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Iron transformations during low temperature alteration of variably serpentinized rocks from the Samail ophiolite, Oman

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Abstract

Partially serpentinized peridotites in the Samail ophiolite in the Sultanate of Oman currently undergo low temperature alteration and hydration both at shallow levels, with water recently in contact with the atmosphere, and at depth, with anoxic, reducing fluids. However, it is unclear how changes in the distribution and oxidation state of Fe are driving the production of energy-rich gases such as hydrogen and methane detected in peridotite catchments. We track the Fe transformations in a suite of outcrop samples representing a subset of the spectrum of least to most altered end-members of the Oman peridotites. We use microscale mineralogical and geochemical analyses including QEMSCAN, Raman spectroscopy, synchrotron radiation X-ray fluorescence (XRF) mapping, and electron microprobe wavelength dispersive spectroscopy. The less-altered peridotites possess a diversity of Fe-bearing phases including relict primary minerals (e.g. olivine, pyroxene, chromite) and secondary phases (e.g. serpentine and brucite). Raman spectroscopy and electron microprobe data (Si/(Mg + Fe)) indicate that much of the serpentine is significantly intergrown with brucite on the sub-micron scale. These data also indicate that the Fe content of the brucite ranges from 10 to 20 wt% FeO. The mineral assemblage of the highly reacted rocks is less diverse, dominated by serpentine and carbonate while olivine and brucite are absent. Magnetite is relatively rare and mainly associated with chromite. Goethite and hematite, both Fe(III)-hydroxides, were also identified in the highly altered rocks. Whole rock chemical analyses reflect these mineralogical differences and show that Fe in the partially serpentinized samples is on average more reduced (~0.40–0.55 Fe^{3+}/Fe_{Total}) than Fe in the highly reacted rocks (~0.85–0.90 Fe^{3+}/Fe_{Total}). We propose that olivine, brucite, chromite and, perhaps, serpentine in the less-altered peridotites act as reactive phases during low temperature alteration of the Oman peridotite. The pervasive oxidation of Fe(II) in the less-altered peridotites to Fe(III) in the most-altered peridotites during water-rock reaction in the subsurface of the Samail ophiolite may produce H_2 which will influence the development of microbial energy sources and habitats, and carbon cycling and sequestration within the (ultra)mafic ocean crust.

Keywords: Serpentinization; Oman ophiolite; Low temperature; Iron; Oxidation state; Synchrotron radiation; Raman spectroscopy

1. INTRODUCTION

The Samail ophiolite in the Sultanate of Oman is an excellent system to study low temperature alteration of ultramafic rocks because it is one of the best and largest exposures of oceanic crustal and shallow mantle rocks on Earth (e.g. Boudier and Coleman, 1981). The partially serpentinized peridotites experience modern day water/rock reactions at low temperatures (23–60 °C – Neal and Stanger, 1983, 1985; Kelemen et al., 2011; Streit et al., 2012; Miller et al., 2016). The rocks interact with fluids with

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diverse chemistries that include rainwater, Mg^{2+}/HCO_3^- -rich fluids, and Ca^{2+}/OH^- -rich fluids (Barnes et al., 1978; Neal and Stanger, 1985). Moderately alkaline (pH ~ 8–9) Type I fluids (terminology from Barnes and O'Neill, 1969; Neal and Stanger, 1985), and hyperalkaline (pH ~ 10–12) Type II fluids rich in H_2 and CH_4 (Barnes et al., 1978; Neal and Stanger, 1983, 1985; Clark and Fontes, 1990; Kelemen and Matter, 2008; Kelemen et al., 2011) are produced by modern day alteration of the ultramafic peridotite.

