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Trace element systematics of pyrite from submarine hydrothermal vents

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ABSTRACT

Submarine hydrothermal sulfide ores occur at mid-ocean ridges, intra-oceanic arcs and in back-arc basins associated with host rocks of highly variable composition. Pyrite is the dominant sulfide mineral in most samples presented within this study, and thus the trace element composition of pyrite may reflect the different metal sources and precipitation processes. Here, we report on a systematic study of minor and trace element contents in pyrite from active and inactive submarine hydrothermal vent fields at different plate-tectonic settings including the Indian and Mid-Atlantic Ridges, the Tonga–Kermadec intra-oceanic arc, the Lau back-arc and the central Okinawa Trough. Our results show that the trace element contents of pyrite from different locations vary significantly but for most elements without any systematic correlation to the concentration in the magmatic host rocks. Only As appears to be depleted in pyrite from ultramafic-hosted vent systems that are affected by serpentinization. These As depleted pyrites preferentially host Au^0 micro- or nano-particles. Bismuth is enriched in pyrite from hydrothermal systems that contain a sedimentary component and micro-inclusions of sphalerite are either due to fluid–sediment interaction or phase-separated fluid venting. Pyrites from individual locations have highly variable concentrations of elements like Au, Co, Cu, Se, Mo, Ag and Sb that are most likely related to fluid evolution and changes in fluid composition. Sub-seafloor hydrothermal fluid–seawater mixing influences the distribution of Au, Co, Cu, Se and Mo in pyrite. Elements like Au, Ag, Sb and Pb often have a characteristic affinity to As, while Cd correlates closely with Zn. A magmatic volatile contribution to the Hine Hina hydrothermal system may result in the precipitation of Cu-enriched pyrite. Our results show that the concentrations of most trace metals in pyrite are a function of the physicochemical parameters of the fluid phase rather than a reflection of the magmatic host rock composition.

1. Introduction

Submarine hydrothermal circulation is caused by cooling of magmatic rocks of the oceanic crust and leads to chemical exchange and heat transfer between the lithosphere and the oceans (e.g., Hannington et al., 2005). Investigations of submarine hydrothermal systems have focused on the composition of hydrothermal fluids (e.g., Schmidt et al., 2007; Koschinsky et al., 2008) and sulfide-bearing bulk ore samples (e.g., Fouquet et al., 1998; Kristall et al., 2011). Previous studies suggested that the composition of hydrothermal sulfides largely depends on the variable composition of the magmatic host rocks and thus on the geological setting. For example, sulfide precipitates in back-arc basins appear to be enriched in Au, Zn, As, Ag, Sb and Pb compared to sulfides from hydrothermal systems at mid-ocean ridges (Herzig et al., 1993; Hannington et al., 1999). The metal content of magmatic rocks in turn depends on the behavior of metals in the magma source and during differentiation (e.g., Doe, 1994; Stanton, 1994). Leaching of metals from the host rocks and their transport in hydrothermal fluids to the seafloor is controlled by temperature, pH, redox conditions, salinity and the availability of ligands to form chloride, sulfide and hydroxide complexes that may enhance metal and trace element solubilities in the fluid phase (Seyfried and Ding, 1993, 1995; Pokrovski et al., 2008). However, elements concentrated in the host rocks are not necessarily concentrated in the associated hydrothermal fluids (Gillis and Thompson, 1993; Schmidt et al., 2007). In addition to leaching from the host rocks, magmatic volatiles may provide another important metal source for hydrothermal systems and elements such as Au, Cu, As and Ag can be transported by such a volatile phase (Williams-Jones and Heinrich, 2005; Simon and Ripley, 2011; Scher et al., 2013). Additionally, the composition of hydrothermal fluids can be affected by phase separating processes (Butterfield et al., 2003; Foustoukos and Seyfried, 2007; Liebscher and Heinrich, 2007). Elements such as Cu mainly fractionate into the vapor phase while Zn, for example, remains in the chloride-rich brine (Koschinsky et al., 2008; Nagaseki and Hayashi, 2008; Pokrovski et al., 2013). Sulfides precipitating from fluids that interacted with sediments were found to have high As, Se, Sb, Pb and Bi contents (Koski et al., 1988; Zierenberg et al., 1993). Bulk sulfide samples are composed of different mineral phases and are thus of limited suitability to determine

