

Mineral assemblages, stable isotopes and fluid inclusions in ore veins from the Macigno Formation at Calafuria (Livorno Mountains, northern Tuscany, Italy)

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ABSTRACT. — The present paper deals with an integrated geological, mineralogical and geochemical study on mineralized faults and fractures recognized in the Macigno Formation at Calafuria in the Livorno Mountains of northern Tuscany. In the field, two main different systems of faults were recognized: an earlier one related to a compressive phase with NE-SW, NW-SE and N-S trending faults, and a younger one related to a relaxation phase with reactivation of N-S and NW-SE trending faults. They distinguish for specific mineral assemblages, consisting mainly of quartz in the former, and barite-marcasite-pyrite in the latter. Minerals were analyzed for fluid inclusions and isotopic composition. Data on fluid inclusions indicate that three main mineralizing episodes affected the fault systems. In the first episode, the fluids deposited quartz in the fault systems related to the compressive phase. The second episode was the main one, and led to the deposition of euhedral quartz in the NE-SW faults, and barite, marcasite and pyrite essentially in the N-S and NW-SE faults. The fluid evolution ended with the deposition of calcite, dolomite and a series of supergene minerals originated by alteration of Fe-sulfides.

The sulfur isotopic composition of minerals (–6.3 to 25.1‰) would seem to exclude a magmatic origin of the sulfur, favoring instead a sedimentary origin. Moreover, a temperature of about 400°C is estimated by sulfur isotope thermometry for the second stage of mineralization. Owing to pressure effects, the homogenization temperature given by the fluid inclusions for this stage of mineralization is considerably lower than the isotopic one.

Lithostatic pressure of 125 MPa is estimated for the barite and sulfide mineralization, this corresponding to a depth of 5 km. Finally, a post-Middle Pliocene age is proposed for the ore veins at Calafuria, that may have formed during tectonic relaxation events from hydrothermal fluids rich in CO₂ and H₂S, as are observed in the Larderello geothermal area at present.

RIASSUNTO. — Il lavoro riguarda un'indagine integrata geologica, mineralogica e geochimica di faglie e fratture mineralizzate nel Macigno di Calafuria, nei Monti Livornesi (Toscana settentrionale). In campagna, sono stati riconosciuti due principali sistemi di faglie, una più antica connessa a una fase compressiva e caratterizzata da faglie con direzione NE-SW, NW-SE e N-S, l'altra più recente relazionata a una fase distensiva con riattivazione delle faglie N-S e NW-SE. I due sistemi si differenziano per la

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presenza di specifici insiemi mineralogici, costituiti prevalentemente da quarzo in quello compressivo, e da barite-marcasite-pirite in quello distensivo. Una serie di minerali è stata analizzata per le inclusioni fluide e per la composizione isotopica. I dati sulle inclusioni fluide individuano tre principali episodi mineralizzanti. Il primo ha depositato quarzo in tutte le faglie connesse alla fase compressiva, il secondo e più importante ha mineralizzato con cristalli di quarzo eudrale le faglie NE-SW, ed essenzialmente con barite, marcasite e pirite le faglie N-S e NW-SE, ed infine il terzo ed ultimo episodio con una deposizione diffusa di calcite, dolomite e prodotti limonitici.

La composizione isotopica dello zolfo sembrerebbe escludere un'origine magmatica dello zolfo, favorendo invece un'origine sedimentaria dello stesso. La temperatura isotopica calcolata per il secondo episodio di mineralizzazione è di $400 \pm 50^\circ\text{C}$. Barite e solfuri metallici dovrebbero essere di età post Pliocene Medio, ed essere stati depositi ad una profondità di 5 km, corrispondenti ad una pressione litostatica di 125 MPa, da parte di fluidi idrotermali ricchi in CO_2 e H_2S , analoghi a quelli attuali dell'area geotermica di Larderello.

KEY WORDS: *vein ores, mineralogy, fluid inclusions, stable isotopes, Macigno Fm., Livorno Mountains, Tuscany.*

INTRODUCTION

The Macigno Formation, outcropping at Calafuria (hereinafter MFC) in the Livorno Mountains in northern Tuscany, facing the Ligurian Sea (Fig. 1), is the site of widespread sulfide and barite mineralization occurring along faults and fractures. The present study was carried out in order to (1) characterize the mineral assemblages in terms of major and minor components, meanwhile describing the tectonic lineaments of the mineralized systems, (2) compare the environment of mineralization with other similar occurrences in Tuscany, and (3) investigate the chemical-physical conditions of the hydrothermal fluids, and the mechanism and timing of mineralization, coupling mineralogical, isotopic and fluid inclusion data.