Iron redox transformations that occur during low temperature (<150 °C) water/rock reactions are a key component of the dynamic chemistry and potential habitability of serpentinizing systems (e.g. Sleep et al., 2004; McCollom and Bach, 2009; Klein et al., 2014). The oxidation of Fe(II) in (ultra)mafic minerals to Fe(III) in secondary phases will reduce water to H_2 gas under anoxic, reducing conditions (e.g. Neal and Stanger, 1983). Hydrogen gas is essential to biologic processes (e.g. Nealson et al., 2005), is one of the most important electron donors for extant chemolithotrophs (Nisbet and Sleep, 2001), and may have been one of the earliest sources of energy on Earth (e.g. Sleep et al., 2004; Russell et al., 2010). Initial experimental and modeling studies of the speciation and partitioning of Fe into the diversity of secondary mineral phases that can form during low temperature serpentinization (<150 °C) have been conducted (Klein et al., 2009; McCollom and Bach, 2009; Mayhew et al., 2013; Bach, 2016). Yet, relatively little is known about the conditions and processes under which different secondary minerals form and accommodate Fe at low temperature. It is often assumed that during serpentinization all Fe(III) is accommodated by magnetite formation (McCollom and Bach, 2009; Cannat et al., 2010; Malvoisin et al., 2012a). Significant Fe(III) substitution into serpentine (up to 70%) has been documented in mid-ocean ridge and continental margin systems (O'Hanley and Dyar, 1993; Andreani et al., 2008; Klein et al., 2009; Evans et al., 2009; Streit et al., 2012; Klein et al., 2014), as well as experimental systems (Seyfried et al., 2007; Marcaillou et al., 2011). Yet, the significance of Fe(III) partitioning into serpentine for H_2 production has been debated (Beard and Frost, 2016). The production of Fe-rich serpentine is often accompanied by the partitioning of Fe(II) into brucite and occurs at low temperatures (150–250 °C) and water-rock ratios (Moody, 1976a,b; Sleep et al., 2004; Bach et al., 2006; Seyfried et al., 2007; Klein et al., 2009; McCollom and Bach, 2009; Klein et al., 2014; Bonnemains et al., 2016). A small degree (up to 10% Fe) of Fe(III)-partitioning into brucite has recently been reported (Beard and Frost, 2016). This differential partitioning of Fe has a significant impact on the possible extent of Fe(II) oxidation and subsequent H_2 generation during water/rock reactions.

The diversity of geochemical conditions and fluid compositions within the Samail ophiolite result in a variety of Fe oxidation pathways, making the ophiolite a natural laboratory in which to investigate the geochemical reactions that give rise to the mineral assemblages and energy-rich by-products associated with low temperature aqueous alteration of ultramafic rocks. Previous characterization of rocks of the Oman ophiolite has revealed that ~90% of Oman peridotites are harzburgites (~85% olivine, 10–15% orthopyroxene, 5% spinel, ≪1% clinopyroxene) while ~10% are dunites (>90% olivine, 5–10% spinel, ≪1% clinopyroxene) that occur in isolated lenses (Boudier and Coleman, 1981; Godard et al., 2000; Monnier et al., 2006; Hanghoj et al., 2010). All Oman peridotites collected from outcrops exhibit some degree of alteration (Kelemen et al., 2011) ranging from minimally serpentinized (~30–60%; Hanghoj et al., 2010; Boudier et al., 2010) to entirely serpentinized and carbonated (e.g. Boudier et al., 2010; Streit et al., 2012; Falk and Kelemen, 2015). Notably, abundant Fe-bearing serpentine, with an Fe(III) component, has been observed in the serpentinized peridotite (Streit et al., 2012; Miller et al., 2016) variably intermixed with Fe-bearing brucite (Miller et al., 2016). A variety of possible formation mechanisms exist to explain the observed alteration phases, which have very different implications for H_2 production. For instance, the hydration of primary olivine to serpentine and other Fe(III)-bearing phases may generate H_2, while the transformation of Fe(III)-oxides to magnetite would consume H_2.

The objective of this current work is to characterize low temperature Fe transformations and mineral alteration pathways recorded in serpentinites from the Samail ophiolite in Oman. A detailed, microscale mineralogical analysis of the less-altered Oman peridotites provides insights into the mineral assemblages and Fe chemistry of partially altered serpentinites that still possess the potential for further oxidation. Characterization of highly altered end-members of the Oman peridotites provides possible end points of alteration for comparison. Combining bulk and microscale geochemical characterization techniques and comparison of least- to most-altered rocks allows us to assess the iron mineralogy associated with low temperature serpentinization, which gives insight into possible H_2-generating and consuming reactions within the Oman ophiolite.

2. METHODS

2.1. Serpentinite samples from the Oman ophiolite

Twelve serpentinite rock samples collected from surface outcrops of the Oman ophiolite were characterized in this study. At the hand sample scale, the samples vary significantly in lithology and extent of alteration. Those that appear to be less-altered include samples OM94-61, a harzburgite collected from the Wadi Tayin massif (Hanghoj et al., 2010), (OM94-61 was not analyzed by bulk techniques because we did not have access to a bulk rock sample.); OM95-35, a dunite from the Samail massif; OM14-06 and OM14-07 dunites from Wadi Lufti; OM14-05 a harzburgite/dunite from Wadi Lufti; OM14-08 a characteristic harzburgite from Wadi Quafifa; OM14-10 a harzburgite fromWadi Dhuli. The highly altered rocks investigated here include OM08-01, OM08-206A and 206D, and OM09-129 which were previously studied by Streit et al. (2012) and OM14-11, a completely serpentinized harzburgite.