Stability of dense hydrous magnesium silicate phase G in the transition zone and the lower mantle

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Abstract

Re-examination of the run products in the $\text{Mg}_2\text{SiO}_4\text{-H}_2\text{O}$ system by Ohtani *et al.* (1995) revealed stability of dense hydrous magnesium silicate, phase G, and brucite at 20 GPa and 800°C, and stability of the assemblage with superhydrous phase B + phase G + fluid at 20 GPa and 1000°C under the water saturated conditions. We reported the Raman spectrum of phase G, which suggests existence of silicon ions in the six coordination sites. Brucite, superhydrous phase B, and phase G are stable at least up to 22.5 GPa and around 1000°C, and are the candidates for the hydrous phases in a cold slab descending into the base of the transition zone and the uppermost part of the lower mantle. The X-ray diffraction and the Raman spectra data revealed that the dense hydrous magnesium silicate, phase G, and phase D re-defined by Yang *et al.* (1997) and Kuroda and Irifune (1998) are identical. Phase F by Kanzaki (1991) and Gasparik (1993) is likely to be identical to phase G.

Introduction

Ohtani *et al.* (1997) and Kudoh *et al.* (1997) reported a dense hydrous magnesium silicate, phase G, which has a high measured density of $3.4 \pm 0.2 \text{ g/cm}^3$ comparable to wadsleyite and ringwoodite, although it has a large amount of water about 14.5–18 wt.%. The single crystal analysis of this phase (Kudoh *et al.*, 1997; Yang *et al.*, 1997) implies that it has a stishovite-like structure with all of the silicon ions in single octahedral site. Ohtani *et al.* (1997) tentatively named this hydrous phase as phase G.

In the previous paper, Ohtani *et al.* (1995) reported the stability relations in the $\text{Mg}_2\text{SiO}_4\text{-H}_2\text{O}$ system based on the electron probe microanalysis without detailed X-ray diffraction study. In this work, we made further X-ray examination of these run products and re-evaluated the stability field of phase G in the $\text{Mg}_2\text{SiO}_4\text{-20.4 wt.\% H}_2\text{O}$ system.

Kuroda and Irifune (1998) and Yang *et al.* (1997) also synthesized the same dense hydrous magnesium silicate and called it “phase D” ignoring differences in the X-ray diffraction pattern from the original phase D reported by Liu (1987). Kanzaki (1991) reported existence of phase F at about 15.5 GPa and 700–800°C, and Gasparik (1993) showed the stability field of phase F in the $\text{MgO-SiO}_2\text{-H}_2\text{O}$ system. We critically evaluated the X-ray powder diffraction data and the synthesis conditions of Kuroda and Irifune’s and Yang’s D, Kanzaki’s F, and phase G in the

MgO-SiO₂-H₂O system, and concluded that all of these phases are identical.

Experimental

Details of the procedures of the high pressure and temperature synthesis experiments are given in Ohtani *et al.* (1995). Several grains of single crystal in the run products were picked up and examined by the X-ray powder diffraction using the Debye-Scherrer camera with the Gandolfi attachment. The Raman spectrum of phase G was obtained by using the micro-Raman spectrometer (NRS-2000). Excitation was provided by the 514.5 nm line of Ar⁺ laser (NEC) with the power of 30mW. The laser beam was focussed to the sample area of around 1 μ m by using the objective lens ($\times$ 100). The scattered light was measured by a single monochromator with the cooled CCD multi-channel detector system. The sampling time was two accumulations of 5 seconds for each measurement. The compositions of the phases were determined by using the electron probe microanalyser (JEOL8800) with the operating condition of 10 nA and 15 kV (the spot size is c.a. 1 μ m).

Results and discussion

Table 1 summarizes the revised experimental results obtained in this work. The results for the other runs are the same as those reported by Ohtani *et al.* (1995). We could observe coexistence of superhydrous phase B and phase G in the higher temperature portion of the charge conducted at 22 GPa and 1000°C. However, brucite and phase G coexist in the lower

TABLE 1. Experimental conditions and the results.

