Fluid inclusion evidence for the development of Zn–Pb–Cu–F skarn mineralization in SW Sardinia, Italy

M. BONI

Dipartimento di Scienze della Terra, Universitá di Napoli, Largo S. Marcellino, 10 80138 Naples, Italy

A. H. RANKIN AND M. SALVADORI

Department of Geology, Royal School of Mines, Imperial College of Science, Technology and Medicine, London SW7 2BP, U.K.

Abstract

New microthermometric data are presented for fluid inclusions in epidote, garnet, hedenbergite, armenite, quartz, fluorite, calcite and baryte associated with skarn-related base metal mineralization in the Iglesiente and Sulcis mining districts of SW Sardinia. Based on a comparison of these data with published results for vein and palaeokarst mineralization a 'two fluid' model is proposed for the mineralization in the area. An early fluid, responsible for skarn-associated sulphide mineralization, developed above 350–400 °C with a salinity generally less than about 10 eq. wt.% NaCl, and on cooling was also responsible for some of the vein and palaeokarst mineralization. The origin of this fluid is, at this stage, speculative (meteoric/magmatic?). A separate fluid regime, characterized by lower temperatures and much higher salinities (Th < 140 °C and >20 eq. wt.% NaCl) was mainly responsible for the bulk of the Permo–Triassic vein and palaeokarst mineralization, and some late-stage skarn mineralization. This low-temperature, saline (basinal or evaporitic?) brine appears to have mixed with more dilute groundwaters during this stage of mineralization. The existence of two (or more) mineralizing fluids with different characteristics at the end of Hercynian tectonic/magmatic events appears to be widespread throughout the whole of Europe.

KEYWORDS: fluid inclusions, skarn mineralization, two-fluid model, Sardinia, Italy.

Introduction

THE Lower Palaeozoic rocks of SW Sardinia host two contrasting types of mineralization. Economically, the most important are the Cambro–Ordovician stratabound Pb–Zn–Cu ores (Boni, 1985). The second group are distinctly epigenetic in character, and comprise a series of late- and post-Hercynian skarn, vein and palaeokarst ores of minor economic importance. The geological setting and mineral paragenesis of both mineralization types are well documented (Boni, 1985; Boni and Amstutz, 1982; Aponte et al., 1988) and the genesis of the vein and palaeokarst mineralization has been discussed in the light of recent fluid inclusion and isotopic studies (Boni, 1986; Boni and Iannace, in press; Cortecci et al., 1989; De Vivo et al., 1987).

Here we report on the results of a combined petrographic and microthermometric study of fluid inclusions in minerals associated with skarn-type mineralization. These data permit discussion of the origins of skarn-associated fluids and their relationship to other mineralizing fluids active in the area since Cambro–Ordovician times.

