SIMS MEASUREMENT OF MAGNESIUM ISOTOPIC RATIOS IN YAMATO-74191 AND -75028 METEORITES

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Abstract: Isotopic ratios of $^{24}Mg/^{25}Mg$ and $^{26}Mg/^{25}Mg$ have been measured for Mg-rich and Al-poor portions of matrix parts of the Yamato-74191 and -75028 meteorites with a Hitachi IMA 2A ion microprobe mass analyzer. Several terrestrial samples of lherzolites and a dunite were also analyzed. A clear evidence for the excess of ^{24}Mg has been found in the portions of Yamato-74191, where Mg/Si ratio is higher than 1.5 and Al/Mg ratio is less than 0.13. This excess ^{24}Mg can be evidence for the heterogeneity of the primordial solar nebula.

1. Introduction

Since the discoveries of isotopic anomalies of ^{16}O (Clayton *et al.*, 1973) and ^{26}Mg (Gray and Compston, 1974) in the Allende carbonaceous chondrite, isotopic anomalies of such elements as S (Rees and Thode, 1977), Ba and Nd (McCulloch and Wasserburg, 1978a), Ca (Lee *et al.*, 1978), Sr (Papanastassiou and Wasserburg, 1978) and Sm (McCulloch and Wasserburg, 1978b) have been observed for Allende. Furthermore, the ^{16}O anomaly has been found even in an ordinary chondrite of the type LL3 (Mayeda *et al.*, 1980). The existence of these anomalies requires a heterogeneous solar nebula and has been interpreted as the result of a supernova explosion that synthesized those elements and injected them into the primordial nebula. If such a supernova had exploded, ^{20}Ne, ^{23}Na, ^{24}Mg and ^{28}Si would have been synthesized according to the theoretical considerations of Arnett (1969). Nishimura and Okano (1981a, b) have reported preliminary results on excess ^{24}Mg in Allende and a few Yamato meteorites.

Searching for excess ^{24}Mg has been carried out for samples of Yamato meteorites belonging to the petrological type 3, and a clear evidence for an excess of ^{24}Mg has been found in Yamato-74191 (L3) chondrite.

2. Experimental

A Hitachi IMA 2A ion microprobe mass analyzer was used. 12 keV O_2^+ ions were used as primaries. The diameter of the primary ion beam was 100 to 200 μm on the sample surface, and the current, 0.3 to 1.2 μA. The ultimate pressure in the analyzer chamber was about 2×10^{-5} Pa, and the pressure during the isotopic measurement was about 3×10^{-5} Pa.

Samples used were Yamato-74191 (L3 (Yanai, 1979)) and Yamato-75028 (H3

part in a brecciated chondrite (YANAI, 1979)) and a few terrestrial lherzolites from Salt Lake, Hawaii, from Oki Island, Japan, and from McMurdo, Antarctica. A terrestrial forsterite in dunite from Ehime Prefecture, Japan was also analyzed as a laboratory standard. Polished and ultrasonically washed surfaces of these samples were used for the isotopic analyses.

Magnesium isotopic analyses for the chondrites were performed on Al-poor and Mg-rich portions in matrix areas where the concentration ratios of Al/Mg were less than 0.13. Mass scannings were repeated 10 to 20 times in one run over the mass range from 24 to 26, and more than 3 runs were carried out at one probed portion. In order to avoid charge build-up due to the positive ion bombardment, electron spray was applied. Moreover, samples were covered with a sheet of tantalum with apertures 3 mm in diameter. A schematic diagram of a sample holder with a cover of tantalum is shown in Fig. 1.
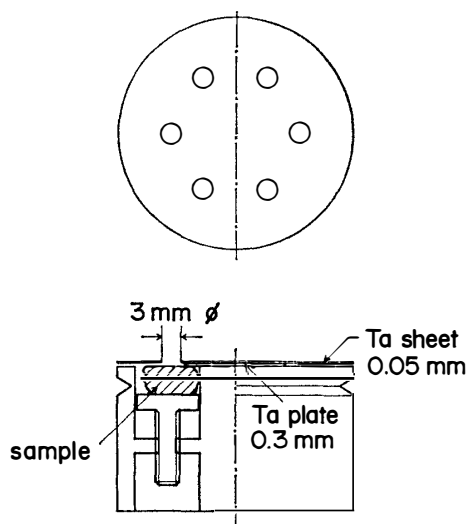

Fig. 1. Sample holder with a cover of tantalum sheet.

