Mg isotopic compositions of stony spherules from deep-sea sediments

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The isotopic compositions of Mg in 5 individual stony spherules from deep-sea sediments have been measured. The spherules are composed of olivine, glass, and magnetite, and considered to be of extraterrestrial origin. No significant mass fractionation of up to 2 per mil per amu was recognized. One sample showed a small but significant non-linear ²⁶Mg isotopic effect ($\delta^{26}\text{Mg} = +1.2$ per mil) similar to that reported in interplanetary dust particles (IDPs). Based on Mg isotopic compositions of the spherules, we suggest that either vaporization mass loss of parent meteoroids of stony spherules was not so large, usually less than ~20%, or ablative mass loss occurred effectively during entry into the Earth's atmosphere, and that physicochemical fractionations took place in parent meteoroids could be related to those of primitive IDPs. The processes responsible for the non-linear effect of ²⁶Mg, however, remain undefined.

INTRODUCTION

The cosmic spherules collected from the ocean floor are important sources of extraterrestrial material (e.g., Brownlee, 1981, 1985 and references therein). As is the case with meteoritic chondrules (e.g., Misawa and Nakamura, 1988), detailed REE patterns may constrain not only the nature of the parent meteoroids but also the melting conditions of these material. In addition, the study of O, Mg, and Si isotopic mass fractionations can help us to better understand melting conditions of parent bodies that enter the Earth's atmosphere. Because of the limited sizes of individual spherules (typically less than 200 μg), the fine structures of trace element abundances, especially REE patterns, and the isotopic compositions of O, Mg, and Si are not well understood except in only a few cases (e.g.,

Nagasawa *et al.*, 1979; Clayton *et al.*, 1986; Davis *et al.*, 1991).

In order to further clarify the chemical and isotopic characteristics of these spherules, we have undertaken isotope dilution analysis of the REE and isotopic measurements of Mg together with instrumental neutron activation analysis (INAA) of major and trace elements, and part of this study will appear elsewhere (Misawa *et al.*, 1992). We present here the Mg isotopic data for 5 individual stony spherules and discuss the implications of the data on melting and vaporization processes during entry into the Earth's atmosphere as well as the physicochemical fractionations that took place on the parent meteoroids. Preliminary data from our study were reported by Misawa and Yamakoshi (1990).

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EXPERIMENTAL

Samples

More than 50 stony spherules were separated magnetically from pelagic clay dredged by the *R/V Hakurei-Marui* near the Hawaiian islands at a depth of ~ 4500 m. The spherules were hand-picked under a binocular microscope. They were weighed using a Cahn-29 automatic electrobalance, and 5 spherules larger than $10\ \mu\text{g}$ were selected for Mg isotopic analysis. After ultrasonic cleaning in distilled water and distilled acetone, each spherule was broken into two parts using an agate mortar. One part was mounted in epoxy resin and polished with diamond paste for SEM observation. The other part was used for the Mg isotope measurement. The spherules were examined by a JEOL JMS-740 electron microprobe. Constituent phases were identified using a Kevex Delta-3000 energy dispersive spectrometer system on the electron microprobe. Textures were observed by back-scattered electron images. All spherules analyzed in this study show barred-dendritic textures (Fig. 1) typically observed in cosmic spherules, and are considered to be of extraterrestrial origin.

Fig. 1. Back-scattered electron image of spherule HWI-5 which is composed of barred-dendritic olivine (medium gray), glass (dark), and magnetite (bright). The texture strongly suggests that the spherule melted totally. Outer surfaces of the spherule have lightly experienced etching by seawater (the darkest areas).

Chemistry

Reagents used during chemistry were purified by the following methods. Acetone was distilled in a Pyrex glass still. H_2O was first distilled in a stainless steel boiling still, then distilled twice in quartz boiling stills, and finally distilled in a quartz sub-boiling still. HCl was obtained by bubbling high purity HCl gas into distilled water. HF and HClO_4 were taken from commercial products (sub-boiling purified reagents; NBS Analytical Chemistry Division).

