Express Letter

Experimental evidence for a hydrous transition zone in the early Earth's mantle

Tatsuhiko Kawamoto [a,*], Richard L. Hervig [a,b], John R. Holloway [a,c]

[a] Department of Geology, Arizona State University, Tempe, AZ 85287, USA
[b] Center for Solid State Science, Arizona State University, Tempe, AZ 85287, USA
[c] Department of Chemistry, Arizona State University, Tempe, AZ 85287, USA

Abstract

Partition coefficients of H_2O between β and γ phases of olivine stoichiometry and coexisting ultra mafic melt have been estimated to be $> 0.1 \pm 0.04$ (1σ) and 0.04, respectively; based on experiments at 15–16.5 GPa, 1300–1500°C in a hydrous KLB-1 peridotite system. The high H_2O contents of β (1.5–3 wt%) and γ phases (0.7 wt%) would form a reservoir for H_2O after cooling and crystallization of a hydrous magma ocean. Subsequent upwelling of this hydrous mantle would release H_2O at the β phase–olivine boundary near 400 km depth, inducing partial melting of the peridotite to produce hydrous ultramafic magma. Most subducting hydrous minerals dehydrate at pressures shallower than 6.5 GPa if the down-dragged hydrous peridotite follows a P–T path hotter than 900°C at 8 GPa and cannot re-hydrate the transition zone. Therefore, the above proposed partial melting would gradually deplete the H_2O reservoir, which is consistent with the decrease in the activity of ultramafic magmatism and the apparent degree of melting of komatiites from the Archean to the Mesozoic.

1. Introduction

The Earth is characterized by the existence of liquid H_2O, which has a significant effect on physico-chemical processes in the planet. Therefore, it is important to know the distribution of H_2O or OH in the solid Earth. Since the pioneering work by Ringwood and Major [1] and Sclar et al. [2], several hydrous phases have been produced in the MgO–SiO_2–H_2O system under high pressure and tempera-

ture conditions and proposed as H_2O reservoirs in the mantle (see Thompson [3] for a comprehensive review). Recently, we have started to address the stability fields of these hydrous phases in a peridotitic system and suggested dense hydrous magnesium silicates such as phase E, clinohumite, chondrodite, and phase A can be stable only in relatively cold subduction zones (< 800°C at 9 GPa) [4]. The most plausible phase to contain a significant amount of H_2O at mantle temperatures and, at the same time, abundant enough to represent a significant reservoir of H_2O, is the β phase [5]. Smyth [5] predicted that the β phase can possess up to 3.3 wt%

* Corresponding author. Fax: + 1 602 965 8102. Tel: + 1 602 965 6598. E-mail: adtxk@asuvm.inre.asu.edu

H_2O with a formula $(Mg,Fe)_{1.75}SiO_4H_{0.5}$. Initial attempts to synthesize β phase under nominally anhydrous conditions demonstrated H_2O contents of up to 0.4 wt% [6,7]. This was followed by the synthesis of a fully hydrated β phase containing several weight percent H_2O at H_2O-saturated conditions [8–10]. In this paper, we will report partition coefficients of H_2O between the β phase and coexisting melt in a hydrous peridotite system and hypothesize the existence of a reservoir for H_2O through cooling and crystallization of a hydrous magma ocean.

2. Experimental

We carried out a series of experiments with hydrous peridotite to determine the H_2O contents of the β phase at higher temperatures than those of previous studies (Table 1, Fig. 1) [6–10]. As a starting material, we used a mixture of a gel of Mg-free KLB-1 peridotite composition [11] and brucite, resulting in an overall H_2O content of 13.7 wt%. Two additional experiments were conducted with 3.4 wt% H_2O. Experiments were performed in a Walker type multi-anvil apparatus at Arizona State University and a uniaxial split sphere anvil apparatus at the State University of New York at Stony Brook (USSA-2000). Grain sizes of minerals were 10–100 μm. Major element compositions of phases were determined by electron microprobe. H concentrations

were determined with a secondary ion mass spectrometer (SIMS) at the Center for Solid State Science, Arizona State University, following the analytical procedures described in Ihinger et al. [12]. The ion beam diameter was ~ 20 μm. Chemical compositions of β and γ phases roughly fall between olivine and phase E. Hence, we used the olivine-phase E calibration to quantify the H^+ signal in the β and γ phase by assuming that olivine is anhydrous and the H_2O content of phase E is 7.6 wt% [9].

