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ION MICROPROBE MEASUREMENTS OF Mg ISOTOPES IN TYPE B1 CAI OF ALLENDE METEORITE

Osamu KOIKE¹, Hisayoshi YURIMOTO¹, Hiroshi NAGASAWA²,
and Shigeho SUENO¹

¹*Institute of Geoscience, University of Tsukuba,
Tsukuba, Ibaraki 305*

²*Department of Chemistry, Gakushuin University,
Mejiro, Toshima-ku, Tokyo 171*

Abstract: Magnesium isotopes in individual mineral grains of a Ca-Al rich inclusion from the Allende meteorite have been measured by secondary ion mass spectrometry. An electrostatic peak switching system was used to make a precise isotopic measurement in high mass resolution mode ($M/\Delta M = \sim 4000$). The inclusion shows excess of ²⁶Mg correlated with the ²⁷Al/²⁴Mg ratio. The results suggest that live ²⁶Al decayed in the inclusion which formed simultaneously in the solar nebula. The relative abundance of ²⁶Al ($^{26}\text{Al}/^{27}\text{Al} = 3.12 \times 10^{-5}$) is close to the “canonical” value ($^{26}\text{Al}/^{27}\text{Al} = \sim 5 \times 10^{-5}$) for coarse-grained CAIs.

1. Introduction

Ca-Al rich inclusions (CAIs) in the Allende meteorite have been studied by many researchers who have been very interested in the origin and evolution of the early solar system. The CAIs are considered as the most primitive phases in primordial gas of the solar composition (LORD, 1965; LARIMER, 1967; MARVIN *et al.*, 1970; GROSSMAN, 1972).

Magnesium isotopic measurements of CAIs have revealed the presence of excess ²⁶Mg which is correlated with the ²⁷Al/²⁴Mg ratio. The relationship indicates that live radioisotope ²⁶Al decayed in the CAIs, and an upper limit of $^{26}\text{Al}/^{27}\text{Al} \sim 5 \times 10^{-5}$ has been established for the early solar nebula (*e.g.*, LEE *et al.*, 1976; HUTCHEON, 1982). The excess is commonly cited in support of the view that CAIs are the first solids to have formed in the solar nebula and that they formed more or less simultaneously, within an interval shorter than the half-life of ²⁶Al. However, the isochron of ²⁶Mg excess, in some CAIs, is disturbed by incomplete re-equilibration processes such as partial melts after all or a significant fraction of the initial ²⁶Al had decayed. The nature and setting for the disturbing event are still unknown (PODOSEK *et al.*, 1991).

In this study, we have measured the excess of ²⁶Mg in HN3-1 Type B1 CAI of the Allende meteorite (NAGAHARA *et al.*, 1987; NAGAHARA and NAGASAWA, 1988) by secondary ion mass spectrometry (SIMS). As the first step for our isotopic analysis by SIMS, we report analytical procedures and the principal results of Mg isotopic measurement.

2. Experimental

2.1. Sample preparation

The sample used in this study was mineral grains separated from Allende HN3-1 Type B1 CAI; some petrological and isotopic studies have been previously made (MAYEDA *et al.*, 1986; NAGAHARA *et al.*, 1987; NAGAHARA and NAGASAWA, 1988). Each mineral grain (spinel, fassaite, melilite, and anorthite) was mounted separately on epoxy disks. The size of each mineral grain was less than 20 μm . The disks were ground with SiC paper and then polished with alumina paste. The polished disks were coated with ~ 20 nm of gold film for SIMS analysis.

2.2. Standards

Three different terrestrial single crystals (spinel, augite, and anorthite) were used as standards for Mg isotopic analysis (Table 1). The spinel, augite, and anorthite grains were from Russia, from Takashima, Japan, and from Miyakejima, Japan, respectively. The surfaces of the standards were coated by carbon film for electron microprobe analyses. Homogeneity of Mg and Al concentration on individual terrestrial standards was confirmed by electron microprobe analysis. The Al/Mg ratios for each crystal are shown in Table 1. After the electron microprobe analyses, the carbon film was removed, and then a gold film was evaporated for SIMS work.