GEOLOGICAL SETTING

The Livorno Mountains constitute a structural high enveloped to the east by normal faults trending NNW-SSE and delimiting Apennine units from Upper Miocene terrains (Giannini, 1962; Bartoletti *et al.*, 1986), to the west by the shoreline extending between the towns of Livorno (Leghorn) and Castiglioncello, to the north by a fault system trending NE-SW, and to the south by faults trending WNW-ESE, that oppose Apennine units to Lower Pleistocene terrains (Bartoletti *et al.*, 1986). Neogene-Quaternary sediments lie conformably on the Apennine units (sands, pebbles and cemented marine deposits), and outcrop as monoclinical sequences deepening toward the NE along the northern and eastern borders of the area, and toward the SW along the southern border.

MFC is the only member of the Tuscan Nappe known throughout the Livorno Mountains (Tavani, 1954; Malatesta, 1954), and extends from 10 km to the south of Livorno for about 3 km along the Ligurian coast. It is overlain by tectonic units of the allochthonous Ligurids complex (Fig. 1), and is limited (1) to the north by a fault system that opposes the MFC to the Antignano formation (sandstones, marls, calcareous-marl flysch) of the lower Ligurids sequence, (2) to the south by the ophiolites of the upper Ligurids complex, and (3) to the west by the Antignano formation (Lazzarotto *et al.*, 1990). Structurally, MFC constitutes a map-scale body that deepens north-westward in its northern portion and north-eastward in its southern portion.

MFC shows a high ratio of sandstone to pelite, and consists of coarse layers up to three meters in thickness, the latter facies being largely predominant with respect to fine-grained thin layers (Bracci *et al.*, 1985; Manasse, 1905). The rock is grey, with local large yellow-reddish stains due to superficial alteration of iron sulfide to iron hydroxide. Barite veins also occur in the Macigno of Calafuria; they were first recorded by Della Valle (1865), and described in more detail by Uzielli (1876), De Stefani (1877), D'Achiardi (1877), Rodolico (1942) and Bracci and Orlandi (1990). These authors did not give any genetic interpretation on these findings.

The whole MFC outcrop was site of intense digging activity that dates back to the Roman

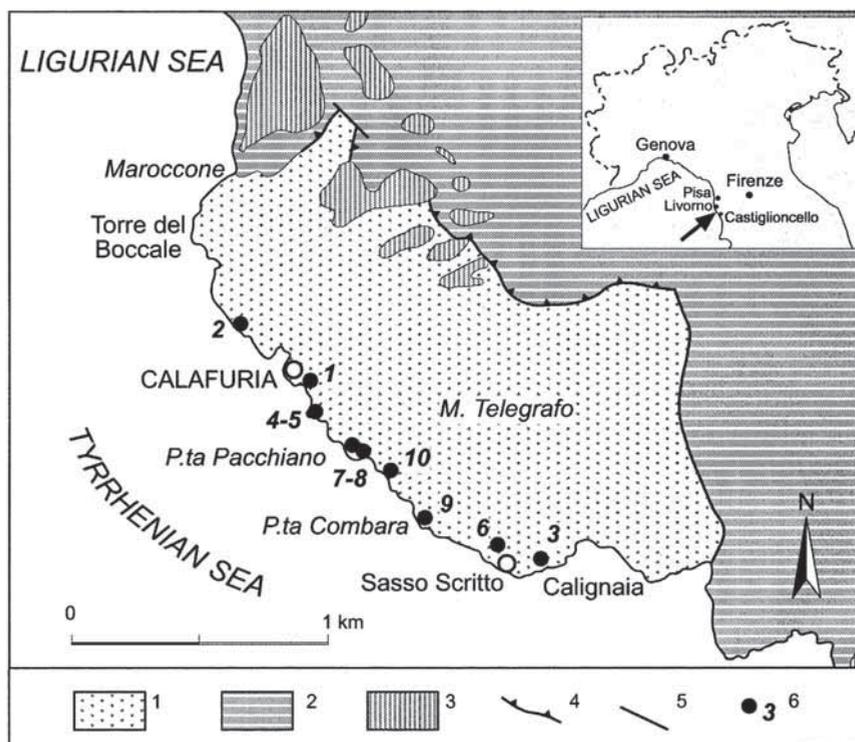


Fig. 1 – Sketch geological map of the Calafuria area, southeast of Livorno town (modified from Galoppini *et al.*, 1996). 1 = Macigno Formation of Calafuria (Tuscan Nappe); 2 = ophiolites (Ligurids Complex); 3 = Pleistocene terranes; 4 = overthrust; 5 = faults; 6 = mineral veins and sampling sites.

Empire (Galoppini *et al.*, 1996). All quarries display generally a staircase architecture and sometimes amphitheatre and pit structures.

