



Geochemical constraints on the modes of carbonate precipitation in peridotites from the Logatchev Hydrothermal Vent Field and Gakkel Ridge

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ABSTRACT

The ultramafic-hosted Logatchev Hydrothermal Field (LHF) at 15°N on the Mid-Atlantic Ridge and the Arctic Gakkel Ridge (GR) feature carbonate precipitates (aragonite, calcite, and dolomite) in voids and fractures within different types of host rocks. We present chemical and Sr isotopic compositions of these different carbonates to examine the conditions that led to their formation. Our data reveal that different processes have led to the precipitation of carbonates in the various settings. Seawater-like $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for aragonite in serpentinites (0.70909 to 0.70917) from the LHF are similar to those of aragonite from the GR (0.70912 to 0.70917) and indicate aragonite precipitation from seawater at ambient conditions at both sites. Aragonite veins in sulfide breccias from LHF also have seawater-like Sr isotope compositions (0.70909 to 0.70915), however, their rare earth element (REE) patterns show a clear positive europium (Eu) anomaly indicative of a small (< 1%) hydrothermal contribution. In contrast to aragonite, dolomite from the LHF has precipitated at much higher temperatures (~100 °C), and yet its $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.70896 to 0.70907) are only slightly lower than those of aragonite. Even higher temperatures are calculated for the precipitation of deformed calcite veins in serpentine–talc fault schists from north of the LHF. These calcites show unradiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.70460 to 0.70499) indicative of precipitation from evolved hydrothermal fluids. A simple mixing model based on Sr mass balance and enthalpy conservation indicates strongly variable conditions of fluid mixing and heat transfers involved in carbonate formation. Dolomite precipitated from a mixture of 97% seawater and 3% hydrothermal fluid that should have had a temperature of approximately 14 °C assuming that no heat was transferred. The much higher apparent precipitation temperatures based on oxygen isotopes (~100 °C) may be indicative of conductive heating, probably of seawater prior to mixing. The hydrothermal calcite in the fault schist has precipitated from a mixture of 67% hydrothermal fluid and 33% seawater, which should have had an isenthalpic mixing temperature of ~250 °C. The significantly lower temperatures calculated from oxygen isotopes are likely due to conductive cooling of hydrothermal fluid discharging along faults. Rare earth element patterns corroborate the results of the mixing model, since the hydrothermal calcite, which formed from waters with the greatest hydrothermal contribution, has REE patterns that closely resemble those of vent fluids from the LHF. Our results demonstrate, for the first time, that (1) precipitation from pure seawater, (2) conductive heating of seawater, and (3) conductive cooling of hydrothermal fluids in the sub-seafloor all can lead to carbonate precipitation within a single ultramafic-hosted hydrothermal system.

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1. Introduction

Seawater circulation within the ocean crust and associated water–rock interactions has profound consequences for the chemical and isotopic compositions of both the ageing ocean crust and seawater (e.g., Elderfield and Schultz, 1996). During the transformation of seawater

into a hydrothermal fluid, calcium (Ca) concentration increases while magnesium (Mg) and sulfate concentrations decrease (e.g., von Damm, 1990). These changes are due to seawater–rock Ca–Mg exchange reactions and to precipitation of carbonate, anhydrite, and hydrous magnesium-silicates (Mottl, 1983; Seyfried, 1987; Teagle et al., 1998). High-temperature vent fluids discharge at or near mid-ocean ridge axes is manifested by the formation of black smokers and massive sulfide deposits (Von Damm, 1990; Tivey, 2007). In contrast, low-temperature alteration follows a different reaction path, characterized by the formation of palagonite, clay minerals, and carbonate minerals (e.g., Staudigel et al., 1981; Alt, 1995). Even at low temperatures (<60 °C), seawater loses Mg while it leaches Ca from the rock (Elderfield et al.,

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1999; Wheat et al., 2000). The increase in Ca in seawater is matched by the decrease in Mg, so that the overall reaction does not significantly change the pH of the circulating seawater. Calcite and aragonite precipitate during low-temperature seawater–rock interactions and represent useful indicators for the determination of water–rock reactions and fluid mixing processes within the ocean crust (Hart et al. 1994; Coggon et al., 2004; Amini et al., 2008). Several previous studies of ultramafic-hosted hydrothermal environments along the Mid-Atlantic Ridge (MAR) report that aragonite has exclusively formed at low temperatures from virtually unmodified seawater (e.g., Bonatti et al., 1980; Blusztajn and Hart, 1996; Ribeiro da Costa et al., 2008). Despite the apparent dominance of carbonates formed at ambient seafloor conditions, there is also evidence for aragonite and calcite precipitating at high temperatures from mixtures of ambient seawater and discharging hydrothermal fluids (Früh-Green et al., 2003; Pichler and Veizer, 2004; Ludwig et al., 2006; Amini et al., 2008).

