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

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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 $\mu^{97}\text{Mo}$ value of $+3 \pm 6$. This value, coupled with a previously reported $\mu^{100}\text{Ru}$ 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.

Keywords

accretionary genetics; BSE; iron meteorites

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.epsl.2018.01.017>.

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 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 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 “nonmagmatic” 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.

Ungrouped iron meteorites Chinga, Dronino, Gebel Kamil, and Tishomingo each have distinct siderophile element compositions (e.g., Honesto et al., 2006; Campbell and Humayun, 2012). Each meteorite is chemically unique, so it is problematic to classify them as magmatic or non-magmatic. Based on the chemical differences of siderophile elements, such as Ni, Ga and Ir, prior studies have concluded that ungrouped meteorites likely originated on different parent bodies that were distinct from one another, as well as from the known iron groups (e.g., Wasson et al., 1989).

To assess the Ru isotope composition of the Earth’s mantle, Fischer-Gödde et al. (2015) reported the Ru isotope composition of a terrestrial chromitite from the Shetland Ophiolite Complex. Subsequently, Bermingham and Walker (2017) reported an estimate of the Ru isotopic composition of the oceanic mantle, which is likely representative of the BSE, from measurements of thirteen different ophiolite chromitites and Os–Ir–Ru alloy grains which sample eight different, mainly Phanerozoic, mantle domains (Table SM1b). The isotopic compositions of these materials were found to be identical, within analytical uncertainties, to a reference material solution used as a standard in studies of meteoritic Ru. The chromitites and alloy grains do not have sufficient Mo to obtain corresponding, high precision Mo isotope data.

In order to broadly assess the Mo isotopic composition of the BSE, we report Mo isotope data for six Phanerozoic molybdenites from five different localities, two Archean (Coronation and Mozaan), one Paleoproterozoic (Makganyene), one Neoproterozoic (Pocatello), and one Paleozoic (Dwyka West) glacial diamictite composites, and two modern ocean island basalts (one from the Canary Islands and one from Hawaii) (Table SM1c). The molybdenites are of hydrothermal origin and represent a variety of molybdenite-formation environments (Pietruszka et al., 2006). Given the range of mass dependent Mo isotopic compositions represented in these samples (Pietruszka et al., 2006), this suite allows assessment of whether mass dependent isotopic variations correspond with mass independent variations. The diamictites have been previously used to evaluate the compositional evolution of the upper continental crust (UCC; Gaschnig et al., 2016), and are

used here to provide an estimate of the corresponding Mo isotopic composition of the UCC through time. Given that continental crust was ultimately derived from the mantle, the diamictites should also provide a record of the Mo isotopic composition of the upper mantle. The Mo isotope compositions of recently erupted ocean island basalts from La Palma (LP15) and Hawaii (Loihi LO-02–04) are also reported. Some Loihi basalts have been determined to have anomalous ^{182}W isotope compositions, suggesting that the source of these basalts likely includes material from the deep mantle (Mundl et al., 2017). Conversely, basalts from La Palma are characterized by normal ^{182}W isotope compositions (Touboul and Walker, 2012). Collectively, the molybdenite, diamictite and basalt data are averaged to provide a preliminary estimate of the BSE composition.

3. Methods

Osmium, Ru, and Mo isolation and purification chemistries and analytical methods followed Walker (2012), Bermingham et al. (2016), and Worsham et al. (2016b, 2017), respectively. Briefly, iron meteorites were digested in 8 M HCl at $\sim 140^\circ\text{C}$, and complete dissolution of iron meteorites was achieved after ~ 48 hrs. Silicates present in some of the IAB iron meteorites were not dissolved; however, incomplete dissolution of these phases is unlikely to affect the bulk sample isotopic composition of Mo and Ru, given the very low relative abundance of siderophile elements in silicates as compared to the metal phase and the absence of presolar phases. After dissolution, the solution was divided into separate aliquots for Mo, Ru, and Os isolation and purification. There were some samples from which Mo, Ru, Os isotope compositions were collected on neighboring pieces (< 2 cm) and these are noted in Table SM1a.

Molybdenites were isolated from the same hand specimens used in Pietruszka et al. (2006). The molybdenites were dissolved in a concentrated $\text{HNO}_3\text{:HCl}$ (2:3) aqua regia mixture over three days at $\sim 120^\circ\text{C}$. Complete dissolution of these samples was not achieved for all samples; however, this is not expected to cause a shift in isotopic composition because the siderophile-hosting phases were likely dissolved during this treatment. After dissolution, the solution was purified for Mo following Worsham et al. (2017), where only the first anion exchange column was required because of the high Mo purity of the samples digested. Glacial diamictites and the La Palma basalt were processed following Worsham et al. (2017). Briefly, powders were dissolved in concentrated HF:HNO_3 (5:1) mixture at $\sim 150^\circ\text{C}$ over 5 days. Complete dissolution of these samples was not achieved; however, this is not expected to cause a shift in isotopic composition because the siderophile-hosting phases were likely dissolved during this treatment. The ocean island basalt sample LO-02–04 was digested following Touboul and Walker (2012). This sample was processed for W isolation and purification (following Archer et al., 2017), during which Mo was also isolated. Subsequent purification of Mo was completed following Worsham et al. (2017).

