Earth and Planetary Science Letters 487 (2018) 221–229

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

New insights into Mo and Ru isotope variation in the nebula and terrestrial planet accretionary genetics

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ARTICLE INFO

Article history:
Received 23 September 2017
Received in revised form 20 January 2018
Accepted 24 January 2018
Available online xxxx
Editor: F. Moynier

Keywords:
accretionary genetics
BSE
iron meteorites

ABSTRACT

When corrected for the effects of cosmic ray exposure, Mo and Ru nucleosynthetic isotope anomalies in iron meteorites from at least nine different parent bodies are strongly correlated in a manner consistent with variable depletion in *s*-process nucleosynthetic components. In contrast to prior studies, the new results show no significant deviations from a single correlation trend. In the refined Mo–Ru cosmic correlation, a distinction between the non-carbonaceous (NC) group and carbonaceous chondrite (CC) group is evident. Members of the NC group are characterized by isotope compositions reflective of variable *s*-process depletion. Members of the CC group analyzed here plot in a tight cluster and have the most *s*-process depleted Mo and Ru isotopic compositions, with Mo isotopes also slightly enriched in *r*- and possibly *p*-process contributions. This indicates that the nebular feeding zone of the NC group parent bodies was characterized by Mo and Ru with variable *s*-process contributions, but with the two elements always mixed in the same proportions. The CC parent bodies sampled here, by contrast, were derived from a nebular feeding zone that had been mixed to a uniform *s*-process depleted Mo–Ru isotopic composition.

Six molybdenite samples, four glacial diamictites, and two ocean island basalts were analyzed to provide a preliminary constraint on the average Mo isotope composition of the bulk silicate Earth (BSE). Combined results yield an average μ^{97}Mo value of $+3 \pm 6$. This value, coupled with a previously reported μ^{100}Ru value of $+1 \pm 7$ for the BSE, indicates that the isotopic composition of the BSE falls precisely on the refined Mo–Ru cosmic correlation. The overlap of the BSE with the correlation implies that there was homogeneous accretion of siderophile elements for the final accretion of 10 to 20 wt% of Earth's mass. The only known cosmochemical materials with an isotopic match to the BSE, with regard to Mo and Ru, are some members of the IAB iron meteorite complex and enstatite chondrites.

1. Introduction

Most bulk meteorite samples are characterized by analytically well-resolved, nucleosynthetic isotope anomalies in Mo (Burkhardt et al., 2011; Poole et al., 2017; Worsham et al., 2017) and Ru (Chen et al., 2010; Fischer-Gödde et al., 2015; Fischer-Gödde and Kleine, 2017). Both of these elements comprise isotopes synthesized by the *p*-process (^{92}Mo, ^{96}Ru, and ^{98}Ru), *s*-process (^{96}Mo, ^{100}Ru), *r*-process (^{100}Mo, ^{104}Ru), both *s*- and *r*-processes (^{95}Mo, ^{97}Mo, ^{98}Mo, ^{99}Ru, ^{101}Ru), or the *p*-process with minor contributions from the *s*-process (^{94}Mo). These intra-element isotope anomalies are consistent with variable depletion in *s*-process components relative to the Earth (Dauphas et al., 2002a, 2002b; Burkhardt et al., 2011; Fischer-Gödde et al., 2015; Worsham et al., 2017). Further, Dauphas et al. (2004) found that anomalies in the Mo and Ru isotope compositions of bulk meteorites are correlated, terming this relationship the Mo–Ru "cosmic correlation". The slope of the Mo–Ru cosmic correlation matches that predicted from nucleosynthetic theory, if disparate regions of the nebula received variable contributions of *s*-process materials (Dauphas et al., 2004). The cause of nucleosynthetic isotope heterogeneity in the nebular disk remains an open question. It may have been a product of selective thermal processing (Trinquier et al., 2009), incomplete mixing of presolar grains in the solar nebula (Carlson et al., 2007), or late injection of diverse nucleosynthetic components (Bizzarro et al., 2007). Regardless of the responsible mechanism for the isotopic heterogeneity, the existence of a Mo–Ru cosmic correlation requires that nucleosynthetic components of these two elements were processed and mixed in the solar nebula in a similar manner.

