MOLYBDENUM ISOTOPE ANOMALIES IN ALLENDE AND MURCHISON METEORITES

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Introduction: The solar nebula has been thought to be isotopically homogenized because presolar materials ejected from pre-existed stars have experienced dynamical processes such as evaporation, condensation and mixing in the nebula. Isotopic compositions of some elements are in fact homogenous in bulk meteorite scale (e.g., Te [1], Os [2]). In contrast, nucleosynthetic isotopic anomalies are reported for some elements, especially in chondrites (e.g. Sr [3], Sm [4]). This indicates that isotopic compositions for these elements were heterogeneous in the solar nebula, although the mechanism which controls the nebular isotopic homogeneity/heterogeneity for individual elements remains unclear.

Molybdenum is one of the promising elements for the study of isotopic anomalies in meteorites. It has seven stable isotopes that were synthesized from three different nucleostynthetic processes (s-, r- and p-process). In the early 2000's, Mo isotopic anomalies were found in some meteorites [5-6], while another study showed that the Mo isotopic composition was homogeneous in the solar nebula [7]. More recently, Mo isotopic anomalies were reported for various meteorites with much higher precision by using a state of the art MC-ICP-MS (multicollector inductively coupled plasma mass spectrometry) [8]. The latest study claimed that the reason for such contradiction was not clear, and may reflect heterogeneities at the sampling scale in the same meteorite. This still remains as an unsolved question because Mo isotopic compositions in meteorites have been reported only in limited studies. If sample heterogeneities, at least for Mo, exist in bulk sampling scale, the isotopic anomalies observed could be caused by the existence of some isotopically distinctive phases rarely exist in the meteorites. As a preliminary stage to produce a new comprehensive dataset of high precision Mo isotopes in bulk meteorites, here we report Mo isotopic compositions in two primitive chondrites obtained by using the N-TIMS (negative thermal ionization mass spectrometry).

Experiments: Powdered bulk chondrites (Allende, CV3.6; Murchison, CM2) were digested in a pressured digestion system (DAB-2, Berghof, Germany) with a mixture of HF and HNO_3 (10:1) at 205°C for 48 hours [9]. After digestion, the sample solution was dried at 80 °C. Then, 0.5M HF was added, and dissolved in an ultrasonic bath for several hours. The solution was centrifuged for two hours, and Mo in the supernatant was purified via a newly developed HF-HCl-HNO_3 chemical separation technique that consists of a two-stage column chemistry using anion exchange resin [10]. This procedure was capable of approximately 100% recovery of Mo.

Molybdenum isotopes were measured as MoO_3^- by N-TIMS (TRITON *plus*, ThermoFisher Scientific Inc., at Tokyo Tech). Mass interferences (^{90}Zr, ^{94}Zr, ^{96}Zr, ^{96}Ru, ^{98}Ru and ^{100}Ru) were negligible throughout this study. Instrumental mass fractionation was corrected by the exponential law (^{98}Mo/^{96}Mo = 1.415363 [11]). The Mo isotopic ratios (^{i}Mo/^{96}Mo) were reported in εMo units (ε^{92}Mo, ε^{94}Mo, ε^{95}Mo, ε^{97}Mo and ε^{100}Mo) which represent 10^4 relative deviation from the terrestrial values.

Results: Molybdenum isotopic composition of bulk Allende and Murchison are shown in Fig. 1. The magnitude of the Mo anomalies decreases in the order of ε^{100}Mo > ε^{94}Mo > ε^{97}Mo > ε^{92}Mo > ε^{95}Mo for Allende, and ε^{94}Mo > ε^{92}Mo > ε^{97}Mo > ε^{100}Mo > ε^{95}Mo for Murchison. The magnitude of isotope anomaly is larger in Murchison than that of Allende except for ε^{100}Mo. The Mo isotope data are plotted on the ε^{94}Mo–ε^{95}Mo diagram (Fig. 2). These chondrites are plotted on a single reference line with positive Mo isotopic deviations from the terrestrial values, indicating the deficit of s-process nuclei (Fig. 2).

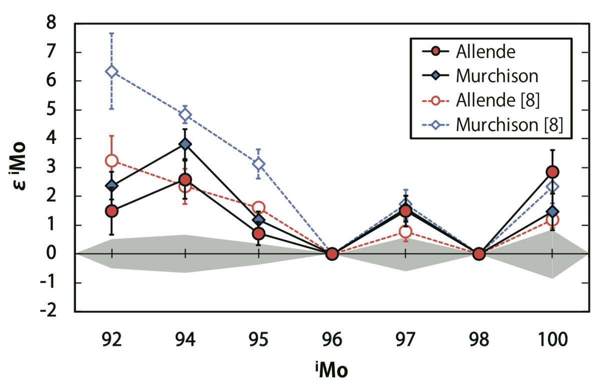

Figure 1. ε^{i}Mo plot for bulk Allende and Murchison. Errors for chondrites are standard error (2SE) of the single isotopic run. Gray shows the reproducibility of terrestrial rock measurements (2SD). Filled and open symbols are from this study and [8], respectively.