The Mo, Ru, and Os isotope compositions were measured using *Thermo Fisher Triton* and *Triton Plus* thermal ionization mass spectrometers (TIMS) operated in negative ionization mode at the Department of Geology, University of Maryland (following Walker, 2012; Bermingham et al., 2016; Worsham et al., 2016b). Each instrument was equipped with nine Faraday cups, seven of which were used to measure the seven Mo or Ru isotopes, or six Os

isotopes, as trioxides (MoO_3^- , RuO_3^- , or OsO_3^-) using a single static line measurement method. The reported data were reduced using one of two different reduction protocols. One protocol utilized an assumed oxygen isotopic composition (obtained from Nier, 1950) for oxide interference corrections, while the other protocol relied on the direct measurement of the oxygen isotopic composition (“Nier reduction method” and “measured oxygen reduction method”, respectively; Walker, 2012; Bermingham et al., 2016; Worsham et al., 2016b; Bermingham and Walker, 2017). The latter reduction scheme became available approximately mid-way through the course of this study with the addition of 10^{12} ohm and 10^{13} ohm resistor amplifiers to the *Triton Plus*. This permitted direct in-run monitoring of the oxygen isotope compositions by measuring $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2^-$ (for Mo) or $^{104}\text{Ru}^{18}\text{O}^{16}\text{O}_2^-$ (for Ru) (see Bermingham et al., 2016; Worsham et al., 2016b). Ruthenium isotope data were corrected using either the “Nier reduction method” or the “measured oxygen reduction method”. Molybdenum isotope data were corrected using the “measured oxygen reduction method”, and Os isotope data were corrected for oxide interferences using the “Nier reduction method”. All data were corrected for instrumental mass fractionation using the exponential law and $^{98}\text{Mo}/^{96}\text{Mo} \equiv 1.453171$ (Lu and Masuda, 1994) and $^{99}\text{Ru}/^{101}\text{Ru} \equiv 0.745075$ (Chen et al., 2010), or $^{192}\text{Os}/^{188}\text{Os} \equiv 3.08271$ (Allègre and Luck, 1980) as the relevant normalizing ratio. To describe isotopic compositions, the μ notation is used which corresponds to the deviation of an isotopic ratio of a sample, relative to the average ratio measured for the repeated analysis of the *Alfa Aesar* standard for that analytical campaign, in parts per million:

$$\mu^x\text{Mo}_{\text{sample}} = \left[\frac{(^x\text{Mo})_{\text{sample}}}{(^x\text{Mo})_{\text{standard}}} - 1 \right] \times 10^6$$

$$\mu^x\text{Ru}_{\text{sample}} = \left[\frac{(^x\text{Ru})_{\text{sample}}}{(^x\text{Ru})_{\text{standard}}} - 1 \right] \times 10^6$$

$$\mu^x\text{Os}_{\text{sample}} = \left[\frac{(^x\text{Os})_{\text{sample}}}{(^x\text{Os})_{\text{standard}}} - 1 \right] \times 10^6$$

In-house single-element *Alfa Aesar Specpure*[®] plasma standard solutions of Mo and Ru, and a Johnson Matthey Os standard were used for this study. For Mo, repeated measurements of the standard yielded external reproducibility for $\mu^{92}\text{Mo}$, $\mu^{94}\text{Mo}$, $\mu^{95}\text{Mo}$, $\mu^{97}\text{Mo}$, and $\mu^{100}\text{Mo}$ ranging from ± 76 , ± 27 , ± 15 , ± 7 , ± 20 to ± 107 , ± 37 , ± 23 , ± 5 , ± 32 (2SD), respectively, using the “measured oxygen reduction method”. For $\mu^{96}\text{Ru}$, $\mu^{98}\text{Ru}$, $\mu^{100}\text{Ru}$, $\mu^{102}\text{Ru}$, $\mu^{104}\text{Ru}$, repeated measurements of the standard using the “Nier reduction method” generated external reproducibility for different measurement campaigns ranging from ± 61 , ± 144 , ± 6 , ± 29 , ± 30 to ± 65 , ± 182 , ± 15 , ± 54 , ± 88 (2SD), respectively. Using a measured oxygen isotope composition, the external reproducibility ranged from ± 51 , ± 109 , ± 7 , ± 40 , ± 63 to ± 80 ,

± 162 , ± 14 , ± 48 , ± 39 (2SD). The generally lower precision on $\mu^{96}\text{Ru}$, $\mu^{98}\text{Ru}$, $\mu^{102}\text{Ru}$, and $\mu^{104}\text{Ru}$, when using a measured oxygen isotope composition, reflects an unaccounted for effect in the oxygen correction scheme (Bermingham et al., 2016; Bermingham and Walker, 2017). Although not desired, this is not relevant to this study because its focus is on the *s*-process only ^{100}Ru isotope, which is measured to the highest, and roughly equal, precision using both methods. For Os, repeated measurements of the standard generated external reproducibility (2SD) for different measurement campaigns ranging from $\mu^{189}\text{Os} \pm 3$ to ± 7 and $\mu^{190}\text{Os} \pm 6$ to ± 13 .

