

Fluid inclusion and stable isotope evidence for the origin of mineralizing fluids in south-west England

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Abstract

The oxygen and hydrogen isotope composition of hydrothermal fluids associated with the Variscan granites of southwest England has been inferred from analysis of various silicate minerals (predominantly quartz) and by direct analysis of fluid inclusions within quartz and fluorite. These data have been combined with the results of a fluid inclusion study to develop a model for the origin and evolution of hydrothermal fluids in the region. Magmatic fluids expelled from the granites had compositions in the range $\delta D = -65$ to -15‰ , and $\delta^{18}O = 9$ to 13‰ . Respective temperature, salinity, fluid δD , and fluid $\delta^{18}O$ values for the (i) early Sn-W mineralization, (ii) later Cu-Pb-Zn sulphide mineralization, and (iii) latest 'crosscourse' Pb-Zn-F mineralization are: (i) 230–400 °C, 5–15 wt.% NaCl equiv., -39 to -16‰ , and 7.0 to 11.2‰, (ii) 220–300 °C, mostly 2–8 wt.% NaCl equiv., -41 to -9‰ , and 2.3 to 8.1‰, and (iii) 110–150 °C, 22–26 wt.% NaCl equiv., -45 to $+2\text{‰}$, and -1.8 to $+5.5\text{‰}$. These data highlight the important role of both magmatic fluids exsolved from the crystallizing granite, and basinal brines circulating within restricted fracture systems.

KEYWORDS: hydrothermal fluids, fluid inclusions, stable isotopes, south-west England.

Introduction

THE Cornubian orefield of south-west England is the most intensely mineralized and economically important of the British Isles. A popular and widespread view is that the polymetallic mineralization in the region was the product of large-scale convective meteoric-hydrothermal fluid circulation around the margins of the cooling granite batholith (Jackson *et al.*, 1989; Simpson *et al.*, 1979), and the role of magmatic fluids is considered to be relatively minor. However, there is a shortage of stable isotopic evidence for the origin of the hydrothermal fluids associated with the mineralization (see Jackson *et al.*, 1982, and Shepherd *et al.*, 1985). Because of this, a combined fluid inclusion and stable isotope study was carried out on a variety of mineralization types within the province.

In Cornubia (Fig. 1) polymetallic (Sn, W, Cu, Pb, Zn) mineralization is spatially associated with

Variscan (290–280 Ma; Darbyshire and Shepherd, 1985) granite plutonism. The hydrothermal activity responsible for this mineralization was repetitive and occurred during granite consolidation and for a long period (at least 100 Ma) afterwards (Halliday, 1980; Jackson *et al.*, 1982). Although the mineralization is locally complex and takes a variety of forms, the majority of deposits occur in steeply dipping veins which are often associated with intense wallrock alteration of the host rocks. Veins located within the granites tend to contain more Sn and W, whilst those in the surrounding aureole rocks tend to contain more Cu, Pb, and Zn. Additionally, a distinctive set of quartz-fluorite veins, with Pb, Zn, and Ag mineralization, cut and displace the earlier vein systems. Although of little economic value, these late veins are important in terms of understanding the metallogenic evolution of the province. Previous geochemical and isotopic studies in the region, which have proposed a