Representative samples of skarn and related high-temperature vein mineralization were collected from mineralized areas of the Iglesiente and Sulcis districts of SW Sardinia (Fig. 1). Unfortunately, due to the overprinting of the early skarn assemblages by later hydrothermal events, only a few of the early skarn minerals showed visible and/or measurable inclusions. Consequently, we had to choose between studying inclusions in skarn minerals from areas barren of mineralization, but much less influenced by later hydro-
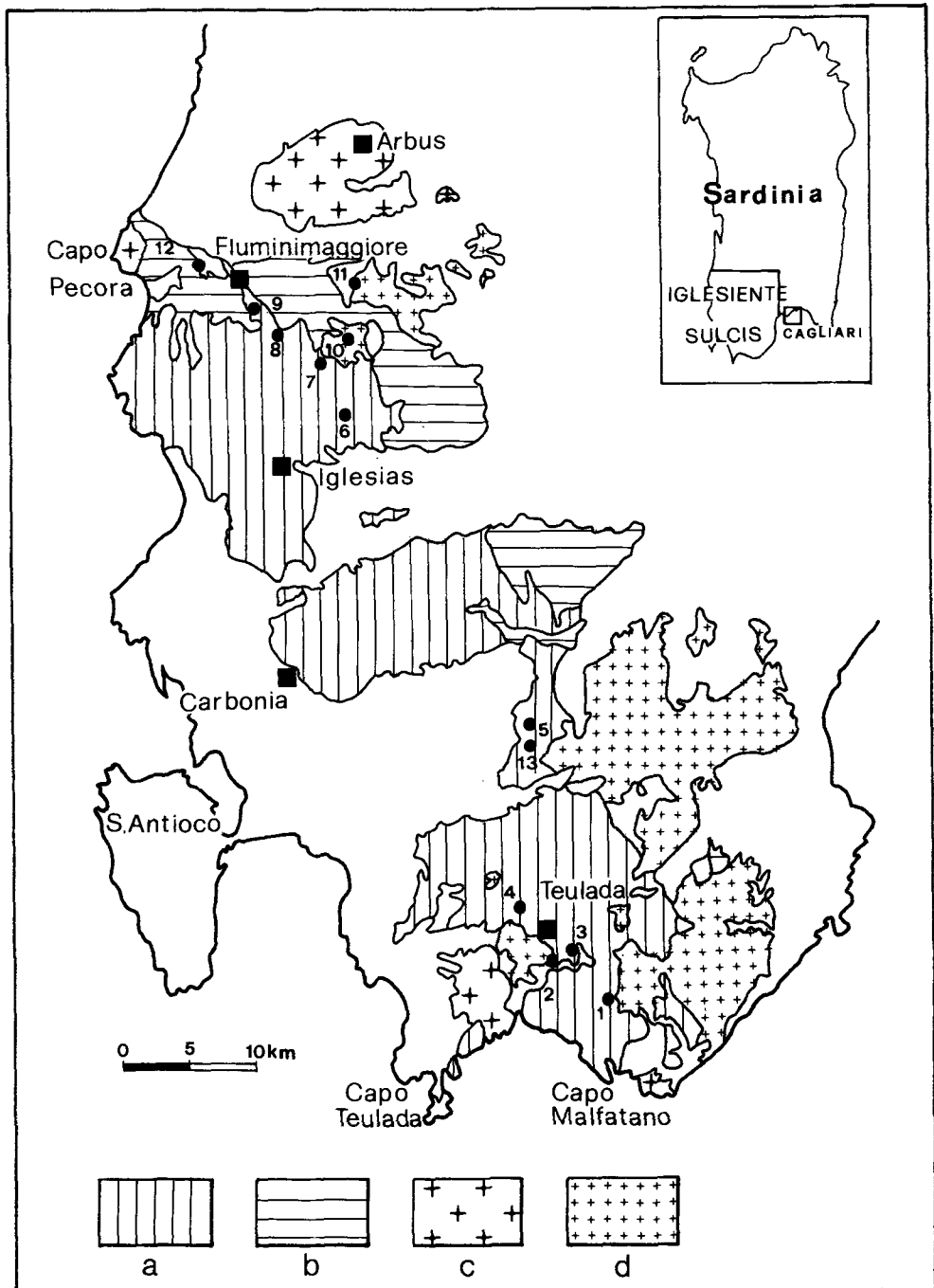
FIG. 1. Geological sketch map of SW Sardinia. The circles indicate the sampling areas. (*a*) Cambrian–Lower Ordovician; (*b*) Upper Ordovician; (*c*) Synkinematic granites; (*d*) Post-kinematic granites (leucogranites). 1 Sa Perdaiola; 2 S. Lucia (Teulada); 3 Filone Morettu; 4 Sideriu Boi; 5 M. Tamara; 6 Reigraxius; 7 Arenas-Tiny; 8 Gutturu Pala; 9 Su Zurfuru; 10 Perda Niedda; 11 Punta Nebidedda; 12 S. Lucia (Flumini); 13 Nuxis.

thermal alteration, and those from areas rich in sulphide ores where late-stage epidote and chlorite overprinted the early stages of skarn development. We chose the latter.

Geological setting of the skarns and associated mineralization

At the end of the Hercynian tectonic cycle, the Lower Palaeozoic basement of SW Sardinia was affected by a complex sequence of multiple intrusive events. These culminated in the emplacement of biotite-bearing leucogranites at shallow depth in the crust (3.8 to 1.5 km) at approximately 289 Ma (Del Moro et al., 1975). A wide variety of hornfels types was produced along the intrusive contacts. Exoskarns also developed in places where carbonate rocks occurred close to the intrusive contacts.

The skarns may be subdivided, according to Kerrick (1977), into metamorphic (along lithological boundaries) and vein types. Both types are mineralized with varying proportions of Pb–Zn–Cu sulphides, baryte and fluorite. Aponte et al. (1988) evaluated the paragenesis and mineral stability fields for these two mineralization types. They recognized and characterized (see Kerrick, 1977, for discussion of terms used) three main mineralogical associations, each reflecting a different evolutionary stage at pressures around 1 kbar:

(1) Metamorphic stage ($T > 550\,°C$), characterized by garnet (andradite > grossularite) + wollastonite and garnet + pyroxene (diopside–hedenbergite); (2) Metasomatic stage ($T \sim 400\,°C$), characterized by epidote and amphibole (actinolite > tremolite); (3) Hydrothermal stage ($T < 375\,°C$), characterized by chlorite, fluorite, quartz and calcite.