4. Results

4.1. Iron meteorites and CRE correction schemes

Exposure to cosmic rays can modify the isotopic composition of a meteorite, with the magnitude of the effects dependent on the neutron capture cross sections and resonance integrals of the relevant isotopes, as well as the depth from the surface from which the sample originates. Corrections for such effects are particularly important for iron meteorites, given that sizable modifications to Ru and Mo isotopic compositions can result from the long-term exposure histories characterizing some iron meteorites (Fischer-Gödde et al., 2015; Worsham et al., 2017). A major issue with published Mo–Ru cosmic correlation data is that none of the data used in the original correlation were corrected for CRE effects (Dauphas et al., 2004), and only the Ru data were corrected in a subsequent re-examination of the correlation (Fischer-Gödde et al., 2015). Hence, some of the scatter in the published correlations may reflect uncorrected cosmic ray effects. Fischer-Gödde et al. (2015) noted that although they found that the IID and IVB groups to be offset from the Mo–Ru cosmic correlation, the Ru isotope and dosimeter data were not always collected on the same pieces of the meteorites, nor were the Mo isotope data corrected for CRE effects. That study recommended that future studies combine high-precision Mo, Ru, and CRE dosimetry measurements (Pt or Os) on the same pieces of irons from these groups to determine if the offsets are an accurate reflection of the isotope composition of the parent bodies.

To obtain accurate Ru and Mo pre-exposure isotope compositions for iron meteorite samples, it is necessary to analyze these elements and an appropriate neutron dosimeter from the same or neighboring meteorite piece, given that CRE effects can vary with depth over short distances in a meteorite (Eugster et al., 2006; Markowski et al., 2006). Here, Os is used as an appropriate neutron dosimeter for siderophile elements because this HSE does not record nucleosynthetic isotope anomalies in iron meteorites, and some Os isotopes (e.g., ^{189}Os) possess large neutron capture cross-sections and resonance integrals (Mughaabghab, 2003; Walker, 2012; Worsham et al., 2017). By correlating the $\mu^{189}\text{Os}$ vs. $\mu^x\text{Mo}$ or $\mu^{100}\text{Ru}$, a single pre-exposure composition for a group of meteorites can be determined from the point of intersection of the resulting trend where $\mu^{189}\text{Os} = 0$ (Fig. SM2), here termed the “intercept-derived group pre-exposure” composition (Bermingham and Walker, 2017; Worsham et al., 2017). The uncertainties associated with these CRE compositions are defined as the extent of the error envelop at $\mu^{189}\text{Os} = 0$ for the trend generated using the ISOPLOT program (Ludwig, 2003) as per Bermingham and Walker (2017) and Worsham et al. (2017). This approach was used to calculate the CRE corrected Mo and $\mu^{100}\text{Ru}$ isotope

compositions of the IAB MG-sLL iron meteorite group (Bermingham and Walker, 2017). The MG and sLL subgroup have been suggested to have originated from the same parent body via impact-generated melts at ~4.6 to 3.5 Ma and ~5.4 Ma, respectively, after calcium aluminum inclusions (CAI) (Wasson and Kallemeyn, 2002; Worsham et al., 2017; Hunt et al., 2018), making it appropriate to combine the isotope compositions of these groups to define a single group pre-exposure composition.

Intercept-derived CRE corrections cannot be used for the ungrouped iron meteorites, because there are no other meteorites that can be assumed to have the same pre-exposure composition with which to define a trend. Nor can the intercept method be used for some magmatic iron meteorites where there was not a large enough range in the $\mu^{189}\text{Os}$ vs. $\mu^x\text{Mo}$ or $\mu^{100}\text{Ru}$ group trends to produce as robust a slope as that defined by the IAB (MG-sLL) group. Instead, the CRE corrected compositions of individual meteorites were determined by projecting the $\mu^x\text{Mo}$ or $\mu^{100}\text{Ru}$ values of a sample to a $\mu^{189}\text{Os}$ of zero using the linear equation and well-defined slopes of the $\mu^{189}\text{Os}$ vs. $\mu^x\text{Mo}$ or $\mu^{100}\text{Ru}$, here termed the “slope-derived pre-exposure” composition (following Qin et al., 2015; Worsham et al., 2017). The most precise and well-defined slopes were then used to correct individual meteorite compositions. In this case, the IAB MG-sLL meteorite group slopes were applied to calculate the pre-exposure compositions for the IC, IIAB, IIIAB, IVA, IVB, and ungrouped meteorites (Fig. SM2). The uncertainties shown for individual meteorites are the 2SD of standards (where $n = 1$ to 2) or samples (where $n = 2$ to 3), or the 2SE of samples (when $n = 4$), propagated through the CRE correction calculation, accounting for the uncertainties of the measurements and the slopes. For samples where $n = 2$, the larger 2SD of the standards or samples was used. For the magmatic groups, individual meteorite compositions were subsequently averaged to provide a group composition, and the uncertainties of the average compositions of the magmatic iron groups are defined as the 2SD of individual meteorite compositions of each group. The CRE corrected $\mu^{97}\text{Mo}$ and $\mu^{100}\text{Ru}$ isotope compositions for the samples and groups analyzed here are presented in Table 1. The Os isotope data collected during this study are reported in Supplementary Materials (Table SM3). Due to a lack of correlation between $\mu^{189}\text{Os}$ and $\mu^{96}\text{Ru}$, $\mu^{98}\text{Ru}$, $\mu^{100}\text{Mo}$, $\mu^{102}\text{Ru}$, or $\mu^{104}\text{Ru}$, these isotopes are not corrected for CRE effects. Cosmic ray exposure uncorrected Mo and Ru data are shown in Tables SM4 and SM5, and CRE corrected data for $\mu^{92,94,95}\text{Mo}$ isotopes are provided in Table SM4b and Fig. SM4c.

