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The cosmic molybdenum–ruthenium isotope correlation

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Abstract

Dauphas et al. [Astrophys. J. 565 (2002) 640–644] reported molybdenum isotopic anomalies in differentiated and bulk primitive meteorites. It is shown here that these isotopic anomalies correlate with one another in exactly the way expected from nucleosynthesis theory if different regions of the nebula received different contributions of *s*-process matter synthesized in low-mass AGB stars. Furthermore, when bulk measurements are grouped by meteorite class, the molybdenum isotopic anomalies correlate with the ruthenium isotopic anomalies recently reported by Chen et al. [Lunar Planet. Sci. XXXIV (2003) #1789], again indicating a heterogeneous distribution of *s*-process matter. As molybdenum is only moderately siderophile, most of the molybdenum presently in the mantle was delivered before the completion of core formation. In contrast, because ruthenium is highly siderophile, nearly all of the mantle ruthenium was delivered by a late veneer, after the end of core formation. Thus, the fact the silicate Earth lies on the Mo–Ru cosmic correlation supports the idea that the Earth accreted homogeneously. Stated otherwise, the feeding zone of the Earth did not change drastically with time, as both the bulk of the Earth and the late veneer accreted from material from the same Mo–Ru isotopic reservoir.

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1. Introduction

With a few notable exceptions [1–3], the bulk isotopic compositions of meteorite parent bodies and the Earth are identical (neglecting the effects of radioactive decay) and it has been argued that the solar nebula was isotopically well mixed due to large

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scale turbulence and gas–dust exchange. As instrumental capabilities improve, the isotopic homogeneity of the nebula can be tested with increasing accuracy and precision. Recent studies [4–9] have addressed the issue of the homogeneity of the nebula for molybdenum, using essentially identical sample sets, but the results are contradictory. Dauphas et al. reported the molybdenum isotopic compositions of bulk undifferentiated and differentiated meteorites [4,5] as well as leachates and complementary residues of primitive meteorites [5]. They concluded that the nebula was not fully homogenized for molybdenum at a planetary scale and that variable contributions of the *s*-process nuclides could explain the observed heterogeneity. Silicon carbide grains condensed in the envelopes of AGB stars [10,11] were suggested to be the hosts of this *s*-process signature [5]. Yin et al. [6] also found isotopic anomalies for molybdenum but the results of these two studies differ in two respects. The latter authors did not observe any isotopic variation in differentiated meteorites and they observed a decoupling between *p*- and *r*-process anomalies that is inconsistent with the *s*-process interpretation of [4,5]. More recently, Chen et al. [7] confirmed the presence of Mo isotope anomalies in primitive and differentiated meteorites. These authors also observe a decoupling between the various *p*- and *r*-process anomalies. Becker and Walker [8] and Lee and Halliday [9] questioned these results, arguing that the solar nebula had been well homogenized for Mo. Because these measurements are at the edge of analytical capabilities, it is important to clearly summarize the arguments supporting the reality of the observed variations.

It is shown here that the molybdenum anomalies observed in several classes of meteorites by Dauphas et al. [4,5] correlate between the various isotopes. These molybdenum anomalies also correlate with isotopic anomalies in ruthenium [12,13], recently measured in a different laboratory (JPL-Caltech), using a different technique (N-TIMS). Furthermore, these correlations lie along lines predicted from nucleosynthetic theory [10,11,14,15]. For these reasons, it is concluded that the isotopic anomalies reported for molybdenum and ruthenium are real effects that have significance not only for our understanding of solar system formation, but also for the accretion of the Earth.

2. Molybdenum isotope correlations

Heavy elements such as molybdenum were synthesized in red giant stars and supernovae by three nucleosynthetic processes (*p*, *r*, and *s*). If the carriers of these three processes were not uniformly mixed during solar system formation or in the interstellar medium, then mass-independent isotopic heterogeneities (anomalies) would survive. Isotopic ratios can be fractionated in the solar system or during analysis in the laboratory. These variations are smooth functions of the mass number and are referred to as mass fractionation. In order to investigate isotopic anomalies, which are not a smooth function of mass number as they are caused by nuclear processes, the isotope ratios must be corrected for natural and instrumental mass fractionation. This can be done by internal normalization, using an assumed constant value for one of the isotopic ratios. In the case of molybdenum, the ratio adopted for normalization is usually $^{98}\text{Mo}/^{96}\text{Mo}$ [4–7] because these two isotopes are predominantly produced by the *s*-process while other isotopes received large contributions from the *p*- and the *r*-processes [10,11,14]. Since the observed anomalies are small, molybdenum isotopic composition is reported in epsilon units (See Fig. 1 caption for notation and Appendix A.1 for calculation of the uncertainties).

