Chemical Geology 258 (2009) 5–16

Contents lists available at ScienceDirect

Chemical Geology

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

Lithium isotope analysis of olivine by SIMS: Calibration of a matrix effect and application to magmatic phenocrysts

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ARTICLE INFO

Article history:
Accepted 3 October 2008

Keywords:
Mantle
Xenolith
Peridotite
Hawai'i
Ko'olau
Tanzania
South Africa
San Carlos
Kilbourne Hole
Geochemistry
Ion microprobe
Secondary ion mass spectrometry

ABSTRACT

High-spatial resolution analysis of light element isotope variations by secondary-ion mass spectrometry (SIMS) has numerous applications in geochemistry and cosmochemistry. Recent attention has focused on ^{7}Li/^{6}Li variations in magmatic phenocrysts to infer the volatile degassing history of their parent magmas, and on minerals from mantle samples to determine source-region processes and the recycling history of mantle reservoirs. In these studies the effect of mineral composition on the ^{7}Li/^{6}Li ratio measured by SIMS has been considered secondary, and generally disregarded. We show, using a suite of nine olivines analyzed by MC-ICP-MS or TIMS, that there is a substantial effect of composition on the ^{7}Li/^{6}Li ratio of olivine measured by SIMS. For magnesian olivine ($74<\mathrm{Fo}<94$) the effect is a linear function of composition, with δ^7Li increasing by 1.3‰ for each mole percent decrease in forsterite component. At higher Fe contents, the relationship ceases to be linear. The composition range over which linear behavior is exhibited appears to depend on instrumental conditions. A calibration of this matrix effect over the linear range is presented, assuming the measurement of ^{7}Li/^{6}Li relative to an olivine standard of known composition. Application of this calibration to a suite of olivines separated from basaltic lavas from Ko'olau, Hawai'i demonstrates that the matrix effect is responsible for a geologically spurious correlation between δ^7Li and Mg#. However, after correction, the olivines retain evidence of Li isotope heterogeneity, the degree and nature of which differs in each of the four separates studied. These results emphasize the importance of compositional correction for SIMS measurement of δ^7Li in olivine, particularly in zoned crystals, and support previous conclusions that Li isotope variability in igneous materials is subject to late-stage disturbance. The significant matrix effect demonstrated for olivine suggests that matrix effects in other minerals require further evaluation.

1. Introduction

Secondary ion mass spectrometry (SIMS) analysis of micro-scale Li isotope and abundance variations in mineral grains plays an important role in establishing mechanisms and scales of isotope fractionation. The microanalyses permit assessment of intra-granular spatial correlations between concentration and isotopic profiles, and can be used to investigate diffusion-related concentration variations and isotopic fractionation, as well as other igneous processes such as volatile element degassing, magma mixing, or contamination. These SIMS analyses commonly traverse widely varying major element compositions of individual mineral grains (e.g., Beck et al., 2004). The effect of these varying matrix compositions on the instrumental capability to produce accurate Li isotope compositions has not been investigated systematically, but most studies conclude the effect to be negligible under the conditions investigated (Decitre et al., 2002; Beck et al., 2006).

A difference of ~4‰ was reported in the δ^7Li values obtained by SIMS for basaltic glasses depending on the use of olivines or clinopyroxene as a standard (Hervig et al., 2004). In that study, low energy secondary ions were collected (0±20 eV). Kasemann et al. (2005) noted a probable matrix effect for Li isotopes in siliceous glasses by observing a shift in instrumental mass fractionation (IMF) as a function of the degree of energy filtering applied to secondary ions, but they did not observe such a shift for basaltic glasses. The combined SIMS and MC-ICP-MS (multi-collector inductively coupled plasma mass spectrometry) study by Jeffcoate et al. (2007) noted possible matrix effects of a few ‰ in the analysis of olivines and pyroxenes from mantle xenoliths.