Discussion: Molybdenum isotopic compositions in chondrites are clearly resolved from that of the terrestrial, which are consistent with the previous study [8] (Fig. 1). Because Murchison did not experience intensive thermal metamorphism on its parent body, refractory presolar grains are abundant in this meteorite. Therefore, one possibility for the Mo isotope anomaly observed in Murchison would be incomplete sample digestion by our technique, leaving behind extremely acid resistant presolar phases rich in s-process Mo isotopes (e.g. SiC). However, a mass balance calculation negates this possibility: Murchison contains ~2 ppm of presolar SiC grains [12], in which the Mo concentration is up to 44 times [13] of the chondritic value (0.88 ppm [8]). Assuming that all SiC undissolved have ~40 ppm Mo with isotopic composition of the mainstream SiC, the complete dissolution of Murchison would shift our data only -0.69ε and -0.26ε for ε^{94}Mo and ε^{95}Mo, respectively. In addition, since Allende meteorite underwent intensive thermal metamorphism on the parent body and thus rarely contains presolar grains [14], the Mo isotope anomaly observed in this meteorite was not attributed to incomplete digestion. Therefore, the bulk-isotopic anomalies in Allende and Murchison indicate that the solar nebula was isotopically heterogeneous for Mo in time and space at least in two locations where carbonaceous chondrite parent bodies and the Earth have formed.

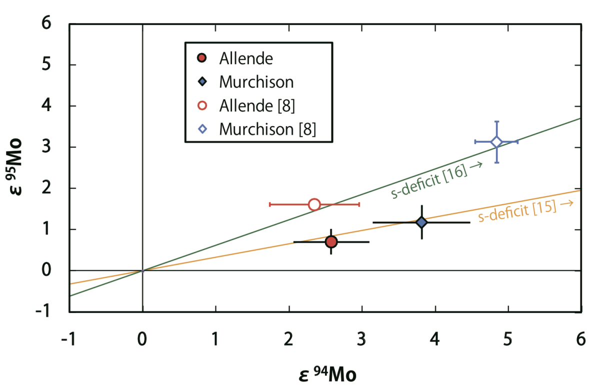

Figure 2. ε^{95}Mo-ε^{94}Mo plot for bulk chondrites. Symbols and errors are the same as in Fig. 1. Terrestrial samples are plotted on the origin (0, 0). Two sold lines (orange [15] and green [16]) are mixing lines of terrestrial component and s-process end-members.

An interesting observation in Fig. 2 is that Mo isotopic data from this and previous studies individually plot on different s-process vs terrestrial mixing lines that are calculated from different nucleosynthetic models [15-16]. The latter model [16] is consistent with the mixing line defined by the Mo isotopic data of mainstream SiC grains [17]. The s-process end-member components of the two models were calculated based on different physical parameters (e.g. metallicity, mass of central star) that produce distinct ratios of s-process nuclei. If Mo isotope data in Fig. 2 are all correct, the discrepancy may reflect the difference of digestion methods between two studies, and/or heterogeneous distributions of the s-process carriers (presolar grains) at least for bulk sampling scale of Murchison.

It has been suggested that main carriers of s-process nuclei in chondrites are not only SiC, but also oxides. SiC and oxide grains are both produced in red giants and AGB stars (in which s-process nuclei were synthesized), depending on C/O ratio in the central star [18]. Therefore, it is likely that presolar oxides have Mo isotopic composition different from that in the mainstream SiC. Two Murchison samples used in this study and [8] may have different abundances regarding presolar SiC and oxides. Selective dissolution of these grains in the acid digestion may enhance the difference in Mo isotope compositions finally obtained.

In the case of Allende, the Mo isotopic difference cannot be explained by the heterogeneous distribution of presolar grains at the sampling scale. Instead, CAIs, enriched in r-process Mo isotopes [8], may play a key role. If the contribution of CAI is different in bulk sampling scale, it is possible to cause the discrepancy of Allende. However, if the sampling heterogeneity is the case for both Murchison and Allende, it remains unclear why Mo isotopic data of individual studies are plotted on the single theoretical lines.

At this point, one can advocate that Allende and Mucrhison meteorites have mainly s-deficit anomalies compared to the terrestrial value for bulk sampling scale. Further Mo isotopic data for the other bulk meteorites and sequential acid leachates from some chondrites would have the potential to elucidate the discrepancy observed in two studies.

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