The skarn lithotypes probably acted as both structural guides and traps for the mineralizing fluids. It is possible that these Pb–Zn–Cu ores represent a remobilization of metals contained in the Lower Palaeozoic stratabound deposits, with a minor contribution of metals from the intruding magmatic bodies and/or intruded host rocks. The metal associations are similar throughout the whole district. The early metasomatic stage contains only small concentrations of pyrite and hematite–magnetite (mushketovite, magnetite pseudomorphs after hematite) coexisting with garnets. Most of the ore minerals are related to the later metasomatic and hydrothermal stages. They comprise several generations of pyrite, magnetite, pyrrhotite, sphalerite, chalcopyrite and galena. The ore minerals appear to have been deposited chiefly together with amphibole and epidote, partially replaced by chlorite.

Sample localities and sampling strategy

Owing to repeated episodes of chloritization and sulphidization, the early skarn minerals (for example garnet) are markedly altered and impoverished in measurable fluid inclusions. However, it was possible to obtain a few relatively fresh crystals of garnet, hedenbergite, epidote, and rare crystals of armenite ($BaCa_2Al_6Si_8O_{28}2H_2O$) from selected areas. Overall the best inclusions were located in quartz, calcite and fluorite and these were sampled from a number of key localities. Baryte was also included in this study despite its limitations as a suitable host for fluid inclusions. Sample localities are listed below (see also Fig. 1).

Hedenbergite and armenite (Balassone et al., 1989) were obtained from the vein skarn at the Su Zurfuru mine (Aponte et al., 1988). The garnets were sampled from Pta. Nebidedda, Tiny, Su Zurfuru (Iglesiente), and Filone Morettu, Sideriu Boi (Sulcis). A single sample of epidote was obtained from Filone Morettu. Quartz was sampled at Sideriu Boi, Mte. Tamara and Sa Perdaiola, and hydrothermal calcite from Su Zurfuru and Mte. Tamara. Several generations of fluorite were sampled from Su Zurfuru and S. Lucia (Fluminimaggiore), from Perda Niedda and Pta. Nebiddeda, and from small stratabound occurrences at Gutturu Pala and Reigraxius mines.

Methodology and description of fluid inclusions studied

Microthermometric analyses were carried out on about 300 primary, pseudosecondary and secondary inclusions in representative samples of garnet, hedenbergite, epidote, armenite, fluorite, quartz, calcite and baryte using a Linkam TH600 heating–freezing stage. The homogenization temperatures (Th) were recorded for all inclusions. However, owing to the small size of most inclusions, freezing measurements were restricted to 70 determinations of the temperatures at which the last transient solid phase, always ice, melted (Tm-ice). Attempts to determine temperatures of first melting (Te) were generally ambiguous and restricted to only a few crude determinations in fluorite. The reported Th and Tm-ice values are believed to be accurate to within $\pm 2\,°C$ and $\pm 0.2\,°C$ respectively. The few reported Te results are probably no better than $\pm 2\,°C$.

With the exception of fluorite and sometimes quartz, where inclusion sizes range up to about 80 μm, the inclusions are generally less than

10 μm. The fluid-inclusion populations in all samples are predominantly two phase (v + l) aqueous types. Liquid CO_2 has not been identified in any inclusion. Occasional, unidentified, rectangular, solid phases were, however, recognized in some fluorite and quartz samples. These failed to dissolve on heating up to 400 °C and are interpreted as captured rather than true daughter phases.

A number of criteria, summarized by Roedder (1984), were used to distinguish primary from secondary inclusions in these samples. The recognition of primary inclusions was most readily apparent in the case of fluorite and garnet, but less easy in other minerals. Unless otherwise stated, all recorded thermometric measurements relate to presumed primary or pseudosecondary inclusions.

Metastability in the inclusions, manifest by the absence of a vapour bubble at room temperature or its disappearance after the inclusion has been frozen and reheated, is comparatively rare and restricted to low-temperature inclusions in fluorite and calcite. Care was taken to ensure that all Tm-ice measurements were recorded in the presence of a vapour bubble. The effects of necking-down and leakage were however frequently apparent, especially in the case of armenite, calcite and baryte. Care was taken to avoid those inclusions where these processes had obviously taken place.

Results

The recorded homogenization temperatures range from <100 °C up to 400 °C. Garnet, fluorite and baryte exhibit the widest Th range (Fig. 2). In the case of fluorite and garnet the range reflects the different generations of host mineral and inclusions sampled (see figure caption for explanation). In the case of baryte, necking-down, leakage and non-elastic stretching are probably responsible. Th data for this mineral must therefore be treated with caution.

