Atacamite and paratacamite from the ultramafic-hosted Logatchev seafloor vent field (14°45′N, Mid-Atlantic Ridge)

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ABSTRACT

Atacamite and paratacamite are ubiquitous minerals associated with Cu-rich massive sulfides at the Logatchev hydrothermal field (Mid-Atlantic Ridge). In this work we provide new details on the mineralogy and geochemistry of these basic cupric chlorides. Our data support the notion that atacamite and paratacamite formation at submarine vent fields is an alteration process of hydrothermal Cu-sulfides. Secondary Cu-sulfides (bornite, covellite) are unstable at ambient seawater conditions and will dissolve. Dissolution is focused at the sulfide–seawater contact, leading to release of Fe^{2+} and Cu^+ and formation of residual chalcocite through an intermediate Cu_5S_4 phase. Most of the released Fe^{2+} oxidizes immediately and precipitates as FeOOH directly on the chalcocite rims whereas Cu as chloride complexes ($CuCl_2^-$, $CuCl_3^{2-}$) remains in solution at the same Eh. Cuprous–chloride complexes migrate from the reaction zone and upon increasing Eh precipitate as $Cu_2Cl(OH)_3$. As a consequence of this, the sulfide–seawater reaction interface is clearly marked by thin chalcocite–FeOOH bands and the entire assemblage is mantled by atacamite (or paratacamite). Our mineralogical, petrographic, geochemical and isotopic studies suggest that there are two types of atacamite (and/or paratacamite) depending on their mode of precipitation. Type 1 atacamite precipitated directly on the parent sulfides as evidenced by mantling of the sulfides, absence of detrital mineral grains, a preserved conspicuous positive Eu anomaly and a negligible negative Ce anomaly similar to those of the parent sulfide. In addition, Au concentrations are slightly lower than those of the parent sulfides, which suggest minimal transport of Au-ions after their release from the sulfides. Furthermore, the low content of the rare earth elements implies short contact time with the ambient seawater. The Sr–Nd–Pb-isotopic signatures of type 1 atacamite confirm the genetic association with the parent sulfides and indicate formation spatially very close to the latter. Type 2 atacamite precipitated at some distance from the parent sulfides, which means that the cuprous–chloride complexes have moved away from the sulfide alteration zone before precipitation. The evidence for this is absence of direct association of atacamite with sulfides. In addition, this atacamite contains a substantial proportion of detrital minerals, which implies precipitation in the sediments, distal to the parent sulfides. As a consequence of the detrital impurities the contents of elements like Cr, Cs, Hf, Nb, Rb, Th and Zr are higher than in type 1 atacamite (and/or paratacamite). Au contents are lower than those of type 1 atacamite (and/or paratacamite) which implies prolonged Au transport in solution before precipitation. Furthermore, the rare earth element distribution patterns have no positive Eu anomaly suggesting that the positive Eu anomaly of the parent sulfide has been erased after dissolution and prolonged contact of the fluid with ambient seawater (with negative Eu anomaly). Finally, the Sr–Nd-isotope signature differs from that of the parent sulfide and indicates a considerable terrigenous input.

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1. Introduction

Atacamite and its trigonal polymorph paratacamite are the most stable copper salts at the pH and Eh of cold (undersaturated in $CaCO_3$) deep seawater (Woods and Garrels, 1986; Hannington, 1993) and it is

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not surprising that these basic cupric chlorides [$Cu_2Cl(OH)_3$] are commonly found at seafloor hydrothermal sites (Bonatti et al., 1976; Scott et al., 1982; Hekinian and Fouquet, 1985; Alt et al., 1987; Alt, 1988a, b; Embley et al., 1988; Fouquet et al., 1988; Thompson et al., 1988; Rona and Clague, 1989; Scott et al., 1990; Herzig et al., 1991; Krasnov et al., 1991; Vanko et al., 1991; Fouquet et al., 1993; Mills and Elderfield, 1995; Langmuir et al., 1997; Butler et al., 1998; Damyanov et al., 1998; Moss, 2000; Severmann, 2000; de Ronde et al., 2003; Rouxel et al., 2004; Glynn et al., 2006; Hrischeva et al., 2007; Eickmann et al., 2009). Although a number of studies report on atacamite and paratacamite occurrences only two of them (Mossman and Heffernan, 1978; Hannington, 1993) are comprehensive investigations addressing the physical and chemical conditions under which these minerals form at the seafloor vent sites. These two papers describe atacamite formation in two contrasting environments: primary precipitation of atacamite in a reduced environment (hydrothermal sediments in the Red Sea hot brine-filled deeps; Mossman and Heffernan, 1978) and secondary atacamite formation during oxidative weathering of massive sulfides under ambient seawater conditions [TAG hydrothermal field, Mid-Atlantic Ridge (MAR); Hannington, 1993]. Nonetheless, our understanding of precipitation of basic cupric chlorides at the seafloor is still very limited especially with respect to our knowledge of their occurrences on the continents (Cameron et al., 2007; Reich et al., 2008, 2009, and references therein). In particular, none of the published works discuss their trace element and isotope compositions. Here we report on the composition of a set of green samples (originally interpreted, and here confirmed to be basic cupric chlorides: atacamite and paratacamite) collected at the ultramafic-hosted Logatchev vent field (14°45′N, MAR) during two cruises (R/V *Yuzhmorgeologiya* in 2000; R/V *Meteor* in 2004). We aim at providing further insight into the origin of basic cupric chlorides at the seafloor vent fields by integrating mineralogical, geochemical and isotopic data.

