Molecular hydrogen in mantle minerals

X. Yang[1]*, H. Keppler[2]*, Y. Li[1]

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Abstract

Current models assume that hydrogen was delivered to Earth already in oxidised form as water or OH groups in minerals; similarly, it is generally believed that hydrogen is stored in the present mantle mostly as OH. Here we show by experiments at 2-7 GPa and 1100-1300 °C that, under reducing conditions, molecular hydrogen (H_2) has an appreciable solubility in various upper mantle minerals. This observation suggests that during the accretion of the Earth, nebular H_2 could have been delivered to the growing solid planet by direct dissolution in a magma ocean and subsequent incorporation in silicates. Moreover, the presence of dissolved molecular H_2 in the minerals of the lower mantle could explain why magmas sourced in this region are rich in hydrogen, despite the fact that lower mantle minerals contain almost no OH groups.

Introduction

The presence of hydrogen in the silicate mantle is a key parameter in influencing Earth's climate, habitability, and geochemical evolution; without some hydrogen in the mantle, plate tectonics would likely not exist on Earth (Regenauer-Lieb et al., 2001; Mierdel et al., 2007). The formation of OH defects in nominally anhydrous minerals (Bell and Rossman, 1992; Keppler and Smyth, 2006) requires a sufficiently high oxygen fugacity, fO_2, to oxidise hydrogen to molecular H_2O or OH groups. However, highly reducing conditions may prevail deep in the modern Earth (Frost and McCammon, 2008), as well as on the Moon and on Mars (Wadhwa, 2008). The early Earth (Yang et al., 2014), especially during its early accretion (Rubie et al., 2011), was likely extremely reduced, with fO_2 far below the Fe-FeO buffer. Under these conditions, hydrogen is not oxidised to H_2O, but is present as H_2, and the retention of H in the early mantle would then

1. State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China
*   Corresponding authors (email: xzyang@nju.edu.cn; hans.keppler@uni-bayreuth.de)
2. Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany

only be possible if H_2 could be directly dissolved in mantle minerals. This does not appear implausible from available data on He solubility in olivine (Parman et al., 2005). In this study, we have investigated the solubility of H_2 in olivine, orthopyroxene (opx), clinopyroxene (cpx) and garnet by experiments at 2-7 GPa, 1100-1300 °C and Fe-FeO buffered conditions. Experiments were conducted on gem-quality single crystals, and recovered large crystals (up to 2-3 mm in size) were studied by Fourier-transform infrared (FTIR) spectroscopy (see Supplementary Information).

H_2 Dissolution and Quantification

Details of the experiments are given in Table 1, and representative spectra are illustrated in Figures 1 and 2. A small peak at ~4062 cm^{-1} was observed for most of the annealed crystals. This peak cannot be caused by gaseous H_2, e.g., in fluid inclusions, because H_2 does not possess a dipole moment and therefore is not infrared active. Also, this peak cannot be attributed to overtones of OH or of any other species, because in an experiment at 2.5 GPa and 1250 °C buffered by Fe_2O_3-Fe_3O_4 (with fO_2 about 9 log units above the Fe-FeO buffer), yielding very oxidising conditions where H_2 in the system is negligible, the annealed thick opx crystal showed strong OH bands, but no band in the 4100-4000 cm^{-1} range (Fig. S-2). We also show that this peak is unrelated to the embedding medium used during sample polishing (Fig. S-3). The only plausible explanation for the peak is therefore that it is due to H_2 dissolved in the lattice of the crystals.

Polarised FTIR determinations on an opx sample along the a, b and c axes show that the absorption of H_2 is anisotropic, with stronger absorbance along a and c than along b axes (Fig. 1). This confirms that H_2 is actually physically dissolved in the crystal lattice. It is known from previous studies on glasses that the interaction with the surrounding silicate matrix can produce an induced dipole in the H_2 molecule, which makes it slightly infrared active (Shelby, 1994; Schmidt and Holtz, 1998; Hirschmann et al., 2012). The H_2 frequency observed in this study is lower than in silicate glasses by 30-70 cm^{-1} (4105-4140 cm^{-1}), which in turn is ~50 cm^{-1} lower than in vapour (Shelby, 1994; Schmidt and Holtz, 1998; Hirschmann et al., 2012). The peak of H_2 in olivine is not obvious at 2.5 GPa and 1250 °C, unlike for opx, cpx and garnet, but is markedly enhanced at 7 GPa and 1300 °C (Fig. 2). This suggests a profound role of pressure on H_2 dissolution in silicate minerals, similar to that observed for silicate glasses (Hirschmann et al., 2012). For the same annealed cpx or garnet sample, the intensity of the H_2 peak, i.e. either the linear or integral absorbance, decreases with crystal thickness upon further polishing (Table 1 and Fig. 2c-d), as expected by the Beer-Lambert Law. However, the garnet sample shows much stronger absorbance at a greater thickness, which may be due to a zoned H distribution in the crystal or some loss of H_2 during the polishing process.

