

# HYDROUS LOWER MANTLE: THE WATER SOURCE FOR WET PLUMES ?

Konstantin Litasov and Eiji Ohtani

*Inst. Mineral. Petrol. Econ. Geol., Tohoku University, Sendai, Japan*

## INTRODUCTION

Recent experimental and theoretical studies suggest that water plays a key role in the geodynamics of the Earth's interior because it significantly affects melting, phase transitions and physical properties of minerals. Ringwood (1977) proposed about 2 wt% of H<sub>2</sub>O in Earth's source material, assuming Earth was formed from a mixture of C1 chondrite- and enstatite chondrite-like components. Although part of H<sub>2</sub>O or molecular H may have been lost since the Earth's birth, many data suggest that a considerable amount of water can be stored in the Earth interior.

The upper mantle, transition zone and lower mantle could have different potentials for storing water. Upper mantle is relatively dry. Transition zone should be an important water reservoir due to significant (2-3 wt% of H<sub>2</sub>O) water solubility in wadsleyite and ringwoodite (Mg,Fe)<sub>2</sub>SiO<sub>4</sub> (e.g. Kohlstedt et al., 1996). Water storage capacity of the lower mantle becomes a matter of debate. At lower temperatures (<1300°C), superhydrous phase B and phase G (D/F) can accommodate water in the uppermost lower mantle. The lower mantle consists of Mg-perovskite, ferropericlase and Ca-perovskite, however the water solubility of these minerals is poorly studied. Meade et al. (1994) reported results of FTIR measurements of water solubility in MgSiO<sub>3</sub>-perovskite and documented two pleochroic hydroxyl absorbance peaks at 3423 and 3483 cm<sup>-1</sup>. Calculation of water content corresponds to 60-70 ppm H<sub>2</sub>O. However, Bolfan-Casanova et al. (2000) showed absence of water (<1 ppm H<sub>2</sub>O) in MgSiO<sub>3</sub>-perovskite. Recent data on water solubility in peridotite-related Al-Fe-Mg-perovskite measured by SIMS and FTIR revealed 0.1-0.4 wt% H<sub>2</sub>O (Murakami et al., 2002). Murakami et al. (2002) also reported 0.3-0.4 wt% H<sub>2</sub>O in Ca-perovskite and about 0.2 wt% H<sub>2</sub>O in ferropericlase. These data however may be doubtful on the basis of the recent studies by Bolfan-Casanova et al. (2002), who reported less 20 ppm H<sub>2</sub>O in ferropericlase at 25 GPa.

In this contribution we study water solubility in Mg-perovskites (pure, aluminous, and those observed in peridotite and former oceanic crust), Ca-perovskite, and

ferropericlase. Using the measured water content we (1) estimate water storage capacity in the Earth's lower mantle and (2) propose role of water in generation of wet mantle plume and transport of lower mantle diamonds to the lithosphere.

The phase relations were determined at 25-26 GPa and the temperature range from 1000 to 1800°C. We used several starting materials (Table 1) corresponding to perovskite and ferropericlase. The hydrous composition was prepared by adding Mg(OH)<sub>2</sub> or Ca(OH)<sub>2</sub> to the synthetic mineral mixtures and adjusting the proportion of MgO and CaO. A Kawai (MA8) multianvil 3000-tons press of Tohoku University, Sendai was used in the experiments. The furnace assemblies and experimental details are described by Litasov and Ohtani (2002). Mineral compositions were measured by the electron microprobe under the operating condition of 15 kV and 10 nA current. Water contents were measured by FTIR. Infrared spectra were measured using Jasco MFT-2000 microsampling FTIR spectrometer (see Litasov et al., 2003, for more details of FTIR). The concentrations of hydroxyl groups were determined by the method of Paterson (1982) where absorption bands were integrated by using the calibration of the extinction coefficient and density factors.

## RESULTS

The results of experiments are summarized in Table 1. Experimental products are represented by polycrystalline aggregates of major mineral according to the starting composition with minor amount of other phases. Selected electron microprobe analyses are shown in Table 2.