Meteorites common to this study and published studies include Campo del Cielo (IAB), Toluca (IAB), Negrillos (IIAB), North Chile (IIAB), Tlacotepec (IVB), Bendego (IC), and Chinga (UNGRP). Group averages (IAB, IIAB, IIIAB, IVA, and IVB) can also be compared. The CRE uncorrected data obtained in this study for $\mu^{97}\text{Mo}$ and $\mu^{100}\text{Ru}$ isotope compositions are generally in good agreement with CRE uncorrected published data (Dauphas et al., 2002a, 2002b; Chen et al., 2010; Burkhardt et al., 2011; Fischer-Gödde et al., 2015; Poole et al., 2017) (SM6), with offsets reaching a maximum of 13 ppm. After correcting for CRE effects for $\mu^{100}\text{Ru}$, group averages determined here overlap within the uncertainties of corrected data reported by Fischer-Gödde et al. (2015). Cosmic ray exposure corrections for $\mu^{100}\text{Ru}$ range from ~1 to ~40 ppm, typically ~9 ppm, while corrections for $\mu^{97}\text{Mo}$ are smaller ranging from ~1 to 10 ppm, typically ~2 ppm. The CRE corrected Mo isotope data reported here cannot be directly compared with the literature because Mo

isotope compositions for iron meteorites reported to date have not been corrected for CRE effects.

4.2. Terrestrial materials

Defining the Mo and Ru isotopic composition of the Earth has typically been achieved by reporting the composition of repeated analyses of commercial plasma standard solutions (Dauphas et al., 2004; Chen et al., 2010; Burkhardt et al., 2011; Fischer-Gödde et al., 2015), and rarely, combining these compositions with those determined from a limited selection of terrestrial rock samples (Fischer-Gödde et al., 2015; Bermingham et al., 2016). Using plasma standards alone to define the composition of the BSE is problematic because the chemical and geological origins of these standards are rarely known.

To provide a more robust estimate of the BSE, the Ru isotopic composition of the oceanic mantle ($\mu^{100}\text{Ru} + 1 \pm 7$; Table 1, Fig. 2) as defined by Bermingham and Walker (2017) is used. The Mo isotope composition of the BSE is estimated from the Mo isotopic composition of a selection of molybdenites, diamictites, and modern ocean island basalts. Samples were measured up to four times ($n = 1 - 4$) by loading purified Mo from a single digestion onto different filaments. The uncertainties for samples measured once are the 2SD of repeat measurements of the standard, or the 2SE of the measurement (internal error), whichever was greater. The uncertainties for sample means, where $n \geq 3$, are reported as the 2SD of the standard or the sample, whichever was greater. The uncertainties for sample means, where $n \geq 4$, are reported as the 2SE associated with the multiple measurements of the sample.

The $\mu^{97}\text{Mo}$ isotopic composition of the six molybdenites are identical within analytical uncertainty and average $\mu^{97}\text{Mo} = +2 \pm 6$ 2SD (where 2SD refers to 38 repeated measurements of the Mo *Alfa Aesar* standard for the relevant analytical session) (Fig. 2, Table SM7). The consistency in Mo isotope composition among these samples suggests that there was limited compositional difference between the molybdenite source regions. Using data from Pietruszka et al. (2006), no correlation between mass dependent ($\delta^{97/95}\text{Mo}$) and mass independent ($\mu^{97}\text{Mo}$) Mo isotope compositions is evident (Fig. SM8).

The Mo isotopic composition of the UCC is defined here by averaging the Mo isotope compositions of glacial diamictite composites measured here. The $\mu^{97}\text{Mo}$ isotope compositions for these samples are identical within analytical uncertainties, indicating that there is currently no resolved compositional difference between crustal samples spanning much of Earth history (Fig. 2, Table SM7). The average $\mu^{97}\text{Mo}$ isotope compositions for all diamictites analyzed here is $+8 \pm 6$ 2SD (where 2SD is as above).

The basalt from La Palma has previously been analyzed for ^{182}W isotope compositions and was found to be identical to the *Alfa Aesar* W standard (Touboul and Walker, 2012). Basalts from Loihi, however, have been previously determined to have anomalous ^{182}W isotope compositions suggesting that the Loihi source includes material from the deep mantle (Mundl et al., 2017). The $\mu^{97}\text{Mo}$ composition for the La Palma basalt is $+2 \pm 6$ and for LO 02–04 is -1 ± 6 2SD (where 2SD is as above) (Fig. 2, Table SM7).

At the current level of precision, the molybdenites, diamictites, and ocean island basalts all have Mo isotope compositions that are identical within analytical uncertainties, and are not resolved from the composition of the Mo *Alfa Aesar* standard. Combining the Mo isotope compositions of these samples provides an average $\mu^{97}\text{Mo}$ value of $+3 \pm 6$ 2SD for the BSE where the uncertainty reflects the 2SD of repeated analysis of the Mo *Alfa Aesar* standard from each measurement campaign.

