



OH solubility in olivine in the peridotite–COH system under reducing conditions and implications for water storage and hydrous melting in the reducing upper mantle



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ABSTRACT

Experimental studies of OH solubility in peridotite minerals are of crucial importance for understanding some key geochemical, geophysical and geodynamical properties of the upper mantle. In reducing depths of the upper mantle, C–O–H fluids are dominated by CH₄ and H₂O. However, available experimental H-annealing of olivine concerning water storage capacity in the reducing upper mantle has been exclusively carried out by equilibrating olivine with H₂O only. In this study, OH solubility in olivine has been investigated by annealing natural olivine crystals under peridotite-bearing and CH₄–H₂O-present conditions with piston cylinder and multi-anvil apparatus. Experiments were performed at 1–7 GPa and 1100–1350 °C and with oxygen fugacity controlled by Fe–FeO buffer, and OH solubilities were measured from polarized infrared spectra. The olivines show no change in chemical composition during the experiments. The infrared spectra of all the annealed olivines show OH bands in the range 3650–3000 cm⁻¹, at both high (>3450 cm⁻¹) and low (<3450 cm⁻¹) frequency, and the bands at ~3400–3300 cm⁻¹ are greatly enhanced above ~3 GPa and 1300 °C. The determined H₂O solubility is ~90–385 ppm for the olivine coexisting with H₂O (1–7 GPa and 1100 °C), and is ~40–380 ppm for the olivine coexisting with CH₄–H₂O (1–7 GPa and 1100–1350 °C). When CH₄ is present in the equilibrium fluid, the H₂O solubility is reduced by a factor of ~2.3 under otherwise identical conditions, indicating a strong effect of CH₄ on the partitioning of water between olivine and coexisting fluid. The storage capacity of water in the reducing upper mantle is, modeled with the measured solubility of olivine and available partition coefficients of water between coexisting minerals, up to ~2 orders of magnitude lower than some previous estimates. Considering the temperature along the geotherm in the reducing oceanic upper mantle, the required H₂O concentration to trigger hydrous melting is 250 and 535 ppm at ~100 and 210 km depth, respectively, and is even larger at greater depths. These values exceed the typical H₂O abundance (~100 ± 50 ppm) in the upper mantle, suggesting that pervasive hydrous melting at reducing depths of the oceanic upper mantle is not likely. Similar arguments may also be casted for the reducing deep upper mantle in the continental regions.

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1. Introduction

It is commonly accepted that water dissolved as H-related point defects in the crystal structure of nominally anhydrous minerals constitutes the main reservoir of water in the mantle. Such water, even of trace amounts, affects strongly some important physico-chemical properties of the host phases and also key geochemical, geophysical and geodynamical processes of the mantle and even

the whole Earth (e.g. Hirschmann, 2006; Keppler and Smyth, 2006; Yang and McCammon, 2012; and references therein). The species and concentration levels of water in olivine, the most abundant mineral in the upper mantle, have attracted broad interest in the past decades, and our knowledge has been greatly enhanced as a result of extensive studies on natural and synthetic samples. Olivine in mantle samples, e.g. xenoliths, xenocrysts or megacrysts, is easily subjected to secondary hydrothermal alteration, and may also undergo significant H loss/gain during ascent to the surface (e.g. Demouchy et al., 2006; Peslier and Luhr, 2006; Peslier et al., 2008), casting doubt whether natural olivine can efficiently preserve initial H information in the mantle. Therefore,

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Table 1
Chemical composition of the starting materials (wt.%).

	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	NiO	Total
Olivine	41.01	0.01	0.02	0.01	9.72	0.11	48.35	0.06	<0.01	<0.01	0.31	99.60
Orthopyroxene	55.06	0.14	4.26	0.51	6.16	0.11	32.01	0.82	0.14	0.01	0.09	99.30
Clinopyroxene	52.81	0.39	6.35	1.10	3.06	0.08	14.89	18.53	1.92	<0.01	0.06	99.21
Spinel	0.02	0.20	48.63	17.86	12.31	0.12	19.72	<0.01	<0.01	<0.01	0.31	99.17

FeO, assuming all Fe as FeO. Data are the average of multi-grain (2–3) and multi-point (6–12) analyses by electron microprobe.

experimental studies under simulated conditions have been playing a critical role in understanding the dissolution of H in olivine.

Experimental H-annealing of olivine and constraints on water storage capacity have been nearly exclusively carried out with H₂O as the dominant, if not only, coexisting fluid, by equilibrating crystals with H₂O or by growing crystals in H₂O-bearing melts (Bai and Kohlstedt, 1993; Kohlstedt et al., 1996; Matveev et al., 2001; Zhao et al., 2004; Berry et al., 2005, 2007; Mosenfelder et al., 2006; Smyth et al., 2006; Grant et al., 2007; Ardia et al., 2012; Férot and Bolfan-Casanova, 2012; Sokol et al., 2013; Novella et al., 2014). However, fluids in the upper mantle are complicated. They are dominated by CO₂–H₂O under oxidizing conditions, e.g. in the modern shallow mantle, and by CH₄–H₂O under reducing conditions, e.g. in the modern upper mantle below ~100–150 km and in regional zones of the early shallow mantle (Rohrbach et al., 2007; Frost and McCammon, 2008; Zhang and Duan, 2009; Stagno et al., 2013; Yang et al., 2014b). Our recent work has shown that, under otherwise identical conditions of the oxidizing shallow mantle, water solubility of olivine coexisting with CO₂–H₂O differs profoundly from that with H₂O, due to the effect of CO₂ on the partitioning of water between olivine and fluid (Yang et al., 2014a). Therefore, knowledge of water storage in olivine in the reducing upper mantle and its effect on mantle properties requires experimental studies under conditions buffered by CH₄–H₂O-bearing fluids.