The samples were dissolved with $2\text{--}3\ \mu\text{l}$ of a HF-HClO_4 mixture in a sealed teflon bomb. After evaporating to dryness and redissolved in 1N HCl , they were passed twice through a $300\ \mu\text{l}$ -volume quartz column packed with Dowex AG 50 W X-12 (200–400 mesh) cation exchange resin. Mg was eluted with 1N HCl . For small samples, HWI-3 and -4, column chemistry was performed once. The total procedural Mg blank was measured by isotope dilution. Using the normal chemistry (two column separations), the final Mg fraction was collected and then spiked with a ^{25}Mg tracer. The total collected fraction (both passes) yielded a blank less than $0.5\ \text{ng}$. We usually loaded $1/4$ to $1/10$ of the collected Mg fraction on the filament per run, and the contribution of the loading blank to the total blank was considered to be small. Since we ran μg of Mg during this work, the data are not corrected for blank.

Mass spectrometry

The isotopic composition of Mg was determined using a VG-354 mass spectrometer with a single Faraday collector. The thermal ionization was carried out by the single Re V-shaped filament mode (Lee *et al.*, 1977 a). Samples ($200\text{--}500\ \text{ng}$ of Mg) were loaded on an out-gassed ($< 1 \times 10^{-7}$ Torr, $4.5\ \text{A}$ for 2 hrs) filament with $2\ \mu\text{l}$ of silica gel and $5\ \mu\text{l}$ of $3\text{N H}_3\text{PO}_4$ as an activator (Schramm *et al.*, 1970), and baked at $\sim 1000^\circ\text{C}$ for 10 hrs to remove Na. The filament temperature was increased gradually to $\sim 1500^\circ\text{C}$. A single charged ^{24}Mg signal larger than $10^{-11}\ \text{A}$ was sustained over a period of 5 hrs with $200\ \text{ng}$ of Mg. During measuring, Na, Mg,

and Al mass regions were monitored. Neither hydrocarbon nor scattering peaks from Na and Al were recognized. Isotopic measurements were carried out with a general peak jumping mode in the cyclic order ^{24}Mg - ^{25}Mg - ^{26}Mg - ^{24}Mg . Fifteen sequential cycles were grouped in one set, and the mean raw ratios and the average of fractionation corrected ratios were calculated. The only selection criterion for these sets was that the standard deviation of the mean must be less than 1 per mil for $^{25}\text{Mg}/^{24}\text{Mg}$ and 2 per mil for

$^{26}\text{Mg}/^{24}\text{Mg}$. Usually over 20 sets were obtained during one analysis. For normalization we used $^{25}\text{Mg}/^{24}\text{Mg}=0.12663$ (Catanzaro *et al.*, 1966), and mass fractionation was corrected using a power law.

