

Water solubility in majoritic garnet in subducting oceanic crust

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Received 8 July 2003; revised 28 August 2003; accepted 28 August 2003; published 22 November 2003.

[1] Water in majoritic garnet synthesized in the mid-oceanic ridge basalt (MORB) + H₂O composition at 20 GPa and 1400–1500°C was measured by secondary ion mass spectrometry (SIMS) and infrared spectroscopy. We found that the majorite contains 1130 to 1250 ppm OH by weight. The infrared absorption band showed that incorporation of the hydroxyl in majorite is most likely due to the hydrogarnet substitution. Our results indicate that water can be transported into the mantle transition zone by nominally anhydrous minerals such as omphacite and majorite in the subducting basaltic crust. Such water may have great influences on the physical properties of slab in the transition zone. **INDEX TERMS:** 3630 Mineralogy and Petrology: Experimental mineralogy and petrology; 3670 Mineralogy and Petrology: Minor and trace element composition; 5139 Physical Properties of Rocks: Transport properties. **Citation:** Katayama, I., K. Hirose, H. Yurimoto, and S. Nakashima, Water solubility in majoritic garnet in subducting oceanic crust, *Geophys. Res. Lett.*, 30(22), 2155, doi:10.1029/2003GL018127, 2003.

1. Introduction

[2] It has been widely accepted that the presence of water significantly affects melting behavior and physical properties of the mantle. Phase relations in the H₂O-bearing basaltic composition were systematically investigated by high pressure and temperature experiments [e.g., *Poli and Schmidt, 1995; Schmidt and Poli, 1998; Ono, 1998; Okamoto and Maruyama, 1999*]. These studies showed that most of H₂O is released upon breakdown of amphibole at shallow depth (<50 km) but trace amounts can be accommodated in lawsonite and carried to deeper mantle in cold subduction zones. However, lawsonite is stable up to a depth of 300 km, and no hydrous minerals are formed in the basaltic composition at deeper levels. On the other hand, the nominally anhydrous minerals can also dissolve substantial amounts of hydroxyl [e.g., *Bell and Rossman, 1992a*]. Garnet and pyroxene from kimberlite xenoliths dissolve up to 400 and 1800 ppm OH (by weight), respectively [*Bell and Rossman, 1992a, 1992b; Smyth et al., 1991*]. Moreover, omphacites found in natural diamond-grade eclogite contain up to 3020 ppm hydroxyl [*Katayama and Nakashima, 2003*]. Subducted basaltic crust includes ~40% omphacite in the diamond-grade eclogite and therefore may carry up to 1200 ppm OH (by weight) before it transforms to garnetite at mantle transition zone, where it is composed predominantly of majoritic garnet with minor amount of stishovite [e.g., *Ringwood, 1967; Irfune et al., 1986*].

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[3] Previous experimental studies reported limited solubility of hydroxyl (up to 200 ppm) in garnets at mantle depths [*Ackermann et al., 1983; Geiger et al., 1991; Lu and Keppler, 1997; Withers et al., 1998*]. Most of these data, however, were restricted to Mg-end-member pyrope composition. Majoritic garnet in the basaltic composition contains trace amounts of Na₂O (up to 2.5 wt%) and TiO₂ (up to 2.1 wt%) as well as almandine and grossular components [*Ono and Yasuda, 1996*]. Such chemical impurities may increase the solubility of water in nominally anhydrous minerals as reported for enstatite [*Rauch and Keppler, 2002*], stishovite [*Pawley et al., 1993; Chung and Kagi, 2002*] and MgSiO₃-perovskite [*Murakami et al., 2002*]. We measured the hydrogen content in majorite synthesized in the natural basaltic composition by using secondary ion mass spectrometer (SIMS) and infrared (IR) spectroscopy. Our results have important implications for the distribution of water at the mantle transition zone.

