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Progress of hydration reactions in olivine–H_2O and orthopyroxenite–H_2O systems at 250 °C and vapor-saturated pressure

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ABSTRACT

We conducted hydrothermal experiments in olivine (Ol; Fo_{91})–H_2O and orthopyroxenite (Opx; composed of 95% of orthopyroxene, En_{66})–H_2O systems under conditions of 250 °C and vapor-saturated pressure (P_{sat}) to examine the temporal evolution of the solution chemistry and products in runs of up to 1008 h in duration. The maximal degree of hydration (i.e., H_2O content in the solid sample) in the Ol–H_2O experiments (3.6 wt.%) was much higher than that in the Opx–H_2O experiments (0.4 wt.%). In the Ol–H_2O experiments, Mg and Si in solution showed an initial increase (stage I) before decreasing (stage II) and finally attaining a steady state after 504 h (stage III). Following a drop in silica activity toward the level of brucite stability field, the products also changed from serpentine + magnetite (stages I and II) to serpentine + brucite + magnetite (stage III). Serpentine minerals also changed from lizardite (stages I and II) to lizardite + chrysotile (stage III). The zoning pattern of the products around olivine at 1008 h (brucite + serpentine at the olivine contact, and serpentine at the outermost rim) is consistent with the temporal changes in the mineralogy of the products, and is similar to the pattern observed in the mesh rims in partly serpentinized dunites. In the Opx–H_2O experiments, chlorite formed after orthopyroxene grains, which differs from the formation of talc and serpentine after orthopyroxene (bastite), as observed in natural hydrated harzburgites. The Opx–H_2O system maintained $10–10^3$ times higher silica activity than Ol–H_2O system, suggesting that brucite does not form after olivine during hydration of peridotites when the Ol–H_2O system is linked to the Opx–H_2O system.

The progress of hydration reactions is affected by mechanical properties of host rocks. The hydration reactions observed in this study produced hierarchical fractures in the reactants, which became filled with reaction products, similar to mesh textures after olivine in natural peridotites. This reaction-induced fracturing produced new reaction surfaces and fluid pathways that enhanced the hydration reactions. The overall reaction producing serpentine + brucite in the Ol–H_2O experiments showed the large volume expansion ($V/V_0 = 1.43$ at stage III), whereas that producing only serpentine proceeded with near constant volume ($V/V_0 = 1.19$ at stage I). The volume expansion is more difficult to occur in the oceanic lithosphere than in our experiments during serpentinization. Thus, in the case that volume expansion is prevented at reaction sites, one of the following outcomes occurs: (1) the hydration reaction stops until new fractures form, or (2) the reaction proceeds with low volume expansion (absence of brucite) by removing Mg from the system. These two outcomes would produce contrasting distributions or extent of hydration in oceanic lithosphere.

1. Introduction

Fluids play a crucial role in global-scale mass transfer, metamorphism, volcanism, and seismic processes in subduction zones (e.g., Hacker et al., 2003; Iwamori, 1998). Serpentine minerals, which are produced by interaction between ultramafic rocks and fluids, contain about 13% water and are the greatest carrier of H_2O into the deep interior of Earth. Therefore, the volume and distribution of hydrated oceanic mantle are of special interest in evaluating the effects of fluids on subduction zone processes.

Mesh and hourglass textures are commonly developed in partly and completely serpentinized ultramafic rocks (e.g., Bach et al., 2004, 2006; Iyer et al., 2008; Katayama et al., 2010; Klein et al., 2009; O'Hanley, 1996; Wicks and Whittaker, 1977). Mesh texture after olivine is commonly characterized by the assemblage serpentine ± brucite ± magnetite. A model reaction of serpentinization in the $MgO–SiO_2–H_2O$ system is as follows:

$$\underset{\text{olivine}}{2Mg_2SiO_4} + \underset{\text{water}}{3H_2O} = \underset{\text{serpentine}}{Mg_3Si_2O_5(OH)_4} + \underset{\text{brucite}}{Mg(OH)_2}. \quad (1)$$

This reaction indicates the production of the same number of moles of serpentine and brucite, and the preservation of all elements in the rocks except for H_2O. Magnetite forms due to the oxidation of

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the fayalite component in olivine. In contrast to reaction 1, the modal abundance and distribution of brucite are variable even in dunite (Wicks and Whittaker, 1977). This suggests that serpentinization after olivine does not always proceed via reaction 1 when element transfer occurs during serpentinization.

