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The Pb-rich sulfide veins in the Boccassuolo ophiolite: Implications for the geochemical evolution of hydrothermal activity across the ocean-continent transition in the Ligurian Tethys (Northern-Apennine, Italy)

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ABSTRACT

Galena bearing sulfide veins have been discovered coexisting with Fe–Cu–Zn dominated veins in the hydrothermal stockwork of the Boccassuolo ophiolite (External Ligurides, Northern Apennine, Italy). The galena-rich veins cut across a volcanic pile composed of pillow lava flows, pillow breccia, and ophiolitic sandstone. Bulk-ore analyses indicate significant enrichment in Pb giving raise to mantle normalized Pb–Ag–Au–Zn–Cu patterns with unusual negative slope, in contrast with the average flat pattern of most sulfide deposits in the Internal Liguride ophiolites which reflect the Fe–Cu–Zn assemblage of ophiolite-hosted Volcanic-associated Massive Sulfide (VMS) deposits all over the world.

A wide literature shows that, in contrast with the Internal Ligurides, plutonic and volcanic rocks of the External Ligurides display less depleted and even enriched geochemical characters, not consistent with common oceanic crust at mid oceanic ridges (MOR), but probably originated in the ocean–continent transition of the Adria continental margin. In this geodynamic context, pillow basalts become locally enriched in Pb with high Pb/Cu ratios, and other crustal-compatible elements such as Mo and U. The Pb enrichment observed in the veins Boccassuolo is interpreted to be a result of leaching of such anomalous volcanics forming the ophiolitic substrate. The case of Boccassuolo supports the conclusion that the geochemical character of hydrothermal activity evolved from Cu–Zn rich in MOR-type assemblages of the Internal Ligurides, towards composition enriched in Pb in the External Liguride domain, representing the transition from the Ligurian ocean to the Adria continental margin.
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1. Introduction

Variation of Pb with respect to its companion metals (Cu, Zn) has become pivotal to the classification and geotectonic interpretation of ancient Volcanic-associated Massive Sulfide (VMS) deposits worldwide (see a summary of the classification criteria in Misra, 2000). The behavior of Pb in a global geochemical cycle indicates higher incompatibility during magmatic processes and preferential mobility in hydrothermal fluids compared with Cu and Zn, thereby reaching continental–crust/primitive-mantle enrichment factors of 10 to 30 times higher than the other chalcophile metals. Basaltic rocks as a whole may have Pb/Cu ratios in the range of 0.005–0.070 in contrast with rhyolites and granites which are characterized by Pb/Cu ratios as high as 2.45 or more (Hofmann, 1988; Wedepohl, 1991). Since the metals in VMS deposits were essentially derived from leaching of intrusive and extrusive igneous rocks in the footwall substrate (Large, 1992; Reed, 1983), their relative abundance is a reflection of the type of magmatism, and indirectly, it indicates the large-scale geotectonic setting of ore deposition (Barrie and Hannington, 1999). A major implication is that VMS deposits associated with mafic–ultramafic rocks in ancient and modern sub-oceanic crust from MOR, to island arc and subduction-influenced settings, are generally Pb-poor and Cu–Zn rich (Barrie and Hannington, 1999; Galley and Koski, 1999). In contrast, VMS associated with transitional basalts and felsic volcanic rocks, in continental arcs and rifted continental margins, exhibit progressive increase of the Pb content with respect to Cu and Zn. There is, however, at least one exception to this rule. In the Chilean Ridge at 38°S, abundant galena is observed in sulfide-mineralized quartz veins associated with a MORB dominated slow-spreading system (Mühe et al., 1977). In this case, the anomalous Pb enrichment is interpreted to be a result of the higher mobility of Pb compared with Cu and Zn, during hydrothermal over-leaching of the oceanic crust. The process removed larger-than-normal proportion of Pb that is now concentrated in the quartz veins, and left the flushed section of oceanic crust, far from the mineralized zone, more depleted in Pb than normal.

