IMPROVEMENTS OF SIMS MG ISOTOPE ANALYSES FOR METEORITIC AND COMETARY SAMPLES USING RF PLASMA ION SOURCE. N. T. Kita[1], A. T. Hertwig[1], C. Defouilloy[1], K. Kitajima[1], and M. J. Spicuzza[1]. [1]WiscSIMS, Department of Geoscience, University of Wisconsin-Madison, Madison, WI 53706 (noriko@geology.wisc.edu).

Introduction: The in-situ decay of the extinct nuclide ^{26}Al (half-life of 0.7 million years) to daughter ^{26}Mg in meteoritic and cometary particles has been applied as a high time resolution (≤0.1 Ma) chronometer of early solar system evolution [e.g. 1]. Analyses of µm-scale Al-rich minerals and glass by Secondary Ion Mass Spectrometry (SIMS) is critical in detecting the correlated excess ^{26}Mg with ^{27}Al/^{24}Mg ratios, which indicates in-situ decay of ^{26}Al in closed system [e.g., 2-4]. However, Mg isotope analyses of small plagioclase grains (≤3 µm) in chondrule mesostasis and cometary particles were very difficult to obtained in the past [5]. We recently upgraded the primary oxygen ion source of WiscSIMS Cameca IMS 1280 to a radio-frequency (RF) Plasma ion source (Hyperion-II [6]), which improves primary beam density and stability compared to the Duoplasmatron (DP) ion source that was originally equipped with the instrument. Here we report the performance and analytical developments in Mg isotope measurements using the new RF plasma ion source.

Analytical Conditions: Primary and secondary acceleration voltages (–13 kV and +10 kV, respectively) as well as parameters for secondary ion optics were set to values similar to previous Mg isotope analyses using the DP source [3-5]. We tested both O^- and O_2^- primary ions by switching the magnetic field of the Primary Beam Mass Filter, because the latter provide faster sputtering rates (×2) and higher secondary ion yields (×3) [7]. Secondary Mg ions were detected using Faraday cups (FC) or electron multipliers (EM) for intensities above or below10^6 cps, respectively.

Primary Beam Size and Intensity: Primary O^- ions from the RF Plasma source were focused to the sample surface under critical illumination mode. Primary beam apertures with the diameters of 750 µm, 400 µm, and 250 µm were used for beam sizes 10-20 µm, 5-10 µm, and <5 µm, respectively. We did not use Köhler illumination mode, which is commonly used for analyses using the DP source. It is because the intense primary ions from RF Plasma source would quickly enlarge primary beam apertures that determine the beam diameters.

The primary O^- beam intensity was evaluated for different beam size based on scanning electron microscope (SEM) images of SIMS pits after 10 minutes of sputtering on olivine standard (Fig. 1). Those of O_2^- were also estimated for 50 pA and 1 nA on plagioclase and olivine standards, respectively (Fig. 2a). These actual spot sizes are 2-3 times larger than those determined by 16%-84% edge resolution method by Cameca. The primary O^- beam intensities were higher by a factors of 5-10 for ≥10 µm beam and as much as ×20 for ≤3 µm beam compared to our studies using the DP source (Fig. 1). Intensity ratios of O_2^-/O^- primary ions were ~1/2 at given primary beam sizes. The primary ion intensity at given primary beam condition was constant (≤1%) for a week long analysis session.

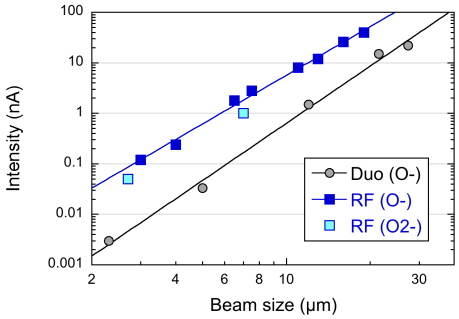

Fig. 1. Intensity of primary ions versus beam sizes of RF Plasma source. DP source data are from [5,8-9].

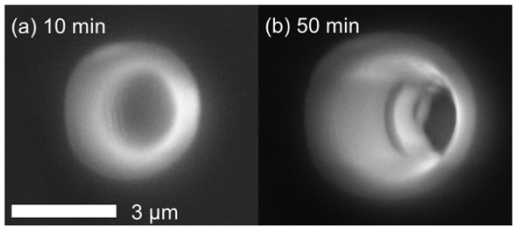

Fig. 2. SEM images of SIMS pits made by 50 pA O_2^- primary ion beam on labradorite standard. (a) 10 min sputtering for alignment. (b) After 50 min of Mg isotope analyses with 1 µm rastering.

Mg Isotope Analyses of Plagioclase: SIMS Al-Mg isotope analyses were performed for several plagioclase standards (natural crystal and synthetic glasses with MgO from 0.1% to 1.0%). We used an O_2^- primary ion beam with ~3 µm diameter at 50 pA intensities (Fig. 2a). The ^{24}Mg ion intensity ranges from 2×10^4 cps for labradorite standard (Lab1) with 0.12% MgO to 2×10^5 cps for anorthite glass (AnG) with 1% MgO. At first, we used an axial EM with magnetic peak switching as in the previous plagioclase analyses [3]. However, due to smaller and more intense primary beam conditions, secondary Mg ion intensity changed abruptly

after 30 minutes to 1 hour of analysis, which resulted in poor statistics in the isotope ratios.

