Chemical Geology 458 (2017) 14–21

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Quantification of oxygen isotope SIMS matrix effects in olivine samples: Correlation with sputter rate

J. Isa*, I.E. Kohl, M.-C. Liu, J.T. Wasson, E.D. Young, K.D. McKeegan

Department of Earth, Planetary, and Space Sciences, University of California, Los Angeles, United States

ABSTRACT

We investigated the magnitude and reproducibility of instrumental mass-dependent fractionation of oxygen isotopes in secondary ion mass spectrometry (SIMS) analyses of olivine crystals of different major element chemistry (from Mg-rich to Fe-rich) in order to improve the accuracy of in-situ O-isotope measurements in geochemical/cosmochemical olivine samples. We found that oxygen isotope SIMS matrix effects are reproducible, and developed a model curve that can be used for correcting instrumental mass fractionation of olivine samples of intermediate chemical composition. The changes in instrumental mass fractionations were likely caused by differing Cs concentrations in the near surface regions of the samples due to different sample sputtering rates.

1. Introduction

Secondary ion mass spectrometry (SIMS) is a useful technique for analyzing isotope abundances in cosmochemical and geochemical samples because of its excellent spatial resolution. For light elements ($m < \sim 60$ amu) with relatively high ionization yields, SIMS can provide high precision (sub-permil) analyses of isotope ratios. As with all mass spectrometers, instrumental biases (e.g., mass-dependent fractionations) are calibrated by the use of standard materials, thereby enabling isotope ratios to be reported on a conventional normalized scale (e.g., Standard Mean Ocean Water, SMOW, for oxygen or hydrogen isotopes). Problems can arise due to a lack of appropriate standard materials; such problems can be particularly acute for SIMS, limiting both precision and accuracy of isotopic analyses. Precision is, in part, dependent on the homogeneity of an isotopic standard at fine spatial scales, a characteristic that typically can be assessed only through repeated SIMS measurements. However, even after homogeneity of a material is established, its suitability as a standard for a given isotopic analysis depends on how well the material matches the mineralogical and chemical composition of the target sample(s). This is because elemental and isotopic fractionations in SIMS are inherent in the sputtering process and thus depend upon the interactions of the primary ion beam with the target material. Ionization yields of sputtered target atoms are a function of the near-surface chemical composition of the target and are generally < 1%, even for sputtering with reactive primary ion beam species. Thus, instrumental fractionations can be discrepant for materials of differing chemical compositions or crystallinity, leading to inaccurate analyses should an inappropriate standard be used for calibration. The resultant error is referred to as a "matrix effect" since it is generated by a mismatch between the matrix of the sample being analyzed and that of the standard used to calibrate instrumental fractionation.

In situ analysis of oxygen isotope abundances was recognized as an important early application of SIMS, and this continues to the present day. Accordingly, significant efforts have been made to develop standard materials and to quantify matrix effects on SIMS oxygen isotope measurements. The most comprehensive work has involved oxygen isotope analyses of various silicate minerals made under energy filtering with selection of high-energy secondary ions (Eiler et al., 1997; Riciputi et al., 1998). This approach was taken in the hope that, by analyzing only secondary ions that were sputtered from a sample with high initial kinetic energy (typically > 325 eV), matrix effects would be reduced and/or instrumental mass fractionation (IMF) would be more stable and could be modeled by systematic parameterization(s). These early investigations demonstrated some general trends between IMF and sample characteristics, for example mean atomic mass. Among related minerals, the IMF was found to correlate with simple chemical parameters; for example, within the olivine solid-solution series the magnitude of oxygen isotope IMF increased linearly with forsterite content by approximately 6‰/amu over a range of ~0.2 in molar Mg/(Mg + Fe) content (Eiler et al., 1997; Riciputi et al., 1998). Interpolation over this limited range in olivine chemistry permitted analytical accuracy in $\delta^{18}O$ of ~1‰, which was commensurate with the precision obtained with this method that utilized magnetic field peak-hopping

---

* Corresponding author.
E-mail address: jisa@ucla.edu (J. Isa).

http://dx.doi.org/10.1016/j.chemgeo.2017.03.020
Received 18 October 2016; Received in revised form 18 March 2017; Accepted 20 March 2017

and ion counting with electron multipliers. However, extrapolation to more Fe-rich compositions showed very large deviations from the linear relationship, resulting in a $\delta^{18}O$ error (matrix effect) ranging up to ~20‰ for pure fayalite (Eiler et al., 1997).

With the development of large-radius, forward-geometry ion microprobes (e.g., the CAMECA ims-1270 and -1280), rapid, high-precision (< 0.5‰) oxygen isotope measurements became possible by measuring isotope beams simultaneously with Faraday cup detectors distributed along the instrument's mass focal plane (e.g., Kita et al., 2009; Kolodny et al., 2003; Treble et al., 2007). To achieve the necessary high intensity signals from small (~10–25 μm) analytical spots, the mass spectrometer must be set to transmit the abundant, low-energy secondary ions, i.e., the peak of the sputtered ion energy distribution. These methods have supplanted the high energy-filtering approach because they enable much faster analyses (3–5 min vs. 15–30 min) that consume less sample while still yielding significantly improved precision. However, higher precision without an equivalent increase in accuracy is always problematic, and therefore today's analyses also require an improved quantification of matrix effects appropriate to the analytical conditions utilized.

