Isotope Variations of Light Elements in Chondrites
–Ion Microprobe Studies–

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1. Introduction

Isotope anomalies in primitive meteorites have been investigated on various refractory and volatile elements during the last three decades. The analyses of these anomalies has played an important role in estimating the formation processes of minerals in the early solar nebula. Among the various processes which are thought to be the origin of the isotope anomalies, the following three processes are closely related to the mineral formation; (1) mass fractionation, (2) mixing of excess stable isotopes, (3) remnants of short-lived radio-active nuclides (extinct nuclides).

The best known example in the mass fractionation process is the one found in the CAI’s of the Allende meteorite (Wasserburg et al., 1977, Clayton et al., 1988). The amount of mass fractionation for Mg and Si found in CAI’s had an order of magnitude larger than those of terrestrial samples, and it was considered to have arisen from an evaporation-condensation process in the primordial solar nebula. However, no definite model has been proposed so far to explain all of the isotopic data consistently. A systematic comparison of isotopic behavior between the products of laboratory experiments and the natural material is required. A preliminary result of such an investigation performed by Uyeda et al. (1989b) is given
in section 3.

The mixing process of an excess stable isotope was first proposed by Clayton et al. (1973) in order to explain the $^{16}$O excess found in the CAI’s of the Allende meteorite. Isotopic and mineralogical studies indicate that the CAI’s consist of at least four components, which are the extra solar gas and solid component, and the solar gas and solid component (Clayton et al., 1988). As for magnesium, Nishimura et al. (1982) and Okano et al. (1986) has reported the $^{24}$Mg excess in a number of primitive meteorites. Recently, the correlation between the mineral species and the $^{24}$Mg excess has been intensively studied by Sakaguchi et al. (1988), and Uyeda et al. (1989a). A review of these results is given in section 2. The third process is the presence of decay-products of now extinct short-lived nuclides, such as $^{26}$Mg from $^{26}$Al, reported by Lee et al. (1976). In this case, the amount of $^{26}$Mg excess is expected to be proportional to the Al/Mg ratio, and the time interval between the nucleo-synthesis of $^{26}$Al and the formation of an $^{26}$Al-bearing mineral was estimated.

In most cases, these isotopic studies on primitive materials have been carried out for each element independently, however, in recent years, the direct comparison between isotope behavior of the different elements has been considered to provide important informations. In the CAI’s of the Allende meteorite, for example, a clear correlation is seen between Si and Mg isotopes, whereas no correlation is seen between Ca and Mg (Clayton et al., 1988). This indicates that Si and Mg were fractionated through the same event, but a different process should be assumed for Ca. Thus the isotope analysis of multiple elements is essentially important for advanced studies on isotope cosmology. However, in order to do this, it is desirable to measure isotope anomalies of different elements for the same micro-portion of a sample, using the same apparatus. Up to now, the isotope analysis using the ion microprobe analyzer (IMA) is one of the most effective methods to carry out such measurements.

In an IMA measurement, a sample surface is bombarded by a primary ion beam with keV energy, and the secondary ions, sputtered from the surface are analyzed by a mass spectrometer. The efficiency of secondary ion production depends strongly on the nature of the primary ion. For example, the $O_2^+$ primary ion is effective for producing secondary ions of Mg, Si, Ca, Ti, Fe, etc. Whereas the efficiency is considerably low for such elements as
C, O, S, Cl, etc. It is desirable to use Cs⁺ primary ions to measure the latter elements. So, in order to compare the isotopic behaviors between the various elements, it is necessary to use two kinds of primary ions. Thus, we introduced a new Cs⁺ ion source in addition to the O₂⁺ source, and constructed a new data processing system for isotope measurement. A preliminary report of the isotope measurement using this IMA system is shown in section 5.

Up to now, extensive studies on isotope anomalies in meteorites have been carried out for many major elements. However, the study of sulfur has not yet been so extensive, in spite that this is also one of the major elements in the primitive meteorites. Therefore, some basic measurements were performed for sulfur, and the result are shown in section 4.

