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Author(s)	Itoh, Shoichi; Makide, Kentaro; Yurimoto, Hisayoshi
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Calculation of radiogenic ^{26}Mg of CAI minerals under high precision isotope measurement by SIMS

Shoichi Itoh*, Kentaro Makide, Hisayoshi Yurimoto

Department of Natural History Sciences, Hokkaido University, Sapporo 060-0810, JAPAN

Abstract

High precision Mg isotope measurements have been performed to determine radiogenic ^{26}Mg of CAI minerals by secondary ion mass spectrometry using faraday cup multi-collection system. Terrestrial samples of spinel and augite, and synthetic glasses of melilite and fassaite, were prepared to correct instrumental mass fractionation. Reproducibility of Mg isotope measurements for each standard were limited to $\sim 0.4\text{‰}$ (2σ). On the other hand, the standard errors for one spot are $\sim 0.05\text{‰}$ (2σ). The poor reproducibility resulted from variations of instrumental mass fractionation among individual measurement spots. We propose novel calculation method of radiogenic ^{26}Mg considering instrumental and natural mass fractionation for each mineral. The overall measurement error of radiogenic ^{26}Mg of the minerals can be calculated less than 0.2‰ (2σ). This provides that the time resolution of early solar system chronometer was improved up to 100kyr for ~ 20 micrometer scale objects formed in the early solar system.

Keywords: SIMS; Magnesium; Al-Mg isochron; Multi-collector; instrumental mass fractionation; CAI

1. Introduction

The ^{26}Al - ^{26}Mg dating using a short-lived radionuclide of ^{26}Al (a half-life of 0.73Ma) is useful to determine the relative ages of materials formed in the early solar system. Recently, multi-collector secondary ion mass spectrometry (SIMS) has made possible high precision magnesium isotope analyses that provide chronologically useful data on low-Al/Mg phases in Ca-Al-rich inclusions (CAIs) and chondrules in primitive chondrites [e.g., 1-6]. Most high precision ^{26}Al - ^{26}Mg SIMS studies are done for CAIs in order to estimate the earliest thermal history in the early solar system. If the radiogenic ^{26}Mg for individual minerals in CAIs could be determined with the precision of less than 0.2‰ , time resolution

of early solar system chronology would be achieved to 100 kyr.

CAI minerals typically have large mass fractionation of few ‰/amu (e.g., $\delta^{25}\text{Mg} > \sim 5\text{‰}$) probably by natural evaporation processes [6-9]. On the other hand, equivalent or larger amounts of mass fractionation occurred during SIMS measurements, mainly by ion sputtering processes. The instrumental and natural mass fractionations depends on mass differences between isotopes, but the mass fractionation factors are slightly different each other. Moreover, the instrumental mass fractionation factors are also different among minerals. These differences can significantly affect the determination of amounts of radiogenic ^{26}Mg in minerals especially in case of high precision isotope analyses with less than 0.5‰ uncertainties and where the degree of natural mass fractionation is larger than few ‰/amu .

In this paper, we present analytical methods of high precision Mg isotope

* Corresponding author. Tel.: +81-11-706-2725; fax: +81-11-706-2725.

E-mail address: sitoh@ep.sci.hokudai.ac.jp (S. Itoh).

measurements and the data correction method for ^{26}Al - ^{26}Mg dating of CAI minerals by multi-collector SIMS.

2. Experimental methods

A Cameca ims-1270 of Hokkaido University has been used in this study. A 13 keV $^{16}\text{O}^-$ primary ion beam focused to 10-20 μm diameter was used. Measurements were done at the high mass resolving power of ~ 2000 , sufficient to resolve all molecular ion interferences (e.g., ^{24}MgH , $^{48}\text{Ca}^{2+}$). The effect of all molecular ion interferences to Mg isotopes was smaller than 0.1‰ levels. The primary ion currents were adjusted to 5-38 nA in order to set that the secondary ^{24}Mg ion counts for each standard mineral were obtained as $\sim 10^8$ cps.