Run No.	Pressure GPa	Temperature °C	time min.	Results
N4	17.4	950(20)* 850**	70	E+fluid SuB+G+fluid+trA?
106	18.5	1000(10)	90	SuB+G+fluid
N5	19.0	940(20)	40	SuB+G+fluid
N9	19.8	845(10)	15	Bc+G+fluid
114	22.5	1000(10) 900**	30	SuB+G+fluid Bc+G+fluid
102#	14	1000(10)	60	A+CEn+fluid
N7#	14.7	925(25) 825**	60	E+fluid A+CEn+fluid
N3#	14.7	945(25) 845**	65	E+fluid A+CEn+fluid
103#	16.0	1000(10)	60	E+fluid
E15H03##	23.0	1300(10)	180	SuB+G+fluid

#, Results from Ohtani *et al.* (1995)

##, Bulk composition of the starting material is MgSiO₃-15wt.%H₂O

*, Numbers in parentheses are temperature fluctuation during the run.

**, Cold end of the Pt capsule; E, phase E; fluid, aqueous fluid; SuB, superhydrous phase B; G, phase G; Bc, brucite; A, phase A; CEn, Clinoenstatite.

FIG. 1. Chemical composition and water content of phase G. The chemical compositions of the similar phase reported by Kanzaki (1991) and Gasparik (1993) are also given in this figure. Runs EH01 and EH04 are from Ohtani *et al.* (1997).

temperature portion of the same charge. The structural formula of phase G was presented by Ohtani *et al.* (1997) as $\text{Mg}_{1.14}\text{Si}_{1.73}\text{H}_{2.81}\text{O}_6$, which suggests that this phase has some non-stoichiometric nature with variation of Mg/Si ratio and water content. Fig. 1 summarizes the variation of the Mg/Si ratio and water content of the dense hydrous magnesium silicate, phase G, in the run products together with those reported by Ohtani *et al.* (1997). The present result implies that the Mg/Si ratio and the water content of phase G differ significantly with the synthesis conditions.

Raman spectra of the hydrous phase G synthesized at 23 GPa and 1300°C in the bulk MgSiO_3 -15 wt.% H_2O composition are given in Fig. 2. We observed a clear Raman spectrum of OH vibration for this phase in the range of the wave number around 2850 cm^{-1} which is consistent with the recent measurement by Frost and Fei (1998). We observed several Raman peaks for phase G with a strong peak at 785 cm^{-1} , which is close to the frequency in the vibration mode of the Si-O bonding (A_{1g} mode) in stishovite SiO_2 (Hemley *et al.*, 1986). The Raman spectrum similar to that of stishovite suggests octahedral silicon in phase G, which is consistent with the single crystal X-ray diffraction analysis of phase G (Kudoh *et al.*, 1997; Yang *et al.*, 1997). Fig. 3 shows the preliminary phase diagram for the Mg_2SiO_4 -20.8wt% H_2O composition at high pressure. The phase diagram is drawn by taking into account of the recent works in the Mg_2SiO_4 - H_2O system (Kanzaki, 1991; Gasparik, 1993; Luth, 1993 and 1995; Inoue, 1994; Kuroda and Irifune, 1998; Frost and Fei, 1998). The reaction of superhydrous phase B and water to brucite and phase G at pressures above 20 GPa can be written as follows; $\text{Mg}_{10}\text{Si}_3\text{O}_{14}(\text{OH})_4$ (Superhydrous phase B) + $8.45\text{H}_2\text{O}$ → $8\text{Mg}(\text{OH})_2$ (Brucite) + $1.73\text{Mg}_{1.14}\text{Si}_{1.73}\text{H}_{2.81}\text{O}_6$ (Phase G). Kudoh *et al.* (1997) reported that the crystal structure

FIG. 2. Raman spectra of the hydrous phase G (23 GPa and 1300°C in MgSiO_3 -15wt.% H_2O composition) in the low frequency (a) and hydroxyl stretching (b) regions.

of phase F in their previous work (Kudoh *et al.*, 1995) was in error, and the phase they analyzed was actually superhydrous phase B instead of phase F. The similarities in the X-ray diffraction patterns (see Table 2) and chemical compositions of phase G and phase F by Kanzaki (1991) and Gasparik (1993) indicate that their phase F is identical to phase G. The chemical

FIG. 3. Stability diagram of the Mg_2SiO_4 -20.4wt.% H_2O system at high pressure. The phase diagram is drawn by taking into account of the recent works in the Mg_2SiO_4 - H_2O system (Kanzaki, 1991; Gasparik, 1993; Luth, 1993 and 1995; Inoue, 1994; Kuroda and Irifune, 1998). α , olivine; L, silicate liquid; fluid, aqueous fluid; Cd, hydroxyl chondrodite (Yamamoto and Akimoto's phase D (Yamamoto and Akimoto, 1974, 1977)); CEn, clinoenstatite; A, phase A; E, phase E; β , modified spinel; SuB, superhydrous B; G, phase G. Phase G, phase F by Kanzaki (1991), and phase D by Kuroda and Irifune (1997) and Yang *et al.* (1977) are identical. The dashed curve, PER, represents the estimated minimum geotherm within the slab in Peru (Helffrich and Brodholt, 1991).

