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The study of Mg isotope compositions of terrestrial rocks and meteorites

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Abstract The study of Mg isotopes has been carried out for about 40 years since 1970's. With analytical progress, the study is not only limited to the excess of ^{26}Mg due to decay of short-lived ^{26}Al in primitive meteorites, also extended to mass-dependent fractionation of Mg isotopes in meteorites and terrestrial rocks. This paper reviews recent development in Mg isotope researches.

Keywords Mg isotopes, MC-ICPMS, solar nebular condensation, planet formation

1 Introduction

Mg is a major element of most terrestrial materials and extraterrestrial rocks. It has three isotopes (^{24}Mg, ^{25}Mg, and ^{26}Mg), with relative mass differences between them greater than 4% per atomic mass unit (amu). Mg isotopic compositions can be changed by both mass-dependent fractionation and decay of short-lived radionuclide ^{26}Al. Hence, Mg isotopes can be used to trace geochemical processes and as an isochronometer.

Mg isotopes of extraterrestrial materials have been extensively studied, especially those formed in the earliest solar system. Because excess ^{26}Mg serves as a proxy for extinct ^{26}Al (half life $T_{1/2}$ = 0.73 Ma), which is one of the most important energy sources of melting asteroids, Al-Mg system holds a promise of being a high-resolution chronometer for early solar system events, given ^{26}Al was uniformly distributed throughout the inner solar nebula. Furthermore, mass-dependent fractionation of Mg isotopes can trace processes in the terrestrial and the solar nebular evolution.

Almost all Mg isotopic compositions were usually measured with thermal ionization mass spectrometry (TIMS) and, especially, secondary ionization mass spectrometry (SIMS)[1-3], 10 years ago. The analysis precisions of both techniques are 1—2‰[4-6], compatible to the range of Mg isotopic compositions due to mass-dependent fractionation. Multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) provides with a possibility of high-precision measurement of Mg isotopic ratios. The reproducibility

of $^{25}Mg/^{24}Mg$ and $^{26}Mg/^{24}Mg$ measured by MC-ICPMS is better than 30 to 60×10^{-6}. Hence, mass-dependent fractionation of Mg isotopes can be used to trace cosmochemical and geochemical processes.

2 Research progress in Mg isotopic compositions

2.1 *Excess ^{26}Mg and the reffered $^{26}Al/^{27}Al$ ratios in the solar nebula*

Assuming a homogeneous distribution of ^{26}Al in the early solar system, Mg isotopic compositions of diverse components in primitive meteorites provide a high-resolution (on the order of 70000 years[7]) chronometer for the earliest evolution of the solar system.

The Ca-Al-rich inclusions (CAIs) and chondrules are millimeter- to centimeter-sized assemblages in chondrites, probably formed at the earliest stage in the solar system hence preserve hints of the solar nebular processes[1, 8, 9]. The accumulated data of ^{26}Al-^{26}Mg isotopes in primitive solar system material (CAIs and chondrules) demonstrate that ^{26}Al existed in the early solar system with a clear cutoff of inferred $^{26}Al/^{27}Al$ ratios of $\sim 5 \times 10^{-5}$ (e.g. MacPherson *et al.* [1]). This inferred $^{26}Al/^{27}Al$ ratio suggests a high abundance of ^{26}Al in the early solar system, which produced enough heat for melting parental asteroids of basaltic achondrites. The systematic difference in the referred $(^{26}Al/^{27}Al)_0$ ratios of CAIs and chondrules implies a forming interval of 2 Ma between them, with CAIs earlier than chondrules.

The initial $^{26}Al/^{27}Al$ ratios of CAIs were usually determined in situ with SIMS. However, the mineral "isochron" could be affected through re-distribution of Mg isotopes between phases during secondary events. In addition, most of chondrules have too lower Al/Mg for SIMS to detect excess of ^{26}Mg. In contrast, MC-ICP-MS provides us with a new technique to obtain the bulk Al-Mg isotopic compositions of CAIs, which may not be significantly affected by the secondary events. In addition, its high precision allows us to determine small excess of ^{26}Mg from samples with low Al/Mg ratios.