2.3. Magnesium isotopic measurement

Magnesium isotopic ratios and Al/Mg ratios were measured by the Tsukuba University CAMECA IMS-3F ion microprobe equipped with electrostatic peak switching system. All Mg isotopic measurements were made with a focused primary ion beam of $^{16}\text{O}^-$. Primary beam currents ranged from 0.5 nA to 12 nA and were

Table 1. Mg isotopic measurement of terrestrial standards.

Samples	$\Delta^{25}\text{Mg}^1$ (‰) ($\pm 2\sigma_{\text{mean}}$)	$\delta^{26}\text{Mg}^2$ (‰) ($\pm 2\sigma_{\text{mean}}$)	$^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ ($\pm 2\sigma_{\text{mean}}$)	$^{27}\text{Al} / ^{24}\text{Mg}^3$
Spinel (Russia)	-11.3 ± 0.7	-0.3 ± 2.6	1.97 ± 0.03	2.58
	-11.7 ± 0.9	2.1 ± 1.2	1.96 ± 0.03	
Augite (Takashima)	-5.3 ± 0.6	-0.5 ± 1.5	0.51 ± 0.02	0.655
	-5.6 ± 0.7	-0.9 ± 1.3	0.51 ± 0.02	
Anorthite (Miyakejima)	-3.0 ± 0.8	2.9 ± 1.5	309 ± 1	423
	-2.8 ± 1.2	-0.9 ± 3.0	317 ± 3	

Each line shows the measured values for a different spot of the given standard.

$$^1 \Delta^{25}\text{Mg} = 1000 \times \left[\frac{(^{25}\text{Mg}^+ / ^{24}\text{Mg}^+)_{\text{MEAS}}}{(^{25}\text{Mg} / ^{24}\text{Mg})_{\text{REF}}} - 1 \right]$$

$$^2 \delta^{26}\text{Mg} = 1000 \times \left[\frac{(^{26}\text{Mg}^+ / ^{24}\text{Mg}^+)_{\text{MEAS}}}{(^{26}\text{Mg} / ^{24}\text{Mg})_{\text{REF}}} - 1 \right] - 2 \times \Delta^{25}\text{Mg}$$

$(^{25}\text{Mg} / ^{24}\text{Mg})_{\text{REF}}$ and $(^{26}\text{Mg} / ^{24}\text{Mg})_{\text{REF}}$ are assumed to 0.12663 and 0.13932, respectively (CATANZARO *et al.*, 1966).

³ Determined by electron microprobe analysis.

