

Fluid inclusions and chlorite geothermometry in Fe-Cu-Zn volcanic-hosted massive sulfide deposits of the Northern Apennine ophiolites (Italy): Preliminary results

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ABSTRACT: Fluid inclusions in quartz and calcite and the mineral chemistry of chlorite in the gangue of (Fe-Cu-Zn) sulfide deposits of the Northern Apennine ophiolites (Italy) have been investigated. Quartz and calcite contain fluid inclusions in the system $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$, with low salinity and homogenization temperatures clustering in three different ranges: $<100^\circ\text{C}$, $120^\circ\text{C}-170^\circ\text{C}$ and $240^\circ\text{C}-360^\circ\text{C}$. Preliminary data indicate that the highest temperatures are found preferentially in stratiform, massive ores, whereas results obtained for stockwork veins mostly reflect temperatures $<170^\circ\text{C}$. Temperatures obtained from chlorite in stockwork veins are remarkably higher ($176^\circ\text{C}-351^\circ\text{C}$). The nature of the fluid inclusions encountered so far, seem do not indicate any contribution of a magmatic source, but suggests that there was some influence by meteoric waters.

1 INTRODUCTION

Several Fe-Cu-Zn sulfide deposits occur in the Mesozoic ophiolites of the Northern Apennines, between Liguria and Emilia Romagna (Fig.1). Some of these deposits were known since the Bronze Age as a source of copper, and were worked at intervals through the 13th and 17th centuries.

Systematic mining activities started in 1875 only, and went through a period of considerable prosperity between 1890 and 1930, during which more than

one million tons of ore with an average grade of 7 % copper were produced (Galli & Penco 1996). Exploitation continued locally up to the sixties, when the last mine was closed at Libiola. In spite of their historical significance as archeological sites and their importance as economic source of copper in the recent past, these deposits have not received much attention by geologists. As a result scientific information is poor and fragmentary and limited to descriptions of the ore mineralogy (Bertolani 1952, 1953) and structural features (Ferrario & Garuti

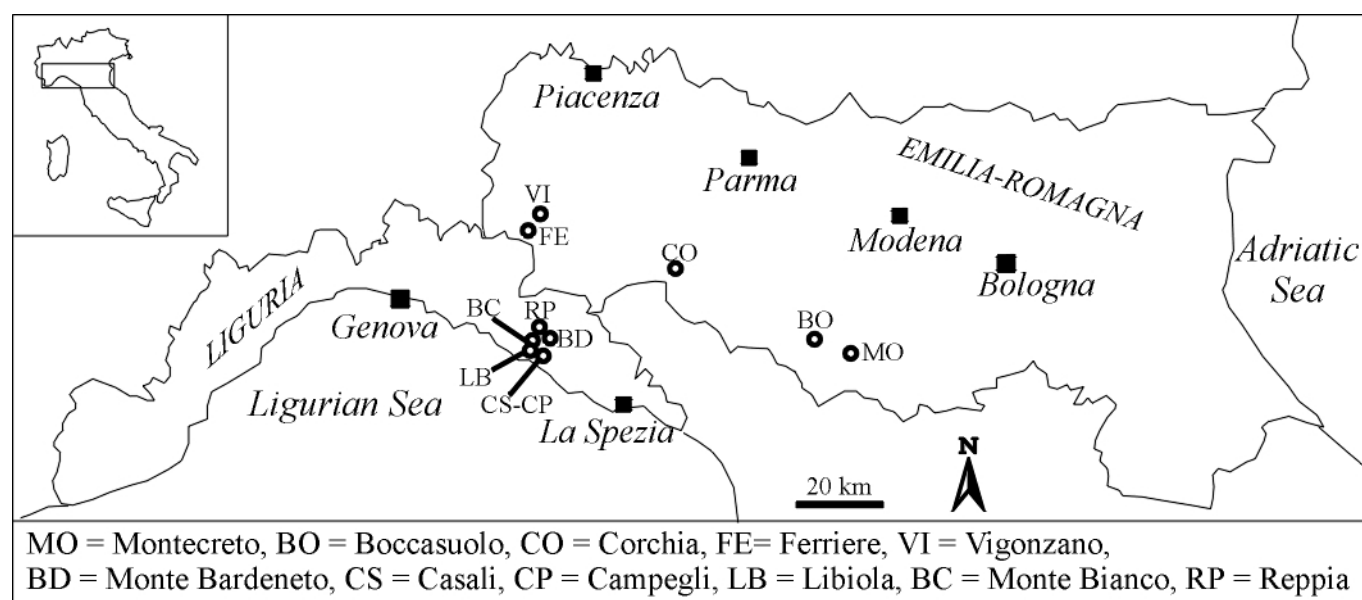


Figure 1. Geographical location of the major sulfide deposits of the Northern Apennine.

1980).