The molybdenum isotopic compositions of bulk meteorites reported by Dauphas et al. [4,5] were averaged over their independently determined meteorite groups and are plotted in Fig. 1. Because the measurements are corrected for natural and instrumental mass fractionation relative to a terrestrial standard, the molybdenum isotopic composition of all terrestrial rocks would plot at the origin of this diagram. The parameters of the correlations investigated in the present contribution were calculated using the method of York [16] implemented in Isoplot [17]. As illustrated, the isotopic anomalies are correlated with one another. Dauphas et al. [4,5] concluded that these variations reflected variable contributions of *s*-process nuclides [14]. If true, then the data points should lie on mixing lines between terrestrial and *s*-process compositions (see Appendix A.2),

$$\varepsilon_{\text{Mo}}^i = \frac{\rho_{\text{Mo}}^i - \rho_{\text{Mo}}^{98} \mu_{\text{Mo}}^i}{\rho_{\text{Mo}}^{92} - \rho_{\text{Mo}}^{98} \mu_{\text{Mo}}^{92}} \times \varepsilon_{\text{Mo}}^{92}, \quad (1)$$

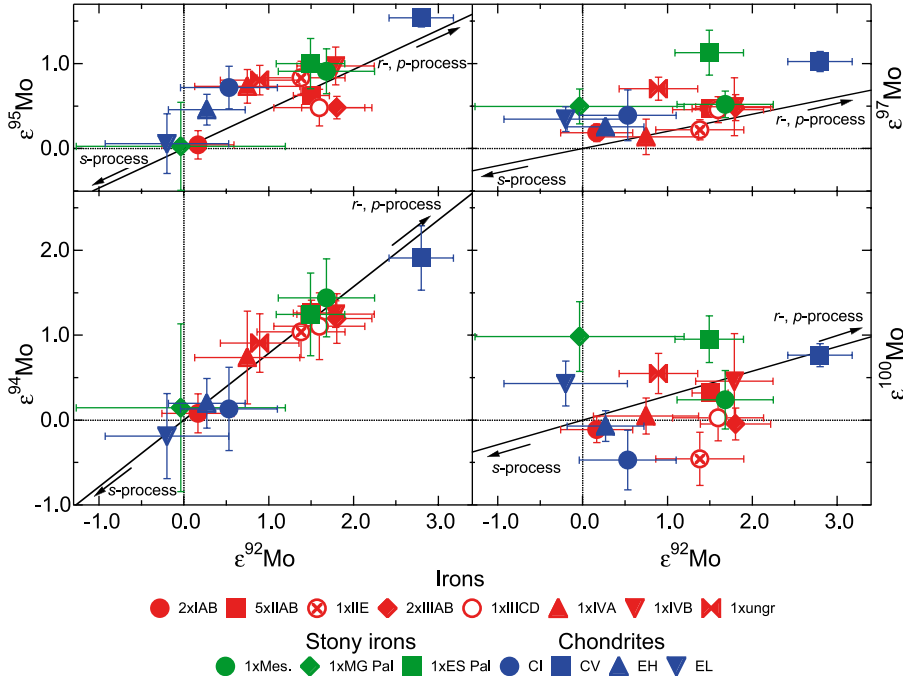


Fig. 1. Molybdenum isotopic compositions of meteorite groups [4,5] are correlated and lie along the lines [Eq. (1)] expected for mixing with *s*-process molybdenum [10,11], $\epsilon_{\text{Mo}}^i = \{[(^i\text{Mo}/^{96}\text{Mo})_{\text{sample}} / (^i\text{Mo}/^{96}\text{Mo})_{\text{terrestrial}}] - 1\} \times 10^4$. Data and *s*-process compositions (calculated from presolar silicon carbide grains from low-mass AGB stars, the major source of the *s*-process) are normalized to $\epsilon_{\text{Mo}}^{98} = 0$. For terrestrial samples, $\epsilon_{\text{Mo}}^i = 0$. Uncertainties are 2σ .

