Measuring H$_2$O concentrations in olivine by secondary ion mass spectrometry: Challenges and paths forward

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Abstract

Trace concentrations of H$_2$O in olivine strongly affect diverse mantle and magmatic processes. H$_2$O in olivine has been difficult to accurately quantify due to challenges in sample preparation and measurement, as well as significant uncertainties in standard calibrations. Here we directly compare secondary-ion mass spectrometry (SIMS) measurements of the olivine standards of Bell et al. (2003, hereafter Bell03) and Withers et al. (2012, hereafter Withers12) upon which most SIMS and Fourier transform infrared (FTIR) spectroscopy analyses are based. In the same SIMS session, we find that the olivine standards from the two studies are offset by ~50%, forming lines of different slope when comparing SIMS measurements to the independent nuclear reaction analysis (NRA) in Bell03 and elastic recoil detection analysis (ERDA) in Withers12. This offset is similar to the ~40% offset that exists in the FTIR absorption coefficients determined by those two studies, and points to the NRA-ERDA data as the cause for the offset more than different IR absorption characteristics of the different olivines. We find that the Withers12 olivine standards form the most precise calibration line, and that the measured Bell03 olivine standards have issues of reproducibility and accuracy due to the presence of hydrous inclusions (as documented previously by Mosenfelder et al. 2011). Owing to the limited availability of the Withers12 olivine standards, however, we recommend using orthopyroxene standards (Kumamoto et al. 2017) to calibrate H$_2$O in olivine by SIMS due to similar calibration slopes. We revise the reference values of current orthopyroxene standards to account for uncertainties in the Bell et al. (1995) manometry data. With these revised values, the orthopyroxene calibration line is within 12% of the Withers12 olivine line, which is within the long-term uncertainty of the SIMS olivine measurements. We apply our SIMS calibration protocol to revise estimates of the partition coefficients for H$_2$O between olivine and melt, resulting in a value of 0.0009 ± 0.0003 at pressures ~0.2–2 GPa. This brings into closer agreement between the partition coefficients determined from experimental studies and those based on natural studies of olivine-hosted melt inclusions.

Keywords: SIMS, water, olivine, nominally anhydrous minerals, calibration, volatiles, standards

Introduction

The presence of hydrogen in nominally anhydrous minerals (NAMs) is known to influence a wide range of mantle and magmatic processes (e.g., Bell and Rossman 1992). The solids of mantle peridotite, for example, varies markedly as a function of the hydrogen concentration in NAMs, which in turn governs the extent and pressure of mantle melting (e.g., Gaetani and Grove 1998; Hirschmann et al. 1999; Sarafian et al. 2017). It should be noted that hydrogen bonded to oxygen in mineral structures is often measured as H$_2$O ppm (µg/g), with some studies colloquially using the term “water.” Here we use H$_2$O to refer to the concentration of structurally bound H in a crystal, and where appropriate, H$^+$ for discussing the diffusing species. Olivine typically has only trace concentrations of H$_2$O (0–60 ppm), yet because it is the dominant upper-mantle mineral, it plays a prominent role in mantle dynamics (Demouchy and Bolfan-Casanova 2016). Rheological studies show, for example, that olivine’s strength may be reduced by up to an order of magnitude with as little as tens of parts per million of H$_2$O (Faul et al. 2016), with profound effects on mantle viscosity and dynamics (Hirth and Kohlstedt 1996). The H$_2$O concentration in olivine is also predicted to be a determining factor in the electrical conductivity of the mantle (Gardés et al. 2017), which is used for geophysical modeling of mantle structure (e.g., Naif et al. 2013). Furthermore, the rates and dynamics of magma ascent are often constrained by studying diffusion-induced concentration profiles of H$_2$O in magmatic and mantle olivine. (Demouchy et al. 2006; Peslier and Luhr 2006; Ferriss et al. 2018; Newcombe et al. 2020).

Despite recent advances in the measurement and quantification of H$_2$O in olivine, there remain several challenges. Some of these challenges arise from difficulties inherent to the analytical techniques used, while others arise from disagreements...