5. Discussion

5.1. Mo–Ru cosmic correlation

The CRE corrected $\mu^{97}\text{Mo}$ vs. $\mu^{100}\text{Ru}$ compositions of all samples analyzed here define a precise linear correlation with a slope $m_{\text{measured}} = -2 \pm 0.2$ (MSWD 0.94), and intercepts at $\mu^{100}\text{Ru}(\mu^{97}\text{Mo} = 0) = +1 \pm 4$ and $\mu^{97}\text{Mo}(\mu^{100}\text{Ru} = 0) = +1 \pm 2$ (Fig. 3; Table 2). All samples

plot within the error envelope of the linear regression of all extraterrestrial data, at the 95% confidence level, as calculated by the ISOPLOT program (Ludwig, 2003). The strong correlation, originally noted by Dauphas et al. (2004), persists for all of the iron meteorite groups and individual ungrouped meteorites examined. The slope of the Mo–Ru correlation is consistent with the $\mu^{97}\text{Mo}$ vs. $\mu^{100}\text{Ru}$ slope predicted from variable depletion in *s*-process material (e.g., presolar silicon carbide, SiC, from AGB stars) in the solar nebula ($m_{s\text{-process}} = -2.2$; Dauphas et al., 2004) (Table 2), as are the slopes of the Mo–Ru correlation when using different Mo isotopes (Table 2). The equivalence between the precisely defined $\mu^{97}\text{Mo}$ vs. $\mu^{100}\text{Ru}$ correlation from meteorite samples and theoretical prediction is consistent with variable depletions in the *s*-process component being the predominant cause of $\mu^{97}\text{Mo}$ and $\mu^{100}\text{Ru}$ isotope variability in the regions of the solar nebula sampled by these meteorites.

Samples studied here from the CC group (IVB, Chinga, Dronino, and Tishomingo) have higher $\mu^{97}\text{Mo}$ ($\sim +53$) and lower $\mu^{100}\text{Ru}$ (~ -108) than NC meteorites (IC, IIAB, IIIAB, Gebil Kamil). Strikingly, CC group meteorites analyzed here are characterized by Mo and Ru isotopic compositions that are indistinguishable from one another, within uncertainties. By contrast, the compositions of NC group meteorites vary in accordance with variable depletion in the *s*-process component. The restricted Mo and Ru isotope compositions in the CC samples indicate that the nebular feeding zone for the four chemically different parent bodies represented here originated from an isotopically homogenized region of the solar nebula characterized by substantial depletions in *s*-process components, relative to the BSE and NC meteorites. Furthermore, rapid homogenization of some materials in the CC nebular feeding area must have happened early in Solar System history, given the ^{182}W model metal segregation age for the IVB parent body of <3 Ma after CAI formation (Kruijer et al., 2014).

Not all CC group meteorites, however, evidently formed from an isotopically homogenized region of the solar nebula. For example, Poole et al. (2017) reported that members of the IIC iron meteorite group have $\mu^{94}\text{Mo}$ and $\mu^{95}\text{Mo}$ isotopic compositions consistent with the CC group, yet possess a more anomalous $\mu^{97}\text{Mo}$ isotope composition ($+82$) than IVB iron meteorites ($+49$). This indicates that there was a heterogeneous distribution of *r*- and/or *p*-process material in at least one part of the CC feeding zone. All measured CC iron

meteorites to date, however, possess the most anomalous Mo and Ru isotope compositions documented in bulk meteorite samples.

The processes causing the highly anomalous Mo and Ru isotopic compositions in CC group iron meteorites could include more vigorous thermal processing of the presolar grain precursors to the group, leading to greater *s*-process depletion, compared to precursor materials sampled by iron meteorites from the NC group. In this case, a high degree of thermal processing of nebular materials could potentially have removed all but the most thermally stable Mo and Ru isotope carriers, thereby leading to the production of more uniform, yet also more anomalous Mo and Ru isotope compositions in the CC reservoir. Thermal processing of precursor materials to carbonaceous chondrites has been previously been proposed to account for, e.g., ^{46}Ti and ^{50}Ti anomalies (Trinquier et al., 2009).