ANALYTICAL METHODS

Identification and characteristics of the mineral assemblages were carried out by means of X-ray diffraction and by EDS-SEM chemical analyses at the Department of Earth Sciences of Pisa. Trace elements in an ore hand-specimen were determined by ICP and AAS analyses at the OMAC Laboratories Ltd (Eire).

The sulfur isotope analysis was performed on barite, marcasite, sphalerite and galena separates from major veins. Sulfur was extracted as SO_2 following the method of Gieseman *et al.* (1994),

and the isotopic composition determined by means of a mass spectrometer. The isotopic composition of sulfur is expressed as $\delta^{34}\text{S}$ unit, in permil, relative to Canyon Diablo Troilite standard, and its analytical precision was about $\pm 0.2\%$. The carbon and oxygen isotope analyses on calcite specimens were carried out on the CO_2 extracted from calcite with 100% H_3PO_4 at 25°C (McCrea, 1950). The isotopic composition is given as $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ units, in permil, relative to PDB and V-SMOW standards, respectively. The analytical precision was better than $\pm 0.1\%$. The oxygen isotopic composition of quartz was determined converting oxygen to CO_2 through fluorination with BrF_5 (Clayton and Mayeda, 1963), and expressed as $\delta^{18}\text{O}$, in permil, relative to V-SMOW. The precision was within $\pm 0.2\%$.

Petrographic and microthermometric analyses were conducted on the fluid inclusions trapped in the quartz, barite, sphalerite and calcite, using doubly-polished sections of thickness variable from 100 to 200 μm . The petrographic analyses were performed using the standard criteria proposed by Roedder (1984), whereas an USGS gas flow heating-freezing stage, assembled on a Leitz microscope, was used for the microthermometric measurements, with accuracy of $\pm 0.2^\circ\text{C}$ on freezing and $\pm 2^\circ\text{C}$ on heating below 400°C . The stage was calibrated at low temperatures with chloroform (-63.0°C), carbon tetrachloride (-22.8°C) and distilled water (0.0°C), and at temperatures above zero with naphthalene (80.5°C), chloroantraquinone (209.03°C), antraquinone (284.59°C) and potassium dichromate (398°C). The temperatures of homogenization (T_h), eutectic (T_e) and final melting of ice ($T_{m_{\text{ice}}}$) were measured at least twice on each inclusion. The T_h values are reported uncorrected for pressure and, therefore, represent the minimum temperature of fluid trapping in the mineral. Fluid inclusion salinity was calculated from $T_{m_{\text{ice}}}$ (Bodnar, 1993).

RESULTS AND DISCUSSION

Tectonic lineaments and mineralization of MCF

In this subsection, the main tectonic lineaments of the MFC are given as recognized in the field at the scale of the outcrop, along with the main mineralogy of fault and fracture fillings.

Faulting and fracturing are intense throughout the whole formation. The faults are concentrated along three main directions and can be grouped as trending N-S, NE-SW and NW-SE, each group developing within 20 to 30° arcs. The deformation history can be described as: 1) a first phase generating NW-SE and NE-SW strike-slip faults, and N-S inverse conjugate faults. Probably these faults are to be connected with the large-scale folding shown in Fig. 1; and 2) a second phase that reactivated the NW-SE and N-S systems as normal faults. The fractures are concentrated around ESE-WNW, NNW-SSE, NNE-SSW directions.

Most faults and fractures are heavily mineralized. In contrast with NE-SW trending faults that are normally filled by quartz and late calcite, the other vein mineral assemblages are constituted by barite,

pyrite, marcasite, and minor galena, sphalerite, calcite, dolomite and quartz. The richest and most interesting assemblages were found in NW-SE and N-S vein fillings. The mineral assemblage can vary from vein to vein and even along a given vein. Note that 1) the NW-SE faults have an Apennine direction, and appear to be reactivated early faults related to the compressive event that originate the Apennines, 2) the NW-SE and N-S faults mineralized with pyrite, marcasite and barite show in places remnants of synkinematic quartz related to the compressive tectonic phase. In some cases, the older mineralization was totally obliterated by the younger one, and 3) the fractures form a conjugate system that shows a variety of orientations, and are normally mineralized with iron sulfides, barite and limonite products. Most of them appear to be related to the younger tectonic phase.

The timing sequence of the mineralizing events can be summarized as follows: (1) iron sulfides and barite in all the faults are younger than quartz, that in places shows boudinage phenomena with cavities and fractures filled by Fe-sulfide (Fig. 2), (2) iron sulfides underwent oxidation to limonite where exposed, this process causing locally pseudomorphic substitution of limonite on calcite crystals, and (3) the final stage of mineralization is recorded by the presence of very small saddle-like dolomite crystals and aragonite, as well as supergene phases like pharmacosiderite and hydromagnesite.

