The effect of Fe on olivine H₂O storage capacity: Consequences for H₂O in the martian mantle

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ABSTRACT

To investigate the influence of chemical composition on the behavior of H_2O in Fe-rich nominally anhydrous minerals, and to determine the difference between H₂O behavior in the martian and terrestrial mantles, we conducted high-pressure H₂O storage capacity experiments employing a wide range of olivine compositions. Experiments were conducted with bulk compositions in the system FeO-MgO-SiO₂-H₂O with Mg no. [Mg no. = $100 \times \text{molar Mg/(Mg+Fe)}$] ranging between 50 and 100 at 3 GPa in a piston-cylinder and at 6 GPa in a multi-anvil apparatus. Experiments at 3 GPa were conducted at 1200 °C, with f_{02} buffered by the coexistence of Fe and FeO, and at 1300–1500 °C in unbuffered assemblies. Experiments at 6 GPa were conducted at 1200 °C without buffers. Experiments at 1200 °C produced olivine+orthopyroxene+hydrous liquid (liq), and higher T experiments produced olivine+liq. Additionally, we synthesized a suite of 7 olivine standards (Mg no. = 90) for low blank secondary ion mass spectrometry (SIMS) analysis of H in multi-anvil experiments at 3-10 GPa and 1250 °C, resulting in large (200-400 µm) homogeneous crystals with 0.037 to 0.30 wt% H₂O. Polarized Fourier transform infrared (FTIR) measurements on randomly oriented grains from the synthesis experiments were used to determine principal axis spectra through least-squares regression, and H contents were calculated from the total absorbance in the OH stretching region. Using these olivines as calibrants for SIMS analyses, the H contents of olivines and pyroxenes from the variable Mg no. experiments were measured by counting ¹⁶OH ions. Ignoring any matrix effects owing to variation in Mg no., H contents of olivine and pyroxene increase linearly with decreasing Mg no. At 6 GPa and 1200 °C, olivine H contents increase from 0.05 to 0.13 wt% H₂O (8360 to 23 900 H/10⁶ Si) as olivine Mg no. decreases from 100 to 68, and at 3 GPa and 1200 °C olivine H contents increase from 0.017 to 0.054 wt% (278 to 10 000 H/106 Si) as Mg no. decreases from 100 to 55. The partition coefficient for H between pyroxene and olivine, $D_{\rm H}^{\rm opx/ol}$, decreases from 1.05 at 3 GPa and 1200 °C to 0.61 at 6 GPa and 1200 °C. The storage capacity of Fe-rich olivines with compositions expected in the martian mantle is ~ 1.5 times greater than those in the terrestrial mantle, suggesting that the geochemical behavior of H_2O in the mantles of the two planets are quite similar. If 50% of the K₂O on Mars remains in its mantle (Taylor et al. 2006), then a similar or greater proportion of the H₂O is also in the mantle. Given accretionary models of the total martian H₂O budget (Lunine et al. 2003), this suggests concentrations of 100–500 ppm H_2O in the martian mantle and 0.1–1.9 wt% H₂O in primary martian basalts.

Keywords: Olivine, H₂O storage capacity, Mars, infrared spectroscopy, ion microprobe

INTRODUCTION

Small concentrations of hydrogen dissolved in mantle minerals play a critical role in the dynamics of planetary interiors. Trace amounts of hydrogen dissolved in nominally anhydrous minerals have a substantial influence on the viscosity of convecting interiors (Karato and Wu 1993; Mei and Kohlstedt 2000a, 2000b) as well as the strength of planetary lithospheres (Kohlstedt et al. 1995; Mackwell et al. 1990), and thereby influence planetary tectonic evolution. Dehydration of nominally anhydrous peridotite may lead to hydrous partial melting in several

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tectonic environments (Hirth and Kohlstedt 1996; Asimow and Langmuir 2003; Hirschmann 2006), including those significantly deeper than the sources of planetary basalts (e.g., Bercovici and Karato 2003; Hirschmann et al. 2005). The storage capacity of hydrogen, considered as H_2O , in planetary mantles is also a key parameter influencing the history of volatile fluxes from planetary interiors to the surface (Rüpke et al. 2004; Hirschmann 2006). Importantly, the H_2O storage capacities of planetary interiors may differ substantially according to compositional and thermal differences between planets.

As in Earth, the upper parts of the martian mantle are composed chiefly of olivine and its higher pressure polymorphs, wadsleyite and ringwoodite. These phases are known to be

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capable of chemically incorporating large amounts of H₂O as hydroxyl (Kohlstedt et al. 1996). For example, the Earth's mantle has the theoretical capacity to store more than two oceans worth of H₂O within these phases alone (Smyth et al. 2006). However, the storage capacity of olivine in the martian mantle may be quite different, as it is richer in FeO. Whereas Earth's mantle has approximately 8.1 wt% FeO (McDonough and Sun 1995), estimates of the martian mantle range from 16.0–18.7 wt% (Morgan and Anders 1979; Dreibus and Wänke 1985; Bertka and Fei 1997). These differences translate to differences in the mean Mg no. of olivine from 89.5 in Earth's mantle to 75–77 in Mars', where Mg no. is defined as 100 times the molar Mg/(Mg+Fe) ratio.

In experiments at 300 MPa, Zhao et al. (2004) observed an exponential increase in H content of olivine with decreasing Mg no. for compositions spanning pure forsterite (Mg no. = 100) to a Mg no. of 83.1. The thermodynamic model of Zhao et al. (2004) predicts that martian composition olivine, at 1200 °C and 6 GPa, could have an H₂O storage capacity in excess of 1 wt% H₂O. If applicable to the martian mantle, this tremendous storage capacity would likely have significant effect on partitioning of H₂O between solid residue and silicate melt, thereby influencing the possible formation of chemical lithosphere (Hirth and Kohlstedt 1996), the possible locus of hydrous melting (Hirschmann et al. 2009), and the flux of H_2O from the martian interior to the surface (Hirschmann 2006). However, it is unlikely that such an extrapolation of the model fit from low-pressure data will be valid at higher pressure. High-pressure studies of olivine H2O storage capacity show little effect of Mg no. on H concentration (cf. Kohlstedt et al. 1996; Mosenfelder et al. 2006; Smyth et al. 2006; Litasov et al. 2007; Bali et al. 2008; Withers and Hirschmann 2008). These previous studies, however, investigated a narrow range of olivine compositions that vary between the Fe-free end-member composition and typical mantle composition olivine with Mg no. of ~90. Thus, no previous study has examined systematically the effect of varying Mg no. on H in olivine at mantle pressures over a range that spans martian mantle compositions.

Development of high-sensitivity, low-blank SIMS analysis of H in nominally anhydrous minerals (Koga et al. 2003; Aubaud et al. 2007; Tenner et al. 2009; Kovács et al. 2010) has provided new opportunities for analysis of H in experimentally annealed olivine and other mantle minerals (Aubaud et al. 2004, 2008; Hauri et al. 2006; Withers and Hirschmann 2007, 2008; Tenner et al. 2009; O'Leary et al. 2010). However, a long-standing issue has been development of a robust set of olivine standards and accurate quantification of SIMS analyses for olivine. Different studies have used distinct (but in some cases overlapping) combinations of natural and synthetic olivine standards and have achieved distinctly different results. For example, whereas Koga et al. (2003) obtained an olivine calibration that agreed well with their results for orthopyroxene, Aubaud et al. (2007) found distinctly different SIMS calibrations for these two phases. But, as pointed out by Aubaud et al. (2007), there are some problems with both natural and synthetic standards used to date. Some natural standards have microscopic intergrowths of hydrous minerals that interfere with comparison between SIMS, FTIR, and bulk analytical techniques, each of which sample different analyte volumes. Some synthetic standards have suffered from similar problems owing to heterogeneity. Aubaud et al. (2009) attempted to improve accuracy

of standards used for SIMS analyses of olivine through elastic recoil detection analysis (ERDA), but Kovács et al. (2010) noted significant discrepancies between the concentrations measured by ERDA and those from independent FTIR and SIMS analyses. Clearly, intercalibration of SIMS with other analytical techniques is required from an improved set of olivine standards.

Here we present ion probe measurements of the H_2O storage capacity of olivine grown in experiments performed at 3 and 6 GPa and 1200–1500 °C, in which the bulk Mg no. was varied systematically between 100 and 50. Together with a new intercalibration of the concentration of H_2O in olivine measured by SIMS and FTIR, these new experiments document the influence of Mg no. on olivine storage capacity.

