

## Geochemistry of the Cornubian tin province

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**Abstract.** The exposed crust of the Cornubian massif in S.W. England has been systematically sampled, and the rocks analysed for a wide range of major and trace elements. Geochemically this region is highly anomalous, with three elements (boron, lithium, tin) occurring at levels several times higher than the average for other parts of the continental crust. The greatest degree of enrichment is found in the rocks of the Cornubian granite batholith, but it is also present in rocks pre-dating the formation of the batholith. The mineral deposits of Cornubia derive their trace elements from different sources: B and Sn from the granite, and Cu and S from the country rocks.

South-west England ("Cornubia") is a highly distinctive metallogenetic province. It is one of the world's major tin-producing areas, and over the past few centuries it has supported over one thousand tin and copper mines. Boron is likewise so abundant that in many of the rocks of the region tourmaline is a major rock-forming mineral, rather than the unusual accessory that it is elsewhere.

Although the mineral deposits of the region have been studied for many years, there is a comparative lack of information on the geochemistry of their host rocks, and consequently it is difficult to evaluate the various mechanisms by which element enrichment can have arisen. Much data exists for particular elements or for particular rock types (Hall 1973; Edwards 1976; Ahmad 1977; Darbyshire and Shepherd 1985), but there is a need for a comprehensive geochemical study of the whole Cornubian crust, including all the major lithologies.

Many authors have commented on the close association between the mineral deposits and the large granite intrusions of the area, and have described the distribution of deposits in terms of "emanative centres", located in or near the granites. It is less clear whether the role of the granites was solely that of a heat source, or whether they are also the material source of the ore-forming elements.

The intention of this study was to characterize geochemically each of the major rock units making up the

exposed crust of the region, and in particular to establish whether the apparent richness in boron, tin and other elements is a characteristic of all the rocks of the region, or just of the Cornubian granite batholith, or just of the hydrothermal vein deposits.

The geology of S.W. England is shown in Figure 1. The sedimentary succession ranges from L. Devonian to U. Carboniferous. Accumulation of sediments was accompanied by volcanicity and in the later stages by folding, and at the end of the Carboniferous a major granite batholith was intruded into the area. Tectonically the province lies on the northern edge of the Variscan (Hercynian) orogenic belt, and the tectonism and granite formation are Variscan. The area which is the subject of this study is delimited to the south by the metamorphic and ophiolitic complexes of the Lizard and Start Point, and to the east by the outcrop of post-Variscan (Permian and later) sediments.

### Method of study

The plan of this study was to collect systematically all the rock types which comprise the Cornubian massif at the present level of exposure, to analyse them for major and trace elements, and to use the data to estimate the average crustal composition of the region before and after granite formation.

The massif was sampled according to a systematic scheme, as follows. The whole region was divided into the 10 × 10 km squares of the UK National Grid, and from each square a typical specimen was collected of the predominant lithology in the lithostratigraphic unit with the largest extent. In the granite areas the specimen collected was of the most widely distributed petrographic type. Supplementary specimens were collected to ensure representation of rocks which were not sufficiently widespread to predominate in any single 10 × 10 km square, i.e. volcanic rocks, limestones and cherts. A high priority was given throughout to freshness, i.e. freedom from weathering and hydrothermal alteration. This last consideration