In this contribution, we focus on oxygen isotope analyses of olivine. We are interested in meteoritic samples that often span a very wide range in FeO contents compared to terrestrial mantle olivines (Criss, 2008 and references therein); for example, olivine phenocrysts in unequilibrated carbonaceous chondrites range from ~Fa0 to Fa80 (e.g., Wasson and Rubin, 2003), olivine in martian meteorites is intermediate from ~Fa20 to Fa50 (e.g., Mikouchi et al., 2001), olivine in HED meteorites is ~Fa30 to Fa90 (Warren et al., 2014 and references therein), and olivine in angrites goes from ~Fa10 to Fa86 (Keil, 2012). Previous studies of matrix effects in meteoritic olivine have come to different conclusions. Valley and Kita (2009) found significant matrix effects that varied non-linearly from forsterite to fayalite, however only a limited number of intermediate composition olivines were investigated with no samples analyzed between Fa40 and Fa100. In contrast, Jogo et al. (2012), using similar analytical methods and instrumentation, found no systematic differences in IMF among terrestrial (Fa11) and meteoritic (Fa35 and Fa63) olivine standards. The reasons for this discrepancy are not apparent.

Our goal here is to investigate oxygen isotope IMF over the entire olivine Fe-Mg solid-solution series. We determined the oxygen isotope compositions of nine separate, homogeneous olivine samples by laser-assisted fluorination isotope-ratio mass spectrometry and then made high precision SIMS analyses of the same samples to define a calibration curve between instrumental mass fractionation and sample compositions. We also investigated whether matrix effects correlate with the concentration of Cs ions implanted in the sample surface. Our results permit interpolation of matrix effects for intermediate olivines, thereby enabling high precision and high accuracy for investigations of cosmochemical samples.

1.1. Sample and analytical technique

Seven terrestrial and two meteoritic olivine samples, covering a wide range of Fe/Mg compositions, were studied (Table 1). The sample descriptions are in the appendix. All samples were handpicked under a binocular microscope. The samples were carefully examined to avoid other phases such as opaque inclusions, or yellow brown to dark brown colored veins that probably consisted of carbonate and Fe-bearing oxide. Some grains were mounted in epoxy resin or indium for SIMS measurements, while other portions of selected grains were used for laser fluorination analysis. Several samples (Day Book dunite, Rockport, and those from the Skaergaard intrusion) were washed prior to laser fluorination analysis to dissolve adhering opaque oxides and other weathering materials. The samples were washed in individual beakers by following a protocol of hydrochloric acid (3 mol/l overnight), deionized water in an ultrasonic bath, nitric acid (2 mol/l overnight), deionized water in an ultrasonic bath, and methanol in an ultrasonic bath. After the acid treatment, the samples looked transparent and had a uniform color (yellow to slightly green in the range Fa0 to Fa70). All samples were dried in an oven at 50 °C for three to five days prior to the laser fluorination analysis.

Quantitative mineral elemental compositions were obtained by electron microprobe analysis (EPMA) with the UCLA JEOL8200, with 20 s counting times for peaks and 5 s counting time for backgrounds. The beam currents used were ~15 nA at 15 kV; ZAF corrections were made.

For laser-assisted fluorination, samples were melted in the presence of fluorine gas by irradiation with an infrared laser and the isotopic composition of liberated oxygen was measured with a Thermo Finnigan Delta Plus gas-source isotope ratio mass spectrometer (IRMS) in Dual Inlet mode at the Stable Isotope Lab, UCLA, following methods most recently described in Young et al. (2016). SIMS analyses were performed on the UCLA 1270 and 1290 ion microprobes by using a primary Cs^+ beam and analyzing low-energy (0–25 eV) negative secondary ions. The measurements were carried out during four different analytical sessions, with the ims-1270 in 2012, 2013 and 2014, and with the ims-1290 in 2017. On the ims-1270, samples were sputtered with a 20 keV Cs^+ primary beam with intensities of 3, 4 and 6 nA focused to spots with a diameter in the range of 20–40 μm; on the ims-1290, primary beam intensities of 2.5 nA and 4 nA were used (spot sizes ~10–20 μm). A normal incidence electron gun was used to compensate for sample charging. Oxygen isotopes ^{16}O and ^{18}O were measured simultaneously by using two Faraday cups (10^{10} and 10^{11} Ω resistors) in the multicollection system. The acquisition times per analysis spot on the ims-1270 were 200 s (12 to 15 cycles of 10 s integration) and resulted in internal uncertainties < 0.1‰. On the ims-1290, secondary ions were counted for ~1 min (10 cycles of 5 s integrations) and internal and external uncertainties between 0.1‰ and 0.2‰ were achieved. The relative sputter rates for individual

Table 1
Olivine standard materials used in this study.

Name of sample	Fa	Locality	Source and sample identifier
Pine River IAB iron meteorite	2	N/A	UCLA, IN 314
Day Book dunite	7	Yancey County, North Carolina, USA	NMNH 119138
Mt. Franklin	8	Victoria, Australia	Paul Warren (UCLA)
San Carlos	9	San Carlos, Gila County, Arizona, USA	Christopher Snead (UCLA)
Urals	16	Lake Itkul, Sverdlovsk, Urals, Russia	NMNH 16257-01
Skaergaard EG 5108	35	Skaergaard Intrusion, East Greenland	Oxford U., EG5108
NWA 6693 achondrite	50	N/A	UCLA, LC 2617 and LC 2618
Skaergaard EG 1907	69	Skaergaard Intrusion, East Greenland	Oxford U., EG1907
Rockport	97	Essex County, Massachusetts, USA	NMNH 85276