Per. Mineral. (2009), 78, 3, 19-35

doi: 10.2451/2009PM0010
http://go.to/permin

PERIODICO di MINERALOGIA
established in 1930

An International Journal of
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY
and applied topics on *Environment*, *Archeometry* and *Cultural Heritage*

Post-Variscan hydrothermal activity and ore deposits in southern Sardinia (Italy): selected examples from Gerrei (Silius Vein System) and the Iglesiente district

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Submitted, July 2009 - Accepted, October 2009

Abstract - The current understanding of post-Variscan hydrothermal activity and mineralization in southern Sardinia (Italy) is reviewed in the framework of the geological evolution of Western Europe. The structural and geochemical data are discussed for both the Southwestern Iglesiente-Arburese-Sulcis district, and for the Southeastern Sarrabus-Gerrei one (Silius mine). In the Southwest part the majority of the deposits, aligned coaxially to crustal extension, can be classified as vein- and palaeokarst-types (sphalerite, Ag-galena and barite). The prevalent mineralizing fluid across the whole mining district is a H_2O-NaCl-$CaCl_2$ fluid with a salinity above 20 wt. % NaCl eq. and $T_h \leq 140$ °C. A similar fluid (T_h mean ≈ 100 °C) also caused the precipitation of the widespread hydrothermal dolomites (*Geodic Dolomite*). Another type of fluid, with much lower salinities and T_h up to 200 °C, has been recorded locally near magmatic intrusions and at the periphery of skarn bodies. In the Southwest area, Pb isotopes of related minerals bear the imprint of a radiogenic "Variscan" component, and of another component derived from the Paleozoic/pre-Paleozoic basement. One of the most impressive vein systems cropping in the Southeast district, exploited in the Silius mine (Gerrei), consists of an association of fluorite, galena and barite. Here most ore minerals were precipitated at temperatures in the range of 120 - 180 °C from a dominant fluid consisting also of an NaCl ± $CaCl_2$ rich brine. The origin of the fluids in both areas is mainly from evaporated seawater, bearing a small contribution from halite dissolution. Ore Pb in the Silius veins could have been derived from a mixture of Pb from the Ordovician metarhyolites and metasediments as well as from the late-Variscan granites. The suggested timing for the hydrothermal events in southern Sardinia are: 1) Middle Permian (270 Ma); 2) Triassic-Jurassic. It has been hypothesized that the Mesozoic events were related to the onset of Tethys spreading.

Riassunto - È stata effettuata una revisione dell'attività idrotermale e delle mineralizzazioni post-Varistiche nella Sardegna meridionale, inquadrate nell'ambito dell'evoluzione geologica dell'Europa occidentale. Vengono discussi i dati strutturali e geochimici esistenti, oltre ad altri ottenuti di recente, sia per i distretti sudoccidentali dell'Iglesiente-Sulcis-Arburese, che per l'area sudorientale del Sarrabus-Gerrei, in cui si localizza la miniera di Silius. Nei distretti sudoccidentali la maggior parte dei depositi metallici (blenda, Ag-galena e barite) si rinvengono sia in vene che in paleokarst idrotermali, controllati da lineamenti strutturali

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impostati su *pattern* di estensione crostale. Il fluido mineralizzante prevalente in tutto il distretto citato è un fluido a composizione H_2O-NaCl-$CaCl_2$, con salinità superiori a 20 wt. % NaCl eq. e $T_h \leq 140$ °C. Un fluido simile H_2O-NaCl-$CaCl_2$ fluid (T_h media ≈ 100 °C) viene considerato anche responsabile della estesa dolomitizzazione idrotermale (*Dolomia Geodica*) nella stessa zona. Un altro tipo di fluido, con salinità molto più basse e temperature di omogeneizzazione fino a 200 °C, è stato misurato nelle mineralizzazioni prossime alle intrusioni granitiche ed alla periferia delle zone di *skarn*. Nei distretti della Sardegna sudoccidentale gl'isotopi del piombo delle mineralizzazioni post-Varistiche hanno sia l'impronta della componente radiogenica "Varistica", che quella derivata dai sedimenti e mineralizzazioni presenti nel basamento pre-Paleozoico/Paleozoico. Nella regione di sudest, uno dei maggiori sistemi di vene idrotermali è il sistema filoniano di Silius (Gerrei), che contiene un'associazione di fluorite, barite e galena. A Silius la maggior parte dei minerali sono precipitati a temperature tra 120 e 180 °C da un fluido principale costituito da brine a componente NaCl ± $CaCl_2$. L'origine dei fluidi mineralizzanti in entrambe le aree di mineralizzazione post-Varistica è prevalentemente da evaporazione di acqua di mare, con un limitato contributo della dissoluzione di evaporiti. Il piombo delle mineralizzazioni di Silius ha un'origine mista comprendente i metasedimenti e le metarioliti (i "Porfiroidi") della roccia incassante e i graniti tardo-Varistici. Si ipotizza che le fasi idrotermali più importanti nella Sardegna meridionale siano databili: 1) Permiano Medio (270 Ma); 2) Triassico-Giurassico. Gli eventi idrotermali Mesozoici sono da mettere in relazione all'apertura della Tetide.

Key words: *hydrothermal fluids; Sardinia; post-Variscan; Arburese; Sarrabus; Iglesiente.*

Introduction

The late- to post-Variscan geological evolution of Europe is characterized by numerous magmatic and hydrothermal mineralizing events, ranging in age from the end of the orogenic compression to the onset of Tethys spreading. Their timing and particular characteristics are different from one area to another throughout Europe but some general features appear to be common. The hydrothermal fluids of ore deposits in many districts of Western Europe have a common origin; they caused the widespread dolomitization of the Paleozoic limestone sequences, and the stratabound (vein- and paleokarst types), Temperature, salinity and composition of the post-Variscan hydrothermal fluids, investigated by fluid inclusion (FI) studies, have been reported for most areas of the Iglesiente ore district (SW Sardinia) (Boni, 1986; Boni *et al.*, 2000; Cortecci *et al.*, 1989), as well as in parts of Sarrabus (SE Sardinia) (Belkin *et al.*, 1984). Altough fair amount of analyses exist on mineralizations like the "Filone Argentifero" (Valera, 1974; Masi *et al.*, 1975; Belkin *et al.,* 1984), data on the Silius vein system have been reported only in the unpublished excursion guidebook prepared for a conclusive "Workshop of the European Science Foundation" (Geode Program), which took place in Sardinia on March 2003 (Boni and Bechstädt, 2003). Moreover, no published FI data exists for the Montevecchio area. This paper aims to fill this gap, carrying out new fluid analyses in the Silius (southeast area) and Montevecchio (southwest area) vein systems. In this study, the nature of the fluids circulating during multiple hydrothermal activity and mineralization events in southern Sardinia (Italy) are analysed and discussed, from the late stages of Variscan compression throughout the Mesozoic. We were able to reconstruct the fluid evolution of Southern Sardinia in the framework of the post Variscan fluid history of Western Europe, by a combination of FI, Pb- and stable-isotopic data.

