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Mineralogical and geochemical investigation of seafloor massive sulfides from Panarea Platform (Aeolian Arc, Tyrrhenian Sea)

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ABSTRACT

Panarea seafloor hydrothermal system is associated with a range of mafic to felsic volcanic rocks. The hydrothermal system is active at present and discharges magmatic–hydrothermal fluids and precipitates massive sulfides. The sulfides exhibit multi-stage deposition, evident in the alternation of several mineral generations that follow a general temporal precipitation sequence: marcasite → alunite → opal. Sr–Nd–Pb isotope data indicate that most of the metals in the sulfides are derived predominantly from the Panarea volcanic rocks with some contribution from ambient seawater and/or local sediments. A remarkable feature of these sulfides is their chondrite-normalized rare earth element (REE_N) distribution pattern with a pronounced negative Eu anomaly, which has not been observed previously. Our study demonstrates that this REE_N pattern reflects the REE fractionation during sulfide deposition. The ionic radius mismatch between Eu^{2+} (the main form of Eu in reduced, high-temperature hydrothermal fluids) and the only possible site for REE substitution in the marcasite, that of Fe^{2+}, suggests a crystallographic control on the REE_N pattern. Apparently, marcasite precipitation can generate a sulfide deposit with a negative Eu anomaly due to discrimination against Eu^{2+} relative to REE^{3+} in the Fe^{2+} crystallographic site.

1. Introduction

Seafloor hydrothermal activity at convergent plate boundaries has increasingly attracted scientific attention over the last 20 years. This is due to the notion that volcanic arc hydrothermal deposits appear to be better modern analogs of volcanogenic massive sulfides than hydrothermal deposits at divergent plate boundaries (Iizasa et al., 1999). In addition, the large variety of substrate rocks (from basalts to rhyolites) leached by the hydrothermal systems as well as the direct magmatic contribution to these systems (Yang and Scott, 1996) provide a setting for processes and deposits that are atypical for the relatively simple mid-ocean ridge (MOR) settings. Findings such as ponds of molten native S at the seafloor (Embley et al., 2006) and emissions of liquid CO_2 (Lupton et al., 2006) show that unique deposits can be found in hydrothermal systems at convergent plate boundaries.

The Aeolian Arc is one of the volcanic arcs most studied for submarine hydrothermal activity in the world (e.g., Dekov and Savelli, 2004). Although many papers report on sulfide–sulfate deposition at this volcanic arc (Dekov and Savelli, 2004) the investigated mineralizations up to date are mostly scattered in sediments (Marani et al., 1997). Only one work investigates from an isotope point of view massive sulfide deposits in the region (Peters et al., 2011). Motivated by the scarcity of research on this type of deposit at the Aeolian Arc and by the anticipated challenges of the arc setting we undertook a mineralogical–geochemical study of a massive sulfide deposit from the Panarea Platform.

2. Geologic setting

The Tyrrhenian Sea (Fig. 1A) is an active back-arc basin of Late Miocene–Holocene age (Kastens et al., 1988). Submarine hydrothermal activity has been documented (Dekov and Savelli, 2004, and references therein) at most of the islands and seamounts that form the Aeolian volcanic arc in the southeastern part of the basin (Fig. 1A, B). Panarea volcanic complex is a mostly submerged, nearly circular and volcanically active platform in the eastern part of the Aeolian arc (Fig. 1B, C). Recent bimodal volcanism (basalts and rhyolites; Gabbianelli et al., 1990) affected the emerged portions of this shallow-water platform represented by the Panarea and Basiluzzo Islands (Fig. 1C). Swath bathymetry (Marani et al., 1997) revealed a shallow depression between these two islands. The islets east of Panarea and south of Basiluzzo Islands (Fig. 1C) are interpreted as remnants of a crater rim (Gugliandolo et al., 2006). Hydrothermal activity has been documented as fumarolic fields (hundreds of shallow gas exhalations) and little

