

Evolution of the hydrothermal system at La Crocetta “feldspar” mine: fluid inclusion and stable isotope constraints on the environment of late stage veins

MARCO BENVENUTI^{1*}, PILARIO COSTAGLIOLA¹, ANDREA DINI², PIERFRANCO LATTANZI³,
GIOVANNI RUGGIERI⁴, ORLANDO VASELLI¹ and GIUSEPPE TANELLI¹

¹ Dipartimento di Scienze della Terra – Università degli Studi di Firenze, Via G. La Pira 4, I-50121 Firenze, Italy

² CNR, Istituto di Geoscienze e Georisorse – U.O. Pisa, Via Moruzzi 1, I-56124 Pisa, Italy

³ Dipartimento di Scienze della Terra – Università di Cagliari, Via Trentino 51, I-09127 Cagliari, Italy

⁴ CNR, Istituto di Geoscienze e Georisorse – U.O. Firenze, Via G. La Pira 4, I-50121 Firenze, Italy

ABSTRACT. — A significant portion (average 200,000 t/y) of the Italian production of feldspathic raw materials for ceramic industries comes from La Crocetta deposit (southern Tuscany, Elba Island). The quarried rocks (so called “eurites”) are pervasively sericitized porphyritic aplites, showing peculiar K-rich (7 to 11 wt% K₂O) and Fe-Ca-S-poor compositions. The main stage of mineralization (i.e., sericitization of the aplites) was described in previous studies. This paper is focussed on the late-stage, post-sericitization veins which crosscut eurite rocks. The development of these N-S striking veins may be associated with conjugate faults related to movements along the Elba Centrale regional fault. Mineralogy of veins includes calcite with subordinate quartz and pyrite. A peculiar rock facies, locally known as “candor”, is made up by particularly abundant calcite-bearing veins, which represent the last hydrothermal event at La Crocetta. Calcite-hosted fluid inclusions show homogenization temperatures (Th) between 197° and 227° C, with salinities between 1.1 and 2.7 wt.% NaCl-equivalent. In agreement with geological background and inferred fluid circulation model, a low pressure regime of vein emplacement can be assumed. Accordingly, these Th should correspond to trapping

temperatures not exceeding 250° C. The carbon ($\delta^{13}\text{C}_{\text{PDB}}$) and oxygen ($\delta^{18}\text{O}_{\text{V-SMOW}}$) values of calcite are -5.4 to -7.4‰, and 6.3 to 10.2‰, respectively. At 250°C, the calculated values of $\delta^{18}\text{O}$ of water, and $\delta^{13}\text{C}$ of CO₂ in equilibrium with vein calcites are in the ranges, respectively, of 1.0 to 2.9‰, and -6.2 to -4.1‰. These data are consistent with formation of the late-stage veins from a dominantly meteoric fluid, mixed with CO₂ from a deep-seated magmatic or metamorphic source.

RIASSUNTO. — La miniera della Crocetta (Isola d’Elba, Toscana meridionale) produce in media circa 200.000 tonnellate/anno di materie prime feldspatiche, contribuendo così in modo significativo a fare dell’Italia il primo produttore europeo del settore. Le coltivazioni minerarie interessano primariamente apliti porfiriche (dette “euriti”) che hanno subito un processo pervasivo di sericitizzazione e conseguente forte arricchimento in potassio (K₂O da 7 a 11% in peso) ed impoverimento in Fe-S-Ca. Il processo di sericitizzazione idrotermale è stato descritto e discusso in studi precedenti. Il presente lavoro si focalizza su uno stadio idrotermale tardivo, post-sericitizzazione, che ha portato ad un’intensa fratturazione dell’“eurite” con sviluppo di vene ad andamento prevalente N-S. Il quadro geostrutturale suggerisce che queste fratture siano connesse alle faglie coniugate associate al

* Corresponding author, E-mail: m.benv@geo.unifi.it

lineamento tettonico regionale della faglia dell'Elba Centrale (CEF). Le vene sono costituite da calcite con subordinato quarzo e pirite. Nella porzione SW della miniera queste vene sono particolarmente abbondanti e sviluppate, tanto da dar luogo ad una facies particolare (detta "candor") che ha un minor valore commerciale. Le inclusioni fluide nella calcite di vena presentano temperature di omogeneizzazione (Th) comprese tra 197° e 227° C, con salinità variabili tra 1.1 and 2.7% in peso (NaCl equiv.). Tenuto conto del quadro geologico regionale, si può supporre che il modello di circolazione dei fluidi tardivi non si discosti significativamente da quello ipotizzato per il processo di sericitizzazione, ovvero che anche lo sviluppo delle vene a calcite sia avvenuto in un regime di basse pressioni. Pertanto, le Th dovrebbero corrispondere a temperature di intrappolamento non superiori a 250°C. La composizione isotopica di carbonio ($\delta^{13}\text{C}_{\text{PDB}}$) e ossigeno ($\delta^{18}\text{O}_{\text{V-SMOW}}$) della calcite varia, rispettivamente, tra -5.4 e -7.4‰ e tra 6.3 e 10.2 ‰. I valori calcolati a 250°C del $\delta^{18}\text{O}$ dell'acqua e del $\delta^{13}\text{C}$ della CO_2 in equilibrio con le calciti di vena variano, rispettivamente, tra 1.0 e 2.9‰, e tra -6.2 e -4.1‰. Questi dati sono compatibili con una formazione delle vene tardive a partire da fluidi di prevalente natura meteorica, mescolati con CO_2 di probabile origine profonda, magmatica o metamorfica.

KEY WORDS: *Feldspathic material, hydrothermal alteration, late-stage fluids, fluid inclusions, C-O isotopes.*

INTRODUCTION

Given their close spatial and temporal relationships with ore-forming systems, sericitic alteration and K-metasomatism of intrusive rocks have been extensively studied in many geological settings (Sheppard and Taylor, 1974; Taylor, 1986, 1992; Sillitoe, 1991; Hedenquist *et al.*, 1998; Lang and Baker, 2001; Juliani *et al.*, 2002). Altered rocks, in these contexts, are associated to the ore minerals, but usually represent a waste material.