Bizzarro[10] measured bulk Mg isotopic compositions of several CAIs and chondrules from Allende using MC-ICPMS. Their Mg isotope data indicate that Allende chondrules formed as earlest the oldest CAIs, and continued for at least 2.5 Myr. The "canonical" $(^{26}Al/^{27}Al)_0$ value of the solar system is $\sim 5 \times 10^{-5}$. Recently, a few of researches suggested a "supra-canonical" value of $\sim 5.85\text{-}7 \times 10^{-5}$ based on high-precision measurements of Mg-isotopic compositions of CAI with MC-SIMS and MC-ICP-MS[11]. In contract, there are other analyese argueing against the "super-canonical" value[12-15].

2.2 *Mg isotope mass-dependent fractionation in Terrestrial and exterrestrial rocks*

Volatility of magnesium is between refractory elements (e.g., Al and Ca) and moderately volatile elements (e.g., Fe) and so should prove useful as an indicator of planetary provenance. Studies of Mg isotopic variations in terrestrial and extraterrestrial rocks can be used to identify the processes of planetary accretion and differentiation. Mg isotopes have been used to estimate the relative contributions of chondrules and CAIs to the formation of the terrestrial planets and asteroids because of their distinctive Mg isotopic composi-

tions[16]. However, Mg isotopic composition of the Earth is still not well-constrained. Some studies on mantle peridotites indicate that the Earth has heavier Mg isotopic compositions compared to chondrites[17] while other studies, also based on mantle peridotites as well as oceanic basalts, reached opposite conclusion[18]. In addition, it is still debated if Mg isotopic fractionation can happen among peridotite minerals. Studies on basalt differentiation reveal limited Mg isotope fractionation during basaltic differentiation[14], which indicates that Mg isotope fractionation should be even smaller at mantle temperatures considering that equilibrium isotope fractionation decreases as the temperature increases. However, significant Mg isotopic fractionation among mantle minerals has been reported in recent studies[16]. If the conclusions of these studies are indeed right, then it is more complicated to constrain the Mg isotopic composition of the earth since many previous studies only use olivine to represent the bulk Earth[16]. Lately, Handler et al.[19] investigated Mg isotopic compositions of olivine and a few coexisting pyroxenes and found limited inter-mineral Mg isotopic fractionation. Based on their data, the earth is chondritic origin.

Up to now, published data on meteorites and terrestrial rocks varied widely[20, 21].

3 Published data of Mg isotopic compositions in China

The research of Mg isotopic compositions started late in China. With the introduction of advanced analytical equipment in recent years, more domestic researchers started to pay attention to this area of reseach and made important progress. The following will introduce some of their research work.

3.1 Analytical methods

A procedure has been developed for separating Mg from bulk meteorite and ultramafic rock samples by Wang *et al.*[22]. Bio-Rad AG50W-X12, 200—400 mesh resin and 1M HNO_3 are used to separate Mg from sample solutions. Purified Mg sample solutions were introduced to a MC-ICPMS to analyze Mg isotope compositions. The new procedure allows for a long-term external reproducibility of δ^{26}Mg and δ^{25}Mg of 0.10 and 0.05‰, and 0.06‰ for δ^{26}Mg* (2σ, n = 211, over a period of 24 months), respectively. Recovery yield of Mg in this separating procedure is > 99%. The total procedural blank for Mg is < 2.0 ng.

3.2 Mg-Al isotopes in meteorites

Hsu *et al.*[23] made Al-Mg isotopic measurements on several CAIs and chondrules from the Ningqiang by SIMS. Their initial $(^{26}Al/^{27}Al)_0$ ratios for the CAIs are generally consistent with the value of 5×10^{-5}. 2 chondrules have the $(^{26}Al/^{27}Al)_0$ values of $0.3—0.6 \times 10^{-5}$.