EXPERIMENTAL METHODS

Synthesis of H-bearing olivine standards

We synthesized 7 new olivine standards for intercalibration of FTIR and SIMS analyses of H. The experiments in which these new standards were created will be referred to as "large volume experiments." Starting materials for the large volume experiments were prepared by homogenizing mixtures of reagent grade MgO, Mg(OH)2, FeO, and SiO2 under ethanol in an agate mortar and pestle. Three mixtures were constructed such that each had a bulk Mg no. of 90 and H2O content of 5 wt%. The anhydrous compositions of the starting materials were equivalent to those of stoichiometric olivine [molar (Mg+Fe)/Si = 2], olivine + 5 mol% orthopyroxene [molar (Mg+Fe)/Si = 1.95] and olivine + 5 mol% ferropericlase [molar (Mg+Fe)/ Si = 2.05]. Reagent mixtures were weighed into 3 mm diameter Au capsules that were mounted in a water-cooled vice and sealed by arc welding. Sealed capsules contained 27-50 mg of starting material. Olivine standards were synthesized by annealing the starting materials at a nominal temperature of 1250 °C for 96 h at pressures that varied from 3 to around 10 GPa. The 3 GPa large volume experiment was carried out in an end-loaded piston-cylinder apparatus using a BaCO3 pressure medium and type D thermocouple. No correction for pressure was applied to thermocouple EMF. Details of pressure calibration for this apparatus are to be found in Xirouchakis et al. (2001). Multi-anvil experiments were performed in a Walker-style module mounted in a 1000 ton hydraulic press. Second stage WC anvils had 12 mm truncations. A modified 12-TEL assembly was used for multianvil large volume experiments. The 12-TEL assembly consists of octahedra with integral gaskets made from a castable ceramic (Ceramacast 584-OS + 5 wt% Cr2O3). For routine experiments the 12-TEL assembly contains a straight walled graphite furnace with dimensions 13 × 4 mm OD × 3.17 mm ID that is capped by stainless steel rings. A type D thermocouple is inserted from one end of the furnace and is separated from the capsule by a 0.3 mm disk of crushable MgO. The interior of the furnace surrounding the capsule and thermocouple is filled with crushable MgO. Details of pressure and temperature calibration for this assembly are given in Dasgupta et al. (2004). The modified 12-TEL assembly has a 13 mm × 5 mm OD × 4 mm ID straight walled graphite furnace to accommodate capsules of up to 3 mm in diameter. The comparatively large capsule is believed to be crucial to the growth of large olivine crystals. The furnace is capped by $1 \times 5 \text{ mm OD} \times 4$ mm ID stainless steel rings. Other than the dimensional changes, materials used in the modified 12-TEL assembly are identical to those in the regular 12-TEL. The modified assembly has not been calibrated for pressure or temperature so experimental conditions reported in Table 1 are based on the force-pressure curve for the regular assembly. In one experiment, the applied force was unintentionally increased beyond the range of the force-pressure calibration curve for the 12-TEL assembly, which resulted in a loss of connection to the thermocouple. In that experiment (M475), the voltage applied to the furnace was increased until power consumption (measured using a true-RMS, true power transducer) was equivalent to the average power drawn in previous large volume experiments at 1250 °C, and the applied voltage was controlled by means of a computer interfaced with the temperature controller to maintain constant power consumption. The pressure of experiment M475 is expected to be at least 10 GPa, but owing to the lack of pressure calibration for applied force >500 tons, together with the absence of a thermocouple reading, the exact P-T conditions for this experiment are uncertain. All experiments were terminated by instantaneously turning off the power to the furnace, followed by slow decompression. After recovery, each capsule was pierced by drilling with a handheld drill bit until water was seen to emerge from the capsule.

TABLE 1.	Results of November 2009 SIMS session: new olivine
	standards (large volume experiments)

		-		-					
Experiment*	[Mg+Fe]	P (GPa)	EMP		SIMS		EMP SIMS		FTIR
			Ol Mg no. n		Ol Mg no. n		OH/Si×	n	C _{H-0} (wt%)
	/Si		-		SiO _{2 [EMP]}		2		
A710	2.05	3	91.9(1)	89	8.5(8)	7	0.0632		
M469	1.95	4	90.4(1)	58	5.1(5)	7	0.0373		
M449	2.00	6	90.8(2)	123	15.7(10)	8	0.1212		
M472	2.00	7	90.7(1)	57	16.3(8)	9	0.1184		
M437	2.00	8	90.6(1)	87	19.8(11)	9	0.1381		
M443	2.05	8	91.1(2)	25	24.1(11)	8	0.1530		
M475	2.00	10†	90.2(1)	56	46.7(22)	12	0.3016		

Note: T and duration for all experiments is 1250 $^{\circ}$ C, 96 h; n = number of analyses; numbers in parentheses represent 1 st.dev. in the least significant digit of measured value.

* A710 run in piston-cylinder, all others in multi-anvil.

 $+ P \ge 10$ GPa, T estimated from furnace power.

Experiments with variable Mg no.

Starting materials for piston-cylinder and multi-anvil experiments were prepared using the same procedure and materials as for the large volume experiments described in the preceding section. Six mixtures were prepared with bulk Mg no. varying from 5 to 100. Each composition has H/Si = 1 (H₂O content of ~5 wt%) and an anhydrous composition equivalent to 90 mol% olivine + 10 mol% orthopyroxene. Starting materials were loaded into Au₈₀Pd₂₀ capsules that were clamped in a water-cooled vice and sealed by arc welding. Capsules for multi-anvil and piston-cylinder experiments were 1.6 and 2 mm in diameter, respectively. For piston-cylinder experiments at 1200 °C, the cylindrical AuPd capsules were embedded in FeO that was packed into a 4.5 mm diameter Fe foil outer capsule. such that the AuPd capsules were not in contact with the Fe foil. Experiments in the multi-anvil were conducted without outer capsules. Each of the starting compositions was annealed at 1200 °C and 3 GPa for 48 h in an end-loaded pistoncylinder apparatus and at 1200 °C and 6 GPa for 12 h in the multi-anvil apparatus. A piston-cylinder experiment with bulk Mg no. 70 was run at 1300 °C and 3 GPa for 12 h in a double capsule, and experiments with bulk Mg no. 70, 80, and 90 starting compositions were performed at 3 GPa and 1500 °C with 3 h duration and without double capsules. Multi-anvil experiments were run in the regular 12-TEL assembly (Dasgupta et al. 2004). Pressure and temperature uncertainties for the 6 GPa experiments are estimated to be ±0.3 GPa and ±40 °C, and for the 3 GPa experiments are ±0.1 GPa and ±12 °C. After retrieval, capsules were sectioned with a wire saw using boron carbide and a 50 um tungsten wire.

ANALYTICAL METHODS

Electron microprobe

Major element concentrations were determined by wavelength-dispersive electron microprobe analysis with the JEOL JXA8900R at the University of Minnesota, using an acceleration voltage of 15 kV and 20 nA beam current, and ZAF data reduction with software supplied by JEOL. Counting times were at least 10 s for each element and 5 s for the background. Mineral standards from Jarosewich et al. (1980) were used. In addition, the electron microprobe was used to make backscatter image maps, together with reflected light images of the same areas, which serve as indispensible navigation aids for SIMS.

Fourier transform infrared spectroscopy

Olivines that were used as standards for SIMS were analyzed with a Bruker Tensor 37 FTIR spectrometer and Hyperion 2000 microscope. At least six crystals—the same crystals that were included on the SIMS sample mounts—were selected from each of the seven large volume experiments for FTIR analysis. The individual crystals were mounted in Crystalbond 509 (Aremco Products) on a brass polishing mount and polished with $1-0.1 \ \mu$ m diamond lapping film. The polishing mount was heated sufficiently (6 s on a 120 °C hotplate) to allow repositioning of the crystal for polishing of a second parallel face. Polished sections of crystals were removed from their mounts and cleaned by dissolving the Crystalbond adhesive in acetone. The thickness of each polished slab was determined using a Zeiss Axio Imager M1 microscope. A 50× objective was focused in reflected light on a glass slide immediately adjacent to the crystal to be measured. Focusing was aided by nearly closing both apertures in the incident light path, and the distance measure ment function of the microscope was used to measure the stage displacement during refocusing on the top surface of the crystal. Repeated measurements between varying locations on the glass slide and crystal surface typically vary by up to 1 μ m.

Sufficiently large crystal sections, typically 200–400 μ m in diameter, were suspended over an aperture for FTIR analysis, and smaller crystals (100-200 µm) were placed on a CaF₂ plate. The Hyperion 2000 microscope is equipped with both a 250 and 50 µm narrow band MCT detector, and has 15× and 36× reflecting optics objectives and condensers. An appropriate combination of detector, objective, and internal aperture setting was selected for each apertured analysis spot. Many of the olivines are twinned, and where possible analyses were made on either side of twin planes, taking care to avoid overlap with regions of a crystal on the other side of inclined twin planes. For each crystal, and where possible for each twin, an unpolarized analysis together with four polarized analyses were made on at least one spot within the crystal. Analysis spots were selected so as to avoid having cracks and inclusions in the beam path. The polarizer was positioned in the incident beam path and rotated in 45° increments between analyses. Owing to the eightfold symmetry (3 mirror planes) of the infrared absorbance indicatrix, the four polarization directions cannot be equally spaced within one octant of the indicatrix (when the incident light direction and two of the polarization directions are coincident with the axes of the indicatrix, the other two polarization directions have equal absorption). But, because the crystals are randomly orientated, the polarization directions are likely to be unique. A background measurement was taken before each sample analysis with a given polarizer orientation. Automated stage positioning was used to return to and switch between analysis positions. For each analysis, an infrared (globar) source was used and at least 64 scans were taken over a spectral range of 600-8000 cm⁻¹ with a sampling interval of 2 cm⁻¹.