The opinion that the Fe-Cu-Zn sulfide deposits of the Northern Apennine formed by hydrothermal processes related with the establishment of convective cells below the ancient oceanic floor (Ferrario & Garuti 1980) has become almost universally accepted, although this model has never been tested with any specific mineralogical and geochemical investigation. Notably, no study has been undertaken so far to investigate the nature of the hydrothermal solutions responsible for the deposition of the sulfide ore. Therefore, as part of a developing project between the Universities of Modena (Italy) and Granada (Spain), aimed to study the ore genesis associated with the ophiolites in the Western Mediterranean basin, we present here preliminary results of an investigation of fluid-inclusions and chlorite geothermometry in the sulfide ore deposits of the Northern Apennine ophiolites.

2 GEOLOGICAL BACKGROUND

The Northern Apennine ophiolites are characterized by anomalous stratigraphy compared with the Tethyan ophiolites in the Eastern Mediterranean basin (Abbate et al. 1988, Lemoine et al. 1987, Robertson 2002). Field evidence indicates that mafic-ultramafic cumulates are extremely thin or absent, and a true sheeted-dike complex never existed in these ophiolites. Instead, the mantle tectonites are intruded by huge gabbro bodies, and both are covered by thick layers of ophiolitic breccias, supporting the view that the plutonic basement in the western wing of the Thetys was exposed at the ocean floor and eroded, prior to the outflow of pillow-lava and deposition of pelagic sediments.

Based on the morphology of the ore bodies and their structural relationships with the host rocks, the Fe-Cu-Zn sulfide deposits of the Northern Apennine can be divided into two main groups (Fig. 2):

- 1) The stratiform mineralization consists of fairly massive, lens-shaped ore bodies laying concordant with lithostratigraphic joints: i) at the top of the pillow lava unit, in contact with the sedimentary cover (Corchia type), ii) at the base of the pillow lavas, inside the ophiolitic breccia, covering the plutonic basement (Monte Bardeneto type), and iii) inside the pillow lava unit (Libiola type).
- 2) The stockwork mineralization consists of a network of quartz + carbonate veins, from one centimeter to some decimeters in thickness, containing low-grade disseminated sulfides. The stockwork mineralization occurs filling cracks

and fractures inside the different units of the ophiolite sequence: i) in the mantle tectonite (Vigonzano type), ii) in the massive gabbro (Campegli type), or iii) in the pillow lava (Bocassuolo type). In some cases, the stockwork passes upwards into a massive, stratiform ore body, usually through a thick zone of hydraulic breccia.

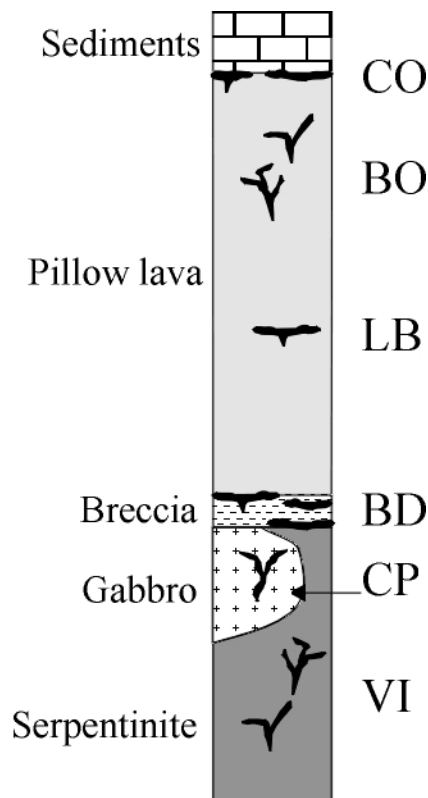


Figure 2. Schematic stratigraphic position of sulfide deposits in the Northern Apennine (see figure 1 for abbreviations).

The mineralogy of the Northern Apennine Fe-Cu-Zn sulfide deposits basically consists of pyrite, chalcopyrite, and sphalerite, in both stratiform and stockwork ore types. Pyrrhotite generally occurs as accessory phase, but may become important in some stratiform ores. Quartz and calcite are ubiquitous gangue minerals, although chlorite and epidote are widespread in quartz-carbonate veins.

4 GEOTHERMOMETRY

Fluid inclusions

The study of the fluid inclusions was carried out at the University of Granada, on samples selected as representatives of the stockwork and stratiform ores, from the localities of Montecreto, Bocassuolo and Corchia. Numerous primary fluid inclusions were observed in quartz and calcite, consisting in both

cases of one phase (liquid) or two phases (liquid + vapor), with a high filling degree (> 0.95). Microthermometric data indicate that most inclusions are metastable under freezing, so that vapor phase reappears at positive temperature values or may even not reappear. Eutectic temperatures are lower than -40°C , indicating that the fluid system was possibly of the type $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$. The melting temperature of the hydrohalite could only be determined in a few inclusions in quartz, giving consistent values indicating a Na/Ca ratio lower than 1. The final ice melting temperature obtained for inclusions in quartz, indicate salinities between 1.1 and 4.0 wt % NaCl equivalents. The homogenization temperatures (T_h) vary in the ranges 64°C - 360°C and 86°C - 256°C for inclusions in quartz and calcite respectively (Fig. 3). Most data from the stockwork veins concentrate below 150°C , being generally higher in the calcite (146°C on average) than in quartz ($< 150^{\circ}\text{C}$).

