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Evidence for Mo isotope fractionation in the solar nebula and during planetary differentiation

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ABSTRACT

Mass-dependent Mo isotope fractionation has been investigated for a wide range of meteorites including chondrites (enstatite, ordinary and carbonaceous chondrites), iron meteorites, and achondrites (eucrites, angrites and martian meteorites), as well as for lunar and terrestrial samples. Magmatic iron meteorites together with enstatite, ordinary and most carbonaceous chondrites define a common $\delta^{98/95}$Mo value of $-0.16 \pm 0.02‰$ (relative to the NIST SRM 3134 Mo standard), which is interpreted to reflect the Mo isotope composition of bulk planetary bodies in the inner solar system. Heavy Mo isotope compositions for IAB iron meteorites most likely reflect impact-induced evaporative losses of Mo from these meteorites. Carbonaceous chondrites define an inverse correlation between $\delta^{98/95}$Mo and metal content, and a positive correlation between $\delta^{98/95}$Mo and matrix abundance. These correlations are mainly defined by CM and CK chondrites, and may reflect the heterogeneous distribution of an isotopically light metal and/or an isotopically heavy matrix component in the formation region of carbonaceous chondrites. Alternatively, the elevated $\delta^{98/95}$Mo of the CM and CK chondrites could result from the loss of volatile, isotopically light Mo oxides, that formed under oxidized conditions typical for the formation of these chondrites.

The Mo isotope compositions of samples derived from the silicate portion of differentiated planetary bodies are heavy compared to the mean composition of chondrites and iron meteorites. This difference is qualitatively consistent with experimental evidence for Mo isotope fractionation between metal and silicate. The common $\delta^{98/95}$Mo values of $-0.05 \pm 0.03‰$ of lunar samples derived from different geochemical reservoirs indicate the absence of significant Mo isotope fractionation by silicate differentiation or impact metamorphism/volatilization on the Moon. The most straightforward interpretation of the Mo isotope composition of the lunar mantle corresponds to the formation of a lunar core at a metal–silicate equilibration temperature of $1800 \pm 200\,^\circ$C. The investigated martian meteorites, angrites and eucrites exhibit more variable Mo isotope compositions, which for several samples extend to values above the maximum $\delta^{98/95}\text{Mo} = +0.14‰$ that can be associated with core formation. For these samples post-core formation processes such as partial melting, metamorphism and in the case of meteorite finds terrestrial weathering must have resulted in Mo isotope fractionation. Estimates of the metal–silicate equilibration temperatures for Mars ($2490 \pm 770\,^\circ$C) and the angrite parent body ($1790 \pm 230\,^\circ$C) are thus more uncertain than that derived for the Moon. Although the Mo isotope composition of the bulk silicate Earth has not been determined as part of this study, a value of $-0.16‰ < \delta^{98/95}\text{Mo} < 0$ can be predicted based on the chondrite and iron meteorite data and by assuming a reasonable temperature range for core formation in the Earth. This estimate is in agreement with four analyzed basalt standards (-0.10 ± 0.10). Improved application of mass-dependent Mo isotope fractionation to investigate core formation most of all requires an improved understanding of potential Mo isotope fractionation during processes not related to metal–silicate differentiation.

1. Introduction

Mass-dependent isotope variations among meteorites and their components have been reported for a variety of elements, including S (Gao and Thiemens, 1993), Zn, Cu, and Ni (Luck et al., 2005; Moynier et al., 2006), Cd (Wombacher et al., 2008), Cr

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(Moynier et al., 2011), Si (Armytage et al., 2011; Fitoussi et al., 2009; Savage and Moynier, 2013), Ca (Simon and DePaolo, 2010), and Sr (Charlier et al., 2012; Moynier et al., 2010; Patchett, 1980). These isotopic variations have been interpreted to reflect fractionation by condensation/evaporation in the nebula and subsequent uneven mixing of the fractionated nebular reservoirs and their products, particularly Ca,Al-rich inclusions (Luck et al., 2005; Moynier et al., 2010; Simon and DePaolo, 2010) or Si-bearing metal (Savage and Moynier, 2013). More recently, mass-dependent isotope fractionation has also been applied to investigate the conditions of planetary core formation. For instance, the Si and Cr isotope compositions of the bulk silicate Earth are fractionated compared to primitive meteorites, and this has been interpreted to indicate Si and Cr partitioning into the Earth's core (Armytage et al., 2011; Fitoussi et al., 2009; Georg et al., 2007; Hin et al., 2014; Moynier et al., 2011; Shahar et al., 2011). Since the magnitude of isotope fractionation depends on the temperature of metal–silicate equilibration, such isotope studies can potentially provide new constraints on the conditions of core formation.

Molybdenum is an interesting element to add to the studies of mass-dependent isotope fractionation in meteoritic and planetary materials. It is refractory and moderately siderophile, and is composed of seven stable isotopes. Mass-independent (i.e., nucleosynthetic) Mo isotope variations in meteorites and their components are well documented and have been used to investigate mixing processes in the solar nebula as well as genetic relationships among meteorites and between meteorites and the larger terrestrial planets (Burkhardt et al., 2011, 2012; Dauphas et al., 2002, 2004). The elemental distribution of Mo in meteorites is dominated by its affinity for the metal phase, but also by its highly refractory character leading to strong enrichments in Ca,Al-rich inclusions (CAI). Although Mo is refractory under the canonical conditions of the solar nebula, it is less enriched than other highly refractory metals in some CAI from the Allende meteorite. This has been interpreted to reflect removal of volatile Mo oxides formed in oxidizing environments (Fegley and Palme, 1985). During planetary differentiation, Mo preferentially partitions into the core and is strongly depleted in the silicate mantle (e.g., Holzheid and Palme, 2007; Newsom and Palme, 1984; Newsom, 1985, 1986; Righter et al., 1998; Wade et al., 2012; Walter and Thibault, 1995). The magnitude of Mo depletion in the mantle, therefore, can help to assess the pressure, temperature and oxygen fugacity conditions of metal segregation during planetary differentiation (e.g., Wood et al., 2006; Wade et al., 2012).