### Mg-PEROVSKITE

We measured water contents in four types of Mg-perovskite samples: (1) pure MgSiO<sub>3</sub> perovskite; (2) Al-rich Mg-perovskite (denoted as Al-Mg-perovskite; Al<sub>2</sub>O<sub>3</sub>=2-7.2 wt%; Mg# = Mg/(Mg+Fe<sub>total</sub>) = 100); (3) Mg-perovskite related to MORB (Al-Fe-Mg-perovskite; Al<sub>2</sub>O<sub>3</sub>=13-17 wt%; Mg#=58-61); and (4) Mg-perovskite related to peridotite (Al-Fe-Mg-perovskite; Al<sub>2</sub>O<sub>3</sub>=5-6 wt%; Mg#=88-90).

**Table 1: Experimental results and water content of perovskites and ferropericlase.**

Run No.	Starting material	Pressure (GPa)	Temp. (°C)	Time (min)	Phase Assemblage	H <sub>2</sub> O content (ppm) <sup>2</sup>
<i>Mg-perovskite</i>						
K-202	MgSiO <sub>3</sub> + 10 wt% H <sub>2</sub> O	25	1300	360	MgPv, L	104 (14)
K-200	MgSiO <sub>3</sub> + 10 wt% Al <sub>2</sub> O <sub>3</sub> + 10 wt% H <sub>2</sub> O	25	1400	360	Al-MgPv, Gt, L	101 (19)
K-201	MgSiO <sub>3</sub> + 10 wt% Al <sub>2</sub> O <sub>3</sub>	25	1400	360	Al-MgPv, Gt	
K-165	Mg <sub>2</sub> SiO <sub>4</sub> + 10 wt% Al <sub>2</sub> O <sub>3</sub> + 5 wt% H <sub>2</sub> O	25	1200	720	Al-MgPv, Gt, NAL, L	1101 (156)
K-164	Mg <sub>2</sub> SiO <sub>4</sub> + 10 wt% Al <sub>2</sub> O <sub>3</sub> + 10 wt% H <sub>2</sub> O	26	1200	900	Al-MgPv, Gt, NAL, L	1440 (160)
K-160	MORB Mg-perovskite <sup>1</sup> + 5 wt% H <sub>2</sub> O	26	1000	1200	Al-Fe-MgPv, L	110 (21)
K-161	same	26	1200	900	Al-Fe-MgPv, L	104 (26)
K-208	Peridotite Mg-perovskite <sup>1</sup> + 10 wt% H <sub>2</sub> O	25	1400	360	Al-Fe-MgPv, St, L	1780 (175)
K-209	same	25	1600	120	Al-Fe-MgPv, St, L	1460 (130)
<i>Ca-perovskite</i>						
K-218	CaSiO <sub>3</sub> + 2 wt% Al <sub>2</sub> O <sub>3</sub> + 10 wt% H <sub>2</sub> O	25	1600	120	CaPv, NAL, L	x <sup>3</sup>
K-227	same	25	1900	30	CaPv, L	~5100
<i>Ferropericlase</i>						
K-223	MgO + 3 wt% Al <sub>2</sub> O <sub>3</sub> + 10 wt% H <sub>2</sub> O	25	1400	120	Pc, Br	21 (8)
K-220	same	25	1600	120	Pc, L	43 (17)
K-225	same	25	1800	5	Pc, L	112 (21)
K-216	(Mg <sub>0.88</sub> Fe <sub>0.12</sub> )O + 3 wt% Al <sub>2</sub> O <sub>3</sub> + 10 wt% H <sub>2</sub> O	25	1400	360	Fpc, Mst, L	25 (14)
K-213	same	25	1600	120	Fpc, Mst, L	71 (23)
K-224	same	25	1800	20	Fpc, L	180 (30)

Phases: MgPv, Mg-perovskite; Al-MgPv, aluminous Mg-perovskite; Al-Fe-MgPv, Al-Fe-Mg-perovskite; St, stishovite; NAL, Na-Al phase; Gt, majorite garnet; CaPv, Ca-perovskite; Pc, periclase; Br, brucite; Fpc, ferropericlase; Mst, magnesite; L, liquid.