Importantly, neither NC nor CC meteorites analyzed here fall off the correlation, unlike the IID and IVB iron groups observed to plot to the left of the *s*-process mixing line in the ^{92}Mo vs. ^{100}Ru correlation reported by Fischer-Gödde et al. (2015). One possible reason for this discrepancy is the absence of CRE correction for the Mo isotope compositions in the Fischer-Gödde et al. (2015) study. While the CRE corrections for ^{97}Mo are small, Fischer-Gödde et al. (2015) used $\mu^{92}\text{Mo}$ which has larger CRE effects to define the Mo–Ru cosmic correlation. Dauphas et al. (2004) and Fischer-Gödde et al. (2015) also reported that some carbonaceous chondrites (CB, CV, CM) deviate substantially from the cosmic correlation, suggesting that the linear correlation may not be universal for all parent bodies. We suggest, however, that it may not appropriate to consider these compositions as representative of their respective parent bodies. Carbonaceous chondrites contain meteoritic components which display large Mo and Ru nucleosynthetic isotope anomalies (e.g., CAIs; Chen et al., 2010; Burkhardt et al., 2011; Fischer-Gödde et al., 2015). These components are heterogeneously distributed in the parent body, evidenced by their random distribution on the bulk sampling scale. Variable sampling of these components through the analysis of separate pieces of a meteorite for Mo and Ru analysis, could lead to isotopic variability between samples on the bulk rock scale, and therefore, an unrepresentative composition of the bulk parent body composition. Additionally, large Mo and Ru (± 30 ppm) isotope variations have been recorded in weak acid leachates of bulk rock chondrites (e.g., L1–L3 leach fractions; Burkhardt et al., 2012; Fischer-Gödde et al., 2015), raising the specter of nucleosynthetic component-specific transport of one element relative to another in the parent body. This means that originally well correlated isotopic compositions of Mo and Ru may have been modified on the local scale by aqueous alteration on the parent body. These elements may be particularly sensitive to such alteration events, given their multiple redox states and sensitivity to redox reactions. This supposition is supported by the absence of a correlation between Mo and Ru isotope compositions of acid leachates from Murchison (CM2) (Fischer-Gödde et al., 2014), and significant intra-group heterogeneity in Ru isotope data for bulk carbonaceous chondrites reported by Fischer-Gödde and Kleine (2017): CM2 ranges from $\mu^{100}\text{Ru}$ –48 to –93, CR2 ranges from $\mu^{100}\text{Ru}$ –61 to –96, CO3 ranges from $\mu^{100}\text{Ru}$ –36 to –125, and CV3 ranges from $\mu^{100}\text{Ru}$ –60 to –140, where the external reproducibility of repeated analysis of reference samples was reported as ± 13 ppm (2SD). Such isotope variability may also be present in the Mo isotope compositions of carbonaceous chondrites (Burkhardt et al., 2011), however, the precision in that study was insufficient to resolve

intra-group isotope variability. In summary, $\mu^{97}\text{Mo}$ and $\mu^{100}\text{Ru}$ isotope compositions of at least nine parent bodies are strongly correlated when using isotope data that are most likely to represent parent body compositions.

5.2. Non-carbonaceous vs. carbonaceous group isotope compositions in the Mo–Ru cosmic correlation

It has been proposed that the CC group composition reflects the mixing between materials incorporating variable *s*- and *r*-process components causing it to be offset from the NC group (Budde et al., 2016; Worsham et al., 2017). Plotting a predominately *p*-process isotope (^{94}Mo) vs. an isotope which has approximately equal contributions from the *s*- and *r*-processes (e.g., ^{95}Mo), reveals that the NC group members have Mo isotope compositions which are consistent with variable incorporation of *s*-process components (Fig. 1). The CC group, however, is slightly offset from the NC *s*-process mixing line. This finding concurs with Poole et al. (2017), which suggested that some CC meteorites (IIC, IIIF, and IVB groups) show an overall excess in *r*- and *p*-process isotopes, relative to *s*-process isotopes.

The offset of the CC group from the NC *s*-process mixing line can be determined by calculating the shift of the measured $\mu^{95}\text{Mo}$ from that predicted from a given $\mu^{94}\text{Mo}$ composition, based on the $\mu^{94}\text{Mo}$ vs. $\mu^{95}\text{Mo}$ relationship ($m = 0.59$) defined by variable *s*-process depletion in the solar nebula (Dauphas et al., 2004). This offset value is termed “CAP μ ” (M), consistent with oxygen isotope terminology:

$$M^{95}\text{Mo} = \mu^{95}\text{Mo}_{\text{measured}} - \mu^{95}\text{Mo}_{s\text{-process}}$$

where $\mu^{95}\text{Mo}_{\text{measured}}$ is the measured ^{95}Mo isotope composition of a sample and $\mu^{95}\text{Mo}_{s\text{-process}}$ is the ^{95}Mo isotope composition of an *s*-process component which falls on the NC *s*-process mixing line. On a plot of $\mu^{94}\text{Mo}$ vs. $\mu^{95}\text{Mo}$, using iron meteorite data from Worsham et al. (2017), the CC group is shifted by $M^{95}\text{Mo} = +19 \pm 14$ (where the error refers to the average error associated with meteorite compositions as defined by Worsham et al., 2017). When plotting isotopes that are similarly anomalous and have approximately equal contributions from the *s*- and *r*-processes only (^{95}Mo vs. ^{97}Mo), however, the $M^{97}\text{Mo}$ offset is smaller, $M^{97}\text{Mo} = +10 \pm 5$ (Fig. 4). The observation that the offset of the CC group is larger when plotting a *p*-process isotope than when plotting *s* and *r*-process isotopes suggests that the addition of a *p*-process component, as well as an *r*-process component, is the cause of the CC group offset from the NC *s*-process mixing line in Mo isotope space.

