Silicon self-diffusion in wadsleyite: Implications for rheology of the mantle transition zone and subducting plates

Akira Shimojuku,[1] Tomoaki Kubo,[1,2] Eiji Ohtani,[1] and Hisayoshi Yurimoto[3]

[1] Si self-diffusion rates in Mg_2SiO_4 polycrystalline wadsleyite were measured at 18 GPa and 1430–1630°C using an isotopic tracer (^{29}Si) and secondary ion mass spectrometry. The volume diffusion coefficient (D_v) and grain-boundary diffusion coefficient (D_{gb}) were determined to be $D_v = 3.44 \times 10^{-11}$ [m²/s] exp (-299 [kJ/mol]/RT) and $\delta D_{gb} = 1.14 \times 10^{-17}$ [m³/s] exp (-248 [kJ/mol]/RT), respectively. Si diffusion rates in wadsleyite are about 5 orders of magnitude slower than Mg-Fe interdiffusion rates at 1400°C. Assuming that Si is the slowest diffusing species in wadsleyite, the geophysical model of the viscosity in the mantle transition zone can be explained by diffusion creep in wadsleyite for a grain size of about 0.5–5 mm. Some portions in cold subducting slabs, where the grain size reduces to less than 1 μm after the olivine-spinel transformation, become weaker than the surrounding mantle. *INDEX TERMS:* 3902 Mineral Physics: Creep and deformation; 3904 Mineral Physics: Defects; 3924 Mineral Physics: High-pressure behavior; 5120 Physical Properties of Rocks: Plasticity, diffusion, and creep; 8162 Tectonophysics: Rheology—mantle. **Citation:** Shimojuku, A., T. Kubo, E. Ohtani, and H. Yurimoto (2004), Silicon self-diffusion in wadsleyite: Implications for rheology of the mantle transition zone and subducting plates, *Geophys. Res. Lett.*, *31*, L13606, doi:10.1029/2004GL020002.

1. Introduction

[2] Mantle convection is accomplished by plastic deformation of its constituent minerals. This plastic deformation occurs through transport of the diffusing atoms (diffusion creep) or motion of dislocations (dislocation creep). To understand the rheological properties of Earth's mantle, it is crucial to determine the diffusion rate of the slowest diffusing species which may control the plastic deformation in silicate minerals undergoing diffusion creep or dislocation climb.

[3] There are numerous studies on diffusivity in olivine, which have shown that Si is the slowest diffusing species [e.g., *Houlier et al.*, 1988, 1990; *Dohmen et al.*, 2002]. However diffusion studies in wadsleyite, a high-pressure polymorph of olivine and one of the major constituent minerals in the mantle transition zone, have been limited to Mg-Fe interdiffusion [*Farber et al.*, 1994, 2000; *Chakraborty et al.*, 1999; *Kubo et al.*, 2004]. In this study,

we report experimental results on Si self–diffusion rates in Mg_2SiO_4 wadsleyite at 18 GPa and 1430–1630°C. Based on these results, the rheology of the mantle transition zone and subducting plates are discussed.

2. Experimental Procedure

[4] High-pressure experiments were performed using a Kawai-type multi-anvil apparatus installed at Tohoku University [*Ohtani et al.*, 1998]. The sample assembly is composed of sintered ZrO_2 pressure medium, Ta electrode and $LaCrO_3$ heater. Temperature was monitored with a W3%Re–W25%Re thermocouple located in the furnace. Uncertainties in pressure and temperature are estimated to be ±0.5 GPa and ±30°C, respectively. The starting material of polycrystalline wadsleyite with a composition of Mg_2SiO_4 was synthesized in 2–3 hours at 18 GPa and 1730°C from powdered forsterite. The forsterite was dried at 130°C for several hours prior to the synthesis experiments. Raman spectroscopy revealed that only wadsleyite is present in the synthesized sample. The polycrystalline wadsleyite was cut into cubes about 500 μm in sizes. Samples with a homogenous grain size and no visible cracks in the cubes were used in diffusion experiments. The surface of the polycrystalline wadsleyite was polished with diamond paste (0.25 μm in diameter) and cleaned using an ultrasonic cleaner with acetone. The polished surface was then coated with a ^{29}Si enriched thin film of about 30 nm in thickness by high-vacuum thermal evaporation of $^{29}SiO_2$ enriched powder ($^{29}Si/^{28+29+30}Si = 99.20$ atomic %). The thickness of the evaporated thin film was evaluated by measuring depth profiling for sample before annealing and was also determined using transmission electron microscopy.