In contrast, quartz from stratiform ores gave temperatures up to 360°C , with a good half of the values falling in the range between 240° and 360°C .

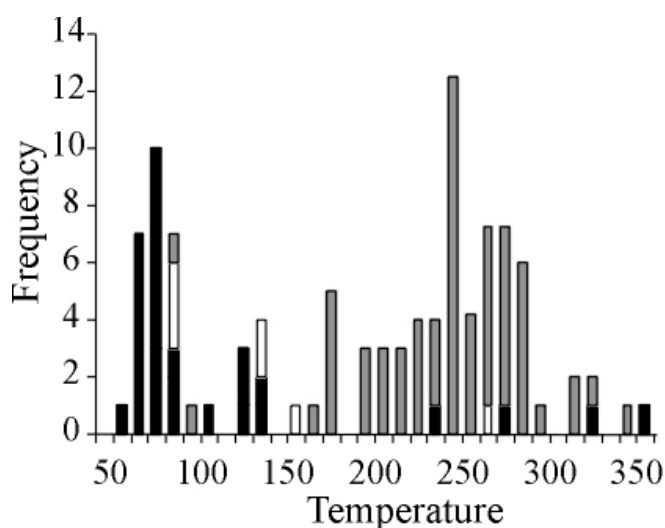


Figure 3. Histogramm of homogenization temperatures for fluid inclusions in quartz (black) and calcite (white) as well as of calculated formation temperatures based on mineral chemistry of chlorite (grey).

Chlorite

Chlorite was analyzed exclusively in stockwork veins, where it occurs as lamellar aggregates included in quartz, calcite, and, less frequently, in the sulfide minerals. Electron microprobe analyses were performed at the University of Modena on ten samples of stockwork ore, taking into examination a set of chlorite crystals representative of the different paragenetic assemblages. The analyzed chlorites correspond to Fe-rich clinocllore, with Al^{IV} contents increasing from 1.48 to 2.57 formula units (based on

$8\text{Si}+\text{Al}^{\text{IV}}$) parallel to the increase in $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio from 0.15 to 0.48. The geothermometer of Cathelineau (1988), based on the extent of Al^{IV} substitution for Si in the tetrahedral site, gave temperatures between 176° and 351°C (Fig. 3).

Notably, data from one single vein, revealed that the temperature of chlorite formation is strictly dependent on its mineralogical association, being remarkably higher in the chlorites crystallized within the carbonate gangue (Table 1) compared with those associated with quartz and sulfide.

Table 1. Crystallization temperature ($^{\circ}\text{C}$) of chlorite from different assemblages within one single vein

Geothermometer	Association		
	Calcite	Quartz	Sulfide
1	336	234	241
2	291	134	144
3	307	238	247

1 = Cathelineau (1988)

2 = Hiller & Velde (1991)

3 = Kranidiotis & MacLean (1987)

5 CONCLUSIONS

The results obtained so far from the study of fluid inclusions and chlorite geothermometry in the Northern Apennine sulfide deposits, although preliminary, are well consistent with the geological context and allow to point out some important problems.

The highest T_h (240° - 360°C) registered by fluid inclusions in quartz of the stratiform deposits are of the same order of the highest temperatures calculated for chlorite in the stockwork veins (240° - 351°C), and probably reflect the initial temperature of ore deposition. In the stockwork veins the temperatures registered by fluid inclusions (256°C) and chlorite (336°C) associated with calcite are systematically higher than those obtained from chlorite (234°C) and fluid inclusions ($< 150^{\circ}\text{C}$) in the quartz matrix. This observation is consistent with the order of deposition calcite-quartz commonly observed in these samples. The lowest T_h $< 150^{\circ}\text{C}$ registered by fluid inclusions in quartz of both deposits, stratiform and stockwork veins, may indicate i) cooling of the hydrothermal system well below 100°C , or ii) alternatively they may correspond to a reopening of the fluid system in a post depositional stage, involving re-crystallization of quartz.

In general, the fluids associated with the sulfide mineralization pertain to the $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$ system, and are characterized by a relatively low salinity, intermediate between seawater and meteoric water, whereas any contribution from a magmatic source seems to be excluded in the light of the present data.

The sulfide deposits in the Northern Apennine ophiolites are believed to have formed at the sea floor, or just below it, from submarine hydrothermal vents, of which the stockwork veins were possible feeders (Ferrario & Garuti 1980). The contribution of relatively cold meteoric waters in this scenario, their mixing with hot hydrothermal fluids, and the possible role they had in the deposition and/or reworking of the sulfide ore will be the focus of further investigation.

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