Geological setting and post-Variscan ores in Sardinia

Sardinia belongs to the Gondwana-derived Iberian-Armorican microplate assemblage (Crowley *et al.*, 2000). Along with the neighboring Corsica, it corresponds to a small segment of the southern flank of the Variscan orogen (Arthaud and Matte, 1977), linked to the "Armorica" fold zone by a narrow suture (Carmignani *et al.,* 1994). The Sardinian Paleozoic basement generally shows strong tectono-stratigraphical and metallogenic analogies with other areas of the European Variscan belt (Boni *et al.,* 1996). The island is one of the oldest mining districts in the world, dating to pre-Roman times; extraction was mainly concentrated in the southern part, while there was only a minor mining activity in the southeastern sectors. Exploitation was initially for silver-lead-copper and later for zinc, fluorite and barite deposits, for the most part limited to the Cambro-Ordovician lithologies of the southwestern part of the island (Boni *et al.*, 1992, 1996). In the first decades of the twentieth century, there were more than thirty active metallic mines in Sardinia; nowadays, due to technical and economical limitations, the only future operational mine may be Silius, which exploits a fluorite-galena-barite vein system in the southeastern Gerrei district (Natale, 1969).

The Variscan basement of southern Sardinia is characterized by rocks from Early Cambrian to Early Carboniferous, involved in a continental collision and deformed under "very-low" to "low-grade" metamorphic conditions. During the compressive phases, subhorizontal N-S and E-W shortening occurred and several tectonic units were thrust and imbricated (Conti *et al.*, 2001).

Within the Paleozoic successions of southwestern Sardinia (Arburese, Iglesiente, Sulcis; Fig. 1A), two tectonostratigraphic units are recognized: 1) Paleozoic sediments of a lower "autochthonous" unit, mainly dominated by sedimentary Paleozoic lithotypes including carbonate sequences; 2) an overlying "allochthonous" unit, consisting of Cambro-Ordovician sediments, mainly clastic, with intercalations of coeval magmatic rocks (Arburese Unit, Carmignani *et al.*, 1994).

The "autochthonous" successions, spanning in age from the early Cambrian to the Devonian and Carboniferous, consist of metamorphic rocks of epizonal facies, and belong to the so-called "External Zones" of the Variscan orogen (Carmignani *et al.*, 1994). Most of the post-Variscan ore deposits occur in the Iglesiente-Sulcis area, which is considered to be the external zone of the Sardinian Variscides. The Lower Cambrian succession (Bechstädt and Boni, 1994) starts here with the basal Nebida Group, consisting of shallow water clastics, followed by the platform carbonates and associated slope deposits of the Gonnesa Group. Middle and Upper Cambrian to Lower Ordovician strata are represented under the Iglesias Group, mainly consisting of slates and recording the deepening of the sedimentary basin. Upper Ordovician-Silurian sediments lie on the previously mentioned successions. These sequences underwent at least two Variscan compressional and one extensional phases of deformation, followed by the intrusion of post-kinematic calc-alkaline granitoids (320 - 290 Ma; Boni *et al.,* 1999, 2002) and differential basement uplift.

The "allochthonous" successions (also called "Southern Nappe Zone") are dominant in southeastern Sardinia (Sarrabus-Gerrei; Fig.1B), where they show a higher metamorphic grade (greenschist facies) than the southwestern successions. These mainly siliciclastic sedimentary rocks, locally containing some thick intercalations of porphyritic meta rhyolites (the so called "Porfiroidi"), have been grouped in the San Vito and Solanas formations (Sarrabus) and in the Gerrei units, respectively (Upper Cambrian-Ordovician; Carmignani *et al.,* 1994). Their age spans from the Upper Cambrian to the Carboniferous. In southeastern Sardinia the emplacement of granitoid batholiths (310-280 Ma, Di Vincenzo *et al.*, 1994 and references therein) followed Variscan compressive events.

The post-Variscan sedimentary record is poorly represented and starts with a clear trend towards crustal attenuation and fragmentation during the

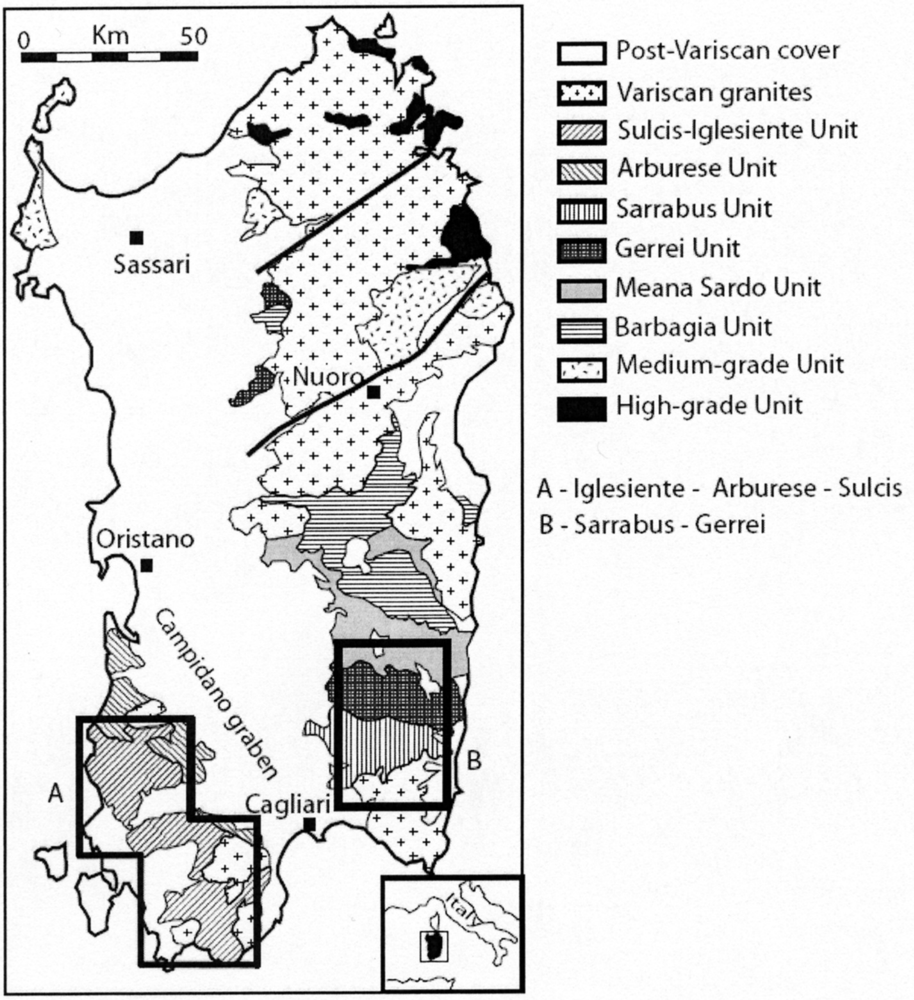

Fig. 1 - Geological sketch map of Southern Sardinia, with the location of both mineralized districts (A = Southwest, B = Southeast) (from Dini *et al.* 2005, modified).

late Carboniferous to Permian. This is possibly related to a large transcurrent mega-shear zone and local basement uplift (Carosi *et al.*, 1992; Cassinis *et al.*, 1999). Recent stratigraphic studies on the Upper Carboniferous-Permian to Middle Triassic sediments of Sardinia, as well as on the petrography and geochemistry of the coeval volcanic units, highlighted three main tectono-sedimentary cycles (Ronchi, 2004). Each one of these sequences is bounded by regional unconformities and mirrors a major geodynamic phase, allowing correlations with other sectors of the southern margin of the European plate (Proto-Tethys to early Alpine Tethys stages). The first cycle can be ascribed to a Late Carboniferous - lower Early Permian time interval, mainly represented by continental sediments deposited in intramontane basins and interfingered with large volumes of calcalkaline volcanic rocks (290-260 Ma; Atzori *et al.,* 2000; Ronca *et al.,* 1999). The second cycle, supposedly spanning from the late Early Permian to the late Permian, is characterized by alluvial formations intercalated by alkaline volcanic rocks. The Mesozoic successions are incomplete and scattered, but point to further crustal thinning (a prelude to Alpidic rifting), as evidenced by Middle- to Upper Triassic marine sediments that locally contain evaporites. The condensed Triassic sequences extend upwards into thicker Jurassic and Cretaceous carbonates. The magmatic counterparts of this extensional period were again identified in sub-alkaline and alkaline dykes (Atzori and Traversa, 1986), dated by Vaccaro *et al*. (1991) at about 230 Ma. The alkaline dykes have a mantle Sr signature and cut repeatedly the Variscan basement at several localities in southern Sardinia.