Prior studies have noted that the Mo and Ru isotopic composition estimate of the bulk silicate Earth (BSE) lies at one end of the

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https://doi.org/10.1016/j.epsl.2018.01.017

Mo–Ru cosmic correlation (Dauphas et al., 2004; Fischer-Gödde et al., 2015). This is noteworthy because the Mo and Ru budgets of the BSE were likely established during different stages of planetary accretion (Dauphas et al., 2004). Molybdenum is a moderately siderophile element (MSE) and consequently a significant portion of its budget was set through high pressure metal-silicate partitioning during the final ~10 to 20% of terrestrial accretion (Li and Agee, 2001; Dauphas et al., 2002c; Righter, 2011). By contrast, the Ru budget in the terrestrial mantle, along with the other highly siderophile elements (HSE), was likely established by late accretion, a process which occurred after the cessation of core formation. It is commonly projected that late accretion added material with a chondritic bulk composition to the mantle accounting for a minimum of ~0.5 wt.% of Earth's mass, (Kimura et al., 1974; Chou, 1978). If the relative timing of the establishment of the Mo and Ru budgets of the BSE were offset in this manner, the observation that the Earth lies on or near the correlation implies there was no major change in the feeding zone of accreting materials during the final ~10 to 20% of accretion (Dauphas et al., 2004).

An important question that has arisen from published Mo–Ru cosmic correlations is whether or not the scatter in these correlations reflects a decoupling of Mo and Ru isotope compositions in the nebula? Alternatively, the scatter could reflect the decoupling of Mo and Ru isotope compositions because of sampling issues which can arise when collecting Mo and Ru isotope data from different pieces and digestions of meteorite samples. All correlations published to date are based on combined datasets for which Mo and Ru isotope data for a meteorite were collected from different pieces of the meteorite which were digested using differing techniques (Dauphas et al., 2004; Fischer-Gödde et al., 2015). This approach does not account for intra-sample heterogeneity, which can occur when sampling iron meteorites with variable cosmic ray exposure (CRE) histories or thermally unequilibrated chondrites. Consequently, the reported Mo–Ru isotope data may not reflect the true Mo–Ru isotope compositions of the parent body in question. Additionally, published studies include only two ungrouped meteorites and a small number of rare meteorite groups, which limited the scope of the nebula being investigated.

Here, these points are addressed by re-examining the Mo–Ru cosmic correlation through the analysis of CRE-corrected Mo and Ru isotope compositions obtained from the same dissolutions or dissolutions of neighboring pieces (<2 cm apart) for twenty-three iron meteorites. The meteorites studied are from the four major magmatic groups, a group IC iron meteorite, the "non-magmatic" IAB iron meteorite complex, and a four ungrouped iron meteorites (Supplementary Materials Table SM1a). The isotopic compositions of most iron meteorites are likely representative of their respective parent bodies given the siderophile nature of Mo and Ru, and the origin of most iron meteorites as planetesimal cores or metal segregated from large volumes of impact-derived melts. Potential problems associated with sample heterogeneity, owing to inadequate correction for CRE effects, are also addressed here by collection of Mo, Ru, and Os (determined as a dosimeter of CRE; Walker, 2012; Worsham et al., 2017) isotope data from the same sample dissolutions or neighboring pieces. We also report Mo isotope data for a selection of terrestrial materials to provide a preliminary estimate of the composition of the BSE in order to determine how it relates to the cosmic correlation.

