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# Growth kinetics of $MgSiO_3$ perovskite reaction rim between stishovite and periclase up to 50 GPa and its implication for grain boundary diffusivity in the lower mantle

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ABSTRACT

The growth rate of $MgSiO_3$ perovskite reaction rims between periclase and stishovite was investigated at 24–50 GPa and 1650–2150 K using a Kawai-type high-pressure apparatus. The textural observations of the recovered samples and rim growth kinetic data revealed that the reaction is controlled by coupled grain boundary diffusion of MgO and grain coarsening in the perovskite reaction layer. Assuming a high diffusivity of O compared with Mg, the grain boundary diffusivity of Mg in the perovskite was determined to be $\delta D_{gb}^{Mg}$ $[\mathrm{m}^3/\mathrm{s}] = 10^{-15.1} \exp\{-[176{,}000 + (P - 24) \times 3.8 \times 10^3]/RT\}$, which is ∼3–5 orders of magnitude faster than that of Si. We found that the bulk diffusivity of Mg in polycrystalline perovskite is affected by the grain boundary when we consider the possible grain sizes and temperatures in the lower mantle. Accordingly, grain boundary diffusion in perovskite may be an effective mechanism for chemical transportation of divalent cations in the lower mantle.

## 1. Introduction

Diffusion rates of elements in minerals provide important constraints for understanding many physical and chemical processes in the Earth's interior, including mantle rheology and chemical transportation (e.g., Holzapfel et al., 2005; Karato and Li, 1992; Poirier, 2000; van Keken et al., 2002; Van Orman et al., 2003; Yamazaki and Karato, 2001). Therefore, diffusion coefficients of mantle minerals have often been studied under high-pressure and high-temperature conditions. These studies have revealed that grain boundary diffusion of mantle silicate is generally several orders of magnitude faster than lattice diffusion (e.g., Farver and Yund, 1995; Shimojuku et al., 2009; Yamazaki et al., 2000). It has also been recognized that Si is the slowest diffusing species in most silicate minerals (Chakraborty, 2010), and therefore the diffusion of silicon likely controls the mantle rheology in the diffusion creep regime.

$MgSiO_3$ perovskite is the most abundant mineral in the lower mantle (Irifune et al., 2010; Stixrude et al., 1992). The rheology in the lower mantle has been discussed on the basis of the Si diffusion coefficient in perovskite assuming that Si is the rate-controlling element (Yamazaki and Karato, 2001). However, recent experimental studies have indicated that Mg lattice diffusion in perovskite is also extremely slow and has very similar diffusivity to Si (Holzapfel et al., 2005; Xu et al., 2011). Accordingly, a coupled motion of Si and Mg may control the actual rheology of perovskite (Xu et al., 2011) different from the other mantle minerals such as olivine, wadsleyite, and ringwoodite (e.g., Dohmen et al., 2002; Shimojuku et al., 2009). Although the characteristic lattice diffusivity of Mg in perovskite has been found, little is known about the rate of its grain boundary diffusion. Furthermore, there is no experimental data on the pressure dependence of diffusivity in perovskite.

Diffusion may control chemical transportation in the lower mantle, including mantle homogenization from the subducting oceanic crust and the chemical interaction between the core and mantle. Previous experimental studies showed that the diffusion rate of elements in ferropericlase is very high compared to that in perovskite (Holzapfel et al., 2003; Yamazaki and Irifune, 2003). In particular, the grain boundary in ferropericlase may be the dominant transport pathway for chemical transportation (Hayden and Watson, 2007; Van Orman et al., 2003). However, grain boundary diffusivity of elements in the predominant phase of perovskite may be more important for understanding chemical transportation in the lower mantle since ferropericlase should be isolated in perovskite matrix in the lower mantle (Yoshino et al., 2008).

Growth kinetics of reaction rims between minerals is often controlled by diffusion of elements. In many cases, grain boundary

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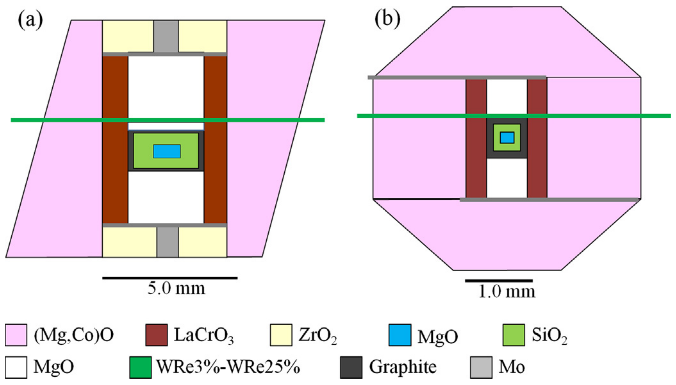

**Fig. 1.** Cross-section of the sample assemblages used for the experiments at (a) 24 GPa and (b) 32–50 GPa.

diffusion was considered to control rim growth in previous experimental studies because it is several orders of magnitude faster than lattice diffusion. Therefore, the grain boundary diffusion coefficient of elements in some polycrystalline minerals has been estimated from rim growth kinetics (e.g., Fisler et al., 1997; Gardés and Heinrich, 2011; Milke et al., 2007; Yund, 1997). In this study, we examined the growth kinetics of the polycrystalline perovskite rim between periclase and stishovite in the MgO–SiO$_2$ system under lower mantle conditions up to 50 GPa. Based on the experimental results, the grain boundary diffusivity of Mg in MgSiO$_3$ perovskite and the chemical transportation in the mantle are discussed.

