourmalines, but not with the earlier (magmatic?) brown tourmalines. Log probability plot analyses were given for data from the Lands End and Carnmenellis granites, with medians of 1.2 ppm for the fresh granite and 4.7 ppm for the tourmalinised variants. A decline in the Bi content was observed in kaolinised lithium mica granites.

Basic igneous and volcanoclastic rocks

A borehole intersected a mineralised zone near Lutton (Figure 1) in which high values of Bi, Ag, W and U were noted (Beer *et al.*, 1981). Rocks penetrated were intrusive greenstone, basic tuffs and Middle Devonian slates. Samples from zones with no obvious mineralisation are summarised in Table 3.

Two boreholes drilled in the Ladywell area (Figure 1) to investigate soil geochemical anomalies penetrated basic tuffs about 4 km from the nearest Dartmoor Granite outcrop. The Sb values in the tuffs in one borehole are higher than those in the other, although the As values are about the same. Sb exceeds the As contents suggesting that there is Sb mineralisation. Summary statistics for the tuffs are given in Table 3.

Location	lithology	No.	Sb mean	Sb max.	Sb min.	As mean	As max.	As min.	As/Sb mean	As/Sb max.	As/Sb min.
Lutton ¹	Greenstone	9	6.55	12	4	55	102	28	8.9	20.4	4
Lutton ¹	Basic tuffs	37	9.3	34	0.5	122	1218	4	18	121	2.8
Chillaton ²	Greenstone	29	6	8	3	48	128	3	n.d.	n.d.	
Chillaton ²	Basic tuffs	4	1			11	18	3	n.d.		
Chillaton ²	Basic lavas	13	n.d.			6.3	41	2	n.d.		
Ladywell ³	Basic tuffs		29.5	136	<1	13.4	49	1	n.d.		
Ladywell ³	B/H1										
Ladywell ³	Basic tuffs		2.3	9	<1	16.3	30	4	n.d.		
Ladywell ³	B/H2										
Mulberry ⁴	Basic tuffs	37	n.d.			23	136	3	n.d.		

Table 3. Summary of analytical data for As and Sb in basic igneous rocks. Sources: (1) Beer *et al.* (1981). (2) Leake *et al.* (1994). (3) Leake and Norton (1993). (4) Central Mining Finance Ltd (1982). Values in ppm.

SEDIMENTARY ROCKS

Data are summarised in Table 4. Mudstones from the Lutton area have very high values of As and Sb. It is uncertain whether these are related to the nearby mineralisation or a sedimentary concentration related to the presence of basic tuffs in the sedimentary column. It is also possible that the data for the Crackington Formation are affected by the presence of mineralisation in the nearby lodes of the Belstone Mine.

Drilling into the Lower Devonian Meadfoot Slates at Royalton (Figure 1, Beer *et al.*, 1986b) revealed evidence for low tenor Sn mineralization. Sb showed no significant correlations with any of the other elements, which were Ce, Ba, Sn, Pb, Zn, Cu, Ca, Ni, Fe, Mn, and Ti.

Multi-element relationships for the Middle Devonian Mylor Slate Formation given in Table 1 accord with data for the same formation given by Stone and Awad (1988) who found a mean of 17 ppm As for background slates around the Tregonning Granite aureole and a range of <1 to 15 ppm for the aureole of the Porthmeor Granite cusp.

It is recognised (e.g. Edwards, 1976; Beer and Scrivener, 1982; Scrivener and Shepherd, 1998) that there are specific metal-rich horizons within the Devonian and Carboniferous. These occur in particular within the middle Devonian volcanic rocks and the lower Carboniferous black shales and cherts with basic tuffs. These are characterised mostly by the presence of bedded Mn ores but are otherwise enriched at sub-economic levels in Pb, Zn, U, Cu, Mo, As and Sb.