As reported by Boni *et al.* (1992, 1999, 2000), several distinct hydrothermal systems were likely active in SW Sardinia. However, they were not only related to the aureole of post-kinematic magmatic intrusions (skarn and retrograde contact metamorphism), but also to distinct periods of post-orogenic crustal extension during the Permian and Mesozoic (Muchez *et al.,* 2005). They resulted in a variety of hydrothermal products, which include a widespread dolomitization and formerly economic ore deposits**.**

Ore Deposits in the Sarrabus-Gerrei and Iglesiente-Arburese-Sulcis Mining Districts

In the Sarrabus-Gerrei (Southeastern Sardinia) the prevailing pre-Variscan mineralization consists mainly of stratabound non-economic volcano-sedimentary orebodies (containing antimonite, scheelite and arsenopyrite) hosted in the Lower Paleozoic lithotypes of the “External Nappes” (Carmignani *et al.,* 1994). Preferential host rocks are the Ordovician porphyritic metarhyolites (“Porfiroidi”), consisting of lava flows, local intrusive dykes and volcanoclastic rocks. These pre-Variscan successions are then cut by Variscan granodiorites (as the San Vito granite) and by Late-Variscan porphyry dykes. In the same area of Sarrabus-Gerrei Ba, Pb, F and Ag have also been exploited in several post-Variscan veins, as in the main structure called “Filone Argentifero del Sarrabus” (Masi *et al.,* 1975; Belkin *et al.,* 1984) and at Monte Genis, while the Silius hydrothermal vein system (F > Ba-Pb) is better known for its fluorite > galena economic concentrations (Natale, 1969). The Silius vein system occurs in the metasandstones and metasiltstones of Gerrei Units (Unità di Monte Lora), with intercalations of a thick complex of weakly metamorphosed acid volcanics of Middle Ordovician age. The fluorite-barite mineralized veins locally cut the Late-Variscan porphyry dykes (Natale, 1969), which allow to set a relative minimum age for the mineralization process. The most important veins (called “San Giorgio” and “San Giuseppe”) generally run parallel, but there are sites where they are clearly interconnected at 250 meters in depth and reach a maximum width of 20 m. Both veins present repeated successive generations of mineral phases with a prevailing ribbon-like geometry, frequently accompanied by breccias and cockade-like features at the intersection points (Fig. 2A, B). The general trends vary from N45E in the southwest, to N65E toward northeast. The San Giorgio vein (the first one to be deposited; Fig. 2A) contains microcrystalline quartz (“chalcedony”), pale colored fluorite, some sphalerite, marcasite and calcite. The San Giuseppe vein (Fig. 2B) contains several generations of fluorite, abundant calcite and galena. Barite was exploited mostly in the upper parts of the mine.

Pre-Variscan stratabound ores, hosted in Lower Cambrian platform carbonates, were the most economically significant deposits in Southwest Sardinia (Boni *et al.,* 1996), having

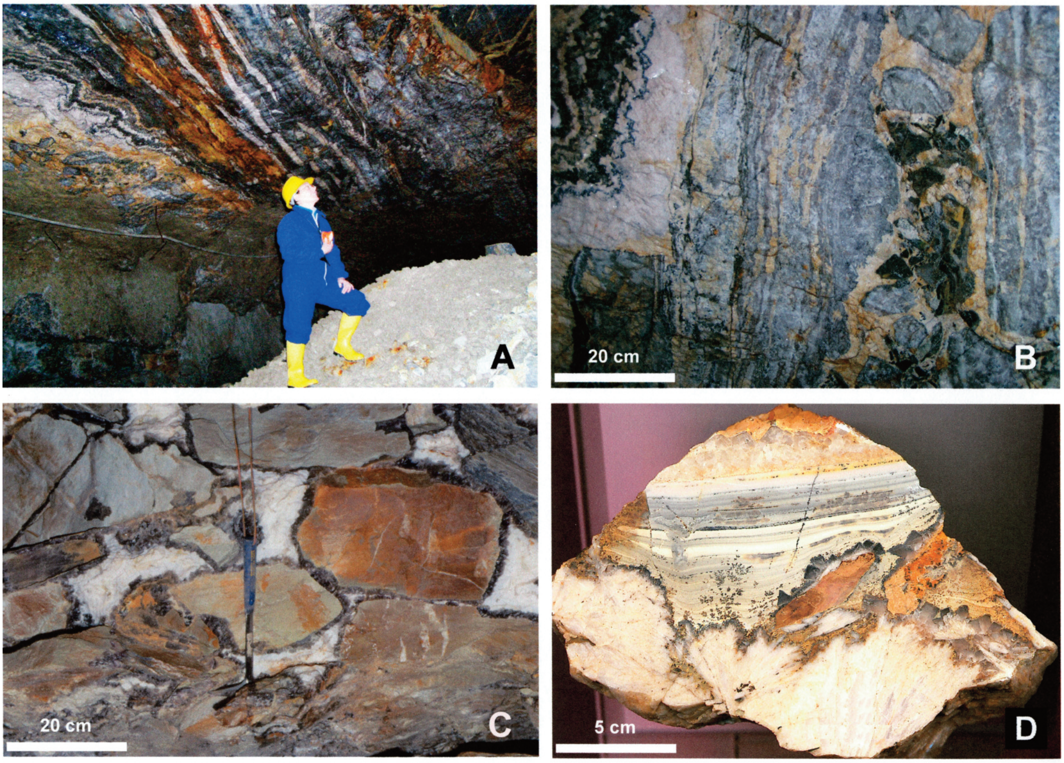

Fig. 2 - Southeast Sardinia, Silius Mine - level +235: A. Ribbon parallel structure (fluorite, calcite, chalcedony) of the San Giorgio vein; B. San Giuseppe vein (fluorite, calcite, galena) cutting and partly replacing the San Giorgio vein. Southwest Sardinia; C. Su Zurfuru mine - Collapse breccia cemented by fluorite and calcite; D. San Giovanni mine – Internal karst sediments.

produced more than 120 million tons of Zn-Pb and 12 million tons of barite ore over the last hundred years. All deposit types were particularly enriched along important paleotectonic lineaments that also controlled the distribution of sedimentary facies. Post-Variscan ore deposits, easily distinguishable from pre-Variscan ones due to the absence of Variscan folding and anchimetamorphic overprinting, were preceded by a strong and pervasive phase of hydrothermal dolomitization (*Geodic Dolomite*) affecting the Cambrian carbonate host rocks (Boni *et al.,* 2000). This dolomite, both replacive and void filling, frequently forms zebra structures with saddle-shaped crystals and occurs in the whole Iglesiente district (more than 500 km^2). The large-scale relationships between dolomite and limestone clearly show the post-deformational origin of this dolomite. *Geodic Dolomite* occurs frequently as bodies clearly cross-cutting the vertical Variscan foliation and apparently controlled by the former, as well as by later extensional faults.