Secondary ions were collected by four faraday cups of the multi-collection system for ^{24}Mg for L'2, ^{25}Mg for C, ^{26}Mg for H1 and ^{27}Al for H'2. Total of 60 cycle measurements for one measurement spot were done in 10 minutes. The last 20 cycles were used to calculate the Mg isotope ratios because the secondary ion intensity ratios between isotopes drifted systematically in the first tens cycles, which would be due to changes of electrostatic charging conditions on sample surface by starting of sputtering. After each sample measurement, we measured background noises of faraday cup detectors to compensate the background drifts to reduce the systematic error.

Russian spinel (SPU), takashima augite (Aug), synthetic melilite-glass (Åk_{40}) (Mel) and synthetic fassaite-glass (Fas) standards were used to correct instrumental mass fractionation for Mg isotopes. The Mg isotope ratios of these standards would be identical each other within the terrestrial igneous isotopic variations (normally $< 0.5\text{‰}$) [9].

3. Results and discussion

3.1. Instrumental mass fractionation

Table 1. Instrumental mass fractionation in one analytical session on August 21, 2006.

sample	$\phi^{25}\text{Mg}_{\text{aug}}$	$2\sigma_m$	$\phi^{26}\text{Mg}_{\text{aug}}$	$2\sigma_m$
SPU	-5.35	0.06	-10.32	0.05
SPU	-5.26	0.06	-10.16	0.04
SPU	-5.16	0.04	-10.09	0.05
SPU	-5.07	0.05	-10.02	0.05
Mel	-6.14	0.07	-12.26	0.07
Mel	-6.32	0.05	-12.53	0.07
Mel	-6.09	0.04	-12.13	0.06
Fas	-2.81	0.05	-5.60	0.05
Fas	-3.12	0.06	-6.15	0.05
Fas	-3.16	0.05	-6.15	0.05
Aug	-0.27	0.06	-0.32	0.08
Aug	0.10	0.04	0.10	0.05
Aug	0.16	0.05	0.22	0.04

σ_m : standard deviation of the mean.

Table 2. Reproducibility of instrumental mass fractionation for standard minerals in one analytical session on August 21, 2006.

sample	$\phi^{25}\text{Mg}_{\text{aug}}^{\text{mean}}$	2σ	$\phi^{26}\text{Mg}_{\text{aug}}^{\text{mean}}$	2σ
SPU	-5.21	0.24	-10.15	0.26
Mel	-6.19	0.24	-12.31	0.41
Fas	-3.03	0.39	-5.97	0.64
Aug	$\equiv 0$	0.47	$\equiv 0$	0.57

σ : standard deviation.

Magnesium isotope ratios are reported for the delta notation,

$$\phi^i\text{Mg}_{\text{ref}} = 1000 \times \ln \left\{ \frac{\left(\frac{i\text{Mg}}{^{24}\text{Mg}} \right)_{\text{unk}}}{\left(\frac{i\text{Mg}}{^{24}\text{Mg}} \right)_{\text{ref}}} \right\} \quad (i = 25, 26)$$

where “unk” denotes unknown samples ratios and “ref” is a terrestrial reference sample. We used the Aug as a reference for discussion of instrumental mass fractionation of SIMS, since the instrumental mass fractionation of the Aug is 0-1 ‰/amu for $\phi^{25}\text{Mg}_{\text{real}}$ under the measurement condition in this study [10, 11].