In some cases, however, potassic or sericitic alteration facies may intrinsically constitute the orebody itself. According to Maineri *et al.* (2003), the La Crocetta deposit (Elba Island, Italy) is a paramount example of how pervasive sericitization

of a magmatic rock can result in the formation of high quality raw ceramic material. La Crocetta mine belongs to the Southern Tuscany district that, with its 600,000 tonnes/year, contributes to making Italy the largest European producer of raw ceramic materials (1.8 Mt/y; Pearson, 1998).

At La Crocetta, a porphyritic aplite was pervasively sericitized to a K-rich rock locally known as "eurite". According to Maineri *et al.* (2003), sericitization took place about 6.7 Ma ago (^{40}Ar - ^{39}Ar dating). Field evidence suggests that the Elba Central fault, a low angle extensional lineament, played a major role as the main channel for the ore-forming fluids.

The ultimate source of ore-forming fluids at La Crocetta, however, remains poorly constrained. In general, potassic/sericitic alteration is ascribed to interaction of altered rocks with "magmatic" ore fluids, either of direct juvenile origin (Sheppard *et al.*, 1969, 1971; Sheppard and Taylor, 1974; Sheppard and Gustafson, 1976; Stein and Hannah, 1985), or deriving from magma degassing (Taylor, 1986, 1992; Hedenquist *et al.*, 1998). At La Crocetta, however, the relatively high K/Rb ratio of eurites is apparently in contrast with a derivation of the hydrothermal fluids from "local" granite (Maineri *et al.*, 2003). On the other hand, a non-magmatic origin of fluids (basinal brines, seawater, meteoric water) has been invoked by many authors on the basis of stable isotope and fluid inclusion studies (Bowman *et al.*, 1987; Dilles *et al.*, 1992; Zaluski *et al.*, 1994; Sheets *et al.*, 1996). At La Crocetta a meteoric contribution to ore fluids is in accordance with both fluid inclusion microthermometric data and trace element composition of eurites (Maineri *et al.*, 2003).

Late-stage (post-ore) carbonate (\pm quartz, \pm sulfide) veins are unevenly distributed in the La Crocetta mine area; if particularly abundant, they give rise to the so-called "candor facies", a rock of lower commercial quality. Preliminary fluid inclusion and geochemical data suggested that these veins were the product of a late-stage circulation of fluids of dominantly meteoric origin (Maineri *et al.*, 2003). In the present paper, we discuss this hypothesis in the light of new microthermometric and stable isotope composition data.

GEOLOGICAL BACKGROUND

The La Crocetta deposit is located in the eastern portion of Elba island, which lies in the northern Tyrrhenian Sea, between the Corsica Island and the Tuscan coast (Fig. 1). In his pioneering study of Elba, Trevisan (1950) recognized five major thrust complexes, numbered (I–V) from the bottom to the top in their structural position. Notwithstanding recent research and detailed field mapping is unravelling a much more complex tectonic and stratigraphic history (e.g. Pandeli and Puxeddu, 1990; Duranti *et al.*, 1992; Corti *et al.*, 1996; Bortolotti *et al.*, 2000), the overall picture proposed by Trevisan (1950), is substantially

valid even now. The five complexes were assigned to either the Tuscan palaeodomain (complexes I, II, and III) or to the Ligurian oceanic realm (complexes IV and V). La Crocetta deposit is embedded in complex V, close to the contact with the underlying complex IV. Complex V, the uppermost structural unit, essentially consists of two members. The lower one, a Palaeocene–Eocene pelitic (argillites, calcarenites and sandy marls) succession, is interbedded with ophiolitic breccias, and is strongly tectonized (Keller and Piali 1990). The upper member consists of Cretaceous flysch, basically made up of limestone beds, calcareous shales, and feldspathic sandstones. Complex IV, on the other hand, consists of Jurassic ophiolitic rocks

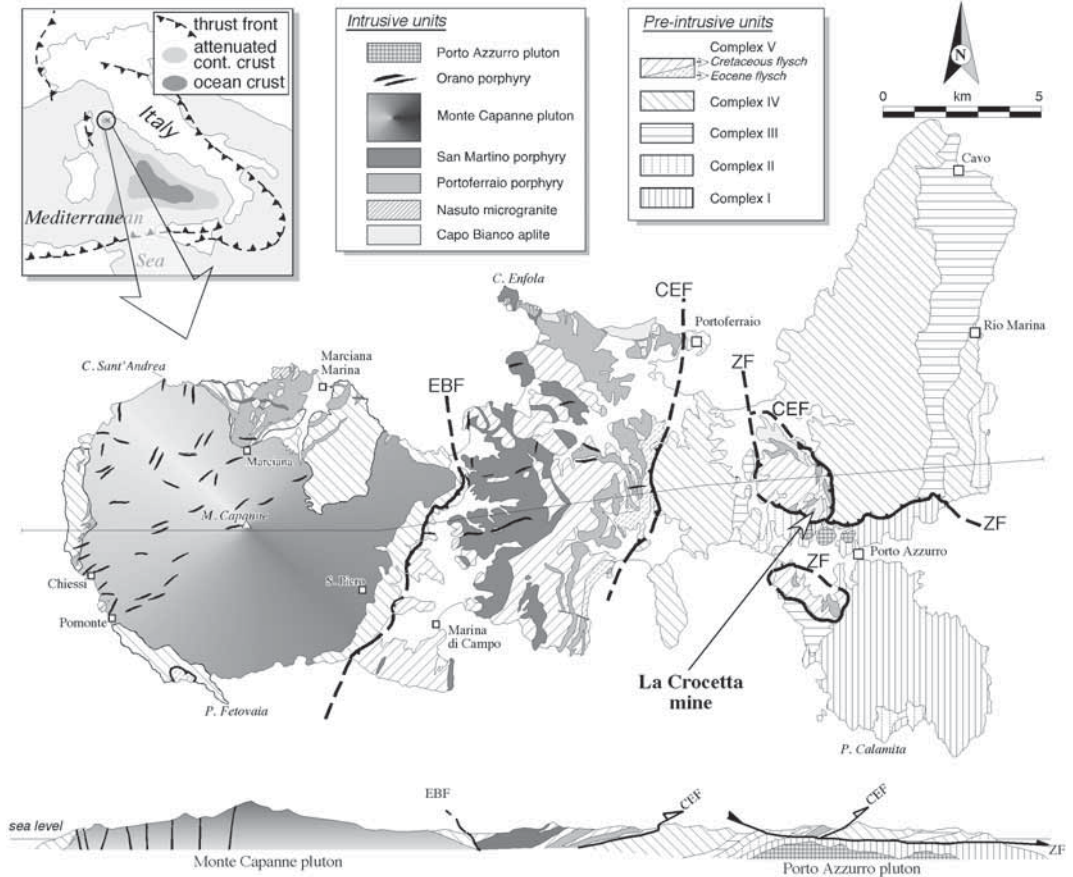


Fig. 1 – Geology of Elba Island.

