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# Application of high precision SIMS $^{26}\text{Al}$ – $^{26}\text{Mg}$ analyses to the early solar system chronology

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## Abstract

High precision SIMS  $^{26}\text{Al}$ – $^{26}\text{Mg}$  isotopic analyses were performed in order to detect the excesses of  $^{26}\text{Mg}$  that derived from in situ decay of  $^{26}\text{Al}$  (half-life of 0.73 million years) in primitive meteorites. The electron multiplier is used to analyze Mg isotopes in Al-rich glass using  $5\ \mu\text{m}\ \text{O}_2^-$  primary ion beam. The EM dead time correction and Al/Mg sensitivity calibration are applied to obtain accurate data. The precisions of  $^{26}\text{Mg}/^{24}\text{Mg}$  isotopic ratios and  $^{27}\text{Al}/^{24}\text{Mg}$  atomic ratios were 2–5% and 10%, respectively. The relative formation time of less than 1 million years among chondrules is able to be determined. Further attempt was made to improve the precision of Mg isotopic ratios using the multi-collector Faraday cups. The preliminary tests showed both internal and external precisions of better than 0.1%.

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## 1. Introduction

Chondrules are millimeter-sized spherical objects in meteorites and one of the oldest objects in the solar system. The chronometer using the short-lived radionuclide  $^{26}\text{Al}$  (the half-life of 0.73 million years) is the useful tool to determine the timing of various events that happened during the earliest million years of the solar system [1–5]. The former existence of  $^{26}\text{Al}$  in a chondrule is now observed as an excess of  $^{26}\text{Mg}$ , and the  $^{26}\text{Mg}/^{24}\text{Mg}$  ratios correlate with  $^{27}\text{Al}/^{24}\text{Mg}$  ratios as shown in an isochron diagram (Fig. 1). The initial  $^{26}\text{Al}/^{27}\text{Al}$  ratio in each chondrule is estimated from the slope of the isochron and converted to a relative

formation time (hereafter called as  $^{26}\text{Al}$  age) by the following equation:

$$\Delta t = \ln\left\{\left(\frac{^{26}\text{Al}}{^{27}\text{Al}}\right)_{\text{initial}} / \left(\frac{^{26}\text{Al}}{^{27}\text{Al}}\right)_{\text{reference}}\right\} \frac{\tau_{1/2}}{\ln(2)},$$

where  $\tau_{1/2}$  is the half-life of  $^{26}\text{Al}$  and  $\left(\frac{^{26}\text{Al}}{^{27}\text{Al}}\right)_{\text{reference}}$  is  $4.5 \times 10^{-5}$ , the highest value among meteoritic materials that is taken from the value of type B CAIs (Ca, Al-rich inclusions) [2]. Because of the low initial abundance of  $^{26}\text{Al}$  ( $^{26}\text{Al}/^{27}\text{Al} < 10^{-5}$ ) in chondrules, the measurable amount of excess  $^{26}\text{Mg}$  can be obtained only from glass or Al-bearing minerals that are normally observed as small grains (a few micrometers to  $20\ \mu\text{m}$ ). Here we present the analytical methods of measuring the Al–Mg isotopic system of chondrules using the Cameca IMS-1270 high sensitivity and high resolution SIMS at the Geological Survey of Japan (GSJ).

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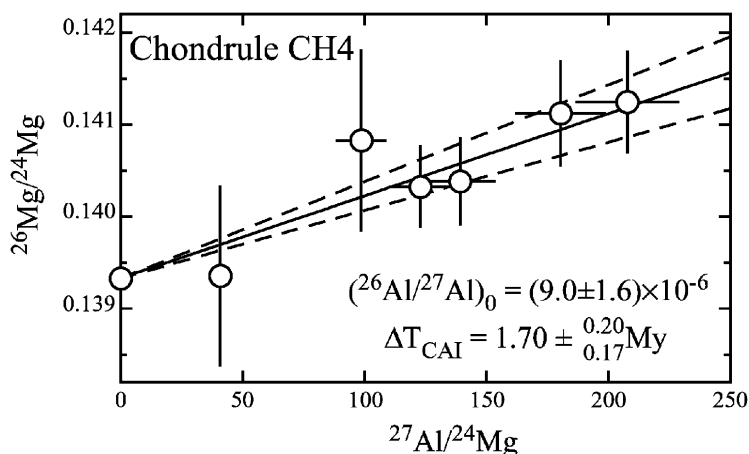