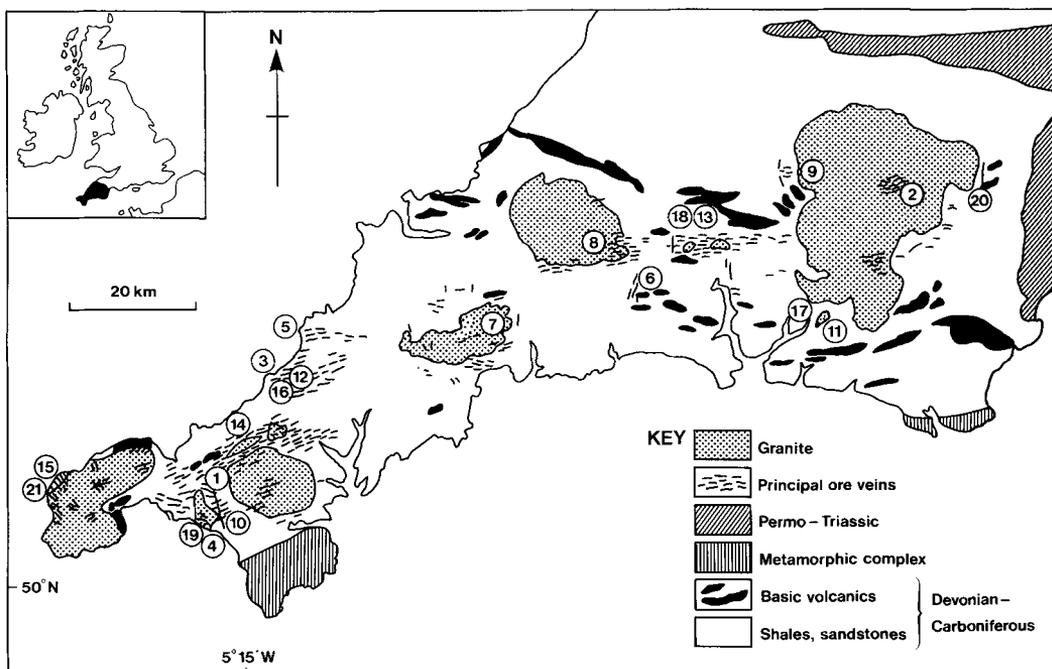


FIG. 1. Location map of the Cornubian orocfield. 1, Pendarves; 2, Birch Tor; 3, Cligga; 4, Wheal Rose; 5, Wheal Golden; 6, Wheal Wrey; 7, Tregarden; 8, Cheeswring; 9, Wapworthy; 10, Wheal Fortune; 11, Hemerdon; 12, Chiverton; 13, Capunda; 14, South Crofty; 15, Wheal Cock; 16, Perran Wheal George; 17, Wheal Lopez; 18, Collacombe; 19, Megalligar; 20, Wheal Exmouth; 21, Bostraze.

predominantly meteoric origin for the mineralizing fluids, have tended to focus on the granites (Sheppard, 1977) and associated early Sn-W mineralization (Jackson *et al.*, 1989; Shepherd *et al.*, 1985; Shepherd and Scrivener, 1987). Less attention has been given to later hydrothermal events (see for example Shepherd *et al.*, 1985, and Shepherd and Scrivener, 1987).

Present study

Samples of mineralized material were collected from various localities in the province (Table 1). For the fluid inclusion study, doubly-polished wafers of quartz and fluorite were subjected to thermometric and compositional analysis using a Linkam TH600 microscope stage. Calibration of the stage was carried out using the known melting points of pure organic and inorganic compounds (Roedder, 1985). Paired measurements of the vapour-liquid homogenization temperature (T_h) and the salinity (expressed as weight % NaCl equivalent) were obtained from approximately 30–40 inclusions in each sample. Salinities were obtained either from the last melting temperatures of ice or hydrohalite, or from the solution

temperatures of halite daughter minerals. Measurements in the vein samples were restricted to primary and pseudosecondary inclusions (using the criteria of Roedder, 1984). Fluid inclusions in the unaltered granites and the K-silicate alteration assemblage could not be easily classified and were probably all secondary in origin. The T_h values represent minimum temperatures of fluid trapping and need a positive temperature correction which is dependent on the pressure during hydrothermal activity. Using independent geothermometers we have determined that this correction does not usually exceed 50 °C, so the errors in using the T_h values to estimate isotopic compositions are minimal.

For the stable isotope study, silicates were analysed by conventional techniques (Clayton and Mayeda, 1963). Fluid inclusions were analysed directly for D/H (in quartz and fluorite) and $^{18}\text{O}/^{16}\text{O}$ (in fluorite) after release of the fluid by crushing or thermal decrepitation. Vein samples were selected so that one generation of predominantly primary inclusions was analysed; in the granites and alteration assemblages, several generations of secondary inclusions were also analysed. The O-isotopic composition of fluids precipitated

Table 1: Fluid inclusion and stable isotope data for granites and associated hydrothermal alteration and mineralization in Cornubia.