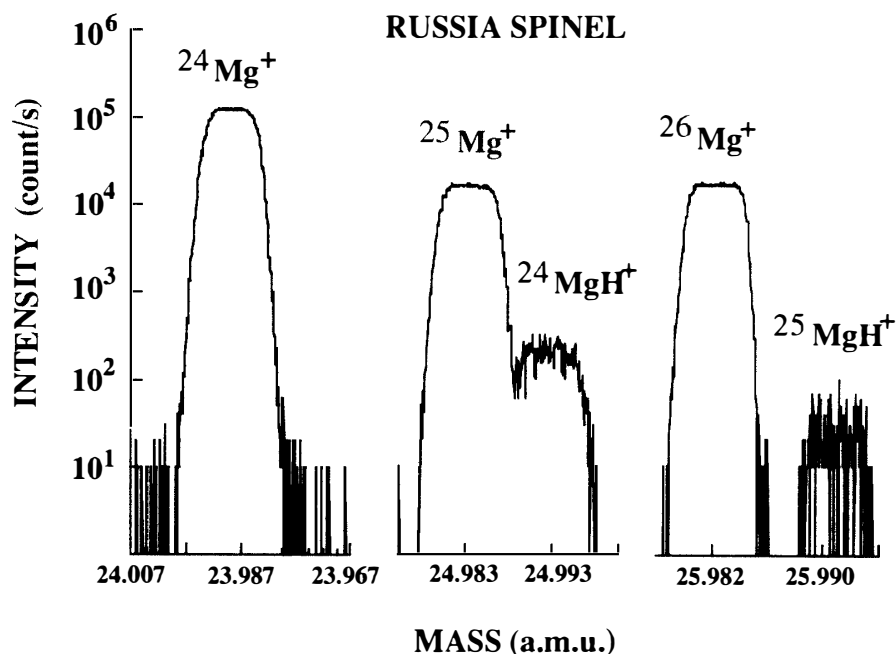


Fig. 1. High resolution mass spectra ($M/\Delta M = \sim 4000$) of positive secondary ions in the atomic mass 24, 25, and 26 regions. Ions were sputtered from a terrestrial spinel single crystal by bombardment with $^{16}\text{O}^-$ ions. The Mg isotope peaks are clearly resolved from all interferences.

adjusted for each run to obtain a $^{24}\text{Mg}^+$ count rate of not more than $\sim 3.0 \times 10^5$ counts per second and typically $\sim 1.5 \times 10^5$ counts per second. The beam size was $10 \sim 20 \mu\text{m}$ in diameter. The transfer optics of the instrument were adjusted to obtain an imaged field of $150 \mu\text{m}$ in diameter. The contrast aperture ($150 \mu\text{m}$) was used and the entrance and exit slits of the mass spectrometer were closed enough to achieve the desired mass resolution. The energy slit was set to select an energy window of 15 eV. A mass resolution power, $M/\Delta M$, of ~ 4000 was sufficient to resolve all significant interferences from MgH^+ (Fig. 1) as well as other possible molecular and doubly-charged ions.

Measurements were made by cycling through the mass sequences 24, 25, 26, and 27 in a peak jumping mode. The peak jumping was achieved by an automatic control of magnetic field strength. To minimize hysteresis effects, the magnet was repeatedly stepped through the set of field values corresponding to the selected masses before starting a measurement run. After the magnetic peak jumping, a precise peak centering of each mass was made by electrostatic peak switching scan. Principle of the electrostatic peak switching equipment was described by SŁODZIAN *et al.* (1984). Small drifts in the position of a peak during the run were compensated by the electrostatic peak centerings every ten cycles through the masses to keep the ion beam centered in the exit slit of the mass spectrometer. Secondary ion signals were detected with an electron multiplier operated in a pulse counting mode. Signals measured in the electron multiplier were corrected for the counting system dead time. The dead time, which was determined by Ti isotopic measurements of a rutile standard, was $33.6 \pm 0.2 \text{ ns}$. The correction was 0.5% when a $^{24}\text{Mg}^+$ count rate was $\sim 1.5 \times 10^5$ counts per second.

Table 2. Mg isotopic measurement of HN3-1 Type B1 CAI.

Phase	$^{27}\text{Al}/^{24}\text{Mg}$ ($\pm 2\sigma_{\text{mean}}$)	$\Delta^{25}\text{Mg}$ (‰) ($\pm 2\sigma_{\text{mean}}$)	$\delta^{26}\text{Mg}$ (‰) ($\pm 2\sigma_{\text{mean}}$)
Spinel # 1	2.45 ± 0.02	3.61 ± 1.99	0.8 ± 1.5
Spinel # 2	2.42 ± 0.01	-1.05 ± 0.84	3.5 ± 1.4
Spinel # 3	2.45 ± 0.06	-1.30 ± 0.38	4.9 ± 1.7
Fassaite # 1	1.99 ± 0.04	-2.28 ± 0.67	3.92 ± 0.39
Fassaite # 2	2.45 ± 0.06	0.48 ± 2.70	-2.0 ± 5.6
Melilite # 1	7.56 ± 0.17	5.67 ± 0.11	10.8 ± 2.7
Melilite # 2	7.08 ± 0.09	5.31 ± 0.03	6.6 ± 6.6
Melilite # 3	8.73 ± 1.00	6.54 ± 0.75	2.2 ± 4.9
Anorthite # 1	718 ± 66	5.4 ± 2.4	163.6 ± 4.0
Anorthite # 2	451 ± 8	1.0 ± 2.1	99.4 ± 7.4
Anorthite # 3	429 ± 6	6.5 ± 3.2	87 ± 12
Anorthite # 4	816 ± 45	2.9 ± 3.4	198.0 ± 9.4
Anorthite # 5	484 ± 31	4.7 ± 3.0	117.6 ± 7.8