where ρ_{Mo}^i represents the *s*-process composition normalized to terrestrial composition,

$$\rho_{\text{Mo}}^i = (^i\text{Mo}/^{96}\text{Mo})_s / (^i\text{Mo}/^{96}\text{Mo})_{\oplus} - 1, \quad (2)$$

and μ_i is the mass difference relative to the normalizing pair (98 and 96),

$$\mu_{\text{Mo}}^i = (i - 96) / (98 - 96). \quad (3)$$

The pure *s*-process composition is well known from the determination of molybdenum isotope abundances in mainstream circumstellar SiC grains [10,11]. Indeed, these grains condensed in the envelopes of low-mass AGB stars, which are the dominant stellar sources for the *s*-process. From these grains it is calculated that the normalized *s*-process compositions (ρ_{Mo}^i) are -1.000 , -0.942 , -0.583 , -0.449 , -0.274 , and -0.995 for the molybdenum isotopes 92, 94, 95, 97, 98, and 100, respectively [11]. The lines in Fig. 1

correspond to addition and subtraction of a pure *s*-process component to the terrestrial composition [Eq. (1)]. As illustrated, the observed correlations are all consistent with variable depletion in *s*-process molybdenum relative to the Earth. The observed slopes for 94, 95, 97, and 100 against 92, taking into account uncertainties on both axes, are 0.75 ± 0.16 , 0.54 ± 0.22 , 0.33 ± 0.18 , and 0.46 ± 0.34 , which are indistinguishable from the predicted slopes, 0.79 ± 0.02 , 0.47 ± 0.01 , 0.20 ± 0.01 , and 0.29 ± 0.02 , respectively (2σ uncertainties). Note that the intercepts of the correlations with the *y*-axis are all equal to 0 within uncertainties (0.02 ± 0.24 , -0.02 ± 0.33 , 0.06 ± 0.25 , and -0.34 ± 0.50 , for 94, 95, 97, and 100 against 92, respectively, 2σ uncertainties).

Various authors have suggested that part [6] or all [8,9] of these variations are due to analytical artifacts but it is very unlikely that such artifacts would produce correlations that closely mimic those expected for a stellar process. Note that the discrepancies between the various laboratories cannot be ascribed to incomplete dissolution. In Refs. [4,5], iron

meteorites were dissolved in 11.2 M HCl–1.7 M HF at 130 °C for 2–3 days and Allende was typically dissolved in 9.4 M HNO₃–8.7 M HF–0.7 M HClO₄ at 130–160 °C for 3–15 days. Iron meteorites are planetary differentiates and are therefore extremely unlikely to be heterogeneous at the sampling scale. Leaching experiments were performed on Allende with acids of increasing strengths and the Mo isotopic composition remains constant, although more resistant phases are being dissolved [5].

The anomalies that were detected in differentiated meteorites were also observed during partial dissolution of the primitive meteorite Orgueil [5], but the latter anomalies are much larger. As shown in Fig. 2, the isotopic anomalies measured in these leaching experiments plot on exactly the same mixing lines. The observed slopes for ⁹⁴, ⁹⁵, ⁹⁷, and ¹⁰⁰ against ⁹² are 0.79 ± 0.03 , 0.49 ± 0.03 , 0.26 ± 0.03 , and 0.31 ± 0.04 , respectively. They are better defined than the bulk meteorite slopes because of the larger anomalies in the Orgueil leachates, and are again in complete agreement with the predictions. The variations in leaching experiments are large enough that instrumental mass fractionation can be corrected by external normalization. The externally normalized ⁹⁸Mo/⁹⁶Mo ratio [18] is in excellent agreement with *s*-process predictions. Dauphas et al. [5] suggested that the hosts of the *s*-process-enriched molybdenum