Sample number	Locality	Mineral *	Temperature (°C) **		Salinity (wt % NaCl equiv.)	δ D H ₂ O # ‰	δ 18O mineral ‰	δ 18O H ₂ O ‰
			Range	Mean				
GRANITES								
BM10	Cheeswring	Q R	100- >550	550	18	-55	11.9	10.5
SA13	Tregarden	Q R	100- >550	550	16	-52	12.1	10.7
D59	Wapsworthy	Q R	100- >550	550	40	-48	11.5	10.1
K-SILICATE ALTERATION								
836HS	Pendarves	M	100- >550	450	11.5	-48	10.9	10.2
OPH7	Pendarves	Q R	100- >550	450	11.5		13.5	10.4
OPH4/1	Pendarves	M	100- >550	450	11.5	-58	10.6	9.9
OPH4/2	Pendarves	F	100- >550	450	11.5		13.0	10.9
OPH4/3	Pendarves	Q R	100- >550	450	11.5		13.4	10.3
TYPE I (Sn - W)								
HW1068F	Hemerdon	Q	360-430	400	15	-30	15.3	11.2
OPH1c	Pendarves	Q	325-370	350	10		14.4	9.1
CH1	Cligga	Q	300-350	320	8	-39	15.6	9.4
OF1/1	Wheal Fortune	Q	290-330	310	10		15.4	8.9
OF1/2	Wheal Fortune	M	290-330	310	10		11.3	8.2
BTV	Birch Tor	Q	280-330	300	7	-39	13.9	7.0
OCH	Cligga	Q	290-304	300	8		14.4	7.5
VM5	Pendarves	Q	285-330	300	10	-34	15.3	8.4
OBTV	Birch Tor	Q	216-240	230	7		14.9	8.0
SC	South Crofty	Q	350-420	400	10	-16		
TYPE II (Cu - Pb - Zn)								
WCO	Wheal Cock	Q	180-300	250	8	-9	11.5	2.6
FI29	Chiverton	Q	210-240	230	5	-41	20.8	8.1
FI36	Capunda	Q	220-240	230	2	-34	15.0	2.3
OPH1a	Pendarves	Q	210-235	220	8		14.5	4.1
FI37	Ferran Wh. George	Q	250-300	275	5	-14	14.0	6.2
FI34	Wheal Lopez	Q	260-310	300	5	-24	13.5	6.6
FI33	Collacombe	Q	210-340	275	5	-20	15.1	7.3
TYPE III (Pb - Zn - Fl)								
QR1	Wheal Rose	Q	130-140	135	26	-36	17.5	0.8
FI38	Wheal Wrey	Fl	140-175	155	23	-45		5.5
FI24	Wheal Golden	Q	115-160	135	22	-33	20.7	4.0
ML	Megalligar	Q	120-170	150		-11	13.5	-1.8
SW89/23B	Wheal Exmouth	Q	100-115	110***	23	-8	11.4	(-8.0)
SW89/23A	Wheal Exmouth	Q	100-115	110***	23	2		
LATE-STAGE ALTERATION								
BOS	Bostraze	Q	140-250	225	1	-20	13.4	3.3

* Q=quartz, QR= relict granitic quartz, M= muscovite/sericite, F= K-feldspar, Fl=fluorite.

** For granitic and alteration fluids this is an estimation based on fluid inclusion studies (see text). For the other fluids this value is based on fluid inclusion Th data. For feldspar and muscovite, the temperatures obtained from co-existing quartz were used.

*** Temperature obtained from co-existing sphalerite. Considering the very low 18-O composition of the fluid this temperature is probably too low, and this sample is not plotted in Fig. 2.

δ D for mineral or inclusion fluid. δ D for fluids in equilibrium with muscovite at stated temperature: 836HS = -28, OPH4/1 = -38 (per mil).

pitating quartz was obtained from the analysis of the quartz and the fluid inclusion-derived temperature data, using established isotopic fractionation relationships (Matsuhisa *et al.*, 1979). The H-isotopic composition of fluids in equilibrium with muscovite was obtained from the fractionation relationship given by Suzuoki and Epstein (1976).

Results

The results of the fluid inclusion and stable isotopic analyses are presented in Table 1, and Figs. 2 and 3.

The isotopic composition of *Cornubian Magmatic Water* was initially defined by Sheppard (1977) on the basis of analyses of micas and quartz

from the granite of the region. These data, together with recent data for granite-associated pegmatites (Jackson *et al.*, 1982) and skarns (van Marcke de Lummen, 1985) have been used to define the *magmatic water* field shown in Fig. 2. Fluid inclusions are abundant in the unaltered granites and reveal that the final stages of crystallization of the granites were associated with the evolution of large volumes of aqueous fluid of variable temperature, salinity, and density (Rankin and Alderton, 1985). The high-temperature ($T_h > 500^\circ\text{C}$) inclusions are the most abundant in quartz from the unaltered granites, and analyses of fluid inclusions from three samples plot within this field. This suggests that the majority of the high-temperature fluid inclusions in these granites are of *magmatic* derivation, that is they were trapped in isotopic equilibrium with the granites at temperatures around 500–600°C and probably represent samples of fluid exsolved from the crystallizing pluton. It is suggested here that the large stable isotope variation for *Cornubian Magmatic Waters* is a result of the differential extent of water vapour separation (through boiling at elevated temperatures) from the crystalliz-

ing granite magmas during and immediately after emplacement (see Viglino *et al.*, 1985). Such a process would also explain the variable salinity of the fluid inclusions and the presence of low-density fluids in these granites (Rankin and Alderton, 1985). The early high-temperature, K-silicate alteration fluids at Pendarves Mine, in the Carnmenellis granite, also plot within the *magmatic water* field defined in Fig. 2.