So far little is known about mass-dependent Mo isotope fractionation during high-temperature processes. This contrasts with the large body of work on such fractionation during low-temperature processes (e.g., Anbar, 2004). In a companion study we have performed liquid-metal liquid-silicate experiments, which demonstrate significant Mo isotope fractionation between metal and silicate up to temperatures of ~3000 °C (Hin et al., 2013). The temperature dependence of this fractionation makes Mo isotopes a tracer to investigate the temperature conditions during planetary core formation.

Here, we present Mo stable isotope data for a variety of chondrites, achondrites, iron meteorites, and lunar samples. These data are used to evaluate the nature and extent of mass-dependent Mo isotope fractionation by solar nebula processes and during planetary differentiation, and to assess whether Mo isotopes can serve as a new tracer for core formation in the terrestrial planets.

2. Analytical methods

2.1. Sample preparation and Mo separation

The samples investigated for this study include eleven chondrites (CV, CM, CO, CR, CK, CB, ordinary and enstatite chondrites), seven iron meteorites (IAB, IIAB, IIIAB, IVA, IVB), three angrites, four eucrites, two martian meteorites, and five lunar samples. In addition four terrestrial basaltic rock standards were analyzed (BHVO-2, BIR-1, W-2a, DNC-1). Whereas the terrestrial rock standards were obtained as powders, all other samples were received as small pieces. They were carefully cleaned with abrasive paper and by sonication in distilled water and ethanol. Several of the meteorite samples are desert finds (Dhofar007, DaG476, NWA4801, NWA4590) and show signs of terrestrial alteration, such as oxidation veins along cracks. When possible, obviously altered parts of these samples were avoided. For NWA4801 this was not possible, however, and for this sample only the grain-size larger than 40 μm was used. All silicate-rich samples were powdered in an agate mortar or mill. For the chondrites Daniel's Kuil, Kernouvé, Allende, Murchison-a and NWA801 aliquots from powders analyzed previously for mass-independent (i.e., nucleosynthetic) Mo isotope anomalies (Burkhardt et al., 2011) were used. The KREEP-rich sample 68115 is the remainder from a W isotope study (Touboul et al., 2007), for which some metal was separated from the powder.

All samples were weighed into 60 ml Savillex beakers, spiked with a ^{100}Mo–^{97}Mo tracer (Hin et al., 2013), and digested in HCl (iron meteorites) or HF–HNO_3–$HClO_4$ (6:3:1) (silicate samples) at 180 °C on a hotplate for several days. This procedure ensured complete spike-sample equilibration. Sample sizes were ~50–100 mg for iron meteorites, ~200 mg for chondrites and ~0.5–2 g for silicate samples. After digestion, samples were dried and re-dissolved in HNO_3–H_2O_2 to attack any remaining organics. Molybdenum was separated from the sample matrix using a three-stage ion exchange procedure employing both anion and cation exchange resins (Burkhardt et al., 2011). Molybdenum was first separated from major elements using a cation exchange column (Bio-Rad AG50W-X8) and 1 M HCl–0.1 M HF (see Patchett and Tatsumoto, 1980). Subsequently, any remaining Fe, Ni and a large part of the Ru was separated from Mo on an anion exchange resin (Bio-Rad AG1-X8) with 1 M HF, while Ti, Zr, Hf and W were eluted using different HCl–HF mixtures (Kleine et al., 2004). Finally, Mo together with some remaining Ru is eluted using 3 M HNO_3. The remaining Ru is removed from the Mo fraction using TRU-Spec resin conditioned in 7 M HNO_3, followed by elution of Mo with 0.1 M HNO_3. This last step was repeated using 1 M HCl and 0.1 M HCl instead of 7 M HNO_3 and 0.1 M HNO_3, resulting in Ru/Mo and Zr/Mo $< 3 \times 10^{-5}$ for most samples. Interference corrections were thus generally <0.02‰, and always <0.05‰ (Cape of Good Hope). Total chemistry yields were 60–85%, highlighting the need for double-spiking to obtain accurate mass-dependent Mo isotope data. Total procedural blanks ranged from 0.3 to 0.9 ng Mo, and were negligible for most samples. However, for some Mo-poor silicate samples blank corrections were necessary (see Table 2).

2.2. Mass spectrometry and data reduction

Molybdenum isotope measurements were performed using a *NuInstruments Plasma1700* MC-ICP-MS at ETH Zürich and a ThermoScientific *NeptunePlus* MC-ICP-MS at the University of Münster. On both instruments all seven Mo isotopes were measured simultaneously in static mode, as well as ^{90}Zr (Zürich) or ^{91}Zr (Münster) and ^{99}Ru to monitor potential isobaric interferences. On the *Nu1700*, samples were introduced via a DSN-100 desolvator equipped with a PFA nebulizer having an uptake rate of ~140 μl/min. When normalized to a 100 μl/min uptake rate,