2. Samples

Warren (2011) divided meteorites into carbonaceous chondrite (CC) and non-carbonaceous (NC) genetic groups, based on the isotopic dichotomy observed for O, Ti, Cr, and Ni. That study concluded that meteorites from the two groups formed in separate regions of the solar nebula. Kruijer et al. (2017) suggested that the

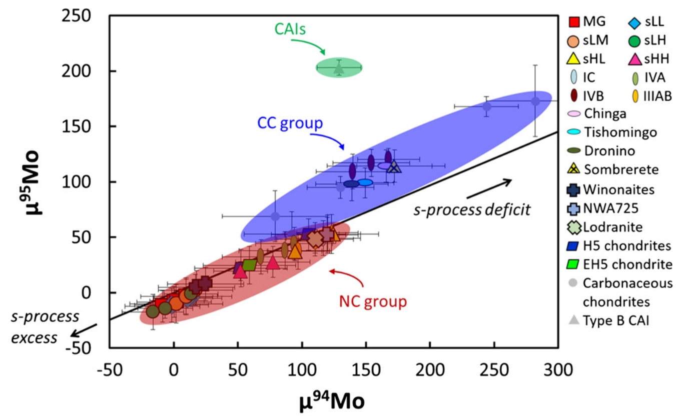

Fig. 1. μ^{94}Mo *vs.* μ^{95}Mo for NC (red field) and CC (blue field) group meteorites. Variations in Mo isotope ratios are due to variable depletions in the *s*-process component, and deviations in the relative abundances of the *r*- and *s*-process components. Type B Allende calcium aluminum inclusions (CAIs), in green, likely have a higher proportion of *r*-process material. The solid black line is a mixing line between a pure *s*-process depleted component (terrestrial) and an *s*-process enriched component (SiC) calculated using equations from Dauphas et al. (2004) and the *s*-process composition of Arlandini et al. (1999). Data fields are constructed using data from Burkhardt et al. (2011), Budde et al. (2016), and Worsham et al. (2017). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

NC and CC regions were segregated early in Solar System history by the presence of a proto-Jupiter. Molybdenum isotopic compositions are particularly useful for resolving CC and NC heritage (Budde et al., 2016; Poole et al., 2017; Worsham et al., 2017). Meteorites can be classified into these groups depending on the relative contributions of *p*-, *r*- and *s*-process material. Both groups possess *s*-process deficits, while the CC group members have an additional *r*-process (and possibly *p*-process) excess. Consequently, the CC group meteorites fall along a distinct *s*-process mixing line that is offset from the *s*-process mixing line on which all NC meteorites fall (Fig. 1). The CC group includes stony carbonaceous chondrites as well as some iron meteorites, indicating that the NC/CC genetic classification applies to both iron and stony meteorites (e.g., Warren, 2011; Budde et al., 2016). Samples analyzed in the present study are from both the CC group (IVB, Chinga, Dronino, and Tishomingo) and the NC group (IAB, IIAB, IIIAB, IVA, IC, and Gebel Kamil). Some of the Mo isotopic data for iron meteorites were previously reported in Worsham et al. (2017), and they are supplemented here with data for additional samples.

Based on chemical and isotopic data, at least nine different parent bodies are represented in the sample suite examined here. The so-called "magmatic" groups IIAB, IIIAB, IVA, IVB, and probably the IC irons, were produced by the fractional crystallization of metallic melts (e.g., Scott and Wasson, 1975). These groups represent five separate parent bodies based on their absolute and relative abundances of siderophile elements, W model ages, and distinct Mo and Ru isotope compositions (Scott and Wasson, 1975; Goldstein et al., 2009; Burkhardt et al., 2011; Kruijer et al., 2014; Fischer-Gödde et al., 2015). Meteorites from the so-called "non-magmatic" IAB iron meteorite complex are different from magmatic iron meteorites in that large variations in their major and trace element compositions cannot be explained by fractional crystallization of a metallic melt. Instead they may have formed as impact derived metal melt pools in chondritic parent bodies (e.g., Wasson and Kallemyn, 2002; Worsham et al., 2016a). Based on HSE abundances and Mo–W–Os isotope systematics, the IAB iron meteorite complex samples at least four different parent bodies (Worsham et al., 2016a, 2017), one of which, consisting of meteorites from Main Group (MG) and the sLL subgroup, comprises part of the present sample suite.