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Magmatic influence on reaction paths and element transport during serpentinization

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ABSTRACT

Small-scale shear zones are present in drillcore samples of abyssal peridotites from the Mid-Atlantic ridge at 15°20′N (Ocean Drilling Program Leg 209). The shear zones act as pathways for both evolved melts and hydrothermal fluids. We examined serpentinites directly adjacent to such zones to evaluate chemical changes resulting from melt–rock and fluid–rock interaction and their influence on the mineralogy. Compared to fresh harzburgite and melt-unaffected serpentinites, serpentinites adjacent to melt-bearing veins show a marked enrichment in rare earth elements (REE), strontium and high field strength elements (HFSE) zirconium and niobium. From comparison with published chemical data of variably serpentinized and melt-unaffected harzburgites, one possible interpretation is that interaction with the adjacent melt veins caused the enrichment in HFSE, whereas the REE contents might also be enriched due to hydrothermal processes. Enrichment in alumina during serpentinization is corroborated by reaction path models for interaction of seawater with harzburgite–plagiogranite mixtures. These models explain both increased amounts of alumina in the serpentinizing fluid for increasing amounts of plagiogranitic material mixed with harzburgite, and the absence of brucite from the secondary mineralogy due to elevated silica activity. By destabilizing brucite, nearby melt veins might fundamentally influence the low-temperature alteration behaviour of serpentinites. Although observations and model results are in general agreement, due to absence of any unaltered protolith a quantification of element transport during serpentinization is not straightforward.

1. Introduction

In recent years, there has been an increasing interest in ultramafic-hosted hydrothermal systems at the seafloor, where peridotites are exposed and interact with seawater (e.g., Gràcia et al., 2000; Kelley et al., 2001; Charlou et al., 2002; Douville et al., 2002; Paulick et al., 2006; Schmidt et al., 2007; Melchert et al., 2008; Klein and Bach, 2009). The resulting serpentinization affects the mineralogy, rheology, seismic and magnetic structure of the oceanic crust (e.g., Miyashiro et al., 1969; Escartín et al., 2001; Fujiwara et al., 2003; O'Driscoll and Petronis, 2009). Additionally, hydration reactions in the abyssal peridotites lead to oxidation of ferrous iron in primary minerals to ferric iron in secondary assemblages (e.g., McCollom and Bach, 2009), and the reducing conditions involved are expressed by formation of hydrogen and methane, which provide fuel for microbial communities (e.g., O'Brien et al., 1998; Kelley et al., 2005; Alt et al., 2007; Delacour et al., 2008).

Fluid flow through the oceanic crust causes redistribution of elements. High-temperature fluids have the potential to leach certain elements from crustal rocks, transport them and lead to precipitation of minerals elsewhere. A profound understanding of the underlying processes and pathways of fluid flow is of interest not only for economic geologists, but also for explanation of the fluid chemistry at hydrothermal vents and for estimating the bulk composition of the oceanic crust, the input into subduction zones. Thus, the detailed study of the character and pressure–temperature framework of serpentinization reactions is relevant for understanding the complex interaction among lithosphere, hydrosphere and biosphere, contributing to comprehensive insights into global geochemical cycles.

The composition and general anatomy of the oceanic crust is believed to be well understood from seismology as well as petrological and geochemical studies on ophiolite complexes and drillcore samples (e.g., Anonymous, 1972; de Wit and Stern, 1976). However, the more detailed the studies get, the more they add knowledge about inhomogeneities to the model of a laterally continuous oceanic crust. Such features, which are particularly common in slow-spreading crust, include chemical heterogeneities, e.g., ultramafic oceanic core complexes (Boschi et al., 2006; Smith et al., 2006; Ildefonse et al., 2007) and intrusions of evolved melts (Coleman and Peterman, 1975; Aldiss, 1981; Koepke et al., 2007; Jöns et al., 2009), but also structural heterogeneities such as detachment faults and fracture zones. Concerning fluid flow and element transport, both sources of heterogeneities are important to consider. Fracturing promotes and focuses fluid flow and thus, to some extent, countervails the volume expansion that accompanies mineral

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hydration reactions. Fracturing therefore allows for fluid-dominated alteration regimes (high water/rock mass ratios), whereas hydration reactions under static conditions promote rock-dominated alteration (lower water/rock mass ratios). Additionally, intrusions of melt generally follow pre-existing fractures (e.g., Kaczmarek and Müntener, 2008; Jöns et al., 2009), resulting in co-occurring chemical and structural heterogeneities. Assuming fluid flow along melt-influenced fractures, the chemical characteristics of the fluid are likely dominated by the interaction with a gabbroic or more evolved melt, even though the host rocks are of distinct chemical composition (e.g., abyssal peridotites).

In the present study, we examine the mineral and bulk-rock chemistry of serpentinized abyssal harzburgites. These rocks host shear zones with abundant magmatic material and are thus an ideal object for studying the combined mineralogical and geochemical effects of serpentinization, magmatism and fluid flow, which might eventually influence vent fluid chemistry of associated hydrothermal systems.