2. Experimental Procedures

2.1. Sample Synthesis

[4] Majoritic garnets were synthesized in the MORB + H₂O composition. Two runs were performed at a pressure of 20 GPa and temperatures of 1400 and 1500°C. Starting material was an oxide mixture with a representative (MORB) composition, which is close to the average MORB composition from the Mid-Atlantic Ridge [*Melson et al., 1976*], plus 13.5 wt% H₂O added by Al(OH)₃, Mg(OH)₂, and Ca(OH)₂ (Table 1). The hydrous phase relations of this composition have been determined at high pressures by *Ono [1998]*. The starting material was loaded into Au₇₅Pd₂₅ capsule of 1 mm diameter and welded. High-pressure syntheses were made using a 1000-ton multi-anvil apparatus (SEDI-1000 at the Tokyo Institute of Technology). A Cr-doped MgO octahedra with 8 mm edge length and tungsten carbide anvils with truncation edge length of 3 mm were used in these experiments. Temperature was monitored using a W₅/W₂₆Re thermocouple inserted into the octahedral assembly. Details of experimental configuration and the pressure calibration were described previously [*Hirose, 2002*]. The samples were compressed to the desired pressure and then the temperature was increased with a rate of about 100°C/min. After heating for 2–3 hours, they were quenched rapidly by switching off the power. The recovered samples were analyzed for major elements by an electron microprobe (JEOL JXA 8800 with 12 nA beam current and 15 kV accelerating voltage), and then further prepared for the measurements of water.

2.2. Hydrogen Analyses

[5] Secondary ion mass spectrometry (SIMS, Cameca ims-3F) was used to quantify the hydrogen content in

Table 1. Experimental Conditions and Chemical Compositions of the Starting Material and the Synthesized Majorites

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO ^a	MgO	CaO	Na ₂ O	K ₂ O	Total	OH ^b
Starting material^c										
MORB	45.50	1.41	17.23	10.29	9.86	12.57	2.93	0.22	100.00	
C295: 20 GPa, 1400°C										
Maj	42.70 (0.64)	0.40 (0.30)	21.65 (0.22)	12.17 (1.25)	13.5 (0.75)	8.22 (0.51)	1.11 (0.08)	n.d.	99.77 (0.70)	0.125 (0.014)
C340: 20 GPa, 1500°C										
Maj	44.51 (0.46)	1.26 (0.15)	22.14 (0.33)	5.47 (0.45)	17.01 (0.95)	7.71 (1.03)	1.29 (0.06)	n.d.	99.47 (0.92)	0.113 (0.018)

The numbers in the parentheses indicate one standard deviations of the multiple analyses. n.d. means no detected.

^aTotal Fe was calculated as FeO.

^bWater concentrations in the majorites were analyzed by SIMS (wt%).

^c13.5 wt% H₂O was adopted to the starting material.

majorites. The samples were coated with Au film of 20 nm thickness to eliminate electrostatic charging. A primary ion beam consisted of mass-filtered ¹⁶O⁻ accelerated by -10 kV with a spot size of 10 μm in diameter and a beam current of about 20 nA. The intensities of the positive secondary ¹H and ³⁰Si ions were measured for 200 cycles to obtain steady state secondary ion emissions. To reduce the background signals, the vacuum level of the sample chamber was maintained at 0.2 μPa, and a cold trap method by liquid nitrogen was employed. For the quantitative analysis, we prepared two standard minerals of natural pyrope (54 ppm OH by weight) and hornblende (3.14 wt% OH). The hydrogen content of the pyrope was calculated from infrared spectra, which concentration was also reported by *Rossmann et al.* [1989] at same locality from Dora Maira Massif, Western Alps. These standards were measured repeatedly to construct a calibration line for each analysis. The adsorbed water on the surface of sample was removed by sputtering the surface and monitoring the profile of the hydrogen intensity with sputter time. Other analytical and instrumental conditions were similar to previous study [*Yurimoto et al.*, 1989].

[6] Infrared spectra of the samples were also obtained at wavenumbers between 1000 and 4000 cm⁻¹ using microscopic Fourier transform infrared (FTIR) spectrometers (JASCO IRT-30). The doubly polished samples with a thickness of less 20 μm were prepared for the IR analysis. The samples were measured by unpolarized radiation with an IR light source, KBr beam-splitter, and an MCT detector. Several hundreds scans were accumulated for each spectrum with a 4 cm⁻¹ resolution. Apertures of 20 × 20 μm were used for selecting sample areas for the measurements.