To obtain better analytical precision, we used multi-collection (MC) EMs for simultaneous detection of Mg 3-isotopes. We applied 1×1 µm raster to improve the stability of secondary ion intensity (Fig. 2b). We use two types of EMs with a pulse counting system: ^{24}Mg and ^{25}Mg on Hamamatsu miniature EM on multi-collector arrays and ^{26}Mg on axial ETP EM, which have different deadtimes of 68 ns and 23 ns, respectively. The discriminator of the pulse counting system, which is normally set to 50 mV to cut off noise, is used to evaluate the pulse-height distribution of individual EM detectors. At the beginning of each analysis, EM high voltages were automatically adjusted so that 50% of pulses were detected at a discriminator level of 400 mV. A single analysis consists of 40 cycles of detecting Mg isotopes on MCEMs (40 s) and ^{27}Al on the axial FC (2 s) by magnetic field scans, which takes ~50 min.

Results of repeated analyses of plagioclase standards are shown in Fig. 3 and compared to those previously obtained using axial EM (5-10 µm, 3-4 hours per spot). Mg isotope ratios of standards plot along a slope ~0.5 line parallel to those of axial EM single collector analyses (Fig. 3a). Systematic differences in measured isotope ratios from previous studies are likely due to differences in detector gains among three EMs.

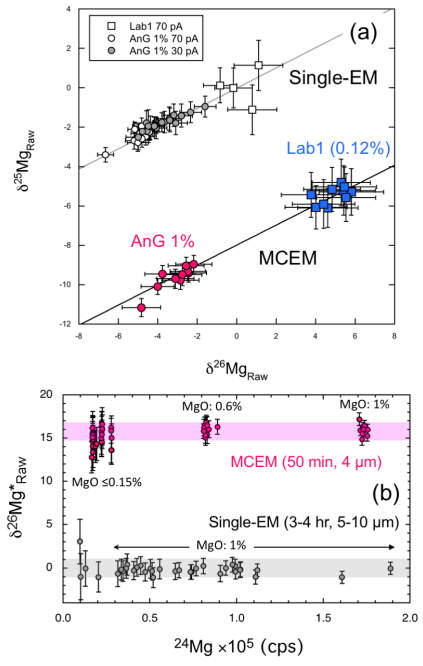

Fig. 3. Mg isotope analyses of plagioclase standards using MCEMs without correcting for relative gains of detectors. Single collector axial EM analyses from [3, 8] are shown for comparison.

The mass independent fractionation of ^{26}Mg from instrumental biases was calculated as, $\delta^{26}Mg^*_{Raw} = (1+\delta^{26}Mg_{Raw}/\ 1000)/(1+\ \delta^{25}Mg_{Raw}/1000)^{1/\beta}$, where we apply β=0.5128 [10]. The $\delta^{26}Mg^*_{Raw}$ values are constant at ~16‰ for several plagioclase standards with a range of secondary ^{24}Mg intensities (2×10^4 to $2\times\ 10^5$ cps; Fig. 3b), indicating that relative gains of three detectors are constant during the analyses, even though they are not unity. Thus, accurate excess $\delta^{26}Mg^*$ of unknowns are estimated by comparison to those of bracketing standard analyses. For standards with lower MgO contents ≤0.15%, repeated analyses of $\delta^{26}Mg^*_{Raw}$ are consistent within 2‰ (2SD, n=28), which is small compared to excess $\delta^{26}Mg^*$ (≥ 5‰) observed in plagioclase from Acfer 094 type II chondrules [11].

Mg Isotope Analyses of olivine: High precision Mg isotope analyses of olivine ($\delta^{26}Mg^*$ ± 0.1‰ or better) have been performed at beam sizes of 12-25 µm using MCFCs using 1×10^{11} ohm resistors on amplifier boards [3, 8]. Using O_2^- primary ions at 1 nA with RF plasma source, the primary beam size of olivine analyses was reduced to 7 µm while maintaining high Mg count rates (2×10^8 cps for ^{24}Mg) and an external reproducibility of ≤ 0.06‰ for $\delta^{26}Mg^*$ (2SD, [11]).

Small cometary olivine analyses require a ≤3 µm beam size for MCFC analyses. Using 50 pA O_2^- primary ions, the secondary ^{24}Mg intensities would be ~1×10^7 cps, while minor isotopes ^{25}Mg and ^{26}Mg would be only ~10^6 cps, which is relatively low for FC analyses. We are currently testing 1×10^{12} ohm resistors to reduce thermal noise of the FC amplifier (≤ 200 cps, 1SD per 60s integrations). Preliminary data suggest that the precisions of $\delta^{25,26}$Mg in olivine could be as good as 0.2‰ (in 2SD) for 3 µm beam size.

Summary: The RF plasma source installed to IMS 1280 improved the quality of SIMS Mg isotope analyses by reducing primary beam sizes and analysis time while achieving similar or better analytical precisions. This new capability allows us to perform Mg isotope analyses of important meteoritic and cometary objects which require smaller primary beam sizes..

References: [1] Kita N. T. et al. (2013) *Meteoritics & Planet. Sci.,* 48, 1383-1400. [2] Kita N. T. et al. (2012) *GCA, 86,* 37-51. [3] Ushikubo T. et al. (2013) *GCA, 109,* 280-295. [4] Ushikubo T. et al. (2017) *GCA, 201,* 103-122. [5] Nakashima D. et al. (2015) *EPSL, 410,* 54-61. [6] Liu M.-C. et al. (2018) *Int. J. Mass Spec. 424,* 1-9. [7] Kita N. T. et al. (2017) *LPS XLVIII,* Abstract #1754. [8] Tenner T. J. et al. (2015) *Meteoritics & Planet. Sci.,* Abstract *#5325*. [9] MacPherson G. J. et al. (2017) *GCA, 201,* 65-82. [10] Davis A. M. et al. (2015) GCA, 158, 245-261. [11] Hertwig A. T. et al. (2018), this meeting.