Fig. 1. Example of the  $^{26}\text{Al}$ – $^{26}\text{Mg}$  isochron of chondrule [4].

## 2. Single collector electron multiplier pulse counting

Glass in some chondrules with high  $^{27}\text{Al}/^{24}\text{Mg}$  ( $\sim 200$ ) shows a  $^{26}\text{Mg}$  excess as high as 1% [4,5]. In these samples, a single collector electron multiplier (EM) is used to measure Mg isotopic ratios with the precision of a few ‰. The primary ion beam of  $\text{O}_2^-$  was used as shaped 5 or 10  $\mu\text{m}$  spot. The mass resolving power is set to 3300 (10% height) with a transmission of secondary ions of larger than 70%. The intensity of the secondary  $^{24}\text{Mg}$  ions from glass with 0.1% MgO is 2000 cps for 33 pA  $\text{O}_2^-$  primary currents. The dead time of the EM pulse counting system is estimated by applying 0.1–0.3 Mcps  $^{24}\text{Mg}$  secondary ions using standard glass with higher MgO (2–8%). The estimated dead time was nearly constant ( $35 \pm 8$  ns) over the long period of time. The uncertainty of the dead time is 5–10 ns for each analytical session and does not affect the isotopic ratios more than 0.1‰ of the analyzed data, if the  $^{24}\text{Mg}$  intensity is less than 10,000 cps. The measured  $^{26}\text{Mg}/^{24}\text{Mg}$  ratio is also corrected for the instrumental mass fractionation by normalizing the measured  $^{25}\text{Mg}/^{24}\text{Mg}$  ratio to be 0.12663 [6]. The measured  $^{25}\text{Mg}/^{24}\text{Mg}$  ratio does not vary during a single measurement and is normally within  $\pm 5\%$  of the literature value. The precision of the corrected  $^{26}\text{Mg}/^{24}\text{Mg}$  ratios is in the range of 2–5‰ for Al-bearing phases in chondrule samples.

The accurate estimate of the initial Al isotopic ratio requires not only a high precision Mg isotopic analysis, but also an accurate determination of the  $^{27}\text{Al}/^{24}\text{Mg}$  ratio. The matrix effect on the SIMS relative sensitivity factor,  $F = (^{27}\text{Al}/^{24}\text{Mg})_{\text{SIMS}} / (^{27}\text{Al}/^{24}\text{Mg})_{\text{True}}$ , was evaluated for geological glass standards and plagioclase mineral standards with known Al and Mg contents. The  $F$ -values of various geological glass standards (basalt, andesite, and rhyolite) agree within 5%, while those of plagioclase standards are higher than glass standard and systematically decrease with increasing Na contents. The range of  $F$ -values for these standards are closed to unity (0.85–1.3), indicating that ionization efficiency of Mg is similar to that of Al for these Al-rich silicates. The reproducibility of  $F$ -values of individual standard is normally  $\pm 10\%$  (in  $2\sigma$ ), which is applied to an uncertainty of the SIMS  $^{27}\text{Al}/^{24}\text{Mg}$  analysis.

Using the above techniques, 16 chondrules in primitive meteorites were so far analyzed in our laboratory [4,5]. It is now possible to discuss a time difference of less than 1 million years among different types of chondrules. This resulted in the new proposal for the formation process of chondrule in the early solar system [5].