3. Results and Discussion

[7] Run products consisted dominantly of majoritic garnet with minor amounts of stishovite and Ca-rich aluminous silicate (CAS phase) as shown in Figure 1. A liquid layer was present in both the run products formed at 1400 and 1500°C. The majoritic garnets contain significant amounts of sodium and titanium, up to 1.6 wt% Na₂O and 1.6 wt% TiO₂. The representative compositions are listed in Table 1. The chemical compositions of majorite obtained in this study are similar to those obtained in the anhydrous experiments on MORB composition at similar P-T conditions [*Irifune et al.*, 1986; *Ono and Yasuda*, 1996]. The trace elements in the garnets have a positive correlation with the Si cation, which can be explained by the majorite substitution [*Ono and Yasuda*, 1996].

[8] Hydrogen ion intensity from the synthesized majorite is shown in Figure 2 as a function of sputtered time. It

rapidly decreased with measurement time and reached a steady state value normalized by the ³⁰Si ion intensity. The high intensity from the sample surface should be due to the adsorbed water on the surface. The SIMS analyses showed that majorites contain 1250 ± 140 ppm OH (by weight) at 1400°C and 1130 ± 180 ppm OH at 1500°C (Table S1¹). There are no significant differences in the hydrogen contents between the two samples, whereas the melt proportion and composition are apparently different in these experiments. This suggests that the water content in coexisting melt has little effect on that in the majorite.

[9] The IR spectra from the synthesized majorites showed hydroxyl absorption around 3350–3650 cm⁻¹ (Figure 3), which are close to those found in the synthesized pyrope [*Ackermann et al.*, 1983; *Geiger et al.*, 1991; *Withers et al.*, 1998] and natural garnets in mantle xenoliths [*Aines and Rossmann*, 1984; *Bell and Rossmann*, 1992b]. The hydroxyl absorptions consist of a sharp peak at 3580 cm⁻¹ and a broad peak around 3450 cm⁻¹. The latter broad band is likely from the surface-adsorbed water as molecular clusters on the majorite crystals, and therefore we attempted to model the spectra mathematically using a Gaussian peak-fitting routine to extract the peak from the molecular water. The OH concentration was calculated from the sharp band at 3580 cm⁻¹ according to Lambert-Beer's law. Using an integral molar absorption coefficient of 3160 ± 330 for pyrope [*Bell et al.*, 1995], it is found that majorite contains 850 ppm OH. This value is semi-quantitative because of the uncertainty in the application of the pyrope molar absorption coefficient and large error for the sample thickness of the very thin sections (<20 μm), but it is similar magnitude to those determined by SIMS analyses.

[10] The hydroxyl peak at 3580 cm⁻¹ is close to that of hydrogarnet substitution SiO₄ = (OH)₄, which is located at 3600 cm⁻¹ observed for pyrope garnet [e.g., *Ackermann et al.*, 1983]. The slightly different peak position is probably due to the chemical complexity in our majorite, which causes multiple coordination of the hydroxyl defect. The large Ca ion in the dodecahedral position may result an increase in interatomic distance and lowering their vibrational energy. The hydrogarnet substitution is therefore the most likely mechanism for hydroxyl incorporation in majoritic garnet under conditions of the transition zone. In previous experiments, *Withers et al.* [1998] showed that hydrogarnet component was absent in end-member pyrope above 7 GPa. On the other hand, *Lu and Keppler* [1997] reported that the solubility of water in pyrope with natural composition

¹ Auxiliary material available at <ftp://ftp.agu.org/apend/gl/2003GL018127>.

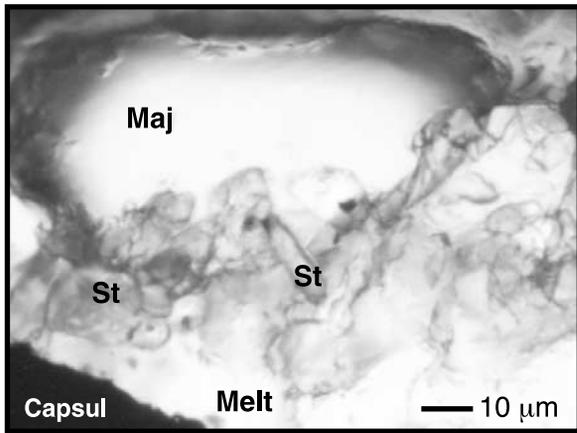


Figure 1. Plane polarized photomicrograph shows the run product at 20 GPa and 1500°C. The sample is mostly composed of majoritic garnet (Maj) with minor stishovite (St) and liquid.

increased with pressure to 200 ppm OH at 10 GPa. *Bolfan-Casanova et al.* [2000] found that the hydroxyl content in tetragonal majorite synthesized in the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$ contained 1280 ppm OH, which is similar to the value obtained in the MORB composition in this study.