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the controlling factors of metal precipitation in a fluid-mineral system. Trace element data on fluid and sulfide phases in hydrothermal systems are required to define the processes of metal mobilization and precipitation and the potential metal sources. The high-resolution trace element data of individual sulfide crystals from active and inactive hydrothermal vents can help to constrain the processes leading to the enrichment of different trace metals in volcanic-hosted massive sulfide (VHMS) deposits, which is also of economic interest.

Pyrite is present in sulfide ores occurring in a wide range of tectonic settings including mid-ocean ridges (e.g., Tivey et al., 1995; Petersen et al., 2000), intra-oceanic arcs (e.g., de Ronde et al., 2011; Berkenbosch et al., 2012) and back-arc basins (e.g., Fouquet et al., 1993; Herzig et al., 1998). Because of the abundance of pyrite in submarine hydrothermal sulfide ores and its ability to incorporate trace metals such as Au, Ni, Co, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Pb and Bi in detectable amounts (Maslennikov et al., 2009; Deditius et al., 2011; Reich et al., 2013) it is possible to compile a global database of pyrite chemistry from a wide range of geological settings. Consequently, we selected pyrite for a systematic trace element study because this mineral represents the most abundant sulfide in submarine hydrothermal vent systems (cf. Fouquet et al., 1998) and it forms from fluids with variable physicochemical composition during different stages of chimney growth (e.g., Maslennikov et al., 2009; Revan et al., 2014).

Here we present minor and trace element compositions of pyrite from submarine hydrothermal vent systems located at different plate tectonic settings and associated with host rocks of variable composition. Our results indicate that the composition of the magmatic host rocks has only little systematic influence on the trace element composition of hydrothermal pyrite. Variations in the physicochemical parameters of hydrothermal fluids and the contribution of magmatic volatiles appear to be the more important factors controlling the trace metal distribution in pyrite.

2. Geological setting and sample localities

Samples from active and inactive submarine hydrothermal vent fields situated at divergent and convergent plate margins (Fig. 1, Table 1) were analyzed. These include the Mid-Atlantic Ridge with the hydrothermal vent sites of the Trans-Atlantic Geotraverse (TAG), Logatchev (IRINA II) and 5°S (Turtle Pits and Comfortless Cove), as well as the Central Indian Ridge with Kairei and the Meso zone. Additionally, we analyzed samples from back-arc basins including the Hine Hina and Jade hydrothermal fields of the Valu Fa Ridge and the central Okinawa Trough, respectively. Submarine hydrothermal systems at intra-oceanic arcs are represented by samples from Brothers volcano and Volcano 19 from the Tonga–Kermadec arc.

2.1. Mid-ocean ridges

The examined mid-ocean ridge vent sites can be generally classified based on their host rock composition into basalt- and ultramafic-hosted hydrothermal systems. The latter include the Kairei (25°19′S/70°2′E) and Logatchev (14°45′N/44°58′W; IRINA II) vent fields of the Central Indian Ridge and the Mid-Atlantic Ridge, respectively. At Logatchev serpentinized ultramafic rocks are exposed on the seafloor (e.g., Kuhn et al., 2004; Paulick et al., 2006), whereas the Kairei vent field (2420–2460 mbsl; Gallant and Von Damm, 2006) is situated on basaltic rocks. However, the chemical composition of the Kairei vent fluids indicates fluid interaction with ultramafic rocks during hydrothermal circulation through oceanic lithosphere (Kumagai et al., 2008; Nakamura et al., 2009). Each of these vent sites is represented by two pyrite-bearing sulfide samples including porous massive pyrite crusts (83GTV-3C3, 3E4; 3019 mbsl) sampled during RV Meteor cruise M60/3 at the north-western base of the IRINA II sulfide mound of the Logatchev 1 vent field (Kuhn et al., 2004). The samples taken during TV-grab station 83 are described as high temperature precipitates although only diffuse fluid venting was identified at the sampling site during cruise M60/3. In contrast, temperature measurements of emanating black smoker fluids at IRINA II revealed fluid temperatures of up to 220 °C (Schmidt et al., 2007). The studied samples from the Kairei vent field are pyrite-bearing massive sulfide samples (105-4-S4, 106-3-S1b) that were recovered during RV Sonne cruise INDEX 2011 (Schwarz-Schampera et al., 2011). The Kairei hydrothermal field is situated in a water depth of 3019 m and the discharging fluids reach temperatures between 315 °C and 365 °C (Gamo et al., 2001; Gallant and Von Damm, 2006; Nakamura et al., 2009).