and overlying Late Jurassic–Middle Cretaceous cherts, limestones and argillites. They show metamorphic aureoles related to the emplacement (between 6.9 and 5.8 Ma; Juteau *et al.*, 1984; Dini, 1997) of the Monte Capanne pluton, a magmatic body belonging to the Tuscan Magmatic Province (TMP), which outcrops in the western part of the island (fig. 1). Other post-orogenic magmatic rocks belonging to TMP include the monzogranitic Porto Azzurro pluton (^{40}Ar – ^{39}Ar age of 5.9 Ma; Maineri *et al.*, 2003), a laccolith complex of subvolcanic porphyritic rocks (PR; Dini *et al.*, 2002; Rocchi *et al.*, 2002), and the Orano granodioritic porphyries (OGP).

On west-central Elba Island, several units can be distinguished in the porphyritic laccolith complex. These include the Capo Bianco porphyritic aplite unit (Rb–Sr age \approx 8 Ma; Dini 1997; Dini *et al.*, 2002), and three different monzogranitic porphyries (Rb–Sr and ^{40}Ar – ^{39}Ar ages of 8.0–7.2 Ma; Dini and Laurenzi, 1999; Dini *et al.*, 2002).

The so called Elba Centrale detachment fault (CEF) is a major tectonic lineament of Elba island. It is a top-to-the-east extension fault, which occurs at the bottom of complex V on the western-central part of the island. This low angle extensional lineament is strongly linked to the emplacement of PR (the subvolcanic porphyritic units) and the Monte Capanne pluton (Bouillin *et al.*, 1994; Daniel and Jolivet 1995; Westerman *et al.*, 2004). Along this major detachment fault, rocks of Complex V, along with the embedded magmatic rocks, were translated approximately 10 km eastward from their original position on the top of the Monte Capanne pluton (Trevisan 1950). The CEF movement is believed to have started after the development of the Monte Capanne thermal aureole and the emplacement of the 6.85-Ma OGP dyke swarms (Dini *et al.*, 2002).

At 5.9 Ma, the emplacement of Porto Azzurro pluton beneath the Elba Centrale fault initiated a new easterly-directed tectonic slip along another major low-angle fault, the Zuccale fault (ZF), localizing the complex V in its present position, 15 km east of Monte Capanne (Pertusati *et al.*, 1993).

N–S-trending high-angle extensional faults finally affected Elba Island and the entire northern Tyrrhenian basin. This tectonism ended before 3.5 Ma (Zitellini *et al.*, 1986; Keller and Pialli, 1990).

LA CROCETTA MINE: GEOLOGY AND SETTING OF LATE-STAGE VEINS

The La Crocetta mine is located in the eastern part of Elba island, about 2.5 km north-west of the town of Porto Azzurro (Fig. 2). The local geology is characterized by the Capo Bianco porphyritic aplites and subordinated monzogranitic porphyries, which are emplaced as large sills and dikes that can vary in thickness from about 10 to 100 m. The intrusions occur within the lowermost part of complex V, at the contact between Cretaceous flysch and Palaeocene–Eocene pelite. The Capo Bianco eurites are located along this contact, and are cut by a small dike of monzogranitic porphyry. Maineri *et al.* (2003) maintain that the contact between the porphyritic rocks and the Porto Azzurro pluton is tectonic, and related to movements of the ZF, which cuts the plane of the older CEF.

The eurite material mined at La Crocetta is a porcelaneous whitish rock with high K_2O and low Na_2O ($\text{K}_2\text{O}/\text{Na}_2\text{O} \approx 60$), arising from a pervasive hydrothermal alteration of the Capo Bianco porphyritic aplite.

The carbonate-rich “candor” facies, is present in the south-western part of the mine (Fig. 2). It is associated with the development of abundant carbonate \pm quartz-pyrite veins, which overprint the pervasive, potassium-rich alteration. These veins strike mainly N–S, have variable dips, and may either be entirely hosted by porphyritic rocks or extend into the surrounding flysch. The timing of formation of this vein system is not clear. It could be related to the regional late-stage, high-angle extensional tectonics or, perhaps more likely, to the development of conjugate faults related to movements along the CEF. The “candor” facies is of lower economic value compared to the “eurite” facies.

MINERALOGY AND TEXTURES OF LATE-STAGE VEINS

Unaltered Capo Bianco porphyritic aplite bodies mainly consist of microphenocrysts of oligoclase–albite, quartz, K-feldspar (Or_{78} – Or_{88}), and muscovite embedded in a very fine groundmass of albite, quartz, K-feldspar, and muscovite (Maineri *et al.*, 2003).