<sup>1</sup>See table 2 for compositions; <sup>2</sup>H<sub>2</sub>O content for major mineral (Mg- and Ca-perovskite and ferropericlase) calculated by FTIR using method of Paterson (1982); <sup>3</sup>The size of the crystals was not enough for FTIR measurements.

Unpolarized IR spectra of pure MgSiO<sub>3</sub> perovskite synthesized at 25 GPa and 1300°C are shown in Fig.1a. IR spectra show several bands: one major at 3448 cm<sup>-1</sup> and three minor at 3397, 3423, and 3482 cm<sup>-1</sup>. The bands at 3423 and 3482 cm<sup>-1</sup> are consistent with data reported by Meade et al. (1994) for MgSiO<sub>3</sub> perovskite synthesized at 27 GPa and 1830°C. Calculated water content corresponds to about 100 ppm H<sub>2</sub>O (Table 1).

IR spectra of Al-Mg-perovskite containing 2 wt% of Al<sub>2</sub>O<sub>3</sub> synthesized at 25 GPa and 1400°C show a broad band near 3400cm<sup>-1</sup>. The spectra are different from those of anhydrous perovskite (Fig.1b) and indicate water content near 100 ppm. Al-Mg-perovskite containing 4-7 wt.% of Al<sub>2</sub>O<sub>3</sub> shows broad IR spectra with poorly identified bands at 3404, 3448, and 3565 cm<sup>-1</sup> (Fig.1b). Calculated water content of single crystal perovskite in samples K-164 and K-165 is 1100-1400 ppm.

The unpolarized spectra of MORB-related Al-Fe-Mg-perovskite are shown in Fig.1c. The spectra are composed of two major bands at 3125 and 3397 cm<sup>-1</sup>

and some minor bands. The minor bands along with possible impurities can affect on broadening of the spectra. The nature of the band at 3125 cm<sup>-1</sup> is not clear. We addressed this band to ringwoodite which has major OH vibration band at 3120 cm<sup>-1</sup>. The water content in MORB-related Al-Fe-Mg-perovskites measured using band at 3397 cm<sup>-1</sup> is 90-110 ppm.

The unpolarized spectra of peridotite-related Al-Fe-Mg-perovskite synthesized at 25 GPa and 1400-1600°C are shown in Fig.1d. The spectra of thick (80-120 μm) samples are broad and composed of two major bands at 3397 and 3690 cm<sup>-1</sup>. The position of major perovskite band at 3397 cm<sup>-1</sup> is close to that determined by Bolfan-Casanova (2000) at 3388 cm<sup>-1</sup>. The band at 3690 cm<sup>-1</sup> is absent in the spectra of thin crystals and may correspond to quench inclusions of brucite (which has a major band at 3698 cm<sup>-1</sup>). The band at 3690 cm<sup>-1</sup> was not used in calculations of H<sub>2</sub>O content. The H<sub>2</sub>O content in Mg-perovskite related to peridotite calculated for samples with average thickness is 1400-1800 ppm.

**Table 2: Average compositions of experimental phases.**

Sample	K-202	K-200	K-201	K-164	K-160	K-161	K-208	K-209	K-227	K-218	K-216	K-213	K-224
	MgPv	Al-MgPv	Al-MgPv	Al-MgPv	MgPv (bas.)	MgPv (bas.)	MgPv (per.)	MgPv (per.)	CaPv	CaPv	Fpc	Fpc	Fpc
SiO <sub>2</sub>	60.10	59.09	59.19	55.37	36.73	38.11	52.77	53.11	48.92	49.24			
TiO <sub>2</sub>					2.18	1.91							
Al <sub>2</sub> O <sub>3</sub>		2.03	1.45	7.16	14.50	13.16	5.50	5.80	2.08	1.49	0.90	1.65	2.00
FeO*					26.23	24.52	7.39	6.09			17.39	18.09	18.11
MgO	40.36	39.77	39.78	38.14	20.15	21.37	34.48	34.94			80.81	81.94	80.30
CaO									47.67	47.33			
H <sub>2</sub> O*	0.01	0.01		0.14	0.01	0.01	0.18	0.15	0.50	0.50	0.00	0.01	0.02
Total	100.5	100.9	100.4	100.8	99.81	99.08	100.3	100.1	99.17	98.56	99.10	101.6	100.4
Si	1.000	0.979	0.985	0.918	0.683	0.709	0.903	0.907	0.951	0.962			
Ti					0.031	0.027							
Al		0.039	0.028	0.140	0.319	0.289	0.111	0.117	0.048	0.034	0.008	0.014	0.017
<sup>5</sup> Fe <sup>3+</sup>					0.245	0.229	0.063	0.052					
Fe <sup>2+</sup>					0.163	0.153	0.042	0.035			0.106	0.108	0.109
Mg	1.000	0.982	0.987	0.942	0.559	0.593	0.880	0.889			0.882	0.871	0.865
Ca									0.993	0.991			
Total	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.010	2.008	0.996	0.993	0.991
H	0.001	0.001		0.015	0.001	0.001	0.021	0.017	0.065	0.065	0.000	0.001	0.002
2V <sub>O</sub>		0.003	0.002	0.025	0.008	0.010	0.019	0.017	0.042	0.029			
Mg#					57.8	60.8	89.3	91.1			89.2	89.0	88.8