The Tm-ice values for inclusions in most minerals fall within the range 0 to −5 °C corresponding to salinities of about 0 to 7.8 equivalent wt.% NaCl (Hall et al., 1988). It was impossible to accurately measure Te values for these inclusions.

A second group of inclusions, characterized by Th values below 150 °C, show a much lower Tm-ice range, mostly between −17 and −32 °C (see field B in Fig. 3). First melting occurred within the approximate temperature range −52 to −57 °C. These Te values are much closer to the eutectics for chloride–water systems containing bivalent metal ions (notably Ca) than those containing only NaCl and/or KCl. Furthermore,

because many of the Tm-ice values fall well below the eutectics within the model system $NaCl-H_2O$ (Hall et al., 1988), it might be more appropriate to interpret the microthermometric freezing data, as others have done, in terms of phase equilibria within the more appropriate system $CaCl_2-NaCl-H_2O$ (Crawford, 1981; Shepherd et al., 1985). Unfortunatley, insufficient thermometric data are available (Te, Tm-hydrate and Tm-ice are required for each inclusion) to estimate both fluid compositions and salinities in this ternary system. However, based on the binary $CaCl_2-H_2O$ system (eutectic at −52 °C; Crawford, 1981) the Tm-ice values would correspond to salinities of 19 to 26 equivalent wt.% $CaCl_2$, or salinities between about 20 to greater than 23 equivalent wt.% NaCl if the model $NaCl-H_2O$ system is used.

The two main groups of inclusions are clearly separated on the Th versus Tm-ice plot (Fig. 3).

Discussion

The two discrete populations of fluid inclusions shown in Fig. 3 are believed to represent two separate fluid regimes (A and B) which were operative at different times during the evolution of the skarns and their associated mineralization. We postulate the existence of four end-member fluids, A1, A2, B3 and B4, to account for the observed trends on the $Th-Tm$ plot.