Reddish limonite, the oxidation product of marcasite and pyrite, occurs along fractures and faults belonging to all the systems recognized. This feature strongly characterizes the appearance of the sandstone, which preserves its natural grey colour only where less affected by fractures and mineralization. In addition, a network of mineralized (and more resistant to weathering) fractures caused a typical cellular pattern which is widespread in the MFC (Fig. 3).

Details on mineral assemblages along major faults of the NW-SE, N-S and NE-SW trending systems

Following the above subsection, a detailed description of the observed mineral assemblages and their relation with the major tectonic lineaments are reported, this allowing to relate



Fig. 2 – Network of mineralized veins depicting a cellular structure. Such pattern derives from preferential weathering of the rock with respect to the enclosing mineralized rims.

the mineralogical composition of veins to specific deformation events.

The most important fault of the NW-SE system (vein 1 in Fig.1) outcrops for about 100 m to the south of the Calafuria bridge. It is a thick mylonite fault of few cm to 1 m in width and about 30 m in length. The fault walls are mineralized by a thin crust of microcrystalline quartz showing tectonic striation. The main mineralogy of the vein filling is represented by marcasite, pyrite, barite and limonite. Marcasite and pyrite are finely granular, and form concentric and alternate layers. Barite occurs in massive veins, as well as in euhedral up to 5 cm long crystals within cavities together with iron sulfides. In spite of their fragility, the barite crystals in these faults are perfectly tabular and undeformed, thus indicating that they were not affected by any important post-depositional tectonic event. On outcrop, most marcasite and pyrite are oxidized to limonite-like minerals. Accessory minerals, also included in barite crystals, are stibnite, cinnabar and tetrahedrite. Rare millimetric pharmacosiderite, gypsum and late tiny tabular strontium-rich barite crystals are also found within limonite. The trace element analysis of a marcasite-pyrite-barite hand specimen from vein 1 gave (ppb): Cu 12÷35, Ag <0.2, Pb 11÷690, Zn 58÷299, As 0.3÷2.2, Sb 0.01÷0.91, Bi <0.01, Hg 9240÷1143000, Au 4. Other two faults of the



Fig. 3 – Boudinage structure of vein quartz (2 cm thick). Cavities and fractures are filled by alteration products of iron sulfides (limonite).

NW-SE system, located between Castel Boccale and Torre di Calafuria (vein 2 in Fig. 1), and between Sassoscritto and Calignaia (vein 3 in Fig. 1) contain euhedral marcasite altered to limonite on the weathered surface. Small cavities within marcasite are lined by vitreous, transparent yellow cubic crystals of pharmacosiderite, prismatic colorless crystals of aragonite, tiny tabular crystals of strontium-rich barite and small milky aggregates of hydromagnesite.

A set of N-S trending faults just a few cm in thickness outcrops over about 10 m in length about 50 m southwest of the Calafuria bridge. The fillings of faults 4 and 5 (Fig. 1) consist of galena, barite and subordinate sphalerite. Some small quartz crystals, in contact with the host rock and included in barite, display an idiomorphic habit in polished section. The central part of the vein is composed of euhedral barite and galena, and subordinate quartz and sphalerite. Galena and sphalerite appear to be crosscut by fractures along which they are altered to cerussite and smithsonite, respectively. Barite and subordinate galena fill another fault of the N-S system (vein 6 in Fig. 1) outcropping for few meters near the Sassoscritto locality.

The NE-SW trending faults are characteristically filled by quartz and calcite. In places, they are intersected by veins made of barite and sulfides. These faults are at the best exposed at Punta Pacchiano and Calafuria. They generally display synkinematic quartz on the walls (vein 7 in Fig. 1) and are associated to cataclastic bands up to two meters wide, crosscut by tension gashes filled with euhedral centimeter crystals of postkinematic quartz (vein 8 in Fig. 1). In the two veins, quartz crystals are covered by scalenohedral crystals of calcite, which, in turn, are encrusted by minute rhombohedra of dolomite. Other veins belonging to the same fault system, and occurring in the Sassoscritto quarry, host millimeter brown tabular brookite on quartz crystals. Millimeter blue bipyramidal crystals of anatase were also observed in some veins near the Calafuria bay.

Sulfur isotope composition of barite and sulfides

The isotopic results on marcasite, sphalerite, galena and barite samples are reported in Table 1. Sulfides show a wide range of $\delta^{34}\text{S}$ values between

-6.3 (galena) and +14.2‰ (marcasite). Likewise, the $\delta^{34}\text{S}$ values of barite vary between +13.6 and +25.1‰.