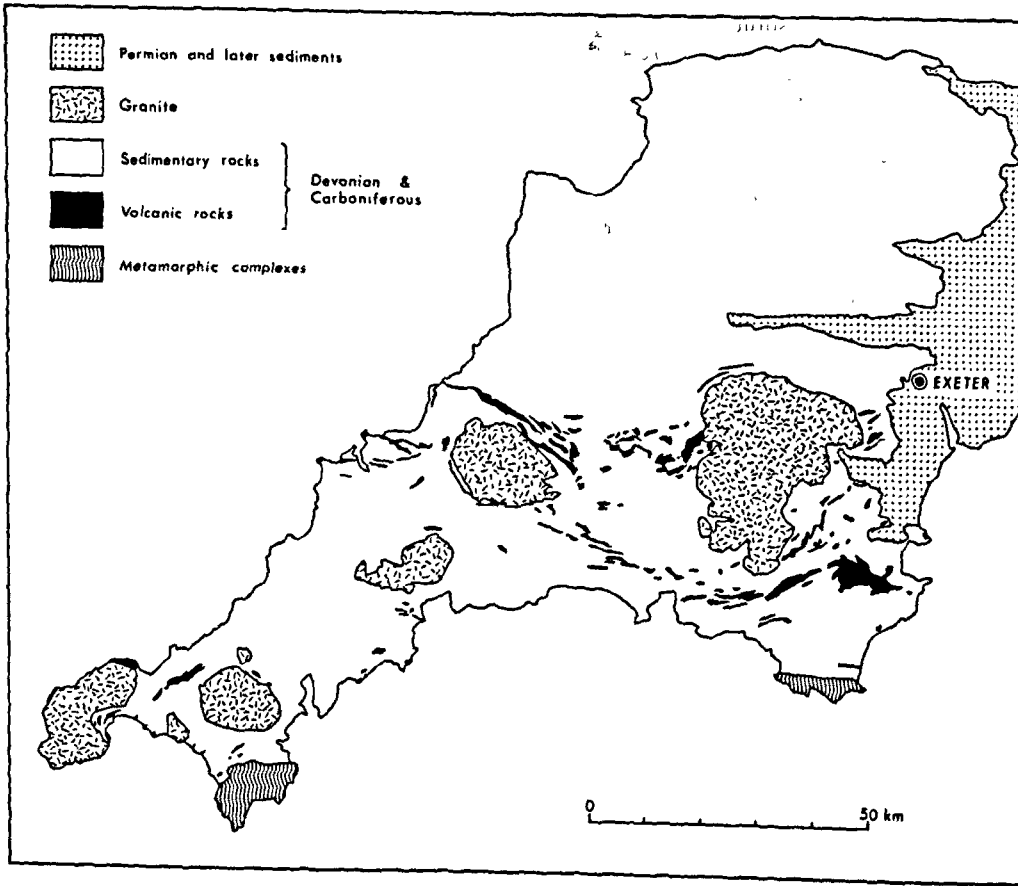


Fig. 1. The geology of S.W. England

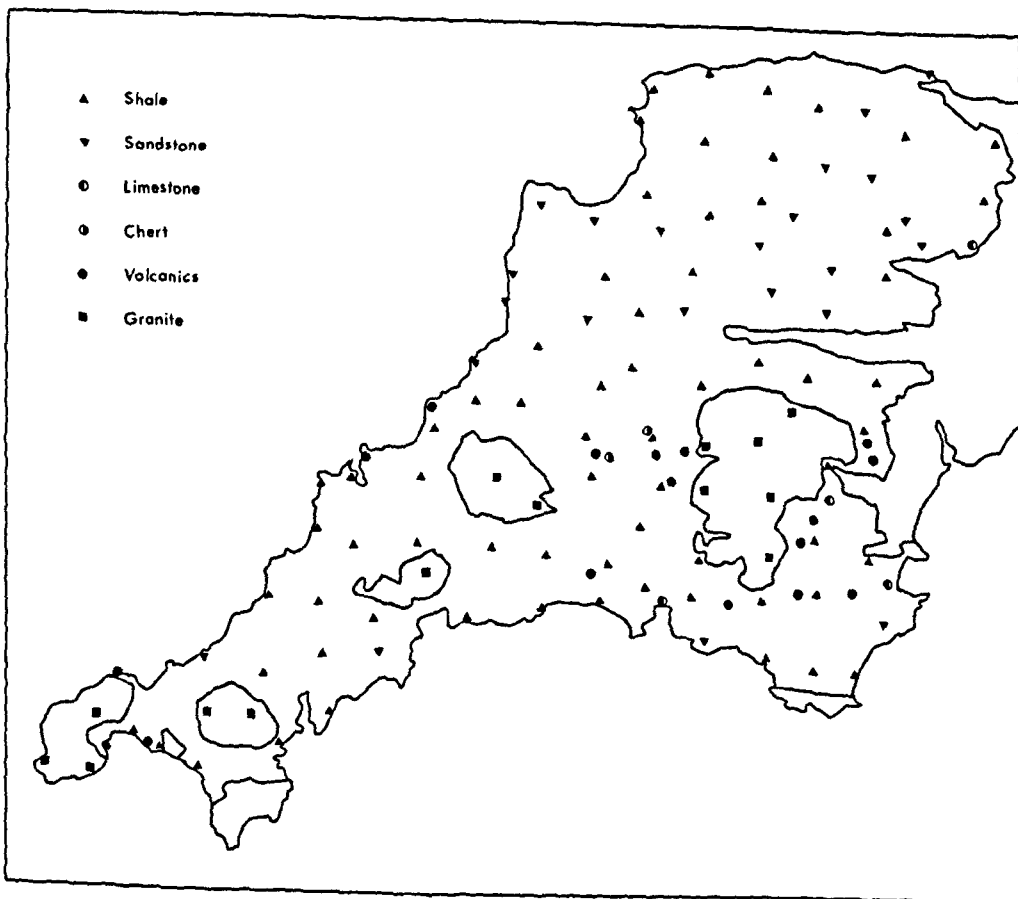


Fig. 2. Localities of the analysed samples

**Table 1.** Average compositions of the major rock groups constituting the Cornubian massif

	Granites	Shales	Sandstones	Limestones	Cherts	Volcanics
SiO <sub>2</sub>	73.40	59.58	78.98	5.17	88.51	47.15
TiO <sub>2</sub>	0.28	0.92	0.62	0.01	0.16	2.24
Al <sub>2</sub> O <sub>3</sub>	13.88	20.69	10.22	0.36	5.94	15.21
Fe <sub>2</sub> O <sub>3</sub>	2.08	7.49	4.73	0.10	1.59	12.75
MnO	0.04	0.07	0.06	0.02	0.05	0.20
MgO	0.42	2.04	0.96	0.58	1.16	5.93
CaO	0.78	0.74	0.40	48.72	0.07	5.54
Na <sub>2</sub> O	2.52	0.82	1.01	0.03	0.04	3.54
K <sub>2</sub> O	4.89	3.70	1.36	0.08	0.63	1.54
P <sub>2</sub> O <sub>5</sub>	0.21	0.12	0.09	0.00	0.04	0.29
S (%)	0.01	0.14	0.04	0.04	0.02	0.07
B	407	107	55	5	30	17
Ba	183	573	266	22	184	371
Ce	58	81	57	9	51	66
Co	5	15	9	0	4	31
Cr	6	107	56	0	28	152
Cu	11	35	13	3	40	53
La	27	39	26	-	25	32
Li	251	102	46	8	35	102
Nb	16	16	9	4	22	53
Ni	19	67	33	0	23	103
Sc	4	20	8	2	5	23
Sn	23	9	4	5	5	9
Sr	76	113	69	262	15	331
V	20	141	60	15	40	215
Y	18	22	16	6	22	32
Zn	43	102	54	19	32	128
Zr	132	181	267	35	92	197
Number of specimens	14	71	23	4	2	20