Fluid A is preserved in most skarn minerals, as well as in quartz (baryte) and some fluorites. With the exception of fluid inclusions in baryte, where necking-down and leakage may account for the spread in Th values shown in Fig. 3, the spread of combined Th and Tm-ice data for fluid A may be interpreted as a cooling, and possibly a dilution, trend involving a high-temperature ($Th > 300$ °C), moderately saline (2–8 equiv. wt.% NaCl) fluid (A1) and a more dilute (almost pure water) lower-temperature fluid (A2). Fluid A1 is best preserved in hedenbergite and garnet. It represents the first detectable pre-ore fluid which cooled and possibly mixed with cooler groundwaters (A2) along the line indicated. The origin of this early fluid is open to speculation, though we tend to favour a meteoric as opposed to magmatic source in view of the low salinities. Fluids between A1 and A2 are clearly linked to early skarn mineralization: quartz crystals which are synchronous with sphalerite afflicted by the 'chalcopyrite disease', are characterized by inclusions which fall along the line A1–A2; most sulphides are also linked to epidotes with Th values which plot towards the A1 end-member on this line. Inclusions in early fluorites also fall along
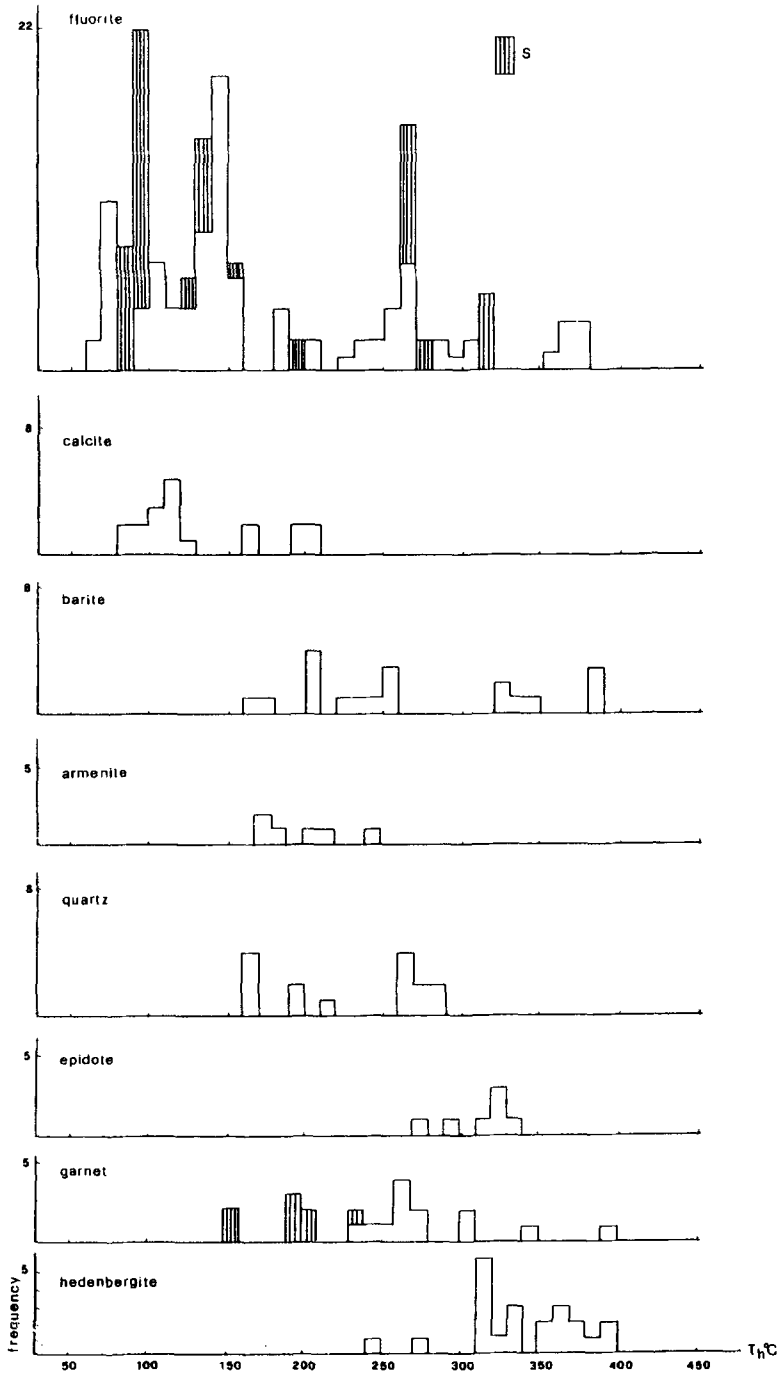
FIG. 2. Histograms of the homogenization temperatures of various skarn and vein minerals from SW Sardinia. 'S' represents secondary inclusions. All others are primary or pseudosecondary. Note the wide spread of data for fluorite, due to the different types of fluorite sampled. The higher temperatures (above about 200 °C) relate mostly to fluorite associated with hedenbergite and the lower temperature inclusions mostly to vein and breccia-hosted fluorite. The data for garnet also represent two generations; early crystals with wollastonite and later idiomorphic crystals.
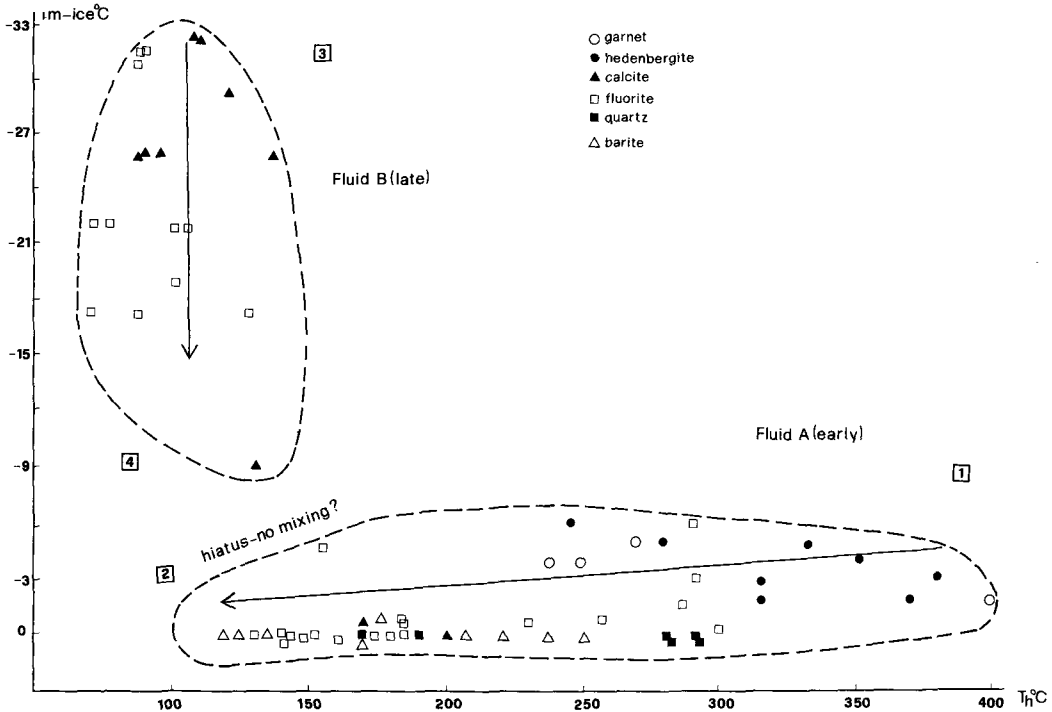
FIG. 3. Diagram of homogenization temperature (Th) versus last melting temperature (Tm-ice) for probable primary inclusions in skarn and vein minerals from SW Sardinia. Numbers 1, 2, 3, and 4 relate to the inferred position (approximate) of end-members within fluid fields A and B respectively. See text for further discussion.

the line A1–A2. Though necking-down and leakage may account for at least part of the spread in Th data for the barytes, it is unlikely that the observed Th range for fluorite can also be ascribed to these processes in view of the lengths taken to avoid these possibilities during thermometric measurements.

