



# Experimental study of carbonate formation in oceanic peridotite

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## Abstract

Interactions of CO<sub>2</sub>-rich aqueous fluids with mantle peridotite have major implications for geochemical budgets and microbial life in the shallow oceanic lithosphere through the formation of carbonate minerals and reduced carbon species. However, the underlying mechanisms controlling the transformation of CO<sub>2</sub> to carbonates in ultramafic-hosted hydrothermal systems remain incompletely understood. A long-term laboratory experiment was conducted at 300 °C and 35 MPa to investigate serpentinization and carbonate formation pathways during hydrothermal alteration of peridotite. Powdered harzburgite was initially reacted with a Ca-rich aqueous fluid for 14,592 h (608 days) and changes in fluid composition were monitored with time. Once the system reached a steady state, a CO<sub>2(aq)</sub>-rich fluid was injected and allowed to react with the system for 5907 h (246 days). Fluid speciation and mineral analyses suggest that serpentinization of harzburgite in the CO<sub>2</sub>-poor system led to the precipitation of serpentine, brucite, magnetite, and minor calcite, in addition to other minor phases including chlorite and sulfur-poor Ni sulfides. The addition of the CO<sub>2(aq)</sub>-rich fluid caused dolomite, Ca-rich dolomite, and high-Mg calcite to form at the expense of olivine, calcite, and brucite, while serpentine remained unreactive. Replacement textures and mineral assemblages mimic those documented in carbonate-altered seafloor serpentinites, particularly those from the Mid-Atlantic Ridge and the Iberia Margin. In contrast to thermodynamic predictions, magnesite did not form in the experiment because the dissolution of clinopyroxene, in combination with the lack of serpentine reactivity, maintained low Mg/Ca ratios in solution. Clinopyroxene dissolution and unreactive serpentine may similarly maintain low Mg/Ca ratios in submarine serpentinization systems and limit magnesite formation in subseafloor environments. Results of this study suggest that the formation of Ca–Mg carbonates by mineral carbonation is favorable in subseafloor serpentinization systems and likely represents a significant, but poorly quantified, carbon sink in hydrothermally altered oceanic lithosphere at slow-spreading mid-ocean ridges.

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## 1. INTRODUCTION

Mantle peridotite is exposed in a range of tectonic settings, including mid-ocean ridges, continental margins, subduction zone fore-arcs, and ophiolites (Fryer et al., 1995;

Bodinier and Godard, 2003; Dick et al., 2003; Cannat et al., 2010). When exposed to aqueous fluids near Earth's surface, peridotite undergoes hydrothermal alteration to form hydrous silicates, carbonates, oxides, and sulfides (e.g., Frost, 1985). The replacement of silicate and hydroxide minerals by carbonates – a process referred to as mineral carbonation – sequesters dissolved CO<sub>2</sub> into solids that can be stable over geologic time (e.g., Kelemen and Matter, 2008). Since hydrothermally altered peridotite is

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thought to comprise 5–9% of the rocks exposed along slow- and ultraslow-spreading mid-ocean ridges (Carlson, 2001; Cannat et al., 2010), mineral carbonation represents a potentially significant sink for carbon in the shallow oceanic lithosphere.

Mineral carbonation has received considerable attention as a means to sequester atmospheric CO<sub>2</sub> and mitigate global warming (e.g., Seifritz, 1990; Kelemen et al., 2011). A number of field, experimental, and theoretical studies have examined carbonation reactions in ultramafic substrates (Bruni et al., 2002; Cipolli et al., 2004; Giammar et al., 2005; Hansen et al., 2005; Kelemen and Matter, 2008; Andreani et al., 2009; King et al., 2010; Klein and Garrido, 2011; Hövelmann et al., 2011; Paukert et al., 2012; Van Noort et al., 2013; Klein and McCollom, 2013; Lafay et al., 2014; Peuble et al., 2015a,b). With only few exceptions, previous experimental studies have focused on the carbonation of olivine to magnesite, which can occur by the simplified reaction:



Magnesite is common in carbonate-altered peridotite (soapstone and listvenite) on land, which is typically associated with convergent plate margins, such as ophiolites in orogenic belts and exhumed mélange rocks in paleo-subduction zones (Naldrett, 1966; Griffis, 1972; Barnes et al., 1973; Dabitzias, 1980; Böhlke, 1989; Schandl and Wicks, 1991; Hansen et al., 2005; Robinson et al., 2005; Spandler et al., 2008; Boschi et al., 2009; Beinlich et al., 2012; Ulrich et al., 2014; Falk and Kelemen, 2015). The carbon in these rocks appears to be dominantly sourced from sedimentary lithologies that were affected by metamorphic decarbonation reactions (Barnes et al., 1973; Dabitzias, 1980; Schandl and Wicks, 1991; Beinlich et al., 2012; Falk and Kelemen, 2015). Magnesite also occurs in completely to incompletely serpentinized peridotite that has undergone low temperature alteration by Mg- and HCO<sub>3</sub>-rich waters (Barnes and O'Neil, 1969; Stanger, 1985; Bruni et al., 2002; Kelemen and Matter, 2008; Kelemen et al., 2011; Paukert et al., 2012; Oskierski et al., 2013; del Real et al., 2016; Schwarzenbach et al., 2016b). Here, fluids appear to be meteoric in origin, with carbon derived mainly from soil or atmospheric CO<sub>2</sub> (Schroll, 2002; Oskierski et al., 2013; Schwarzenbach et al., 2016b).