Typical results for the standards are shown in Table 1. Representative error for the 20 cycles of one measurement spot is estimated to 0.06‰ (2σ). Because the statistical counting error of secondary ions

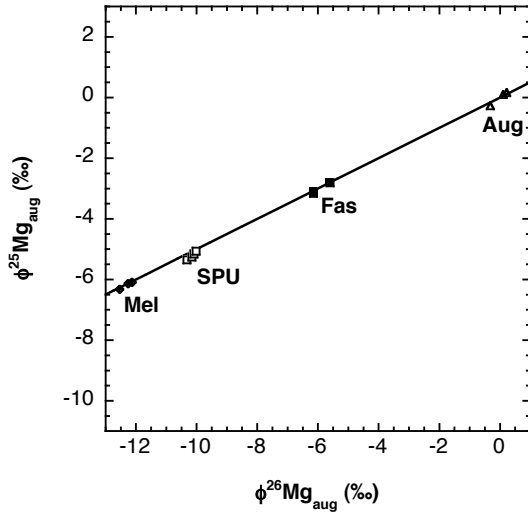


Fig. 1. $\phi^{25}\text{Mg}_{\text{aug}}$ vs. $\phi^{26}\text{Mg}_{\text{aug}}$ plot for standard minerals. A line denotes a representative instrumental mass fractionation line.

for the 20 cycles is inferred to be 0.04‰ (2σ), the measurement error is nearly comparable to the statistical uncertainty. On the other hand, representative reproducibility for each standard is 0.34 (2σ) for $\phi^{25}\text{Mg}_{\text{aug}}^{\text{mean}}$ and 0.46 (2σ) for $\phi^{26}\text{Mg}_{\text{aug}}^{\text{mean}}$ (Table 2), which are 6-8 times larger than the measurement uncertainty of one point. We refer the delta value calculated from repeated measurements for each standard as $\phi^{25,26}\text{Mg}_{\text{aug}}^{\text{mean}}$. The poor reproducibility would be due to small changes of sample surface conditions of point by point, but the variations are controlled by mass-dependent fractionation law (Fig. 1). The instrumental mass dependent fractionation factors are slightly different for each mineral (Table 3).

These results indicate that the isotope ratio for these minerals can be determined in the precision of $\sim 0.4\text{‰}$ (2σ). We refer the intrinsic delta value as $\phi^{25,26}\text{Mg}_{\text{real}}$. Using this intrinsic precision, we can determine radiogenic ^{26}Mg with $\sim 0.4\text{‰}$ (2σ) precision. However, amounts of radiogenic ^{26}Mg could be determined more precisely than the case based on the intrinsic precision of $\phi^i\text{Mg}_{\text{real}}$ if the mass-dependent fractionation relationship among the data is considered.

Table 3. The linear regression of $\phi^{25}\text{Mg}_{\text{aug}}$ and $\phi^{26}\text{Mg}_{\text{aug}}$ between two terrestrial standard minerals.

	α	2σ	β	2σ
SPU-Aug	0.5141	0.0043	-0.006	0.064
Mel-Aug	0.5030	0.0035	-0.004	0.060
Fas-Aug	0.5096	0.0075	-0.010	0.062

α : instrument mass fractionation factor for each mineral as $\phi^{25}\text{Mg} / \phi^{26}\text{Mg}$.
 β : $\phi^{26}\text{Mg}$ at $\phi^{25}\text{Mg} = 0$.
 σ : standard deviation.

3.2. Calculation of radiogenic ^{26}Mg

The instrumental mass fractionation factor α_{SIMS} for spinel, fassaite and melilite are calculated from pairs of SPU-Aug, Fas-Aug and Mel-Aug, respectively (Table 3). Although the small instrumental mass fractionation of Aug introduces a systematic error for α_{SIMS} , the instrumental mass fractionation of Aug is inferred less than 1‰ for $\phi^{25}\text{Mg}_{\text{real}}$ under this measurement condition (Fig. 1) [10, 11]. Therefore, the induced systematic error for α_{SIMS} is negligible for the regression parameters (Table 3).