2. Geological setting

Samples for this study were drilled during ODP Leg 209 (Kelemen et al., 2004), which is located at the slow-spreading Mid-Atlantic ridge (MAR) near the prominent 15°20′N fracture zone (Fig. 1). Leg 209 drilled mainly abyssal peridotites and gabbros exposed in the footwalls of major detachment faults on the flanks of the MAR. Fluids issuing from the active Logatchev hydrothermal field, located between Sites 1268 and 1270, are characterized by high concentrations of dissolved dihydrogen and methane, indicative of peridotite–seawater interactions. The widespread fluid–peridotite interaction is also evidenced by H_2 and CH_4 anomalies in the water column (Charlou et al., 1991; Bogdanov et al., 1997). Based on structural and lithological observations, Schroeder et al., (2007) interpret the MAR in the 15°N area as a non-volcanic ridge with abundant localized faulting. At Site 1270 of Leg 209, four holes were drilled near the top of an exposed long-lived normal fault on the side of the rift valley (Kelemen et al., 1998; Schroeder et al., 2007). Although this part of the MAR is volcanically starved, gabbroic intrusions and melt veins are abundant (Kelemen et al., 2004). Veins containing zircon and apatite have been found in small-scale shear zones, and they are interpreted as plagiogranitic melts derived from hydrous partial melting of gabbroic rocks (Jöns et al., 2009). In the present study, we use serpentinite samples adjacent (max. 2 cm distance) to such evolved melt veins (the corresponding host rocks to samples used by Jöns et al., (2009), sample locations given in Table 1).

3. Methods

3.1. Phase identification

Mineral phases were identified by polarizing microscopy. In addition, whole-rock samples were pulverized and examined with a Panalytical X'Pert PRO X-ray diffractometer (XRD) at the University of Bremen with Cu K_α radiation. Each powder pellet was scanned from $2\Theta = 4°$ to 75° with a voltage of 45 kV and a current of 40 mA. Data evaluation was done using R. Petschick's MacDiff software (version 4.2.5; available for download from `http://servermac.geologie.uni-frankfurt.de/Staff/Homepages/Petschick/RainerE.html`). XRD patterns of selected samples can be found in Appendix A.

3.2. Electron microprobe analyses

Major element mineral chemical compositions have been determined using a JEOL JXA-8900 electron microprobe at the University of Kiel (Germany). For most silicate minerals an accelerating voltage of 15 kV was used, with exception of olivine and spinel (20 kV). Measurement spot sizes were typically 1–5 μm in diameter. Standards were either natural minerals or synthetic materials. The CITZAF method of Armstrong (1995) was used for correction of the raw counts.

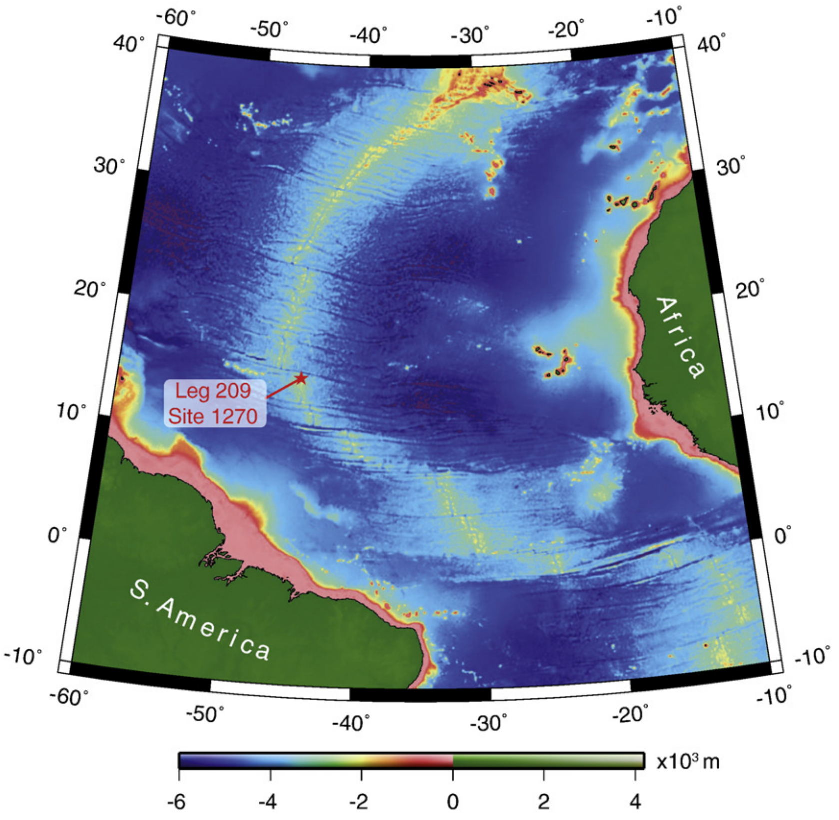

Fig. 1. Bathymetric map (prepared using the Generic Mapping Tools of Wessel and Smith, 1991, 1998) of the central Atlantic Ocean showing the location of ODP Leg 209 Site 1270 (equidistant conic projection).