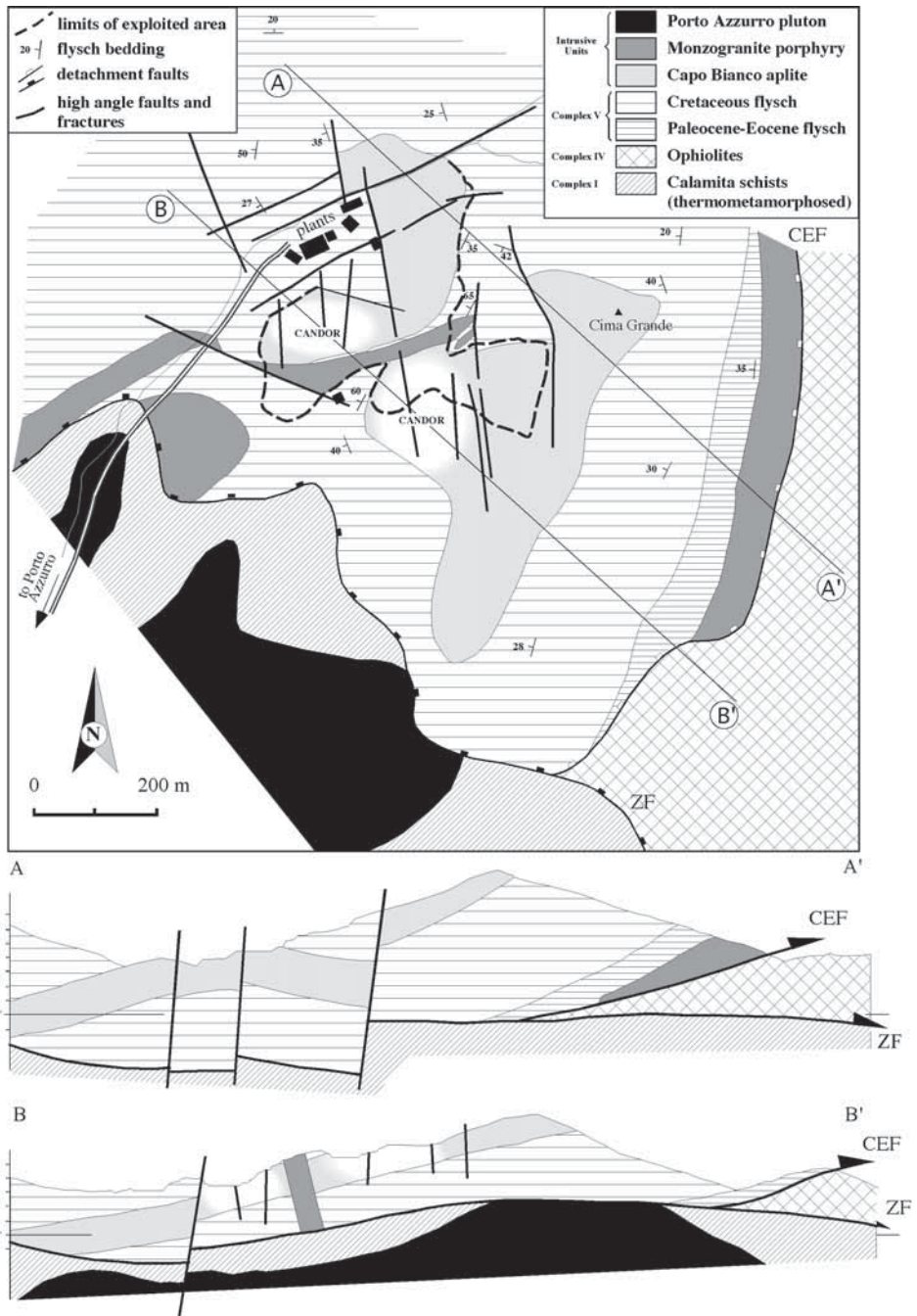


Fig. 2 – Simplified geological map of La Crocetta mine (modified after Maineri *et al.*, 2003). “Candor” alteration facies is indicated by the white shading.

The sericitization of the Capo Bianco aplite represents the ore stage at La Crocetta mine, which actually can be regarded as a hydrothermal sericite deposit. Hydrothermal alteration produced an extensive replacement of albitic plagioclase and feldspars by fine-grained sericite and quartz. These mineralogical and textural changes were accompanied by strong enrichment in bulk K_2O and LOI, whereas Na_2O , CaO and Sr were apparently leached during sericitization (Maineri *et al.*, 2003). The loss of Na_2O (and possibly CaO) is in agreement with the textural observation of plagioclase replacement by sericite.

The development of late-stage veins has been observed exclusively at La Crocetta mine: where they are particularly abundant, the resulting rock (of lower economic value) is the candor facies. The veins occur at all scales, with thickness varying from some hundreds of microns up to some decimeters. They do not show any alteration halo. Mineralogy of veins includes calcite with subordinate quartz and pyrite, cutting through the earlier mineral assemblage formed during sericitization. Locally, the magmatic quartz phenocrysts of the Capo Bianco aplites are cut by the late-stage microveins. More rarely, late-stage quartz occurs as small overgrowths on magmatic quartz phenocrysts. According to Maineri *et al.* (2003), CaO , Sr and MgO , Fe_2O_3 and LOI increased in sericitized rocks affected by this late-stage carbonatization event.

ANALYTICAL METHODS

Microthermometry analyses of fluid inclusions were carried out on 100- μ m-thick, doubly polished wafers at Dipartimento di Scienze della Terra, Firenze, and at Istituto Geoscienze e Georisorse (IGG) of CNR in Pisa, by using the Chaixmea and Linkam THMSG 600 heating-freezing stages. Both stages were calibrated with pure H_2O synthetic fluid inclusions, and natural pure CO_2 inclusions. Accuracy is estimated in the order of ± 0.2 °C during freezing below 10 °C, and ± 2.0 °C when heating in the temperature range of 50–350 °C.

Carbon and oxygen isotope compositions of calcites were determined at the Dipartimento di Scienze della Terra, Firenze, using a Finnigan MAT

250 Delta S mass spectrometer. Data are reported as δ -values, in ‰, relative to PDB standard and V-SMOW standard, respectively. Analytical precision was within ± 0.1 ‰ for oxygen and ± 0.05 ‰ for carbon.

FLUID INCLUSIONS

Fluid inclusions related to the sericitization

Maineri *et al.* (2003) carried out a detailed study on these inclusions which have been found along trails within magmatic quartz phenocrysts. They were, at least in part, trapped during fluid immiscibility processes, as evidenced by microthermometric data and by the coexistence of liquid-rich and vapor-rich inclusions. The study also suggested that the potassium-metasomatism can be related to the circulation of fluids with temperatures mostly between 190° and 240°C, characterized by variable salinity (4–17 wt% NaCl equiv.) and CO_2 contents (X_{CO_2} molar fraction = 0.025–0.027 or $X_{CO_2} \leq 0.014$). Fluids were locally boiling: their volumetric properties indicate that pressure probably oscillated between lithostatic (280–310 bar) and hydrostatic (100–110 bar) values, corresponding to a depth for sericitization of about 1100–1200 m (Maineri *et al.*, 2003). The significant salinity variations displayed by liquid-rich inclusions can be only in part ascribed to adiabatic boiling processes; rather, these fluctuations are most likely the result of an influx of external saline fluids into the hydrothermal system (Maineri *et al.*, 2003).