## 2. Experimental procedures

We performed high-pressure and high-temperature experiments using a Kawai-type high-pressure apparatus (Orange 3000 and MADONNA II) installed at Ehime University, Japan. WC cubes with 32 mm edge length (EL) and 5 mm truncated edge length (TEL) were used as the second stage anvils for the experiments at 24 GPa, while sintered diamond cubes with 14 mm EL and 1.5 mm TEL were used for the experiments at 32–50 GPa with a similar setup to Stagno et al. (2011). Single crystals of periclase with sizes of $\sim 1.0 \times 1.0 \times 0.5$ mm$^3$ and $\sim 0.25 \times 0.25 \times 0.20$ mm$^3$ and a fine powder of quartz were used as the starting materials for the reaction experiments. The largest faces of periclase single crystals were oriented along the [100] direction. In order to determine the mobile component controlling the overall reaction progress, a small amount of Pt paste was placed onto the flat surface of the periclase. The periclase and Pt paste were dried at 1273 K for 3 h in order to remove any volatiles. Details of the sample assembly are shown in Fig. 1. The sample assembly was composed of sintered (Mg,Co)O and ZrO$_2$ pressure mediums, a cylindrical LaCrO$_3$ heater, a molybdenum electrode, and a graphite sample capsule. Temperature was monitored with W3%Re–W25%Re thermocouples located in the LaCrO$_3$ heater without correction for the pressure effect on the thermocouple emf. The starting materials, the pressure mediums and the heater were dried at 1273 K for 3 h before assembling. All parts of the sample assembly were then stored at 393 K in a vacuum oven before the experiments.

Samples were compressed at room temperature, and then heated to the desired temperature at high pressure. Then, temperatures were maintained for 15–1500 min, after which the temperature was decreased. The heating and cooling rate was controlled to be ~100 K/min in all experiments. After the experiments, recovered samples were cut perpendicular to the sample interface. Then, the surface of the cross-section was polished using one micrometer diamond powder. Thicknesses of reaction layers ($\Delta x$) and corresponding grain widths ($a$) were observed by a Field-Emission Scanning Electron Microprobe (FE-SEM) (JEOL JSM-7000F) equipped with an Energy Dispersive Spectrometer (EDS) and a transmission electron microscope (TEM) (JEOL JEM-2010) at Ehime University. Raman spectroscopy revealed that the reaction rim consisted of perovskite.

The water concentrations of some of the recovered samples after the reaction experiments performed at 24 GPa were measured by Fourier-transform infrared spectroscopy (FTIR) using a Mercury Cadmium Telluride (MCT) detector. The samples were polished to disks with a thickness of ~250 µm. After polishing, the disks were washed with acetone and dried at 393 K in a vacuum oven for more than 10 h. The aperture size was 20 × 20 µm. Because the thickness of the MgSiO$_3$ perovskite reaction rims were too thin for reliable FTIR measurement, only the water contents of the periclase contacting perovskite layers were estimated on the basis of the method of Libowitzky and Rossman (1997). The infrared spectra were taken from 3–10 points in each sample. Background corrections of the absorbance spectra were carried out by subtracting the linear baseline of the OH stretching vibration region.

## 3. Results and discussion

### 3.1. *Microstructural observations and the rate-controlling component*

We carried out reaction experiments at 24–50 GPa and 1650–2150 K, where MgSiO$_3$ perovskite is the stable high-pressure phase in the SiO$_2$–MgO system. The experimental conditions, the thicknesses of the MgSiO$_3$ perovskite layers ($\Delta x$), and the corresponding grain widths ($a$) are summarized in Table 1. The grain widths were measured in the direction parallel to the interfaces of the perovskite layers. Back-scattered electron (BSE) images of recovered samples in the reaction experiments are shown in Fig. 2(a–d). Precise measurement of the grain widths $a$ was difficult because of the presence of many fractures in the perovskite layers. TEM observations (Fig. 2(e)) show that the grain boundaries basically run normal to the interfaces of the reactant. Also, the angles of the triple junctions between reactants and perovskite grain boundaries were balanced by the surface tension (Fig. 2(f)). The grain widths in the present experiment were carefully measured according to the characteristics of the grain boundary ignoring the other fractures (e.g., black arrows in Fig. 2(e) and (f)).

The perovskite reaction rim was observed between stishovite and periclase due to the following reaction:

$$\mathrm{MgO(periclase)} + \mathrm{SiO_2(stishovite)} = \mathrm{MgSiO_3(perovskite)}. \qquad (1)$$

SiO$_2$ quartz transforms to stishovite before the formation of perovskite because of the rapid transformation kinetics of the low-pressure SiO$_2$ phase (Zhang et al., 1996). Both the thickness of the reaction layers and the corresponding grain widths are almost constant across all rims in a single run.

The position of Pt-markers traces the interface between reactants and provides information on the direction of mass transport in the reaction rim during the reaction process. The Pt-markers were always observed at the perovskite–periclase interface in the run products (Fig. 2). In this case, mass balance indicates that MgO is the mobile component that diffuses through the rim and then the component reacts with stishovite at the opposite interface to produce perovskite. Thus, perovskite rims preferentially grew at the stishovite–perovskite interface by the following reaction:

$$\mathrm{SiO_2(stishovite)} + \mathrm{MgO(mobile)} = \mathrm{MgSiO_3(perovskite)} \qquad (2)$$

where MgO (mobile) is the MgO component released from periclase through the perovskite layer (Fig. 3). Both Mg and O ions are forced to diffuse at the same rate because opposite electric charges require coupling of both ions during diffusive transport. Therefore,