The metallic ore deposits occur mainly in the same Cambrian carbonates as the pre-Variscan ones, while only occasionally are hosted in Cambrian to Silurian shales. They can be subdivided in vein- and palaeokarst-types and are controlled by structural lineaments following a pattern of crustal extension (Boni *et al.,* 2002).

The mineral assemblages in the veins range from sphalerite > galena > chalcopyrite to fluorite-barite > Ag-rich galena, while the ore minerals in the palaeokarsts are limited to barite and Ag-rich galena. In the latter types, the ore minerals occur as multistage cement of collapse breccias (Fig. 2C) or replace karst internal sediments (Fig. 2D). The porosity of hydrothermal dolomites can also be fully obliterated by newly precipitated ore and gangue minerals. The most important vein deposits in the Southwest are the Montevecchio-Ingurtosu vein system (Salvadori and Zuffardi, 1973; Zn > Pb >> Cu) in the northernmost Arburese area, the Su Zurfuru-Santa Lucia veins (F-Ba-Pb) near the village of Fluminimaggiore (Bakos and Valera, 1972), and the Barega and Mont'Ega barite veins in Sulcis (Boni, 1986). The palaeokarstic network hosting the barite and Ag-rich galena ores is typical of the areas around Iglesias and along the western coast (Boni *et al*., 2002).

Previous data on fluid inclusions and lead isotopes of late- to post Variscan ores and epigenetic dolomite

In the Southeast, the most common hydrothermal fluid system is represented by highly saline, Ca-rich fluids. In the Sarrabus mining district these fluids were detected by Belkin *et al.* (1984) in several mineral occurrences, as the Tacconis, S'Arcu Mannu, Su Casteddu and Is Crabus F-Ba-Zn-Pb complex veins. In the Serra S'Ilixi F-Ba-Pb(Ag) vein, belonging to the "*Filone Argentifero*", the main fluid is much less saline (around 0 °C last melting), but also relatively low in homogenization temperature (90 to 150 °C). This deposit may have resulted from a meteoric water plumbing system (Belkin *et al*., 1984).

The Pb-isotopic signatures measured in the galenas of Sarrabus-Gerrei vein deposits do not display a very broad range. They vary from 18.26 to 18.28 for $^{206}Pb/^{204}Pb$ and from 38.35 to 38.37 for $^{208}Pb/^{204}Pb$ (Dini *et al*., 2005) and fall in the same field as the high temperature veins of the Iglesiente-Arburese district (Boni *et al.,* 1992). The set of measured galenas from all orebodies shows an intermediate signature between the values recorded in the magmatic feldspars of the San Vito Variscan granite and the feldspars contained in the meta-rhyolitic "porphyroids" of Ordovician age, that are the common host rocks of most vein deposits.

Fluid inclusion studies of post-Variscan ore and gangue minerals in Southwest Sardinia have been published by Valera (1974), Boni (1986), De Vivo *et al.* (1987), Cortecci *et al.* (1989), and Boni *et al.* (1990, 1992, 2000). In the whole mining district, a H_2O-NaCl-$CaCl_2$ fluid with high salinities (above 20 wt. % NaCl eq.) and $T_h \leq 140$ °C, was responsible for the precipitation of most of the vein and palaeokarst ores, where the homogenization temperatures (T_h) represent fluids minimum trapping temperatures (Boni, 1986). However, independent geological constraints in this area support the assumption that pressure correction in the case of both veins and palaeokarst fillings is very small (Boni *et al*., 1992).

A similar H_2O-NaCl-$CaCl_2$ fluid (T_h mean ≈ 100 °C) caused the precipitation of the widespread hydrothermal dolomites in the same area (Boni *et al*., 2000), which preceded the deposition of most ores. Another type of fluid, with lower salinities and T_h up to 200 °C, has been locally recorded in the veins located near magmatic intrusions and at the periphery of skarn bodies (Boni *et al*., 1990, 1992, 2002). Inclusions in calcites and barites, possibly related to the latest stages of low temperature vein- and palaeokarst deposits, contain H_2O-NaCl type fluid, characterized by very low salinities (0 - 1 wt. % NaCl eq. and T_h values in the 70 -130 °C range; Boni *et al.*, 1992).

Pb-isotope ratios of galenas from skarn- and high temperature vein ores and from low temperature vein- and palaeokarst deposits in

SW Sardinia, form two distinct groups (Boni *et al*., 2002; Fig. 3). The first group is characterized by $^{206}Pb/^{204}Pb$ = 18.01 - 18.29 and $^{208}Pb/^{204}Pb$ = 38.17 - 38.47, whereas the second group yields values of $^{206}Pb/^{204}Pb$ = 17.86 - 18.07 and $^{208}Pb/^{204}Pb$ = 37.95 - 38.20, respectively (Swainbank *et al*., 1982; Boni and Köppel, 1985; Ludwig *et al*., 1989). Pb-ratios of galenas from the first group are similar to the values measured in the feldspars of Variscan granites, while the isotopic values of the second group are near to the compositions of the Cambrian stratabound ore-lead and to those of hydrothermal dolomites ($^{206}Pb/^{204}Pb$ = 17.80 - 17.95, $^{208}Pb/^{204}Pb$ = 37.84 - 38.05, Boni and Köppel, 1985; Fig. 3). These Pb-isotopic signatures indicate that in this area, for the late- to post Variscan hydrothermal products there has been a mixed contribution of Cambrian ore lead and of Variscan lead. The latter might have been derived from interaction of the hydrothermal fluids either with Lower Paleozoic clastic sediments and/or with Variscan granites (Boni *et al*., 1992). A strong isotopic similarity between feldspar-lead in the Early Cambrian basal sandstone and ore-lead in the carbonates exists, pointing to a direct involvement of the pre-Cambrian (not outcropping) crystalline basement as metal source (Boni *et al*., 1992, 1996). On the other hand, the Pb-isotope signatures of the post-Variscan ores show that they are mixtures of the Cambrian (basement-derived) ore-lead and of the highly radiogenic, Upper Cambrian-Ordovician sediment-derived lead (Boni *et al*., 1992).

Analytical Methods

More than 300 inclusions were measured in fluorite, calcite, sphalerite and quartz samples representative of the Silius (Sarrabus) and Montevecchio (Arburese) vein systems. In the Montevecchio system only the quartz-sphalerite association of the S. Antonio Vein has been investigated. Some inclusion-rich samples were also subjected to preliminary crush-leach analysis (D. Banks), to determine the composition and the origin of the mineralizing fluids.

Microthermometric analytical measurements on fluid inclusions have been carried out at the Dipartimento di Scienze della Terra of the University of Napoli Federico II, using the Linkam TH 600 stage. The stage was calibrated using synthetic fluid inclusions (Bodnar and Sterner, 1987). The inclusions are primary and secondary in origin (some of the inclusions can also be considered pseudosecondary); the secondary inclusions are derived from post-crystallization trapping of fluids in different generations of fractures.

Vapor and liquid-rich fluid inclusions are irregular in shape and range in length from 1µm to 10µm. Leakage and stretching was detected mainly in calcite and corresponding inclusions were avoided.