compositions of the dense hydrous magnesium silicate reported by Kanzaki (1991) and Gasparik (1993) are also given in Fig. 1. The present phase relation shown in Fig. 3 is generally consistent with the phase relation of serpentine reported by Kubo *et al.* (1997). Our result strongly suggests that brucite and dense hydrous magnesium silicate phase G are the candidates for hydrous phases at least in a locally water-enriched slab descending into the base of the transition zone and the uppermost part of the lower mantle.

There are some confusions on the name of the present dense hydrous magnesium silicate phase G. Yang *et al.* (1997) and Kuroda and Irifune (1998) also synthesized the same phase and called it as phase D, although they could not specify the origin of the differences between the X-ray diffraction patterns of this phase and that of the original phase D reported by Liu (1987). The X-ray diffraction data of phase G, "phase D" reported by Kuroda and Irifune (1998), the original phase D by Liu (1987), and phase F by Kanzaki (1991) are given in Table 2. The X-ray diffraction patterns in this table imply that phase G, "phase D" by Kuroda and Irifune (1998), and phase F by Kanzaki (1991) are likely to be identical.

Table 2 shows clear differences in the X-ray diffraction patterns between phase G and the original phase D by Liu (1987). There are three possibilities on existence of Liu's phase

Table 2. X-ray diffraction data of ultradense hydrous magnesium silicate, phase G, D and F.

Phase G*, Run 106 (18.5GPa, 1000°C)			Phase D by Kuroda and Irifune (1998)		Phase F by Kanzaki (1991)		Phase D by Liu (1987)	
hkl	d _{obs}	I _{obs}	d _{obs}	I _{obs}	d _{obs}	I _{obs}	d _{obs}	I _{obs}
001	4.330	20	4.31	20	4.34	100	9.5	10
100	4.118	10	4.11	15			4.3	15
							3.37	15
101	2.977	100	2.996	100	2.991	10	3.00	100
							2.53	15
110	2.372	5	2.391	10				
11-1	2.085	100	2.098	90				
021	1.8596	20	1.867	25				
112	1.6001	100	1.608	60	1.603	5	1.61	80
202	1.4903	2	1.499	10			1.496	20
21-1	1.4650	20	1.472	20				
300	1.3747	50	1.38	30			1.39	20
103	1.3621	5	1.368	10				
301	1.3100	5	1.316	5				
113	1.2356	20	1.238	10				
203	1.1823	20	1.186	10				
302	1.1496	10	1.152	10				
31-1	1.1066	20	1.109	10				
004	1.0846	10	1.087	5				
21-3	1.0605	10	1.063	10				
22-2	1.0448	10	1.047	10				
40-1	1.0054	2	1.006	5				

*, Cell parameters are calculated with a hexagonal unit cell, $a=4.760(5)\text{\AA}$, $c=4.333(6)\text{\AA}$, $V=85.0(3)\text{\AA}^3$. Trigonal symmetry; Space group $P\bar{3}1m(\text{No.162})$ measured density $3.4\pm0.2\text{g/cm}^3$.

D; (1) it is a mixture of phase G and some contaminated phases, (2) it is a metastable phase formed in the diamond anvil cell due to a short run duration, a large temperature gradient, and/or no sealing of water during heating, and (3) it really exists stably at higher pressure (Ohtani *et al.*, 1998), i.e., it could be a superlattice of phase G as was suggested by Frost and Fei (1998). We need further detailed studies to clarify the origin of the differences between the X-ray diffraction data of phase G and the original phase D defined by Liu (1987).

Acknowledgements—The authors thank Y. Ito of Tohoku University for EPMA analysis, and A. Suzuki and H. Mizobata of Tohoku University and Y. Ohkubo of JASCO corporation Ltd. for micro-Raman spectroscopic measurement of the run products. This work was supported by a grant-in-aid of Scientific Research (A) from Ministry of Education, Science, Sports, and Culture of the Japanese Government No. 09304051 to E. Ohtani.

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Received November 5, 1997; accepted October 2, 1998