During an extensive program of Li isotope analyses of olivines from various mantle samples and meteorites, we observed a strong correlation between olivine composition (forsterite [Fo] content = Mg# = 100 Mg/[Mg+Fe] on a molar basis) and δ^7Li, prompting the systematic investigation of a possible matrix effect in this mineral. In this study we compare SIMS and MC-ICP-MS or thermal ionization mass spectrometry (TIMS) analyses of olivine samples with a range of

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doi:10.1016/j.chemgeo.2008.10.008

compositions to calibrate the effect of Mg# in olivine on the $^7Li/^6Li$ measured by SIMS. We then apply the calibration to a suite of olivine phenocrysts in basaltic lava (originally intended for use in the matrix calibration but found to be heterogeneous) to assess the degree of Li isotopic variability.

2. Samples

Sample details appear in Table 1. Most olivines used to calibrate the matrix effect were separated from peridotite xenoliths from Tanzania (89-773, LB29, LB51, LB59) and the SW USA (KBH-1, SC1-OL, SC-OL2). They include samples studied previously by Bell and Rossman, 1992; Rudnick et al., 1994; Seitz and Woodland, 2000; Seitz et al., 2004; Aulbach et al., 2008. Sample KPL-2 is a cumulate dunite xenolith from the 1800 Ka'upulehu Flow (Hualalai, Hawai'i). PMD99-149 is an Fe-rich olivine megacryst from the Gansfontein kimberlite, South Africa (Doyle, 1999). These samples range in composition from Fo74.1 to Fo93.6 and most are compositionally homogeneous. Minor heterogeneity in Fe/Mg was recorded in KPL-2 and LB51 (Table 1, Table A1). In KPL-2, two compositionally different groups of grains occur, and were treated as separate data points, although both were assigned the same bulk solution value for δ^7Li. In LB51 one grain had a different Fo content from other homogeneous grains and one grain was zoned. Consequently, the formal uncertainties that reflect this heterogeneity are greater for LB51 than for other samples. An additional sample of olivine with composition Fo52 is from a dunite from the Mooihoek pipe of the Bushveld Igneous Complex (Scoon and Mitchell, 2004). The grain sizes in these samples vary from ~2 mm to >1 cm.

A suite of phenocrysts separated from basalts of Ko'olau, Hawai'i was also analyzed in detail. These are grains remaining from the separates prepared and studied by Chan and Frey (2003) and are mostly in the size range of 0.5–1 mm. 68 analyses on 15 olivine grains drawn from four mineral separates were performed. A further 15 analyses were performed on four grains from separate KOO49, which subsequently proved to be either orthopyroxene or clinopyroxene. Originally, we planned to use both mantle olivines and the suite of olivines separated from Hawaiian basalts to calibrate the matrix effect.

During the study it became apparent that many of the separated phenocrysts (and a minor proportion of the mantle peridotite grains) showed variability in both Fo content and δ^7Li, rendering them less suitable as calibration standards than the more homogeneous mantle samples. Consequently, the matrix effect was calibrated using only the latter. After this matrix effect calibration was applied to the phenocrysts it was found that significant real variation in their Li isotopic composition exists. These variations are documented here and the implications for processes of Li isotope fractionation in basalts, and for the Li isotope analysis of such materials, are discussed.

3. Analytical methods

3.1. Sample preparation

Grains were extracted from crushed peridotite or megacryst fragments by handpicking under the optical microscope, mounted in epoxy and polished using standard procedures, including SiC and Al_2O_3 grinding and polishing grits. After polishing the mounts were washed in ethanol and carbon- or gold-coated for analysis.

3.2. Bulk analysis

Pure separates of the olivine grains were prepared by handpicking crushed, sieved and washed portions of the peridotite samples under the binocular microscope, excluding extraneous phases and altered grains, and keeping cracked grains to a minimum. Most separates were analyzed at the University of Maryland using techniques described by Aulbach et al. (2008). Li abundances and δ^7Li values for SC1-OL determined by MC-ICP-MS are from Seitz et al. (2004), and for the Ko'olau olivines by TIMS from Chan and Frey (2003).