Whereas magnesite commonly occurs in ultramafic outcrops on land, it is rarely found in association with carbonate-altered mantle rocks in oceanic settings (Gablina et al., 2006). Serpentinized peridotite in the shallow oceanic lithosphere commonly contains Ca-bearing carbonates such as calcite, aragonite, and dolomite instead of magnesite (Bonatti et al., 1974; Ludwig et al., 2006; Eickmann et al., 2009; Kelemen et al., 2011; Bach et al., 2011; Schwarzenbach et al., 2013; Schroeder et al., 2015). Carbonates can form in several ways in the oceanic lithosphere, including homogeneous precipitation from pore fluids, and replacement of silicate and hydroxide minerals via mineral carbonation (Bonatti et al., 1974; Andreani et al., 2009; Eickmann et al., 2009; Bach et al., 2011; Bach et al., 2013; Schroeder et al., 2015). Homogeneous

carbonate precipitation in the subsurface can occur during conductive heating of seawater, conductive cooling of hydrothermal fluid, or mixing of seawater with hydrothermal fluid (Bonatti et al., 1974; Eickmann et al., 2009; Bach et al., 2011; Klein et al., 2015b; Schroeder et al., 2015). Mineral carbonation can take place during low temperature, oxidative alteration of peridotite at ridge flanks and passive margins, or at higher temperatures in ridge crest environments. Several studies have documented the replacement of olivine and pyroxene in these environments by Ca-bearing carbonates, including calcite, high-Mg calcite, and dolomite (Alt and Shanks, 1998; Müntener and Manatschal, 2006; Andreani et al., 2009). On the basis of experimental results, Hövelmann et al. (2011) recognized that calcite can readily replace olivine and its weathering products during alteration by CO<sub>2</sub>-saturated and Ca-rich fluids at 200 °C, whereas magnesite is favored if the reacting fluid is Ca-poor. While dolomite was supersaturated in one Ca-bearing experiment, it did not precipitate, possibly due to kinetic factors impeding the formation of Mg-bearing carbonates relative to Ca-carbonates (Hövelmann et al., 2011). Peuble et al. (2015a,b) reported the formation of both magnesite and dolomite in a set of reactive percolation experiments involving injection of CO<sub>2</sub>-rich and Ca-poor fluid into olivine aggregates at 190 °C. Formation of carbonate minerals appeared to be controlled by hydrodynamic processes, with dolomite and magnesite precipitating in regions of moderate and high fluid flow, respectively. The authors note that differences in fluid flow impact the local solution chemistry, which in turn affect carbonate precipitation. Jones et al. (2010), who conducted a laboratory serpentinization experiment at 200 °C using olivine, chromite, and evolved seawater rich in dissolved Ca and HCO<sub>3</sub>, reported calcite and siderite as the dominant carbonate minerals, whereas dolomite and magnesite did not reach saturation. To our knowledge, siderite has not been detected in oceanic serpentinite and it remains unclear what role it plays in active serpentinization systems in the seafloor. Whether magnesite, dolomite, or calcite forms in seafloor serpentinization systems appears to be ultimately controlled by the Mg/Ca ratio of the reacting fluid at the mineral scale (cf. Jones et al., 2010; Hövelmann et al., 2011; Klein and McCollom, 2013; Peuble et al., 2015a,b). However, it remains unclear what role fluid-rock reactions play in controlling the Mg/Ca ratio during interactions of CO<sub>2</sub>-bearing hydrothermal fluids and peridotite in natural systems.

The purpose of this study was to investigate reaction pathways and modes of carbonate formation during hydrothermal alteration of harzburgite in the presence of a Ca-rich fluid under strongly reducing conditions, typical of seafloor serpentinization systems. We conducted a long-term (~2.5 years) laboratory experiment, performed detailed analyses of fluid composition and mineralogy, and compared our experimental results to thermodynamic models and natural samples. The present study highlights the important roles that protolith and fluid composition play in regulating carbonate formation pathways during interactions of CO<sub>2</sub>-rich fluids and peridotite.

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