[5] Diffusion annealing experiments were conducted at 18 GPa and 1430–1630°C at conditions where Mg_2SiO_4 wadsleyite coexists with SiO_2 stishovite. Wadsleyite coated with ^{29}Si enriched thin film was enclosed by NaCl powder in the graphite capsule. The coated surface was surrounded with Au foil to avoid reacting with NaCl. The sample was pressurized at room temperature and heated to the desired temperature with a controlled heating rate of 10°C/s above 400°C.

[6] Concentration profiles of ^{29}Si were measured by the depth profiling method using secondary ion mass spectrometry (SIMS, Cameca IMS-3F) at the Tokyo Institute of Technology [*Yurimoto et al.*, 1989]. The primary ion beam was mass filtered $^{16}O^-$ accelerated to 10 kV with a beam current of 18–29 nA and a beam spot size 25 μm in diameter with 100 μm rastering. Secondary ions from the central 10 μm of the sputtered crater (150 μm square) were collected. Counts of secondary ions ^{26}Mg, ^{28}Si, ^{29}Si and ^{30}Si were obtained as a function of time. Counts as a

[1]Institute of Mineralogy, Petrology and Economic Geology, Faculty of Science, Tohoku University, Sendai, Japan.
[2]Now at Department of Earth and Planetary Sciences, Faculty of Sciences, Kyushu University, Fukuoka, Japan.
[3]Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Tokyo, Japan.

function of depth were estimated based on the relation between the depth of the crater and the sputtering time. The concentration profile was obtained at one point in each sample from runs SID07 and SID110, and at two points in the sample from run SID05.

[7] Water contents in polycrystalline wadsleyite before and after the diffusion annealing were estimated using fourier transformed infrared spectroscopy (FTIR). FTIR measurements were carried out in air. The concentrations of hydroxyl groups were determined by integrating the absorption bands using the calibration by *Paterson* [1982].

3. Results

[8] Experimental conditions and results on diffusion experiments are summarized in Table 1. The average grain size of polycrystalline wadsleyite in the cubes before and after the diffusion experiments for all runs was measured to be 12 (±6) and 10 (±6) μm, respectively, which indicated that significant grain growth did not occur during the diffusion annealing. This is reasonable because the cubes had been synthesized at higher temperature than those of diffusion annealing. Water content in the starting material of polycrystalline wadsleyite was estimated to be 353–507 weight ppm H_2O and the water contents decreased to 14–143 weight ppm H_2O after the diffusion annealing. We confirmed all recovered samples have no visible cracks after the diffusion experiments.

[9] One of the depth profiles in the sample annealed at 18 GPa and 1430°C for 50 hours (Run SID05) is shown in Figure 1. We always measured the diffusion profiles in areas including a grain boundary. Two segments were recognized in the diffusion profiles, indicating that the diffusion occurred within a type B kinetic regime described by *Harrison* [1961]. In the region near the sample surface, volume diffusion is the dominant diffusion mechanism, whereas in the deeper region, grain-boundary diffusion is dominant.

[10] The volume diffusion coefficient was determined using the solution of thin film diffusion model [*Crank*, 1975]:

$$c(y) - c_0 = M/(\pi D_v t)^{1/2} \exp\left(-y^2/(4D_v t)\right) \quad (1)$$

where $c(y)$ is the concentration of ^{29}Si at depth y, c_0 is the initial concentration of ^{29}Si, M is the total number of diffusion sources, t is time of diffusion annealing and D_v is the volume diffusion coefficient. The grain–boundary diffusion coefficient was estimated by the following equation [*LeClaire*, 1963]:

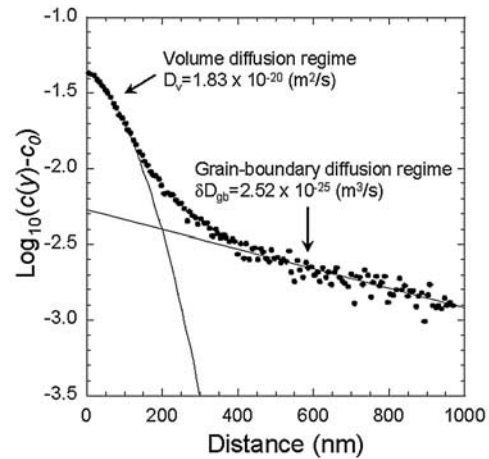$$\delta D_{gb} = 0.66\left(\partial \ln(c(y) - c_0)/\partial y^{6/5}\right)^{-5/3}(4D_v/t)^{1/2} \quad (2)$$