Because the instrumental mass fractionation for each mineral follows the corresponding regression parameters, the radiogenic ^{26}Mg is defined as the deviation from the regression curve if the sample has the same Mg isotope ratios to the standard. Following equation,

$$\phi^{26}\text{Mg}_{\text{excess}} = \phi^{26}\text{Mg}_{\text{aug}} - \frac{\phi^{25}\text{Mg}_{\text{aug}}}{\alpha_{\text{SIMS}}}$$

However, natural minerals often fractionated their isotope ratios under natural processes according to α_{natural} . For example, CAI minerals have been believed to be experienced evaporation, and evaporation mass fractionation factor of CAI composition liquid has been experimentally determined as 0.51400 (24) [1], which is different from the instrumental mass fractionation factors of SIMS α_{SIMS} in this study. Therefore, correction by natural mass fractionation α_{natural} is also essentially after correction by α_{SIMS} to determine radiogenic ^{26}Mg in minerals. Following equation may be applicable to calculate the

amounts of radiogenic ^{26}Mg , $\phi^{26}\text{Mg}_{\text{excess}}$ of minerals:

$$\phi^{26}\text{Mg}_{\text{excess}} = \phi^{26}\text{Mg}_{\text{aug}} - \frac{\phi^{25}\text{Mg}_{\text{aug}}}{\alpha_{\text{SIMS}}} + \frac{\phi^{25}\text{Mg}_{\text{real}}}{\alpha_{\text{SIMS}}} - \frac{\phi^{25}\text{Mg}_{\text{real}}}{\alpha_{\text{natural}}} \pm \varepsilon(\phi^{26}\text{Mg}_{\text{excess}})$$

$$\varepsilon(\phi^{26}\text{Mg}_{\text{excess}}) = \left[\varepsilon_0^2 + \left(\frac{\varepsilon_1}{\alpha_{\text{SIMS}}} \right)^2 + \left(\frac{(\alpha_{\text{natural}} - \alpha_{\text{SIMS}})}{\alpha_{\text{SIMS}} \times \alpha_{\text{natural}}} \times \varepsilon_2 \right)^2 \right]^{\frac{1}{2}}$$

where “ $\varepsilon(\phi^{26}\text{Mg}_{\text{excess}})$ ” denotes the error in $\phi^{26}\text{Mg}_{\text{excess}}$, “ ε_0 ”, “ ε_1 ” and “ ε_2 ” are the errors in $\phi^{26}\text{Mg}_{\text{aug}}$, $\phi^{25}\text{Mg}_{\text{aug}}$ and $\phi^{25}\text{Mg}_{\text{real}}$, respectively. The errors for α_{SIMS} and α_{natural} are negligible for the error propagation under the experimental precisions in this study.

For example, since representative error values (‰) for melilite in this study are followed as, $\varepsilon_0=0.06$, $\varepsilon_1=0.06$, $\varepsilon_2=0.24$, $\alpha_{\text{SIMS}}=0.5030$ and $\alpha_{\text{natural}}=0.5140$, the $\varepsilon(\phi^{26}\text{Mg}_{\text{excess}})$ could be calculated as 0.13‰ (2σ), which is more than four times smaller than the uncertainty calculated from the errors of $\phi^{25,26}\text{Mg}_{\text{real}}$.

4. Conclusions

High precision Mg isotope measurements of CAI minerals (spinel, fassaite and melilite) are performed by the Cameca ims-1270 SIMS instrument using four faraday cups of the multi-collection system. In order to determine amounts of radiogenic ^{26}Mg more precisely than the case based on precisions of $\phi^i\text{Mg}_{\text{real}}$, we propose that the radiogenic ^{26}Mg for CAI minerals can be calculated as the deviation from the equation of instrumental mass fractionation of SIMS. Natural mass fractionation is also corrected after correcting the instrumental mass fractionation. This procedure allows reducing calculating the error of radiogenic ^{26}Mg because variations of $\phi^{26}\text{Mg}_{\text{aug}}$ correlate with those of $\phi^{25}\text{Mg}_{\text{aug}}$ during SIMS measurements. As results, the overall uncertainties of the radiogenic ^{26}Mg can be estimated as less than 0.2‰ (2σ).

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