2. Geological setting

Detachment faulting and core complex formation play a key role in the crustal accretion at slow-spreading centers (Escartín et al., 2008). These processes expose lower crustal and upper mantle rocks at the seafloor (Smith et al., 2006). This type of setting hosts hydrothermal systems in which upper-mantle ultramafics have significant impact on the thermal regime, and on both fluid and deposit composition (Kelley et al., 2001; Douville et al., 2002). Today we know of only five ultramafic-hosted high-temperature hydrothermal fields in the Atlantic Ocean (Logatchev, Batuev et al., 1994; Rainbow, German et al., 1996; Ashadze, Beltenev et al., 2003; Semyonov, Beltenev et al., 2007; Nibelungen, Melchert et al., 2008) and three of them (Logatchev; Semyonov; Ashadze) occur along a single segment of the MAR between the Fifteen-Twenty and Marathon fracture zones (FZ).

The Logatchev hydrothermal field is located south of the Fifteen-Twenty FZ at a section of 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 and comprises 2 active hydrothermal fields, Logatchev-1 and -2 (Fig. 1) some ~7 and ~12 km away from the spreading axis, each of them having several active and inactive vent sites. The hydrothermal activity at both fields is structurally controlled and, at least for Logatchev-1, localized in debris flows consisting of heterogeneous ultramafic and mafic intrusive rock clasts (Augustin et al., 2008; Petersen et al., 2009). Basaltic volcanism and associated gabbroic intrusions beneath the eastern flank of the rift valley 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: (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 Cu and Au rich (Krasnov et al., 1995; Murphy and Meyer, 1998; Mozgova et al., 1999); (5) the hydrothermal fluids have high concentrations of dissolved CH_4 and H_2 (up to 3.5 mM and 19 mM, respectively; Schmidt et al., 2007). The sulfide rubble that composes both the smoking crater bodies and the sulfide mounds at Logatchev-1 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. Atacamite is also present at the outer surface of many weathered sulfide talus samples and occurs in larger accumulations associated with Fe–oxyhydroxide-bearing sediments distal to massive sulfides.

3. Material and methods

We studied 2 TV-grab samples taken at 2 sites from the Logatchev hydrothermal field: one from Logatchev-1, another from Logatchev-2 (Table 1, Fig. 1). The video-controlled hydraulic grab is lowered to the seafloor on a cable and is capable of sampling almost 1 m^2 of the seafloor of interest to a depth of ~50 cm, providing representative samples not only of the surface material, but also from the immediate sub-seafloor. After a preliminary macroscopic description of these samples we divided them into 8 sub-samples (each sample into 4 sub-samples) on the basis of color and texture.

The mineralogy of the samples was studied by X-ray diffractometry (XRD) (Philips X-ray diffractometer PW 1710 with automatic divergence slit and with both monochromatic Co K$_\alpha$ and Cu K$_\alpha$ radiation, 40 kV, 35–40 mA) of random powder mounts: scans from 2 to 80°2θ, with 0.01°2θ step, at 2 s/step. Peak positions were determined with the X'Pert Graphics and Identify program.

Mössbauer spectra of selected samples (after preliminary XRD study and identification of Fe-containing minerals) were obtained at room temperature (ca. 295 K) using a constant acceleration system working in conjunction with a 1024 Multi Channel Analyzer. A nominal 50 mCi ^{57}Co/Rh-source and a gas-filled proportional counter were used as source and detector in these experiments. The sample absorbers consisted of self-supporting pressed discs of sample powders mixed with polymeric transoptic powder. In order to minimize texture effects, all spectra were recorded with the absorber at an angle of 54.7° to the incident gamma-rays (Ericsson and Wäppling, 1976). The obtained raw data were folded and fitted using a computer program (Jernberg and Sundqvist, 1983) assuming resonance absorption lines of Lorentzian shape and equal intensity and line width of the components of each quadrupole doublet. The velocity range of the sample spectra was calibrated against metallic iron (α-Fe) at room temperature.

Four specimens representing both samples (2 specimens from each) were prepared as polished thin sections and studied by optical microscopy (to investigate mineralogy and texture) with a Zeiss Axioplan 2 polarizing microscope. Microphotographs were taken at different magnifications with a Canon Powershot A 80.

Secondary electron images (SEI) and energy dispersive X-ray spectra (EDS) were obtained on small (~1 × 1 cm) sub-samples dried at lab temperature (~20 °C), mounted on aluminum stubs using carbon tape and coated with either Au–Pd or C using a CamScan CS44 scanning electron microscope (SEM) (V = 15 kV, I = 12 nA, electron beam diameter of 2 μm) and Hitachi S4300 SEM (V = 10–20 kV, I = 5–8 μA, electron beam diameter of 1 μm), respectively. Back-scattered electron images (BEI), X-ray mapping (in Cu K$_\alpha$, Fe K$_\alpha$, O K$_\alpha$, S K$_\alpha$ and