CONCLUSIONS

Most sedimentary rocks showed As concentrations that accord with published "world" averages. Concentrations of about 15 ppm were recorded for mudstones, and perceptibly higher values of slightly above 20 ppm in black shales. Pelites associated with basic tuffs and cherts in the Middle Devonian and Lower Carboniferous commonly have As values of >30 ppm. Sandstones are lower and accord with dilution of the argillaceous component by quartz.

Among the igneous rocks, granites showed As concentrations above world averages at about 12 ppm, with marked increases associated with alteration, especially tourmalinisation. This type of

	Number	Sb			As		
		Mean	Median	Max.	Mean	Median	Max.
Chillaton, Lr. Carboniferous ⁽⁵⁾							
Pelites	23	4		8	<1	30.5	107
Cherts	20	-		-	-FS	7.8	43
Belstone, Lr. Carboniferous ⁽⁵⁾							
Crackington Fm.	12					26	23.5
Lutton, Upper Devonian ⁽¹⁾							
Slates	21	12.7	11.5	26	2	353	234
Ladywell, Upper Devonian ⁽³⁾							
Slates, B/H2	-	0.6	<1	3	<1	13.1	13.8
Slates, B/H3	-	2	<1	9	<1	18	15
Royalton, Middle Devonian ⁽⁶⁾							
Meadfoot Slates	-	2.7	3	10	<1		
Mulberry, Middle Devonian ⁽⁴⁾							
Meadfoot Slates	100					33	28
Tuffaceous Slates	38					36	30
Brownstones, Lower Devonian ⁽⁷⁾							
Staddon Fm. Pelites	79					12	12
Staddon Sandstones	39					6.5	4

Table 4. Sb and As data for sedimentary rocks. Sources: See also Table 3. (5) Beer *et al.* (1989). (6) Beer *et al.* (1986a). (7) Leake *et al.* (1982a, b). Values in ppm.

alteration also effects the aureole rocks and introduces high levels of As into a zone surrounding granite cusps that extends to about 500 m. Basic lavas and tuffs exhibit levels of about 10 ppm. Intrusive greenstones show much higher concentrations, but they appear to be very susceptible to alteration with, in particular, widespread and pervasive alkali metasomatism (Floyd and Lees, 1972; Ball *et al.*, 1998).

Bi largely mirrors the behaviour of As. Mineralogically it is most common as inclusions of discrete Bi minerals included in arsenopyrite. By comparison with world averages it is enriched in the granites (1.5 ppm) and increases markedly with tourmalinisation (to about 5 ppm), but seems unaffected by greisenization or haematization. Even higher levels are seen within the aureoles surrounding granites and in mineralised zones with values of several tens of ppm (see also Ball *et al.*, 1982).

The widespread alterations of granite and aureole may be regarded as simply versions of the more confined channelling that gives rise to lode mineralisations. Greisenization and tourmalinisation of both granites and aureole rocks often affect the same specimens and are accompanied by introduction of substantial quantities of As and Bi but only low levels of Sb.

Sb data are sparse. For unaltered granite, a mean of about 1-2 ppm accords with world averages but again there is a slight increase with increasing tourmaline content. Within the aureoles a spatial and numerical correlation with As suggests a similar behaviour with metasomatism, but the concentrations are low. Most of the mudstones are low in Sb, the exceptions being those associated with some volcanoclastic rocks that also exhibit moderately high As. The highest values were observed in volcanic rocks and associated shales of middle Devonian and lower Carboniferous age and with dispersion around stratigraphically associated mineralised zones of the same age.

It is concluded that high As (and Bi) is ultimately sourced from late stage granite derived fluids on the basis of its association with those elements that, under the present knowledge, are granite derived. Sb is enriched in association with volcanic basic rocks.

ACKNOWLEDGEMENTS

We are grateful to Drs C.J. Moon, R.K. Shail and D. Pirrie for many very helpful comments on an earlier version of the paper, which is published with the approval of the Director of the British Geological Survey.

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