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Invited research article

Redox changes in a seafloor hydrothermal system recorded in hematite-chalcopyrite chimneys

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ABSTRACT

Hydrothermal chimneys composed of hematite and chalcopyrite grow at the Irina II vent site (Logatchev hydrothermal field, Mid-Atlantic Ridge). Hematite and chalcopyrite form layers that repeatedly alternate within the chimney wall. The repeating alternation of hematite and chalcopyrite implies for repeating changes in the physico-chemical parameters of the vent fluid. The modeled stability diagrams of hematite and chalcopyrite at the physico-chemical conditions of the Irina II hydrothermal site showed that the precipitation of these two Fe-minerals is primarily governed by the activity of H_2S and pH. Fe-isotope studies suggest that the successive deposition of chalcopyrite ($\delta^{56/54}\text{Fe} = \sim 0.20‰$) and hematite ($\delta^{56/54}\text{Fe} = \sim 0.60‰$) layers in the Irina II chimneys is a result of redox changes in the hydrothermal fluid. The replacement of hematite by either magnetite or chalcopyrite at some places also suggests for a redox inversion in the hydrothermal system from oxic to reduced. Chondrite-normalized rare earth element distribution patterns of the hematite layers show a strong negative Eu anomaly, which is interpreted to be a result of crystal-chemical control on the rare earth element fractionation during hematite precipitation. Sr isotope systematics indicate significant and variable incorporation of seawater (from ~40% to ~80%) in the hydrothermal system. Nd-Pb-isotope studies show that Nd and Pb in chalcopyrite and hematite layers are derived mainly from the underlying mafic and ultramafic rocks. The chimneys are young (5.13 ± 1.28 kyrs B.P.) and their wall thickened inward. The duration of redox cycles (oxic and reducing) within the scale of a single chimney is about several hundred years. The hematite layers are enriched in W, In, Sn and U indicating that primary hematite hydrothermal deposits at the seafloor may be a potential source for these strategic trace elements. High concentrations of these elements in the studied hematite layers can be explained by their (easy) ion substitution for Fe^{3+} in the hematite crystal lattice. Whereas the most plausible source of the elevated W, In and Sn contents are the hydrothermal fluids, the seawater is the possible major source of U.

1. Introduction

Since the discovery of seafloor hydrothermal activity (Corliss et al., 1979; Spiess et al., 1980), > 300 seafloor vent fields have been investigated over the past decades (Hannington et al., 2011). In general, there is a good understanding of the basics of how a seafloor hydrothermal system operates (German and Von Damm, 2006). However, a number of details that are critical for functioning of this system and eventually, for the type of deposit it precipitates below and on the seafloor are still not well understood. According to the conventionally accepted model for a seafloor hydrothermal system (German and Von Damm, 2006) the reduced, acidic, and hot hydrothermal fluids venting at the seafloor, deposit mainly sulfides and sulfates upon mixing with ambient oxic, alkaline, and cold seawater. This model is challenged when minerals known to precipitate in oxic environment (e.g., oxides) are detected as primary phases at seafloor hydrothermal sites. Reports of primary Fe-oxide mineral occurrences at seafloor hydrothermal deposits are rare. Hematite (α-Fe_2O_3) was observed as an accessory

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mineral in the Juan de Fuca (Koski et al., 1984), Broken Spur (Rickard et al., 1994), Snake Pit (Thompson et al., 1988; Krasnov et al., 1995b) and Logatchev (Krasnov et al., 1995b), and as a major mineral in the Turtle Pits (Haase et al., 2007; Pašava et al., 2007) seafloor hydrothermal deposits. Geochemical modeling by Palandri and Reed (2004) demonstrated that hematite precipitates and is stable and abundant at very high water/rock ratio during the serpentinization of mafic and ultramafic rocks by water passing through the lower crust and upper mantle. In such conditions, the operating hydrothermal system is oxidizing. With decreasing water/rock ratio the system evolves towards a reduced system and the hematite is further replaced by magnetite and later by Fe-sulfides. High water/rock ratios required for the development of oxidizing conditions in a hydrothermal system are attained at spreading centres with shallow heat source (Haymon, 1996). These spreading centres are known as magma-rich. At the other type hydrothermally active spreading centres, magma-starved, the hydrothermal activity is generally controlled by crustal permeability structure. Hence, a spreading setting where the shallow heat source is combined with enhanced crustal permeability is favorable for development of highly oxidizing hydrothermal system that precipitates oxides instead of sulfides.

Recent investigations revealed that this particular combination of shallow heat source and high rock permeability may occur at ultramafic-hosted hydrothermal fields (Petersen et al., 2009). At the Logatchev hydrothermal field [Mid-Atlantic Ridge (MAR)] the high crustal permeability related to the detachment faulting is combined with shallow sitting gabbroic intrusions (heat source) (Petersen et al., 2009). Detailed analysis of the geological setting of the Logatchev hydrothermal field (Petersen et al., 2009) suggests that among all the hydrothermal sites of this field the Irina II is the most promising for exploration of a potentially oxidizing hydrothermal system.

Hydrothermal deposits from the Irina II vent site were sampled during two research cruises of the French Research Institute for Exploitation of the Sea (Ifremer, Brest). As theoretically expected, hydrothermal chimneys composed of hematite (Fe-oxide, formed in oxic environment) concentric layers, which alternate with chalcopyrite (Fe-sulfide, formed in reduced environment) layers were collected. Investigation of these deposits is expected to provide an opportunity to gain insights into an active hydrothermal system characterized by changes of the redox conditions. In this work, we present a detailed study of mineral chemistry and isotope systematics (Fe-Sr-Nd-Pb-U-Th) of these chimneys aiming to decipher the redox evolution of the hydrothermal system that formed them.