If the cause of the isotopic difference between the NC group and the CC group is variable incorporation of *s*-, *r*- and *p*-process nuclides, samples from the CC group should plot off the Mo–Ru slope, which reflects variable depletion in pure *s*-process material in the solar nebula. For example, with the addition of *r*- and *p*-process material, CC samples may shift off the *s*-process line towards higher and more variable Mo isotope compositions than ^{100}Ru compositions because *s*- and *r*-process Mo isotopes are plotted vs. the *s*-process only ^{100}Ru . On a $\mu^{97}\text{Mo}$ (*s*- and *r*-process) vs. $\mu^{100}\text{Ru}$ (*s*-process) diagram, however, samples from the CC group plot within error of the Mo–Ru cosmic correlation. When plotting $\mu^{94}\text{Mo}$, (*p*-process enriched isotope) vs. $\mu^{100}\text{Ru}$ or $\mu^{100}\text{Mo}$, (*r*-process enriched isotope) vs. $\mu^{100}\text{Ru}$, the

CC group compositions also overlap within the error of the *s*-process mixing line and the Mo–Ru cosmic correlation (Table 2; Fig. SM9). The $\mu^{100}\text{Mo}$ isotope compositions, however, are not corrected for CRE effects due to the poor correlation between $\mu^{189}\text{Os}$ vs. $\mu^{100}\text{Mo}$, and consequently the $\mu^{100}\text{Mo}$ compositions may shift to slightly higher $\mu^{100}\text{Mo}$ values after CRE correction. The covariation in Mo and Ru isotope anomalies in the feeding zones sampled by the present sample set requires that the nucleosynthetic carriers for Mo and Ru were housed in the same presolar carrier, or Mo and Ru were held in different presolar carriers that were similarly mixed in the nebula or thermally processed such that the similar degrees of isotope variability in both Mo and Ru isotopes resulted. Study of additional materials representative of their parent bodies, however, is needed to assess whether or not there are bodies in which the isotopic systematics of Mo and Ru were decoupled.

5.3. Silicate Earth and the Mo–Ru cosmic correlation

The different siderophile natures of Mo and Ru require that their budgets in the BSE were established during different phases of Earth's accretionary history. The MSE Mo budget of the BSE was likely set during the final ~10 to 20% of terrestrial accretion (Li and Agee, 2001; Dauphas et al., 2002c, 2004; Wade et al., 2012), whereas, the HSE budget, including Ru, was likely established by late accretion of a minimum of a final ~0.5 wt.% of Earth's mass to the mantle (Kimura et al., 1974; Chou, 1978; Bottke et al., 2010). The difference in when these budgets were established in the BSE provides a tool to investigate if there was a change in the genetic characteristics of materials added during these two different phases of accretion. If there was a significant change in the isotopic composition of the accretionary feeding zones between when Mo and Ru were accreted, here termed heterogeneous accretion, then the BSE would not plot on the Mo–Ru cosmic correlation (Dauphas et al., 2004). This is because the Mo and Ru feeding zones would presumably have different proportions of *s*-process depletion, causing a decoupling between Mo and Ru compositions in the BSE from the relationship defined by the Mo–Ru cosmic correlation. If, however, there was no change in accretionary feeding zones between the different phases of Mo and Ru accretion, then the composition of the BSE would fall on the Mo–Ru cosmic correlation because it would have the same relative proportions of *s*-process Mo and Ru that there was in the accreted material.

The Mo and Ru isotopic composition of terrestrial materials reported here ($\mu^{97}\text{Mo} +3 \pm 6$ and $\mu^{100}\text{Ru} +1 \pm 7$), tentatively presumed to define the composition of the BSE, indicate that the composition of the BSE overlaps with the Mo–Ru cosmic correlation as defined in this study, to a high level of precision (Fig. 2). This finding concurs with that of Dauphas et al. (2004). The concordance of these materials with the Mo–Ru cosmic correlation indicates that there was no significant change in the composition of materials contributing to the accessible silicate Earth before and after core formation.

Several prior studies have proposed that the Mo and Ru isotopic composition of IAB iron meteorites and enstatite chondrites are a cosmochemical match to the Earth (Chen et al., 2010; Fischer-Gödde et al., 2015; Bermingham and Walker, 2017; Dauphas, 2017; Fischer-Gödde and Kleine, 2017; Worsham et al., 2017). Using the isotopic composition for terrestrial materials obtained in this study, this observation is confirmed and members of the

IAB iron meteorite complex or enstatite chondrites remain the only meteorite groups which have the same Mo and Ru isotopic composition as the silicate mantle (Fig. 2). This suggests that the nebular feeding zones for these IAB iron meteorite parent bodies or enstatite chondrites and the latter stages of Earth accretion were genetically related.

6. Conclusions

Cosmic ray exposure corrected Mo and Ru isotope data collected for twenty-three iron meteorites strongly correlate. The equivalence between the precisely defined $\mu^{97}\text{Mo}$ vs. $\mu^{100}\text{Ru}$ relationship using measured materials and an *s*-process mixing line indicates that the predominant cause of $\mu^{97}\text{Mo}$ and $\mu^{100}\text{Ru}$ isotope heterogeneity is the variable depletion in the *s*-process component, in agreement with previous work. The overlap of all samples with the precisely defined $\mu^{97}\text{Mo}$ vs. $\mu^{100}\text{Ru}$ correlation is likely a reflection of correction for CRE effects. It may also reflect an absence of intra-sample or -group isotope heterogeneity, which is prevalent in carbonaceous chondrites because of the heterogeneous distribution of meteoritic components and variable degrees of alteration. The Mo–Ru isotope composition of the accessible silicate Earth, defined here using glacial diamictites and oceanic island basalt, falls on the refined Mo–Ru cosmic correlation. This implies that there was no significant change in the composition of materials contributing to the accessible silicate Earth before and after core formation. From the nine different parent bodies studied here, members of the IAB iron meteorite group and enstatite chondrites provide the only cosmochemical match to the Mo and Ru isotope composition of the accessible silicate Earth which suggests that these bodies shared a common nebular feeding zone during accretion.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.