[11] Water is introduced into the basaltic crust by hydrothermal alteration at the mid-oceanic ridge up to about 5 wt%, being incorporated in hydrous minerals and as interstitial water [e.g., *Staudigel et al.*, 1995]. The trapped water in oceanic crust is transported into the mantle at the subduction zone, but the descending basaltic crust releases most of H_2O by the amphibolite-eclogite transformation at relatively shallow depths (~ 50 km). Trace water can be accommodated in lawsonite in the eclogite along a low temperature geotherm [*Schmidt and Poli*, 1998; *Ono*, 1998; *Okamoto and Maruyama*, 1999] (Figure 4). In further deep, even along such a cold geotherm, the subducted oceanic crust becomes “dry” eclogite including no hydrous phases at depths deeper than 300 km. However, recent study on the diamond-grade eclogites from the Kokchetav ultrahigh-pressure metamorphic terrane revealed that considerable amounts of water were included in the nominally anhydrous minerals such as omphacite (~ 3020 ppm OH) and garnet

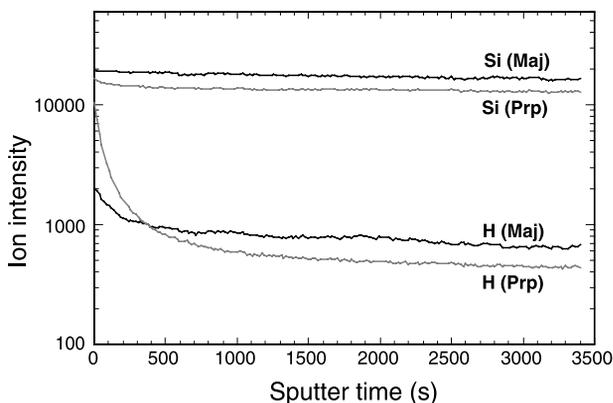


Figure 2. Secondary ion intensities of ^1H and ^{30}Si of the synthesized majorite (black line) and standard pyrope (gray line), as a function of sputter time.

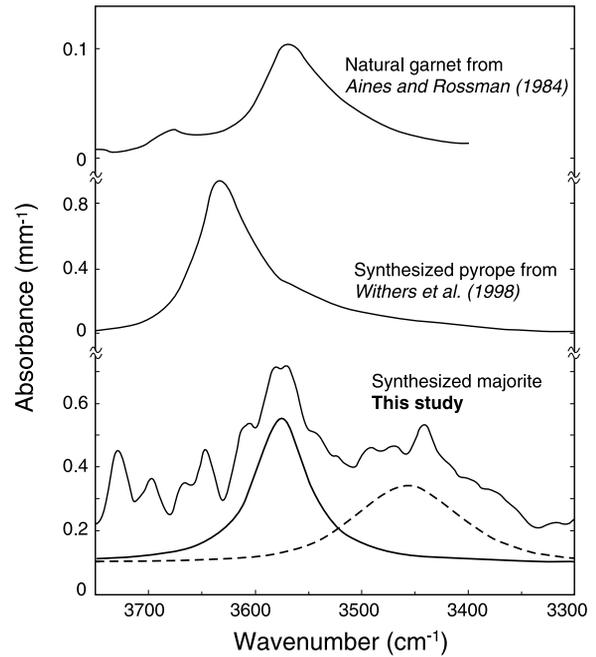


Figure 3. Infrared spectra of the synthesized majorite (bottom line), composed of sharp peak at 3580 cm^{-1} and broad peak at 3450 cm^{-1} , with a result of peak fitting routine. The broad peak may represent valence vibration of H_2O clusters. Interference fringes appear in the spectra because of small absorbance in our thin sample ($<20\text{ }\mu\text{m}$). Hydroxyl spectra of natural garnet from mantle xenolith [*Aines and Rossman*, 1984] and of synthesized pyrope at 3 GPa and 1000°C [*Withers et al.*, 1998] were shown for comparison.