RESULTS AND DISCUSSION

Normals

Standards of normal Mg composition, reagent MgO , separated Mg from KLB-1 lher-

Table 1. Results of Mg analyses

Sample (weight)	$^{25}\text{Mg}/^{24}\text{Mg}$ $\pm 2\sigma$ [#]	measured raw ratios $^{26}\text{Mg}/^{24}\text{Mg}$ $\pm 2\sigma$ [#]	frac. corrected [§] $^{26}\text{Mg}/^{24}\text{Mg}$ $\pm 2\sigma_{\text{mean}}$
MgO	0.124636 ± 92 0.124621 ± 98 0.124568 ± 134 0.124505 ± 138 0.124603 ± 112 0.124550 ± 186 0.124539 ± 278 0.124574 ± 92 0.124618 ± 100 0.124609 ± 94 0.124646 ± 140 0.124654 ± 118 0.124567 ± 144 0.124710 ± 128	0.135452 ± 290 0.135416 ± 268 0.135286 ± 190 0.135126 ± 360 0.135328 ± 108 0.135245 ± 476 0.135202 ± 648 0.135279 ± 292 0.135417 ± 146 0.135393 ± 206 0.135521 ± 226 0.135510 ± 310 0.135367 ± 330 0.135571 ± 206	0.139869 ± 56 0.139878 ± 66 0.139749 ± 196 0.139804 ± 74 0.139797 ± 137 0.139760 ± 54 0.139800 ± 52 0.139858 ± 68 0.139810 ± 54 0.139815 ± 36 0.139873 ± 84 0.139845 ± 40 0.139881 ± 40 0.139780 ± 42
KLB1-OL	0.124745 ± 84 0.124818 ± 104 0.124764 ± 180	0.135655 ± 124 0.135812 ± 292 0.135665 ± 532	0.139753 ± 74 0.139743 ± 52 0.139779 ± 52
Peace River	0.124630 ± 216 0.124783 ± 88	0.135431 ± 336 0.135734 ± 284	0.139833 ± 84 0.139812 ± 82
Av. of Normals	0.124639 ± 171 [¶]	0.135443 ± 360 [¶]	0.139813 ± 21 [‡]
HWI-1 (81.8 µg)	0.124808 ± 152	0.135817 ± 390	0.139850 ± 50
HWI-2 (35.2 µg)	0.124761 ± 76 0.124808 ± 134	0.135828 ± 158 0.135934 ± 210	0.139956 ± 52 0.139991 ± 44
HWI-3 (8.5 µg*)	0.124739 ± 140	0.135778 ± 246	0.139877 ± 76
HWI-4 (17.3 µg)	0.124862 ± 126 0.124905 ± 56	0.135947 ± 236 0.136026 ± 122	0.139789 ± 64 0.139804 ± 56
HWI-5 (58.8 µg)	0.124945 ± 120	0.136196 ± 226	0.139902 ± 52

[#]Errors correspond to the last digits shown and are 2σ for raw ratios or 2σ mean for fractionation corrected $^{26}\text{Mg}/^{24}\text{Mg}$ ratios.

[§]Corrected for fractionation according to $(^{26}\text{Mg}/^{24}\text{Mg})_c = (^{26}\text{Mg}/^{24}\text{Mg})_{\text{meas}} / \alpha^2$, where 'meas' is the measured ratio during the set, $\alpha = (^{25}\text{Mg}/^{24}\text{Mg})_{\text{meas}} / (^{25}\text{Mg}/^{24}\text{Mg})_c$, and $(^{25}\text{Mg}/^{24}\text{Mg})_c = 0.12663$ reported by Catanzaro *et al.* (1966). After corrected for mass fractionation, the mean ratios were calculated.

*Fragment of spherule. Original mass was $> 10 \mu\text{g}$.

[¶]Average of 19 runs. Errors are 2σ .

[‡]Average of 19 runs. Errors are 2σ mean.

Fig. 2. Mass spectrometric measurements of normal Mg (reagent MgO, KLB-1 lherzolite olivine, and the Peace River meteorite). Shaded areas for (a), (b), and (c) are ± 2 per mil, ± 4 per mil, and ± 0.5 per mil error bands, respectively. (a) Uncorrected $^{25}\text{Mg}/^{24}\text{Mg}$ ratios. The grand mean value of uncorrected $^{25}\text{Mg}/^{24}\text{Mg}$ is 0.12464. (b) Uncorrected $^{26}\text{Mg}/^{24}\text{Mg}$ ratios. The grand mean value of uncorrected $^{26}\text{Mg}/^{24}\text{Mg}$ is 0.13544. (c) Fractionation corrected $^{26}\text{Mg}/^{24}\text{Mg}$ ratios. The grand mean value of fractionation corrected $^{26}\text{Mg}/^{24}\text{Mg}$ is 0.139813. Mass fractionation was corrected according to $(^{26}\text{Mg}/^{24}\text{Mg})_c = (^{26}\text{Mg}/^{24}\text{Mg})_{\text{meas}} / \alpha^2$, where 'meas' is the measured ratio during the set, $\alpha = (^{25}\text{Mg}/^{24}\text{Mg})_{\text{meas}} / (^{25}\text{Mg}/^{24}\text{Mg})_c$, and $(^{25}\text{Mg}/^{24}\text{Mg})_c = 0.12663$ reported by Catanzaro *et al.* (1966).