Preliminary ionic composition of fluid inclusions was determined by crush-leach analysis on several samples from the Iglesiente and Sarrabus mining districts. The analyses were carried out at the laboratories of the School of Earth Sciences of the University of Leeds (UK) by Louise Fisher, using the procedure described by Banks and Yardley (1992) and Banks *et al.* (2002). The samples comprised the hydrothermal dolomites from Iglesiente (*Geodic Dolomite*, Boni *et al*., 2000), quartz and calcite from the paleokarst ores of the San Giovanni mine (Iglesiente) (Boni, 1986), fluorite and calcite from the Silius veins (Sarrabus). Samples between 0.5 and 1 g were crushed to a grain size of 1 to 2 mm, cleaned in distilled water and hand-picked. The samples were then cleaned by repeated boiling and rinsing, crushed to a fine powder and leached in doubly distilled water for anion and alkali analysis. The final leachates obtained from the powder were analyzed for Cl^-, Br^- and SO_4^- using ion chromatography, and Na^+, K^+, and Li^+ by flame emission spectroscopy (FES). Detection limits for Cl, Br, SO_4, Na, K,

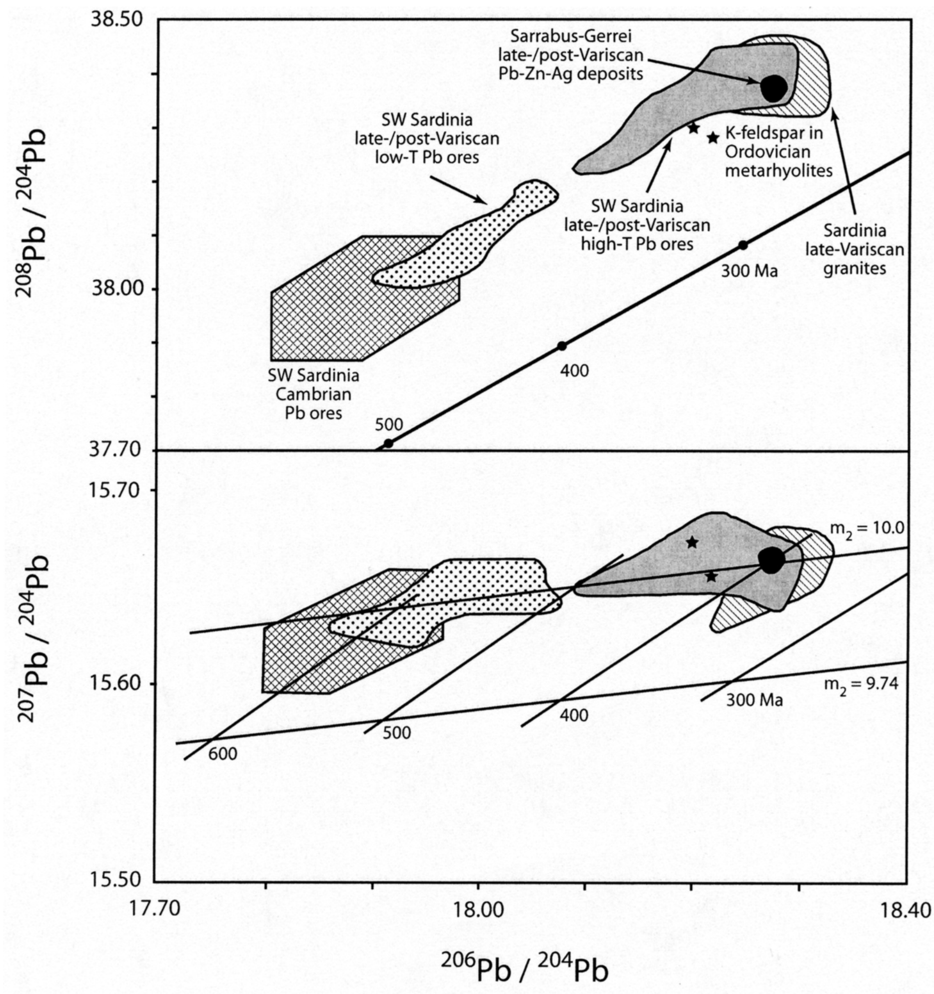

Fig. 3 - Fields of Pb-isotope diagrams for the southwest Sardinia post-Variscan vein- and paleokarst deposits (from Boni *et al.* 1992), and for the vein ores in the Southeast (Dini *et al.* 2005). Fields of isotopic composition of the Paleozoic stratabound ore deposits, of Ordovician "porphyroids" and of late Variscan granites in Sardinia are also shown.

and Li were 10, 0.2, 10, 30, 30, and 0.1 ppb, respectively.

Four calcite samples from the Silius veins were analysed for O and C isotope ratios at the University of Erlangen (Germany). Carbonate powders reacted with 100% phosphoric acid at 75 °C (Wachter and Hayes, 1985) in an online carbonate preparation line, connected to a Finnigan Mat 252 mass spectrometer. $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios were measured simultaneously on the CO_2 gas produced. Calibration was accomplished by assigning a $\delta^{18}O$ value of -2.20 ‰ and a $\delta^{13}C$ value of 1.95 ‰ to the NBS-19 standard. The $\delta^{13}C$ values for carbonates are reported in ‰ V-PDB and $\delta^{18}O$ values in ‰ V-SMOW. Reproducibility was checked by replicate analysis of laboratory standards and is better than ±0.02.

Results

Monophase inclusions were found both at Silius and Montevecchio; they are also more common in calcite. Microthermometric data are reported in Tables 1 and 2.

The homogenization versus last ice-melting temperatures from primary and secondary inclusions in fluorite and calcite in the Silius veins are depicted in Fig. 4. At Silius, microthermometric measurements have been carried out on fluid inclusions in fluorite and calcite from the San Giorgio and San Giovanni veins, mainly sampled in the Gennas Tres Montis mine, at the level +300 around the shaft. More than two hundred primary and secondary liquid-rich fluid inclusions were measured in fluorite and calcite samples, representative of the two different vein systems of the mine. The data led us to the conclusion that at least two fluids circulated during the mineralization event(s) at Silius.

The first was a $NaCl \pm CaCl_2$ fluid, trapped in primary FI in fluorite from both veins, which precipitated mainly fluorite in the 120 -150 °C temperatures range. The second fluid circulated after fluorite deposition, precipitating mainly calcite at temperatures in the 130 -180 °C range. This fluid was trapped in primary FI in calcite (in the San Giorgio vein) and secondary FI in fluorite (in the same vein). The salinity of this fluid can be only estimated (0 - 18 wt.% NaCl equiv.) due to the undiscernible overlap of different generations of FI. Other fluids probably circulated after the main phase of calcite deposition and their presence is recorded in secondary FI in calcite in both veins. The very low first melting temperatures (i.e. estimated eutectics ~ -50 °C) recorded in both fluorite and calcite, suggest the presence of Ca-rich fluids, similar to those measured not only in the ores of southwestern Sardinia (Iglesiente, Arburese), but also in the hydrothermal (*Geodic*) dolomites.

Preliminary stable isotopes data measured in the calcite from the veins are quite puzzling (Table 3). In fact C-isotopes show fairly negative values in all samples (-4.80 to -5.30 $\delta^{13}C_{V\text{-}PDB}$). These low values are possibly due to the interaction of the circulating fluids with the organic-rich Ordovician-Silurian formations, while O-isotopic data have an ample spread between -16.50 and -22.00 $\delta^{18}O_{V\text{-}SMOW}$. Referring in first approximation to the calcite-water equilibrium curves of O'Neil *et al.* (1969), it is possible to argue that the fluids involved in the Silius mineralization were salty brines of undefined nature, either of basinal, or even meteoric origin, that have been heavily modified by interaction with a wide series of sedimentary and/or magmatic host rocks.