Aponte et al. (1988), on a petrological basis, concluded that the main sulphide stage of skarn mineralization took place between about 320 and 200 °C, prior to the onset of massive chloritization. The fluid inclusion homogenization temperatures for the minerals related to this sulphide stage (quartz, epidote, amphibole, calcite and fluorite baryte) fall within a slightly broader and somewhat lower range, from 120 to 300 °C. The discrepancies (20 to 80 °C, average 50 °C) between the thermometric data and mineral stability data of Aponte et al. (1988) are best explained by the need to apply a 'pressure correction' to the Th data. For example, a pressure correction of 50 °C applied to a fluid composition of 5 wt.% NaCl would correspond to pressures, on average, between about 0.4 and 0.6 kbar (Potter, 1977).

This estimate is for illustrative purposes only: the spread of Th data is far too great to allow a more precise estimate of pressures based on fluid inclusion geobarometry alone.

Fluid B, subdivided into B3 and B4, occurs only as inclusions in fluorite and calcite. These are characterized by much higher, but more variable, salinities (generally > 20 equiv. wt.% NaCl), and substantially lower Th values (<140 °C) compared to fluid A. The high-salinity end-member fluid, B3, is thought to represent a late-stage, hypersaline brine possibly originated from a Permo–Triassic (evaporitic?) reservoir as discussed below. The end-member fluid, B4 characterized by secondary inclusions in late fluorite, probably represents a less saline groundwater of similar age. Fluid inclusions of intermediate salinity plot along a dilution trend shown by the arrow in Fig. 3 which represents a mixing line between the two end-member fluids, B3 and B4. The timing and depth (pressure) of emplacement of these fluids is uncertain and it is therefore impossible to apply a pressure correction to these data. Based on geological evidence (e.g. Boni, 1986) these saline
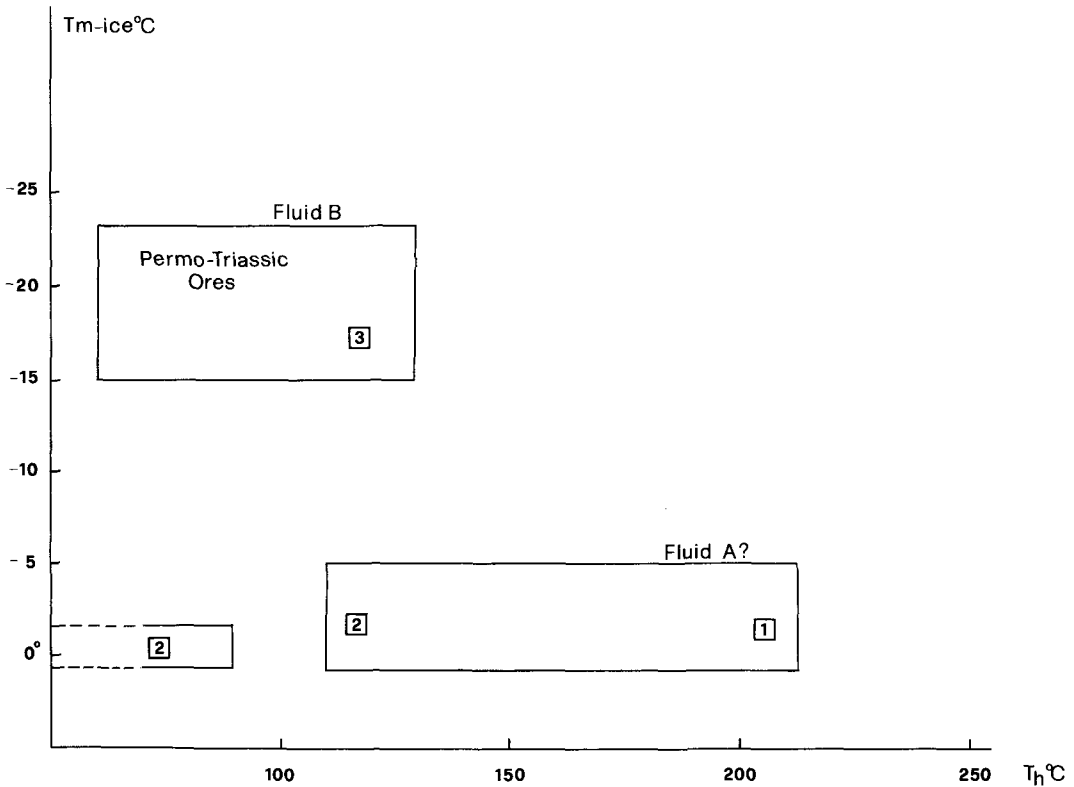
FIG. 4. Fields of homogenization and last melting temperatures (*Th* versus *Tm*-ice) in fluid inclusions from the Permo–Triassic ores of SW Sardinia (based on data from Boni, 1986). The numbers 1, 2, and 3 correspond to the fluid endmembers for fluid fields A and B defined in Fig. 2.

