MAGNESIUM ISOTOPE ANALYSIS OF OLIVINE BY SIMS: CALIBRATION OF MATRIX EFFECTS.

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Introduction: Magnesium has three naturally occurring stable isotopes (^{24}Mg, ^{25}Mg, and ^{26}Mg) allowing one to study mass-dependent and mass-independent isotope fractionation induced by natural processes. While Secondary Ion Mass Spectrometry (SIMS) can potentially provide high precision (sub per mil) Mg isotope data with ~3-40 µm spatial resolution [e.g., 1-6], SIMS instrumental mass fractionation (IMF) of Mg isotope analysis tend to be much larger than that of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) [7 and references therein]. The magnitude of IMF is a function of the chemical composition of the sample [e.g., 8], and this is referred to as a 'matrix effect'. Thus, matrix-matched standards are required and IMF must be evaluated for accurate measurements by SIMS.

Recently, we investigated SIMS matrix effects on Mg isotope analysis of olivine and observed a complex IMF for δ^{25}Mg as a function of Mg#60-100 [9]. In this study, we conducted additional SIMS Mg isotope and minor element concentration analyses of 17 terrestrial and meteoritic olivines for further evaluation of SIMS matrix effects. Mg isotope ratios of 7 out of 17 olivines have been determined by solution MC-ICP-MS [10, 11], and the rest of the olivines have been measured by laser ablation MC-ICP-MS [9]. Our goal is to develop a protocol of high accuracy and high spatial resolution Mg isotope analysis and to apply this for meteoritic olivine (e.g., in chondrules and amoeboid olivine aggregates) as well as small and precious particles obtained by sample return missions (e.g., *Stardust*, *Hayabusa2*, and *OSIRIS-REX*).

Multi-FC Mg isotope analysis: Magnesium three-isotope analyses of 17 olivine samples were performed with the Cameca IMS 1280 at the University of Wisconsin-Madison (WiscSIMS) equipped with a radio-frequency plasma ion source. The analytical conditions are generally similar to those described in [6]. A 7 µm diameter (1 nA) primary O_2^- beam was used for analyses. The secondary ion intensity of $^{24}Mg^+$ on San Carlos olivine ($Fo_{88.8}$) was typically ~2 × 10^8 cps. The external reproducibilities (2SD) of raw δ^{25}Mg, δ^{26}Mg, and δ^{26}Mg* of San Carlos olivine were 0.09‰, 0.16‰, and 0.07‰, respectively.

Single-EM minor element concentration analysis: Minor element concentration analyses of 17 olivine samples were performed with the Cameca IMS 1280. A ~1.3 µm diameter (6 pA) primary O_2^- beam was used for analyses. Secondary $^{23}Na^+$, $^{24}Mg^+$, $^{27}Al^+$, $^{28}Si^+$, $^{40}Ca^+$, $^{52}Cr^+$, $^{55}Mn^+$, $^{56}Fe^+$, and $^{60}Ni^+$ ions were detected by an axial EM that operated by peak jumping.

Results and Discussion: Olivine IMF ranges over ~3‰ in δ^{25}Mg as a function of Mg#60-100. The IMF is not a smooth function of Mg# but rather the IMF jumps by 1.2 and 1.5‰ between Mg#86 and 88, and 97.5 and 100, respectively. We also observed systematic differences in magnitudes of IMF by 0.3‰ between two olivine samples with similar Mg#s (94.7 and 94.9, respectively), suggesting that the IMF is not solely controlled by Mg (and Fe) contents. In order to examine the additional factor(s) that effect the IMF, we compared the magnitude of IMF, minor element abundances, and ionization efficiencies of each element. Large and non-linear variabilities in ionization efficiencies of Mg and Si were observed against Mg#s. The relationship between $^{24}Mg^+/^{28}Si^+$ ratios and Mg#s are similar to the complex IMF as a function of Mg#s, suggesting that the part of IMF results from differences in the ionization efficiencies of Mg and Si. The observed relationships imply that the IMF correction for δ^{25}Mg in olivine can be constrained by using a combination of Mg contents and $^{24}Mg^+/^{28}Si^+$ ratios. It is unclear why ionization efficiencies of Mg and Si vary between different olivines but one possibility is differences in minor element abundances. For instance, olivine samples with higher Mg contents (Mg#>90) and Cr-bearing (CrO ~0.40 wt%) olivine samples show higher magnitudes of IMF and also higher $^{24}Mg^+/^{28}Si^+$ ratios than those of the other olivine samples. The results suggest that minor element abundances create a secondary, but important effect on the IMF.

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