INVESTIGATION OF INSTRUMENTAL FRACTIONATION IN SIMS ANALYSES OF MAGNESIUM, SILICON, AND OXYGEN ISOTOPES IN SILICATES AND OXIDES.

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Introduction: Secondary ion mass spectrometry (SIMS) fractionates elemental and isotopic abundances of a sample during measurements. Physical models to describe the formation of sputtered ions in chemically complex solids are too immature to accurately correct for the elemental and isotopic fractionation of secondary ions. As a result, quantitative analyses for elemental and isotopic abundances require empirical corrections of the instrumental mass fractionation (IMF) using standard materials having similar matrix to the samples to be measured and well-determined elemental and isotope compositions. Here we describe IMF in Mg- and Si-isotope analyses in suites of olivines and low-Ca pyroxenes obtained with Cameca ims-1280 SIMS at University of Hawai‘i, and our progress to develop O-isotope standards for variety of minerals.

Magnesium-isotope IMF: We used ~3−5 nA primary $^{16}O^-$ beam produced by the duoplasmatron or Hyperion-II ion source (installed in August 2019), and 4 Faraday cups (FCs) to measure simultaneously ^{24}Mg, ^{25}Mg, ^{26}Mg, and ^{27}Al. Typical internal precision for δ^{25}Mg is ~0.1−0.15‰ (2-standard-error, 2SE), and typical external reproducibility is ~0.1−0.2‰ (2-standard-deviation, 2SD). We investigated IMF in δ^{25}Mg (Fig. 1) using natural olivine and low-Ca pyroxene from terrestrial peridotites and achondrites (aubrite, pallasite, angrite, diogenite) having Mg-isotope compositions previously reported [1 and refs. therein]. Magnesium-isotope IMF in olivines changes depending on their forsterite contents, generally similar to the observations by [2,3]. However, while we observed a smoothly curved trend against Fo content between Fo_{65-100}, and constant IMF for Fo>65, more complex trend with abrupt changes at $Fo_{\sim 87}$ and $Fo_{\sim 97}$ was found by [2,3]. We need more samples to investigate these anomalous IMF changes. Mg-isotope IMF in pyroxenes also depends on their enstatite and/or wollastonite contents. While our results are generally consistent with those in [4], we investigated more samples and found a curved trend with a bump around $En_{\sim 75}$ in low-Ca pyrorxene IMF. We will try to find more pyroxenes, especially with En~80 to fill gaps between the data in this study.

Silicon-isotope IMF: We developed high-precision Si-isotope measurement protocol with ims-1280 SIMS using conditions similar to [5,6]. We used ~3 nA primary Cs^+ beam with ~10 μm spot and 3 FCs to collect ^{28}Si, ^{29}Si, and ^{30}Si simultaneously. Typical internal precision for δ^{30}Si is ~0.2‰ (2SE) and typical external reproducibility is ~0.2‰ (2SD). We investigated IMF in δ^{30}Si (Fig. 2) using natural olivine and low-Ca pyroxene from terrestrial peridotites and achondrites (aubrite, pallasite, angrite, diogenite) having Si-isotope compositions previously reported [7 and refs. therein]. Si-isotope IMF in olivines highly depend on their forsterite contents, similar to the observations by [6]. As the observed trend is smooth, it seems possible to correct Si-isotope IMF using Fo contents of unknown samples with the standard samples we investigated. Si-isotope IMF in pyroxene also depends on their enstatite and/or wollastonite contents. While our results are generally consistent with those in [6], we investigated more samples and observed the curved trend, instead of a simple linear trend [6]. The curved trend in low-Ca pyroxenes is smooth and it seems possible to correct Si-isotope IMF using En contents of unknown samples.

Oxygen-isotope standards: In addition to standards established earlier [8], we have been working on establishing O-isotope standards to accurately measure O-isotope compositions in secondary minerals formed through metasomatism on chondritic asteroids, such as andradite, grossular, nepheline, sodalite, and wollastonite [9]. We have collected minerals listed in Table 1, measured their chemical compositions with EPMA, and checked isotopic homogeneity in mm-scale (~0.2–0.4‰ in δ^{18}O, 2SD) with the UH ims-1280 SIMS. Their bulk O-isotope compositions were measured using laser fluorination at KOPRI, Korea, using the technique described in [10]. We prepared 2 sets of ~2–3 mg pieces from each mineral and made two measurements for each mineral. Overall uncertainty of these measurements are ~0.14‰, ~0.26‰, and ~0.025‰ for δ^{17}O, δ^{18}O, and Δ^{17}O (n=81, 2SD), respectively, based on the long-term measurements of the KOPRI internal standard (obsidian). The duplicate measurements of each mineral were consistent within the uncertainty, except for sodalite. Table 1 also lists those reported by [8], marked with *.

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Ushikubo et al. (2013) *GCA*, 109, 280-295. [5] Liu et al. (2019) *J. Anal. At. Spectrom.*, 34, 906-914. [6] Villeneuve et al. (2019) *Rapid Commun. Mass Spectrom.* 33, 1589–1597. [7] Poitrasson (2017) *RiMG*, 82, 289–344. [8] Thomen et al. (2016) *Goldschmidt 2016*, #3122. [9] Krot et al. (2020) *51st LPSC*, #1831. [10] Kim et al. (2019) *Rapid Commun. Mass Spectrom.*, 33, 641–649.