Each polarized FTIR spectrum has two separate regions of interest: the OH absorption region from 2800–3800 cm⁻¹, and the region of silicate overtone absorptions at ~1500–2200 cm⁻¹. Baselines for each of these regions were fitted separately. For the silicate overtone region, a suitable spectral region either side of the peaks between 1525 and 2080 cm⁻¹ was selected and a linear baseline was fit through that region for each of the spectra from a given sample. A least-squares fitting algorithm was used, and fitting and baseline subtraction was performed without user interaction. For the OH stretching region, cubic baselines were employed. An interactive fitting routine was used to fit a cubic spline through four points, with two nodes positioned below and two above the frequency range of the region. This is functionally equivalent to fitting a cubic curve through a point either side of the region of interest and specifying the derivatives at those points.

As demonstrated by Lemaire et al. (2004) and Asimow et al. (2006), absorptions in the silicate overtone region of olivine vary systematically with the direction of polarization, and can be used to determine that direction. To determine the orientation, reference spectra from oriented standards are compared with the sample measurement. Our method for determining crystallographic orientation differs somewhat from that employed by Asimow et al. (2006), in that we fit simultaneously the four polarized measurements in the silicate overtone region, which simplifies the fitting procedure, allowing us to use a Levenberg-Marquardt algorithm to fit in the absorption domain. The method for fitting is described below.

The transmission (*T*) in a given direction, as a function of frequency (λ), is related to the transmission along the three principal axes of the absorption indicatrix (e.g., Libowitzky and Rossmann 1996; Asimow et al. 2006; Sambridge et al. 2008), and is given by

$$T(d, \theta, \phi, \lambda) = [T_a(\lambda)]^d \cos^2\theta \sin^2\phi + [T_b(\lambda)]^d \sin^2\theta \sin^2\phi + [T_c(\lambda)]^d \cos^2\phi \quad (1)$$

where *d* is the sample thickness; φ is the angle between the c axis of the crystal and the polarization vector; θ is the azimuth of the polarization vector in the ab plane; and *T*_a, *T*_b, and *T*_c are transmission in the **a**, **b**, and **c** crystallographic directions, respectively. Absorption (*A*) is related to transmission as

$$A(\lambda) = -\log[T(\lambda)].$$
⁽²⁾

To determine crystallographic orientation, we denote the incident light direction in the crystallographic coordinate system as (θ_i, φ_i) , and define α to be the angle between the polarization vector of the first polarized measurement and the projection of the crystallographic **a** axis onto the plane perpendicular to (θ_i, φ_i) . Since the polarization vectors for the subsequent analyses simply increment α by 45°, it is straightforward to regress the four polarized measurements to determine $d, \theta_i, \varphi_i, \text{and } \alpha$. In practice, we used Igor Pro software from Wavemetrics, Inc. to implement the Levenberg-Marquardt fitting algorithm. Principal-axis silicate overtone spectra from Asimow et al. (2006) were used as reference spectra. Singular matrix errors were avoided by manually specifying the " ε " values used to calculate partial derivatives with respect to the fit coefficients. Having determined the values of θ_{α} , ϕ_{α} , and α , the polarization vectors for the four polarized measurements can be readily calculated. Figure 1 shows a comparison of measured sample thickness and the thickness determined by including thickness as a fit coefficient. A relationship such as that shown in Figure 1 could be used to determine sample thicknesses in cases where it is difficult to make independent measurements. Crystals oriented such that the angles between the incident light direction and each of the crystallographic axes are close to being equal result in less constrained fit coefficients. Polarized spectra from such samples are of little use in calculating principal axis spectra, since all spectra have a significant contribution from each principal direction and offer little leverage to help constrain the fit coefficients. Such samples were therefore excluded from the fitting to calculate principal axis spectra. In contrast, spectra with polarization vectors close to a crystallographic axis provide a strong constraint on the principal axis spectrum.

For each experiment, principal axis spectra were calculated by fitting between 20 and 36 polarized spectra, representing from 5 to 9 samples. The fitting method is similar to that described by Asimow et al. (2006). For each frequency of measurement over the OH stretching region, the principal axis absorptions were calculated by setting $T_{\rm ax}$, $T_{\rm b}$, and $T_{\rm c}$ as fit coefficients (Eqs. 1 and 2). The absorbance measurements were fit directly using the Levenberg-Marquardt algorithm. A visual comparison of measured spectra and spectra calculated from the synthetic principal axis spectra shows good agreement, with no systematic under or over estimation of integrated area. In cases where a crystallographic axis lays within 10° of the plane of polarized measurements, an extra spectrum was recorded with the polarizer oriented as close as possible to the crystallographic axis. Comparison of such spectra with the synthetic principal axis spectra shows good agreement, confirming that the fitting method works well in these cases to constrain the relevant absorption coefficient. The sum of the integrated areas of the principal axis spectra was used to calcu-

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late the H content of the standards using the calibration of Bell et al. (2003).

Sample preparation

Where possible, the exposed faces of sectioned capsules were polished using diamond lapping film. Crystalbond was used to adhere the capsules to polishing mounts and to fill spaces



FIGURE 1. Thickness of doubly polished glass chips used for FTIR determinations, calculated by fitting angles of principal vibration directions from unoriented, polarized FTIR spectra (see text), compared to the thickness measured optically for each sample. The non-zero intercept is likely related to small differences in baseline treatment of measured spectra vs. the reference spectra. (Color online.)

between crystals. After polishing, the adhesive was removed by dissolution in acetone, followed by successive soaking periods in acetone and ethyl alcohol to remove hydrocarbon residue. Further details of the cleaning procedure are given in Koga et al. (2003) and Aubaud et al. (2007). The run products of experiments at 3 GPa with bulk Mg no. \geq 80 were too loosely aggregated to allow polishing of a sectioned face, so individual crystals from these experiments were extracted, mounted in Crystalbond and polished. Polished capsules, individual crystals from experiments and mineral and glass standards were pressed into indium for ion probe analysis.

SIMS analysis

Run products were analyzed using a Cameca IMS 6f secondary ion mass spectrometer at the GeoSIMS lab at Arizona State University. The SIMS analyses were performed during two different visits to the ASU SIMS laboratory, one in December 2008 and the second in November 2009. Analyses of the high-pressure experiments with variable Mg no. were performed during the visit in December 2008. However, as detailed in the Discussion, the quantitative calibration for olivine proved unsatisfactory. This led to the synthesis and FTIR characterization of the new standards. Calibration using the new standards and analysis of AC94, AC87, and four of the experimental samples during the session in November 2009 provided a cross-calibration between sessions that allowed quantification of the H content of all the experimental samples referenced to the new standards described in this study.

The two sample mounts analyzed in December 2008 included the run products from the variable Mg no. experiments, together with olivine, orthopyroxene, and glass standards described in Aubaud et al. (2007). The standards used in this mount were: olivine standards AC94, AC87, AC58, AC56, and Fo100; orthopyroxene standards Bamble dry, Bamble opx, San Carlos opx, Damaping, Kenya, KBH1, ROM273-OG2; glass standards JDF D10 and KN54Sta51. Full descriptions of these standards are given in Tables 1, 2, and 3 of Aubaud et al. (2007). Another two sample mounts, analyzed in November 2009, contained repolished halves of capsules from experiments M389, M393, M397, and M398, the orthopyroxene standards listed above, the chips of olivine AC94 and AC87 that were analyzed in the previous session and at least 6 olivine crystals from each of the large volume experiments.

Prior to each analytical session, and before the samples were introduced, the SIMS was heated for 24 h to minimize background H. The pressure in the sample chamber was approximately 8×10^{-10} Torr during the analytical sessions. A Cs⁺ primary ion beam with a current of 5–10 nA and an impact energy of 19 keV was tuned in critical illumination mode. Beam diameter at the sample surface was ~35 µm, and a 100 µm field aperture inserted in the secondary beam path allowed ions sputtered from the central ~10 µm of the sputtered area to enter the mass spectrometer. A –9000 V potential was applied to the sample and the energy bandpass was centered and wide open. Secondary ions were counted by electron multiplier and the count rates corrected for background and counting system deadtime. Background count rates for H determined by analysis of dry forsterite standards were equivalent to 7 and 19 ppm H₂O in forsterite in the 2008 and 2009 analytical sessions, respectively. Further details of the analytical setup and protocol are described in Tenner et al. (2009).

Raman spectroscopy

Prior to removing the polished and gold-coated experimental capsules from the SIMS sample mount, Raman spectroscopy was used to check crystal homogeneity and to discriminate between olivine and pyroxene grains in SIMS analysis pits that were located in fine-grained areas of some charges. This was a useful precaution where ion imaging had been used to align the ion beam over pyroxene crystals that were <50 μ m in diameter. Spectra were collected with a Witec Alpha300R confocal Raman microscope using the excitation from a 514.5 nm laser and a 1800 mm⁻¹ grating. The laser power, measured at the source, was 40 mW. Spectra were averaged from 2–4 accumulations, each with a counting time of 30–90 s.

