In-situ infrared spectra of hydroxyl in wadsleyite and ringwoodite at high pressure and high temperature

XIAOZHI YANG1,2,*, HANS KEPPLER2, LEONID DUBROVINSKY2 AND ALEXANDER KURNOSOV2

1State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210046, PR China
2Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

ABSTRACT

The infrared spectra of hydroxyl in synthetic hydrous wadsleyite ($\beta$-Mg$_2$SiO$_4$) and ringwoodite ($\gamma$-Mg$_2$SiO$_4$) were measured at room temperature up to ~18.8 GPa for wadsleyite and up to ~21.5 GPa for ringwoodite. High-temperature spectra were measured in an externally heated diamond-anvil cell up to 650 °C at ~14.2 GPa for wadsleyite and up to 900 °C at ~18.4 GPa for ringwoodite. The synthetic samples reproduce nearly all the important OH bands previously observed at ambient conditions. Only subtle changes were observed in the infrared spectra of both minerals, both upon compression at room temperature and upon heating at high pressure. For wadsleyite, upon compression to ~18.8 GPa, the frequencies of the bands at ~3600 cm$^{-1}$ remain almost unchanged, while the main bands at 3200–3400 cm$^{-1}$ shift to lower frequencies. During heating at 14.2 GPa to 650 °C the bands at 3200–3400 cm$^{-1}$ broaden and shift to slightly lower frequencies. For ringwoodite, upon compression to ~21.5 GPa, the main bands at 3115 cm$^{-1}$ progressively shift to lower frequencies. During heating at 18.4 GPa to 900 °C, no frequency shift was observed for the band at ~3700 cm$^{-1}$, but the band initially at ~3115 cm$^{-1}$ shifted very slightly to higher frequencies, which should yield almost the same band positions at 1300–1400 °C as those measured at ambient conditions. Our data suggest that water speciation in hydrous wadsleyite and ringwoodite at ambient conditions may be comparable to that under mantle conditions, except perhaps for subtle changes in hydrogen bonding. The low OH-stretching frequencies in wadsleyite and ringwoodite under transition zone conditions imply a large H/D fractionation during degassing of the deep mantle. This may explain the apparent disequilibrium between the hydrogen isotopic composition of the upper mantle and the ocean.

Keywords: Hydroxyl, wadsleyite, ringwoodite, infrared spectra, high-pressure, high-temperature, diamond-anvil cell

INTRODUCTION

Wadsleyite ($\beta$-Mg$_2$SiO$_4$) and ringwoodite ($\gamma$-Mg$_2$SiO$_4$), the high-pressure polymorphs of olivine ($\alpha$-Mg$_2$SiO$_4$), are the most abundant minerals in the transition zone of Earth’s mantle, between 410 and 660 km depth. Both minerals are able to accommodate up to several percent (by weight) of water as hydroxyl groups in their structure, and they likely constitute the most important water reservoir in Earth’s interior (e.g., Smyth 1987; Kohlstedt et al. 1996; Bolfan-Casanova et al. 2000). Water strongly affects many physical and chemical properties of wadsleyite and ringwoodite, including elastic moduli, seismic velocities, molar volume, rheological strength, thermal expansion, and electrical conductivity (Inoue et al. 1998, 2004; Kavner 2003; Smyth et al. 2003; Jacobsen et al. 2004; Huang et al. 2005; Ye et al. 2009). The water contents in wadsleyite and ringwoodite can be high enough to shift phase boundaries between solid phases and to drastically reduce melting temperatures. As such, they may affect the structure of the transition zone, in particular the depth and width of the 410 km discontinuity and they may influence convection and dynamics of the whole mantle (Wood 1995; Bercovici and Karato 2003; Frost and Dolejs 2007; Richard and Bercovici 2009; Deon et al. 2013).

Structural models of the incorporation of H into wadsleyite and ringwoodite are indispensable for understanding water storage in the mantle and for predicting the effect of hydrogen on physical and chemical properties of the transition zone. Infrared spectroscopy is particularly useful for revealing the speciation of H in minerals, and so far models of the dissolution of H in wadsleyite and ringwoodite have been derived mostly from infrared spectra (e.g., Bolfan-Casanova et al. 2000; Jacobsen et al. 2005; Deon et al. 2010; Panero et al. 2013). Neutron diffraction (Sano-Furukawa et al. 2011) and NMR studies (Stebbins et al. 2009; Griffin et al. 2013) have generally confirmed the structural models derived from infrared spectroscopy, although they have added several important details. Water dissolution in wadsleyite is generally well understood. The wadsleyite structure contains an Si$_2$O$_7$ group and one oxygen atom (O1) not attached to silicon. Smyth (1987) pointed out that this oxygen atom is electrostatically underbonded and should be a suitable site for protonation. In hydrous wadsleyite, protonation of O1 is charge compensated by Mg$^{2+}$ vacancies. The intense bands between 3300 and 3400 cm$^{-1}$ in the infrared spectrum of hydrous wadsleyite can be assigned to substitution mechanism, with the OH vector pointing from the O1 atom to the O4 atom along a vacant M3 octahedral site. The weaker bands at ~3600 cm$^{-1}$ may be due to benz hydrogen bonds along the M3 edge, and the bands at ~3000 cm$^{-1}$ may be assigned to protonation of the tetrahedral edge of the Si$_2$O$_7$ group (Smyth 1987; Bolfan-Casanova et al. 2000; Jacobsen et