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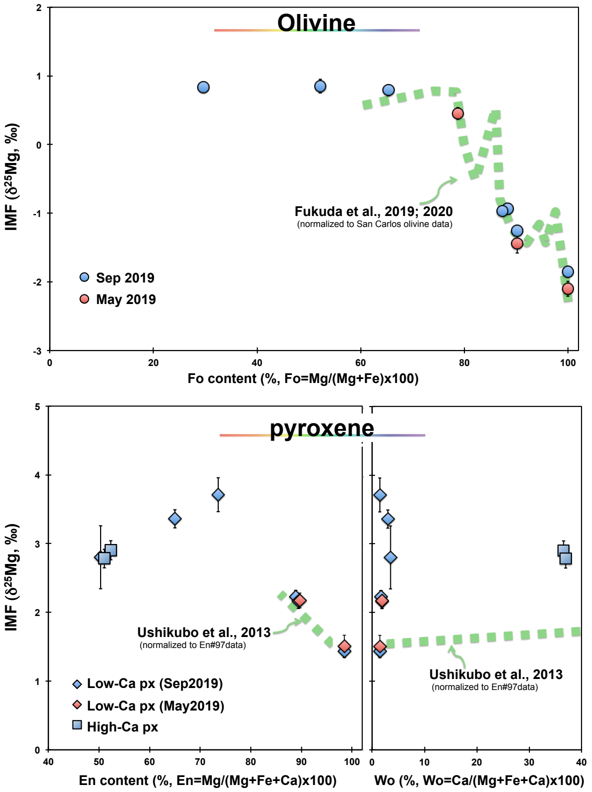

Fig. 1. Magnesium-isotope IMF in olivine and pyroxene.

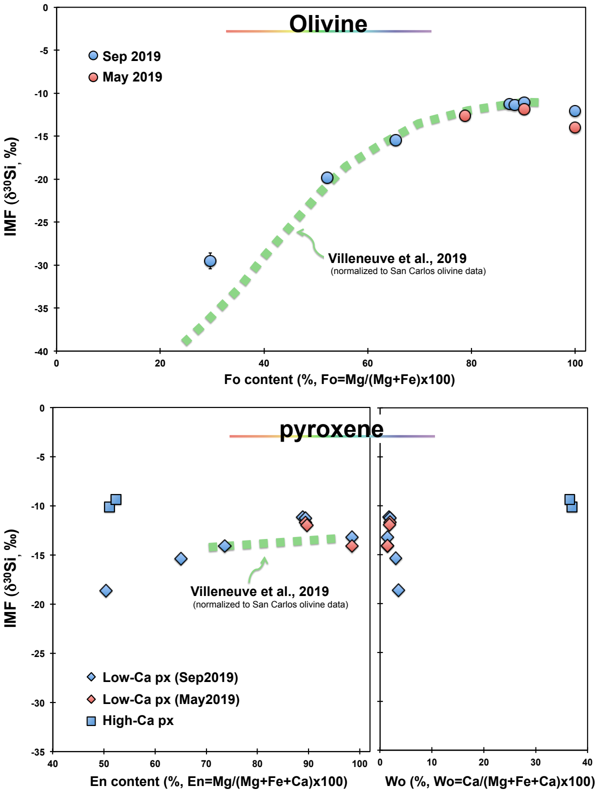

Fig. 2. Silicon-isotope IMF in olivine and pyroxene.

Table 1. Oxygen isotope standards developed in this study and [8].

mineral	description	composition	$\delta^{18}O_{V\text{-}SMOW}$ (‰)
andradite	NMNH C6160 (Smithsonian), Franklin, Sussex Co., New Jersey, USA	andradite: ~95	2.7
anorthite	Miyakejima, Tokyo, Japan	anorthite: ~95	5.9 *
augite	NMNH 164905 (Smithsonian), Black Rock Summit Flow, Nye Co., Nevada, USA	En: ~54, Wo: ~38	5.3 *
baddeleyite	M49571 (Museums Victoria), Myanmar	nearly pure ZrO_2	20.8
Cr-spinel	Stillwater complex, Montana, USA	Cr# ~63, Fe# ~58	3.1
grossular	Jeffrey, Quebec, Canada	grossular: ~98	4.3
hibonite	NMNH R11608 (Smithsonian), Madagascar	TiO_2: ~9, FeO: ~5, MgO: ~3%	10.9 *
magnetite	El Laco volcano, Chile	nearly pure Fe_3O_4	4.3
Na melilite	678H (MNHN Paris), Vesuve, Italy	Na_2O: ~4, MgO: ~6, FeO: ~2%	12.2 *
nepheline	185,149 (MNHN Paris), Davis Hill, Bancroft, Ontario, Canada	K_2O: ~5%	10.4 *
opx	118317 (Smithsonian), Kilbourne Hole, New Mexico, USA	En: ~90, Wo: ~2	5.8
perovskite	NMNH R10703 (Smithsonian), San Benito, California, USA	nearly pure $CaTiO_3$	-1.3
saphhire	NMNH 126321 (Smithsonian), Montana, USA	nearly pure Al_2O_3	5.0 *
sodalite	2286.S (MNHN Paris), Bancroft, Ontario, Canada	nearly pure sodalite	10.9
spinel	NMNH R18112 (Smithsonian), Mogok, Burma	FeO: ~6, Cr_2O_3: ~12%	18.5 *
wollastonite	Wakefield, Quebec, Canada	nearly pure $CaSiO_3$	16.8

*$\delta^{18}O$ values were determined at CEREGE, France [8].