Fluid inclusions related to late-stage calcite deposition

These fluid inclusions, later than sericitization, were also preliminarily investigated by Maineri *et al.* (2003). They have been observed in late-stage vein calcite and quartz, but also as secondary inclusions within magmatic quartz in eurite. The latter phase almost systematically hosts, along healed fractures, randomly-oriented trails of (secondary) 5 to 20- μ m inclusions. In addition, late-stage inclusions occur in the overgrowths on magmatic quartz phenocrysts, aligned along fractures that are apparently continuations of the late-stage microveins.

Maineri *et al.* (2003) analyzed only a limited number of fluid inclusions in vein calcites (samples S5, S6 and CG4). In the present study we have obtained new microthermometric data from both a previously studied sample (S5), and a new sample (CG5) of calcite.

All the inclusions observed in calcite are two-phase liquid-rich inclusions. Some of them occur as solitary inclusions, and can be considered primary in origin following the criteria of Roedder (1984); most inclusions in calcite, however, occur along trails (Fig. 3). A summary of microthermometric

results obtained from different calcite samples is reported in Table I. Salinities (expressed in wt. % NaCl equivalent) were computed from final melting temperatures of ice (T_{mi}) using the equation of Bodnar and Vityk (1994). T_{mi} are in the range of $-1.6/-0.6^{\circ}\text{C}$. Upon heating, all inclusions homogenized to the liquid phase, at temperatures (T_h) of $197/227^{\circ}\text{C}$. A plot of T_h vs. T_{mi} is presented in Fig. 4. Microthermometry did not reveal any significant difference between solitary inclusions and those aligned along trails. Clathrate was not observed in any of the examined

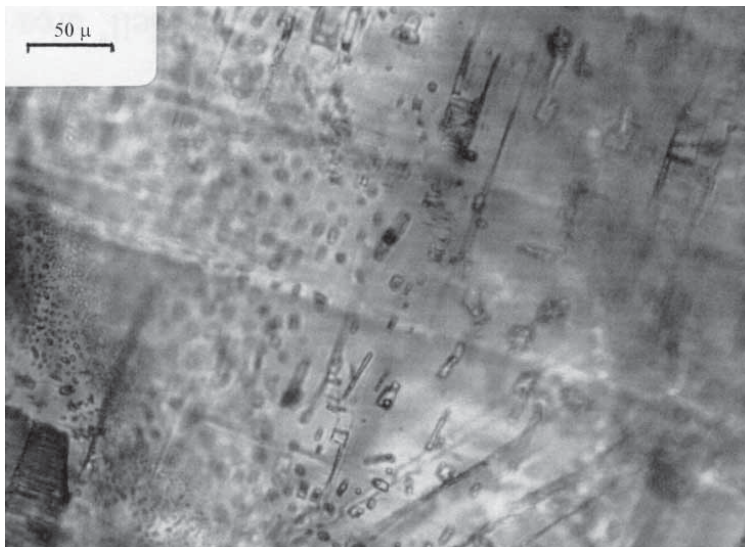


Fig. 3 – Microphotograph of L+V fluid inclusion trails from a vein calcite sample.

TABLE I – Summary of fluid inclusion microthermometric results on late-stage vein calcite. T_{mi} = final ice melting temperatures; T_h = homogenization temperatures. Number of measurements are within brackets.

| Sample | T_{mi} ($^{\circ}\text{C}$) range | T_{mi} ($^{\circ}\text{C}$) average | T_h ($^{\circ}\text{C}$) range | T_h ($^{\circ}\text{C}$) average | Salinity range (wt.% NaCl eq.) |
|----------------------|---------------------------------------|---|------------------------------------|--------------------------------------|--------------------------------|
| CG4AP ⁽¹⁾ | $-0.9 \div -0.8$ | -0.9 (8) | $211 \div 223$ | 216 (8) | $1.4 \div 1.6$ |
| CG5AP | $-1.6 \div -0.6$ | -1.4 (8) | $197 \div 202$ | 199 (8) | $1.1 \div 2.7$ |
| S5 ⁽²⁾ | $-1.5 \div -0.6$ | -0.9 (10) | $205 \div 227$ | 218 (10) | $1.1 \div 2.6$ |
| S6 ⁽¹⁾ | $-1.6 \div -1.4$ | -1.5 (5) | $197 \div 220$ | 207 (7) | $2.4 \div 2.7$ |

⁽¹⁾ Data from Maineri *et al.* (2003).

⁽²⁾ Data from Maineri *et al.* (2003) and this work.

inclusions. Eutectic temperature (Te) was measured in few inclusions, with values in the -38 to -21°C range. The lowest values of Te are indicative of the presence of divalent cations (i.e. Mg²⁺ and/or Ca²⁺) in addition to Na⁺ in the solution (Crawford, 1981).

STABLE ISOTOPES

To constrain the nature of fluids circulating in the last alteration stage, six samples of calcites from late-stage veins, two of “candor” (total rock), plus one sample (total rock) of Complex V carbonatic flysch have been analyzed for carbon and oxygen isotopic composition. The results are reported in Table II.

Compositional ranges of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ for vein calcites are between -5.4 and -7.4‰ and between 6.3 and 10.2‰, respectively. Carbonatic flysch host rock isotopic values are $\delta^{13}\text{C} = -1.5‰$ and $\delta^{18}\text{O} = 12.7‰$. The latter value appears to be significantly lower than Cretaceous carbonates worldwide (Veizer and Hoefs, 1976; Voigt and Wiese, 2000) and Tuscan platform limestones (Carrara Marbles; Cortecchi and Orlandi, 1975; Herz and Dean, 1986). This could reflect some re-equilibration of flysch carbonates in a post-depositional (hydrothermal?) stage. Whole rock analysis of “candor” facies, made up of abundant calcite-bearing microveinlets cutting through

the eurite alteration assemblage, provided values comprised within the compositional ranges of vein calcites.