A variety of mineralization phenomena are spatially associated with the Cornubian granites. Although complex on the scale of an individual deposit, three distinct associations are recognized. The most important volumetrically are veins which have an orientation roughly parallel to the axis of the granite batholith. Within this group of 'mainstage' veins there are clear examples of broad spatial and temporal mineralogical zonation. Early *type I* (Sn–W) veins tend to occur within or adjacent to the granites and are characterized by moderate to high fluid inclusion homogenization temperatures (230–400°C) and moderate salinities (5–15 wt.% NaCl equivalents). Three different parageneses are observed within the type I veins: greisen-asso-

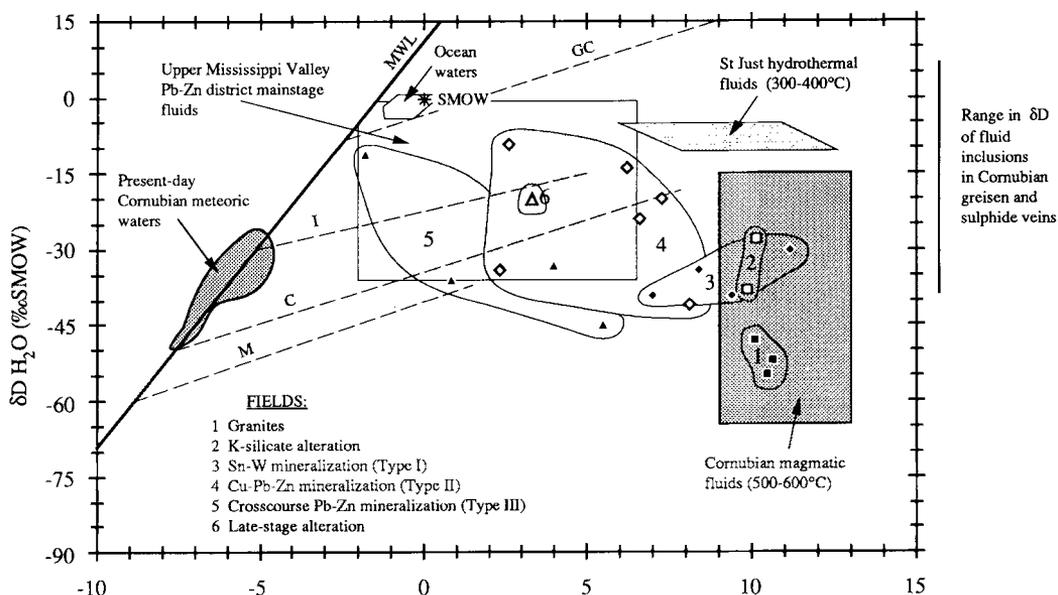


Fig. 2. $\delta\text{D}-\delta^{18}\text{O}$ plot showing the isotopic composition of hydrothermal fluids associated with the Cornubian granites, alteration, and mineralization. MWL = meteoric water line (Craig, 1961). Also shown are the fields for Cornubian magmatic water (this study), present-day Cornubian meteoric and thermal mine waters (Edmunds *et al.*, 1984), hydrothermal fluids from St. Just (Jackson *et al.*, 1982), and the range in δD for fluid inclusions in quartz associated with Cornubian sulphide and greisen veins (Shepherd *et al.*, 1985; Bray, 1980). Field for Mississippi-Valley-type fluids is taken from McLimans (1977). Dashed lines show the approximate positions of basin waters from the Gulf Coast (GC), Illinois (I), California (C), and Michigan (M) (from Sheppard, 1986).

ciated, Sn–W–As; Sn–tourmaline–Fe-oxide; and Sn–tourmaline–chlorite–base-metal-sulphide assemblages (Jackson *et al.*, 1989). *Type II* Cu–Pb–Zn mineralization occurs either within the granites, often superimposed on earlier *Type I* veins, or in the country rock peripheral to the granite. This base-metal assemblage lacks Sn and formed at lower temperatures (220–300 °C) and variable salinities (predominantly 2–8, but up to 26 wt.% NaCl eq.; Shepherd and Scrivener, 1987). A series of distinct Pb–Zn–F veins (*type III*), with a N–S orientation, cut the mainstage veins (types I and II) throughout the region. This *crosscourse* mineralization occurred at low temperature (110–150 °C) from high-salinity fluids (22–26 wt.% NaCl eq.). Fluid–rock interactions have produced a wide range of alteration phenomena, the most important of which are the extensive deposits of kaolinite (*china clay*) associated with the granite batholith.