isotopic component in Orgueil leachates were presolar silicon carbides. The concentration of Mo in SiC required for explaining the anomalies observed in Orgueil leaching experiments is $33 \pm 15 \mu\text{g g}^{-1}$ [5] while the average concentration measured by synchrotron X-ray fluorescence is $31.4 \pm 7.9 \mu\text{g g}^{-1}$ [19] (note that the concentration of Mo in SiC is erroneously given as 9 ± 6 ppm in Ref. [5] because the ppm by atom abundance of Ref. [19] had been taken as ppm by weight). From a mass balance point of view, the presolar SiC grains contain enough *s*-process molybdenum to contribute to the bulk isotopic composition of meteorites at the level of the measured variations. The anomalies detected at a planetary scale in differentiated meteorites would then reflect heterogeneity in the SiC/Mo ratio of the nebula (on the order of a few tens of percent) resulting from gas–dust decoupling, sorting of different kinds of grains in the solar nebula, or inheritance of heterogeneity of the parent molecular cloud. The main difficulty with the SiC interpretation is that the largest anomalies detected during sequential digestion of Orgueil were released in a medium that is not expected to dissolve SiC (HF–HCl). The previous step in the dissolution sequence of Ref. [5] contained HNO₃ and it is possible that some of this oxidizing acid remained, allowing the dissolution of these chemically resistant grains (HNO₃ helps oxidize C while HF reacts with

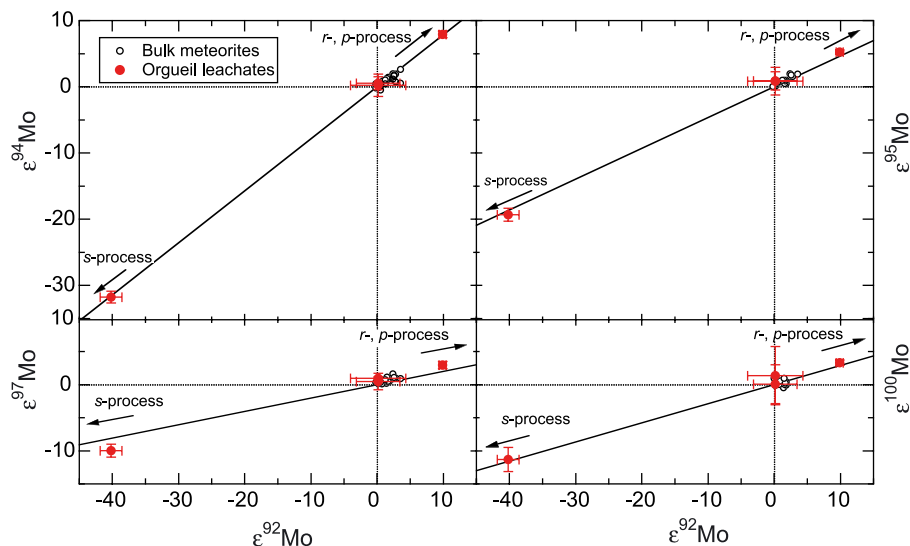


Fig. 2. Same as Fig. 1 for leaching experiments done on the primitive meteorites Orgueil (CI1) [5]. Uncertainties are 2σ .

Si). Even without complete dissolution, the Mo in the SiC grains may be mobile if the lattice is sufficiently disrupted. If the SiC interpretation is correct, then collateral isotopic anomalies should be observed for other elements that are present in significant amounts in circumstellar dust [12,13,20,21].

3. The molybdenum–ruthenium cosmic correlation

Ruthenium and molybdenum share many similarities. They are close to each other in the periodic table, they are present in similar concentrations in SiC ($31.4 \pm 7.9 \mu\text{g g}^{-1}$ Mo and $21.8 \pm 2.3 \mu\text{g g}^{-1}$ Ru [19]), their cosmic abundances are nearly identical ($0.928 \mu\text{g g}^{-1}$ Mo and $0.714 \mu\text{g g}^{-1}$ Ru in Orgueil [22]), they both have seven isotopes (92, 94, 95, 96, 97, 98, and 100 for molybdenum and 96, 98, 99, 100, 101, 102, and 104 for ruthenium), and the isotopes are formed by the same processes, p , p , s and r , s only, s and r , s and r , and r , respectively [14]. Ruthenium therefore appears to be the most promising candidate to search for isotopic effects collateral with those in molybdenum [12,13,23].