## 3. Multi-collector Faraday cup measurement

Many chondrules only contain glass with low  $^{27}\text{Al}/^{24}\text{Mg}$  ratios ( $< 30$ ) as an Al-bearing phase. The

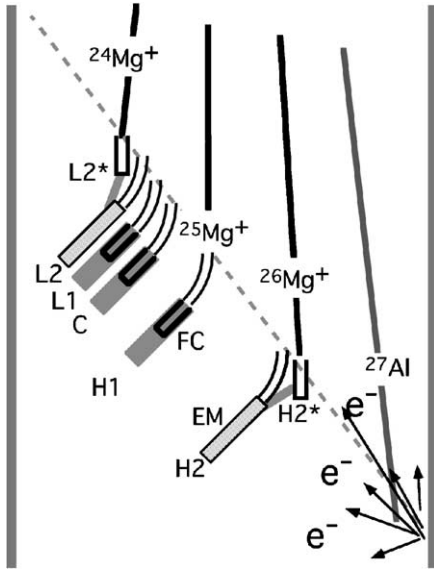


Fig. 2. Multi-collector system for Mg isotopic analyses.

$^{26}\text{Al}$ -ages could not be obtained for these chondrules because of small excess  $^{26}\text{Mg}$  (less than 1%). For high precision determination of Mg isotopic ratios, we use the multi-collector Faraday cups (FCs) system and tested its performance by analyzing mineral and geological glass standards. The IMS-1270 at GSJ is equipped with five detectors: three in the middle are FCs and two others are EMs with additional FC (Fig. 2). A small electrostatic analyzer is attached to each detector except for two external FC detectors. Three exit slit widths can be selected and correspond

to mass resolutions of 2000, 4500 and 6000. At the beginning of this study, we had only three FCs (at L2\*, H1 and H2\* positions) that were used for Mg isotopic analysis.

By using 12 and 25  $\mu\text{m}$   $\text{O}_2^-$  primary beam (0.5–0.8 and 2–3 nA, respectively), the secondary  $^{24}\text{Mg}$  ion current was obtained in the range of  $10^8$  cps ( $10^{-11}$  A) for Mg silicate minerals and  $5 \times 10^6$ – $10^7$  cps ( $10^{-12}$  A) for Al-bearing glass with 2 wt.% MgO. The mass resolution was set to 2000 by using the largest exit slit, though the entrance slit width was the same as the single collector analysis. The effects of hydride, oxide, and doubly charged ions (such as  $^{48}\text{Ca}^{2+}$ ) to Mg isotopes were smaller than 0.1% level. The base line drifts of the FC detectors are in the level of 1000 cps (or  $2 \times 10^{-16}$  A) and carefully examined at the mass 0.2 amu lower than the Mg isotope mass. By switching the magnetic field between  $^{25}\text{Mg}$  and 24.8 (base line) for the central detector, total of 80 cycles measurements are done in 1 h.

The repeated analyses of various Mg silicate standards showed the precision and reproducibility of 0.1% for the  $^{26}\text{Mg}/^{24}\text{Mg}$  ratios (Fig. 3). The precision of Mg isotopic analyses of Al-bearing glass was in the range of 0.2–0.5%, though the  $^{26}\text{Mg}/^{24}\text{Mg}$  ratios of Al-rich glass standards showed a systematic decrease in the level of 0.2–0.6% with increasing  $^{27}\text{Al}/^{24}\text{Mg}$  ratios (2–10). This systematic deficit of the  $^{26}\text{Mg}$  is comparable to the expected  $^{26}\text{Mg}$  excess in meteoritic samples. The data from the same glass standard gave identical values for different primary ion sizes with different Mg secondary ion currents. For this reason,