Since the apparatus used in the present study (a modified Hitachi IMA 2A) has a mass resolution of about 300, and mass peaks corresponding to interfering atomic, molecular and multiply-charged ions could not be directly separated from those of the isotopic peaks of interest. Although it is possible to carry out precise isotopic analysis by subtracting the contributions of these interfering ions numerically, the procedure becomes rather complicated in some cases. Moreover, the isotope analysis is difficult in the trace elements, since contributions of interfering ionic species become serious in such cases. For this reason, a new ion microprobe analyzer was developed by one of the authors (H.N.). The mass resolution of this apparatus is expected to be more than 3000, which can separate almost all the possible interfering ionic species. The progress of the instrumental development is shown in section 5.

2. Measurement of $^{24}\text{Mg}$ excess

According to the Mg isotopic data for various chondrites measures by Nishimura et al. (1982) and Okano et al. (1986), it was seen that most of the data points in the three isotope plot diagram for the primitive meteorites (type 3) had positive deviations with respect to the terrestrial mass fractionation line (TMFL). The data can be interpreted either as the excess of $^{24}\text{Mg}$ or $^{26}\text{Mg}$, with respect to the TMFL. It is noted that these deviations are not caused by the decay of $^{26}\text{Al}$, since all the measured points were Al poor portions and the Al/Mg ratio was less than 0.5. In general,
excess of $^{26}\text{Mg}$ due to decay of $^{26}\text{Al}$ is observed in portions where Al/Mg ratio is more than 500. So, the most simple and straight-forward explanation for the anomaly reported by Nishimura et al. is the mixing of excess $^{24}\text{Mg}$ component into the terrestrial component. The excess can be one of the evidences of the heterogeneous primordial solar nebula. However, the characterizations of the mineral phases were not performed in these studies, and so it was difficult to discuss the mechanism of the mixing process of $^{24}\text{Mg}$ from these data. In order to clarify the relation between the $^{24}\text{Mg}$ excess and the mineral phases, we selected several minerals from the Allende meteorite which had a suitable size for the IMA measurement and identified their mineral phases before measuring Mg isotope anomalies.

Three portions of forsterite-rich olivine grains were selected from polished pieces of the Allende meteorite. A JEOL JCPA-733 electron probe micro-analyzer (EPMA) was used for the observation of SEM images and for quantitative elemental analyses, and the mineral phases as well as the chemical compositions of these grains were identified. Among them, two grains were identified as forsterite-rich aggregates and abbreviated as OLI1 (Fo$_{95}$) and OLI2 (Fo$_{85}$), whereas the third grain was identified as an olivine chondrule and abbreviated as OLC (Fo$_{95}$). For the isotope measurements, a modified Hitachi IMA-2A ion microprobe analyzer was used. 9 keV, O$_2^+$ ions was used as primary ions, and the diameter and current of the beam was 100–200 $\mu\text{m}$ and 0.5–2 $\mu\text{A}$, respectively, at the sample surface. A cold finger with liquid nitrogen temperature was put aside the sample holder to minimize the contamination of hydro-carbons and H$_2$O vapor. The amounts of possible interfering atomic, molecular and multiply-charged ionic species were investigated carefully, and it was concluded that the interferences were less than 1 % (Sakaguchi et al., 1988).

The measured results of isotopic variations for the olivine inclusions with respect to the laboratory standard, a terrestrial Fo-rich olivine (Fo$_{94}$, from Ehime Prefecture, Japan) is shown in Fig. 1. In the cases of OLI1 and OLI2, most of the plotted points distributed to the right hand side, with respect to the terrestrial standard. The weighted mean falls on the point about +5 permil apart from the origin in both specimens. In the case of OLC, the data points scattered over a wide range from the left to the right hand side of the figure, compared to the cases of OLI1 and OLI2. This scattering could not be concluded whether it was intrinsic or
Fig. 1. Three isotope plots of Mg for olivine inclusions from the Allende meteorite. The results of OLI1, OLI2 and OLC are given in (a), (b) and (c), respectively. Horizontal and vertical axes show $\Delta$ values given in permil by the following equation,

$$\Delta(m/25) = \left( \frac{^{m}Mg/^{25}Mg}_{sample} / \left( ^{m}Mg/^{25}Mg\right)_{ref} - 1 \right) \times 1000$$

($m = 24$ for horizontal, 26 for vertical). The mean value of the laboratory standard forsterite (Ehime Prefecture, Japan) is taken as, $(^{24}Mg/^{25}Mg)_{ref} = 8.0082$, $(^{24}Mg/^{25}Mg)_{ref} = 1.0083$ at the origin. Open circles correspond to a mean value of one portion, which include 10 to 15 scans over a mass range of 23.5 to 26.5. Error bars are $\pm \sigma_{mean}$. A solid squares are the weighted mean values of all runs.
instrumental. However, the mean value seems to have a the similar value as those of OLI1 and OLI2. Thus, it was seen that the excess of $^{24}$Mg existed in the inclusions of forsterite-rich olivine of the Allende meteorite especially for OLI1 and OLI2, although the amount of excess is considerably small compared to those observed in the matrices of the Allende meteorite (Nishimura et al., 1982).