In a given vein, the order of ^{34}S enrichment obeys the equilibrium sequence, i.e., barite > marcasite > sphalerite > galena (Ohmoto and Rye, 1979). However, the application of the sulfur isotope thermometry (Ohmoto and Goldhaber, 1997) yields consistent temperature from $374 \pm 25^\circ\text{C}$ to $461 \pm 45^\circ\text{C}$ only for paired minerals from veins 1 and 4. In vein 1, an unrealistic temperature ($> 880^\circ\text{C}$) is calculated on an additional barite-marcasite pair, as well as in vein 6 on a barite-galena pair ($>1000^\circ\text{C}$). These features, coupled with the large variability of the $\delta^{34}\text{S}$ values, suggest different generations of minerals likely crystallized under distinct temperature and oxygen fugacity conditions of the fluids. Temperature controls the isotope fractionation between oxidized and reduced species of sulfur in solution, and the oxygen fugacity controls the sulfate-to-sulfide ratio. Therefore, the observed isotopic non-equilibria between barite and sulfides may be caused by a sampling bias, or by redox reactions at the site and time of ore deposition, possibly due to mixing of the rising hydrothermal fluid with shallow water. If so, the isotopic equilibrium between the mineral pairs under question was not achieved, due to the lower rate of sulfur isotope exchange between phases in solution compared to the rate of mineral deposition.

One may argue that the isotopic dishomogeneity for sulfur in the studied veins may be due to different contributing sources of distinct $\delta^{34}\text{S}$. Although a similar hypothesis cannot be excluded, it is known that small variations in the oxygen fugacity can influence strongly the $\delta^{34}\text{S}$ values (Ohmoto, 1972), because of the large isotope fractionation between sulfate and sulfide even at relatively high temperature (Ohmoto and Rye, 1979). Possibly, the barite and marcasite from the main ore occurrence (vein 1; see Table 1) crystallized from a fluid with a total sulfur in the range +9.4 to +25.1‰, thus favoring a sedimentary source as opposed to a deep-seated magmatic source.

Sulfur isotope geothermometry

The most reliable thermometric estimates are obtained from sulfur isotopic fractionation of

the barite-marcasite pair from vein 1, and for the barite-sphalerite, barite-galena and sphalerite-galena pairs obtained combining the analyzed minerals from nearby veins 4 and 5 (Table 1). As the isotopic fractionation factor of mineral pairs involving barite are large even at high temperature, the corresponding thermometric result are not significantly affected by small impurities in the mineral separates. This may be not the case for the sphalerite-galena fractionation factor, which is small even at low temperature. Therefore, a temperature of formation of $400 \pm 50^\circ\text{C}$ can be assigned to veins 1, 4 and 5. Instead, the sphalerite-galena thermometric estimate of $461 \pm 45^\circ\text{C}$,

obtained combining mineral phases from veins 4 and 5, may be too high, compared to the estimate of $374 \pm 25^\circ\text{C}$ yielded by the barite (vein 4)-galena (vein 5) pair.

Oxygen and carbon isotope compositions of quartz and calcite

Coexisting vein quartz and calcite from two different sites were analyzed for oxygen and carbon isotopes (Table 1). They show comparable $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, which are in keeping with the hydrothermal origin of the minerals (e.g. Shemesh *et al.*, 1992). Calcite is enriched in

TABLE 1 – Isotopic composition (in ‰) of sulfur (vs CDT standard), carbon (vs PDB standard) and oxygen (vs V-SMOW standard) in minerals from vein fillings in the Macigno Formation of Calafuria, Livorno Mountains, northern Tuscany.

Fault system	Vein	Mineral	$\delta^{34}\text{S}(\text{‰})$	$\delta^{13}\text{C}(\text{‰})$	$\delta^{18}\text{O}(\text{‰})$	$\Delta^{34}\text{S}^{(1)}$	$T_i(^{\circ}\text{C})^{(2)}$
NW-SE	1	Barite	+25.1			15.7	423 ± 35
	1	Marcasite	+9.4			(Ba-Ma)	
NW-SE	1	Barite ⁽³⁾	+19.9			5.7	883
	1	Marcasite ⁽³⁾	+14.2			(Ba-Ma)	
NW-SE	3	Marcasite	-4.7				
	3	Marcasite	+9.4				
	3	Marcasite	+11.5				
N-S	4	Barite	+14.3			17.1	406 ± 30
	4	Sphalerite	-2.9			(Ba-Sp)	
						3.4	461 ± 45
						(Sp-Ga) ⁽⁴⁾	
N-S	5	Galena	-6.3			20.6	374 ± 25
N-S	6	Barite	+13.6			0.9	>1000
		Galena	+12.7			(Ba-Ga) ⁽⁴⁾	
N-S	9	Sphalerite	-2.8				
NE-SW	7	Quartz			+22.8		
	7	Calcite		-3.2	+23.3		
NE-SW	8	Quartz			+23.1		
	8	Calcite		-3.5	+25.7		

(1) $\Delta^{34}\text{S}$ = sulfur isotope fractionation, i.e. $\delta^{34}\text{S}_A - \delta^{34}\text{S}_B$.

