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Origin of isotopic heterogeneity in the solar nebula by thermal processing and mixing of nebular dust

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ABSTRACT

We have investigated Mo and W isotope compositions in acid leachates and an insoluble residue from the Murchison carbonaceous chondrite. The new data reveal variable enrichments of *s*- and *r*-process isotopes and demonstrate that several isotopically diverse presolar components are present in Murchison. The insoluble residue is enriched in *s*-process Mo and W, evidently due to the enrichment of presolar SiC grains. In contrast, Mo and W released by leaching with weak acids are depleted in *s*-process isotopes, most likely reflecting the isotope composition of the homogenized portion of the protosolar nebula. The Mo and W isotope compositions of the different leach steps are broadly correlated as expected from *s*-process nucleosynthesis theory, indicating that Mo and W are presumably hosted in the same carriers. However, at the bulk meteorite scale, no nucleosynthetic W isotope anomalies have been identified (except for IVB iron meteorites) in spite of large Mo isotope heterogeneities among the same samples. This decoupling of Mo and W isotopes in bulk meteorites may reflect physical mixing of varying proportions of isotopically diverse presolar components with a "normal" solar nebula component. Due to the high W/Mo ratio and near-terrestrial W isotope composition of the latter, such mixing has no measurable effect on W isotopes, but results in large Mo isotope variations. Alternatively, thermal processes within the solar nebula imparted Mo isotope heterogeneity on an initially homogeneous mixture of presolar dust, while W was not affected. Removal of volatile Mo oxides during the thermal destruction of fragile presolar components would have created isotopically heterogeneous reservoirs of nebular dust. Accretion of meteorite parent bodies from such variably processed dust would thus result in Mo isotope heterogeneities at the bulk meteorite scale. Other elements such as Os and W were not or only slightly affected because they were more refractory during thermal processing and, therefore, remained isotopically homogeneous. Thermal processing of presolar dust within the solar nebula can thus account for both isotope heterogeneities observed for some elements *and* the lack of such isotopic heterogeneity for other elements.

1. Introduction

Bulk meteorites exhibit small but resolvable mass-independent isotopic anomalies in various elements (*e.g.*, Ca, Ti, Cr, Ni, Mo, Ru, Nd, Sm) (Chen et al., 2011a, Niemeyer and Lugmair, 1984; Trinquier et al., 2007; Regelous et al., 2008; Dauphas et al., 2002b; Burkhardt et al., 2011; Chen et al., 2010; Andreasen and Sharma, 2006) that are commonly interpreted as reflecting incomplete homogenization of isotopically diverse presolar dust in the solar nebula. In contrast, uniform and terrestrial isotopic compositions were reported for some other elements (*e.g.*, Os, Hf) (Brandon et al., 2005; Sprung et al., 2010; Yokoyama et al., 2007; Walker, 2012), indicating that the presolar carriers of at least these elements were well mixed in the nebula. These contrasting isotopic characteristics of different elements are poorly understood but are key for constraining the origin of nucleosynthetic isotope anomalies in bulk meteorites.

Several models have been proposed to account for the isotopic heterogeneity observed at the bulk meteorite scale. It has been suggested that this is a primordial feature of the solar nebula inherited from a heterogeneous presolar molecular cloud core (Clayton, 1982; Dauphas et al., 2002b), or caused by the late injection of freshly synthesized matter into the nebula (Trinquier et al., 2007). Furthermore, processes within the solar nebula, such as separation of dust grains of different types (*e.g.*, silicates and sulfides) (Regelous et al., 2008), size-sorting (Dauphas et al., 2010) or selective destruction of thermally labile presolar components

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(Trinquier et al., 2009), may have been important in generating isotopic anomalies in bulk meteorites. For fluid-mobile elements, the selective destruction of presolar grains during parent body processes may also have played a role in modifying the isotopic composition of chondrites (Yokoyama et al., 2011). Models that invoke nebular or parent-body processes for generating the isotopic heterogeneity observed among bulk meteorites can potentially account for the disparate isotope systematics of different elements because elemental fractionation may have occurred during such processes. However, the specific behavior of different elements during nebular or parent-body processes is not known, nor has a systematic study been conducted comparing isotopic variations in elements that may have responded differently during nebular or parent-body processing.

Here we present the first Mo isotopic data for acid leachates and an acid-resistant residue of the Murchison chondrite. Aliquots from the same leachates were also investigated for W (Burkhardt et al. 2012) and Os isotope compositions (Reisberg et al., 2009). Combined with available Mo, W and Os isotope data for bulk meteorites, the Mo and W leachate data are used to assess the origin of both, heterogeneous Mo isotopes in bulk meteorites, *and* near-uniform Os and W isotope compositions in the same bulk samples.

2. Analytical methods

The Mo isotopic measurements were performed on aliquots from six different samples obtained by the sequential dissolution of a ~16.5 g whole-rock powder of the carbonaceous chondrite Murchison. The dissolution was performed at the University of Chicago using the following sequence (see Reisberg et al. (2009)):

L1: 9 M HAc (acetic acid), 1 day, 20 °C;
L2: 4.7 M HNO_3, 5 days, 20 °C;
L3: 5.5 M HCl, 1 day, 75 °C;
L4: 13 M HF/3 M HCl, 1 day, 75 °C;
L5: 13 M HF/6 M HCl, 3 days, 150 °C;
L6: insoluble residue.