2. Geologic setting

The Logatchev seafloor hydrothermal field is located south of the Fifteen-Twenty Fault Zone (FZ) at a section of the MAR (~14°45′N) characterized by detachment faulting and core complex formation (Bougault et al., 1993; Cannat et al., 1997). Logatchev lies at the eastern inner flank of the rift valley wall, about 7 km away from the spreading axis and has several active and inactive vent sites (Fig. 1). The hydrothermal activity is structurally controlled and localized in debris flows consisting of heterogeneous ultramafic and mafic intrusive rock clasts (Augustin et al., 2008; Petersen et al., 2009). Gabbroic intrusions beneath the eastern flank of the rift valley and associated basaltic volcanism are inferred to be the heat source driving the hydrothermal circulation at Logatchev (Petersen et al., 2009). Detailed bathymetric mapping, geological sampling and seafloor observations have shown that the Logatchev hydrothermal field has a number of characteristics that are uncommon on the modern seafloor (Petersen et al., 2009): (1) it is located off-axis, away from the neovolcanic zone, in an area of axis-parallel ridges and detachment faulting; (2) basaltic pillow volcanoes occur off-axis in close proximity to the field; (3) venting occurs mainly in so-called smoking craters and is related to small, fragile sulfide chimneys at the crater rim or occurs directly from holes in the crater floor without chimney formation; (4) the massive sulfides are extremely rich in Cu and Au (Krasnov et al., 1995a; Murphy and Meyer, 1998; Mozgova et al., 1999); (5) the hydrothermal fluids have high concentrations of dissolved CH_4 and H_2 (Schmidt et al., 2007, 2011). The sulfide rubble that composes both the smoking crater bodies and the sulfide mounds at Logatchev consists of massive chalcopyrite and isocubanite partially altered to covellite and bornite by percolation of low-temperature hydrothermal fluids and cold seawater (Petersen et al., 2009). Weathered breccias are characterized by clasts of secondary Cu-rich sulfides such as bornite, chalcocite and digenite set in a matrix of cemented pelagic sediment containing native copper, cuprite and atacamite.

The Irina II site is located at 14°45.17′N/44°58.75′W and consists of an elongated mound structure rising over 15 m above the surrounding seafloor (Fig. 1). It has a basal diameter of ~50 m in NW-SE and 25 m in NE-SW direction. The basement consists of altered ultramafic rock talus (Petersen et al., 2009). A complex of black smokers marks the top of the mound. It consists of five big and numerous smaller chimneys. Apart from some small inactive sulfide chimneys in the west and northwest of the complex the smokers are active (Petersen et al., 2009). In addition to the black smoke emanating chimneys, beehive diffusers emit clear fluids (Petersen et al., 2009). At the southeastern margin of the smoker complex there is a single small and active black smoker (Microsmoker; Schmidt et al., 2011). Subsamples from the talus at the base of this smoker consist of chalcopyrite with rare magnetite and hematite inclusions (Petersen et al., 2009). This mineral association has not been studied before at any seafloor hydrothermal system, and the inferred oxidizing conditions were previously unknown at ultramafic-hosted mid-ocean ridge (MOR) vent sites. Petersen et al. (2009) concluded that the reaction zone of the magma body driving the hydrothermal system at the Irina II site was very close to the seafloor. The hematite-chalcopyrite mineral assemblage implies strong changes in the venting conditions (from oxic to reduced) that may imply that the Irina II hydrothermal system has evolved from pre-intrusion to post-intrusion stage (e.g., Haase et al., 2007).

3. Samples and methods of investigation

We investigated nine samples from two active chimneys [6 from the LGV-BIO chimney (Fig. 2), and 3 from the MS 21-3 chimney (photo not provided)] from the Irina II site (Logatchev hydrothermal field). Chimney fragments were collected during the R/V *L'Atalante* cruise Microsmoke (1995) using the Deep Submersible Vehicle (DSV) *Nautile* (one chimney fragment) and during the R/V *Pourquoi Pas?* cruise Serpentine (2007) using the Remotely Operated Vehicle (ROV) *Victor 6000* (one chimney fragment).

Sub-samples from each sample were prepared as polished sections and their mineralogy and textures were investigated using an Olympus BX60 polarizing transmitted and reflected light microscope.

Bulk mineralogical composition of the finely powdered sub-samples was determined by X-ray diffraction (XRD) analysis (Philips X-ray diffractometer PW 1820 with monochromatic Co K_α radiation) of random mounts with scans from 4 to 75° 2θ, with 0.02° 2θ step, and 1 s/step. XRD patterns were interpreted by using the XPowder® software.

After preliminary observations with a stereo-microscope (WILD M8), small crystals from the two major mineral phases (blackish-gray and yellow, both with metallic lustre) were selected from one sample and mounted on a carbon fiber (5 μm in diameter) attached to a glass rod. Single-crystal X-ray investigations were performed with an Oxford Diffraction Xcalibur3 CCD single-crystal diffractometer using Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). Operating conditions were: $V = 40$ kV, $I = 40$ nA, 20 s exposure time per frame, and 6 cm detector-to-sample distance.

Secondary electron images (SEI) and energy dispersive X-ray spectra (EDS) were obtained on small (~0.5 × 0.5 cm) sub-samples, mounted on aluminum stubs using carbon tape and coated with Au using a FEI