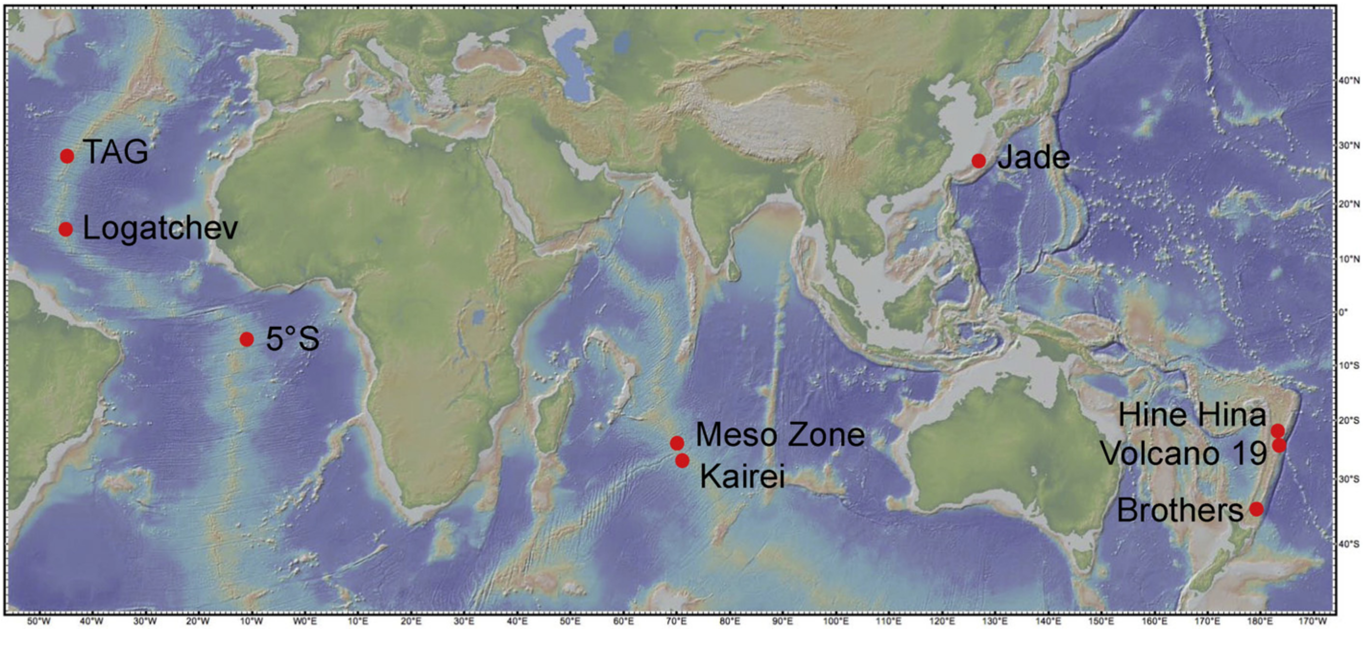

Fig. 1. Global distribution of the sample localities processed in this study. Seafloor map generated using GeoMapApp (http://www.geomapapp.org).