(2) T_i = isotopic temperatures from Ohmoto and Rye's (1979) equations.

(3) Barite and marcasite from different points along the vein.

(4) Mineral pairs as combination of samples from the nearby N-S veins 4 and 5.

^{18}O with respect to quartz, as expected for non-equilibrium mineral pairs (e.g. Clayton *et al.*, 1989; Zeng, 1999), i.e. sampled quartz and calcite refer to different episodes of vein deposition. Based on their nearly identical $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, calcite from both sites may be related to a common mineralizing event. A common but distinct event can be concluded for the quartz samples, based on their nearly identical $\delta^{18}\text{O}$ signature. This is in contrast with mineralogical evidence, by which quartz 8 should be postkinematic and then later than quartz 7 that should be synkinematic. The discrepancy may be conciliated assuming that quite similar conditions in terms of temperature and $\delta^{18}\text{O}$ of fluids were operating during the two tectonic phases, i.e. quartz 7 deposited near the end of the compressive phase and quartz 8 at the early beginning of the relaxation phase.

Fluid inclusions of quartz, barite, sphalerite and calcite

On the basis of the optical observations at room temperature and the microthermometric measurements on crystals of quartz, barite, sphalerite and calcite, three types of fluid inclusions were recognized (Table 2).

Type-I inclusions were observed in quartz; they are aqueous, two-phase (L+V), liquid-rich

inclusions and the vapour phase typically occupies 10-15 vol % of the total inclusion volume. The morphology is variable from tabular to ellipsoidal, and size usually ranges from <10 to 40 μm . Small fluid inclusions (<10 μm) are prevailing. The inclusions occur both as isolated single bubbles and as clusters, suggesting a primary origin. They were observed in the synkinematic quartz of vein 7, and in the idiomorphic quartz grown at the contact with the host rock of vein 5. In these inclusions the homogenization temperatures (T_h) to the liquid phase were in the narrow range 289-332°C and correspond to the highest ones measured in the study area. In contrast, salinity is low (1.4-2.6 wt % NaCl eq.). A few measurements of the eutectic temperature were from -19.9 to -21.9°C, suggesting a NaCl-H₂O composition of the liquid phase (Sheperd *et al.*, 1985).

Type-II inclusions were found in barite, sphalerite and quartz. They are aqueous, two-phase (L+V) and liquid-rich, with a degree of filling ($F = V_{\text{liquid phase}}/V_{\text{total FI}}$) between 0.85 and 0.95. Their shape is usually ellipsoidal, and size ranges from <10 to 80 μm . Fluid inclusions with negative-crystal shape were also observed but only rarely. Type-II inclusions appear to be primary in barite from vein 6 and sphalerite from vein 9, as well as in the euhedral postkinematic crystals of

TABLE 2 – Homogenization temperature and salinity of fluid inclusions in minerals from vein fillings in the Macigno Formation of Calafuria, Livorno Mountains, northern Tuscany.

Fault system	Vein	Mineral	Inclusion type	Th (°C)	Salinity (wt % NaCl eq.)
NE-SW	7	quartz	Type I	289-332	1.4-1.9
N-S	5	quartz	Type I	291-325	1.7-2.6
N-S	6	barite	Type II	155-280	13.2-16.0
N-S	9	sphalerite	Type II	135-152	14.2-15.7
NE-SW	8	quartz	Type II	161-165	14.5-15.0
NE-SW	8	quartz	Type II	138-188	14.7-16.2
NE-SW	8	quartz	Type II	186-201	15.5-16.4
NE-SW	10	calcite	Type III	137-182	0.5-1.6
NE-SW	7	quartz	Type III	158-212	0.7-2.1
NE-SW	8	quartz	Type III	167-224	0.7-2.4
NE-SW	8	quartz	Type III	228-245	1.2-1.6
NE-SW	8	quartz	Type III	172-221	1.4-2.6

quartz from vein 8. Fluid inclusions with similar features were also found in barite crystals from veins 1 and 4. Unfortunately, microthermometric determination on the latter fluid inclusions was impossible to be carried out, owing to turbidity of crystals, shortage of inclusions (usually of small size) and decrepitation phenomena during the heating-freezing stages. Moreover, fluid inclusions in barite frequently showed leaching and stretching processes that determine post-entrapment changes on their volume, thus yielding erroneous T_h values. In this context, in order to obtain consistent and reasonable data, the microthermometric study was conducted on carefully selected inclusions that exhibited no evidence of necking-down and leakage, and only on those trapped in barite crystals from vein 6. The microthermometric measurements gave T_h values from 135 to 280°C and moderate salinity in the range 13.2 to 16.4 wt % NaCl eq. As shown in Fig. 4, the inclusions display a slight dilution trend during cooling, the tail of this trend referring to fluid trapped in sphalerite, with T_h and salinity values of 135-152°C and 14.2-15.7 wt % NaCl eq., respectively. The eutectic temperature was determined in few inclusions trapped in quartz from vein 8. The T_c values were between -20.1 to