RESULTS

Standards synthesis

Once it had been verified that water was present in each of the recovered experimental capsules, the end of the capsule that was situated next to the thermocouple was opened to reveal finegrained quench material overlying loosely aggregated crystals. Crystals varied in size up to 500 μ m, and those located in the center of the capsule were, in general, extracted as pristine grains with few fractures, few inclusions, and little tendency to break apart. The crystals located at the end of the capsule opposite the thermocouple were more likely to contain opaque inclusions. Olivine stoichiometry was confirmed by electron microprobe analysis and Mg no. of the crystals that were analyzed using FTIR and SIMS are presented in Table 1.

Synthetic principal axis FTIR spectra from large volume experiments at 3, 4, 8, and >10 GPa are shown in Figure 2. The synthetic spectra from large volume experiments at 6-8 GPa that are not shown in Figure 2 have the same shape as the spectra from the 8 and 10 GPa experiments and vary only in intensity. The spectra from two lowest pressure large volume experiments (M469 and A710) are somewhat different in appearance from the higher pressure olivine spectra. The three peaks at 3450-3500 cm⁻¹ that are easily seen in the 3 and 4 GPa spectra with polarization in the a direction (//a) are present also in the higher pressure spectra, but are dwarfed by the peaks at 3579-3613 cm⁻¹. The peak at 3353 cm⁻¹ in the 4 GPa //a spectrum is not present in the spectra from other experiments. This peak is likely related to a coupled substitution with Fe3+ (Berry et al. 2007; Kovács et al. 2010). The low-pressure synthetic principal axis spectra are well constrained by polarized measurements that were close (within 10°) to alignment with a crystallographic axis, so the difference between these spectra and those of the higher pressure samples cannot be attributed to the fitting technique. Peak positions in the low-pressure spectra are 3353, 3454, 3481, 3502, 3529, 3579, 3599, and 3613 cm⁻¹ in the //a spectra. In the //b spectra additional peaks are present at 3175 and 3302 cm⁻¹, and in the //c spectra a peak appears at 3567 cm⁻¹. In the high-pressure (6–10 GPa) olivine spectra the major peaks are those at 3579, 3599, and 3613 cm⁻¹ in the //a spectra, 3546 cm⁻¹ in the //b spectra,

FIGURE 2. Infrared spectra of new olivine standards grown in large volume experiments. The principal axis infrared spectra were calculated by fitting the OH stretching region of between 20 and 45 polarized FTIR spectra with known orientation. Spectra are arranged in groups of three, representing polarization parallel to each of the crystallographic axes; //a, //b, and //c represent polarization parallel to a, b, and c crystallographic axes; respectively. The four groups of spectra are from experiments M475, M437, A710, and M469. Spectra are vertically offset for clarity and those from A710 and M469 are expanded by a factor of three in the vertical direction. Annotations above each group of spectra give experiment pressure and molar [Mg+Fe]/Si of the bulk composition. All experiments were run at 1250 °C. (Color online.)

and 3567 cm⁻¹ in the //c spectra. No changes in peak positions were observed in olivines from experiments that had bulk molar (Mg+Fe)/Si of 2.05.

A SIMS calibration for analysis of H in olivine is established by linear regression of the H₂O content of the olivines determined by FTIR against background corrected SIMS measurements of ¹⁶OH/³⁰Si in each of the olivine standards normalized against SiO₂ contents of the crystals determined by EPMA (OH/Si×SiO_{2[EMP]}; Table 1; Fig. 3). The calibration coefficient is the slope of the regression line that is constrained to pass through the origin. The calibration shown in Figure 3a is representative of calibrations that were established on a day-to-day basis within a fortnight



long analytical session in November 2009. After sample changes, or whenever significant retuning of the ion optics was needed, recalibration was effected by analyzing standards interspersed with experimental samples. Even under nominally similar analytical conditions, it was found that the calibration could drift by up to 9% from one day to another.

Cross calibration between analytical sessions

The calibration based upon the new standards synthesized in this study (Fig. 3a) was used to determine H contents of olivine fragments used in previous SIMS sessions and to reanalyze olivines from four of the experiments that had been analyzed in the December 2008 SIMS session (Table 2). Twenty measurements of AC94 give a revised H content of 0.203 ± 0.02 wt% H₂O, and 16 measurements of AC87 result in 0.078 ± 0.01 wt% H₂O. These values are nearly identical to those proposed Kovács et al. (2010) (0.2278 and 0.0808, respectively), based on comparison with natural standards. The scatter in the ion probe measurements of the new standards (Table 1), together with the goodness of fit of the individual IR measurements, suggest that variation in H contents of



FIGURE 3. Representative SIMS calibrations for H in olivine and pyroxene. (a) Calibration for new olivine standards, from Nov. 2009 analyses. (b) Calibrations for olivine and pyroxene from Dec. 2008, using corrected values for AC94 and AC87. Gray symbols represent values reported by Aubaud et al. (2007), and arrows point to the corrected values. Olivine data are shown as red circles and pyroxene as green diamonds. Solid red line shows olivine calibration based on corrected values for AC94 and AC87 and black dashed line shows calibration based on uncorrected values. (c) Expanded view of shaded area from plot **b**. (d) Updated calibration from Tenner et al. (2009). Red circles represent updated values for AC94 and AC87; other synthetic olivines from Aubaud et al. (2007) are plotted as green squares. Blue triangles represent natural samples listed by Tenner et al. (2009). The three natural standards that lie above the regression line are ROM177, ROM250-2, and ROM250-13 (Bell et al. 2004). (Color online.)

 TABLE 2. Results of November 2009 SIMS session: analysis of H in olivine

Sample	n	H ₂ O (wt%)			
AC94	20	0.203(20)			
AC87	16	0.078(10)			
M393	2	0.117(9)			
M389	2	0.117(5)			
M397	2	0.094(1)			
M398	2	0.052(1)			
<i>Note:</i> n = number of analyses; numbers in parentheses represent 1 st.dev. in the					

least significant digit of measured value.

the new standards from a given large volume experiment is <10%in total. Thus, with a range of H contents that spans 0.037–0.3 wt% as H₂O, the new standards provide a cross calibration of SIMS and FTIR for olivines from high-pressure experimental studies that have H contents of hundreds to thousands of parts per million of H₂O.

It should be noted that the experimental methods used to synthesize olivine standards for SIMS were optimized for growth of large, well-equilibrated crystals, at the cost of accuracy in pressure and temperature measurement. The temperature distribution within the 3 mm capsules used in these large volume experiments has not been characterized, but is likely to range over 100 °C, considering that parts of the capsule are situated more than 2 mm from the thermocouple junction. So, while it appears that the H contents of the crystals selected for FTIR and SIMS analysis are constant within the uncertainties of the analytical techniques, the measured H₂O concentrations are not well suited to investigate the details of thermodynamic conditions on H incorporation in olivine. Nevertheless, we observe an increase in H with increasing pressure and decreasing SiO₂ activity (a_{SiO_2}) that is consistent with previous studies (Table 1; Kohlstedt et al. 1996; Lemaire et al. 2004; Mosenfelder et al. 2006; Smyth et al. 2006; Withers and Hirschmann 2008; Bali et al. 2008).

The revised values for the H contents of the fragments of AC94 and AC87 that were used as standards in December 2008, based on the November 2009 analyses, allow us to determine a calibration for olivine that can be applied to the 2008 analyses (Fig. 3b). The calibration for 2008 is significantly different to the 2009 calibration (calibration coefficient of 0.0067 ± 0.0001 in 2009 vs. 0.011 ± 0.0006 in 2008, Figs. 3a and 3b). Thus it appears that the effective calibrations for our analytical sessions spaced apart by one year vary by much more than the variation of up to 9% that was observed within a fortnight session. The calibration coefficients for orthopyroxene established in each of the analytical sessions $[0.0102 \pm 0.0003$ in December 2008, Fig. 3c; 0.0065 ± 0.0002 in November 2009, Tenner et al. (in review)] are indistinguishable from the olivine calibration coefficients for the respective sessions. The validity of the respective calibrations for H in olivine is also confirmed by a reanalysis of olivine from the variable Mg no. experiments (Table 2), which are in good agreement (≤10% relative) with the results described in the following section.

Variable Mg no. experiments

The persistence of the Fe and FeO f_{O_2} buffering materials surrounding the capsules in the experiments at 3 GPa and 1200 °C was observed at the end of each experiment. A monomineralic layer of olivine, in which grain size ranges up to ~300 µm, is present in all of the experiments. Orthopyroxene was found in experiments at 1200 °C, where it is intergrown with olivine and, in experiments with Mg no. \leq 70, metallic Fe. Orthopyroxenes have grain sizes ≤40 µm. Experiments at 1500 °C and 3 GPa consist of olivine and quenched hydrous liquid. The quenched liquid is located at the top of the capsule in piston-cylinder experiments, and at the sides of capsules in multi-anvil experiments, owing to different thermal profiles in the different apparatuses. A piston-cylinder experiment in a double-capsule run at 3 GPa and 1300 °C for 12 h resulted in significant alloving of Fe with the AuPd inner capsule and contamination of the inner capsule (Fig. 4). Iron from the Fe+FeO oxygen buffer entered the inner capsule from the top end, as can be seen in Figure 4. The presence of olivine with Mg no. = 87, seen as darker colored crystals in the backscattered electron image (Fig. 4b), in the bulk of the capsule indicates that the olivine had grown prior to ingress of Fe, which resulted in Fe-enrichment of olivine at the top end of the capsule (bright colored crystals in Fig. 4b). Analysis of Mg no.87 and Mg no.44 crystals, situated either side of the Fe diffusion front, show H₂O contents that are greater by a factor of 3.6 in the more Fe-rich olivine (Table 3; Fig. 5). Olivine H₂O content increases with pressure, and at both 3 and 6 GPa decreases linearly with increasing Mg no. (Table 3; Fig. 5). At 3 GPa, there is no significant variation in the H₂O content with temperature variation from 1200-1500 °C.