Table 1. Contribution of $^{24}MgH^+$ to the mass peak at mass number 25, in cases that without and with a cold finger of liquid nitrogen aside the sample.

Liq. N_2	$^{24}MgH^+/^{25}Mg^+$*	Pressure (Pa)
Without	3×10^{-2}	4×10^{-5}
With	4×10^{-4}	3×10^{-5}

* The estimate of $^{24}MgH^+/^{25}Mg^+$ was carried out based on hydride ion formation ratio which was calculated according to eqs. (1) and (2).

In order to decrease the interferences due to the molecular ions that would come from the environment of hydrocarbons and water vapor, a cold finger of liquid nitrogen was put aside the samples. A remarkable effect of this cold finger was found, as shown in Table 1.

Interferences of multiply-charged and molecular ions with mass peaks at masses 24, 25 and 26 were examined. The second column of Table 2 lists the main ionic species which are liable to overlap. The maximum contributions of these interfering ionic species to the subject ionic species are shown in the third column of the table.

Table 2. Interferences of doubly-charged and molecular ionic species with the mass peaks at mass numbers of 24, 25 and 26.

Subject ionic species	Overlapping ionic species	Maximum contribution to the subject peak
$^{24}Mg^+$	$^{12}C_2^+$	3×10^{-5}
	$^{22}NaH^+$	1×10^{-6}
	$^{48}Ca^{2+}$	2×10^{-5}
	$^{48}Ti^{2+}$	7×10^{-5}
$^{25}Mg^+$	$^{12}C^{13}C^+$	5×10^{-6}
	$^{12}C_2H^+$	7×10^{-6}
	$^{23}NaH_2^+$	1×10^{-6}
	$^{50}Ti^{2+}$	4×10^{-5}
	$^{50}Cr^{2+}$	1×10^{-6}
	$^{24}MgH^+$	4×10^{-4}
$^{26}Mg^+$	$^{13}C_2^+$ $\left.\begin{array}{c} \\ \\ \\ \end{array}\right\}$	
	$^{12}C^{13}CH^+$	1×10^{-6}
	$^{12}C_2H_2^+$	
	$^{12}C^{14}N^+$	7×10^{-6}
	$^{52}Cr^{2+}$	5×10^{-4}
	$^{25}MgH^+$	5×10^{-5}

Table 3. $^{12}C_2^+/^{12}C^+$, $^{12}CN^+/^{12}C^+$ and $^{12}CH^+/^{12}C^+$ ratios measured for the carbon-containing samples.

Sample	$^{12}C_2^+/^{12}C^+$	$^{12}CN^+/^{12}C^+$	$^{12}CH^+/^{12}C^+$
Silicon carbide	0.016	0.0004	0.013
Calcite	0.003	0.0001	0.026
Charcoal	0.040	0.0010	0.031
Graphite	0.054	0.0013	0.005
Dolomite	~ 0	~ 0	0.077

