Water diffusion-transport in a synthetic dunite: Consequences for oceanic peridotite serpentinization

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ABSTRACT

A series of San Carlos olivine aggregates, sintered at high pressure and high temperature, with two different porosities (around 1 and 10%) and grain sizes (1–5 μm and 0–38 μm) were reacted at 300 °C and 500 bars in the presence of pure water. The reaction progress was monitored magnetically and the composition and distribution of the reaction products were analyzed at the end of each experiment. Brucite formation mainly occurred at the aggregate surface as a result of both congruent olivine dissolution and aqueous Mg and Si buffering by the reaction products, i.e. brucite and lizardite. The measured reaction progress did not exceed 2.6% after 290 d, which strongly contrasts with previous studies performed on San Carlos olivine powders (i.e., isolated grains in aqueous solution). Hence, limited water transport through the intergranular region of the aggregate drastically decreased the olivine surface area accessible to water and thus slowed down the whole serpentinization process. When extrapolated to peridotite relevant olivine grain sizes, our experimental results indicate that the water diffusion rate will become so slow that the first layer of primary minerals exposed to water within a mesh structure must fully react before the next mineral layer starts reacting ("layer by layer" mechanism). This type of reaction-transport mechanism is obviously not consistent with the micro-scale serpentine distribution in the mesh of oceanic peridotite samples, therefore additional water transport pathways are required. Cracks formed under extensional thermal stresses are good candidates since, in comparison to grain boundary or reaction-induced fractures, they are wide enough to drastically enhance water transport in oceanic peridotites and therefore account for the observed textures. The 'layer by layer' mechanism inferred here can only set a lower time bound for serpentinization completion. Assuming a mesh size of 1 mm and an initial grain size of 100 μm and considering a temperature ranging from 100 to 300 °C with permanent water saturation, completion should take place within 100–1000 yr. Surprisingly, this duration represents only 1 to 10% of the estimated timescale of the natural serpentinization process, emphasizing the central role played by water availability in the natural reaction process.

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1. Introduction

Hydrothermal circulation through upper-mantle rocks exhumed at slow-spreading ridges leads to the formation of serpentine minerals, $(Mg, Fe)_3Si_2O_5(OH)_4$ as the result of olivine and pyroxene hydration. The "serpentinization" reactions typically occur at temperatures below 450 °C and can produce, besides serpentine group minerals, variable amounts of magnetite, Fe_3O_4, brucite, $(Mg, Fe)(OH)_2$, and talc, $(Mg, Fe)_3Si_4O_{10}(OH)_2$.

The kinetics of the serpentinization process is expected to constrain a range of chemical and physical properties of the oceanic lithosphere: heat structure (Allen and Seyfried, 2004; Delescluse and Chamot-Rooke, 2008), hydrothermal circulation (Emmanuel and Berkowitz, 2006), hydrogen fluxes in slow-spreading centres (Charlou et al., 2002), deformation (Escartin et al., 1997) and magnetic signal build-up (Tivey and Dyment, 2010; Maffione et al., 2014).

For the sake of understanding its kinetics, serpentinization must be seen as a reaction-transport process which can be artificially decomposed into a sequence of steps: water is transported up to the peridotite minerals, typically olivine, $(Mg, Fe)_2SiO_4$, and orthopyroxene, $(Mg, Fe)_2Si_2O_6$ (step 1), which are then dissolved (step 2) and the produced aqueous species are transported (step 3)

Table 1
Experimental conditions and results.

Run	IGS (µm)	Duration (h)	S (%)	Porosity (%)	# Mg serp	# Mg bru	Polymorph	T_{RZ} (µm)	T_{RF} (µm)	NS
S1	0–38	1652	1.64	9 ± 2	0.96 ± 0.02	n.d.	Lizardite	44.6 ± 8.3	51.3 ± 15.3	121
S2	0–38	3434	1.32	0.7 ± 0.1	0.98 ± 0.01	0.95 ± 0.01	Lizardite	61.7 ± 11.6	41.0 ± 9.9	122
S3-1	1–5	1748	0.61	0.5 ± 0.1	0.98 ± 0.01	0.96 ± 0.01	Lizardite	20.8 ± 6.1	13.0 ± 5.3	125
S3-2	1–5	4104	1.12	0.5 ± 0.2	0.98 ± 0.01	0.96 ± 0.01	Lizardite	38.4 ± 9.1	16.5 ± 7.8	119
S3-3	1–5	6956	2.66	0.5 ± 0.3	0.99 ± 0.01	0.97 ± 0.01	Lizardite	48.8 ± 10.9	15.2 ± 6.2	88

Abbreviations are as follows: IGS, initial grain size; S, reaction progress; # Mg serp, Mg/(Mg + Fe) in serpentine; # Mg bru, Mg/(Mg + Fe) in brucite, Polymorph, serpentine polymorph; T_{RZ}, thickness of the reaction zone; T_{RF}, thickness of the reaction front; NS, number of sections across the sintered rim used for calculating the different parameters n.d.: not determined.

up to the locus of the reaction products precipitation (step 4). Each of these steps can potentially be rate limiting regarding the overall serpentinization process.

Serpentinization reactions have been widely studied experimentally in order to evaluate the respective role of temperature, pressure, grain size and starting composition on the chemistry and mineralogy of the reaction products and on their kinetics of formation (e.g., Martin and Fyfe, 1970; Moody, 1976; Wegner and Ernst, 1983; Seyfried et al., 2007; Marcaillou et al., 2011; Malvoisin et al., 2012b). In order to achieve significant extends of reaction at the laboratory timescale, these studies were quite exclusively performed using rock or mineral powders as starting material and, consequently, stages (1) and (3) were not investigated.