Type I fluids have compositions in the range $\delta D = -39$ to -16‰ and $\delta^{18}O = 7.0$ to 11.2‰ , which fall largely within the field for Cornubian magmatic waters in Fig. 2. Some of these early hydrothermal mineralization events show evidence of boiling (Shepherd *et al.*, 1985), and this phenomenon could explain the large D/H variations seen in previous studies (Jackson *et al.*, 1989; Shepherd *et al.*, 1985; Bray, 1980). However, vapour-phase separation cannot explain the lower $\delta^{18}O$ values of the *Type I* fluids, a feature which is best explained by fluid mixing. It is probable that those fluids which plot outside the magmatic water field represent fluids which were expelled from the crystallizing granite and subsequently mixed with an ^{18}O -depleted fluid of surface derivation. The proposal that the earlier hydrothermal fluids were dominantly magmatic in derivation fits more easily with the distinctive chemical character of these fluids (high Li, B, Sn; Alderton *et al.*, 1982) and many of the observed field relationships attributed to hydrofracturing in a magma-dominated system (Halls, 1987).

Type II fluids have compositions in the range $\delta D = -41$ to -9‰ and $\delta^{18}O = 2.3$ to 8.1‰ . Although there is some overlap in the isotopic compositions of the *Type I* and *Type II* fluids, the *Type II* fluids exhibit much greater isotopic variation and typically have higher δD and lower $\delta^{18}O$ values. The systematic variation observed in salinity–temperature–isotope plots (Fig. 3) for granite, high-temperature alteration, *Type I*, and *Type II* fluids suggests a continuum from a magmatic–hydrothermal system to one dominated by more dilute, surface-derived fluids. The scatter in isotopic compositions does not support the concept of a simple mixing process between

homogeneous end-members; rather mixing between a magmatic fluid of relatively homogeneous composition and a variety of heterogeneous country rock fluids is implied. The single analysis of fluid from a quartz vein associated with kaolinized granite would suggest that the alteration at Bostraze took place at a temperature of around 200 °C, from a dilute fluid (1 wt.% eq. NaCl) that was isotopically similar to the low salinity end-member of the *Type II* fluids.

The *Type III* fluids have a distinctive high salinity (Fig. 3) and marked enrichment in Ca (Shepherd and Scrivener, 1987). In this respect they bear a striking resemblance to the fluids associated with Mississippi Valley-type, carbonate-hosted Pb–Zn–F deposits (Roedder, 1984; Hall and Friedman, 1963) which are thought to be derived from compaction of sedimentary basins and the consequent expulsion of indigenous fluids. Their isotopic compositions are highly variable, ranging from $\delta D = -45$ to $+2\text{‰}$, and

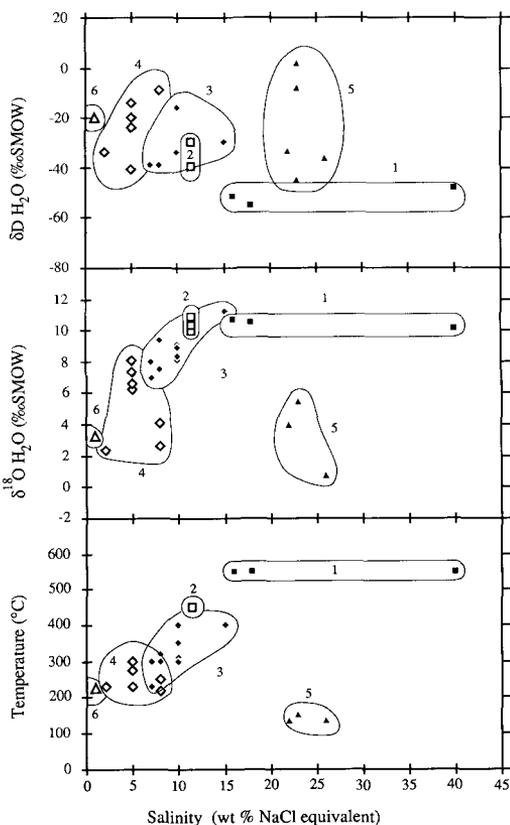


FIG. 3. Plots of salinity of the hydrothermal fluids against δD content, $\delta^{18}O$ content, and temperature. Symbols and fields as in Fig. 2.