The interferences of $^{12}C_2^+$, $^{12}C^{13}C^+$, $^{12}C_2H^+$, $^{13}C_2^+$, $^{12}C^{13}CH^+$, $^{12}C_2H_2^+$ and $^{12}C^{14}N^+$ were estimated in the following way. The ratios of $^{12}C_2^+/^{12}C^+$, $^{12}CN^+/^{12}C^+$ and $^{12}CH^+/^{12}C^+$ were first evaluated for samples of silicon carbide, calcite, charcoal, graphite and dolomite, as shown in Table 3. The largest values in the table for each ionic species, the intensities for the samples at masses 12, 12.5, 13, 24, 25 and 26, and the diatomic ion formation ratio for carbon isotopes (NISHIMURA and OKANO, 1981a) gave us an estimate of the maximum contributions, as shown in Table 2. As for the contribution of $^{23}NaH^+$, the estimate could be made by using the intensities at masses 23 ($^{23}Na^+$), 24 ($^{23}NaH^+$ and $^{24}Mg^+$) and 25 ($^{25}Mg^+$) for a terrestrial anorthite sample. The estimate of doubly-charged ions of Cr, Ti and Ca was carried out by referring to the intensities of $^{53}Cr^{2+}$, $^{47}Ti^{2+}$, $^{49}Ti^{2+}$ and $^{40}Ca^{2+}$ at masses 26.5, 23.5, 24.5 and 20, respectively. The hydride ion formation ratio, MgH^+/Mg^+, was evaluated based on the following equations.

$$\frac{I_{25}}{I_{24}} = \frac{A_{25}}{A_{24}}(1-\alpha)+x, \tag{1}$$

$$\frac{I_{26}}{I_{24}} = \frac{A_{26}}{A_{24}}(1-\alpha)^2+\frac{A_{25}}{A_{24}}x, \tag{2}$$

where I_m: secondary ion intensity at mass m

$\quad\quad$ A_m: natural isotopic abundance of ^mMg

$\quad\quad$ α: mass discrimination factor

$\quad\quad$ x: hydride ion formation ratio.

Using this value of x, the contribution of hydride ions to the subject mass peaks were estimated.

The maximum contribution of the interferences as a whole was estimated to be less than 1×10^{-3} of the subject peak.

An example of the secondary ion mass spectrum obtained for the Yamato-74191 meteorite is shown in Fig. 2. Isotopic ratios of $^{24}Mg/^{25}Mg$ and $^{26}Mg/^{25}Mg$ were calculated from raw secondary ion intensities, and the deviations of these ratios, $\Delta_{24/25}$ and $\Delta_{26/25}$, from the laboratory standard values were evaluated in permil from eq. (3).

$$\Delta_{m/25} = \left[\frac{(^mMg/^{25}Mg)_{sample}}{(^mMg/^{25}Mg)_{lab.std.}} - 1 \right] \times 1000 \ (m=24, 26) \ . \tag{3}$$

The calculations and statistical procedures as well as the control of mass scannings were done automatically by using a micro-computer controlling system which was constructed by the authors. The control contains: (1) scan speed switching, slow at the top of a mass peak and fast at the bottom, (2) data read-in by ten point running mean method, (3) peak height calculation by a top value minus a bottom value, (4) correction for intensity variation with time, (5) calculation of peak height ratios and Δ values, (6) statistical procedures which are the calculation of a mean and a standard deviation (σ and σ_m), the exclusion of data exceeding $\pm 2\sigma$, recalculation of a mean
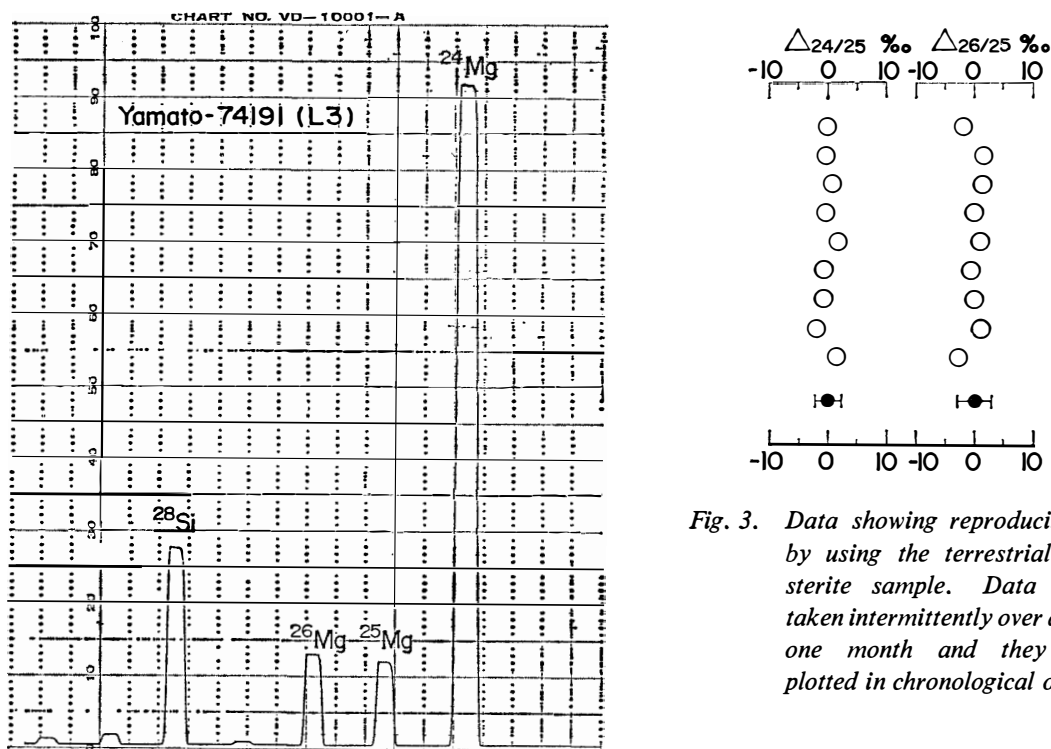