The relation is studied between the chondrule textures and the amount of $^{24}$Mg excess. sixteen chondrules are chosen from the Allende meteorite. Among them, five are porphyritic, three are radial pyroxene, six are barred olivine and two are glassy. Figure 2 shows the mean isotope values of each

![Graph](image)

Fig. 2. The relation between Mg isotope ratios and the chondrule textures. Horizontal and vertical axes show $\Delta$ values in permil given by the following equation.

$$\Delta(m/25) = \{(m^{25}\text{Mg}/^{25}\text{Mg})_{\text{sample}}/(m^{25}\text{Mg}/^{25}\text{Mg})_{\text{standard}} - 1\} \times 1000$$

($m=24$ for horizontal, $26$ for vertical). Isotope ratios reported by Catanzaro et al. (1966) are taken as the standard. A solid line with gradient $-1$ is the normal mass fractionation line (NMFL). A open circle on NMFL shows the uncorrected mean value of the laboratory standard forsterite (Ehime Prefecture, Japan) which was measured prior to each measurement for meteorites. Open symbols are the mean values for each chondrule textures. Error bars are $\pm \sigma_{\text{mean}}$. The temperature in the parentheses are the cooling rate of each texture estimated from reproduction experiment. According to the experiments reported by Tsuchiyama et al. (1970), glassy and barred olivine chondrules were produced from completely molten temperature with a rapid cooling rate of more than $10^{24}\text{C/hr}$. Whereas, the porphyritic chondrules were produced from an incompletely molten temperature.
of the chondrule textures. It was seen that each mean value corresponding
to each texture distributes along a line with a gradient of $-0.34$. There
is a tendency that chondrules formed under a relatively intense heating
conditions, such as glassy or barred olivine chondrules (Tsuchiyama et al.,
1980), have high amount of $^{24}\text{Mg}$ excess. This indicates that the injection
process of $^{24}\text{Mg}$ excess is closely related to the formation of chondrules.

Finally, the present result is compared to that of the oxygen isotope
anomalies. According to the measurement of oxygen isotopes reported by
Clayton et al. (1983), porphyritic chondrules distribute along the so-called
“Allende mixing line”, while the barred olivine chondrules distributed near
the terrestrial fractionation line. So, the tendency between the chondrule
textures and $^{16}\text{O}$ excess is quite different from that of $^{24}\text{Mg}$ excess, and it
would be interesting to perform a direct comparison between $^{16}\text{O}$ and $^{24}\text{Mg}$
anomalies using the same chondrule samples. As mentioned in section 4, a
new system for measuring oxygen isotopes by using the same IMA is now
under construction. The measurement can be done by changing the $\text{O}_2^+$ ion
source into a $\text{Cs}^+$ source. It is expected that direct comparison of isotopic
behavior between the different elements may provide useful information on
the chondrule formation process.

3. Mass fractionation process through laboratory experiments

As it is mentioned in the introduction, large mass fractionations are
observed in refractory inclusions of primitive meteorites for Mg, Si, Ti, and
other elements, which are considered to arise from evaporation-condensation
processes in the solar nebula. In the present study, the mass fractionation
of Mg in the condensation process is studied in detail, considering vari-
ous conditions. Fractionation of Mg in the condensation process is studied
in detail, considering various conditions. A condensation experiment for a
Si-Mg-O-H system was done by Tsuchiyama (1988) using a new vacuum
furnace. Synthesized $\text{Mg}_2\text{SiO}_4$ was used as the evaporation source, which
was evaporated congruently at about 1630°C ($T_{ev}$). A rod of cold finger was
attached above the source, which had various temperatures along the rod
from 1500°C down to room temperature. Under these conditions various
minerals condensed on the cold finger from $T_c = 1400$°C to room temper-
ature. The condensates were collected separately from different temperature
Fig. 3. The relation between condensation temperature $T_c$, and the mass fractionations of the condensates produced through laboratory recondensation experiments. $\Delta 26$ is calculated in permil as,

