Re-configuration and interaction of hydrogen sites in olivine at high temperature and high pressure

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ABSTRACT

Fingerprinting hydrogen storage sites in olivine at high temperature and high pressure is fundamental to understand water distribution and its impact on the upper mantle. We carried out in situ high-temperature and high-pressure IR spectroscopic investigations on hydrogen storage sites in the natural olivine and synthetic Fe-free forsterite. Based on in situ observations of hydrogen in both the natural olivine and synthetic Fe-free forsterite at high temperatures and high pressures, we find that hydrogen does not transfer between storage sites with increasing temperature, but displays disordering at temperatures over 600 °C. In contrast, pressure can induce re-configuration of hydrogen storage sites corresponding to the 3610 and 3579 cm⁻¹ bands. Hydrogen storage sites also exhibit disordering at high pressure. In addition, the dehydrogenation experiments of the natural olivine indicate interacts of hydrogen storage sites. Protons released from titanium-clinohumite defects move to pure Si vacancies, and also to Mg vacancies coupling with trivalent cations. This study is the first attempt to fingerprint hydrogen storage sites in olivine at high temperature and high pressure using in situ IR spectroscopy. The implications of the temperature- and pressure-induced disordering and re-configuration of hydrogen storage sites are discussed. The disordering and re-configuration of hydrogen storage sites at high temperature and high pressure favor better understanding of the water effects on physical properties of olivine. The interactions of hydrogen storage sites during dehydrogenation warn that some hydrogen, if observed in dehydrated mantle-derived samples may not be original and also make hydrogen diffusivity complex.

Keywords: Hydrogen sites, olivine, high temperature, high pressure, in situ IR spectroscopy, water, upper mantle

INTRODUCTION

Water in the form of hydrogen defects can be incorporated into olivine, and strongly influences the physical properties of olivine (Karato 1990; Yang et al. 2015; Faul et al. 2016; Chang et al. 2017), thereby being responsible for physical/chemical processes in the deep Earth (Peslier et al. 2010; Demouchy and Bolfan-Casanova 2016). However, the importance of water effects on some physical properties is still controversial (Wang et al. 2006; Yoshino et al. 2006; Costa and Chakraborty 2008; Fei et al. 2013; Faul et al. 2016; Cline et al. 2018). One of the important reasons may be the complex hydrogen storage sites in olivine. At least four incorporation mechanisms of hydrogen have been identified in olivine (e.g., Beran and Putnis 1983; Berry et al. 2005, 2007a, 2007b; Walker et al. 2007): hydrogen in pure Si vacancies, hydrogen in Mg vacancies, hydrogen associated with titanium-clinohumite, or trivalent cations in tetrahedral or octahedral sites. Recently, hydrogen linked to boron and fluoride in synthetic Fe-free forsterite and natural olivine also has been reported (Ingrin et al. 2014; Crépissone et al. 2014). Hydrogen with different incorporation mechanisms is expected to have different properties, such as diffusivities (Padrón-Navarta et al. 2014), infrared absorption coefficients (Kovács et al. 2010), and solubility (Ingrin et al. 2013; Padrón-Navarta and Hermann 2017). Thus, the water effects obtained from experiments in a regime where one mechanism is dominant may not be directly compared to those where hydrogen is incorporated by a different mechanism. Consequently, understanding hydrogen storage sites in olivine is fundamental to explore water distribution at depth and its impact on mantle dynamics.

A principal advantage of Fourier transform infrared (FTIR) spectroscopy is that it can fingerprint hydrogen of different incorporation mechanisms. Depending on the crystallographic environment, O-H stretching bands in the infrared spectra will have different frequencies. For example, hydrogen with different incorporation mechanisms has distinct absorption bands in the IR spectra of olivine: the bands at 3630–3400 cm⁻¹ are assigned to hydrogen substituting for Si vacancies (e.g., Lemaitre et al. 2004; Walker et al. 2007; Kovács et al. 2010; Umemoto et al. 2011); the bands at 3300–3100 cm⁻¹ are assigned to hydrogen substituting for Mg vacancies (Lemaitre et al. 2004; Berry et