3. H_2O concentrations of β and γ phases

The H_2O concentrations were determined in β and γ phases synthesized at 1300–1500°C, 13.5–16.5 GPa. The results are shown in Fig. 2, plotted with the data of Inoue et al. [9], obtained in the MgO–SiO_2–H_2O system for comparison. Some of our data deviate from the theoretical line between the anhydrous and fully hydrated β phase compositions [5]. This indicates that vacancies also play a role [8] and/or the mechanism of hydration of $(Mg, Fe)_2SiO_4$ could be different from Mg_2SiO_4 [10]. The degree of hydration of the β phase decreases as run temperature increases (Fig. 2). This decrease is the result of an increase in the melt proportion with temperature. Based on the modal compositions of coexisting phases and H_2O contents of β phases, we estimated

Table 1
Summary of experimental conditions and results

Number	H_2O [a]	P	T	t	Capsule	Mineral phases [b]	H_2O in β or γ	H_2O in melt [c]	Partition coefficient [d]
	(wt%)	(GPa)	(°C)	(h)					
1	13.7	15.5	1500	0.3	AuPd	L, Gt, En, β	1.52 (22)	26.2	0.06
2	13.7	15.5	1500	0.9	AuPd	L, Gt, En, β	1.52 (16)	22.7	0.07
3	13.7	15.5	1360	1.0	AuPd	L, Gt, β, Ph E	3.13 (25)	38.0	0.08
4	13.7	15.5	1600	1.0	AuPd	L, Gt			
5	13.7	13.5	1425	3.0	AuPd	L, Gt, En, β, Ph E	2.89 (14)	21.5	0.13
6	13.7	16.5	1400	3.3	AuPd	L, Gt, Stish, β, Ph E	2.61 (14)	41.9	0.06
7	3.4	15.5	1450	1.0	AuPd	L, Gt, β	1.95 (25)	11.1	0.18
8	3.4	15.5	1300	4.0	Au	L, Gt, β, γ, Stish	1.83 (23) β, 0.73 (10) γ	17.4	0.11 β, 0.04 γ

[a] H_2O abundance in a starting material. [b] Order from hot part to cold one along thermal gradient, L = liquid, Gt = garnet, En = enstatite, Ph E = phase E, Stish = stishovite. [c] Calculated H_2O content in partial melts. [d] Partition coefficient of H_2O between β or γ phase of olivine and melt.
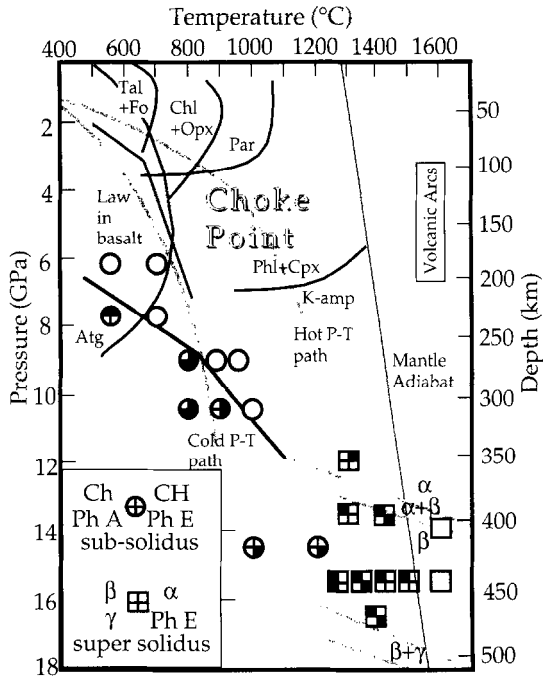
Fig. 1. A $P-T$ projection of the stability of dense hydrous magnesium silicates in H_2O-saturated KLB-1 peridotite at sub-solidus [4] and supersolidus conditions (this work). $\bigcirc$ = a dehydrated assemblage of olivine, two pyroxenes, garnet and H_2O fluid; $\square$ = an assemblage: liquid and garnet (and enstatite at 14 GPa). Two experiments at 1300 and 1450°C and 15.5 GPa were conducted in the 3.4 wt% total H_2O KLB-1 system. The thermal gradient along the capsule was estimated to be 200°C at pressures greater than 12 GPa [8]. Other data are lawsonite in a basaltic system [15]; antigorite [14] and other hydrous minerals in relevant systems for peridotite [13]. Schematic $P-T$ paths in the down-dragged hydrous mantle and the averaged mantle adiabat [30] are also shown. Phase boundaries among α, $\alpha + \beta$, β, and $\beta + \gamma$-$(Mg_{0.9}Fe_{0.1})_2SiO_4$ are after Katsura and Ito [31]. Tal = talc; Atg. = antigorite; Fo = forsterite; Chl = chlorite; Opx = orthopyroxene; Par = pargasite; Phl = phlogopite; Cpx = clinopyroxene; K-amp = K-richterite; CH = clinohumite; Ch = chondrodite; Ph A = phase A; Ph E = phase E.
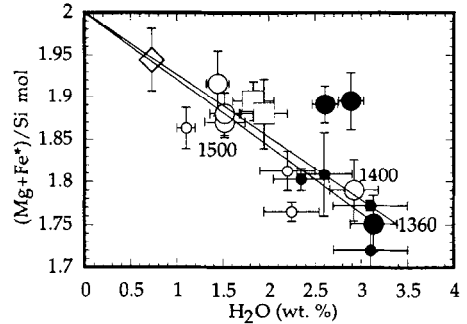