zolite olivine, and from the Peace River meteorite (L6) were analyzed regularly during these experiments (Table 1 and Fig. 2). The raw measured ratios of $^{25}\text{Mg}/^{24}\text{Mg}$ and $^{26}\text{Mg}/^{24}\text{Mg}$ for 19 separated runs are 0.12464 ± 0.00017 (2σ) and 0.13544 ± 0.00036 (2σ), respectively. As shown in Fig. 2, the variation of raw measured isotopic ratios of these reference samples were within ± 2 per mil for $^{25}\text{Mg}/^{24}\text{Mg}$ and ± 4 per mil for $^{26}\text{Mg}/^{24}\text{Mg}$, indicating that the instrumental mass fractionation was ± 2 per mil per amu. From the fractionation corrected $^{26}\text{Mg}/^{24}\text{Mg}$ ratios of all normals (19 separate runs) we get the grand mean value of 0.139813 ± 0.000021 (2σ mean). For each run we calculated

$\Delta(^{25}\text{Mg}/^{24}\text{Mg})$ and $\delta^{26}\text{Mg}$ using the following equations:

$$\Delta(^{25}\text{Mg}/^{24}\text{Mg}) = [(^{25}\text{Mg}/^{24}\text{Mg})_m / (^{25}\text{Mg}/^{24}\text{Mg})_s - 1] \times 1000$$

and

$$\delta^{26}\text{Mg} = [(^{26}\text{Mg}/^{24}\text{Mg})_c / 0.139813 - 1] \times 1000,$$

where 'm' is the measured $^{25}\text{Mg}/^{24}\text{Mg}$, 's' is the grand mean value: $^{25}\text{Mg}/^{24}\text{Mg} = 0.12464$ for raw data determined from standards, and 'c' is the fractionation corrected ratio. We can thus resolve differences in $^{26}\text{Mg}/^{24}\text{Mg}$ of $\delta^{26}\text{Mg} = \pm 0.5$ per mil.

Fig. 3. Mg isotopic compositions of 5 stony spherules from deep-sea sediments. (a) Mass fractionation effects of Mg for the spherules are within a ± 2 per mil per amu instrumental resolution band. $\Delta(^{25}\text{Mg}/^{24}\text{Mg}) = [(^{25}\text{Mg}/^{24}\text{Mg})_m / (^{25}\text{Mg}/^{24}\text{Mg})_s - 1] \times 1000$, where 'm' is the measured raw $^{25}\text{Mg}/^{24}\text{Mg}$ ratios during the set, 's' is the grand mean value: $^{25}\text{Mg}/^{24}\text{Mg} = 0.12464$ for raw data determined from standards. (b) Spherule HWI-2 shows a small but significant non-linear effect outside of a ± 0.5 per mil resolution band. $\delta^{26}\text{Mg} = [(^{26}\text{Mg}/^{24}\text{Mg})_c / 0.139813 - 1] \times 1000$, where 'c' is the value corrected for fractionation according to $(^{26}\text{Mg}/^{24}\text{Mg})_c = (^{26}\text{Mg}/^{24}\text{Mg})_{\text{meas}} / \alpha^2$, where $\alpha = (^{25}\text{Mg}/^{24}\text{Mg})_{\text{meas}} / (^{25}\text{Mg}/^{24}\text{Mg})_c$, and $(^{25}\text{Mg}/^{24}\text{Mg})_c = 0.12663$ reported by Catanzaro *et al.* (1966), and 0.139813 is the grand mean value for all standards normalized using a power law. Errors are 2σ for $\Delta(^{25}\text{Mg}/^{24}\text{Mg})$ or 2σ mean for $\delta^{26}\text{Mg}$.

Mass fractionation

The Mg isotopic data for the spherules are summarized in Table 1 and shown in Fig. 3. The ± 2 per mil band in a $\Delta(^{25}\text{Mg}/^{24}\text{Mg})$ diagram represents the limits of variation for raw $^{25}\text{Mg}/^{24}\text{Mg}$ ratios for standards. Ratios outside of this limit are attributed to intrinsic mass fractionation rather than an artifact during the measurements. Mass fractionations of Mg for three spherules (HWI-1, -2, and -3) range from 0.8 to 1.4 per mil per amu and are within the range of instrumental mass fractionation. The other two spherules, HWI-4 and -5, show larger mass fractionations of 1.8 to 2.5 per mil per amu. However, they are marginal and indistinguishable within errors from the instrumental mass fractionation.