3.3. SIMS analysis

Li isotope microanalyses were obtained on the Cameca IMS-3f and IMS-6f SIMS at Arizona State University. The primary beam was $^{16}O^-$ (15–30 nA, 30–50 µm diameter). Positive secondary ions with excess kinetic energies of 0±20 eV were detected in pulse counting mode. The mass spectrometer was operated at a mass resolving power that varied from ~600 to 1200 ($M/\Delta M$). Mass scans run at $M/\Delta M \sim 1200$ to separate ^6LiH from ^7Li consistently detected no hydride ion, even on hydrous glasses and clay minerals, so that most analyses were performed at lower mass resolution in order to maximize count rates and minimize counting statistics errors. Counting times were 10 s for ^6Li and 1 s for ^7Li in each cycle, with 50 to 200 cycles per analysis, and the largest contrast aperture (400 µm) was used. Typically a pre-sputter period of 3–5 min per point was employed. For the most recent analyses, including most analyses used in the matrix-effect calibration, charge compensation was evaluated every 20 cycles, and ranged from 0 to 30 V.

All raw $^7Li/^6Li$ isotope ratios and ^7Li intensity data were plotted as a function of cycle number to facilitate the screening of outliers and analyses affected by surface contamination or changes in primary ion intensity (as revealed by systematic trends or fluctuations in ^7Li count

Table 1
Olivine sample details

Sample no.	Fo±2σ	δ^7Li±2σ	Locality	Rock type	Reference
Mantle olivine samples used in matrix correction					
KBH-1	90.5±0.1	3.4±1.0	Kilbourne Hole, NM	Spinel lherzolite xenolith in basalt	1
SC1-OL	89.7	3.4±0.5	San Carlos, AZ	Spinel lherzolite xenolith in basalt	2
KPL-2	86.1±1.7	7.3±0.4	Hualalai, Hawai'i	Dunite xenolith in basalt	
LB51	85.5±1.7	6.6±0.3	Labait, Tanzania	Wehrlite xenolith in olivine melilitite	3, 5
LB29	92.4±0.3	3.5±0.7	Labait, Tanzania	Garnet lherzolite xenolith in olivine melilitite	3, 5
LB59	84.7±0.3	6.6±0.4	Labait, Tanzania	Wehrlite xenolith in olivine melilitite	3, 5
89-773	93.6±0.2	3.0±0.5	Olmani, Tanzania	Spinel harzburgite xenolith in ankaramite	4
PMD99-149	73.9±0.3	2.3±0.2	Gansfontein, South Africa	Olivine megacryst in kimberlite	6
MHK-1	52.4±0.3	−0.8±0.5	Mooihoek, South Africa	Dunite from pipe in Bushveld Complex	
Olivine phenocrysts from Hawaiian basalts					
KOO-17A	86.1–88.4	5.0±0.5	Makapu'u, O'ahu	Phenocrysts in lava flow	7
KOO-30A	81.8–88.3	2.6±0.5	Makapu'u, O'ahu	Phenocrysts in lava flow	7
KOO-49	78.1–85.5	2.3±0.7	Kamehame Ridge, O'ahu	Phenocrysts in lava flow	7
KOO-55	82.1–88.2	4.6±0.5	Kamehame Ridge, O'ahu	Phenocrysts in dike	7

Errors on olivine compositions represent compositional variability determined from numerous analyses (see text and Table A1). References refer to previous work on these olivines. Further references to the localities may be found in the text. 1. Bell and Rossman (1992), 2. Seitz et al. (2004), 3. Lee and Rudnick (1999), 4. Rudnick et al. (1994), 5. Aulbach et al. (2008), 6. Doyle (1999), 7. Chan and Frey (2003).