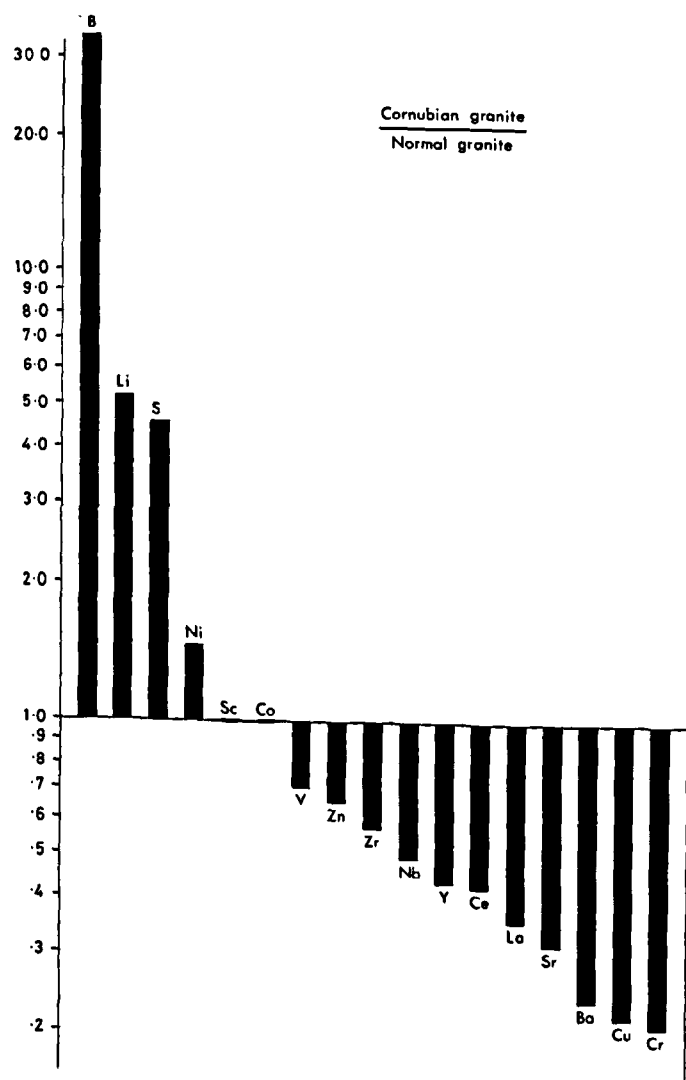
Trace element contents are given in parts per million; all Fe given as Fe<sub>2</sub>O<sub>3</sub>

was particularly important because several elements of interest are liable to redistribution by hydrothermal activity, so no sample was collected which showed any sign at all of hydrothermal alteration or veining. All the sampling localities are shown in Figure 2.

The number of specimens analysed was 134, and all the analyses were carried out by ICP spectrometry. Four separate specimen preparations were used: (1) most major and trace elements were determined directly after decomposition by HF-HClO<sub>4</sub>; (2) silicon, titanium and zirconium were determined after lithium metaborate fusion and digestion in dilute nitric acid; (3) boron and sulphur were determined by ICP spectrometry after a potassium carbonate fusion and separation of insoluble carbonates and perchlorates (Walsh 1985); (4) tin was determined after conversion to stannic hydride following lithium metaborate fusion (Hall 1980).

#### Compositions of the main Cornubian rock types

Table 1 shows the average (arithmetic mean) compositions of the six main categories of rock type. Their principal features are as follows.



**Fig. 3.** Trace element enrichment or depletion in Cornubian granites, compared with the worldwide average for granites (see Table 3)

The *granites* have a normal major element chemistry for this type of rock, the most distinctive feature being a rather low Na<sub>2</sub>O/K<sub>2</sub>O ratio, but their trace elements are much more unusual. Barium, strontium and rare earths are unusually low for granites, whereas boron, lithium and tin are very high. Boron is enriched to an extreme degree, with an average concentration 20–30 times that of the average granite outside this region. The enrichment is not confined to a single intrusion but is shown by all the granites in the Cornubian batholith.

It might be thought that the high average for boron could be caused by a few anomalously high values associated with hydrothermal alteration, but this is not the case. The number of granites in each range of boron content is as follows:

0– 200 ppm	1 sample
200– 400 ppm	7 samples
400– 600 ppm	3 samples
600– 800 ppm	2 samples
800–1,000 ppm	1 sample

It is true that in this region there are tourmalinized granites and tourmalinites with much more than