Becker and Walker [8] suggested that their finding of uniform solar system molybdenum isotopic composition was consistent with their earlier report of uniform ruthenium isotopic composition among the Earth and meteorites [24]. However, a recent study [12,13] indicates that ruthenium isotopes are not uniform in the solar system. When individual isotopic analyses of bulk meteorites are grouped by meteorite class (Fig. 3), these ruthenium anomalies [12,13] correlate with molybdenum anomalies [4,5]. Compared to the case of intercorrelations between Mo isotopes, a complication arises with molybdenum–ruthenium systematics because an assumption must be made concerning the chemical composition of the s -process end member (the Mo/Ru ratio would affect the curvature of the mixing while the Tc/Ru trapped in the grains would have affected the ruthenium isotopic composition at mass 99 from decay of s -process ^{99}Tc). The simplest assumption is that molybdenum, technetium, and ruthenium were trapped in the host phase with no chemical fractionation relative to the circumstellar gas. The expected relationship between the molybdenum and ruthenium isotopic compositions is then

(see Fig. 1 caption for ε notation and Appendix A.3 for the demonstration),

$$\varepsilon_{\text{Ru}}^{100} = \frac{\rho_{\text{Mo}}^{100} - \rho_{\text{Ru}}^{99} \mu_{\text{Ru}}^{100}}{\rho_{\text{Mo}}^{92} - \rho_{\text{Mo}}^{98} \mu_{\text{Mo}}^{92}} c \times \varepsilon_{\text{Mo}}^{92}, \quad (4)$$

where c is the curvature coefficient of the mixing relationship,

$$c = ({}^{101}\text{Ru}/{}^{96}\text{Mo})_s / ({}^{101}\text{Ru}/{}^{96}\text{Mo})_{\text{solar}}, \quad (5)$$

ρ_{Ru}^i is the s -process composition of ruthenium normalized to terrestrial composition,

$$\rho_{\text{Ru}}^i = ({}^i\text{Ru}/{}^{101}\text{Ru})_s / ({}^i\text{Ru}/{}^{101}\text{Ru})_{\oplus} - 1, \quad (6)$$

and μ_{Ru}^i is the mass difference relative to the normalizing pair (99–101),

$$\mu_{\text{Ru}}^i = (i - 101) / (99 - 101). \quad (7)$$

The curvature coefficient is estimated to be 0.15 [14]. When the curvature coefficient of the mixing is different from unity, a straight line is not expected. The linear relationship between $\varepsilon_{\text{Ru}}^{100}$ and $\varepsilon_{\text{Mo}}^{92}$ depicted in Eq. (4) results from the fact that the data points lie very close to the solar end member (the isotopic variations are quantified in parts per ten thousand, Appendix A.1). The s -process ruthenium isotopic compositions normalized to terrestrial compositions, ρ_{Ru}^{99} and ρ_{Ru}^{100} , are 0.40 and 4.71, respectively [15]. As discussed previously, the isotopic composition of ruthenium at mass 99 (ρ_{Ru}^{99}) depends on the assumption that the Tc/Ru ratio was not fractionated during condensation because part of ^{99}Ru was produced by the decay of ^{99}Tc after grain formation. Using the data available [10,11,14,15] for the molybdenum and ruthenium isotopic compositions and the ${}^{101}\text{Ru}/{}^{96}\text{Mo}$ ratio of the pure s -process, we calculate a slope between $\varepsilon_{\text{Ru}}^{100}$ and $\varepsilon_{\text{Mo}}^{92}$ of -0.44 . The observed correlation has a slope of -0.58 ± 0.28 , indistinguishable from the predicted one. This remarkable agreement confirms that the isotopic anomalies that are observed result from a variation in the s -process contribution and that the s -process was very uniform judging from the coherence of the ratios between bulk rocks and single grains. It also indicates that the Mo/Ru and Tc/Ru ratios in the host phase, presumably SiC, were not very fractionated relative to the gas

