ANALYTICAL DEVELOPMENT FOR SIMS HIGH PRECISION OXYGEN AND MAGNESIUM ISOTOPE ANALYSES OF METEORITIC AND COMETARY SAMPLES.

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Introduction: Secondary Ion Mass Spectrometers (SIMS) are used to determine high precision isotope analyses of extraterrestrial objects that are limited to small volumes, such as CAIs, chondrules and returned samples from space missions [e.g., 1-9]. Using the University of Wisconsin IMS 1280 (WiscSIMS), the oxygen isotope ratios of cometary olivine and pyroxene particles (Stardust samples and IDPs) were determined using ~2 µm spot sizes with 1-2‰ precisions [2-4]. Some of these particles are found to have ^{16}O-enrichments similar to those of CAI and AOAs in primitive meteorites [3-4], which might be condensates from the early Solar nebula. As unmelted CAIs and AOAs sometimes show negative stable Mg isotope fractionation as large as −2‰ in δ^{25}Mg [e.g., 9], it is important to obtain stable Mg isotope analyses to test this possible condensation origin.

Currently, it is not possible to obtain SIMS Mg isotope ratios in olivine at 2 µm spot sizes and sub-‰ precisions. Primary O^- ion intensity of 2 µm spots are only a few pA for IMS 1280 [7] corresponding to secondary $^{24}Mg^+$ intensity of 2×10^5 (3×10^{-14} A), which are not high enough compared to the noise levels of multicollection Faraday cup (FC) amplifier (2×10^3 cps; 3×10^{-16} A [1]). By using a new RF plasma source that will be installed to WiscSIMS in 2017, the primary O^- ion beam brightness will be improved significantly compared to current Duoplasmatron source. To estimate the optimum analytical conditions for Mg isotope measurements with spot sizes of ~2 µm, we examined sputter rates and Mg ionization efficiency of olivine standards. Furthermore, we evaluated FC amplifier boards with lower thermal noise in order to improve analytical uncertainty.

Sputter Rates: Two olivine standards (San Carlos: Fo_{89} and Orikabe olivine: Fo_{60} [1]) were used for sputtering tests. The polished surface of these standards was sputtered to be ~1 µm deep using a ~30 µm diameter beam, either by large Koehler illumination mode or rastering. The sputtered volumes were then estimated by surface profilometer. We first compared sputter rates of Fo_{89} olivine between O^- and O_2^- primary ions at 23 keV impact energy (−13 kV and +10 kV for primary and secondary accelerating voltages, respectively), and compared secondary ion yields ($^{24}Mg^+$ cps per nA primary ions) between both conditions. Secondly, we compared sputter rates of Fo_{89} and Fo_{60} olivine for impact energy of 23 keV and 15 keV (−7 kV and +8 kV) using O^- primary ions. The results are shown in Fig. 1.

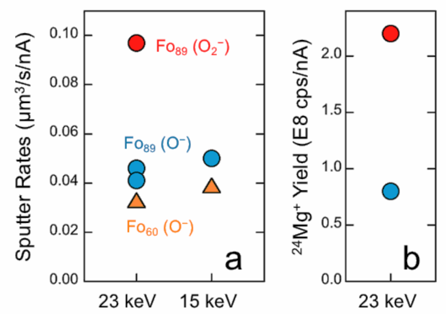

Fig. 1. Sputter rates (a) and secondary ion yield (b) of olivine under oxygen primary ion beam.

The sputter rates are twice as high with O_2^- than with O^- primary ions and the secondary ion yield is also higher by a factor of 2.8. From these data, we estimate Mg ionization efficiency in Fo_{89} to be 8% (O^-) and 11% (O_2^-). The sputter rates did not change significantly between both olivine standards, nor between 15 keV and 23 keV impact energy. Based on these data, we concluded that the optimum analysis condition is to use O_2^- primary ions at 23 keV impact energy.

Faraday Cup Amplifier Noise: The FC amplifier thermal noise is the main source of uncertainties for secondary ion intensity below 10^7 cps ($<10^{-12}$ A). The IMS 1280 at WiscSIMS uses amplifier boards manufactured by Finnigan MAT with 10^{11} or 10^{10} Ω resistors. Successor model "IMS 1280-HR" uses newer amplifier boards manufactured by Cameca with switchable 10^{11} and 10^{10} Ω resistors. We compared amplifier noise levels of both amplifiers with 10^{11} Ω resistors. We also replaced the resistor-capacitor pair on the original IMS 1280 FC amplifier boards with a 10^{12} Ω resistor (glass sealed) and a 1pF capacitor from Finnigan/ MAT251 stable isotope mass spectrometer. We tested another 10^{12} Ω resistor from Ohmite (Epoxy coated; MOX112523100AK). Their noise levels were also examined.

The FC amplifier board housing is kept under rough vacuum and thermally insulated. We modified the vacuum line so that the housing is continuously pumped by a dry pump at pressure <0.1 Torr, which minimizes the noise from radioactivity in residual gas. Noise level is expressed as standard deviation (1SD) of repeated signal measurements of 4 s and 60 s integration time without applying secondary ions to the detectors. The theoretical limit of thermal noise (Johnson-Nyquist noise) for 10^{11} and 10^{12} Ω resistors are 2×10^{-16} A and 6.5×10^{-17} A, respectively for 4 s integration. The results of tests are shown in Table 1.