As mentioned above, "supra-canonical" value of $(^{26}Al/^{27}Al)_0$ is in question. The origin of CAIs is also a long-standing issue. Wang *et al.*[24] measured Mg isotopic compositions of CAIs from both Ningqiang (ungrouped[25]) and Allende (CV3) carbonaceous

chondrites with MC-ICPMS, to confirm the canonical value of $(^{26}Al/^{27}Al)_0$, and to clarify Mg mass-dependent fractionation of CAIs. In addition, several amoeboid olivine aggregates (AOAs) from Allende were analyzed to illuminate the interval of solar nebular condensation, because AOAs probably sampled later condensates in comparison with normal CAIs[26].

The result shows that CAIs from Allende have a relatively closed Al-Mg system in the CAIs and no significant Mg isotope exchange with ambient materials; they have an inferred initial $(^{26}Al/^{27}Al)_0$ ratio of $(4.77 \pm 0.39) \times 10^{-5}$ close to the canonical value. The AOAs contain excess ^{26}Mg and plot close to the CAI regression line, which is suggestive of their contemporary formation. None of the CAIs and AOAs studied in this work shows significant mass fractionation with enrichment of the heavier Mg isotopes, arguing against an evaporation origin.

3.3 *The comparison Mg Isotopic compositions between terrestrial and exterrestrial materials*

It is still few and inconsistent for the published Mg-isotope data on terrestrial and extraterrestrial samples. In addition, whether terrestrial materials of Mg isotopic characteristics is similar to chondrites or non-chondrites has been disputed. Wang et al[27] analyzed some Mg isotopic data of the mantle rocks, and four bulk meteorites analyzed by MC-ICPMS. Their data indicate that terrestrial mafic and ultramafic rocks that probably derived from the mantle display significant variation of $\delta^{26}Mg$ from $-0.52‰$ to $0.19‰$, suggestive of heterogeneous compositions of Mg isotopes of the terrestrial mantle. These variations may not be due to simple partial melting and/or fractional crystallization, because mineral separates (including olivine, clinopyroxene and orthopyroxene) of the peridotites show no fractionation of Mg isotopes. Mg isotopic compositions of 3 chondrites are rather homogeneous. However, to deduce whether the earth Mg isotopic compositions origin from chondrites or not, still need more data.

Yang *et al.*[28] have studied a set of well-characterized mantle peridotite xenoliths from Sanyitang and Beiyan, North China craton, which have diverse origins with different mineralogy, chemical composition and degree of partial melting and metasomatism. The results display a small variation in Mg isotopic composition. The Mg isotopic compositions of the coexisting olivine, orthopyroxene and clinopyroxene in all peridotites are identical within their external precision (~ $\pm 0.1‰$, 2SD), suggesting that Mg isotope fractionation between olivine and pyroxenes at the temperatures of > 900℃ is insignificant. These results are thus consistent with the absence of Mg isotope fractionation during basalt differentiation. Overall, the $\delta^{26}Mg$ of the mantle is estimated to be -0.26 ± 0.16 (2SD). This value is similar to two chondrites (Allende and Murchison) (~ -0.3). Their data show the silicate earth has a chondritic Mg isotopic composition.

Li *et al.*[29] found the $\delta^{26}Mg$ relative to the original solution range from -2.03 to $-0.33‰$, positively correlated with pH.

4 Questions and directions

There is a lot of confusion on the research of Mg isotopes in early solar system and ter-

restrial process. The questions focus on:

(1) Whether the upper limit of initial $(^{26}Al/^{27}Al)_0$ ratio of 5×10^{-5} is true;

(2) Whether ^{26}Al is homogenous in early solar nebular;

(3) Whether terrestrial materials show Mg isotopic characteristics similar to chondrites or non-chondrites;

(4) The origin of CAIs is also a long-standing issue. Mg isotope compositions can provide better evidence.

Further research is beneficial to address these issues.

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