Partition coefficients for H between orthopyroxene and olivine decrease from a weighted average value of 1.05 at 3 GPa and 1200 °C to 0.61 at 6 GPa and 1200 °C (Table 3; Figs. 5 and 6), owing to the strong increase in olivine H content with increasing pressure. Thus, H becomes less incompatible in olivine than in Al-free orthopyroxene at pressures greater than 3 GPa. The orthopyroxene/olivine partition coefficient does not show any observable dependence upon Mg no. over the range of compositions investigated in this study.

DISCUSSION

New olivine standards

To be useful as standards for SIMS, synthetic crystals have to be sufficiently large and robust that they can be extracted from the indium mounts, repolished, cleaned, and remounted for reuse. Accordingly, grain growth in the large volume standards synthesis experiments was maximized by performing long duration experiments with bulk compositions that are sufficiently close to olivine stoichiometry that the crystalline aggregates in the experiments are monomineralic. The absence of secondary phases prevents grain boundary pinning that would inhibit growth of large crystals (Ohuchi and Nakamura 2007). No mineral apart from olivine was identified in any of the experiments that were optimized for grain growth, so variations in a_{SiO_2} in the 1250 °C large volume experiments are unlikely to extend to those defined by coexistence with either pyroxene or ferropericlase. Even so, the variable (Mg+Fe)/Si ratios in the starting bulk composition likely influence a_{SiO_2} owing to associated variations in coexisting fluid composition, and a_{SiO2} variations influence H storage capacities. For example, among the two lowest pressure large volume experiments, A710 had low a_{SiO_2} [bulk molar (Mg+Fe)/Si = 2.05] and produced olivine



FIGURE 4. Backscattered electron images of experimental charges. (a) Experiment M393 at 1200 °C and 3 GPa. OI = olivine crystal; OI+opx+Fe = olivine, orthopyroxene, and iron metal intergrowth; AuPd = capsule material; Liq = quench crystals and voids representing quenched hydrous silicate liquid. (b) Experiment B220 at 1300 °C and 3 GPa in which iron from the external buffer assemblage entered from the top end of the inner capsule. Fe = iron metal; Fo₄₄ = Fe-enriched olivine crystal (Mg no. = 44) from upper part of capsule; Fo₈₇ = olivine crystal with Mg no. of 87 from lower part of capsule. Bright speckles outlining horizontal cracks in the crystal aggregate are an artifact of polishing. Black areas in A and B are void spaces where material has been plucked from the surface during polishing. The scale bar in the lower left corner of each image is 500 μ m in length.

with greater H content (0.063 wt% H₂O) than experiment M469 (0.037 wt%), which had higher a_{siO_2} [bulk molar (Mg+Fe)/Si = 1.95], although the former was performed at lower pressure (3 GPa) than the latter (4 GPa) (Table 1).

Differences in a_{SiO_2} may also explain why the 6 GPa olivine standard (M449) has 0.12 wt% H₂O, while the olivine in experiment M406 from the variable Mg no. suite of experiments has 0.08 wt% H₂O, despite having a similar Mg no.: the large volume experiment, M449, had stoichiometric olivine bulk composition, whereas a_{SiO_2} in experiment M406 was buffered by coexistence with pyroxene. The large volume experiment at

6 GPa produced olivine with a higher apparent H content than the 7 GPa experiment, as opposed to the increasing H content that one might expect with increasing pressure (Kohlstedt et al. 1996), which could indicate inaccuracy in the H content determined by FTIR. Alternatively, uncertainties in temperature and pressure of the large volume experiments, together with the high variance of the two-phase experiments, may be the cause of such non-systematic variation. The correlation between FTIR and SIMS analyses nevertheless suggests that the measurements are precise and that the olivines are well suited for use as crosscalibrating standards for SIMS.

TABLE 3. Variable Mg no. experiments

Experiment	P (GPa)	T (°C)	Bulk	Olivine			Pyroxene				D _H ^{opx/ol}	
			Mg no.	Mg no.	H ₂ O (wt%)	H/10 ⁶ Si	n	Mg no.	H ₂ O (wt%)	H/10 ⁶ Si	n	
M393	6	1200	50	60.13	0.121(5)	22300	5	69.24	0.075(1)	9130	4	0.62(3)
M389	6	1200	50	60.38	0.130(4)	23900	4	70.09	0.074(3)	9070	4	0.57(3)
M394	6	1200	60	68.06	0.129(19)	23100	4	76.10	0.082(1)	9830	4	0.63(10)
M407	6	1200	70	74.89	0.114(8)	19900	2	80.30	0.078(2)	9220	4	0.68(5)
M397	6	1200	80	82.13	0.101(6)	17100	5	85.60	0.059(3)	6920	4	0.59(4)
M406	6	1200	90	90.02	0.079(9)	12800	4	91.66				
M398	6	1200	100	100.00	0.053(9)	8360	5	100.00	0.040(0)	4420	2	0.74(13)
B218	3	1200	50	55.44	0.054(5)	10000	6	66.10	0.063	7720	1	1.17
A637	3	1200	50	57.56	0.048(2)	9000	4	64.69	0.055(10)	6850	2	1.14(21)
A642	3	1200	60	62.68	0.045(2)	8260	3	70.44	0.045(7)	5520	4	1.00(15)
A638	3	1200	70	71.82	0.050(6)	8750	8	74.75	0.052(1)	6310	2	1.05(14)
A641	3	1200	80	80.30	0.029(2)	4860	3					
B217	3	1200	90	90.40	0.023(1)	3710	3					
A647	3	1200	100	100.00	0.017(0)	2630	3					
B224	3	1500	60	79.79	0.029(9)	4960	4					
B225	3	1500	70	85.65	0.028(5)	4730	4					
B223	3	1500	90	94.80	0.019(0)	3060	3					
B220, top	3	1300	80	44.22	0.062(8)	12100	3					
B220, bottom	3	1300	80	86.88	0.017(2)	2780	2					

Note: Mineral compositions determined by electron microprobe and hydrogen contents by SIMS in December 2008. n = number of analyses; numbers in parentheses represent 1 st.dev. in the least significant digit of measured value; the calibrations used to calculate olivine H₂O contents were constructed using revised values for olivine standards AC94 and AC87.



FIGURE 5. Hydrogen contents of olivine and pyroxene determined using SIMS. Hydrogen concentrations, expressed as wt% H₂O, are plotted against the Mg no. of the host mineral. Lines connect olivine and pyroxene measurements from the same experiment. Olivine data are plotted as circles and pyroxene as diamonds. Dash-dotted lines are fit to the 1200 °C data at 3 and 6 GPa, with the exception of the two 6 GPa data at Mg no. ~60. The 3 GPa line is extrapolated over the range of all the data. Data from 6 GPa, 1200 °C experiments are shown in blue, 3 GPa and 1200 °C in red, 3 GPa and 1500 °C in orange, and two measurements from different parts of experiment B220 at 3 GPa and 1300 °C in violet. Reanalysis of olivines from experiments in the second SIMS analytical session are shown in green. See text for further details. Shaded bands represent the range of possible Mg no. for olivine in the mantles of Earth and Mars (Morgan and Anders 1979; Dreibus and Wänke 1985; Bertka and Fei 1997). (Color online.)



FIGURE 6. Partition coefficient for H₂O between orthopyroxene and olivine plotted against olivine Mg no. Weighted averages of data from 6 GPa (red squares) and 3 GPa (blue diamonds) are shown as red dot-dashed line and blue dashed line, respectively. (Color online.)

Choice of FTIR extinction coefficients

The accuracy of any cross calibration of SIMS to FTIR depends on accurate knowledge of the extinction coefficient for the OH absorption bands. The concentration of H expressed as weight proportion of H₂O, $C_{\rm H_2O}$, can be calculated from the integrated peak area, A, by application of the Bouguer-Beer-Lambert law

$$C_{\rm H_{20}} = (A \times c \times M) / (d \times \rho \times \varepsilon)$$
(3)

where M is the molar mass of H_2O , c is a constant for conversion to parts per million (c = 10⁶) or percent (c = 100) proportions, *d* is thickness in cm, ρ is density in g/L, and ε is the integral extinction coefficient, or the integral molar absorptivity, with units of L/(mol·cm²). For samples with constant density, the constants on the right hand side of Equation 3 can be replaced by k, the "absorption coefficient," as defined by Kovács et al. (2010)

$$C_{\rm H2O} = (\mathbf{k} \times A)/d. \tag{4}$$

Accordingly, k has dimensions of cm² and is inversely proportional to the extinction coefficient. A decrease in extinction coefficient or increase in absorption coefficient corresponds to an increase in the number of absorbers per unit of absorption intensity.