$\delta^{18}\text{O} = -1.8$ to $+5.5\%$, and in Fig. 3 fall within the field of ore-forming fluids of the S.W. Wisconsin Mississippi-Valley-type Pb-Zn deposits (McLimans, 1977). Many deep oilfield and basinal brines have a similar isotopic character (Sheppard, 1986; Kharaka and Carothers, 1986) that is attributed to a variety of mechanisms such as isotopic exchange with minerals in the host sediments, by near-surface evaporation, by membrane filtration, or by mixing of connate and meteoric fluids. As with high-temperature boiling, evaporation of surface waters leads to the loss of water vapour and consequent isotopic fractionation (Vigilino *et al.*, 1985). Large shifts in the original H- and O-isotopic composition of the fluids can occur, to higher δD and $\delta^{18}\text{O}$ values (Knauth and Beeunas, 1986), and Connolly *et al.* (1990) have recently suggested that combined mixing-evaporation processes can lead to large variations in the δD contents of formation waters. Deep sedimentary basins containing thick accumulations of Permo-Triassic Red Beds and evaporite horizons are present adjacent to the Cornubian Massif (Smith, *in press*) and, therefore, could have produced such fluids.

Discussion

The overall trend of dilution and cooling in successively younger phases of hydrothermal activity (Fig. 3) appears to be a natural consequence of the intrusion and crystallization of a granite melt in a water-saturated crust, and as such is seen in other mineralized granitic terrains (Taylor, 1977). On intrusion, the granite melt would have initially caused local dehydration and the incorporation of such fluids (the 'metamorphic' waters of Primmer, 1985) into the hydrothermal system, but the earliest activity would have been dominated by *magmatic* fluids, concentrated and expelled during the late stages of granite crystallization. The variable salinities of the granite fluids (Fig. 3) and the difference in isotopic composition between the granite fluids, and early K-silicate alteration and type I Sn-W fluids (Fig. 2) are attributed to variable amounts of boiling in response to differential pressure release on hydrofracturing (Burnham, 1979). Surface-derived fluids present in the aureole rocks were also drawn into the hydrothermal circulation by convective action and mixed with the magmatic fluids. However, it is likely that the convective fluid systems were local rather than pervasive, and essentially restricted to major fracture systems. This scenario therefore differs from the large convective systems advocated by Simpson *et al.* (1979) in which pervasive altera-

tion of the country rocks takes place and which collapse in on itself. Modelling of the fluid flow around selected granite plutons in Cornubia (Samms and Thomas-Betts, 1988) has illustrated how the removal by erosion of the overlying insulating layer of sedimentary cover would tend to cause the fluid temperatures to decrease, and the locus of convective circulation to move from the granites into the surrounding aureole sediments. It is hardly surprising therefore that mineral zonations (Dewey, 1925) around the granites are observed. Furthermore, whilst the Sn and W were probably derived by extraction from the granite melt, the derivation of the Cu, Pb, and Zn most likely lies in leaching of the low-grade sedimentary rocks of the metamorphic aureole.

The influx of Ca-rich basinal brines, and the associated Pb-Zn-F mineralization were imprinted on the granite-related hydrothermal activity, presumably because the region represented a structural 'high' adjacent to the subsiding sedimentary basins. Mineralization with identical characteristics appears in post-Variscan strata throughout northern Europe (Behr and Gerler, 1987; Dill and Nielsen, 1987). Although the distinctive crosscourse mineralization in Cornubia tends to be restricted to major N-S structures at some distance from the granites, there is also evidence to suggest that these fluids started to become incorporated into the main-stage veins during the final phases of this mineralization (Shepherd and Scrivener, 1987). These fluids can also be recognized in the youngest fluid inclusion populations of the unaltered granites of the region (Rankin and Alderton, 1985). Widespread interaction between granites and more recent basinal brines is therefore envisaged, and this feature was probably common in other areas where granite intrusions controlled the localization and flow of more recent basinal brines (e.g. the North Pennines region of England; Brown *et al.*, 1987).

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