Table 1. FC amplifier thermal noise (unit: 10^{-16}A)

Amplifier board	Resistor	4s	60s
A: Finnigan (1280)	E11	3.1	0.64
B: Cameca (1280-HR)	E11	1.9	0.39
C: Finnigan (1280)	E12 MAT251	1.9	0.28
D: Finnigan (1280)	E12 Ohmite	1.9	0.35

The newer amplifier board for 1280-HR (B) shows improved noise level for 10^{11} Ω resistor, close to theoretical limit. The noise level for original 1280 amplifier board (A) improved by using 10^{12} Ω resistors (C, D). However, these noise levels are 3 times higher than theoretical limits and very similar to that of 1280-HR amplifier board with 10^{11} Ω resistor.

Application to Oxygen Isotope Analyses: To verify the performance of the FC amplifier boards with lower noise levels, the precisions of O 3-isotope measurements were compared using 3 different amplifier/resistor configurations for $^{17}O^-$ detections. General analytical conditions are similar to [1] using multi-collector FC detectors. Three different configurations were tested (A, B, and C in Table 1). ^{16}O and ^{18}O are detected by using FC and original IMS 1280 amplifier board with 10^{10} and 10^{11} Ω resistors, respectively. For A and C, each analysis takes ~7 min including 100 s of baseline and 200 s of signal acquisition. For B, the analysis time was reduced to ~4 min including 60 s of baseline and 100 s of signal acquisitions. Spot sizes are 15 µm for A and B and 10 µm for C. Fig. 2 shows examples of FC baseline stability in a ~3 day session.

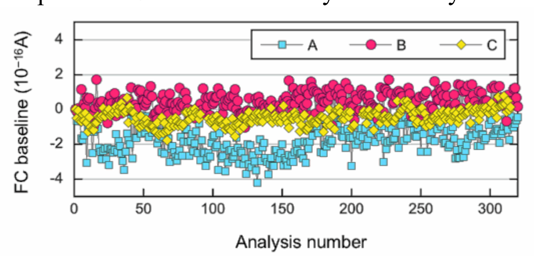

Fig. 2. FC baseline stability during O 3-isotope analyses relative to the first analysis. Stability is improved for amplifier configurations of B and C in Table 1.

San Carlos olivine standard was analyzed repeatedly in each session (4 spots every 16-20 unknowns; total 80-180 for each session). To evaluate the performance of different amplifiers, we use 2SD of the bracket standard $\Delta^{17}O_{Raw}$ (= $\delta^{17}O_{Raw} - 0.52\times \delta^{18}O_{Raw}$), which is usually very similar to the internal error (two standard error, 2SE) of $\delta^{17}O_{Raw}$ value. Using data from 5 different SIMS sessions over the past 3 years, we plot the session average 2SD of bracket standard $\Delta^{17}O_{Raw}$ against the average ^{17}O intensities of the standard (Fig. 3). By using lower noise amplifiers (B and C), we achieved a similar analytical uncertainty to the original configuration (A) even with a reduced acquisition time (B) or with a smaller spot sizes at lower ^{17}O signal intensity (C). These conditions are applied successfully to O 3-isotope analyses of extraterrestrial samples presented in this meeting [10-13].

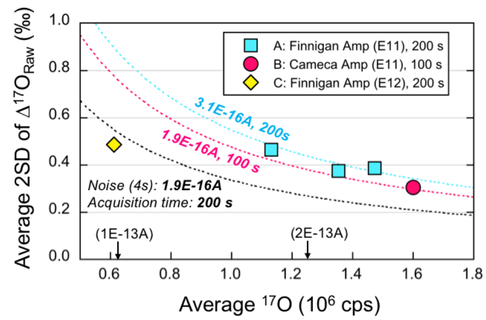

Fig. 3. Average 2SD of $\Delta^{17}O_{Raw}$ values of bracket San Carlos olivine standard from five SIMS sessions as a function of the average ^{17}O intensity. Predicted uncertainty of ^{17}O measurements with given noise level and acquisition time are shown as dashed lines that decrease inversely with ^{17}O signal intensity.

Towards Mg isotope analyses of cometary particles: Using the sputter rates estimated in this study, O_2^- primary ions that are focused to 1-2 µm diameters and 0.04-0.13 nA intensity would sputter olivine 1 µm deep in 4 min of SIMS analyses. Under these conditions, $^{24}Mg^+$ intensities would be from 8×10^6 to 3×10^7 cps, corresponding to $^{25}Mg^+$ intensities from 1×10^6 to 4×10^6 cps. Based on the relationship between analytical uncertainties and signal intensity (Fig. 3), the internal precisions (2SE) of δ^{25}Mg values would be better than 0.1-0.3‰ in using configuration B or C and an acquisition time of 200 s.

References: [1] Kita N. T. et al. (2010) *GCA, 74,* 6610-6635. [2] Nakamura T. et al. (2008) *Science, 321,* 1664-1667. [3] Nakashima D. et al. (2012) *EPSL, 357-358,* 355-365. [4] Defouilloy C. et al. (2016) *LPS XLVII,* Abstract #1584. [5] Kita N. T. et al. (2012) *GCA, 86,* 37-51. [6] Ushikubo T. et al. (2013) *GCA, 109,* 280-295. [7] Nakashima D. et al. (2015) *EPSL, 410,* 54-61. [8] Ushikubo T. et al. (2017) *GCA, in press*. [9] MacPherson et al. (2012) *EPSL, 331-332,* 43-54. [10] Hertwig A. et al. (2017) *LPS, XLVIII,* Abstract #1227. [11] Chaumard N. et al. (2017) *LPS, XLVIII,* Abstract #1610. [12] Heck P. R. et al. (2017) *LPS, XLVIII,* Abstract #1694. [13] Boyle S. et al. (2017) *LPS, XLVIII,* Abstract #1219.