Table 1   Details of H_2 dissolution experiments.

Sample	P (GPa)	T (°C)	fO_2 buffer	fH_2 (bar)	Duration (hr)	Thickness (mm)[a]	Area (cm⁻²)	Height (cm⁻¹)	ppm H_2O[b]	ppm H_2O[c]	wt.% H_2O[d]
unpolarised FTIR											
opx	2	1100	Fe-FeO	5.45E+4	24	2.27	2.58	0.065	15	14	0.137
opx	2.5	1250	Fe-FeO	8.25E+4	24	1.42	3.11	0.079	18	17	0.167
opx	2.5	1250	Fe_2O_3-Fe_3O_4	4.68E+0	24	1.31	-	-	-	-	-
olivine	2.5	1250	Fe-FeO	8.25E+4	24	1.99	-	-	-	-	-
olivine	7	1300	Fe-FeO	3.02E+6	16	1.72	2.95	0.077	17	16	0.161
garnet	2.5	1250	Fe-FeO	8.25E+4	24	2.46	3.51	0.131	20	27	0.275
garnet	2.5	1250	Fe-FeO	8.25E+4	24	2.94	6.34	0.232	37	48	0.486
cpx	2.5	1250	Fe-FeO	8.25E+4	24	1.41	4.52	0.128	26	27	0.268
cpx	2.5	1250	Fe-FeO	8.25E+4	24	2.49	4.66	0.149	27	31	0.313
polarised FTIR											
opx $E//a$	2	1100	Fe-FeO	5.45E+4	24	2.27	2.78	0.079	5	6	0.056
opx $E//b$	2	1100	Fe-FeO	5.45E+4	24	2.06	1.41	0.047	3	3	0.033
opx $E//c$	2	1100	Fe-FeO	5.45E+4	24	2.27	3.53	0.089	7	6	0.062
total							7.72	0.215	15	15	0.151

To facilitate comparison, all H_2 contents are given as the equivalent contents of H_2O. Height and area are the linear and integral absorbance of the ~4062 cm⁻¹ peak, respectively normalised to 1 cm thickness. Unpolarised and polarised data of opx annealed at 2 GPa and 1100 °C are for the same sample from the 1st stage H_2 dissolution run (see Supplementary Information). Data labelled 'total' are the sum along *a*, *b* and *c* axes. For the opx crystal, the absorbance of unpolarised analysis is about 1/3 the total absorbance of polarised analyses, probably due to the orientation effect. fH_2 is the calculated equilibrium H_2 fugacity (see details in Yang, 2016).
- The peak is too weak for any quantitative evaluation (see Fig. 2a).
[a] Thickness of doubly-polished crystals.
[b] Estimated by the integrated area of the ~4062 cm⁻¹ peak with the determined extinction coefficient of 4.63 ppm⁻¹ H_2O cm⁻² for opx.
[c] Estimated by the height of the ~4062 cm⁻¹ peak with the determined extinction coefficient of 0.13 ppm⁻¹ H_2O cm⁻¹ for opx.
[d] Estimated by the reported extinction coefficient of 0.26 L/mol cm for SiO_2 glass by Shelby (1994).