FeO\*, total Fe as FeO. Mg#=100Mg/(Mg+Fe<sub>total</sub>). H<sub>2</sub>O\*, suggested H<sub>2</sub>O content from Table 1. <sup>5</sup>Fe<sup>3+</sup> was calculated from Fe<sup>3+</sup>/ΣFe ratio by EELS (Litasov et al., 2003). 2V<sub>O</sub>=(1-Si-Ti)-(1-Mg-Fe<sup>2+</sup>-Ca)=M<sup>3+</sup><sub>B</sub>-M<sup>3+</sup><sub>A</sub>, is amount of oxygen vacancies in ABO<sub>3</sub>-perovskite, which can be filled by hydrogen atoms. Bas., MORB; Per., peridotite. See table 1 for other abbreviations.

### CA-PEROVSKITE

The unpolarized spectra of aluminous Ca-perovskite synthesized at 25 GPa and 1900°C are shown in Fig.2. The spectra composed of two major bands at 3343 and 3607 cm<sup>-1</sup>. The H<sub>2</sub>O content in Ca-perovskite is near 5100 ppm. Ca-perovskite contain more Al<sub>2</sub>O<sub>3</sub> with increasing temperature, therefore water solubility may increase also.

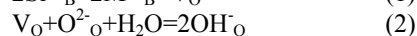
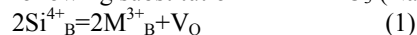
### FERROPERICLASE

IR spectra of periclase show weak bands at 3299, 3308, and 3404 cm<sup>-1</sup>. Ferropericlase has major bands at 3299 and 3474 cm<sup>-1</sup> (Fig.3). Calculated H<sub>2</sub>O content in periclase is 21 ppm at 1400°C (Al<sub>2</sub>O<sub>3</sub> in periclase is 0.7 wt%) and 112 ppm at 1800°C (Al<sub>2</sub>O<sub>3</sub>=1.2 wt%). The H<sub>2</sub>O content in ferropericlase is 25 ppm at 1400°C (Al<sub>2</sub>O<sub>3</sub>=1.0 wt%) and 180 ppm at 1800°C (Al<sub>2</sub>O<sub>3</sub>=2.2 wt%). These data indicate that (1) ferropericlase (Mg#=88) contains more water and Al<sub>2</sub>O<sub>3</sub> relative to periclase and (2) water content in ferropericlase increases with increasing temperature and Al<sub>2</sub>O<sub>3</sub>.