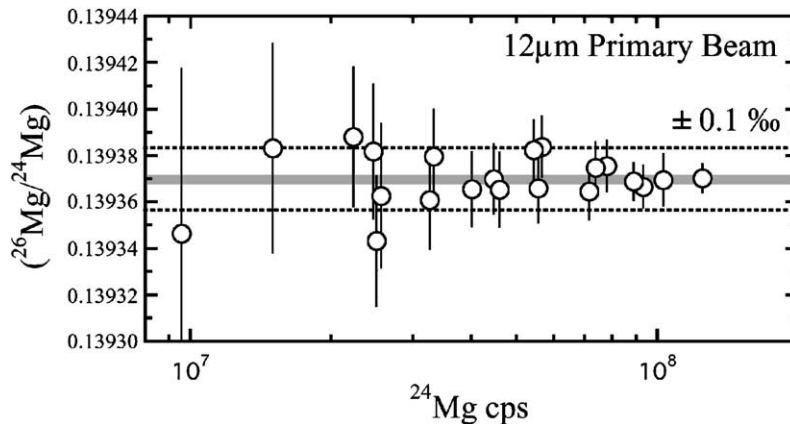


Fig. 3. Test analyses of Mg silicate standards using multi-collector FCs.

we currently speculate that the FC detector for  $^{26}\text{Mg}$  ( $\text{H2}^*$ ) is exposed by secondary electrons produced at the wall of the detection chamber by the bombardment of intensive  $^{27}\text{Al}$  ions. Because  $\text{H2}^*$  does not have a small electrostatic analyzer, secondary electrons cannot be suppressed.

To solve this problem, two additional FC detectors are installed to the multi-collector system so that the  $^{27}\text{Al}$  ions can be simultaneously detected. However, we found a new problem on baseline measurements during the test analyses of the Mg silicate mineral standards. When  $^{24}\text{Mg}$  and  $^{25}\text{Mg}$  are measured by using two adjacent detectors such as H1 and C, the baseline of  $^{25}\text{Mg}$  measured at mass 24.8 decreased significantly, resulted in unusually high  $^{25}\text{Mg}/^{24}\text{Mg}$  ratios. It seems that the secondary  $^{24}\text{Mg}$  ions hit a part of the housing of the detector and cause some effect, as the detector housing is curved to the lower mass side. This effect was not observed when Mg isotopes were analyzed by detectors  $\text{L2}^*$ , H1 and  $\text{H2}^*$ , probably because the detector housing of H1 was shielded from  $^{24}\text{Mg}$  ion beam by other detectors (L1 and C) and the  $\text{H2}^*$  detector was shielded from  $^{25}\text{Mg}$  ion beam by a small EM detector (H2) fixed to the lower mass side.

The baseline of the FC detector was carefully examined at a mass between 24.5 and 25.5. The baseline was found to be normal at the mass 24.96, which is  $\sim 0.026$  amu lower than the mass of  $^{25}\text{Mg}$  (24.9858). Because there is no interference ions or tailing from the Mg isotopes, we chose this magnetic field to measure the baseline of the FC detectors. Using this baseline position, further tests on both Mg-mineral standards and Al-bearing glass standards are now under the investigations.

#### 4. Discussion and conclusions

Using the high sensitivity and high resolution SIMS (IMS-1270), new sets of  $^{26}\text{Al}$ – $^{26}\text{Mg}$  analyses of chondrules were obtained by using the single collector EM pulse counting method. However, because of a small  $^{26}\text{Mg}$  excess in many chondrules, new analytical techniques with the precision of 0.1–1‰ are required. One approach may be to improve the precision of EM detectors by applying higher secondary ion intensities ( $\sim 10^5$  cps) or by using the multi-collector system. There are some difficulties using EM detectors with 0.1‰ accuracy and precision, such as dead time correction and gain calibration. Another approach is to use the multi-collector FC detectors, described above. Despite that the reproducibility and precision of the system is satisfactory, there are some systematic errors on the measured isotopic ratios for Al-rich glass standards. These problems are to be solved by a careful examination of the analytical conditions.

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