One can expect a large mass loss of spherules from parent meteoroids due to vaporization during melting events. Based on elemental abundances of one of the glassy spherules analyzed by INAA, Nagasawa *et al.* (1979) suggested that more than 80% of the original weight of the

parent materials was lost during melting when meteoroids entered the Earth's atmosphere. Recent laboratory distillation experiments (Esat *et al.*, 1986; Esat and Ringwood, 1990; Misawa and Tsuchiyama, 1990; Davis *et al.*, 1990) revealed that Mg mass fractionation of 2 to 30 per mil per amu was produced when mass loss of 20 to 85% occurred. If spherules represent vaporization residues of their parent meteoroids, the mass loss of spherules from parent materials by vaporization during entry into the atmosphere is considered to be less than $\sim 20\%$ by analogy to results from the distillation experiments. Davis *et al.* (1991) also analyzed Mg isotopes of 7–250 μm silicate spherules using an ion microprobe, and found that there is little mass fractionation of Mg in the spherules.

On the other hand, as pointed out by Davis *et al.* (1991), diffusion coefficients of divalent cations in molten silicate melt considered to be small enough to prevent complete Mg isotopic equilibration during relatively short periods of heating. Recent numerical calculations for the at-

atmospheric entry of micrometeoroids showed that the peak temperatures experienced these materials usually less than 1700°C, and that micrometeoroids spend ~2 sec at above liquidus temperatures (Love and Brownlee, 1991). The diffusion coefficients of divalent cations in basalt melt range from 10^{-7} to 10^{-6} cm² s⁻¹ between 1260 and 1440°C at 1 atm (Hofmann and Magaritz, 1977). Since the diffusion coefficient of Mg may not be so much different from that of Ca, we can estimate the diffusion coefficient of the order of 10^{-6} to 10^{-5} cm² s⁻¹ for Mg based on the extrapolated values from Hofmann and Magaritz's experimental data for Ca at the temperature range from 1400 to 1700°C. If high temperature melting of parent meteoroids occurred on the timescale of ~1 sec (Love and Brownlee, 1991), the transport distance of mass fractionated Mg is less than 30 µm even though they totally melted. In this case mass fractionations due to distillation were limited in the outer shell of the molten droplet, therefore, an effective ablative mass loss from parent material may be remained the Mg isotopic compositions of the inner portion undisturbed. Such an occurrence may be consistent with the observed Mg isotopic compositions for the spherules.

Non-linear effect

One sample, HWI-2, shows a small but significant (out of the limit of resolution) non-linear effect. Repeated analyses suggest that the deviation in this spherule from the normal is real ($+1.02 \pm 0.37$ per mil; $+1.27 \pm 0.31$ per mil), however, it is impossible to determine which isotope is enriched or depleted. We first assumed $^{25}\text{Mg}/^{24}\text{Mg}$ is normal. Of course, the non-linear effect observed here is not due to any chemical fractionations in the deep-sea environment.

Mg isotopic anomalies have been recognized in several meteoritic constituents. Al-correlated ^{26}Mg excess in Ca, Al-rich inclusions (CAIs) in carbonaceous chondrites (e.g., Lee *et al.*, 1977 b) and in an igneous clast from the Semarkona LL3.0 chondrite (Hutcheon and Hutchison, 1988) are considered to be due to *in situ* decay of now extinct ^{26}Al (half-life $T_{1/2} = 0.72$ Ma).

