Measurement of water contents in olivine using Raman spectroscopy

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ABSTRACT

We have measured the water contents in forsterites and olivines synthesized in the multi-anvil press using confocal Raman spectroscopy. These samples were previously characterized for water contents by polarized FTIR and contain from 75 to 1300 ppm wt H2O. We find that both forsterite and olivine follow the same trend in water content vs. integrated Raman OH/Si intensity. In addition three synthetic enstatites also display a linear trend in water vs. OH/Si integrated Raman intensity but with a different slope than for olivine, indicating that the calibration for measuring water by Raman is matrix dependent. Three glasses of different compositions (two rhyolites and one basalt) and different water contents were also analyzed. Comparison with the forsterites and olivines shows that the Raman cross-section of these glasses is very different and their intensities must be corrected by different factors. Therefore, to be able to use glasses as external calibrants, prior knowledge of their behavior compared to well-characterized NAM standards is necessary.

Keywords: Raman spectroscopy, quantification, water content, olivine

INTRODUCTION

To constrain the deep water cycle, the knowledge of the storage capacity of water in nominally anhydrous minerals (NAMs) of the mantle is a key issue (e.g., Bolfan-Casanova 2005; Férot and Bolfan-Casanova 2012; Tenner et al. 2012). This is tackled by studying hydroxyl abundances in natural samples on one hand, and by investigating experimentally the high-pressure and high-temperature solubility of the water component in NAMs. Compared with natural samples, high-pressure synthetic samples are smaller in size, which introduces a limitation on the accuracy of water content measurements because the techniques developed so far, such as Fourier transform infrared spectroscopy (FTIR, Libowitzky and Rossman 1996; Kovacs et al. 2010; Asimow et al. 2006), secondary ion mass spectroscopy (SIMS, Aubaud et al. 2004; Demouchy et al. 2005), elastic recoil detection analysis (ERDA, Bureau et al. 2009; Withers et al. 2012), and proton-proton scattering (P-P, Maldener et al. 2003) provide a spatial resolution that is quite good but not always sufficient for polycrystalline samples. Among these techniques, infrared spectroscopy, being a site-specific technique, provides useful information about the different sites of protonation within the mineral structure, one pitfall being that sufficient thickness is necessary to detect small amounts of water and thus the grain size is a limiting factor (typically thicknesses of 50 to 100 μm are necessary, implying grain sizes of the same order). The beam size of SIMS or ERDA, which are bulk methods, is comparable to that of FTIR. SIMS is also very useful to measure water-rich samples, i.e., that are too absorbing for FTIR, as is the case of wadsleyite for example (Demouchy et al. 2005; Bolfan-Casanova et al. 2012), and has in addition achieved quite low-detection limits down to 50 ppm wt H2O (see Koga et al. 2003; Mosenfelder et al. 2011). A limitation of the method is that it relies on external calibrants with a significant matrix effect (Koga et al. 2003; Mosenfelder et al. 2011). Both SIMS, ERDA, or P-P techniques have recently been used to calibrate the infrared absorption coefficients of the Mg2SiO4 polymorphs [Withers et al. (2012) for olivine; Deon et al. (2010) for wadsleyite; Koch-Müller and Rhede (2010) for ringwoodite]. Especially ERDA and P-P are calibration-free methods.

In the past, we have used FTIR to analyze samples that were synthesized in chemically simple systems such as MgO-SiO2-H2O, MgO-FeO-SiO2-H2O, and MgO-FeO-Al2O3-SiO2-H2O, and with relatively high-bulk water contents from 5 to 1 wt% H2O. In these cases grain sizes are relatively large and allow absorbance techniques such as FTIR to be used. However, if the peridotite system is to be studied, and also with lower water contents that are more realistic for the mantle, grain sizes may be reduced and the spatial resolution becomes an important issue to measure water contents. Using Raman spectroscopy beam sizes of 1 × 3 μm can be achieved (see Thomas et al. 2009) competing with the diffraction limit of infrared spectroscopy.

In the recent years, Raman spectroscopy has been developed to measure water in glasses (Thomas 2000; Di Muro et al. 2006; Thomas et al. 2008) and has also been used to calibrate the water content in garnets (Thomas et al. 2008) down to 50 ppm wt H2O. In this study we report for the first time Raman spectra of OH in enstatite end-member Mg2SiO4 and iron-bearing olivine (Mg,Fe)2SiO4. We also present preliminary data for enstatite, showing that the method can be extended to any NAM.