DISCUSSION AND CONCLUSIONS

Fluid inclusions in vein calcites provide information on the physical-chemical nature of the fluid responsible for late-stage alteration and carbonate deposition. The salinity range computed from Tmi varies from 1.1 to 2.7 wt. % NaCl equiv. (Table I). These values, however, should be considered as maximum values; in fact, Tmi depends not only on the presence of ionic species in solution, but also on the occurrence of dissolved gasses (mainly CO₂ in shallow depth hydrothermal systems), which depresses the Tmi value by as much as 1.4°C (Hedenquist and Henley, 1985). The absence of clathrate after Tmi in the examined inclusions indicates XCO₂ values of ≤ 0.014 (Hedenquist and Henley, 1985).

The Th vs. Tmi plot of Fig. 4 shows that, except for a single inclusion of the CG5 sample (which may be a necked inclusion), the other ones define a rough trend of decreasing Th and Tmi. This type of correlation may be explained by a boiling process causing a salinity increase (i.e. decrease of the Tmi), and a concomitant temperature decrease. However, as previously noted by Maineri *et al.* (2003), and confirmed in the present study, no

TABLE II – Carbon and oxygen isotope analyses on rock carbonate and vein calcite. The $\delta^{18}\text{O}(\text{H}_2\text{O})$ and $\delta^{13}\text{C}(\text{CO}_2)$ values in equilibrium with calcite are calculated at 250°C (see text for fractionation factors). wr = whole rock analysis

| Samples | Description | $\delta^{18}\text{O}$ ‰ | $\delta^{18}\text{O}(\text{H}_2\text{O})$ (‰) | $\delta^{13}\text{C}$ ‰ | $\delta^{13}\text{C}(\text{CO}_2)$ (‰) |
|--------------|----------------------------|-------------------------|---|-------------------------|--|
| F1 (wr) | Complex V flysch limestone | 12.7 | 5.4 | -1.5 | -0.2 |
| Candor1 (wr) | candor facies | 7.5 | 0.2 | -6.9 | -5.6 |
| Candor2 (wr) | candor facies | 9.1 | 1.8 | -5.9 | -4.6 |
| CG5 | late-stage vein | 6.4 | -0.9 | -7.4 | -6.2 |
| G9 | late-stage vein | 6.6 | -0.7 | -5.4 | -4.1 |
| G10 | late-stage vein | 6.7 | -0.6 | -7.1 | -5.8 |
| S1 | late-stage vein | 7.4 | 0.1 | -7.0 | -5.7 |
| S5 | late-stage vein | 6.3 | -1.0 | -7.3 | -6.0 |
| S6 | late-stage vein | 10.2 | 2.9 | -6.1 | -4.8 |

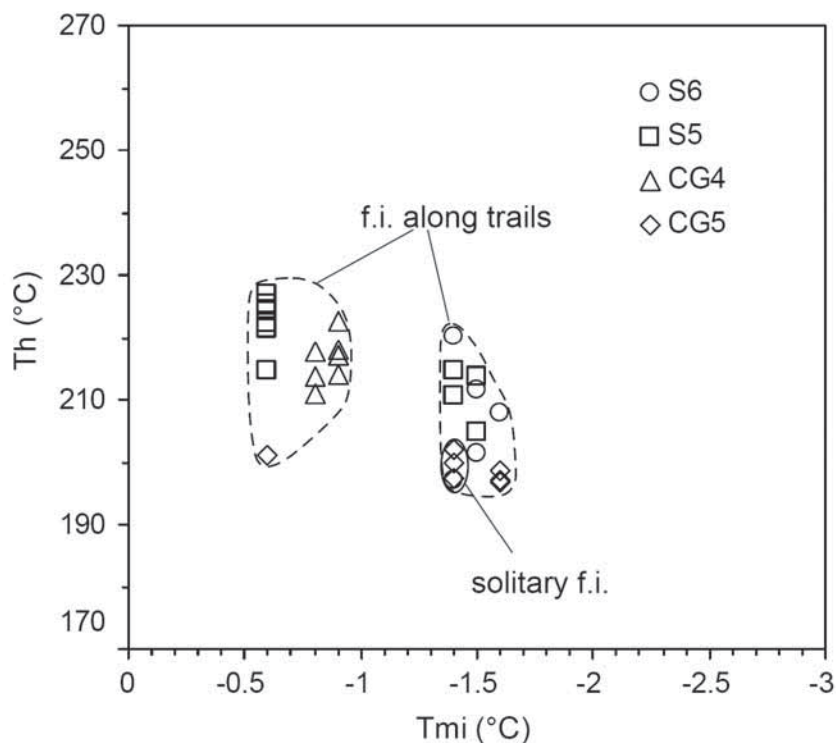


Fig. 4 – Plot of homogenization temperatures (T_h) vs. final ice melting temperatures (T_{mi}) for fluid inclusions in calcite related to late-stage alteration event at La Crocetta. Solitary and trail inclusions are distinguished.

vapor-rich inclusions that may testify boiling processes have been observed in the analyzed calcite crystals. Since boiling cannot be proved, the trend of Fig. 4 can be better explained by a mixing process between fluids characterized by different salinities and/or CO_2 contents. T_{mi} variation due to the mixing of fluids of contrasting salinities were also reported by Maineri *et al.* (2003) for fluid inclusions related to sericitization. However, the latter inclusions showed higher salinities (up to 17 wt% NaCl equiv.), whereas inclusions in late-stage vein calcite have relatively low salinities (≤ 2.7 wt. % NaCl equiv.), suggesting that the trapped water should be largely of meteoric origin.

As said above, there are no evidences of boiling for fluids trapped in calcite inclusions. Therefore, pressure corrections should be added to T_h to obtain the trapping temperatures. These corrections were estimated on the basis of the volumetric

properties of the system H_2O -NaCl (since the CO_2 content in the inclusions is relatively small), using the data of Zhang and Frantz (1987). Assuming that the depth of formation of the inclusions in vein calcites was similar to that estimated at the time of sericitization (slightly more than 1 km), the corrections are $\leq 6^\circ\text{C}$ for hydrostatic conditions and $< 20^\circ\text{C}$ for lithostatic conditions. The temperature of formation of the calcite veins, therefore, should be comprised in the 200-250°C range, i.e. approximately the same shown by fluids responsible for the sericitization (ore) stage (e.g. Maineri *et al.*, 2003).