Quantification of H_2 in these samples is not easy; methods such as ion microprobe (SIMS) are unsuitable, as SIMS can only measure the total H content, including the contribution from OH. To quantify H_2, we therefore carried out two-stage annealing experiments on an opx crystal (see Supplementary Information). The crystal was first annealed in H_2 and then re-annealed at high fO_2 to convert the dissolved H_2 into OH; the increased OH absorbance was measured by FTIR and converted into water contents. Blank experiments confirmed the reliability of the method. This yields absorption coefficients for polarised FTIR measurements of H_2 in opx of ~4.63 ppm⁻¹ H_2O cm⁻² for the integral intensity and of ~0.13 ppm⁻¹ H_2O cm⁻¹ for the linear intensity, where the concentration of dissolved H_2 is

expressed as the equivalent form of H_2O. By applying these values together with an orientation factor of 1/3 to the unpolarised spectra, H_2 contents in the samples can be estimated. The use of the same extinction coefficient for different minerals is justified, since the position and shape of the H_2 band is virtually the same. Observed hydrogen contents are mostly ~15-40 ppm H_2O. The data for olivine clearly show that hydrogen solubility increases with pressure, as expected from the increase of hydrogen fugacity. Moreover, the hydrogen contents given in Table 1 should be considered as minimum values. This is because the hydrogen contents are so small that it is conceivable that in the two-stage calibration runs, not all the H_2O produced by oxidation of H_2 was re-dissolved in the crystal; some may remain adsorbed on the surface. This could lead to some systematic underestimation of hydrogen solubility. Only for reference, Table 1 also contains hydrogen contents calculated using the linear calibration coefficient for H_2 in SiO_2 glass (Shelby, 1994). This would yield numbers higher by a factor of ~100. However, the position of the H_2 peak differs between SiO_2 glass and minerals, and accordingly, the extinction coefficient is likely also different.
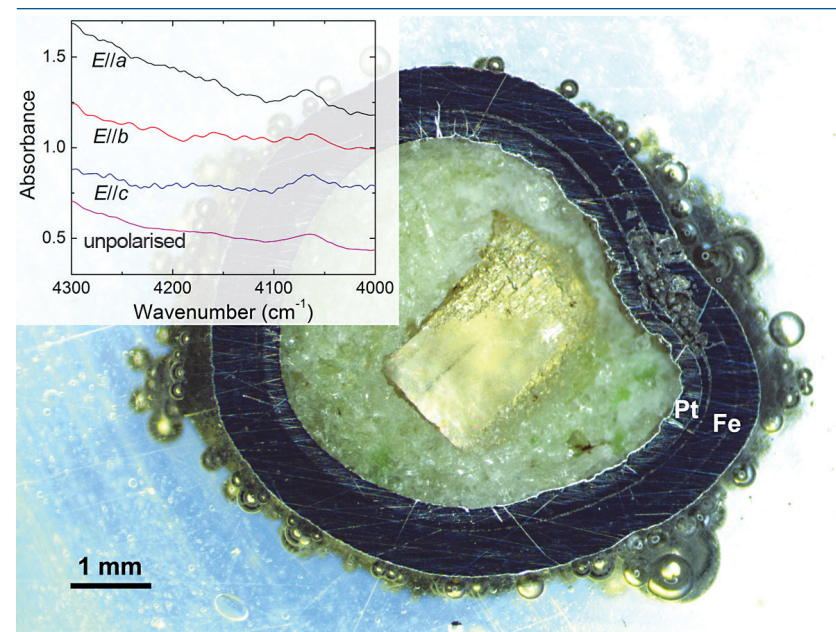
Figure 1   Recovered orthopyroxene crystal annealed at 2 GPa and 1100 °C and polarised and unpolarised FTIR spectra of the crystal containing molecular H_2. The spectra were normalised to 1 cm thickness and vertically offset. Blank experiments confirmed the reliability of the method. The crystal was surrounded by fine powder of spinel peridotite of broadly equilibrium composition (*e.g.*, with similar composition between the crystal and orthopyroxene in the peridotite). The capsule was embedded in epoxy resin, and the crystal remained nearly intact after the run.
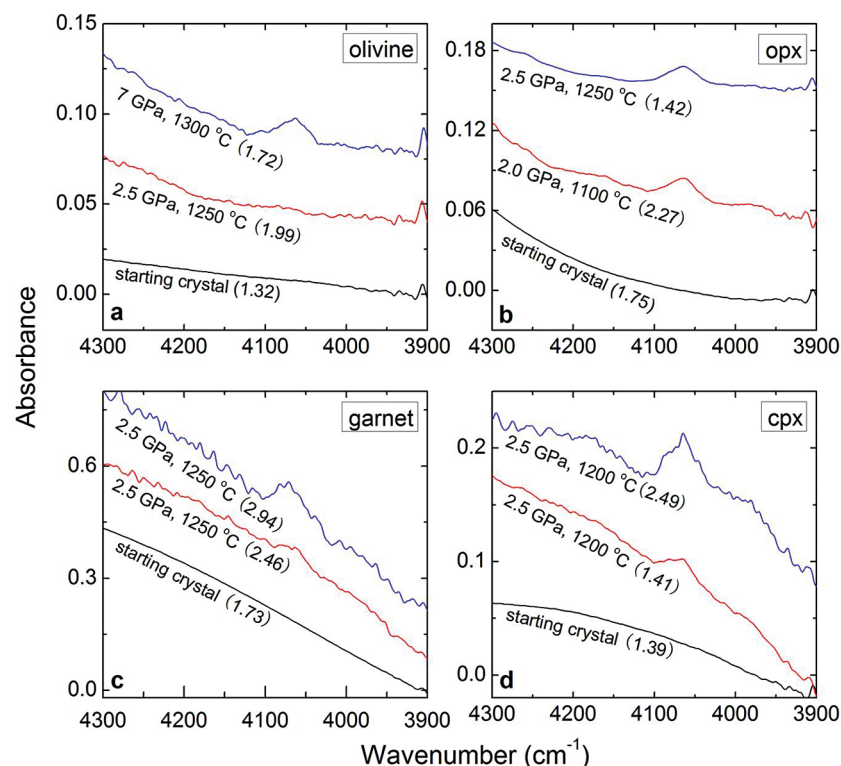
Figure 2 Unpolarised FTIR spectra of **(a)** olivine, **(b)** orthopyroxene, **(c)** garnet, and **(d)** clinopyroxene containing dissolved molecular H_2. Experimental conditions are given below each spectrum; numbers in parentheses are the thickness (mm) of the polished crystal. The spectra were not normalised to constant thickness, but vertically offset. The two spectra for either the annealed **(c)** garnet or **(d)** clinopyroxene were measured on the same recovered crystal after polishing to different thickness.