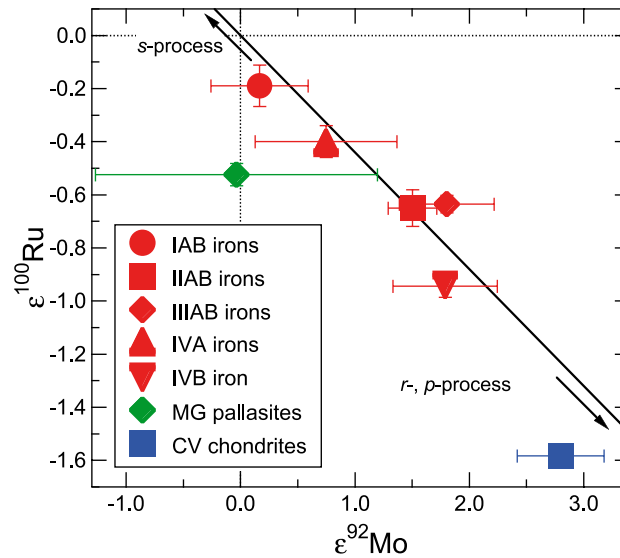


Fig. 3. Molybdenum [4,5] and Ru [12,13] isotopic compositions of meteorite groups lie along the line expected for mixing with *s*-process molybdenum and ruthenium [Eq. (4)] [10,11,14,15], $\epsilon_{\text{Ru}}^i = \{[(^i\text{Ru}/^{101}\text{Ru})_{\text{sample}} / (^i\text{Ru}/^{101}\text{Ru})_{\text{terrestrial}}] - 1\} \times 10^4$. Data and *s*-process predictions are normalized to $\epsilon_{\text{Mo}}^{98} = 0$ and $\epsilon_{\text{Ru}}^{99} = 0$. Uncertainties are 2σ .

from which the grains condensed. Kashiv et al. [19] measured the trace element composition of mainstream SiC and concluded that molybdenum and ruthenium were not fractionated relative to each other when trapped. Based on the determination of the ruthenium isotopic composition of individual SiC grains, Savina et al. [15] came to the similar conclusion that the Tc/Ru ratio was not fractionated during condensation in the envelopes of AGB stars. These results agree with our observations.

Despite contradictory evidence for part [6] or all [8,9,24] of the molybdenum and ruthenium isotopic variations, the presence of the cosmic ruthenium–molybdenum correlation further strengthens the case that the observed effects [4,5,7,12,13] are real. It is indeed very unlikely that analytical artifacts affecting different elements, in different laboratories, on different instruments, would correlate with each other and would mimic so closely a process governed by stellar physics (Fig. 4). A recent study by Chen et al. [7] has confirmed the presence of nucleosynthetic anomalies in iron and carbonaceous meteorites. Together with Ref. [6], these authors observed a decoupling between the various *p* and *r* isotopes that would be inconsistent with the *s*-process interpretation presented here. The measurements of Mo in leaching experiments show

that the *p* and *r* isotope anomalies are coupled in Orgueil and that the *s*-process must be responsible for the observed variations. The effects on the *r*-process isotopes in bulk meteorites are at the limit of detection

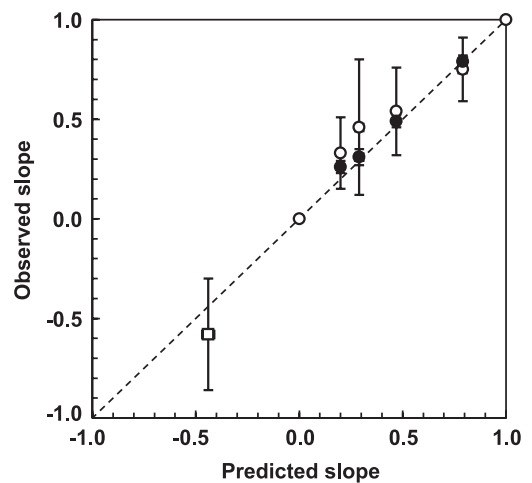


Fig. 4. Comparison between the predicted (*s*-process) and the observed slopes of the correlations investigated in the present study. Empty circles: Mo–Mo correlations in bulk meteorites (Fig. 1). Filled circles: Mo–Mo correlations in leaching experiments (Fig. 2). Empty square: Mo–Ru correlation in bulk meteorites (Fig. 3). Uncertainties are 2σ .

and some of the correlations are noisy. Although there is no indication of *p*- and *r*-process decoupling in our data on bulk meteorites, we cannot exclude the possibility of some decoupling.