Fig. 2. Example of secondary ion mass spectrum for the matrix of Yamato-74191.

Fig. 3. Data showing reproducibility by using the terrestrial forsterite sample. Data were taken intermittently over about one month and they are plotted in chronological order.

and an error and the iteration of these procedures, and (7) data print out.

The reproducibility of the magnesium isotopic measurement has been examined by analyzing the laboratory standard sample of forsterite intermittently over about one month. The Δ values obtained for these analyses are plotted in chronological order in Fig. 3. From the plot, the reproducibility was found to be about ± 3 permil as $\pm 2\sigma$, as shown by the error bars for the closed circles in the figure.

3. Results and Discussion

Data obtained for three samples of terrestrial lherzolites and for a spinel lherzolite are shown in Fig. 4 as a three isotope plot. In the figure, a straight line with the slope
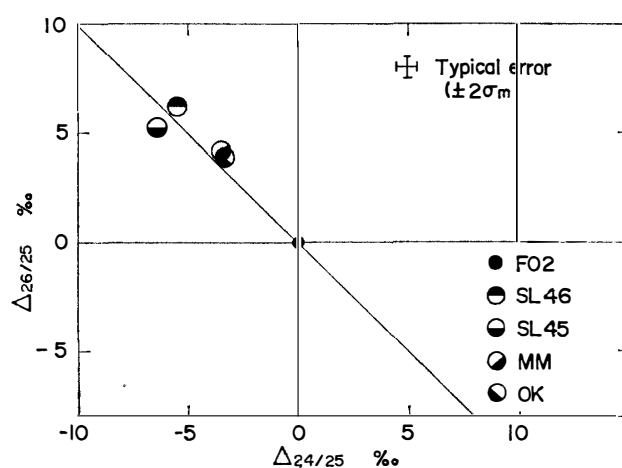