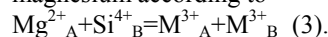
## DISCUSSION

### STRUCTURAL POSITION OF WATER

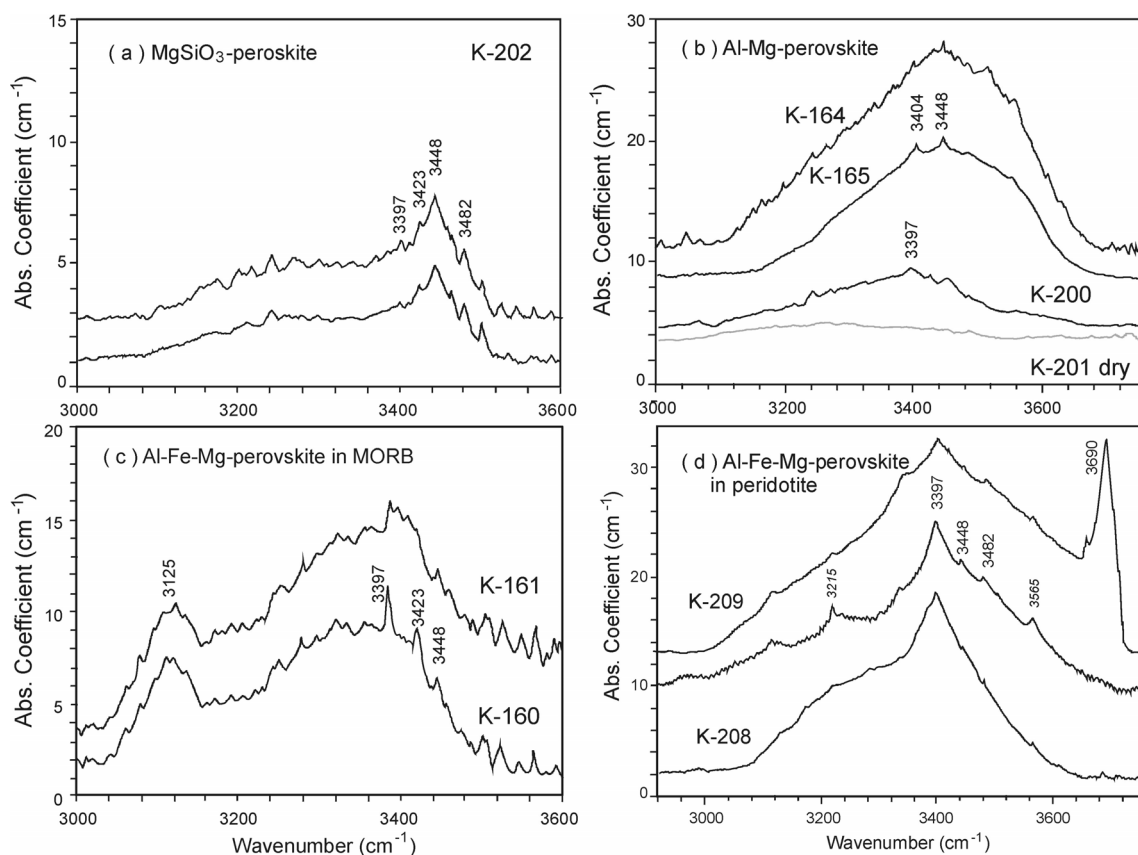
Substitution of Al or Fe<sup>3+</sup> for Si in perovskite and Mg in periclase can create oxygen defects, which potentially absorb hydrogen. Therefore, H<sub>2</sub>O solubility increases with increasing Al<sup>3+</sup> or Fe<sup>3+</sup> content. This is not true for Al- and Fe-rich Mg-perovskite related to MORB. The defect equilibria in perovskites are dominated by the following substitution in A<sup>2+</sup>B<sup>4+</sup>O<sub>3</sub> (Navrotsky, 1999):



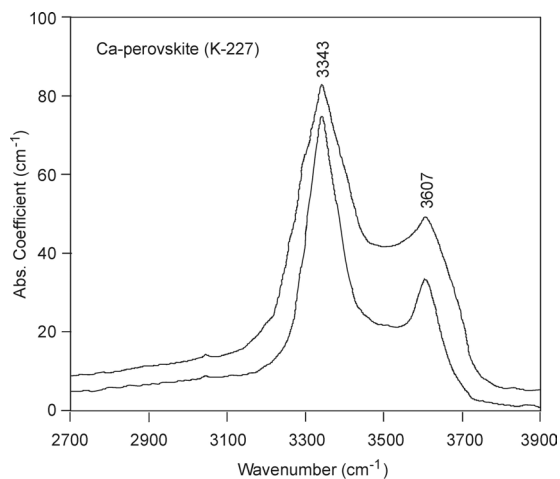
where subscripts O and B denote oxygen and B-cation sites respectively and M<sup>3+</sup> = Al<sup>3+</sup> or Fe<sup>3+</sup>. Eq. (1) creates oxygen vacancies, V<sub>O</sub>, which can be and eq. (2) fills them. Incorporation of trivalent cations such as Al and Fe into MgSiO<sub>3</sub> perovskite can follow a coupled substitution of two trivalent ions for silicon and magnesium according to