Figure 1. The depth profile of ^{29}Si in polycrystals wadsleyite annealed at 18 GPa and 1430°C for 50 hours (Run SID05) as a function of distance from the surface of a wadsleyite cube. The solid lines show the best fitting of equations (1) and (2) to the data in volume diffusion and grain–boundary diffusion regime, respectively.

where δ is grain-boundary width and D_{gb} is the grain-boundary diffusion coefficient. The calculated diffusion coefficients are summarized in Table 1. Uncertainties in diffusion coefficients were estimated by taking into account the fitting error and uncertainties in the relation between the crater depths and the sputtering time.

4. Discussion

[11] Figures 2a and 2b show Si volume diffusion and Si grain-boundary diffusion coefficients as a function of inverse temperature. Temperature dependence of diffusion coefficients is given by the Arrhenius equation:

$$D = D_0 \exp(-E^*/RT) \quad (3)$$

where D_0 is the pre–exponential factor, E^* is the activation energy, R is the gas constant and T is the absolute temperature. A least-squares fit of equation (3) to the data of volume diffusion and grain-boundary diffusion coefficients yields pre-exponential factors of 3.44×10^{-11} m^2/s (log $D_{v0} = -10.5 \pm 3.6$) and 1.14×10^{-17} m^3/s (log $\delta D_{gb0} = -16.9 \pm 4.0$) and activation energies of 299 (±122) and 248 (±135) kJ/mol, respectively. Uncertainties in pre-exponential factor and activation energy were estimated by taking into account the uncertainties of diffusion coefficients and temperatures. Although one would expect activation energy for volume diffusion to be much larger than that for

Table 1. Experimental Conditions and Estimated Values of Si Self-Diffusion Coefficients at 18 GPa

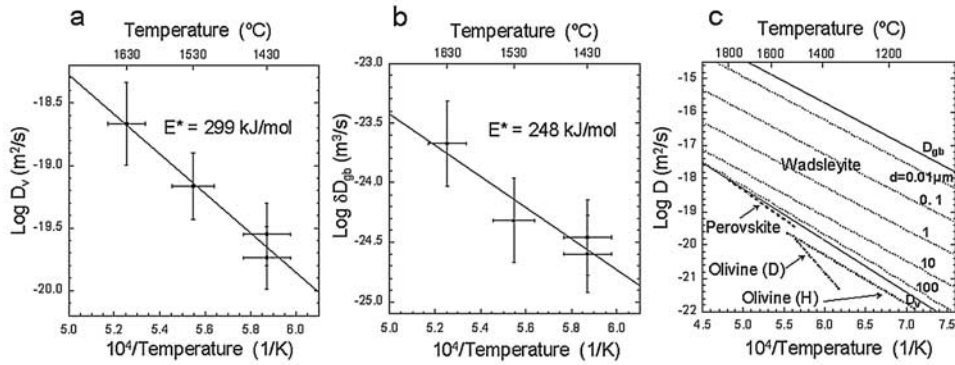| Run No.	T (°C)	Time (hr)	Water Contents (wt. ppm H_2O) Before	After	D_v (m^2/s)	δD_{gb} (m^3/s)
SID05	1430	50	353(11)	14(1)	$1.83(^{+0.92}_{-0.80}) \times 10^{-20}$	$2.52(^{+1.79}_{-1.31}) \times 10^{-25}$
					$2.82(^{+1.40}_{-1.23}) \times 10^{-20}$	$3.47(^{+2.45}_{-1.80}) \times 10^{-25}$
SID110	1530	56	507(51)	143(9)	$6.86(^{+2.25}_{-3.13}) \times 10^{-20}$	$4.84(^{+2.24}_{-2.70}) \times 10^{-25}$
SID07	1630	1	353(11)	58(7)	$2.16(^{+1.37}_{-1.15}) \times 10^{-19}$	$2.13(^{+1.67}_{-1.20}) \times 10^{-24}$

Numbers in parentheses represented the uncertainties.

