Molybdenum isotopic evidence for the origin of chondrules and a distinct genetic heritage of carbonaceous and non-carbonaceous meteorites

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A B S T R A C T

Nucleosynthetic isotope anomalies are powerful tracers to determine the provenance of meteorites and their components, and to identify genetic links between these materials. Here we show that chondrules and matrix separated from the Allende CV3 chondrite have complementary nucleosynthetic Mo isotope anomalies. These anomalies result from the enrichment of a presolar carrier enriched in *s*-process Mo into the matrix, and the corresponding depletion of this carrier in the chondrules. This carrier most likely is a metal and so the uneven distribution of presolar material probably results from metal–silicate fractionation during chondrule formation. The Mo isotope anomalies correlate with those reported for W isotopes on the same samples in an earlier study, suggesting that the isotope variations for both Mo and W are caused by the heterogeneous distribution of the same carrier. The isotopic complementary of chondrules and matrix indicates that both components are genetically linked and formed together from one common reservoir of solar nebula dust. As such, the isotopic data require that most chondrules formed in the solar nebula and are not a product of protoplanetary impacts.

Allende chondrules and matrix together with bulk carbonaceous chondrites and some iron meteorites (groups IID, IIIF, and IVB) show uniform excesses in ^{92}Mo, ^{95}Mo, and ^{97}Mo that result from the addition of supernova material to the solar nebula region in which these carbonaceous meteorites formed. Non-carbonaceous meteorites (enstatite and ordinary chondrites as well as most iron meteorites) do not contain this material, demonstrating that two distinct Mo isotope reservoirs co-existed in the early solar nebula that remained spatially separated for several million years. This separation was most likely achieved through the formation of the gas giants, which cleared the disk between the inner and outer solar system regions parental to the non-carbonaceous and carbonaceous meteorites. The Mo isotope dichotomy of meteorites provides a new means to determine the provenance of meteoritic and planetary materials, and to assess genetic links between chondrites and differentiated meteorites.

1. Introduction

Nucleosynthetic isotope anomalies in meteorites and their components provide unique insights into the formation and early evolution of the solar system (see Dauphas and Schauble, 2016 for an overview). These anomalies arise through the heterogeneous distribution of isotopically diverse presolar materials in the solar protoplanetary disk and as such can be used to assess potential genetic relationships among meteorites and their components. For instance, on the basis of Cr, Ti, and O isotopic data, Warren (2011)

distinguished between carbonaceous and non-carbonaceous meteorites and argued that this distinction reflects a fundamental dichotomy in the provenance of meteoritic and planetary materials. This dichotomy may reflect a temporal change in the composition of the solar nebula, perhaps caused by episodic accretion of material to the solar nebula (e.g., Wasson, 2000), or, alternatively, is due to the formation of carbonaceous and non-carbonaceous meteorites in spatially distinct regions of the solar nebula (e.g., Warren, 2011).

Nucleosynthetic isotope anomalies also exist at a smaller scale among the components of primitive meteorites; these isotope anomalies are most prominent in Ca–Al-rich inclusions (CAIs) (e.g., Dauphas and Schauble, 2016), but are also present in chondrules and matrix, the major components of most primitive chon-

drites. For instance, chondrules and matrix from the Allende carbonaceous chondrite (CV3) have complementary nucleosynthetic W isotope anomalies, indicating that presolar material is unevenly distributed between these two components (Budde et al., 2016). This isotopic complementarity confirms earlier conclusions based on the chemical complementarity of chondrules and matrix (Becker et al., 2015; Bland et al., 2005; Ebel et al., 2016; Hezel and Palme, 2008, 2010; Palme et al., 2015) that both components are genetically linked and formed from the same reservoir of solar nebula dust. As such, these data would rule out the formation of chondrules by protoplanetary impacts and would instead indicate a solar nebula origin of chondrules. However, the heterogeneous distribution of presolar material between chondrules and matrix should lead to collateral isotopic variations for elements other than W. Thus, given the importance of the isotopic chondrule–matrix complementarity for constraining chondrule formation models, it is necessary to identify such anomalies also for other elements. Demonstrating isotopic chondrule–matrix complementarity for several elements, and the absence of such anomalies for some other elements, may also help to better understand the nature of the presolar carrier that is unevenly distributed between chondrules and matrix, as well as the processes leading to this uneven distribution. Such information is critical for better constraining the nature of the chondrule-forming process.

Here we report Mo and Ba isotopic data for the same Allende chondrule and matrix samples analyzed previously for W isotopes (Budde et al., 2016). Molybdenum is particularly useful because it exhibits large and distinctive nucleosynthetic isotope anomalies in bulk meteorites (Burkhardt et al., 2011; Dauphas et al., 2002a). Of note, *r*- and *s*-process variability result in different Mo isotope patterns, making it possible to distinguish, for instance, a deficit in *s*-process from an excess in *r*-process Mo nuclides (Burkhardt et al., 2011). Barium is useful because it can provide additional constraints on the nature of the presolar carrier causing the isotopic anomalies in chondrules and matrix. Because Ba is lithophile while Mo and W are siderophile, the combined isotopic data can help to distinguish between different grain types (e.g., metal versus silicates) as the carrier of the observed isotope anomalies.