Additional evidence for an appreciable solubility of H_2 in mantle minerals comes from two recent studies. At otherwise similar conditions (1.5 GPa and 1200 °C), the OH solubility of olivine measured by FTIR is ~50 % lower for experiments buffered by Fe-FeO than by the more oxidising Ni-NiO buffer (Yang, 2016). This may reflect the higher water fugacity at Ni-NiO buffer conditions, where the fluid consists of nearly pure water, while at the Fe-FeO buffer, the fluid consists of a mixture of H_2O and H_2 in comparable molar fractions (Yang, 2016). However, SIMS measurements that measure total H (*i.e.* OH + H_2) found only a reduction of bulk hydrogen contents of ~5 % in the Fe-FeO as compared to the Ni-NiO buffer runs (Gaetani *et al.*, 2014). This would be consistent with a significant dissolution of H_2 in the sample under reducing conditions, which nearly compensated for the decrease in OH content.

Discussion

The solubility of H_2 measured in this study is about one order of magnitude lower than the water/OH solubility in minerals under comparable conditions (Keppler and Smyth, 2006). However, the observed solubility is not small on a planetary scale. While the measured contents are only ~15-40 ppm of H_2O (Table 1), they will increase with pressure and hydrogen fugacity in the deeper mantle so that solubilities of hundreds of ppm should easily be achievable at higher pressures. 100 ppm of H_2O in the bulk mantle would already be equivalent to 0.3 ocean masses. The data in Table 1 suggest that the H_2 solubility in minerals of very different structure and composition is quite similar. This is in line with the observation that the peak of H_2 in the FTIR spectra is always at the same position, irrespective of structural details. Very likely, H_2 does not substitute on a specific cation/anion site, but due to its small size, it fills interstitial positions. This would imply a broadly similar mechanism of H_2 dissolution in all silicate minerals of the entire mantle.