The EELS spectra of Al-Fe-Mg-perovskite related to MORB indicate that it contains a large amount of ferric



**Figure 1:** Examples of unpolarized FTIR spectra of Mg-perovskite synthesized at 25-26 GPa.



**Figure 2:** Examples of unpolarized FTIR spectra of Ca-perovskite synthesized at 25 GPa and 1900°C.

iron,  $\text{Fe}^{3+}/\Sigma\text{Fe} \approx 0.6$  (Litasov et al., 2003). Therefore, trivalent cations favors substitution of Mg and Si sites by the mechanism of eq.3. In MORB-related perovskite only 2-4% of trivalent cations in site B create oxygen

vacancies by Eq.1. This evidence explains restricted water solubility in MORB Mg-perovskite, which contains less than 0.010 p.f.u. of oxygen vacancies (Table 2). The cation values of peridotite Mg-perovskite (samples K-208 and K-209 in Table 2) indicate that 12-20% of the  $\text{M}^{3+}$  cations in site B create 0.012-0.017 p.f.u. oxygen vacancies according to Eq.1.

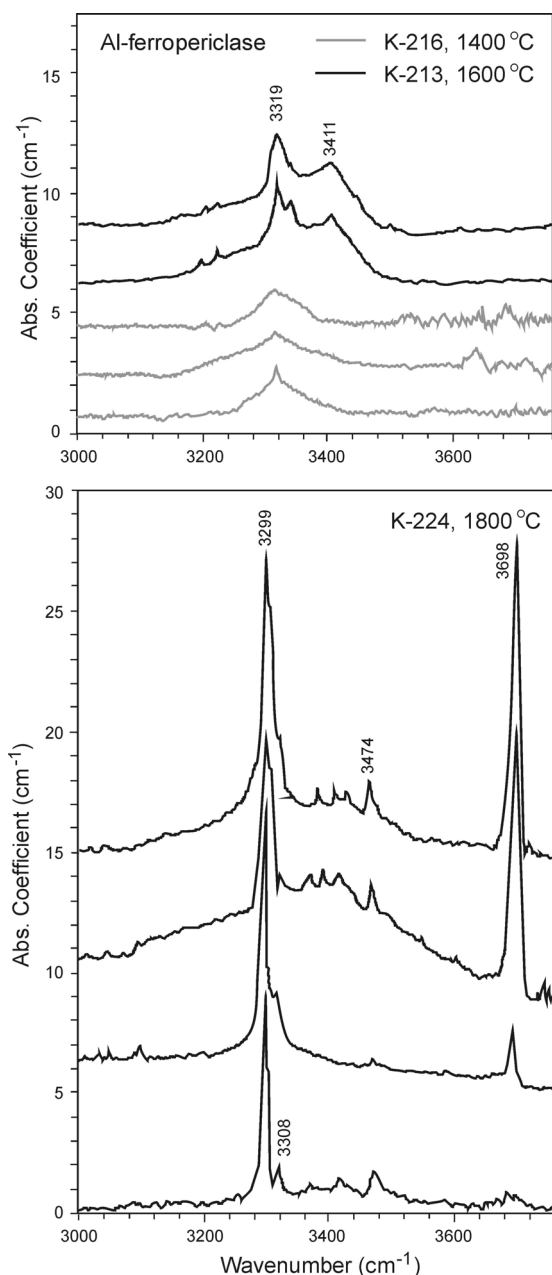
The cation values of Ca-perovskite indicate that most of Al occupies Si site creating oxygen vacancies. However,  $\text{H}_2\text{O}$  content in Ca-perovskite is higher than the amount of vacancies (Table 2). This indicates that other substitutions are involved for hydroxyl incorporation in Ca-perovskite.