The main subjects of this study are carbonate minerals from the Logatchev Hydrothermal Field (LHF) at the MAR at 14°45'N. Aragonite hosted in serpentinites from the Gakkel Ridge (GR) in the Arctic Ocean was also included in the study. This paper investigates the chemical aspects of precipitation of carbonate minerals at both sampling sites using Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) and minor and trace element concentrations of aragonite, calcite and dolomite formed during water–rock interaction. Our previous study (Eickmann et al., 2009) revealed that $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values agree with aragonite precipitation at low temperatures, similar to other seafloor weathering environments (Bonatti et al., 1980) and moderate-temperature hydrothermal sites (Kelley et al., 2005). In contrast, low $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of serpentinites-hosted calcite from the LHF indicate precipitation from hydrothermal solutions dominated by magmatic CO_2 (Eickmann

et al., 2009). The study of LHF carbonate minerals consequently provides a good opportunity to investigate both calcite precipitation at high temperatures and aragonite precipitation at low temperatures within the same hydrothermal field. Here, we demonstrate that calcite was precipitated from conductively cooled hydrothermal fluids, whereas dolomite has been precipitated from conductively heated seawater. Although aragonite precipitated from near end-member seawater, REE reveal a minor hydrothermal influence.

2. Geological background

Both the slow-spreading MAR and the ultraslow-spreading GR (Fig. 1) are characterized by the exposure of upper mantle rocks along detachment faults (Cannat, 1993; Tucholke and Lin, 1994; Dick et al., 2003). The area south of the Fifteen-Twenty Fracture Zone is typified by extensive exposure of peridotite and gabbroic rocks on both flanks along the spreading axis of the MAR (Cannat et al., 1997; Fujiwara et al., 2003). Widespread fluid–rock interaction in the sub-seafloor is evident from extensive methane and hydrogen anomalies in the water column and high-temperature fluid discharge in the LHF (Charlou et al., 1998, 2002; Schmidt et al., 2007). The LHF is located on the rift valley wall of the MAR (Fig. 2) at a water depth of 3060 m to 2900 m. Several active and inactive vents are distributed along a NW–SE direction. The active LHF comprises seven high-temperature vent sites (Fig. 2), including two black smokers (Irina II and Site 'A'), and five smoking craters (Quest, Site 'B', Irina, Anna-Louise and Candelabra). Basement rocks mainly consist of serpentinized peridotites (dunites and harzburgites), with dikes and intrusions of coarse-grained websterites, orthopyroxenites and Opx-rich pegmatoidal norites (Augustin et al., 2008; Petersen et al., 2009). Furthermore, the LHF exhibits abundant copper and iron deposits

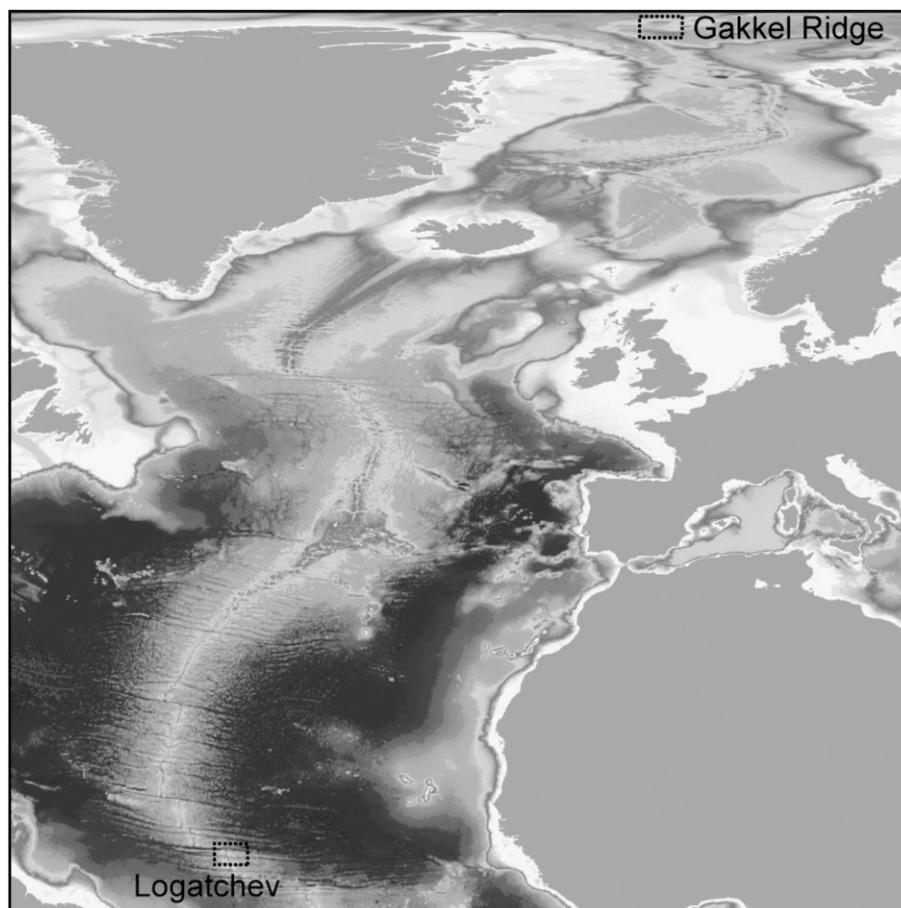


Fig. 1. Locations of the Logatchev Hydrothermal Field on the Mid-Atlantic Ridge (14°45'N) and of the Gakkel Ridge in the Arctic Ocean.

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