By using piston-cylinder and multi-anvil apparatus, the solubility of water in olivine has been for the first time investigated, with natural gem-quality olivine crystals as starting material, under peridotite-bearing, CH₄–H₂O-present, and Fe–FeO-buffered conditions at 1–7 GPa and 1100–1350 °C. For comparison, experiments of water solubilities in olivine in equilibrium with H₂O under otherwise identical conditions were also conducted. The results are of crucial importance for understanding the water storage capacity and hydrous melting in reducing depths of the “actual” upper mantle, as well as other relevant properties.

2. Water dissolution in olivine and CH₄ in upper mantle

The upper mantle is dominated by peridotite, and olivine constitutes about 60–70% of lherzolite to >90% of dunite. Water is dissolved mainly as OH in olivine. The infrared spectra of olivine exhibit great complexity, and >50 bands have been identified in the Mid-IR region (Miller et al., 1987; Matsyuk and Langer, 2004). Bai and Kohlstedt (1993) divided the bands into group I bands at high frequency (3650–3450 cm⁻¹) and group II bands at low frequency (3450–3000 cm⁻¹), however, subsequent studies have led to significant debates about the OH assignments (Supplementary material). Berry et al. (2005, 2007) have recently suggested that four substitution mechanisms may be commonly important, namely protonation associated with octahedral Ti (bands at ~3572 and 3525 cm⁻¹), Mg vacancies (bands at ~3300–3100 cm⁻¹), trivalent cations (bands at ~3400–3300 cm⁻¹) and Si vacancies (other group I bands, especially those at ~3610, 3579, 3567 and 3480 cm⁻¹), respectively. Despite the complexity, the terms of group I and group II bands are still widely used, and in most cases, they are only used to distinguish the high and low frequency bands, not involving their incorporation mechanisms initially considered by Bai and Kohlstedt (1993).

The amount of water dissolved in olivine is affected by olivine composition, pressure, temperature, oxygen fugacity and chemical environment, such as coexisting phases and water activity (Bai and Kohlstedt, 1993; Kohlstedt et al., 1996; Matveev et al., 2001; Zhao et al., 2004; Berry et al., 2005, 2007; Mosenfelder et al., 2006; Smyth et al., 2006; Grant et al., 2007). In this paper, water storage capacity and water solubility of olivine are equally used to refer to the maximum content of OH dissolved in this mineral under peridotite- and fluid-bearing conditions and at a given pressure and temperature, corresponding to fluid-saturated conditions in the reducing upper mantle. This resembles those used in Yang et al. (2014a) for peridotite- and CO₂–H₂O-bearing conditions in the relatively oxidizing shallow mantle.

C–O–H fluids play a key role in affecting many mantle processes, including melting, metasomatism and diamond genesis, and the speciation and composition of C–O–H fluids in the mantle are controlled by oxygen fugacity, pressure, temperature and other factors (e.g. Simakov, 1998; Frost and McCammon, 2008; Zhang and Duan, 2009). If present, C–O–H fluids in the reducing upper mantle contain a lot of CH₄, although the exact fraction, which may vary largely between different tectonic settings, remains unknown. Evidence for this includes: (1) theoretical models – empirical estimation and thermodynamic calculations have shown that CH₄ is an important component of C–O–H fluids under reducing conditions (Frost and McCammon, 2008; Zhang and Duan, 2009), e.g. for a system at 2.4 GPa, 1000 °C and buffered by Fe–FeO, the molar fraction of CH₄ in the equilibrium fluid is ~0.8 as shown by Zhang and Duan (2009); (2) natural samples – fluid inclusions in mantle samples are of unique importance for understanding mantle C–O–H fluids, and CH₄-rich fluid inclusions have been observed for peridotite formed at a depth of ~200 km (Liu and Fei, 2006) and a >0.5 molar fraction of CH₄ has been reported for fluid inclusions in diamonds (Simakov, 1998).

3. Experimental and analytical methods

3.1. Starting materials

The starting material was a fresh lherzolite xenolith from Lihue (eastern China), and, the constitutive minerals are olivine, orthopyroxene, clinopyroxene and spinel, with volume fractions of ~72%, 20%, 7% and 1%, respectively. The chemical composition is uniform for each mineral, as determined by electron microprobe analyses (Table 1). Gem-quality olivine crystals, with grain sizes of ~0.7–1.5 mm, were separated from the xenolith by handpicking under a binocular microscope. Several small pieces of the xenolith, caused by gentle crushing, were ground in an agate mortar with alcohol into fine powder (mostly <50 μm). The powder was used to produce peridotite-bearing conditions in the upper mantle and also used as pressure media surrounding olivine crystals in the experimental capsules, as well as shielding layers separating olivine crystals from the capsules and other materials loaded into the capsules, as employed by Yang and Keppler (2011) and Yang et al. (2014a) for olivine and by Yang (2012b) for feldspar. By the protection of peridotite powder and Au foil (see below), the composition of non-H elements in the olivine crystals could be maintained nearly not changed in the runs, so that the effect of C–O–H

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