-22.0 °C and, therefore, close to the eutectic of the NaCl-H₂O system (Sheperd *et al.*, 1985).

Type-III inclusions were observed in crystals of calcite and quartz. They are aqueous, two-phase (L+V) and liquid-rich, with F values of 0.90-0.95. Morphology varies from polygonal to sub-rounded, and size is usually below 40 µm. The inclusions appear to be primary in calcite from vein 10, and secondary in quartz from veins 7 and 8. T_h values are between 137 and 245°C, and salinity is low in the range 0.5-2.6 wt % NaCl eq. As shown in Fig. 4, also this type of inclusions depicts a dilution trend, with the coolest (T_h = 137-182°C) and least saline (0.5-1.6 wt % NaCl eq.) inclusions being trapped in calcite.

An additional type of fluid inclusion was observed. It consists of aqueous, single phase, liquid inclusions found only in barite crystals from veins 1, 4 and 6. These inclusions are usually arranged in clusters together with type-II ones. They are sub-rounded to irregular in shape and <10 to 80 µm in size, and usually gave rise to a gas bubble during the freezing stage and were constantly affected by leakage or decrepitation phenomena.

As a whole, the microthermometric data indicate that the evolution of the hydrothermal

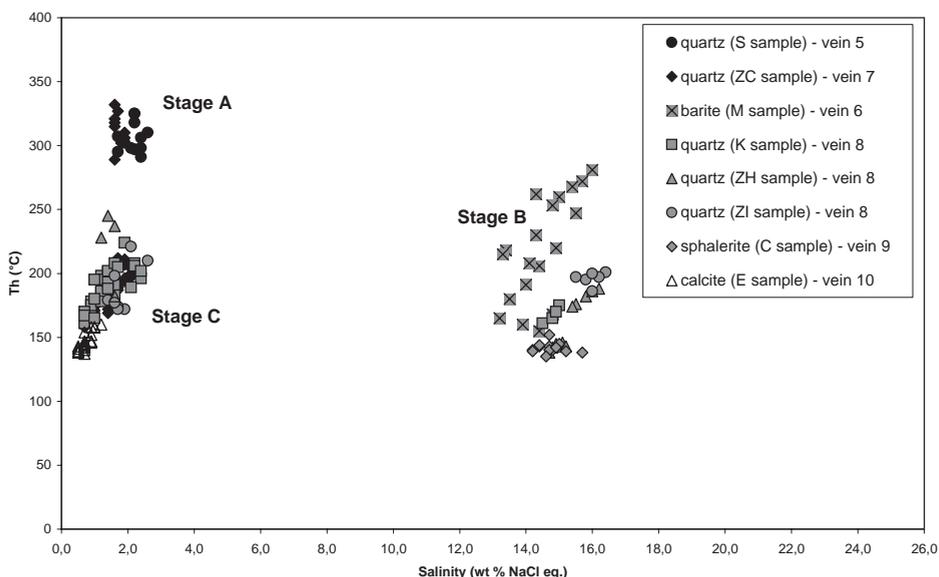


Fig. 4 – Homogenization temperature and salinity of fluid inclusions in minerals filling the fault systems at Calafuria. The data show three main stages of ore deposition, the time sequence being from stage A to stage B to stage C.

fluid circulating along the fault systems crossing the MFC is centered on three main stages (A, B, C), as shown in the T_h vs salinity plot (Fig. 4). These stages appear to be related to distinct fluid phases.

Stage A is focused on hydrothermal fluids of moderate temperature (289-332°C) and low salinity (1.4-2.6 wt % NaCl eq.) responsible of deposition of synkinematic quartz in NE-SW faults and quartz on the surface of N-S and NW-SE faults.

Stage B is related to hydrothermal fluids of low temperature (135-280°C) and moderate salinity (13.2-16.4 wt % NaCl eq.) that deposited euhedral postkinematic quartz in the NE-SW faults as well as barite and sphalerite in NW-SE and N-S faults.

Stage C likely represents the final step of the fluid evolution at Calafuria. During this phase, circulation of low-temperature (137-245°C) and low-salinity (0.5-2.6 wt % NaCl eq.) hydrothermal fluids affected all the fault systems at Calafuria (NE-SW, N-S and NW-SE faults), and was responsible of deposition of calcite.