New measurements in the quartz-sphalerite association of the Sant'Antonio vein at Montevecchio show data not very different from those recorded in the Iglesiente post-Variscan ores (Table 2). Average T_h values of primary inclusions in quartz and sphalerite are in the 75 -104 °C range, while salinities range from 20 to 22 wt. % NaCl eq. Secondary inclusions have a larger temperature spread (50-110 °C) and are generally more saline (from 21 to >23.18 wt. % NaCl eq.). From the very low values of the eutectic temperatures (-57 - -46 °C), the fluids depositing both quartz and sphalerite in the Montevecchio vein should belong to the $NaCl\text{-}CaCl_2$ system.

Preliminary crush-leach data on the minerals of SW and SE Sardinia (L. Fisher)

The fluid inclusions in the measured samples are both primary and secondary, with quite similar salinities. As a consequence, mixing between primary and secondary fluids during the bulk crush-leach analysis is minimal in most samples, and the analyses so obtained are considered to be representative of the highly saline fluids that precipitated the hydrothermal minerals.

The relative Na-Cl-Br composition of the fluids provides important information on their

TABLE 1
Fluid inclusions in fluorite and calcite from the Silius veins system.

Fluorite								**Calcite**							
S. Giorgio Vein				*S. Giuseppe Vein*				*S. Giorgio Vein*				*S. Giuseppe Vein*			
Primary		Secondary		Primary		Secondary		Primary		Secondary		Primary		Secondary	
T_h	T_m	T_h	T_m	T_h	T_m	T_h	T_m	T_h	T_m	T_h	T_m	T_h	T_m	T_h	T_m
121.2	-36.7	126.7	-22.7	148.4	-22.1	128.4	n.a.	97.6	-6.0	124.0	n.a.	76.8	-12.3	91.5	-43.4
120.6	-36.4	154.3	-13.3	149.9	-19.2	147.9	n.a.	130.0	-6.1	150.0	n.a.	74.8	-10.6	95.1	-38.0
108.9	-36.4	161.2	-13.1	149.3	-18.5	145.1	n.a.	167.0	-5.9	175.0	n.a.	84.1	-8.0	116.8	-32.8
120.4	-36.2	149.3	-11.6	155.1	-17.9	174.1	n.a.	81.0	n.a.	102.2	-16.7	81.5	-6.9	77.0	-18.8
119.8	-36.1	113.6	-7.9	156.1	-17.2	153.5	n.a.	125.0	-8.2	94.0	-16.8	87.9	-18.9	106.1	-30.0
118.3	-36.0	135.2	-1.7	154.2	-16.9	139.2	n.a.	85.9	-8.0	91.9	-16.6	79.9	-9.0	94.4	-48.1
118.9	-36.0	170.1	-0.1	151.6	-16.5	131.6	n.a.	77.2	-1.6	122.5	-16.4	75.8	-17.6	55.5	-36.6
119.5	-35.9	173.4	-0.3	153.6	-16.3	136.3	n.a.	83.4	-1.4	102.2	-16.3	89.1	-4.3	95.8	-12.0
119.4	-36.6	137.1	-0.4	158.3	-15.6	156.8	n.a.	159.9	-1.3	99.4	-16.9	88.9	-7.1	84.4	-23.0
121.6	-35.5	119.9	-0.2	162.4	-14.5	171.2	n.a.	165.9	-1.2	72.7	-16.2	67.9	-17.5	80.3	-28.0
115.8	-36.7	143.5	-14.2	119.7	-18.1	153.3	n.a.	105.1	-1.7	92.5	-17.0	83.3	-17.2	76.9	-17.0
117.8	-36.1	128.9	-13.4	116.7	-17.6	144.9	n.a.	102.6	-1.5	76.1	-3.1	88.4	-17.3	75.3	-20.0
122.1	n.a.	131.8	-12.4	121.6	-17.5	154.9	n.a.	107.2	-8.7	107.6	-2.9	87.2	n.a.	76.5	-27.0
117.1	n.a.	127.9	-1.3	123.1	-17.5	132.5	n.a.	111.9	-8.8	115.9	-3.0	74.6	n.a.	85.3	-23.0
120.0	n.a.	141.3	-1.1	120.6	-16.9	146.0	n.a.	106.3	-8.9	86.3	-3.2	67.0	n.a.	90.3	-21.1
128.4	n.a.	137.2	-0.8	129.9	-16.7	147.9	n.a.	122.5	-11.5	143.7	-3.1	82.5	n.a.	90.4	-21.1
130.7	n.a.	159.9	-0.5	122.7	-16.5	141.8	n.a.	90.4	-11.3	96.2	-3.3	103.1	n.a.	116.5	-12.4
132.9	n.a.	130.6	-1.2	117.8	-16.1	171.7	n.a.	110.2	-8.7	98.6	-2.8	88.5	n.a.	110.1	-12.6
122.1	n.a.	146.7	-1.5	118.9	-15.9	181.1	n.a.	120.6	n.a.	108.1	n.a.	90.0	n.a.	103.1	n.a.
88.3	n.a.	163.8	-1.8	119.4	-15.6	145.8	n.a.	104.0	n.a.	102.7	n.a.	90.0	n.a.	92.0	n.a.
98.0	n.a.	137.1	-1.8	120.0	-15.4			134.6	-8.7	128.2	-8.9	79.7	n.a.	114.5	n.a.
99.4	n.a.	172.6	-2.0	125.4	-15.3			111.2	-8.8	120.0	-8.9	77.0	n.a.	100.3	n.a.
115.3	n.a.	140.0	-2.2	123.6	-15.1			104.2	n.a.	121.0	-8.7	87.1	n.a.	94.4	n.a.
116.6	n.a.	164.0	-2.5	116.9	-14.9			107.9	-6.9	111.4	-9.0	107.9	n.a.	85.0	n.a.
122.0	n.a.	158.5	-2.6	115.8	-14.4			118.8	n.a.	113.4	-10.8	114.3	n.a.	94.4	n.a.
117.0	n.a.	137.7	-2.7					133.5	-13.9	129.5	-10.9	87.1	n.a.	77.8	n.a.
120.0	n.a.	173.3	-3.0					123.1	n.a.	113.5	n.a.	78.6	n.a.	58.2	n.a.
120.4	n.a.	146.5	-5.0					86.8	-6.7	100.8	n.a.	79.2	n.a.	82.8	n.a.
120.3	n.a.	105.5	n.a.					108.0	-9.0	99.2	n.a.	76.1	n.a.	84.0	n.a.
122.0	n.a.	134.4	n.a.					112.0	-9.0	116.3	n.a.	66.9	n.a.	77.0	n.a.
119.0	n.a.	122.6	-16.5					111.9	-8.2	87.2	-25.0	71.3	n.a.	92.3	n.a.
122.3	-42.8	169.4	-16.3					112.1	-8.1	89.2	-25.1			79.4	n.a.
107.2	-36.4	119.9	-13.9					119.2	-9.0	116.8	-8.5			76.6	n.a.
108.9	-31.3	103.0	-13.7					118.3	-8.6	86.2	-50.0			85.1	n.a.
119.8	-29.8	120.8	-12.1					122.1	-8.7	97.2	-48.6			70.7	n.a.
120.6	-28.7	145.0	-10.6					127.9	-9.1	103.1	-43.3			79.1	n.a.
115.9	-25.1	174.4	-10.4					98.9	-10.7	116.0	-45.7				
112.5	-24.5	160.2	-7.5					102.6	-9.0						
109.7	-23.6	124.6	-4.3					97.2	-7.0						
113.9	-27.2	158.5	-1.1												
118.9	-28.7	137.7	-0.9												
115.7	-26.7	173.3	-0.6												

n.a. = not analyzed

Table 2
Fluid inclusions in sphalerite and quartz from Sant'Antonio vein (Montevecchio).