fluids are likely to have been active in the near-surface environment (<1 kbar), suggesting a pressure correction below 50 °C.

Comparison with published fluid inclusion data for SW Sardinia

The hiatus between the fields for fluids A and B on the *Th/Tm*-ice plot supports the textural and mineralogical evidence that two quite separate fluid regimes were involved at different times in the evolution of skarn mineralization. This plot exhibits broad similarities to the *Th/Tm*-ice plot for the Permo–Triassic vein and palaeokarst ores of SW Sardinia as summarized in Fig. 4 (Boni, 1986). Two contrasting fluid types represented by fields A and B are again recognized. Field A, however, extends only up to about 220 °C, in contrast to 400 °C for the skarn ores. This shows that higher temperature 'metasomatic' fluids were not so involved in the development of the vein and

palaeokarst ores and are more related to the early skarnification processes in the skarn-type ores. A separate field of low-temperature, low-salinity inclusions is also apparent just beyond the main field of fluid A for the palaeokarst and vein ores. As noted by Boni (1986) and others (De Vivo *et al.*, 1987; Cortecci *et al.*, 1989) late-stage calcite and baryte from these environments are characterized by abundant, low-temperature, mono-phase inclusions. It is most likely that these fluids represent an extension of field A down to <70 °C, rather than a totally separate field or continuum from field B.

The 'two fluid' model proposed above for both the skarn and the palaeokarst and vein ores of SW Sardinia is not applicable to the results recently presented by Giamello *et al.* (1989) for the Funtana Raminosa (Central Sardinia) hydrothermal field, where similar contact-metamorphic/metasomatic processes have taken place. A single evolutionary trend is indicated by these

authors, with inclusions showing a progressive decrease in salinity with decrease in temperature.

Conclusions

The fluid inclusion evidence for SW Sardinia supports the paragenetic evidence of an evolving skarn process and superimposed mineralization involving fluids of contrasting compositions and origins. The dilute, high-temperature fluids (magmatic and/or meteoric) responsible for the formation of the skarn ores were probably still active during the development of some of the vein and palaeokarst mineralization. However, at this point they were somewhat cooler, either because of their distance away from the intrusive bodies or because of mixing (and some dilution) with lower temperature groundwaters. At a much later stage, probably accompanying a phase of extensional tectonics, a more saline brine was introduced into the system. This fluid was responsible for the development of the main stage 'Permo–Triassic' vein and palaeokarst ores, and also for preceeding epigenetic dolomitization in the area (Boni and Iannace, in press).

A similar situation of two (or more) fluids with different characteristics at the end of Hercynian tectonic and magmatic events, seems to be widespread throughout the whole of Europe. It has been described by Rankin and Criddle (1985) in Wales, Behr *et al.* (1987) in Germany, by Mullis (1987) and Mullis and Stalder (1987) in Northern Switzerland, and by Hein *et al.* (1989) in the southern Alps. As is the case for SW Sardinia, the sudden arrival of very saline brines into a hydrothermal system and the concomitant deposition of ore minerals has, to date, been ascribed to the high-level circulation of Permo–Triassic formation waters derived from evaporitic sediments. For SW Sardinia the timing of this event is certainly later than the main phase of granite intrusion (289 ± 1 Ma) and prior to the deposition of the Middle Triassic carbonates (Campumari Formation). The origin of saline ore fluids from a 'Permo–Triassic evaporitic reservoir', for SW Sardinia is, however, purely speculative at this stage in view of the sparcity of outcrops of appropriate age throughout the island. Nevertheless, an alternative or additional source for these fluids may be envisaged from the extensive evaporitic sediments of continental Europe at a time when the Corso-Sardic massif was still connected to it.