Fig. 2. $(Mg + Fe^*)/Si$ atomic ratios vs. H_2O contents of hydrous β and γ phases. The present data (large circles, squares and a diamond) and those from Inoue et al. conducted in the SiO_2-MgO-H_2O system (small circles) [9] roughly lie on the line between the theoretical end member: $(Mg, Fe)_2SiO_4$ and $(Mg, Fe)_{1.75}SiH_{0.5}O_4$ (3.3 wt% H_2O for $Mg/(Mg + Fe) = 1$, and 3.2 wt% for 0.9) [5]. Solid symbols represent samples coexisting with phase E. The diamond represents the γ phase. Most β phase determinations are from runs conducted in the 13.7 wt% total H_2O KLB-1 system. One γ phase and two β phases (open squares) with 1.83 and 1.95 wt% H_2O were from runs in the 3.4 wt% total H_2O KLB-1 system. Numerals represent run temperatures in 13.7 wt% H_2O-bearing system at 15.5 GPa.

the proportion of melt to range from 15% to 60% and calculated the H_2O concentration in partial melts to range between 10 and 40 wt% (Table 1). The greatest source of error for the calculation of the partition coefficient was the estimation of the modal compositions, and we estimated the error in the modal amounts of each phase to be $\pm 20\%$ relative. The partition coefficient of H_2O between the β phase and melt was calculated to be 0.1 ± 0.04 (1σ) (Fig. 3). We assumed that all excess H_2O was

dissolved in the partial melts and no H_2O was lost through capsule walls during experiments. These two assumptions may not be true. Therefore, we should point out that the calculated partition coefficient is a minimum value. In an experiment at 1300°C, 15.5 GPa, in the 3.4 wt% total H_2O-bearing KLB-1 system, a β phase with 1.8 wt% H_2O, 1.90 $(Mg + Fe^*)/Si$ mol, and 0.93 $Mg/(Mg + Fe)$ mol coexists with a γ phase with 0.73 wt% H_2O, 1.94 $(Mg +$
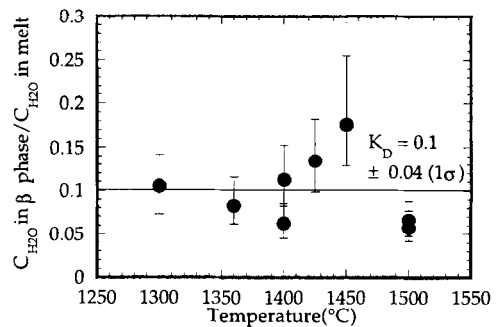

Fig. 3. Calculated partition coefficient of H_2O between β phase and coexisting hydrous melts vs. temperature. The thermal gradient along a capsule was estimated to be 200°C. See text for limitation of this estimation.