Interactions between ultramafic rocks and fluids have been extensively investigated based on hydrothermal experiments (e.g., Allen and Seyfried, 2003; Janecky and Seyfried, 1986; Martin and Fyfe, 1970; Normand et al., 2002; Seyfried and Dibble, 1980; Seyfried et al., 2007; Wegner and Ernst, 1983; Yada and Ishii, 1974). Martin and Fyfe (1970) and Wegner and Ernst (1983) conducted batch experiments in the Ol–H_2O system with low ratios of water to rock mass (0.2–0.3). Based on the loss of ignition in solid samples, the authors showed that the hydration reactions proceeded significantly within several weeks (conversion rate of several tens of percent), with a maximum conversion at 250–300 °C. Martin and Fyfe (1970) also reported that hydration in the Opx–H_2O system occurs at a higher rate with increasing temperature. However, details of the reaction stoichiometry in both systems were not constrained because of a lack of data on solution chemistry.

The time evolution of solution chemistry during interaction between seawater and ultramafic rocks has been investigated in batch experiments with periodic fluid sampling (Allen and Seyfried 2003; Janecky and Seyfried, 1986; Seyfried and Dibble, 1980; Seyfried et al. 2007), revealing that the change in solution chemistry is dependent on the system of interest. Reactions in a system comprising seawater and natural peridotite (lherzolite, hurzburgite, and dunite) involve many ionic species and minerals; consequently, the reactions are complex. In addition, these previous studies provided no information on the amount and mineralogy of solid products during intermediate stages of the experiments.

In the present study, we examined the hydration reactions in the olivine (Ol)–H_2O and orthopyroxenite (Opx)–H_2O systems by performing hydrothermal experiments under conditions of 250 °C and vapor-saturated pressure ($P_{sat} = 3.98$ MPa). At this temperature, a high degree of hydration is expected in both systems after a reasonable duration of the experiment (Martin and Fyfe, 1970). Vapor-saturated pressure was selected for simplicity, given the nature of the experimental apparatus. Although P_{sat} is lower than the pressures at sites of hydrothermal alteration on the seafloor, the phase relations at P_{sat} do not differ significantly from those at 50 MPa, as employed in previous experiments (e.g., Allen and Seyfried, 2003; Seyfried and Dibble, 1980). Based on the occurrences and amounts of hydrous products, and on solution chemistry, we examine how the hydration reactions and reaction textures evolved with time, and discuss the implications of the results for hydration processes in oceanic lithosphere.

2. Experiments and analyses

Natural olivine sand and orthopyroxenite were crushed and sieved to obtain the <125 μm fraction. The forsterite (Fo) component in olivine was 0.91 (Table 1). The orthopyroxenite consisted of 95 vol.% orthopyroxene (enstatite (En) component = 0.66) with minor plagioclase, ilmenite, and hornblende. The orthopyroxene used in this study was richer in Fe^{2+} than is the case for typical mantle peridotites (En component > 0.8). We mixed 3.45 g of olivine or orthopyroxenite powder with 3.45 g of distilled water in the stainless steel (SUS 316) reaction vessel (capacity of 8.8 cm^3). The water/rock mass ratio was 1.0. The water filling ratio was 0.45 at room temperature, corresponding to a ratio of 0.55 under in situ conditions (250 °C and P_{sat}). The maximum run time was 1008 h. H_2O in the vessel was consumed by the hydration reactions; however, the pressure inside the vessel was maintain at P_{sat} and all the mineral samples were always located in the liquid H_2O, because of the relatively high water/rock ratio.