The isotopic composition measured in the ion microprobe differs from true isotopic composition of the sample by the matrix dependent instrumental mass fractionation. The instrumental mass fractionation varies with the geometry of the sample measured, tuning condition of the instrument, and the position of the energy window, *etc.* In addition, the instrumental mass fractionation changes during the course of the measurement, inferred that this is the result of changes in the distribution of ion sputtered from a deepening hole (FAHEY *et al.*, 1987). From these reasons, it is very difficult to determine precisely the intrinsic mass fractionation of the sample. In this study, no special efforts were made to determine precisely the mass-dependent Mg isotopic fractionation. Therefore, $\Delta^{25}\text{Mg}$ values reported in Table 2 (and in Table 1) include the intrinsic and instrumental mass fractionational effects. The primary goal of the Mg isotopic measurements in this study is the determination of “non-linear” ^{26}Mg excess.

For the measurement of non-linear effects in ^{26}Mg , a few independent runs were usually made on a given spot. The measured $^{26}\text{Mg}/^{24}\text{Mg}$ ratios were corrected for an assumed linear mass fractionation relationship on the basis of the measured $^{25}\text{Mg}/^{24}\text{Mg}$ ratios and the normal Mg isotopic ratios given by CATANZARO *et al.* (1966). As shown in Table 1, most $\delta^{26}\text{Mg}$ values on different spots for the terrestrial standards are zero within $2\sigma_{\text{m}}$; although two $\delta^{26}\text{Mg}$ values are not. There are no significant discrepancy between variations for those original data; smaller errors of $\delta^{26}\text{Mg}$ values for each of spinel and anorthite standards arise occasionally when these data are statistically dealt in. Therefore, the linear fractionation correction and the chosen normal ratios agree with our SIMS data on the terrestrial standards (Table 1).

A run consisted of 90 cycles through the mass sequence, 24, 25, 26, and 27. A measurement run was divided into “blocks” of 10 cycles each for the purpose of time interpolation and peak centering. In order to minimize instrumental instabilities, time interpolation was made for the mass intensities every ten cycles. The mass fractionation

correction was applied to each block and the average of the individual $\delta^{26}\text{Mg}$ value was computed at the end of the run. This procedure minimized the $\delta^{26}\text{Mg}$ error, since it accounts for variations in the instrumental mass fractionation during a run. The $\delta^{26}\text{Mg}$ values reported in Table 1 and in Table 2 are averages over a series of a few runs on a single spot.

The relative sensitivity factor of Mg^+ and Al^+ for each mineral under the analytical conditions used was determined with terrestrial standards of spinel, pyroxene, and anorthite. The $^{27}\text{Al}/^{24}\text{Mg}$ ratios for CAI minerals were calculated from $^{27}\text{Al}^+/^{24}\text{Mg}^+$ intensity ratios multiplied by the relative sensitivity factors. Sensitivity factors determined from analyses of the respective standard minerals were 1.31, 1.26, and 1.33 for spinel, pyroxene, and anorthite, respectively.

3. Results and Discussion

The results of the Mg-Al analysis are given in Table 2. Mg-Al evolution diagrams showing $^{26}\text{Mg}/^{24}\text{Mg}$ versus $^{27}\text{Al}/^{24}\text{Mg}$ are shown in Fig. 2. All data points are plotted in Fig. 2. Individual anorthite grains are numbered in the figure. In this study, we assumed the same sensitivity factor for anorthite and for melilite because no terrestrial standard of melilite was prepared. Therefore, $^{27}\text{Al}/^{24}\text{Mg}$ values for melilite in Table 1 may shift systematically.