(~ 240 ppm OH) that sums up to 1300 ppm OH in the bulk rock [*Katayama and Nakashima*, 2003]. The eclogite transforms to garnetite around 400 km depth, which is predominantly composed of majorite (90 vol%) with minor amounts of stishovite [*Irifune et al.*, 1986]. This study shows that such

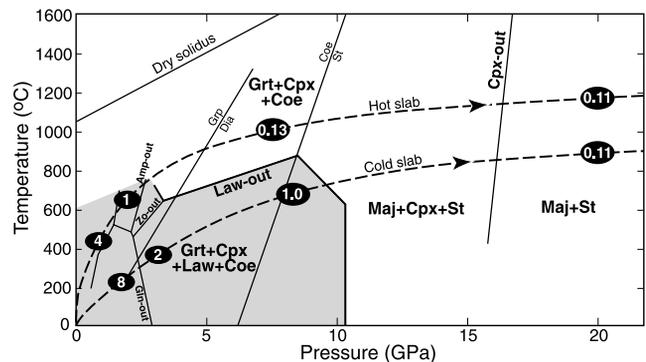


Figure 4. Water content of the basaltic crust along hot and cold subduction. The phase relations in the MORB composition were taken from *Okamoto and Maruyama* [1999] and *Irifune and Ringwood* [1993]. Shaded area represents stability fields of hydrous minerals in the MORB composition. The water contents (circled number as wt% OH) were estimated from this study (20 GPa), *Katayama and Nakashima* [2003] (7 GPa, 1000°C), and from *Okamoto and Maruyama* [1999].

majoritic garnet can contain 1130 to 1250 ppm OH. Stishovite can also incorporate trace hydroxyl coupled with the aluminum substitution up to ~ 150 ppm OH that is one order of magnitude lower than the maximum solubility of OH in the majorite [Pawley *et al.*, 1993]. However, Chung and Kagi [2002] recently reported relatively higher hydrogen in stishovite in the MORB composition (up to ~ 810 ppm OH). These suggest that water included in omphacite and garnet in eclogite can mostly be transferred to majorite and stishovite at the eclogite-garnetite transition. In such a way, more than 1000 ppm OH can be transported into the mantle transition zone (Figure 4). The water in basaltic crust may be further transferred to perovskite in the lower mantle [Murakami *et al.*, 2002; Litasov *et al.*, 2003].

[12] We estimated the total mass of water transported by subducting basaltic crust into the mantle transition zone. The volume of the produced oceanic crust would be 1.0×10^{11} km³ during the last four billion years, assuming the average production rate of 25 km³/y at mid-oceanic ridge [Turcotte and Schubert, 1982]. If these basaltic crusts mostly subducted into the mantle, their total volume is equivalent to that of mantle transition zone. Taking the density into calculation, 2.23×10^{20} kg H₂O could have been carried into the mantle transition zone. This corresponds to about 16 percent of the total water in the present hydrosphere. The mantle transition zone can accommodate large amounts of water, where wadsleyite and ringwoodite can contain up to 3.3 wt% and 2.7 wt% H₂O, respectively [Inoue *et al.*, 1995; Kohlstedt *et al.*, 1996], and therefore this value is approximately only 2% of the maximum solubility of water in the mantle transition zone. Despite of a small amount of water in the nominally anhydrous minerals, it significantly enhances the mobility of point defect and causes mechanical weakening [e.g., Griggs and Blacic, 1965]. The trapped water in the majoritic garnet have therefore great influences on the physical properties of slab in the transition zone.

[13] **Acknowledgments.** We thank Y. Nishihara, S. Ono, M. Murakami and Y. Kuwayama for technical suggestions on experiments, and K. Nagashima and A. Utsunomiya for SIMS analyses. We also appreciate S. Maruyama and S. Omori for discussions on water distribution in the upper mantle. Constructive comments by J.R. Smyth and an anonymous reviewer helped to improve the manuscript. This research is supported by a research fellowship of the Japan Society for the Promotion of Science for Young Scientists to the first author.

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