Current models of the origin of water on Earth usually assume that hydrogen was contained in the chondritic material from which Earth accreted, with a possible contribution from icy objects that formed beyond the snow line in the outer solar system and were later scattered inward (Morbidelli *et al.*, 2000; Marty and Yokochi, 2006; Rubie *et al.*, 2011; Marty, 2012). Such models necessarily imply that planets formed close to the sun are relatively dry, compared to those formed at larger heliocentric distances. The observation of significant solubility of H_2 in mantle minerals of this study suggests that some of the hydrogen on Earth could also have been sequestered directly from the solar nebula, in agreement with the recent discovery of a component with very low D/H ratio in the deep mantle (Hallis *et al.*, 2015). Hydrogen from a dense nebular atmosphere (Ikoma and Genda, 2006; Genda and Ikoma, 2008) could have first dissolved in the magma ocean (Hirschmann *et al.*, 2012) and then have been trapped in the silicate minerals of the mantle (Fig. 3a). Such a mechanism would allow sequestration of hydrogen into a planet at any heliocentric distance, implying that planets close to the sun do not necessarily have to be poor in hydrogen.

Mantle plumes reaching down to the lowermost mantle are believed to be the source of ocean island basalts (McKenzie and O'Nions, 1995; French and Romanowicz, 2015). There is ample evidence showing that this deep mantle source is also a major reservoir of volatiles (Dixon *et al.*, 2002; Saal *et al.*, 2002), with hydrogen contents that are several times higher than in the MORB source of the upper mantle. This observation is, however, in striking contrast to experimental data, which show that (Fe,Mg)O ferropericlase and (Mg,Fe)SiO_3 bridgmanite, the main minerals of the lower mantle, may dissolve at most a few ppm of OH in their structure (Bolfan-Casanova *et al.*, 2000, 2002, 2003; Panero *et al.*, 2015). The presence of some H_2 in the lattice of these two minerals could easily reconcile these observations (Fig. 3b). Upon upwelling from the lower mantle, fO_2 changes (Frost and McCammon, 2008), partially due to the phase change
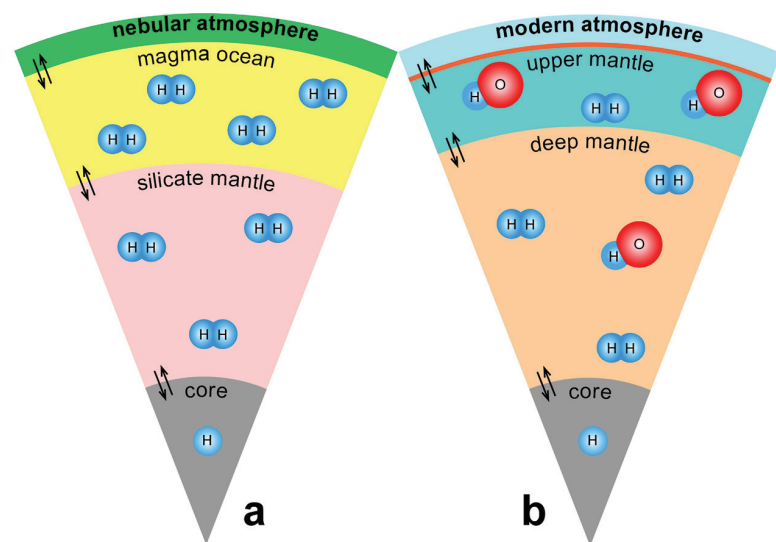
Figure 3 Schematic illustration of water storage **(a)** in the early mantle during the magma ocean stage and **(b)** in the modern mantle (not to scale). In the early Earth, where highly reducing conditions were prevailing, H_2 might have been distributed between different reservoirs through equilibrium partitioning. In the modern Earth, where plate tectonics and mantle redox stratification are present, hydrogen in the oxidised shallow upper mantle is mostly dissolved in minerals as OH groups, while significant amounts of H_2 are likely still present in the deep reduced mantle.

from bridgmanite, which stabilises Fe^{3+}, to upper mantle minerals that mainly incorporate Fe^{2+}. Accordingly, molecular H_2 stored in the lower mantle may be converted to H_2O or OH during the ascent of the mantle plume ($H_2 + Fe_2O_3 = H_2O + 2FeO$). It therefore appears that not only the deep cycle of carbon, but also the deep hydrogen cycle may be strongly coupled to the redox state of the mantle. Similar to carbon (Stagno *et al.*, 2013), the oxidation of H_2 to H_2O could also trigger partial melting, since H_2O is much more soluble in silicate melts than H_2 (Hirschmann *et al.*, 2012).

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Additional Information

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