All data points for anorthite grains lie on a single correlation line. A least square fit to 13 data gives a line with slope $^{26}\text{Al}/^{27}\text{Al} = (3.12 \pm 0.13) \times 10^{-5}$ and intercept $\delta^{26}\text{Mg} = 3.37 \pm 0.75$. The relative abundance of ^{26}Al ($^{26}\text{Al}/^{27}\text{Al} = 3.12 \times 10^{-5}$) is close to the "canonical" value ($^{26}\text{Al}/^{27}\text{Al} = \sim 5 \times 10^{-5}$) for coarse-grained CAIs.

The increases or decreases of Mg intensities during measurement have been observed in some spots of anorthite grains. The variation gives the larger error, especially in anorthite #1. The instability of Mg intensity corresponds to heterogeneous distribution

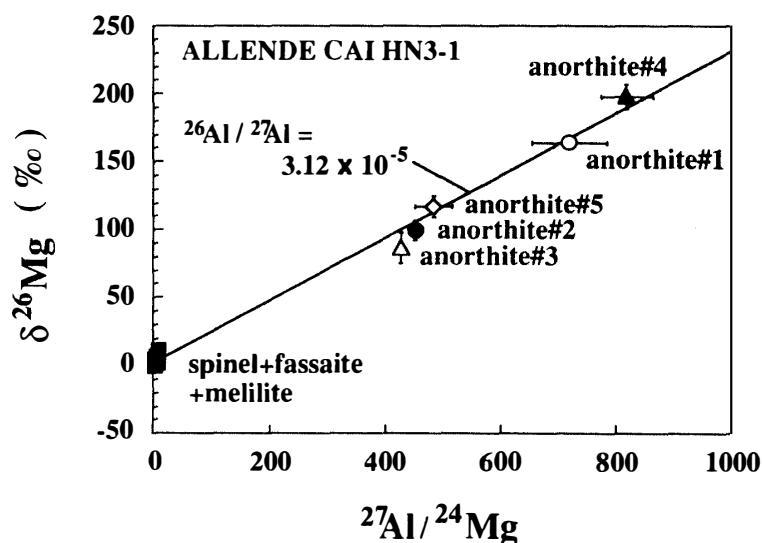


Fig. 2. ^{26}Al - ^{26}Mg plot for Allende HN3-1 Type B1 CAI, showing a correlation of $\delta^{26}\text{Mg}$ with $^{27}\text{Al}/^{24}\text{Mg}$ ratio due to the in situ decay of ^{26}Al . A least square fit to 13 data points gives a slope of $^{26}\text{Al}/^{27}\text{Al} = (3.12 \pm 0.13) \times 10^{-5}$. All errors are $2\sigma_{\text{mean}}$.

of Mg in anorthite, but not instrumental instability. Nevertheless, there are not any significant scatters from the isochron line. The results indicate that the internal isochron of anorthite is essentially equal to the mineral isochron in the CAI, and strongly suggest that live ^{26}Al decayed in the anorthite crystal and that CAIs formed simultaneously in the solar nebula.

Data points for one spinel, one fassaite pyroxene, and one melilite crystal fall slightly off the isochron line. We can not conclude that these scatters from isochron line are intrinsic effects or due to instrumental instabilities, although PODOSEK *et al.* (1991) suggested that melilite crystals in Type B1 CAIs migrated upward from the isochron probably by isotopic re-equilibration. Data points for the other melilite crystals (melilite #2, #3) lie on this line within $2\sigma_m$. The $\delta^{26}\text{Mg}$ values for two melilites (melilite #2, #3) and one fassaite (pyroxene #2) have larger errors. We consider that these uncertainties are attributed to instrumental instabilities during Mg isotopic measurements. The large Al/Mg error for melilite #3 is due to the chemical zoning of melilite solid solution. These results indicate that abundant data points obtained by much precise measurements are required to determine the intercept which represents the initial $^{26}\text{Mg}/^{24}\text{Mg}$ ratio at the CAI formation and that *in situ* magnesium isotope measurements combined with petrological studies are also necessary to discuss the CAI formation. As the next step, *in situ* magnesium, oxygen, and other isotopic measurements are required in a thin section sample of CAI, and the results should be combined with petrological studies.

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