Quartz				Sphalerite			
Primary		*Secondary*		*Primary*		*Secondary*	
T_h	T_m	T_h	T_m	T_h	T_m	T_h	T_m
76.4	-18.3	58.0	-21.2	n.a.	-21.4	98.5	-22.4
82.3	n.a.	63.4	-17.7	101.9	-19.9	105.1	-11.1
88.6	n.a.	69.4	-17.7	66.7	n.a.	109.8	-20.2
104.3	n.a.	75.2	n.a.			78.8	-24.7
82.2	-17.7	76.9	n.a.			89.3	n.a.
82.2	-17.5	92.1	n.a.			124.5	n.a.
85.8	-17.2	104.5	n.a.			94.5	-22.8
89.3	-17.1	114.6	n.a.			96.5	-19.1
80.1	-17.5					101.2	-17.1
						105.6	-15.6
						109.8	n.a.
						81.6	n.a.

n.a. = not analyzed

Table 3
Stable isotope data for selected calcite samples from the Silius ore deposit.

sample #	δ^{13}C V-PDB (‰)		δ^{18}O V-SMOW (‰)	
	$\delta^{13}C$	*std.dev.*	$\delta^{18}O$	*std.dev.*
SGG 1	-4.86	0.02	19.25	0.03
SGG 2	-5.13	0.02	17.08	0.02
SGP 1	-5.15	0.03	22.45	0.04
SGP 2	-5.30	0.01	16.51	0.03
SGP 3	-5.05	0.02	16.67	0.02

origin (Muchez *et al.*, 2005). The Cl/Br vs. Na/Br diagram from fluid inclusion leachates of both ore and gangue minerals is shown in Fig. 5; in this plot, most analyses form a cluster with Na/Br and Cl/Br values significantly lower than those of seawater. These data indicate that both the dolomitising fluids, as well as the fluid precipitating the post-Variscan ores derive from strong evaporation of seawater (seawater evaporation brine). Three samples from the San Giovanni mine and one from the Silius veins show somewhat higher ratios. This could be indicative of mixing between a bittern brine and a halite dissolution brine, or between a bittern brine and seawater (D. Banks, personal communication).

Additional data on ionic composition of the Montevecchio-Ingurtosu minerals have recently been determined also through crush-leach analysis at the University of Leoben, Austria (Honisch, 2008). Crush-leach data of quartz, calcite and barite from the Ingurtosu vein show a significant evaporation trend that is confirmed by the presence of anhydrite crystals within quartz. The galena- and sphalerite-mineralization seem to derive from a distinct fluid event that shows no trend in the Na/Cl-Br/Cl diagram.

Discussion and conclusions

Based on comparative investigation on the peculiar physico-chemical characteristics of the fluids of ore and gangue minerals, as well as on the probable metal sources deduced from Pb-isotopes, it appears that post-Variscan hydrothermal activity and mineralization in southern Sardinia can be assigned to at least two temporally and spatially distinct fluid systems.

The main hydrothermal system acting in the Southwest (low-temperature veins and palaeokarst, 70 - 150 °C) is represented by highly saline, Ca-rich fluids (Fig. 6). These fluids circulated over a large area, generally detached from known intrusive bodies. The Pb isotopic signatures (Fig. 3) of the ore and gangue minerals are dominated by values similar to Cambrian stratabound ores and carbonate host rocks, with only a minor contribution of a radiogenic "Variscan" source, probably as a result of a low temperature regime and/or of lower water/rock ratios (Boni *et al.*, 1992). At least part of the Montevecchio ores belong to the same fluid system. A second system (skarn aureoles and high temperature vein deposits, 150

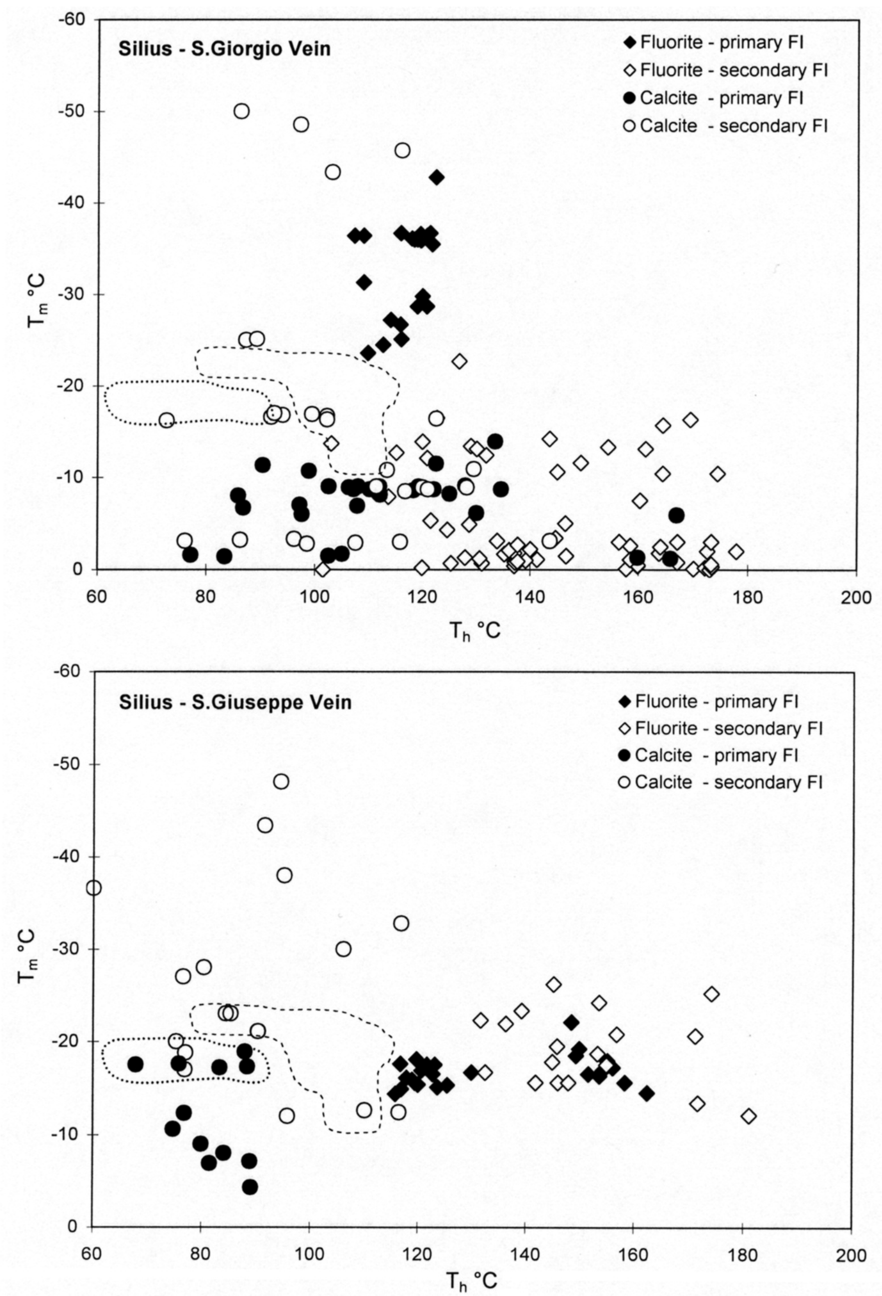

Fig. 4 - Plots of last ice-melting *vs* homogenization temperatures from primary and secondary inclusions in fluorite and calcite in the San Giorgio and San Giuseppe veins, Silius mine. Dotted fields are related to the T_m *vs* T_h values from primary and secondary inclusions in Montevecchio quartz, dashed fields are those of Montevecchio sphalerite.

