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Measuring H_2O concentrations in olivine by secondary ion mass spectrometry: Challenges and paths forward

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Abstract

Trace concentrations of H_2O in olivine strongly affect diverse mantle and magmatic processes. H_2O 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_2O 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_2O 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