After the individual runs, the reaction vessel was cooled to room temperature within 1 h, and the solution was removed from the vessel. The solid samples (products + unreacted olivine/orthopyroxenite) were dried at 70 °C for 2 days. The surface morphology of the products was observed by scanning electron microscope (SEM). Serpentine minerals were identified using a Raman spectrometer (HoloLab 5000; Kaiser Optical Systems) equipped with an Olympus BX51 microscope, housed at Tohoku University, Japan. The size of the laser spot on the sample surface was about 2.0 μm. For several samples, thin sections of the products were prepared for detailed textural observations and chemical analyses by electron probe microanalyzer (EPMA; Jeol 8200) at the University of Tokyo, Japan.

Table 1
Representative chemical compositions of the reactant and product minerals.

	O1–H_2O				Opx–H_2O	
	Ol	Srp	Brc	Mt	Opx	Chl
SiO_2	39.8	36.9	1.0	4.8	51.9	38.5
TiO_2	0.0	0.0	0.0	0.2	0.1	0.2
Al_2O_3	0.0	0.4	0.1	0.0	2.0	8.1
Cr_2O_3	0.0	0.0	0.0	0.0	0.0	0.0
FeO	9.0	1.5	6.4	86.9	21.5	20.9
MgO	50.3	36.8	72.3	2.0	23.3	14.6
MnO	0.1	0.0	0.5	0.4	0.4	0.2
CaO	0.3	0.4	0.3	0.5	0.3	2.2
Na_2O	0.0	0.0	0.0	0.0	0.0	0.0
K_2O	0.0	0.0	0.0	0.0	0.0	0.2
Total	99.7	76.1	80.6	94.9	99.6	84.9
X_{Mg}[a]	0.91	0.98	0.95		0.66	0.56

[a] $X_{Mg} = Mg/(Mg + Fe)$.

About half of the solid sample in each experiment was ground to a powder for analyses by X-ray powder diffraction and thermogravimetry. X-ray powder diffraction analysis was performed by XRD diffractometry (Rigaku RINT-220VL), using Cu–Kα radiation. Samples were scanned with 2θ step sizes of 0.02°. The water content in the solid samples was measured by thermogravimetry (TG; Rigaku Thermo Plus DSC8120) as the weight loss measured when increasing the temperature from room temperature to 1000 °C at a rate of 20 °C/min.

In all experiments, the amount of solution taken from the vessel was 1.0–1.5 ml. We used 0.1 ml of the solution for the measurement of cations; the remainder was used for measurements of pH. Gaseous species and anions were not analyzed. The concentrations of Si, Mg, Ca, Fe, Al, Cr and Ni were measured by inductively coupled plasma-mass spectrometry (ICP-MS; Perkin Elmar Tech, Elan DRC) at Tohoku University. The solution pH was measured at room temperature (~25 °C). In situ pH values (250 °C) and aqueous speciation were computed using the program SOLVEQ (Reed, 1981; Reed and Spycher, 1983) and using thermodynamic data from Holland and Powell (1998) for minerals and from the SUPCRT92 database (Johnson et al., 1992; Shock and Helgeson, 1988; Shock et al., 1989, 1997) for inorganic aqueous species. Because we did not analyze anions, three possible cases were considered for in situ pH calculations, in which the charge was balanced by HCO_3^-, HS^-, or SO_4^{2-}. The distilled water is likely to have contained HCO_3^-. In addition, sulfur species (HS^- or SO_4^{2-}) may have been present because a small amount of sulfur was included in the stainless steel vessel used in the experiments. Although it is known that serpentinization with the formation of magnetite results in reducing conditions in fluids (e.g., Klein and Bach, 2009), we cannot exclude the possibility that SO_4^{2-} was present as a sulfur species that leached from the vessel, because the initial distilled water would have been a relatively oxidizing medium.

3. Results

3.1. Characterization of products

3.1.1. Olivine–H_2O system

Eleven experiments with different run times were carried out in the Ol–H_2O system (Table 2). The XRD analyses and SEM observations