We can thus calculate the isotopic composition ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) of hydrothermal fluids in equilibrium with late-stage hydrothermal calcites. Calculations were performed by using the calcite-water curve of O'Neil *et al.* (1969), and the calcite- CO_2 curve of Botting (1968). At 250°C,

the calculated $\delta^{18}\text{O}$ (H_2O) and $\delta^{13}\text{C}$ (CO_2) of vein calcites give values in the ranges -1.0 to 2.9% and -6.2 to -4.1% , respectively (Table II). The observed $\delta^{18}\text{O}$ (H_2O) range would confirm that hydrothermal fluid from which calcite precipitated was basically meteoric water, that was enriched in ^{18}O by isotopic exchange with country rocks. The $\delta^{13}\text{C}$ values apparently rule out an origin of carbon from local carbonatic flysch, as well as any significant flysch–fluid equilibration with respect to carbon. It would seem thus likely that CO_2 was derived from a deep-seated source (magmatic or metamorphic).

In conclusion, oxygen and carbon isotopic compositions of late-stage calcites, coupled with fluid inclusion data, suggest that the last hydrothermal event at La Crocetta involved a dominantly meteoric fluid, mixed with CO_2 from a deep-seated source. Therefore, both the sericitization and late-stage carbonatization events were accomplished by fluids of nearby the same origin (meteoric with magmatic or metamorphic contribution), and took place under the same PT conditions ($P=300\text{-}100$ bars; $T=200\text{-}250^\circ\text{C}$).

ACKNOWLEDGEMENTS

We thank Gianni Cortecchi and another anonymous referee for reviewing the manuscript and for critical comments that helped to improve the paper. Some field and chemical data reported here were collected during undergraduate thesis work at Università di Firenze by M. Luccarini and L. Peruzzi. Mr A. Bertoni and the whole EURIT mine staff are thanked for their kind assistance during fieldwork and sample collection. Financial support by MIUR (“ex-60% Funds”) is acknowledged.

REFERENCES

- BODNAR R.J. and VITYK M.O. (1994) – *Interpretation of microthermometric data for H_2O -NaCl fluid inclusion*. In: De Vivo B, Frezzotti ML (eds.) “*IMA '94: Short Course on fluid inclusions*”, Virginia Polytechnic Institute & State University, 117-130.
- BORTOLOTTI V., FAZZUOLI M., PANDELI E., PRINCIPI G., BABBINI A. and CORTI S. (2000) – *Geology of central and eastern Elba Island*. *Ofioliti*, **26**, 79-96.
- BOTTINGA Y. (1968) – *Calculation of fractionation factors for carbon and oxygen exchange in the system calcite-carbon dioxide-water*. *J. Phys. Chem.*, **72**, 800-808.
- BOUILLIN J.P., POUPEAU G. and SABIL N. (1994) – *Etude thermo-chronologique de la dénudation du pluton du Monte Capanne (Ile d'Elbe, Italie) par les traces de fission*. *Bull. Soc. Geol. France*, **165**, 19-25.
- BOWMAN J.R., PARRY W.T., KROPP W.P. and KRUEER S.A. (1987) – *Chemical and isotopic evolution of hydrothermal solutions at Bingham, Utah*. *Econ. Geol.*, **82**, 395-428.
- CORTECCI G. and ORLANDI P. (1975) – *Oxygen- and carbon-isotopic composition of gypsum-calcite-dolomite crystals and metamorphic marble assemblages*. *Chem. Geol.*, **15**, 309-314.
- CORTI S., DINI C., PANDELI E. and PRINCIPI G. (1996) – *Le unità tettoniche dell'Isola d'Elba orientale (Toscana): nuovi dati e ipotesi di correlazione*. In: 78^a Riunione Estiva S.G.I. “*Geologia delle Dolomiti*”, Abstr. Vol., 65-66.
- CRAWFORD M.L. (1981) – *Phase equilibria in aqueous fluid inclusion*. In: Hollister LS, Crawford ML (eds.) “*Short Course in fluid inclusion*”. Mineral Ass. Canada, **6**, 75-100.
- DANIEL J.M. and JOLIVET L. (1995) – *Detachment faults and pluton emplacement: Elba Island (Tyrrhenian Sea)*. *Bull. Soc. Geol. France*, **166**, 341-354.
- DILLES J.H., SOLOMON G.C., TAYLOR H.P. and EINAUDI M.T. (1992) – *Oxygen and hydrogen isotope characteristics of hydrothermal alteration at the Ann-Mason porphyry copper deposit, Yerington, Nevada*. *Econ. Geol.*, **87**, 44-63.
- DINI A. (1997) – *Le rocce porfiriche dell'Isola d'Elba: geologia, geocronologia e geochimica*. Unpublished Ph.D Thesis, Università di Pisa, Italy, 217 p (English abstr. in *Plinius*, **17**, 130-136).
- DINI A. and LAURENZI M.A. (1999) – *$^{40}\text{Ar}/^{39}\text{Ar}$ chronology of shallow-level granitic intrusions, Elba Island, Italy*. In: “*Geoitalia, 2nd Forum FIST*”. Abstr Vol, 288-290.
- DINI A., INNOCENTI F., ROCCHI S., TONARINI S. and WESTERMAN D.S. (2002) – *The magmatic evolution of the laccolith-pluton-dyke complex of Elba island, Italy*. *Geol. Mag.*, **139**, 257 - 279.
- DURANTI S., PALMIERI R., PERTUSATI P.C. and RICCI C.A. (1992) – *Geological evolution and metamorphic petrology of the basal sequences of eastern Elba (Complex II)*. *Acta Vulcanol.*, **2**, 213-229.