Figure 2. (a) Arrhenius plot for Si volume diffusion in Mg_2SiO_4 wadsleyite. (b) Arrhenius plot for Si grain–boundary diffusion in Mg_2SiO_4 wadsleyite. (c) Grain-size dependence of Si diffusion rates in wadsleyite calculated from equation (4) and Si volume diffusion rates in various mantle minerals. Diffusion data of olivine (H), olivine (D) and perovskite are from *Houlier et al.* [1990], *Dohmen et al.* [2002] and *Yamazaki et al.* [2000], respectively.

grain-boundary diffusion, our results show those activation energies are relatively similar. Similar activation energies for the Si volume diffusion and Si grain-boundary diffusion were also reported in perovskite examined at 25 GPa [*Yamazaki et al.*, 2000]. These results imply pressure may have a larger effect in grain-boundary diffusion than volume diffusion as discussed by *Bejina et al.* [2003].

[12] Assuming that the average width of grain boundary is 1 nm, the grain-boundary diffusion is about 4 orders of magnitude faster than the volume diffusion at the experimental conditions. We have evaluated the effective diffusion coefficient (D_{eff}) in polycrystalline wadsleyite using the equation:

$$D_{eff} = D_v + \pi \delta D_{gb}/d \qquad (4)$$

where d is the grain size [*Raj and Ashby*, 1971]. Grain–boundary diffusion starts to have an effect when the grain size is smaller than 100 μm (Figure 2c).

[13] In the present study, the polycrystalline wadsleyite contains up to 500 weight ppm H_2O (Table 1). Because water possibly promotes the atomic diffusion in crystals, it is important to consider differences in water contents when comparing to other diffusion data. In wadsleyite, Si diffusion rates are about 5 orders of magnitude slower than the Mg-Fe interdiffusion rate at 1400°C [*Kubo et al.*, 2004], although water contents in the Si diffusion experiments were larger than those in the Mg–Fe interdiffusion experiments (50–90 weight ppm H_2O). The activation energy for Si self–diffusion is larger than that of the Mg–Fe interdiffusion (~172 kJ/mol).

[14] We compared Si volume diffusion rates obtained in this study with those previously reported in mantle olivine [*Houlier et al.*, 1990; *Dohmen et al.*, 2002] and $MgSiO_3$ perovskite [*Yamazaki et al.*, 2000] (Figure 2c). Si self–diffusion rates of wadsleyite for volume diffusion are almost identical with that of perovskite and about 0.5–1 orders of magnitude faster than that of olivine at 1400°C, although it is necessary to consider differences in iron and water contents for quantitative comparison.

[15] We make the following two assumptions to discuss the rheology of the mantle transition zone and subducting plates. (1) Si is the rate-controlling species in wadsleyite

and controls the plastic deformation. Although there is a lack of oxygen diffusion data for wadsleyite, Si is a good candidate for the slowest diffusion species in wadsleyite, as it is in olivine [*Houlier et al.*, 1988; *Dohmen et al.*, 2002]. (2) Si self-diffusion rate of ringwoodite is identical with that of wadsleyite. Similar diffusivity between wadsleyite and ringwoodite has been confirmed for Mg-Ni and Mg-Fe interdiffusion rates [*Farber et al.*, 1994, 2000]. Electrical conductivity of wadsleyite and ringwoodite, which is controlled by atomic diffusion, are also similar [*Xu et al.*, 1998]. Under these assumptions, we have calculated the viscosity η for diffusion creep using the following equation:

$$1/\eta = 13.3\Omega D_{eff}/(RTd^2) \qquad (5)$$

where Ω is the molar volume [*Raj and Ashby*, 1971]. Changes of viscosity for diffusion creep in wadsleyite are plotted with temperature and grain size in Figure 3. Using creep law parameters of analogue spinel [*Lawlis et al.*, 2001; *Karato et al.*, 2001], we also calculated the viscosity for dislocation creep as a function of stress in Figure 3. The temperature and the viscosity of the mantle transition zone have been estimated to be 1400–1600°C [*Ito and Katsura*, 1989], and 10^{20-21} Pa·s [e.g., *Peltier*, 1996]. Figure 3 indicates that the geophysical model of the viscosity in the mantle transition zone can be explained by diffusion creep with a grain size of 0.5–5 mm and dislocation creep with a stress of 1–10 MPa, which are consistent with petrological and geophysical estimates for the mantle transition zone. Our results suggest that both diffusion creep and dislocation creep mechanisms may be dominant in the mantle transition zone. Transitions between the two deformation mechanisms may easily occur by slight changes or heterogeneities in grain size and stress at the mantle transition zone.