As mentioned above, the sulfur isotope thermometry (i.e. barite-marcasite, barite-sphalerite and barite-galena sulfur isotopic fractionation factors) suggests a temperature of $400 \pm 50^\circ\text{C}$ for the fluids that mineralized the NW-SE and N-S faults. This isotopic temperature is notably higher than the highest temperature of homogenization of 280°C , measured in fluid inclusions in barite. This discrepancy can be ascribed to pressure effects on fluid inclusions (Roedder, 1984).

Assuming the isotopic temperature as reference value, a pressure of 125 MPa is estimated during the emplacement of the mineralization. Under lithostatic conditions, this pressure corresponds to about 5 km depth. Based on this depth and the presumed post-Middle Pliocene age of the mineralization (see next subsection) a quite rapid exhumation of the MFC should have occurred, possibly exceeding 1.9 mm a^{-1} . Therefore, concurrent and important uplift and exogenic processes should be admitted during the last 2.6 Ma. However, the true trapping temperature of fluid inclusions in barite may be appreciably higher than the measured one of 280°C . Then the given depth of the mineralizing event and the exhumation rate of the Macigno Fm. could be even considerably lower.

Age of mineralization

With reference to the case study, analogous ore veins are hosted elsewhere in Tuscany (magnesite at Miemo, Val d'Elsa and Monterufoli; polymetallic sulfides at Sassa) within Apennine faults of similar orientation. In some cases, the veins cut both Mesozoic terranes of the Tuscan Nappe and overlying Pliocene sediments, like at Jano, Montignoso and Casciana Terme. In the latter locality barite and marcasite veins cross-cut both Lower Pliocene conglomerates and Lower-Middle Pliocene clays (Orlandi *et al.*, 2005). Therefore, it may be concluded that also the vein barite and iron sulfides at Calafuria, which appear not to have suffered any post-depositional tectonic event and comparatively show similar orientation, should have emplaced during post-Middle Pliocene, and possibly originated from hydrothermal fluids rich in CO_2 and H_2S , as is observed in the Larderello geothermal area at present.

CONCLUSIONS

The NW-SE barite and iron sulfide veins studied in this work show the same orientation of veins cutting the ophiolitic complex bordering the MFC in the southern part of the Livorno Mountains (Marinelli, 1955). These veins are filled mainly by magnesite and marcasite. The exactly same orientation of the veins in the two different geological settings, suggests that they are coeval and younger than the tectonic dislocation responsible for the present-day stratigraphic position of the ophiolites. In this context, the vein barite crystals appear to be undeformed, this also excluding any significant post-depositional tectonic event.

The deformation history of MFC can be described as follows: 1) a first phase generating NW-SE, NE-SW strike-slip faults, and N-S inverse conjugate faults, and 2) a second phase that reactivated the NW-SE and N-S systems as normal faults. Most faults and fractures are heavily mineralized. The richest and most interesting mineral assemblages are found in veins filling NW-SE and N-S systems. These veins are mineralized with barite, pyrite, marcasite and minor galena, sphalerite, calcite, dolomite and quartz.

Fluid inclusions indicate three main ore-forming stages characterized by hydrothermal fluids with distinct salinity and/or temperature. The first stage involved a hydrothermal fluid of low salinity (1.4-2.6 wt % NaCl eq.) and moderate temperature (289-332°C), and was responsible of deposition of synkinematic quartz in the NE-SW faults, and quartz on the walls of N-S and NW-SE faults. The fluids of the second stage were of moderate salinity (13.2-16.4 wt % NaCl eq.) and low temperature (135-280°C), and deposited euhedral postkinematic quartz in the NE-SW faults as well as barite, iron sulfides and sphalerite in NW-SE and N-S faults. Finally the third stage fluids of low salinity (0.5-2.6 wt % NaCl eq.) and temperature (137-245°C) affected all the fault systems and deposited calcite as an additional mineral phase.

The sulfur isotopic composition of minerals would seem to exclude a magmatic origin of the sulfur, favoring instead a sedimentary origin. In addition, a temperature of about 400°C is estimated by sulfur isotope geothermometry for the second stage of mineralization. The discrepancy between the isotopic and fluid inclusion thermometric data is probably due to pressure effects on inclusions.

A lithostatic pressure of 125 MPa is estimated for the barite and sulfide mineralization, this corresponding to a depth of 5 km. Finally, a post-Middle Pliocene age is proposed for the ore veins at Calafuria, that may have formed during tectonic relaxation events from hydrothermal fluids rich in CO₂ and H₂S, as are observed in the Larderello geothermal area at present.

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