Kovács et al. (2010) used a combination of FTIR and SIMS analysis to show that FTIR extinction coefficients for the various OH absorption bands in olivine spectra may differ considerably. In that study, a SIMS calibration based on five natural olivine crystals was used to determine the H content of olivines that were synthesized under varying experimental conditions, and therefore have distinct IR absorption bands. The integrated intensity of the various OH absorption bands present in those samples was calculated by averaging unpolarized FTIR measurements of unoriented samples and applying a correction for thickness of strongly absorbing samples. Kovács et al. (2010) determined effective extinction coefficients for the absorption bands present in their experimental samples by regression of FTIR integrated absorbance measurements against $C_{\rm H_{2O}}$ determined by SIMS. Extrapolation of the SIMS calibration based on olivines with <0.025 wt% H₂O to measure H concentrations in excess of 0.4 wt% H2O, together with the FTIR uncertainties related to baseline fitting and "correction factor" for highly absorbing samples, add significant uncertainty to the calculated FTIR extinction coefficients. Notwithstanding these limitations, it is clear that applying the same extinction coefficient to the natural samples and to the FTIR spectra of the synthetic olivines of Kovács et al. (2010) that, like our olivine spectra, have high wavenumber peaks between 3400 and 3630 cm⁻¹, would result in significant mismatch. When the misfit is interpreted solely in terms of variation in extinction coefficient, an increase by a factor of 3 in integral absorption coefficient for high wavenumber absorption bands is required to reconcile the SIMS analyses of natural olivine standards and the experimental samples of Kovács et al. (2010).

We have chosen to use mineral-specific extinction coefficients for quantification of OH in pyroxene and olivine (Bell et al. 1995, 2003). Other approaches, such as applying a frequencydependent extinction coefficient (Paterson 1982; Libowitzky and Rossmann 1997), or the peak specific extinction coefficients for olivine (Kovács et al. 2010) would result in significantly different results, far outside of the analytical uncertainties discussed below. Following the reasoning of Kovács et al. (2010), we evaluate the possibility of error in the extinction coefficient applied to the FTIR spectra of our new olivine standards by comparison with SIMS analyses of natural olivine standards later in this discussion.

Analytical uncertainty arising from baseline fitting

Assuming that the extinction coefficient is appropriate for the absorption bands of interest, the uncertainty in H content estimated from uncertainty in the extinction coefficient is 6.4% (Bell et al. 2003). Additional systematic error is, however, possible. The greatest uncertainty is derived from the choice of baseline, which can lead to large systematic errors, as discussed by Bell et al. (2003). Our baseline fitting leads to principal axis spectra that are similar in appearance to those produced in Mosenfelder et al. (2006) by similar fitting techniques and, crucially, do not appear to remove more broad components than baselines used by Bell et al. (2003) in determining the extinction coefficient. Using concave-downward baselines beneath the peaks would result in significantly lower H concentrations (as much as 20% reduction in integrated area), but we did not consider such procedures to be warranted, since resultant baseline-corrected spectra appear quite different to the spectra used to determine the extinction coefficient (Bell et al. 2003). We therefore estimate a 10% uncertainty in the FTIR measurements, based on reproducibility of our measurements, with the caveat that alternative baseline fitting procedures could result in measurements that lie outside of this bound.

Revisiting earlier SIMS calibrations for H₂O in olivine

In the light of several observations, reconsideration of the H in olivine standards AC94, AC89, and AC87 [the "low a_{SiO_2} " standards of Aubaud et al. (2007), which were hydrated by annealing in the presence of ferropericlase] seems required. First, as pointed out by Kovács et al. (2010), the calibration of Aubaud et al. (2007), owing to strong leverage by these three standards, likely produces a significant underestimate of olivine H contents compared to those that would be obtained by giving greater weight to the three olivines from the Monastery kimberlite, analyzed previously by Bell et al. (2004), and also included in the Aubaud et al. (2007) study. Second, and as also discussed by Kovács et al. (2010), calibrations for orthopyroxene and olivine might be expected to be similar, based on ion sputtering theory (Williams 1979), as has been the case in studies that do not include these low a_{SiO_2} standards (e.g., Koga et al. 2003; Kovács et al. 2010). Third, calibrations for H in olivine that have included the low a_{SiO2} standards (e.g., Aubaud et al. 2007; Tenner et al. 2009) show poor correlation (e.g., Fig. 3b), such that the H contents of standards lying close to the origin are underestimated, as illustrated in Figure 3c. Each of these observations suggests that H contents of the low a_{SiO_2} standards are significantly greater than those given by Aubaud et al. (2007). As noted by Aubaud et al. (2007), the H contents of the 2 mm crystals of these standards are not homogeneous, and significant H enrichment was seen in the outermost 500 µm rims. We suspect that the polarized FTIR measurements were not limited to these outermost parts of the crystal, since it is nearly impossible to find an infrared beam path that does not pass through the interior of the crystal. The fragments of these standards that were used in SIMS mounts, however, were likely taken from the highly H-enriched rims. Owing to repeated extraction from sample mounts, repolishing, and remounting, the crystals have gradually disintegrated and several fragments have been lost, making it difficult to prepare the remaining pieces for reanalysis with FTIR. Initial attempts to make FTIR measurements on the remaining fragments of AC94 suggested an H content of ~0.21 wt% H₂O, but, because this measurement was made by application of the Bell et al. (2003) calibration to unoriented and unpolarized spectra, it cannot be considered to be accurate (Bell et al. 2003). Thus, we used our newly synthesized olivine standards to determine the H contents of AC94 and AC87, which allows us to correct previous calibration curves that have used those standards. We have not reanalyzed AC89, but expect that the H content of that sample was likewise underestimated by Aubaud et al. (2007). AC89 was not used in the calibrations described in this study. The new values for the H contents of AC94 (0.203 wt% H₂O) and AC87 (0.078 wt% H₂O) are factors of 2.2 and 1.6 greater than the concentrations given by Aubaud et al. (2007) for the rims of these crystals (0.091 and 0.048 wt% H2O, respectively). Correspondingly, calibration coefficients that were established using the Aubaud et al. (2007) values (Aubaud et al. 2007; Withers and Hirschmann 2007, 2008) increase by a factor of 2. Based on reanalysis of AC94 using unpolarized FTIR, Tenner et al. (2009) assigned a value of 0.149 wt% H₂O to AC94, but used the Aubaud et al. (2007) H content for AC87, which resulted in a calibration coefficient of 0.008 ± 0.003 for olivine. Reconstructing the Tenner et al. (2009) calibration using our updated values leads to a factor of 1.4 increase in calibration coefficient (Fig. 3d). Preferred values for the H contents of olivines that were calculated using these calibrations [5 measurements from Withers and Hirschmann (2007), 12 from Withers and Hirschmann (2008), and 1 from Tenner et al. (2009)] are tabulated in the Appendix to this paper.

Comparison of natural and synthetic standards

The validity of applying the Bell et al. (2003) extinction coefficient for olivine to our synthetic olivines that have principally high wavenumber absorption bands (Fig. 2) can be checked by comparing SIMS analyses of the different types of olivine. Three of the natural olivine standards analyzed by Kovács et al. (2010), ROM177, ROM250-2, and ROM250-13, were also analyzed by Aubaud et al. (2007) and Tenner et al. (2009). These samples originate from the Monastery kimberlite and were characterized by Bell et al. (2004). The recalculated SIMS calibration lines from Aubaud et al. (2007) and Tenner et al. (2009) show improved, although still imperfect, agreement with the Monastery kimberlite olivines (e.g., Fig. 3d). In each case, the natural samples lie above the calibration lines, and linear regression of the Monastery kimberlite olivine analyses alone from Aubaud et al. (2007) and Tenner et al. (2009) results in calibration coefficients that are 23 and 43% greater, respectively, than those calculated by regression of the entire standard sets. These differences reflect the mismatch between the natural olivine standards and

our new synthetic standards, whose H contents were quantified using the extinction coefficient of Bell et al. (2003). This observation contrasts with that of Kovács et al. (2010), who show that synthetic olivines with FTIR spectra that are similar to those of our new standards, when compared with natural olivine samples that include the same three Monastery kimberlite olivines, would produce SIMS calibrations that differ by a factor of 3 when the Bell et al. (2003) extinction coefficient is applied to each sample set. The limited number of natural olivine standard analyses available to compare with the calibrations derived from our new synthetic olivine standards prohibit us from speculating with any certainty as to the need for a distinct extinction coefficient for high wavenumber absorption bands. The good correlation between our SIMS measurements and areas of OH bands having widely varying peak locations suggests, however that the effective extinction coefficient for our experimental olivine spectra is unlikely to differ from the value that we have used by more than the analytical uncertainty. We therefore continue to use the Bell et al. (2003) extinction coefficient for both natural and experimental olivines, but note that future refinements of sitespecific infrared extinction coefficients could affect our results, together with almost all previously published measurements of H in olivine from high-pressure experiments.