[16] It has been suggested that the strength of subducting slabs significantly decreases due to grain size reduction after the olivine-spinel transformation [e.g., *Rubie*, 1984; *Karato et al.*, 2001]. *Riedel and Karato* [1997] calculated that the grain size of spinel could be reduced to about 0.1 μm when the olivine–spinel transformation occurs at relatively low temperature. Figure 3 shows that spinel with a grain size less than about 1 μm can become weaker than the surrounding mantle. Therefore some portions in subducting slabs are
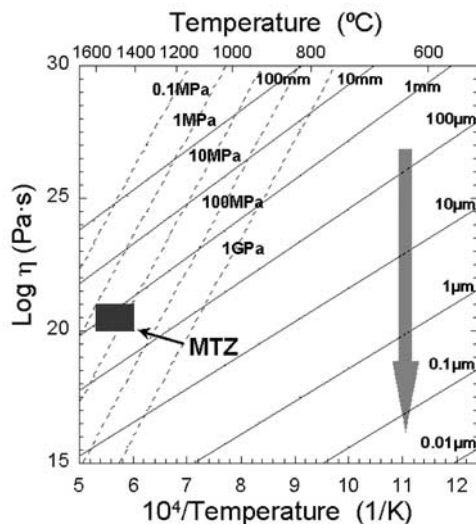
Figure 3. Temperature-viscosity relations with diffusion creep calculated from Si self-diffusion rates in wadsleyite and dislocation creep calculated using creep law parameters of analogue spinel [*Lawlis et al.*, 2001; *Karato et al.*, 2001]. The solid lines show viscosity profiles deformed by diffusion creep as a function of grain size (0.01 μm–100 mm). The dotted lines show viscosity profiles by dislocation creep as a function of stress (0.1 MPa–1 GPa). The black square shows the range of temperature [*Ito and Katsura*, 1989] and viscosity [e.g., *Peltier*, 1996] in the mantle transition zone. The arrow shows weakening of plates due to grain size reduction after the olivine-spinel transformation.

possibly weaker than the surrounding mantle, although the viscosity estimated at lower temperatures has a large uncertainty because of relatively large error in the activation energy in our diffusion data.

[17] We also compared the viscosity for the diffusion creep derived from our diffusion data with that from the rheological data of analogue spinel [*Lawlis et al.*, 2001; *Karato et al.*, 2001]. These are similar at the temperature of 1400–1600°C in the mantle transition zone. When extrapolating to lower temperatures in subducting slabs, the viscosity derived from our diffusion data gives much lower viscosity than that from *Karato et al.* [2001] because of a difference in temperature dependence.

[18] Our rheological implications based on the Si diffusivity in direct high–pressure phase of wadsleyite are almost consistent with previous discussions on rheology at the mantle transition zone and subducting slabs based on an analogue spinel [*Lawlis et al.*, 2001] and numerical modeling [*Karato et al.*, 2001].

[19] Discussions on rheology of the mantle transition zone and subducting slabs may strongly be affected by water content and chemical environment in the mantle transition zone. Experiments with better controlled water fugacity, oxygen fugacity, and silica activity using iron–bearing wadsleyite are needed to assess these issues.

References

Bejina, F., O. Jaoul, and R. C. Liebermann (2003), Diffusion in minerals at high pressure: A review, *Phys. Earth Planet. Inter.*, *139*, 3–20.

Chakraborty, S., R. Knoche, H. Schulze, D. C. Rubie, D. Dobson, N. L. Ross, and R. J. Angel (1999), Enhancement of cation diffusion rates across the 410-kilometer discontinuity in Earth's mantle, *Science*, *283*, 362–365.

Crank, J. (1975), *The Mathematics of Diffusion*, 2nd ed., 414 pp., Oxford Univ. Press, New York.

Dohmen, R., S. Chakraborty, and H.-W. Becker (2002), Si and O diffusion in olivine and implications for characterizing plastic flow in the mantle, *Geophys. Res. Lett.*, *29*(21), 2030, doi:10.1029/2002GL015480.

Farber, D. L., Q. Williams, and F. J. Ryerson (1994), Diffusion in Mg$_2$SiO$_4$ polymorphs and chemical heterogeneity in the mantle transition zone, *Nature*, *371*, 693–695.