Extrapolation of serpentinization kinetic data derived from powder experiments predicts that grains of ~100 µm, i.e., the typical grain size in peridotites, should react completely within tens of years. Consequently, serpentinization would represent an instantaneous process at the geological timescale (Malvoisin et al., 2012b). This inference is, however, not consistent with serpentinization reaction progresses estimated for abyssal peridotites, which are generally comprised between 40 and 100% (Oufi et al., 2002).

Consequently, water availability and/or species transport, i.e. step (1) and/or (3), are the likely rate limiting steps of the natural process and, the relevance of experimental studies performed on powders must therefore be questioned. Water involved in large scale hydrothermal circulation is mainly expected to flow (advection). Advection is an efficient process in oceanic lithosphere hydration as shown by the development of an hydrothermal circulation (Douville et al., 2002) which can only be reproduced numerically by using high peridotite permeability (10^{-14} to 10^{-13} m^2 Emmanuel and Berkowitz, 2006). Obviously, the high permeability of serpentinized peridotite is a consequence of rock fracturing which results from the combination (Rouméjon and Cannat, 2014) of deformation at mid-ocean ridges (McCaig et al., 2007; Hirose and Hayman, 2008), thermal cracking (Boudier et al., 2005; Demartin et al., 2013) and reaction-induced fracturing (Iyer et al., 2008; Jamtveit et al., 2008; Kelemen and Hirth, 2012; Plümper et al., 2012). However, the way serpentinization kinetics can be enhanced by fracturing remains controversial since volume increase associated to rock hydration should lead to pore clogging which will in turn decrease the rock permeability. The simulation of water advection in serpentinized peridotites is a complicated task since it will depend, in particular, on the geometry and the permeability of the fracture network. Numerical simulation (e.g., Emmanuel and Berkowitz, 2006; Iyer et al., 2012) is certainly the most appropriate mean to account for such complexity. At a smaller scale, microtextures of the serpentine veins in serpentinized peridotites suggest that advection occurs in the mesh network (cm scale and beyond) whereas hydration of the mesh cells (mm scale and below) is rather expected to operate through diffusion along mineral boundaries and microcracks, eventually through gel-like protoserpentine in the early serpentinization stages (Andreani et al., 2007; Boudier et al., 2010). In

order to assess the respective part of reactivity and water diffusion (transport) on the kinetics of the serpentinization process, we followed an experimental approach; a synthetic dunite aggregates (sintered San-Carlos olivine) was reacted with pure water at 300 °C and 500 bars for various run durations. Reaction rates were compared to data collected with the same method, i.e., magnetic monitoring and analysis of scanning electron microscopy (SEM) images, under identical P–T conditions, on the same olivine material run as separate grains (powders) by Malvoisin et al. (2012b). Mass transfer of water/aqueous species during the serpentinization process was inferred from mineral phase distribution at the micrometer scale using again field emission-SEM data (FE-SEM data). The present set-up which involves as boundary condition the sample free surface in contact with water will prevent building up of significant deviatoric stress at the reaction interface. Processes such as reaction-induced fracturing which promote rock permeability will consequently not operate here.

2. Methods

Gem-quality San Carlos olivine (Fo$_{91}$) was finely crushed in an agate mortar and then calibrated at two initial grain sizes (IGS = 0–38 µm and 1–5 µm) with sieving and Stokes separation, respectively. Around 60 mg of calibrated powder were placed in a 3.5 mm diameter graphite sleeve and sintered in a piston–cylinder apparatus (see Brunet et al., 2003 for experimental set-up) at 1.5 GPa and 800 °C during 2 to 5 h to produce two cylinder aggregates of low porosity (ϕ), S1 and S3, with $\phi = 0.6 \pm 0.2\%$ (Table 1). An additional aggregate, S2, of higher porosity ($\phi = 9 \pm 2\%$) was prepared with the 0–38 µm powder in the same conditions but with a heating period limited to 10 min. Even if much of the deformation was accommodated by the protective graphite sleeve, decompression in the piston–cylinder apparatus at the end of the run led to disking of the sintered aggregate into 5 to 6 slices with a thickness between 1 and 2 mm. However, fracturing perpendicular to the slices was not observed. For each run, one of the slices was embedded in epoxy and polished parallel to its basal surface. Back-scattered electron images (BSE images) with a resolution of 0.28×0.28 µm^2 on a 1×1 mm area were acquired on the corresponding polished sections using the FE-SEM (Zeiss Sigma^{TM}, ENS, Paris). The surface area of both pores and olivine grains was computed by image analysis in order to retrieve a porosity estimate (Table 1). The remaining 4 to 5 slices were either loaded together (S1 and S2) or loaded separately as three different samples (S3) in Au-capsules (Malvoisin et al., 2013; 2 cm in length, 4.8 mm outer diameter and 4.4 mm inner diameter) together with deionized water (resistivity of 18 MΩ.cm) in a water to rock ratio of 2 for S1 and S2 and 4.5 for S3. Once welded shut, the capsules were placed in horizontal cold seal pressure vessels at a temperature of 300 °C ± 5 °C monitored with a Ni–NiCr thermocouple and regulated to within 1 °C (Brunet and Chopin, 1995). A pressure of 500 ± 50 bars was achieved by pumping argon into the vessel. Saturation remanent magnetization was also monitored *in-situ* with a cryogenic magnetometer (2G) available at ENS (Paris)