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

JED L. MOSENFELDER,1,* MARION LE VOYER,1 GEORGE R. ROSSMAN,1 YUNBIN GUAN,1 DAVID R. BELL,2,3 PAUL D. ASIMOW,1 AND JOHN M. EILER1

1Division of Geological and Planetary Sciences, California Institute of Technology, M/C 170-25, Pasadena, California 91125-2500, U.S.A.
2Department of Chemistry and Biochemistry, Box 871604, Arizona State University, Tempe, Arizona 85287-1604, U.S.A.
3School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287, U.S.A.

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 H2O give highly reproducible results; in contrast to previous studies, the data are fit to well-constrained calibration lines with high correlation coefficients (r2 = 0.98–1). However, four kimberlitic megacrysts with 140–245 ppm H2O sometimes yield 16O/H/32Si 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 H2O, other volatiles (including fluorine), and/or hydrous phase precipitates. Ionization of the contents of the pores contributes variably to the measured 16O/H, resulting in analyses with erratic depth profiles and corresponding high uncertainties (up to 16%, 2σmean). 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

INTRODUCTION

The accurate analysis of trace concentrations of hydrogen in nominally anhydrous minerals (NAMs) and glasses is a long-standing problem (Aines and Rossman 1984; Rossman 1990, 2006; Ihinger et al. 1994; Hauri et al. 2002), with wide-ranging applications to geology and planetary science (e.g., Bell and Rossman 1992; Smyth and Jacobsen 2006; Saal et al. 2008; Hirschmann et al. 2009). Much of the work on NAMs has concentrated on olivine, the most abundant mineral in the Earth’s upper mantle. Although experimental studies have shown that olivine can incorporate large amounts of hydrous components—up to nearly 1 wt% (as H2O) at pressures of ~13 GPa (Mosenfelder et al. 2006a; Smyth et al. 2006)—typical concentrations in natural crystals are orders of magnitude lower, ranging from 0–20 ppm H2O (by weight, as used throughout this paper) for samples derived from the upper-most mantle (plagioclase- or spinel-hexerlotite facies) to 50–400 ppm H2O for xenocrysts from diatremes or kimberlites (garnet-hexerlotite facies) (Miller et al. 1987; Bell and Rossman 1992; Bell et al. 2004; Matsuak and Langer 2004; Koch-Müller et al. 2006; Mosenfelder et al. 2006b).

Fourier transform infrared (FTIR) spectroscopy is the most commonly applied tool for measuring such low concentrations. An increasingly popular and powerful technique is secondary ion mass spectrometry (SIMS), which has benefited from recent improvements in instrumentation, analytical protocols, and sample preparation techniques (Kuroswa et al. 1997; Hauri et al. 2002; Koga et al. 2003; Aubaud et al. 2007). FTIR and SIMS are complementary methods, each with its own advantages and disadvantages. FTIR provides constraints on mechanisms of H incorporation. In glasses, speciation into H2O and OH molecular groups can be readily and quantitatively determined. In minerals, it is possible—though with less certainty than in glasses—to assign different O-H absorption bands to intrinsic defects (point defects, substitutions) or extrinsic defects (inclusions or extended defects comprised of hydrous phases, fluid inclusions). Under ideal conditions, with thick samples (on the order of 1 cm) in transmission mode, the detection limit for IR is very low, less than 1 ppm H2O (Fig. 1). SIMS, on the other hand, offers enhanced spatial resolution (particularly with NanoSIMS), with the ability to examine much smaller, near-surface volumes of material, and the convenience and power of simultaneous analysis of other elements. SIMS can also be used for samples that are too fragile and/or small in grain size to analyze practically using FTIR, which requires double-polished sections to acquire high-quality data.

Recently published SIMS and NanoSIMS calibrations for hydrogen in olivine (Tenner et al. 2009; Kovác et al. 2010; O’Leary et al. 2010) suffer from scatter in excess of analytical precision (Fig. 2), to a greater degree than for other minerals and/or glasses calibrated in the same studies. We assessed the causes