- HEDENQUIST J.W., ARRIBAS A. and REYNOLDS T.J. (1998) – *Evolution of an intrusion-centered hydrothermal system: Far Southeast Lepanto porphyry and epithermal Cu-Au deposits, Philippines*. *Econ. Geol.*, **93**, 374–404.
- HEDENQUIST J.W. and HENLEY R.W. (1985) – *The importance of CO₂ on freezing point measurements of fluid inclusions: Evidence from active geothermal systems and implications for epithermal ore deposition*. *Econ. Geol.*, **80**, 1379–1406.
- HERZ N. and DEAN N.E. (1986) – *Stable isotopes and archaeological geology: the Carrara marble, northern Italy*. *Appl. Geoch.*, **1**, 139–151.
- JULIANI C., CORRÊA-SILVA R.H., MONTEIRO L.V.S., BETTENCOURT J.S. and NUNES C.M.D. (2002) – *The Batalha Au-granite system-Tapajós Gold Province, Amazonian craton, Brazil: hydrothermal alteration and regional implications*. *Prec. Res.*, **119**, 225–256.
- JUTEAU M., MICHARD A., ZIMMERMANN J.L. and ALBAREDE F. (1984) – *Isotopic heterogeneities in the granitic intrusion of Monte Capanne (Elba Island, Italy) and dating concepts*. *J. Petrol.*, **25**, 532–545.
- KELLER J.V. and PIALLI G. (1990) – *Tectonics of the Island of Elba: a reappraisal*. *Boll. Soc. Geol. It.*, **109**, 413–425.
- LANG J.R. and BAKER T. (2001) – *Intrusion-related gold systems: the present level of understanding*. *Miner. Deposita*, **36**, 477–489.
- MAINERI C., BENVENUTI M., COSTAGLIOLA P., DINI A., LATTANZI P., RUGGIERI G. and VILLA I.M. (2003) – *Sericitic alteration at the La Crocetta deposit (Elba Island, Italy): interplay between magmatism, tectonics and hydrothermal activity*. *Miner. Deposita*, **38**, 67–86.
- O'NEIL JR., CLAYTON R.N. and MAYEDA T. (1969) – *Oxygen isotope fractionation in divalent metal carbonates*. *J. Chem. Phys.*, **51**, 5547–5558.
- PANDELI E. and PUXEDDU M. (1990) – *Palaeozoic age for the Tuscan upper metamorphic sequences of Elba and its implications for the geology of the northern Apennines*. *Eclogae Geol. Helvet.*, **83**, 123–142.
- PEARSON K. (1998) – *Italy's minerals. Poised for ceramic markets*. *Industrial Minerals*, **374**, 21–39.
- PERTUSATI P.C., RAGGI G., RICCI C.A., DURANTI S. and PALMERI R. (1993) – *Evoluzione post-collisionale dell' Elba centro-orientale*. *Mem. Soc. Geol. Ital.*, **49**, 223–312.
- ROCCHI S., WESTERMAN D.S., DINI A., INNOCENTI F. and TONARINI S. (2002) – *Two-stage growth of laccoliths at Elba Island, Italy*. *Geology*, **30**, 983–986.
- ROEDDER E. (1984) – *Fluid inclusions*. *Reviews in mineralogy*, **12**, Mineral Soc Am, Washington, DC, 640 p.
- SHEETS R.W., NESBITT B.E. and MUEHLENBACHS K. (1996) – *A meteoric water component in magmatic fluids from porphyry copper mineralization, Babine lake area, Br. Columbia*. *Geology*, **24**, 1091–1094.
- SHEPPARD S.M.F. and GUSTAFSON L.B. (1976) – *Oxygen and hydrogen isotopes in the porphyry copper deposit at El Salvador, Chile*. *Econ. Geol.*, **71**, 1549–1559.
- SHEPPARD S.M.F., NIELSEN R.L. and TAYLOR JR H.P. (1969) – *Oxygen and hydrogen isotope ratios of clay minerals from porphyry copper deposits*. *Econ. Geol.*, **64**, 755–777.
- SHEPPARD S.M.F., NIELSEN, R.L. and TAYLOR JR H.P. (1971) – *Hydrogen and oxygen isotope ratios in minerals from porphyry copper deposits*. *Econ. Geol.*, **66**, 515–542.
- SHEPPARD, S.M.F. and TAYLOR JR H.P. (1974) – *Hydrogen and oxygen isotope evidence for the origins of water in the Boulder batholith and the Butte ore deposits*. *Econ. Geol.*, **69**, 926–946.
- SILLITOE R.H. (1991) – *Gold metallogeny of Chile-an introduction*. *Econ. Geol.*, **86**, 1187–1205.
- STEIN H.J. and HANNAH, J.L. (1985) – *Movement and origin of ore fluids in Climax-type systems*. *Geology*, **13**, 469–474.
- TAYLOR B.E. (1992) – *Degassing of H₂O from rhyolite magma during eruption and shallow intrusion, and the isotopic composition of magmatic water in hydrothermal systems*. *Geological Survey of Japan Report*, **279**, 190–194.
- TAYLOR JR H.P. (1986) – *Isotope geochemistry of oxygen and hydrogen-a brief review*. *Trans. Am. Geophys. Union*, **47**, 287–290.
- TREVISAN L. (1950) – *L'Elba orientale e la sua tettonica di scivolamento per gravità*. *Mem. Ist. Geol. Univ. Padova*, **16**, 1–36.
- VEIZER J. and HOEFS J. (1976) – *The nature of O¹⁸/O¹⁶ and C¹³/C¹² secular trends in sedimentary carbonate rocks*. *Geochim. Cosmochim. Acta*, **40**, 1387–1395.
- VOIGT S. and WIESE F. (2000) – *Evidence for Late Cretaceous (Late Turonian) climate cooling from oxygen-isotope variations and palaeobiogeographic changes in Western and Central Europe*. *J. Geol. Soc. London*, **157**, 737–743.
- WESTERMAN D.S., DINI A., INNOCENTI F., ROCCHI S. and TONARINI S. (2000) – *Christmas-trees in the shallow crust: the nested laccolith complex*

- from Elba Island, Italy.* In: "Geoscience 2000", Manchester (UK), Abstr. Vol., 11.
- ZALUSKI G., NESBITT B. and MUCHLENBACHS K. (1994) – *Hydrothermal alteration and stable isotope systematics of the Babine Porphyry Cu deposits, Br. Columbia: Implications for fluid evolution of porphyry systems.* Econ. Geol., **89**, 1518-1541.
- ZHANG Y.G. and FRANTZ J.D. (1987) – *Determination of the homogenization temperatures and densities of supercritical fluids in the system NaCl-KCl-CaCl₂-H₂O using synthetic fluid inclusions.* Chem. Geol., **64**, 335-350.
- ZITELLINI N., TRINCARDI F., MARANI M. and FABBRI A. (1986) – *Neogene tectonics of the Northern Tyrrhenian Sea.* Giornale di Geologia, **48**, 25-40.