Table 2. Comparison of Cornubian trace element compositions with global averages

	Cornubian shales and slates			Average shale	Cornubian greenstones	Average tholeiite	Average alkali basalt
	(black)	(grey)	(all)				
B (ppm)	118	102	107	100	17	6	—
Ba	519	597	573	650	371	246	528
Ce	71	85	81	80	66	33	105
Co	15	15	15	23	31	48	43
Cr	112	104	107	110	152	168	202
Cu	40	33	35	50	53	90	85
La	35	41	39	38	32	15	54
Li	99	103	102	75	102	7	12
Nb	16	16	16	19	53	13	69
Ni	68	66	67	55	103	134	145
Sc	19	20	20	16	23	30	20
Sn	10	8	9	4	9	1.5	—
Sr	127	107	113	200	331	328	530
V	148	138	141	150	215	251	213
Y	19	24	22	27	32	28	33
Zn	89	109	102	85	128	100	108
Zr	179	182	181	210	197	137	189
S (%)	0.40	0.03	0.14	—	0.07	—	—

Average shale = Taylor and McLennan's (1985) average post-Archaean shale

Average tholeiite and alkali basalt = Wedepohl and Muramatsu's (1979) averages

1,000 ppm B, but none of these rocks have been sampled, and the analyses represented here are of typical granites and not abnormal ones.

The relative abundance of trace elements in the Cornubian granites compared with those of other regions are summarised in Figure 3. Assessment of the degree of enrichment or depletion is complicated by the fact that published estimates of the average granite composition are in serious need of revision. By comparison with Taylor's (1964) average values, the Cornubian granites would appear to be very rich in Co and Ni and normal for Cr and Cu, but I believe Taylor's averages to be low by a factor of 5 or more for all four elements. Instead, I have used an average of the recommended value for 9 international geochemical reference samples of normal granitic composition from Abbey's (1983) compilation. On this basis the Cornubian granites are not particularly enriched in Co or Ni but are very depleted in Cr and Cu.

The *argillaceous* rocks are either shales or slates, the intensity of the cleavage increasing southwards. In major element composition they are low in both Ca and Na, reflecting the low contents of carbonate minerals and detrital feldspar respectively, but none of the trace elements is strikingly high or low compared with shales from other regions (Table 2). Those elements which are extremely high in the Cornubian granites (B, Li, Sn) are moderately high in the shales, and those elements which are very low in the granites (Ba, Sr) are moderately low in the shales. When the shales were divided into two groups by colour (22 black shales and 49 grey shales) and their averages calculated separately, only small differences were apparent, even for such chalcophile elements as Co, Cu, Ni and Zn, even though the black shales have an appreciably higher sulphur content. The shales vary in their boron content from about 50 to 150 ppm, and there

are none which are low in boron. This element has been used by many workers to distinguish marine and non-marine clays, and by comparison with Recent sediments all the Cornubian slates resemble normal marine clays.

The *sandstones* are likewise low in Ca and Na, reflecting low carbonate and detrital feldspar contents, but their major and trace element compositions do indicate the presence of an appreciable clay content in all the sandstones. The same is true of the *cherts*. The *limestones* which were analysed are relatively free of clay impurities and show no unusual geochemical features.

The *volcanic rocks* are much more variable than the granites, and the 20 specimens for which the average has been calculated include extrusive basalts and spilites, intrusive dolerites and albite-dolerites, trachybasalt, picrite, epidiorite, amphibolite, and several tuffs. All of them have undergone at least some degree of low temperature alteration and their original form and mineralogy is often obscured. Collectively they may be described as greenstones. Their average composition does not closely correspond to any particular type of fresh igneous rock, being somewhat similar to hawaiiite (Le Maitre 1976), but obviously also reflecting the spilitic alteration superimposed on their original magmatic parentage. The most obvious feature of the trace element chemistry is that they are enriched in the same three elements as the granites, namely B, Li and Sn (Table 2). The enrichment is particularly great for lithium, although its absolute abundance is no greater than in the granites or the argillaceous sediments.