Comparison with other independent analytical techniques

Further independent measurements of the H contents of AC94, AC87, and AC89 were made by Aubaud et al. (2009) using ERDA. As noted by Kovács et al. (2010), it is difficult to reconcile these with SIMS measurements of these samples, as the mismatch between SIMS measurements of natural olivine standards and these low a_{SiO_2} experimental samples is exacerbated by the low H contents determined by ERDA. Our new measurements of the H concentrations of AC94 and AC87 are significantly higher than the ERDA measurements of these samples. We suspect that the $200 \times 50 \,\mu\text{m}$ areas at the sample surface analyzed by ERDA do not sample solely the highly Henriched rims of the crystals, so the ERDA measurements cannot be compared directly with our reanalysis of the fragments of these samples that were extracted from SIMS sample mounts, or with the corresponding SIMS measurements. Additional ERDA measurements using more homogeneous crystals such as those synthesized in the present study would be required to establish improved correspondence between ERDA, SIMS, and FTIR.

Effect of Mg no. on olivine and orthopyroxene H₂O storage capacities

Perhaps the most striking feature of our experimental results is the modest increase in H in olivine with decreasing Mg no., compared to the large exponential increase found by Zhao et al. (2004) in experiments at 300 MPa. Thus, whereas our data suggest that olivine with a Mg no. of 50 has a storage capacity $\sim 3 \times$ that of pure Mg₂SiO₄, the exponential relation found by Zhao et al. (2004) predicts a factor of 50. Apart from the large differences in pressures of the studies [300 MPa for Zhao et al. (2004) vs. 3–6 GPa in this study], the reasons for these profound differences are not completely clear. We note, however, that the parameterization of Zhao et al. (2004) is based chiefly on experimental data from a much narrower range of olivine compositions, with Mg nos. no lower than 83. Also, the H concentrations determined by Zhao et al. (2004) for pure Mg_2SiO_4 appear to be anomalously low when compared to their Fe-bearing samples, perhaps owing to kinetic impediments to hydrating the gem-quality single crystals of forsterite that they employed.

In applying SIMS calibration coefficients for H in olivine and pyroxene to our variable Mg no. experimental run products, we ignore possible matrix effects owing to the compositional differences. By comparing calibration coefficients for nominally anhydrous minerals, amphiboles, and micas, Koga et al. (2003) found a small decrease in slope with increasing Fe content, although they also found considerable scatter for Fepoor compositions. If similar matrix effects apply to olivines and orthopyroxenes of variable Mg no., then the variations in H₂O storage capacity that we measure may be overestimated slightly. However, the differences between 3 and 6 GPa and variable temperature results and the relative difference between pyroxene and olivine results are unlikely to be affected by these compositional effects, and while the slope of the olivine and pyroxene dependencies upon Mg no. could be modified, the relatively small influence of Mg no. (Fig. 5) compared with the exponential effect observed in 300 MPa experiments (Zhao et al. 2004) is robust. Thus, at mantle pressures the incompatibility of H may be slightly lower during melting of martian mantle compared with the case for Earth, but will not be as significantly different as would be implied by extrapolation of the low-pressure exponential changes in H storage capacity.

Another potential influence on H contents of olivines and pyroxenes in the variable Mg no. experiments could be that of changing melt composition. Withers and Hirschmann (2007, 2008) suggested that the significant decreases in H contents of olivine and pyroxene with increasing T in high-pressure experiments is caused by increasing dilution of the hydrous component of the liquid phase in the experiments, leading to reduced H₂O fugacities in the melt and coexisting crystal. As the bulk Mg no. is changed in our isothermal experiments, the degree of solidus depression is likely different, so one might question whether the observed dependence upon Mg no. may be related primarily to differences in the liquids, rather than the crystalline phases. That the primary influence is that of crystal composition is demonstrated by the results from experiment B220, which was contaminated by an influx of Fe from the top end of the capsule in the course of the experiment. Because the diffusion rate for H in olivine is several orders of magnitude faster than Fe-Mg interdiffusion (Mackwell and Kohlstedt 1990; Kohlstedt and Mackwell 2008), we expect the H contents of olivine either side of the Fe-Mg diffusion front to be equilibrated with respect to H. The different H contents of olivine above and below the diffusion front must therefore be solely attributable to crystal chemical effects, since the activity of the H2O component in the liquid is constant (both crystals coexist with the same liquid). Because the results from olivines in experiment B220 lie on the same trend as the 3 GPa variable Mg no. experiments at 1200 and 1500 °C (Fig. 5), we conclude that there is no observable effect of changing melt composition over the range of Mg no. investigated in our experiments. The lack of measurable influence of temperature on the 3 GPa results is likely due to balancing of the competing effects of H₂O dilution with increasing melt fraction and increasing "solubility" in the crystal, since at 2.5 GPa a moderate increase in olivine H content is seen with increasing temperature between 1100 and 1400 °C (Bali et al. 2008), while at higher pressure olivine H contents decrease with temperature (Withers and Hirschmann 2008).

Partitioning of H between orthopyroxene and olivine

Comparison of experiments at 3 and 6 GPa shows that the H partition coefficient between orthopyroxene and olivine, given by

$$D_{\rm H}^{\rm opx/ol} = \frac{C_{\rm H}^{\rm opx}}{C_{\rm H}^{\rm ol}} \tag{5}$$

increases with pressure (Fig. 6). The effect of pressure on H storage capacities of olivine and pyroxene are described by

$$C_{\rm H}^{\rm phase} = A^{\rm phase} f_{\rm H_2O}^{\rm n} \exp\!\left(\frac{-P\!\left(\Delta V^{\rm phase}\right)}{RT}\right) \tag{6}$$

(Kohlstedt et al. 1996; Rauch and Keppler 2002), where A^{phase} is a constant unique to each phase, $f_{\text{H}2\text{O}}$ is the fugacity of H₂O, n depends on the nature of the hydrous defect and the charge neutrality condition, and ΔV^{phase} is the volume change associated with the hydration reaction between the mineral and fluid. The value of the fugacity exponent, n, is unity for both olivine (Kohlstedt et al. 1996) and orthopyroxene (Rauch and Keppler 2002). Therefore, the orthopyroxene/olivine partition coefficient, $D_{\text{H}}^{\text{opviol}}$, is given by

$$D_{\rm H}^{\rm opx/ol} = \frac{A^{\rm opx}}{A^{\rm ol}} \exp\left(\frac{-P\left(\Delta V^{\rm opx} - \Delta V^{\rm ol}\right)}{RT}\right) \tag{7}$$

and so the decrease in $D_{\mu}^{\text{px/ol}}$ indicates that the volume of hydration of olivine is smaller than that for orthopyroxene.

Partitioning of H between orthopyroxene and olivine does not show a strong dependence on Mg no. Linear regression does indicate modest changes in $D_{\rm H}^{\rm opx/ol}$ with varying Mg no. (Fig. 6), although the departures from a slope of zero are not statistically significant. However, one might expect a small dependence upon Mg no. in the senses shown (increasing with Mg no. for $D_{\rm H}^{\rm opx/ol} > 1$ and decreasing with Mg no. for $D_{\rm H}^{\rm opx/ol} < 1$) if the storage capacity trends for olivine and orthopyroxene are parallel, owing to the influence of Fe-Mg partitioning between olivine and orthopyroxene, which creates greater disparities in Mg nos. between the individual phases at lower bulk Mg no. As can be seen in Figure 5, the difference in Mg no. of coexisting olivine and orthopyroxene increases with decreasing Mg no., which leads to a larger vertical offset in H₂O concentration (i.e., increase in $D_{\rm H}^{\rm opx/ol}$) for $D_{\rm H}^{\rm opx/ol} > 1$ and smaller vertical offset (i.e., decrease in $D_{\rm H}^{\rm opx/ol}$) for $D_{\rm H}^{\rm opx/ol} < 1$ with decreasing Mg no., if the H contents of each mineral follow parallel trends with Mg no.

The modest values of $D_{\rm H}^{\rm opx/ol}$ determined in this study contrasts with the much greater values (~10) determined at 1–2.5 GPa from minerals crystallized from basaltic liquids (Koga et al. 2003; Aubaud et al. 2004; Hauri et al. 2006) or from natural peridotitic xenoliths (Bell and Rossman 1992). Much of the difference is related to the influence of Al, which greatly increases the H storage capacity of pyroxene owing to a coupled substitution mechanism (e.g., Mierdel and Keppler 2004; O'Leary et al. 2010). With increasing pressure, the Al content of peridotitic pyroxene diminishes (Brey et al. 1990; Hirschmann et al. 2009), thereby reducing strong H fractionation between pyroxene and olivine. Our results show that there is also an intrinsic reduction in opx/ol fractionation of H with increasing pressure that occurs in the absence of Al. Thus, in contrast to lower pressure conditions, where opx is the principal reservoir of H₂O in nominally anhydrous mantle, in the deeper parts of the upper mantle olivine may be the more important host (Tenner et al. in review).