After drying down, the aliquots of samples L1–L5 were treated with aqua regia, dried and then re-dissolved in 6 M HCl. To completely dissolve all presolar grains remaining in the insoluble residue (L6), this sample was first fused by a CO_2 laser under a reducing atmosphere (see Burkhardt et al. (2011)), and then digested in HNO_3–HF–$HClO_4$. After drying down, sample L6 was completely dissolved in 6 M HCl. Small aliquots of all samples were spiked with a mixed ^{97}Mo–^{180}Hf–^{183}W tracer for concentration measurements by isotope dilution. Purification of Mo (+W, Hf) from the sample matrix was performed by ion exchange chromatography in HCl–HF media (Burkhardt et al., 2011; Kleine et al., 2004). Total procedural Mo blanks were ~400 pg for the unspiked and ~48 pg for the spiked aliquots and no blank correction was required. The blank introduced by the leaching procedure itself could not be assessed, but is expected to be small because only ultra-pure acids and Milli-Q water was used (see Reisberg et al. (2009)).

Molybdenum isotope measurements on the unspiked aliquots were performed using the large-geometry *Nu Plasma* 1700 MC-ICP-MS at ETH Zürich, equipped with a Cetac Aridus II desolvating nebulizer (for details see Burkhardt et al. (2011)). Molybdenum isotopic compositions were typically measured at ion beam intensities of ~$2–3 \times 10^{-11}$ A on ^{96}Mo, which was obtained for a ~75 ppb Mo solution at an uptake rate of ~100 µl/min. Due to its low Mo content, sample L5 was measured at ~5×10^{-12} A on ^{96}Mo. The Mo isotopic data are reported as ε^{i}Mo, which is the part per 10^4 deviation of the ^{i}Mo/^{96}Mo ratio from the mean of the two bracketing runs of the terrestrial standard. The external reproducibility of the ~75 ppb Mo standard (Alfa Aesar Mo) was ±0.75 ε^{92}Mo, ±0.50 ε^{94}Mo, ±0.41 ε^{95}Mo, ±0.23 ε^{97}Mo and ±0.44 ε^{100}Mo. Corrections for isobaric interferences of Zr and Ru on Mo masses were smaller than 2 ε for all samples and assumed terrestrial isotopic composition for these elements. Instrumental mass bias was corrected using the exponential law and ^{98}Mo/^{96}Mo = 1.453171 (Lu and Masuda, 1994). This normalization is best suited to resolve nucleosynthetic anomalies (Burkhardt et al., 2011).

3. Results

The concentrations of Mo and W in the various leachate fractions and the insoluble residue (Table 1) were calculated by dividing the quantity of Mo or W in the leachates by the total mass of the Murchison sample. While the majority of the Mo (~68%) is released in the second leaching step, the largest fraction of W (~48%) is contained in leaching step 4 (Fig. 1). The total Mo and W concentrations, calculated as the sum of the concentrations determined for each leaching step, are in good agreement with results for bulk rock analyses (1.15 ppm Mo here *vs.* 1.27 ppm in Burkhardt et al. (2011); 123 ppb W here *vs.* 130 ppb in Kleine et al. (2004)), indicating that all components of Murchison were digested in the leaching procedure.

The Mo isotopic data are listed in Table 1 and plotted on ε^{i}Mo versus atomic mass ^{i}Mo (Fig. 2) and ε^{92}Mo versus ε^{i}Mo diagrams (Fig. 3). All samples exhibit large Mo isotopic anomalies ranging from +30.5 ε^{92}Mo for L1 (HAc leachate) to −79.3 ε^{92}Mo for L6 (insoluble residue). The weighted average of the leachates yields ε^{92}Mo = 4.39 ± 0.53, slightly lower than ε^{92}Mo = 6.44 ± 0.39 reported for bulk Murchison (Burkhardt et al., 2011). This difference may reflect sample heterogeneity or loss of a small fraction of isotopically anomalous Mo from the leachates. The Mo isotopic compositions of the different leaching steps are consistent with deficits (L1–L3) and excesses (L4–L6) in *s*-process isotopes. A deficit in *s*-process Mo relative to terrestrial Mo leads to positive ε^{i}Mo values (for normalization to ^{98}Mo/^{96}Mo) and is characterized by a *w*-shaped pattern in a ε^{i}Mo–^{i}Mo diagram. Conversely, an *s*-excess results in negative ε^{i}Mo values and a corresponding *m*-shaped pattern (Burkhardt et al., 2011; Dauphas et al., 2002a). Note that a variable distribution of *r*-process Mo isotopes would result in different patterns, *i.e.*, an additional kink in ^{94}Mo (Burkhardt et al., 2011).

4. Presolar carrier phases of Mo and W isotope anomalies

4.1. Nature and origin of Mo isotope anomalies

The Mo isotopic data reveal large internal isotope variations and demonstrate that several presolar, isotopically diverse components are present in Murchison. A previous leaching experiment on the CI chondrite Orgueil revealed similar Mo isotope patterns, albeit of smaller magnitude (Dauphas et al., 2002a). The different magnitude of the isotope anomalies might be caused by the slightly different leaching procedures used in the two studies, but more likely is due to the higher degree of parent body alteration of Orgueil compared to Murchison. In ε^{92}Mo versus ε^{i}Mo diagrams (Fig. 3), the data for all the leaching steps plot along positive correlation lines that pass through the terrestrial Mo isotopic composition. Molybdenum isotopic data for acid leachates of Orgueil (Dauphas et al., 2002a) as well as a Ca, Al-rich inclusion (CAI) from Allende (A-ZH-5; a type A CAI characterized by