Summarizing the geochemistry of the main rock types, there are three elements which stand out as having abnormally high concentrations in Cornubian rocks, namely boron, lithium and tin. It is clear that the granites (and associated mineral deposits) are very strongly en-

**Table 3.** Comparisons between Cornubian and normal upper crust, and Cornubian and normal granites

	Cornubian upper crust (present day)	Cornubian upper crust (pre-granite)	Normal upper crust	Cornubian granites	Normal granites
SiO <sub>2</sub>	66.65	65.44	66.0	73.40	71.30
TiO <sub>2</sub>	0.75	0.83	0.5	0.28	0.31
Al <sub>2</sub> O <sub>3</sub>	16.14	16.56	15.2	13.88	14.32
FeO	5.26	5.88	4.5	1.87	2.73
MnO	0.06	0.07	0.1	0.04	0.05
MgO	1.54	1.74	2.2	0.42	0.71
CaO	1.32	1.41	4.2	0.78	1.84
Na <sub>2</sub> O	1.20	0.96	3.9	2.52	3.68
K <sub>2</sub> O	3.08	2.75	3.4	4.89	4.07
B (ppm)	135	85	15	407	12
Ba	410	452	550	183	754
Ce	70	72	64	58	135
Co	12	13	10	5	5
Cr	74	87	35	6	28
Cu	25	27	25	11	51
La	33	34	30	27	76
Li	108	82	20	251	48
Nb	15	14	25	16	32
Ni	49	55	20	19	13
Sc	14	16	11	4	4
Sn	10	7	5.5	23	5
Sr	101	105	350	76	241
V	98	113	60	20	28
Y	20	20	22	18	41
Zn	78	85	71	43	65
Zr	197	209	190	132	228

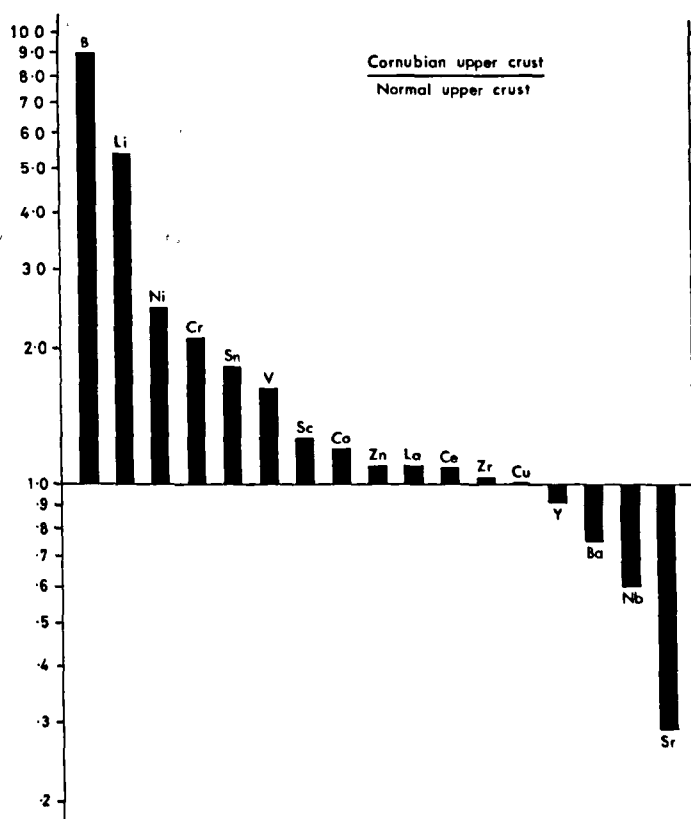
Normal upper crust = Taylor and McLennan's (1985) average for the upper continental crust (major elements given on a volatile-free basis)

Normal granites = Average granite composition derived from Le Maitre (1976) for major elements and Abbey (1983) for trace elements

riched in these elements, and although the concentrations of these elements in the sedimentary and volcanic country rocks are not nearly so extreme they are nevertheless somewhat enriched compared with similar rocks from other regions (Table 2). The conclusion must be that the geochemically anomalous features of this region pre-date the formation of the granite batholith.

#### *Overall composition of the Cornubian crust*

Because of the anomalous trace element concentrations in the Cornubian massif it is of interest to estimate its overall composition. The method used to calculate the average composition of the upper crust in Cornubia at the present day was to measure the areas occupied by each major lithology at outcrop throughout the massif, convert to weight percentages after making an allowance for assumed density differences between the rock types, and then calculate the average composition weighted accordingly. I have also calculated the mean composition of all the crustal rocks that pre-date the main granite intrusions. These averages are given in Table 3, and compared with the average composition of the upper continental



**Fig. 4.** Trace element enrichment or depletion in the present-day upper crust of Cornubia compared with the worldwide average for upper crust, as calculated by Taylor and McLennan (1985)

crust worldwide, as estimated by Taylor and McLennan (1985).