Fig. 4. Three isotope plot of magnesium for terrestrial samples. FO2: forsterite in dunite (Ehime, Japan); laboratory standard, SL46: lherzolite (Salt Lake, Hawaii), SL45: spinel lherzolite (Salt Lake, Hawaii), MM: lherzolite (McMurdo, Antarctica), OK: lherzolite (Oki Island, Japan).
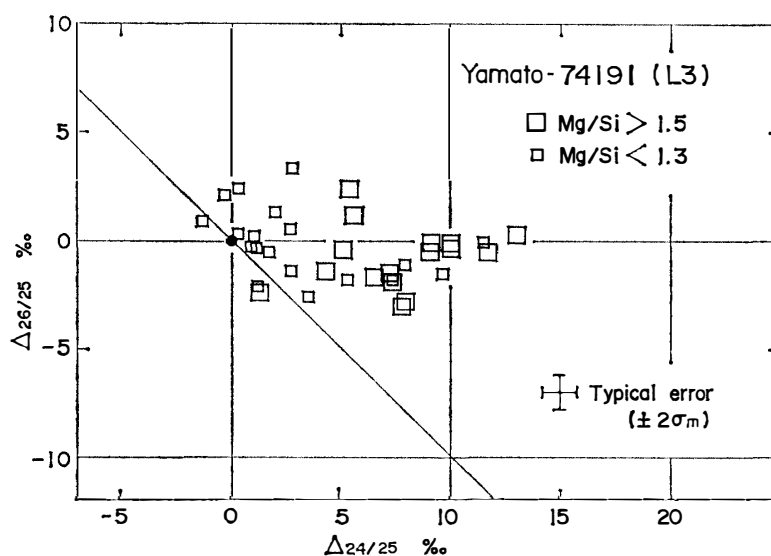

Fig. 5. Three isotope plot of magnesium for the matrix of the Yamato-74191 (L3) chondrite.
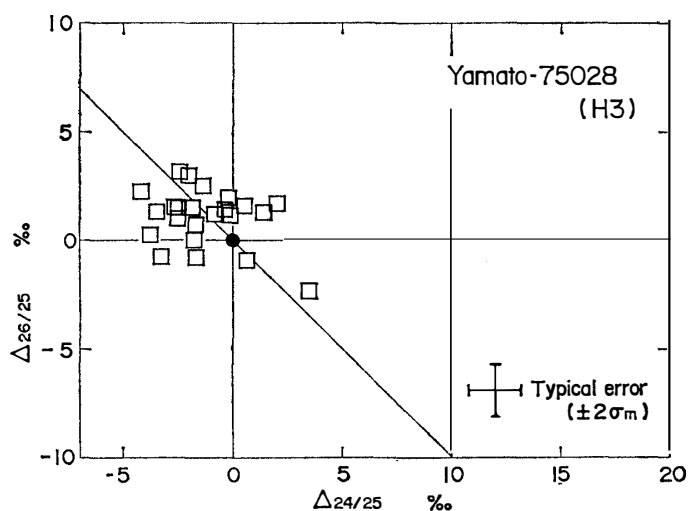
Fig. 6. Three isotope plot of magnesium for the matrix of the Yamato-75028 (H3 part of breccia)
         chondrite.

of -1 corresponds to the normal mass fractionation depending on the mass difference. A typical error shown in the figure represents twice a standard deviation of a mean. The plotted points fall well along the normal mass fractionation line.

Figure 5 gives the three isotope plot of magnesium for the sample of Yamato-74191. It contains two types of data; one is for the portions where the concentration ratio of Mg/Si is higher than 1.5, and the other is for the portions where Mg/Si is less than 1.3. At every portion Al/Mg ratios are less than 0.13. From Fig. 5, the excess of ^{24}Mg is clear for high Mg/Si portions, and for low Mg/Si portions, some of the plotted points also have a tendency for excess ^{24}Mg, but the excess is not so clear.

The data for H3 part of Yamato-75028 are shown in Fig. 6. Almost all data plot near the normal mass fractionation line. No tendency for anomalous ^{24}Mg is found from this figure.

4. Conclusion

Clear evidence for an excess of ^{24}Mg has been found for the matrix part of the Yamato-74191 (L3) chondrite. The excess ^{24}Mg can be explained as the addition of almost pure ^{24}Mg, produced in a supernova explosion, to the original magnesium preexisting in the primordial solar nebula.

This result can be a clearer experimental evidence for the heterogeneity of the solar nebula, together with the results of ^{16}O and ^{26}Mg anomalies.

Acknowledgments

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