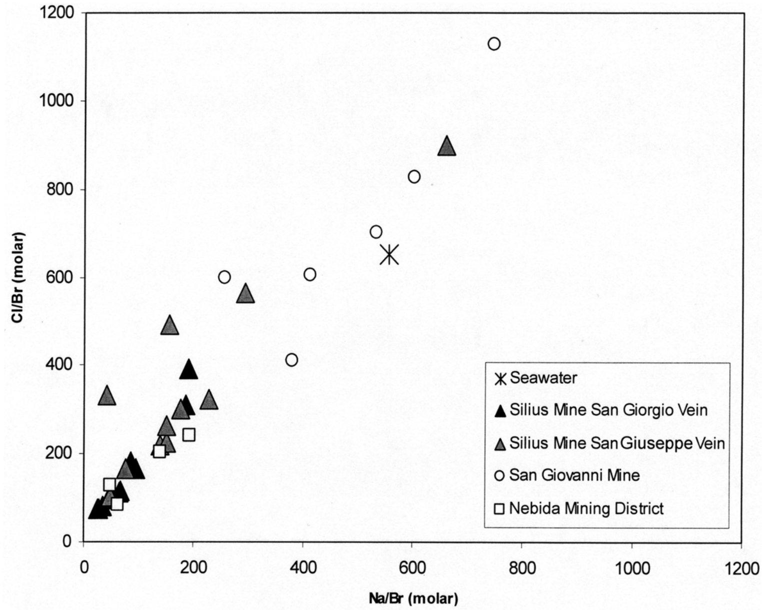

Fig. 5 - Na-Cl-Br composition of mineralizing fluids from the districts quoted in text. Seawater evaporation trend after McCaffrey *et al.* (1987).

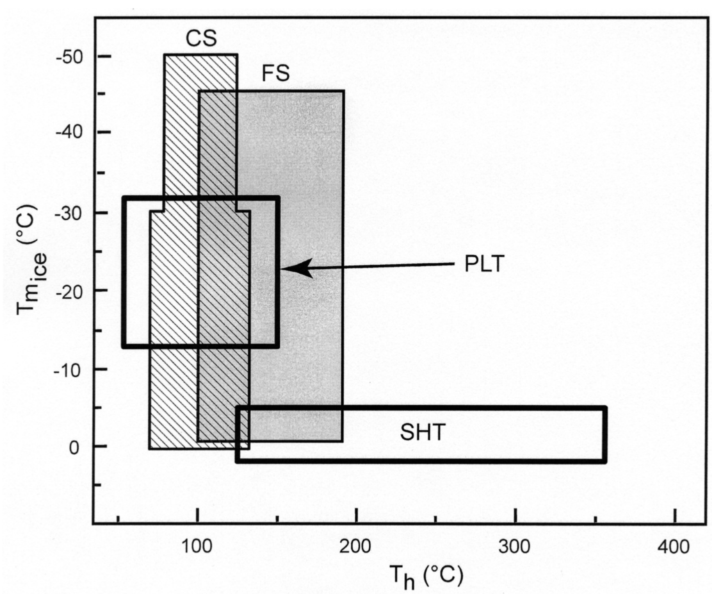

Fig. 6 - Schematic T_h *vs* T_m fields for the primary and secondary inclusions measured in S. Giorgio and S. Giuseppe Veins fluorite (FS) and calcite (CS) of the Silius mine (Southeast Sardinia), compared to the fields of skarn/high temperature veins (SHT) and paleokarst/low temperature veins (PLT) in Iglesiente-Arburese (Southwest Sardinia).

- 350 °C; Fig. 6) was active in close proximity of post kinematic leucogranite intrusions. It is characterized by "magmatically heated", meteoric fluids of relatively low-salinity. Pb isotopes of related minerals (Fig. 3) bear the imprint of a radiogenic "Variscan" component, associated either with the late-Variscan magmatic rocks, or with the low-grade metamorphic Paleozoic or pre-Paleozoic basement. According to the unpublished data on Montevecchio ore reported by Honisch (2008), the paleotemperatures estimated with Na-K thermomenter vary around 300 °C for PbS and almost all ZnS samples.

Pb-isotopes from sulfides in post-Variscan veins in Sarrabus-Gerrei have an intermediate signature between the K-feldspars of the Variscan leucogranites and the feldspars from the Ordovician metarhyolites ("Porphyroids"). Specifically, the ore lead could have been derived by a mixture in various proportions of lead from the Ordovician metarhyolites and metasediments and the late-Variscan granites.

In conclusion, it appears that the deposits, both in the southwest and in southeast of Sardinia, tapped their lead (and possibly other elements as well, as fluorine, that could have been originated from the leucogranites and/or the "porphyroids") from a single homogeneous source (or at least from a homogenized mixture of different sources), during several mineralizing stages broadly defined as the "post-Variscan hydrothermal event". However, at the moment we cannot precisely constrain the timing and duration of this hydrothermal activity in southern Sardinia. In particular it is not known whether the fluid circulations are the expression of only one long lasting tectonothermal event over the time span between the end of the Variscan orogeny and the onset of the Alpine cycle, or they are the result of temporally and genetically distinct thermal pulses (Boni *et al*., 2002).

It has to be noticed, however, that the precipitation from highly saline brines is a common feature of post-Variscan mineralizations throughout Western and Central Europe (Boni *et al*., 2002), where the origin of corresponding fluids has been interpreted as related to the expulsion of formation waters from Permian (and Triassic?) intercontinental basins and/or of Paleozoic brines from basement rocks (Muchez *et al*., 2005).

Many ore deposits throughout Europe reflect an important Lower- to Middle Permian hydrothermal event (isotopic ages of ~ 270 Ma), that has also been proposed for Sardinia by Boni *et al.* (1999, 2002). This age reflects a first post-orogenic period of pronounced crustal extension, related to dextral wrenching and plate reorganization in the Laurasia-Gondwana realm, that was characterized by intense rifting and hydrothermal activity (Arthaud and Matte, 1977; Ziegler, 1990). Other, much younger events were possibly active throughout the Mesozoic.

Finally Boni *et al*. (2002) and Muchez *et al*. (2005) have discussed how the metallic brines penetrated the basement and caused the formation of even more important economic deposits in western Europe during the Mesozoic. Isotopic ages of mineralizations precipitated from these fluids found mainly all over the European plate are Triassic and Jurassic. As in most parts of Europe, the veins and palaeokarst fillings in southern Sardinia seem typically to have been precipitated from highly saline H_2O-$NaCl$-$CaCl_2$ fluids during the Mesozoic. Especially Jurassic fluid systems have generally been interpreted as an expression of continent-wide rifting and concomitant regional fluid circulation reflecting major tectonic disturbances that enhanced the heat flow preceding the opening of the North Atlantic Ocean. Taking into account the paleogeographical position of the island of Sardinia, close to the southern boundary of the European plate, it seems quite logical to identify a genetic link between the hydrothermal activity and the evolving margin of the Tethys.

Acknowledgements

We would like to thank David Banks for permission to quote the unpublished crush-leach data from the Master Thesis of L.Fisher. We also thank A. Gianfagna, Principal Editor of the Periodico di Mineralogia, and the two referees, Q.G. Crowley and G. Iezzi, for their helpful comments.

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