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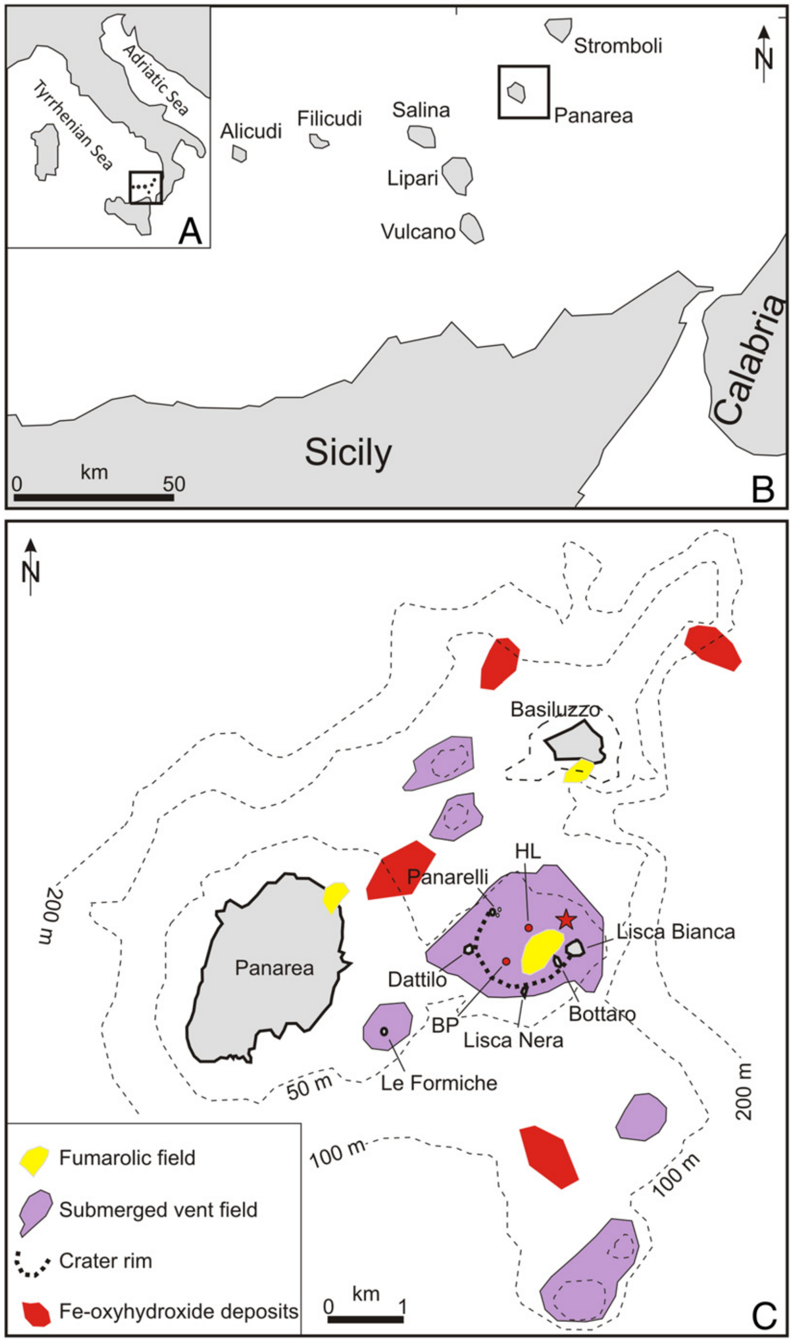

Fig. 1. (A) Sketch map of the Tyrrhenian Sea with the Aeolian Islands (box). (B) Close-up of the SE Tyrrhenian Sea [area in the box at (A)] with the Aeolian Islands and sampling area at Panarea Platform (box). (C) Simplified bathymetric map of the Panarea Platform with the hydrothermally active areas, sampling site (star), and hydrothermal vents Black Point (BP) and Hot Lake (HL) (red dots). Based on Marani et al. (2004), Chiodini et al. (2006) and Tassi et al. (2009).

hydrothermal vents, and as deposits of Fe-oxyhydroxides and polymetallic sulfides scattered within the sediment at the summit of the platform (Fig. 1C) (Gabbianelli et al., 1990; Calanchi et al., 1995; Marani et al., 1997; Capaccioni et al., 2007; Sieland, 2009; Tassi et al., 2009). Investigations have revealed that the Panarea hydrothermal system is complex, with evidence of intense water–rock interaction in the reaction zone, sub-seafloor phase separation and magmatic volatile contribution (Sieland, 2009; Tassi et al., 2009). Hydrothermal fluids investigated in detail at two vent sites [Hot Lake (Pa3 in Tassi et al., 2009) and Black Point (Pa5 in Tassi et al., 2009)] have moderate exiting temperatures (70–96 °C and 130–135 °C, respectively), high calculated temperatures in the reaction zone (345 °C and 310 °C) and low measured pH (5 and 2.5–6). The fluids are reducing and strongly enriched in Na^+, K^+, Ca^{2+}, Li^+, Mn^{2+}, Fe^{2+}, Cl^- and H_2S relative to seawater (Sieland, 2009; Tassi et al., 2009). Black Point (BP) is a black-colored, sulfide-rich hydrothermal vent found at 23 m depth in 2002 (Fig. 1C). It vented black smoke until late 2004. A ridge 2 m long and ~1 m high, covered with hard, black encrustations is located around the BP and implies active sulfide deposition around the vent. Since the end of 2004, the BP has been emitting clear fluids with almost constant T ~ 130 °C, but with variable pH (2.5–6.0) and major ion concentrations (Tassi et al., 2009).