Recently, ion microprobe analyses also demonstrated that interstellar grains preserved in chondritic meteorites, especially the CM clan, often show Mg isotopic anomalies derived from pre-solar ^{26}Al (Zinner *et al.*, 1991). If precursors of the spherules were primitive early solar system material, and the ^{26}Mg excess in HWI-2 is due to *in situ* decay of ^{26}Al , we can estimate an initial $^{26}\text{Al}/^{27}\text{Al}$ ratio using the following equation:

$$(^{26}\text{Mg}/^{24}\text{Mg})_p = (^{26}\text{Mg}/^{24}\text{Mg})_0 + (^{26}\text{Al}/^{27}\text{Al})_0 \times (^{27}\text{Al}/^{24}\text{Mg})_p,$$

where 'p' is the isotopic abundance in the phase or system, and '0' is the isotopic ratios at the time of homogenization. Assuming $(^{26}\text{Mg}/^{24}\text{Mg})_0$ in the system is normal, and using low $(^{27}\text{Al}/^{24}\text{Mg})_p$ values of 0.1 to 0.35 from chemical compositions of spherules (Misawa *et al.*, 1992), we obtained $(^{26}\text{Al}/^{27}\text{Al})_0$ values of 1.5×10^{-3} to 5×10^{-4} . They are 10 to 30 times larger than an *upper limit* of $\sim 5 \times 10^{-5}$ reported for many CAIs in carbonaceous chondrites (e.g., Lee *et al.*, 1977 b). Moreover, there are plenty of differences in their chemical and petrological characteristics between CAIs and stony spherules. CAIs possessing ^{26}Mg excesses mainly consist of high temperature minerals such as Al-Ti-rich pyroxene, anorthite, melilite, and spinel, which are very different from constituents of stony spherules. Major and trace element abundances for stony spherules are chondritic even if they melted during the atmospheric entry, but elemental abundances for CAIs are enriched in both refractory lithophile and siderophile elements. We thus believe this is not the case.

The effects of substantial interactions with nuclear active particles are second possibilities for the Mg isotopic anomalies. A subset of IDPs, chondritic aggregates, exhibits similar but larger anomalies in Mg. Esat *et al.* (1979) and Esat and Taylor (1987) measured 18 IDPs and found 6 particles that show statistically significant excesses in $^{26}\text{Mg}/^{24}\text{Mg}$ ranging from 3 to 4 per mil. Esat (1988) suggested that these anomalies could be related to physicochemical effects such as sputtering of the solar wind and solar flare particles. The application of this

mechanism cannot totally explain the Mg isotopic effect observed in the stony spherule, since the mass of the spherules analyzed in this study is 3 to 4 orders of magnitude larger than that of IDPs. If the parent meteoroids of stony spherules were small (~ 10 – $100 \mu\text{g}$ in weight) and irradiated for 10^5 – 10^7 years in interplanetary space (Raisbeck *et al.*, 1983; Nishiizumi *et al.*, 1991), sputtering by galactic cosmic rays and solar cosmic rays may have occurred only at the surface of the meteoroids.

Isotopic anomalies induced by the distillation-condensation processes are another possibilities for the non-linear isotopic effects. Esat *et al.* (1986) and Misawa and Tsuchiyama (1990) reported on non-linear Mg isotopic effects ($\delta^{26}\text{Mg}$ ranges from +1 to +2.3 per mil) for silicates condensed from gas phases. Since these condensates show large mass fractionations highly enriched in the light isotope, ^{24}Mg , this mechanism appears to be incompatible with the normal $^{25}\text{Mg}/^{24}\text{Mg}$ data for spherules.

The origin of the non-linear effect on Mg isotopes observed in HWI-2 remains obscure. Therefore, a more complicated mechanism should be considered.

CONCLUSIONS

We analyzed the Mg isotopes of 5 individual stony spherules collected from deep-sea sediments. All spherules show normal $^{25}\text{Mg}/^{24}\text{Mg}$ ratios within the range of instrumental mass fractionation (2 per mil per amu), suggesting that either mass loss from parent meteoroids of spherules by vaporization was not so large, or ablative mass loss from parent meteoroids occurred effectively during entry into the Earth's atmosphere. One spherule shows a small but significant non-linear effect of ^{26}Mg ($\delta^{26}\text{Mg} = +1.2$ per mil) similar to those observed in IDPs. Since physicochemical fractionation effects in interplanetary space may be responsible for the observed Mg isotopic effect, further laboratory distillation and sputtering experiments as well as detailed studies on chemical and isotopic compositions for primitive

meteorites, IDPs, and micrometeorites are required.

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