In this paper, we present results of a detailed study of sulfide mineralized quartz veins cutting across pillow-basalt and basalt

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breccia in the Boccassuolo ophiolite complex (Ligurian Tethys, Northern Apennine). The study has revealed that veins dominated by the Cu–Zn assemblage typical of ophiolite-hosted VMS deposits, coexist with others carrying abundant galena in the sulfide assemblage. The case of Boccassuolo apparently represents a further exception to the assumption that VMS deposits associated with mafic–ultramafic rocks in ophiolite complexes are depleted in Pb. However, the reasons for the observed Pb-anomaly, do not seem to be related with over-leaching of Pb from the rock substrate, they rather reflect a change in the chemistry of the hydrothermal activity related with geochemical changes in the leached basalts across an ancient ocean–continent transition zone. Evidences in support of this interpretation are discussed.

2. Geological setting and petrologic background

2.1. The ophiolite sequences of the Ligurian basin

The ophiolites exposed in the Northern Apennine (Fig. 1) represent fragments of the oceanic lithosphere that floored the Ligurian basin in the western limb of the Jurassic Tethys (Piccardo et al., 2002, and references therein). The ophiolites and their sedimentary cover are conventionally divided into Internal and External Ligurides. In the Internal Ligurides, ophiolites form the base of deeply folded northeast-verging blocks bounded by southwest-dipping fault planes, in which stratigraphic relations between the plutonic basement and sedimentary cover are still preserved (Abbate et al., 1980; Barrett, 1982; Elter, 1975). In contrast, ophiolites of the External Ligurides occur as un-rooted and dismembered blocks floating in a mélange of argillaceous rocks and disrupted fragments of carbonaceous flysch and siliciclastic turbidite. Noteworthy, the two domains are believed to represent oceanic crust in two different paleogeographic contexts: one in proximity of the rifting zone (Internal Ligurides), the other closer to the Adria continental margin (External Ligurides) (Piccardo et al., 2002, and references therein). Consistent with this view, mantle peridotites in External Ligurides are sub-continental spinel lherzolite having a less depleted character compared with those in Internal Ligurides (Rampone et al., 1995). Basaltic rocks have MORB-type REE-trace element geochemical signature in both Internal and External Ligurides, although the latter appear systematically less depleted displaying transitional-MORB affinity in some cases (Ottonello et al, 1984; Venturelli et al., 1981).