$\mu^{94}\text{Mo}$ vs. $\mu^{95}\text{Mo}$ 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.)

Fig. 2. $\mu^{97}\text{Mo}$ and $\mu^{100}\text{Ru}$ data for terrestrial materials. Molybdenum data are from the present study and Ru data are reproduced from Bermingham and Walker (2017). The enstatite chondrite (Ru from Fischer-Gödde et al., 2015; Mo from Worsham et al., 2017) and CRE corrected IAB compositions for Mo and Ru are shown for comparison. Open symbols represent single analyses and filled symbols represent the mean of multiple analyses of the sample. For $\mu^{97}\text{Mo}$, the BSE composition is the average composition of samples analyzed here and the uncertainty reflects the 2SD of repeated analysis of the *Alfa Aesar* standard during the respective analytical campaign. For $\mu^{100}\text{Ru}$, the BSE composition is the average composition of samples analyzed in Bermingham and Walker (2017) and the uncertainty reflects an average of the 2SD of repeated analysis of the *Alfa Aesar* standard during the respective analytical campaigns. The light gray fields represent the 2SD of the standards measured during the relevant analytical campaigns and the dark gray fields represent the 2SE of the same standards.

Fig. 3.

The Mo–Ru cosmic correlation defined by $\mu^{97}\text{Mo}$ and $\mu^{100}\text{Ru}$ for meteorite groups and individual meteorites from this study. All data are CRE corrected, and all data were collected from the same $\sim 2\text{ cm}^2$ portions of the meteorites. The circles denote NC groups and the triangles denote CC groups, defined by Mo isotopic compositions. The solid black line is the linear regression through the data and the error envelop is indicated by the gray dotted lines. The uncertainties associated with group averages are described in Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. ^{95}Mo vs. ^{97}Mo (in ppm) for meteorites which cluster into two groups, the NC group (red) and the CC group (blue). 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). NC and CC data are from this study and Worsham et al. (2017). Carbonaceous chondrite data (gray) and Allende CAI data (green) are from Burkhardt et al. (2011). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Cosmic ray exposure corrected $\mu^{97}\text{Mo}$ and $\mu^{100}\text{Ru}$ values for iron meteorites. n refers to the number of analyses of multiple loads onto different filaments of material from the same chemistry.

Sample	n	$\mu^{97}\text{Mo}$	$\pm$	n	$\mu^{100}\text{Ru}$	$\pm$
Non-magmatic irons						
IAB						
MG-sLL (intercept)	7	0	2	6	0	3
Magmatic irons						
IIAB						
Bennett County	1	30	3	1	-39	9
Negrillos	1	24	3	2	-40	9
North Chile ^b	1	24	5	2	-47	14
Group average		26	7		-42	8
IIIAB						
Casas Grandes ^b	1	26	6	1	-59	8
Tamarugal ^b	3	23	11	1	-66	14
Trenton ^b	1	22	5	1	-51	14
Group average		24	4		-58	15
IVA						
Charlotte	1	17	5	1	-28	15
Maria Elena	1	17	6	1	-36	13
Yanhuitlan	1	23	5	2	-42	12
Group average		19	5		-36	14
IVB						
Hoba	2	56	8	2	-114	12
Skookum	4	56	3	3	-103	12
Tlacotepec ^b	3	52	4	2	-91	16
Group average		55	5		-103	22
IC						
Bendego ^b	2	24	7	2	-35	15
Ungrouped irons						
Chinga	2	55	5	1	-107	12
Dronino	1	54	6	1	-109	16
Gebel Kamil	1	4	8	1	-12	7
Tishomingo ^b	2	47	6	3	-105	14
Terrestrial samples						
BSE ^a	34	3	6	34	1	7

Uncertainties are described in the main text and SM.

^aRu data from Bermingham and Walker (2017).

b_{Ru} data obtained using the “measured oxygen reduction method”.

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Table 2

Linear regressions and intercepts of the measured isotopes for the Mo–Ru cosmic correlation and the slopes expected for mixing a pure *s*-process depleted component (terrestrial) and an *s*-process enriched component (SiC) calculated using equations from Dauphas et al. (2004).

	Slope _{predicted}	Slope _{measured}	±	y-intercept _{measured}	±	MSWD _{measured}
$\mu^{92}\text{Mo}$ vs. $\mu^{100}\text{Ru}$	−0.4	−0.5	0.1	+4	14	0.96
$\mu^{94}\text{Mo}$ vs. $\mu^{100}\text{Ru}$	−0.6	−0.7	0.2	+8	17	3.60
$\mu^{95}\text{Mo}$ vs. $\mu^{100}\text{Ru}$	−0.9	−0.9	0.1	−5	5	1.14
$\mu^{97}\text{Mo}$ vs. $\mu^{100}\text{Ru}$	−2.2	−2.0	0.2	+1	4	0.94
$\mu^{100}\text{Mo}^a$ vs. $\mu^{100}\text{Ru}$	−1.5	−1.4	0.3	+4	6	0.74

^a $\mu^{100}\text{Mo}$ data have not been corrected for CRE effects.