Consequences for Mars

Nominally anhydrous minerals in Earth's mantle constitute a significant reservoir in the global H_2O cycle (Hirschmann 2006) and have a critical influence on the locus of partial melting (Hirschmann 2006) and on rheologic structure (Hirth and Kohlstedt 2003). The role of H_2O in the martian mantle is less clear, in part because the concentration of H_2O in the martian mantle is subject to considerable uncertainty and vigorous debate (Dreibus and Wänke 1989; Dann et al. 2001; McSween et al. 2001; Lunine et al. 2003; Chaklader et al. 2006; Treiman, et al. 2006) and in part because the geochemical behavior of H_2O in the martian mantle has been poorly constrained.

At the outset of this study, the only available constraints on the behavior of H in Fe-rich olivines were from the experiments of Zhao et al. (2004). These implied about an order of magnitude greater H storage capacity stability in Fe-rich olivines of martian composition compared to more forsteritic terrestrial olivines, which could have meant that H was much less incompatible during partial melting of the martian mantle than is true on Earth. This could have meant that a greater proportion of martian H was retained in the interior than would be estimated based on analogies with highly incompatible elements such as K, La, or Ce (Dreibus and Wänke 1985) and that the influence of H on the locus of partial melting would be less than that on Earth (Hirschmann et al. 2009). Our experimental results do not confirm the findings of Zhao et al. (2004), suggesting instead that H is about a factor of two more compatible in the martian mantle compared to terrestrial values (Fig. 5). Consequently, incompatible elements such as K and LREE remain good proxies for the behavior of H₂O during martian magmatic processes and the influence of H₂O on melting in the source regions of martian basalts may be similar to terrestrial equivalents.

We note that we have not measured directly mineral/melt partition coefficients applicable to martian basalt petrogenesis. However, to a first approximation the residue/melt partition coefficients for H are proportional to the H "storage capacities" for the residues (Hirschmann et al. 2009). In detail, of course, the relevant partition coefficients must be measured for minerals and melts of the correct composition for mantle melting. However, storage capacity measurements such as those presented here, where the melt composition is set by equilibrium with olivine and orthopyroxene in the FeO-MgO-SiO₂-H₂O system, provide a reasonable measure of relative incompatibility, since mineral/ melt partitioning is most strongly linked to crystal chemistry (e.g., Blundy and Wood 1994).

During partial melting of the terrestrial mantle, the coefficient for partitioning of H₂O between spinel peridotite residues and partial melts, $D_{\rm H}^{\rm perid/melt}$, varies between 0.006 and 0.009, depending on pressure (Aubaud et al. 2004, 2008; Hauri et al. 2006; Hirschmann et al. 2009; Tenner et al. 2009; O'Leary et al. 2010), and so H₂O behaves similarly to La (e.g., Workman and Hart 2005). The slightly lower incompatibility in Fe-rich peridotite suggests that values of $D_{\rm H}^{\rm perid/melt}$ applicable to Mars should be about a factor of two greater, or 0.009-0.014, and that the behavior of H should be intermediate between that of La and Ce in the martian mantle. Importantly, applicable values of $D_{\rm H}^{\rm perid/melt}$ are smaller than the extent of melting for martian basalts, which are typically in the range of 0.02-0.1 (Norman 1999; Borg and Draper 2003). Consequently, ratios of H to elements with similar incompatibility (e.g., La, Ce) will not be fractionated appreciably during partial melting. Fractionations of elements more incompatible than H, such as K, will also be small, or, will result in preferential retention of H in the residue.

These constraints on the relative behavior of H and K during partial melting of the martian mantle allow estimates of the minimum concentration of H_2O in the martian mantle. Based on average K contents of the martian crust from the Mars Odyssey γ -ray spectrometer, Taylor et al. (2006) concluded that half of the K₂O on Mars remains in the mantle. This is consistent with the estimated inventory of radioactive elements in the interior based on observed magma production rates (Kiefer 2003). If this is the case, then at least half of the martian H₂O must also remain in the mantle, unless there was a mechanism early in martian history that recycled K₂O but not H₂O to the interior. In contrast, Hauck and Phillips (2002) argued that ~95% of martian H₂O still resides in its mantle because extraction of H₂O from a one-plate planet is highly inefficient. Simulation



FIGURE 7. Concentrations of H_2O in primary martian magmas calculated assuming sources with 100–500 ppm H_2O (see text), ranges of melt fractions (0.02–0.1) plausible for origin of martian basalts as judged from SNC meteorites (Borg et al. 1997; Norman 1999; Borg and Draper 2003) and likely H_2O peridotite/melt partition coefficients applicable to partial melting of the martian mantle (see text). (Color online.)

of the cosmochemical and accretionary origin of Mars suggests an initial H_2O inventory similar to 0.06–0.27 terrestrial oceans (Lunine et al. 2003), which is equivalent to 200–1000 ppm H_2O for bulk silicate Mars. If a minimum of 50% of this remains in the mantle, then the mean martian mantle contains at least 100–500 ppm H_2O . The low end of this estimate is similar to that presently in the depleted mantle source for mid-ocean ridge basalts (Michael 1995; Dixon et al. 2002; Hirschmann 2006), and the high end is comparable to concentrations in sources of oceanic island basalts (Dixon et al. 2002).

Our estimate of the bulk martian mantle H₂O concentration is consistent with the estimate (288 ppm) of Lodders and Fegley (1997), based on oxygen isotopes of SNC and chondritic meteorites, but considerably more than the 36 ppm value favored by Dreibus and Wänke (1987) and Carr and Wänke (1992), based chiefly on observed H2O contents of SNC meteorites and, indirectly, on their Cl contents. Modest amounts of partial melting (e.g., 2-10%; Borg et al. 1997; Norman 1999; Borg and Draper 2003) of a source with the most hydrous mean concentration (500 ppm) would produce primary magmas with 0.4-1.9 wt% H₂O (Fig. 7), which, allowing for enrichment by fractional crystallization, would be sufficient to account for the ~2 wt% H₂O inferred in some Shergottite magmas based on phase equilibria constraints (Johnson et al. 1991; Dann et al. 2001; Dalton et al. 2007; Draper 2007) or concentrations of other volatiles in SNC phase distributions (McSween et al. 2001). However, there are alternative interpretations of these observations that do not require H₂O-enriched magmas (Treiman et al. 2006; Filiberto and Treiman 2009). At the less hydrous end, higher degrees of partial melting (0.10) of a martian mantle with 100 ppm H_2O would produce primary martian basalts with ~0.1 wt% H₂O (Fig. 7). We emphasize, however, that our estimates are for the average martian mantle and do not necessarily apply to the source regions of SNC meteorites, which may be depleted (or enriched) compared to the mean.

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APPENDIX 1

Revisions to previously published measurements of H in olivine

In this study, we have determined revised values for the H contents of olivine standards AC94 and AC87 that were characterized by Aubaud et al. (2007). In addition, we believe that the H content of standard AC89 may be underestimated by Aubaud et al. (2007). These three standards were used by Withers and Hirschmann (2007, 2008) and Tenner et al. (2009) to calibrate SIMS for measurement of H in olivine. Here we recalculate H concentrations of olivines analyzed in those studies, by reconstructing the calibrations used in those studies using revised values for AC94 and AC87 and excluding AC89, for which we have no revised value. The Withers and Hirschmann (2007, 2008) olivine H concentrations are increased by a factor of 2.05, and the Tenner et al. (2009) olivine measurement by a factor of 1.40. Note that these revisions correct the previously published SIMS values for consistency with the FTIR calibration of Bell et al. (2003), but do not address any potential difference between the FTIR extinction coefficients that apply to the OH absorption bands present in the natural olivines of Bell et al. (2003) and bands in the synthetic olivines of this study.

APPENDIX TABLE 1. Revised values for previously published SIMS measurements of H in olivine

Experiment	Study*	Experiment	Experiment	Olivine C_{H_2O}	Olivine C _{H2O}			
label		pressure	temperature	(wt% H ₂ O)	(wt% H_2O)			
		(GPa)	(°C)	(Published)	(Revised)			
AC87	1	2	1300	0.0478	0.08(1)			
AC94	1	3	1300	0.0910	0.20(2)			
M266	2	8	1200	0.11	0.23(2)			
M268	2	8	1400	0.08	0.16(1)			
M255	2	10.2	1200	0.19	0.39			
M262	2	10.2	1400	0.09	0.18(1)			
M273	2	11.6	1400	0.12	0.25(3)			
M280	3	8	1400	0.070	0.14(2)			
M288	3	8	1520	0.057	0.12(3)			
M281	3	8	1400	0.081	0.17(3)			
M287	3	8	1400	0.079	0.16(2)			
M283	3	8	1400	0.109	0.22(2)			
M286	3	8	1400	0.096	0.20(3)			
M300	3	8	1000	0.159	0.33(8)			
M292	3	8	1400	0.056	0.12(1)			
M298	3	8	1500	0.047	0.10(1)			
M303	3	8	1550	0.044	0.090(6)			
M297	3	8	1600	0.033	0.068(8)			
M293	3	8	1400	0.065	0.13(1)			
M373	4	3	1380	0.0029	0.0040(2)			
<i>Note:</i> Numbers in parentheses represent 1 st.dev. in the least significant digit of the measured value.								