$$\Delta 26 = \{(^{26}\text{Mg}/^{24}\text{Mg})_{\text{meas}}/(^{26}\text{Mg}/^{24}\text{Mg})_{\text{starting}} - 1\} \times 1000$$

where $(^{26}\text{Mg}/^{24}\text{Mg})_{\text{meas}}$ is the mean value of each sample, and $(^{26}\text{Mg}/^{24}\text{Mg})_{\text{starting}}$ is the mean value of the evaporation source before the experiment.

phases and mounted on the sample holder with indium metal for IMA measurement. The relation between the condensation temperature $T_c$ and the mass fractionation with respect to the starting material, $\Delta 26$, is shown for the measured condensates in Fig. 3. It is seen that $\Delta 26$ of the condensates change considerably with $T_c$. The residue was enriched with the heavy isotope and $(\Delta 26)_{\text{res}}$ was around +8 %. According to the previous result of laboratory distillation performed by Esat et al. (1986), the evaporated condensates are fractionated only toward the light isotope with respect to the standard values. Our results show that the condensates can also be fractionated toward the heavy isotope under a certain condition, and it suggests that one should be careful in estimating the mineral formation process from the isotopic data. The mechanism of this large mass fractionation of the condensates can be explained in terms of fractionation between the re-condensed solid phase and the residual gas phase (Uyeda et al., 1990).

4. Detection of sulfur isotopes using Cs$^+$ ion source

Up to now, microprobe studies on sulfur isotopes are not so extensively
done. According to the measurements of Kaplan and Hulston (1966), the variations of sulfur isotopes of bulk chondrites (type 1 to 6) were considerably small (about 3 %). However, the isotopic variations between the various sulfur containing mineral grains may provide useful information in estimating the thermal history of the chondrite precursor especially in the low temperature region, since sulfur, as well as oxygen, is much more volatile compared with other major elements.

A Cs\(^+\) primary ion source is newly attached to the present IMA in the place of the O\(_2^+\) ion source, in order to measure the isotope abundances of various elements from the same portion of a meteorite sample. A data processing system for measuring sulfur and oxygen isotopes were newly constructed and used with the Cs\(^+\) ion source. Table I shows the measured results for the \(^{34}S/^{32}S\) ratio of NBS standard samples (NBS20: barium sulfate) with respect to the sulfur standard. The amount of measured variation of NBS20 with respect to the Canyon Diablo troilite (CDT) agrees well with the published data of NBS.

A point to point analysis on the section of the CDT is performed in order to examine whether a troilite inclusion of the Canyon Diablo meteorite is isotopically homogeneous. The homogeneity of the CDT is important when one intends to collect the troilite inclusion as a standard sample. Figure 4 show the results of two different inclusions of CDT, TR1 and TR2. The spatial scattering of isotopic ratio (\(^{34}S/^{32}S\)) is less than ±0.7 % for both TR1 and TR2, although the C/S and O/S ratios show a considerable variation in TR1. The mean isotope value of TR2 with respect to TR1 is

<table>
<thead>
<tr>
<th>sample</th>
<th>run no.</th>
<th>(\delta) (34/32) %</th>
<th>(\sigma_m)</th>
<th>(\Delta) (34) %**</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD, TR1</td>
<td>6</td>
<td>-23.6</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>CD, TR2</td>
<td>11</td>
<td>-23.2</td>
<td>0.4</td>
<td>+0.4</td>
</tr>
<tr>
<td>Mund**</td>
<td>21</td>
<td>-24.0</td>
<td>0.7</td>
<td>-0.4</td>
</tr>
<tr>
<td>MoS(_2)</td>
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<td>-23.8</td>
<td>1.6</td>
<td>-0.2</td>
</tr>
<tr>
<td>NBS20***</td>
<td>12</td>
<td>-3.3</td>
<td>1.1</td>
<td>+20.3</td>
</tr>
</tbody>
</table>

\(\delta\) (34/32) = \((^{34}S/^{32}S)_{\text{sample}} - (^{34}S/^{32}S)_{\text{CD, TR1}}\), where \(\delta\) (34/32) = \([(^{34}S/^{32}S)_{\text{sample}}/(^{34}S/^{32}S)_{\text{standard}} - 1]\) \times 1000(\%), \((^{34}S/^{32}S)_{\text{standard}} = 0.04431\) (IUPAC data of 1984).