Compared with other parts of the continental crust, the Cornubian upper crust was already highly differentiated before the arrival of the granite batholith. It was very low in Ca, Na and Sr, and particularly rich in B and Li. The granite magmatism even further accentuated the divergence of the upper crust from the bulk crustal composition. Figure 4 shows how the present-day trace element contents of the Cornubian upper crust compare with those of other regions.

It is of great interest to compare the unusual trace element geochemistry of Cornubia with that of the Erzgebirge, which has been comprehensively studied by Pälchen and co-workers (1987). The elements which are particularly enriched (B, Li, Sn) or depleted (Ca, Na, Sr) in Cornubian rocks are similarly enriched or depleted in the Erzgebirge, and moreover in both areas these enrichments and depletions were already present before the Variscan granites were intruded. Despite the 1,200 km separation of the two regions along the northern edge of the Variscan orogenic belt, their geochemical development has evidently been very similar. The degrees of enrichment in Sn and Li have been about the same, but the enrichment in B has been much greater in Cornubia.

#### *Significance of the granites*

In this, as in several other geochemically anomalous regions, it is the granites that show the most extreme ele-

ment enrichments, and the abundance of tin has attracted particular attention because of its economic importance. Opinion on the origin of "tin granites" has been divided between those who regard them as products of extreme fractional crystallization (Groves and McCarthy 1978; Lehmann 1982, 1987) and those who believe the magma was derived from a pre-existing tin-rich source (Plimer 1980). The results of this study show that the Cornubian geochemical anomaly definitely pre-dates the formation of the granite batholith, even though it is in the batholith that the most extreme trace element enrichments are found.

Table 3 compares the element enrichments and depletions of the Cornubian granites with those of the upper crust as a whole. Considering just the trace elements which show the anomaly to the greatest degree, it appears that the Cornubian granites are enriched in B, Li and Sn compared with the pre-existing Cornubian upper crust by about the same amount as that crust was enriched over normal upper crust. These differences imply a two-stage process of trace element enrichment in which granite formation merely accentuated anomalies which were already in existence.

#### Implications for mineralization

The data on trace element distribution in the different rock types shed further light on the origin of the very extensive Cornubian mineral deposits. This mineralization has been described elsewhere (Dines 1956), but the main features are that the deposits are predominantly of hydrothermal type, the main elements of economic interest are Sn and Cu, and that apart from cassiterite most of the ore minerals present are sulphides. The ore deposits occur in both country rocks and granites, more abundantly in the former than the latter, but concentrated close to the granite margins. Quartz, chlorite and tourmaline are the commonest gangue minerals.

The ore deposits are particularly abundant where the country rocks are black slates, or contain volcanic rocks, and these rocks have hitherto been under strong suspicion of being a prime source of the ore metals; in fact Ahmad (1977) showed that the black shales and volcanic rocks have higher copper contents than the granites, which is confirmed here. However, the results for tin and for boron show that neither black shales nor greenstones can be the immediate source of these elements.

Isotopic studies (Jackson et al. 1982; Darbyshire and Shepherd 1985) have shown that the ore-bearing fluids were essentially of meteoric origin, although they have interacted with both the granites and their country rocks. This study shows that tin and boron are high in the granite but low in the country rocks, whereas copper and sulphur are low in the granites but high in the country rocks. The ore deposits are therefore the products of a hydrothermal system which has mobilized components from different sources.

*Acknowledgements.* The author would like to thank Dr. J.N. Walsh and Miss C. Lowe for advice and assistance with the analytical work and Dr. D.H.M. Alderton for comments on the manuscript of this paper. The collection of specimens for analysis was assisted by a grant from the Central Research Fund of London University.

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Received: December 22, 1988

Accepted: September 26, 1989