Acknowledgements

References

Aponte, F., Balassone, G., Boni, M., Costamagna, L. and Di Maio, G. (1988) Variscan skarn ores in SW Sardinia: their relationships with Cambro–Ordovician stratabound deposits. *Rend. Soc. Ital. Min. Petr.* **43**, 445–62.

Balassone, G., Boni, M., Di Maio, G. and Franco, E. (1989) Armenite in South-West Sardinia: first recorded occurrence in Italy. *Neues Jahrb. Mineral., Mh.*, 49–58.

Behr, H. J., Horn, E. E., Frentzel-Beyme, K. and Reutel, C. (1987) Fluid inclusion characteristics of the Variscan and post-Variscan mineralizing fluids in the Federal Republic of Germany. *Chem. Geol.* **61**, 273–85.

Boni, M. (1985) Les gisements de type Mississippi Valley du Sud Ouest de la Sardaigne (Italie): une synthèse. *Chron. Rech. Min.*, **479**, 7–34.

——(1986) The Permo–Triassic vein and paleokarst ores in south-west Sardinia: contribution of fluid inclusion studies to their genesis and paleoenvironment. *Mineral. Deposita*, **21**, 53–62.

——and Amstutz, G. C. (1982) The Permo–Triassic paleokarst ores of South-West Sardinia (Iglesiente-Sulcis). An attempt at a reconstruction of paleokarst conditions. In *Ore Genesis, the State of the Art* (Amstutz, G. C., eds.) Springer, Berlin, 73–82.

——and Iannace, A. (in press) Epigenetic dolomitization and mineralization in SW Sardinia. *Documents du BRGM*.

Cortecci, G., Fontes, J. C., Maiorani, A., Perna, G., Pintus, E. and Turi, B. (1989) Oxygen, sulfur and strontium isotope and fluid inclusion studies of barite deposits from the Iglesiente-Sulcis mining districts, South-Western Sardinia, Italy. *Mineral. Deposita*, **24**, 34–42.

Crawford, M. L. (1981) In *Fluid Inclusions—Applications to Petrology* (Hollister, L. S. and Crawford, M. L., eds.) Mineral. Soc. Canada Short Course Handb. **6**, 75–100.

Del Moro, A., Di Simplicio, P., Ghezzo, C., Guasparri, G., Pellizzer, R., Ricci, C. A., Rita, F. and Sabatini, G. (1975) Il metamorfismo e il magmatismo paleozoico nella Sardegna. *Rend. Soc. Ital. Min. Petr.* **30**, 979–1068.

De Vivo, B., Maiorani, A., Perna, G. and Turi, B. (1987) Fluid inclusion and stable isotope studies of calcite, quartz and barite from karstic caves in the Masua mine, Southwestern Sardinia, Italy. *Chem. Erde*, **46**, 259–73.

Giamello, M., Protano, G., Riccobono, F. and Sabatini, G. (1989) Fluid evolution in the Funtana Raminosa hydrothermal field, Central Sardinia, Italy. *Abstract, Ecrofi X*, London, April 1989, p. 36.

Hall, D. L., Sterner, S. M. and Bodnar, R. J. (1988) Freezing point depression of NaCl–KCl–H$_2$O solutions. *Econ. Geol.* **83**, 197–202.

Hein, U. F., Luders, V. and Dulski, P. (1989) The

fluorite-vein mineralization of the Southern Alps, Italy: combined application of fluid inclusions and *REE* distribution. *Abstract, Ecrofi X*, London, April 1989, p. 47.

Kerrick, D. M. (1977) The genesis of zoned skarn in the Sierra Nevada, California. *J. Petrol.* **18**, 144–81.

Mullis, J. (1987) Fluideinschluss-Untersuchungen in den Nagra–Bohrungen der Nordschweiz. *Ecl. Geol. Helv.* **80**, 553–68.

——and Stalder, H. A. (1987) Salt-poor and salt-rich fluid inclusions in quartz from two boreholes in northern Switzerland. *Chem. Geol.* **61**, 263–72.

Potter, R. W. III (1977) Pressure corrections for fluid inclusion homogenization temperatures based on the volumetric properties of the system NaCl–H$_2$O. *U.S.G.S. J. Res.* **5**, 603–7.

Rankin, A. H. and Criddle, A. J. (1985) Mineralising fluids and metastable low-temperature inclusion brines at Llanharry iron deposit, South Wales. *Trans. Inst. Min. Metall. B.* **94**, 126–32.

Roedder, E. (1984) *Fluid Inclusions*. Mineral. Soc. Amer. *Revs. in Mineralogy*, **12**, 644 pp.

Shepherd, T. J., Rankin, A. H. and Alderton, D. H. M. (1985) *A practical guide to fluid inclusion studies*. Blakie and Sons, Glasgow, 235 pp.