**Troilite phase of the Mundrabilla iron meteorite.

***The published data of isotope ratio for NBS20 with respect to the Canyon Diablo troilite is \(\Delta\) (34) = +20.38 %.
Fig. 4. Results of point to point analysis on troilite phases of the Canyon Diablo iron meteorite. Isotopic and elemental analyses were performed for two inclusions. They are denoted as TR1 and TR2 and are described in (a) and (b), respectively. A expression of $\delta$ (34/32) is given in Table I. In these inclusions, secondary ions of C, O, F, Cl, Fe and Ni were also detected besides S, however except for C and O, their intensities were three orders of magnitude less than that of S. For TR1, C/S and O/S ratio show considerable spatial variation within a area of about 2 mm. The variation is probably due to the weathering effect. For TR2, the variation is very small.

$\pm 0.4\%$. According to the present measurement, the homogeneity of CDT is better than $\pm 1\%$. The same analysis will be carried out in the future for a number of CDT inclusions to confirm the present result. It is seen that the data processing system is capable for performing the point to point isotope analysis with the spatial resolution of about 100 $\mu$m. Furthermore, a system for performing point to point analysis on $^{18}$O/$^{16}$O is also under construction, since the efficiency of oxygen secondary ions is also relatively high by using the Cs$^+$ ion source.
5. Development of ion microscope analyzer with high mass resolution

The ion optical parameters for a new mass spectrometer were determined, taking the following three points into account,

(1) The mass resolution is above 3000 so that the interfering atomic, molecular and multiply-charged ionic species can be almost separated.

(2) Mass dispersion is about 4 mm at the position of the focal plane of the double focusing mass spectrometer in order to detect three isotopes at the same time.

(3) The apparatus should be compact and handled easily.

The ion optical parameters were determined by using a modified program, which was originally reported by Matsuda (1983). This program determines an ion locus by the product of several transfer matrices, which

Fig. 5. Schematic diagram of a newly designed IMA. The system consists of an ion source for producing primary ions (A, B) a target part (C, D), a sample introducing system (E), a double focusing mass spectrometer (F), pumping system (G) and other few parts.
express the aberrations, the focusing and the dispersion effects by the electrostatic and magnetic fields. The mass spectrometer was designed as a double focusing type. The theoretical mass resolution of the system is 3418 (slit width 100 μm). The calculated mass dispersion for 1% mass difference is 4.2 mm at the position of the focal plane of the mass spectrometer. Moreover, a position bombarded by the primary ion beam on the sample surface can be easily adjusted to the optimum point, which would be directly indicated through the secondary ion detecting system by a light beam. The main parts of the apparatus were made of stainless steel. The schematic diagram of the apparatus is shown in Fig. 5. Up to now, the alignment of the system shown in Fig. 5 has almost completed. The ultimate pressure of the sample chamber was $2.0 \times 10^{-5}$ Pa. A ion current of the primary ions measured at the drawing-out electrode was about 40 μA. Here, O$_2^+$ was used as the primary ion species and the accelerating voltage was 5 kV. Adjustments of the secondary ion optics are now carried out.

6. Conclusions

Ion microprobe studies on primitive meteorites have been performed for magnesium and sulfur isotopes, and the relation was discussed between isotopic behavior and the formation process of mineral phases in the primordial solar nebula. It was seen that the IMA (ion microprobe analyzer) is effective for studying the origins of individual mineral phases which compose the primitive meteorites. Especially, IMA is useful for comparing isotopic behavior between different elements, which is essential for advanced studies in isotope cosmology. Comparison between products of laboratory processes and natural primitive materials is effective for the quantitative investigation of the formation process of minerals in the primordial solar nebula.

Acknowledgements

This work was supported by the Grant-in-aid for Scientific Research on Priority Areas (Origins of the Solar System) of the Japanese Ministry of Education, Science and Culture (Nos. 62611003, 63611003 and 01611003).

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