Farber, D. L., Q. Williams, and F. J. Ryerson (2000), Divalent cation diffusion in Mg$_2$SiO$_4$ spinel (ringwoodite), β phase (wadsleyite), and olivine: Implications for the electrical conductivity of the mantle, *J. Geophys. Res.*, *105*, 513–529.

Harrison, L. G. (1961), Influence of dislocations on diffusion kinetics in solids with particular reference to the alkali halides, *Trans. Faraday Soc.*, *57*, 1191–1199.

Houlier, B., O. Jaoul, F. Abel, and R. C. Liebermann (1988), Oxygen and silicon self-diffusion in natural olivine at T = 1300°C, *Phys. Earth Planet. Inter.*, *50*, 240–250.

Houlier, B., M. Cheraghmakani, and O. Jaoul (1990), Silicon diffusion in San Carlos olivine, *Phys. Earth Planet. Inter.*, *62*, 329–340.

Ito, E., and T. Katsura (1989), A temperature profile of the mantle transition zone, *Geophys. Res. Lett.*, *16*, 425–428.

Karato, S., M. R. Riedel, and D. A. Yuen (2001), Rheological structure and deformation of subducted slabs in the mantle transition zone: Implications for mantle circulation and deep earthquakes, *Phys. Earth Planet. Inter.*, *127*, 83–108.

Kubo, T., A. Shimojuku, and E. Ohtani (2004), Mg-Fe interdiffusion rates in wadsleyite and the diffusivity jump at the 410 km discontinuity, *Phys. Chem. Miner.*, in press.

Lawlis, J. D., Y. H. Zhao, and S. Karato (2001), High-temperature creep in a Ni$_2$GeO$_4$: A contribution to creep systematics in spinel, *Phys. Chem. Miner.*, *28*, 557–571.

LeClaire, A. D. (1963), The analysis of grain boundary diffusion measurements, *Br. J. Appl. Phys.*, *14*, 351–356.

Ohtani, E., A. Suzuki, and T. Kato (1998), Flotation of olivine and diamond in mantle melt at high pressure: Implications for fractionation in the deep mantle and ultradeep origin of diamond, in *Properties of Earth and Planetary Materials at High Pressure and Temperature, Geophys. Monogr. Ser.*, vol. 101, edited by T. Yagi, pp. 227–239, AGU, Washington, D. C.

Paterson, M. S. (1982), The determination of hydroxyl by infrared absorption in quartz, silicate glasses and similar materials, *Bull. Mineral.*, *105*, 20–29.

Peltier, W. R. (1996), Mantle viscosity and ice-age ice sheet topography, *Science*, *273*, 1359–1364.

Raj, R., and M. F. Ashby (1971), On grain boundary sliding and diffusional creep, *Metall. Trans.*, *2*, 1113–1127.

Riedel, M. R., and S. Karato (1997), Grain-size evolution in subducted oceanic lithosphere associated with the olivine-spinel transformation and its effects on rheology, *Earth Planet. Sci. Lett.*, *148*, 27–43.

Rubie, D. C. (1984), The olivine-spinel transformation and the rheology of subducting lithosphere, *Nature*, *308*, 505–508.

Xu, Y., B. T. Poe, T. J. Shankland, and D. C. Rubie (1998), Electrical conductivity of olivine, wadsleyite, and ringwoodite under upper-mantle conditions, *Science*, *280*, 1415–1418.

Yamazaki, D., T. Kato, H. Yurimoto, E. Ohtani, and M. Toriumi (2000), Silicon self-diffusion in MgSiO$_3$ perovskite at 25 GPa, *Phys. Earth Planet. Inter.*, *119*, 299–309.

Yurimoto, H., M. Morioka, and H. Nagasawa (1989), Diffusion in single crystals of melilite: I. Oxygen, *Geochim. Cosmochim. Acta*, *53*, 2387–2394.

———————————

T. Kubo, Department of Earth and Planetary Sciences, Faculty of Sciences, Kyushu University, Fukuoka 812-8581, Japan.

A. Shimojuku and E. Ohtani, Institute of Mineralogy, Petrology and Economic Geology, Faculty of Science, Tohoku University, Sendai 980-8578, Japan. (simojuku@ganko.tohoku.ac.jp)

H. Yurimoto, Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Tokyo 152-8551, Japan.