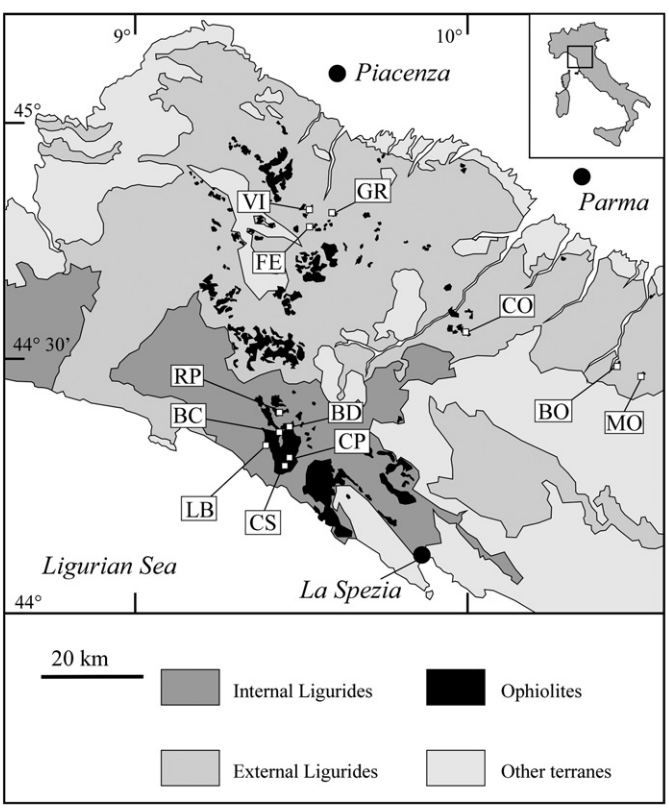

Fig. 1. Sketch structural map of the Internal and External Ligurides and location of the major copper sulfide deposits in the Northern Apennine. RP = Reppia, BD = Monte Bardeneto, BC = Monte Bianco, LB = Libiola, CP = Campegli, CS = Casali, VI = Vigonzano, GR = Groppallo, FE = Ferriere, CO = Corchia, MO = Montecreto, BO = Boccassuolo.

In the Modena province, including the Boccassuolo ophiolite, basaltic rocks display variable compositions suggesting different magmatic source and mixing. Typical N-MORB basalts similar to those of the Internal Ligurides are rare. Basalts commonly display slightly depleted or even enriched bulk geochemistry, with high Zr/Hf ratios (Capedri and Toscani, 2000). Zaccarini et al. (2008) have shown that basalts from six localities of the External Ligurides display N-MORB type distribution of the REE, but are variably enriched in Pb, and Mo, and depleted in Cu and Ni with respect to N-MORB (Table 1). These geochemical anomalies have been tentatively interpreted by Capedri and Toscani (2000) as possible evidence supporting the origin of the basalts in a subduction-related, back-arc/inter-arc setting. Paleo-geographic evolution of the Ligurian Tethys indicates that the basin was still expanding or in a steady state during late Jurassic–Cretaceous times. Intra-oceanic subduction and obduction of Ligurian units onto the Adria continental margin occurred in the southern segment of the oceanic basin corresponding to the Northen Apennine, when a compressive regime started to be active (in Upper Cretaceous?). We do not exclude the possibility that some fragments of subduction-related assemblages might have been sampled by the obducting system. In the External Liguride ophiolites, however, upper mantle assemblages typical of subduction zones (harzburgite–dunite–chromitite) are absent, as well as high-Mg volcanics (i.e. boninite) that frequently accompany subduction-related volcanism (Crawford et al., 1989). Structural and geochemical lines of evidence indicate that the External Liguride ophiolites mostly formed in a pre-collisional stage (Marroni et al., 2001; Piccardo et al., 2002). The observed geochemical deviation from typical N-MORB is not necessarily related to a subduction setting. The close spatial association with almost undepleted sub-continental mantle strongly supports the conclusion that these hybrid MORB-type melts might have generated in the final stages of the extensional regime, in an ocean–continent transition similar to the modern non-volcanic rifted margins of Iberia (Marroni et al., 1998, 2001, 2002; Montanini et al., 2008; Rampone and Piccardo, 2000; Robertson, 2002; Tribuzio et al., 2000, 2002).

2.2. VMS deposits in the Internal and External Ligurides

The Northern Apennine ophiolites contain a number of hydrothermal sulfide deposits known as a major source of copper since 3500 BC (Maggi and Pearce, 2005; Pearce, 2007). The deposits pertain to the VMS class (Volcanic-associated Massive Sulfide deposits), and because of their genetic relation with basaltic volcanics and a dominant Cu–Zn metal assemblage, they have been ascribed to the Mafic type of Barrie and Hannington (1999), resembling VMS deposits of the Cyprus sub-type associated with Phanerozoic ophiolites worldwide (Garuti and Zaccarini, 2005; Garuti et al. 2008; Zaccarini and Garuti, 2008).

The sulfide deposits of the Internal and External Ligurides display different structural styles varying from seafloor-stratiform and seafloor-stratabound massive ore bodies to sub-seafloor stockwork veins with high-grade disseminated sulfides (Ferrario and Garuti, 1980; Garuti and Zaccarini, 2005; Garuti et al., 2008). The best representative examples of the Internal Ligurides concentrate in the large ophiolite complex of Val-di-Vara, in the inland of Sestri Levante (eastern Liguria) whereas the deposits associated with the External

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