Using the new isotopic data, we will assess the extent of isotopic complementarity of chondrules and matrix, evaluate the carrier causing this complementarity and discuss the implications of these constraints for the origin of chondrules. In addition, the Mo isotope data provide new insights into the genetic heritage of distinct meteorite parent bodies and the origin of the dichotomy observed between carbonaceous and non-carbonaceous meteorites, which in turn bears testimony to the early dynamical evolution of the solar nebula and formation of the gas giants.

2. Samples and analytical methods

The chondrule, matrix, and bulk rock samples from the Allende CV3 chondrite analyzed here are the same samples previously analyzed for their Hf–W isotopic compositions (Budde et al., 2016). In total three matrix separates, six chondrule fractions, and two bulk rock samples of Allende were analyzed. The chondrule fractions comprise between 155 and ∼3000 chondrules each and differ in grain size (C2 > C3 > C4) and magnetic susceptibility (C3m > C3i > C3n). Details about the preparation of these samples are given in the supplementary material.

All samples (0.3–0.5 g) were digested in closed Savillex® beakers on a hotplate using HF–HNO$_3$(–HClO$_4$), followed by inverse *aqua regia*. The samples were then passed through a two-stage anion exchange chemistry used for the separation of W in our previous study (Budde et al., 2016). The Mo and Ba analyzed in the present study were separated from column washes collected during the W separation, which was accomplished following

slightly modified procedures outlined in Burkhardt et al. (2011, 2014) and Carlson et al. (2007). In short, Mo was collected during the W anion exchange chemistry using 3 M HNO$_3$, and was then further purified using Eichrom® TRU Resin and HCl and HNO$_3$. Barium was separated from the matrix using AG50-X8 cation resin and various strengths of HCl, with Ba eluted in 2.5 M HNO$_3$ (see supplementary material for details).

The Mo isotope measurements were performed on the Thermo Scientific® Neptune *Plus* MC-ICP-MS at the Institut für Planetologie at the University of Münster. The samples were introduced using a Savillex® C-Flow PFA nebulizer connected to a Cetac® Aridus II desolvator. Standard Ni sample and (H) skimmer cones were used and total ion beam intensities of ∼1.3×10^{-10} A were obtained for a ∼100 ppb Mo solution at a ∼50 µl/min uptake rate. Each measurement consumed ∼100 ng of Mo and consisted of 40 baseline integrations (on-peak zeros) of 8.4 s each, followed by 100 Mo isotope ratio measurements of 8.4 s each. Instrumental mass bias was corrected by internal normalization to ^{98}Mo/^{96}Mo = 1.453173 using the exponential law. This normalization is preferred because it results in large Mo isotope anomalies and distinctive isotope patterns (Burkhardt et al., 2011). Isobaric interferences of Zr and Ru on Mo masses were corrected by monitoring ^{91}Zr and ^{99}Ru (see supplementary material for details). The Mo isotope data are reported as ε^iMo values relative to the mean of bracketing runs of the Alfa Aesar® solution standard, where ε^iMo = $[(^i$Mo/^{96}Mo$)_{sample}/(^i$Mo/^{96}Mo$)_{standard} - 1] \times 10^4$. For samples analyzed several times, reported values represent the mean of pooled solution replicates. The accuracy and precision of the Mo isotope measurements were assessed by repeated analyses of the BHVO-2 rock standard (Table S2), several digestions of which were processed through the full analytical protocol and analyzed together with each set of samples. The ε^iMo values obtained for BHVO-2 are indistinguishable from the Alfa Aesar standard, demonstrating that the Mo isotopic data are accurate. The external reproducibility of the Mo isotope measurements, as determined by repeated measurements of BHVO-2, ranged from ±0.14 for ε^{97}Mo to ±0.39 for ε^{92}Mo (2 s.d., *n* = 24). Total procedural blanks were between 0.7 and 1.2 ng and thus negligible, given that several hundred ng of Mo were analyzed for each sample.

The Ba isotope measurements were made on the Thermo Scientific® Triton *Plus* TIMS at the Institut für Planetologie at the University of Münster. Barium was analyzed using zone-refined double Re filaments with Ba loaded directly on the filament in 2 M HCl. Due to the setup of the specific instrument, the alignment of all Ba isotopes and required interference monitors was not possible on a single line and therefore no data is reported for ^{132}Ba. However, all other isotopes of Ba, along with La and Ce, which have direct isobaric interferences with Ba, were monitored during the measurements. Each run consisted of 300–600 ratios with 16 s integration times. ^{134}Ba, ^{135}Ba, ^{136}Ba, ^{137}Ba, ^{138}Ba, and ^{140}Ce were measured during a single static run utilizing 10^{11} Ω resistors; 10^{12} Ω resistors were used to measure ^{130}Ba and ^{139}La. Data are fractionation corrected to ^{134}Ba/^{136}Ba = 0.3078 using the exponential law (Carlson et al., 2007). The external reproducibility of the Ba isotope measurements was assessed using the long-term reproducibility of terrestrial basalt samples put through the same chemical and measurement procedures as the samples from this study, ranging from ±0.13 for ε^{135}Ba to ±0.31 for ε^{138}Ba (2 s.d., *n* = 14). All run data are given in Tables 1 and S4.

3. Results

The Mo concentration and isotope data for the investigated Allende samples are provided in Table 1. Compared to bulk Allende, the matrix samples are enriched in Mo, while the chondrule separates are variably depleted in Mo. The largest variations in Mo