The  $\text{Al}_2\text{O}_3$  impurity can create oxygen vacancies in ferropericlase by substitution of two Mg atoms. However, water solubility in ferropericlase related to natural fertile peridotite, is restricted. This is consistent with data by Bolfan-Casanova et al. (2002). Ferropericlase can not be considered as important water reservoir in the lower mantle. It is important to note that

increase of H<sub>2</sub>O solubility in ferropericlasite with increasing temperature (and Al<sub>2</sub>O<sub>3</sub>) may be very important for water distribution in the lower mantle.

#### WATER STORAGE CAPACITY OF THE LOWER MANTLE

The present results indicate that Ca-perovskite has highest water solubility among the lower mantle minerals following by Mg-perovskite and ferropericlasite.



**Figure 3:** Examples of unpolarized FTIR spectra of ferropericlasite synthesized at 25 GPa.

Average fertile lower mantle peridotite consists of 80 wt% of Mg-perovskite, 15 wt% ferropericlasite, and 5 wt% of Ca-perovskite. Taking into account possible decrease of water content in the phases with increasing temperature up to the mantle geotherm, we can estimate that the average lower mantle peridotite can contain 0.12 wt.% of H<sub>2</sub>O. Therefore, the maximum amount of water in the lower mantle is estimated as  $3.62 \times 10^{21}$  kg. This is 2.6 times of the present ocean mass and comparable with the amount of water potentially concentrated in the transition zone. This indicates that lower mantle can produce hydrous fluid for arising mantle plumes. Hydrous conditions increase transport ability of the plume materials and, therefore, facilitate delivery of the lower mantle diamonds to the lithosphere.

#### REFERENCES

- Bolfan-Casanova, N., Keppler, H., Rubie, D., 2000. Water partitioning between nominally anhydrous minerals in the MgO-SiO<sub>2</sub>-H<sub>2</sub>O system up to 24 GPa: implications for the distribution of water in the Earth's mantle. *Earth Planet. Sci. Lett.* 182, 209-221.
- Bolfan-Casanova, N., Mackwell, S., Keppler, H., McCammon, C., Rubie, D., 2002. Pressure dependence of H solubility in magnesiowustite up to 25 GPa: Implications for the storage of water in the Earth's lower mantle. *Geophys. Res. Lett.* 29, 10.1029/2001GL014457.
- Kohlstedt, D.L., Keppler, H., Rubie, D.C., 1996. Solubility of water in the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases of (Mg,Fe)<sub>2</sub>SiO<sub>4</sub>. *Contrib. Mineral. Petrol.* 123, 345-357.
- Litasov, K., Ohtani, E., 2002. Phase relations and melt compositions in CMAS-pyrolite-H<sub>2</sub>O system up to 25 GPa. *Phys. Earth Planet. Inter.* 134, 105-127.
- Litasov, K., Ohtani, E., Langenhorst, F., Yurimoto, H., Kubo, T., Kondo, T., 2003. Water Solubility in Mg-perovskites and Water Storage Capacity in the Lower Mantle. *Earth Planet. Sci. Lett.*, submitted.
- Meade, C., Reffner, J.A., Ito, E., 1994. Synchrotron infrared absorbance measurements of hydrogen in MgSiO<sub>3</sub> perovskite. *Science* 264, 1558-1560.
- Murakami, M., Hirose, K., Yurimoto, H., Nakashima, S., Takafuji, N., 2002. Water in Earth's lower mantle. *Science* 295, 1885-1887.
- Navrotsky, A., 1999. Mantle geochemistry: A lesson from ceramics. *Science* 284, 1788.
- Paterson, M.S., 1982. The determination of hydroxyl by infrared absorption in quartz, silicate glasses and similar materials. *Bull. Mineral.* 105, 20-29.
- Ringwood, A.E., 1977. Composition of the core and implications for origin of the earth. *Geochem. Jour.* 11, 111-135.

Contact: KD Litasov, Inst. Mineral. Petrol. Econ. Geol., Tohoku Univ., Sendai, 980-8578, Japan, E-mail: klitasov@ganko.tohoku.ac.jp