Fe*)/Si mol and 0.86 Mg/(Mg + Fe) mol (Table 1, Fig. 2). Our result indicates that the partition coefficient of H_2O between the γ phase and melt is about 0.04.

4. Choke point of subducting hydrous minerals

While some H_2O is transported into the Earth's interior in hydrous minerals through subduction processes, most hydrous minerals dehydrate at pressures shallower than 6.5 GPa when the down-dragged hydrous peridotite follows a hot $P-T$ path [13] (> 900°C at 8 GPa, Fig. 1). Only in a cold subduction zone can dense hydrous magnesium silicates be formed in the down-dragged flow of the base of the mantle wedge, by release of H_2O from decomposing antigorite [14] and lawsonite in the basaltic layer [15,4] (Fig. 1). However, the scarcity of magmatism above subducting slabs deeper than 200 km [16] suggests that downgoing peridotite and basalt almost completely dehydrate at 3.5–6.5 GPa (the choke point) to form volcanic arcs (Fig. 1). Beyond the dehydration of phlogopite, H_2O is carried by K-richterite and nominally anhydrous minerals. Because the atomic H/K ratio of K-richterite is unity, 0.1 wt% K_2O in the down-dragged peridotite will allow 200 ppm H_2O to be carried down into the K-richterite-bearing peridotite. Similarly, nominally anhydrous pyroxenes can contain 200–500 ppm H_2O as impurities [17] and introduce a few hundred ppm H_2O to the deep mantle. Therefore, subduction processes are not able to bring more than several hundred ppm H_2O into the transition zone.

5. Crystallization of hydrous magma ocean

Based on the present results, we hypothesize that a hydrous mantle transition zone could have existed in the early Earth. Calculations of the partitioning of H between the Earth's magma ocean and the primary fluid released from planetesimals, with or without consideration of the effect of metallic iron, have suggested that the Earth's magma ocean could contain up to 1–3 wt% H_2O [18,19]. During the cooling of such a hydrous magma ocean, hydrous β and γ phases would precipitate at depths of 400–670 km,

forming an H_2O reservoir. Assuming modal 60% β phase and the above partition coefficient, the amount of H_2O in the transition zone would be > 0.06–0.18 wt%. Subsequent upwelling of this hydrous mantle would release H_2O at the β phase–olivine boundary. The H_2O lowers the peridotite solidus temperature from 2000°C [20] to 1300°C at 15 GPa, inducing partial melting of the peridotite to produce hydrous magma. Due to the choke point, we estimate that subduction processes can add at most several hundred ppm H_2O to the transition zone, far less than a few weight percent contained in the magma ocean. The subduction processes do not re-hydrate the transition zone to the levels attained just after the cooling of hydrous magma ocean. This partial melting process would, therefore, gradually deplete the H_2O reservoir. Based on thermodynamic calculations and seismic data on the olivine–β phase boundary, Wood suggested that the β phase possesses less than 200 ppm H_2O at the present mantle transition zone [21], which is concordant with our hypothesis.

Recently, high-pressure studies [22,8,23] have demonstrated that partial melts of hydrous peridotite at temperatures near the solidus and at pressures greater than 7 GPa are more Mg-rich than those in a dry system, suggesting a wet origin for komatiite. Although direct measurement of the H_2O content of melt inclusions in olivine in 2.7 Ga Zimbabwe komatiite indicates only 0.2 wt% H_2O at 25 wt% MgO in the rock [24], there is some evidence supporting the existence of wet komatiites. Lapilli tuff and volcanic breccia are reported in some Archean komatiites, indicating that those magmas contained volatiles [25]. Based on experimental duplication of spinifex textures, Grove et al. suggested that komatiites were hydrous melts and the nucleation density of olivine crystals was lowered [26]. Generation of komatiites could be triggered by the above proposed melting model, which is consistent with the decrease in the activity of ultramafic magmatism and the apparent degree of melting of komatiites from the Archean to Mesozoic [27–29]. If this is the case, primary komatiites should have 0.5– ~ 1 wt% H_2O, but their values would have been lowered through chemical reaction with upper mantle peridotite during migration to the surface. The chemistry of partial melts in the wet peridotite system at pressures greater than 3 GPa still remains unknown and should be

obtained with similar precision to that of dry experiments in order to evaluate our hypothesis.

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