American Mineralogist, Volume 96, pages 1725–1741, 2011

Analysis of hydrogen in olivine by SIMS: Evaluation of standards and protocol

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ABSTRACT

We measured hydrogen concentrations in 12 olivines using secondary ion mass spectrometry (SIMS and NanoSIMS), cross-calibrated against Fourier transform infrared (FTIR) spectroscopy and nuclear reaction analysis (NRA). Five of these samples are routinely used for calibration in other laboratories. We assess the suitability of these olivines as standards based on over 300 SIMS analyses, comprising 22 separate calibrations. Seven olivines with 0–125 ppm H_2O give highly reproducible results; in contrast to previous studies, the data are fit to well-constrained calibration lines with high correlation coefficients ($r^2 = 0.98$–1). However, four kimberlitic megacrysts with 140–245 ppm H_2O sometimes yield $^{16}O^1H/^{30}Si$ ratios that have low internal precision and can vary by up to a factor of two even in sequential analyses. A possible cause of this behavior is the presence of sub-microscopic inclusions of hydrous minerals, such as serpentine. In most cases, however, we link the anomalous results to the presence of sub-micrometer to micrometer-scale pores (as small as 100 nm), which we imaged using SEM and NanoSIMS. These pores are interpreted to be fluid inclusions containing liquid H_2O, other volatiles (including fluorine), and/or hydrous phase precipitates. Ionization of the contents of the pores contributes variably to the measured $^{16}O^1H$, resulting in analyses with erratic depth profiles and corresponding high uncertainties (up to 16%, $2\sigma_{\text{mean}}$). After filtering of these analyses using a simple criterion based on the error predicted by Poisson counting statistics, all the data fit well together. Our results imply that the Bell et al. (2003) calibration can be applied accurately to all olivines with IR bands from ~3400–3700 cm^{-1}, without the need for band-specific IR absorption coefficients.

Keywords: Secondary ion mass spectrometry, spectroscopy, infrared, water, mantle, olivine, calibration