4. The cosmic correlation and scenarios of planetary accretion

While secondary processes can obscure isotopic variations produced by mass fractionation, these processes have no effect on mass independent nucleosynthetic anomalies. This characteristic makes these anomalies useful tracers of genetic relationships. When used together, molybdenum and ruthenium provide important clues concerning the accretion of terrestrial planets, including the Earth. As discussed above, the isotopic anomalies for ruthenium [12,13] correlate with the molybdenum isotopic anomalies [4,5]. This correlation is a mixing line between a pure *s*-process component and the solar composition. It apparently holds for all the meteorite groups analyzed so far. The nebula can be described as a soup with circumstellar SiC grains playing the role of the salt [25]. The grains were not fully homogenized in the nebula and some regions appear to be more or less salty than others. It is very likely that the Earth as a whole lies on the cosmic correlation.

Interestingly, there is no requirement for the Earth's mantle to plot on this line. This can be illustrated by examining the molybdenum and ruthenium budget of the Earth's mantle. Because highly siderophile ruthenium was almost completely partitioned into the Earth's core during its segregation, essentially all of the ruthenium now present in the mantle was added after core formation. This is consistent with the fact that noble metals are overabundant in the Earth's mantle compared to what is expected from experimental determination of the metal/silicate partition coefficients [26]. It is also consistent with the fact that noble metals are present in chondritic proportions in the Earth's mantle [27,28]. Thus, the most widely accepted hypothesis is that ruthenium was delivered to the mantle after completion of core formation, as part of a late veneer. Other hypotheses [29,30] involving inefficient core formation during homogeneous Earth accretion have also been proposed. These hypotheses are not in contradiction with the following discussion.

In contrast to ruthenium, as molybdenum is only moderately siderophile, most of the molybdenum now present in the mantle predates core formation. Dauphas et al. [31] estimated that between 87% and 95% of the molybdenum inventory of the mantle had been delivered before core formation, the rest being accreted as part of the late veneer.

It is possible to infer the nature of the material that accreted late in Earth history by examining the elemental and isotopic composition of noble metals in the mantle. Thus, the isotopic composition of osmium, which is variable in meteorites [32] due to early fractionation of the Re/Os ratio (^{187}Re decays to ^{187}Os with a half-life of 43.5 Gy), has proven very useful for constraining the nature of the late veneer [33–35]. The conclusion of these studies is that the material accreted by the Earth in late stages was closer to enstatite or ordinary chondrites than carbonaceous chondrites, (see Ref. [36] for an alternative explanation of the mantle osmium isotopic composition). One must be cautious when trying to tie the undifferentiated meteorite samples presently available to planet forming materials. Indeed, the molybdenum and ruthenium isotopic compositions of differentiated meteorites lack, to a large extent, equivalents among primitive meteorites, suggesting that our sampling of primitive solids in the nebula is far from complete. To summarize, the great majority of mantle molybdenum was delivered before core formation while essentially all mantle ruthenium was delivered as part of a late veneer. Core formation occurred while ^{182}Hf ($t_{1/2}=9$ Ma) was still alive (2ϵ radiogenic ^{182}W in the Earth's mantle, relative to chondritic composition), within a few tens of million years of solar system formation [31,37–39]. Molybdenum and ruthenium record the isotopic composition of accreting material at different times, before and after the completion of core formation (corresponding to the first 99% and last 1% in mass of the Earth, respectively).

Various dynamical and geochemical models have advocated a change with time of the feeding zone of the Earth. If the Earth accreted heterogeneously (the materials accreted before and after core formation having different compositions), then there would be no requirement for the terrestrial mantle to plot on the molybdenum–ruthenium cosmic correlation because these two elements were delivered to the mantle at different times. On the contrary, if the Earth accreted

homogeneously, then the silicate Earth must lie on the cosmic correlation. The intercept of the cosmic correlation with the y -axis, corresponding to normal mantle molybdenum, is $\varepsilon_{\text{Ru}}^{100} = 0.14 \pm 0.47$, indistinguishable from normal mantle ruthenium (Fig. 3). Stated otherwise, the mantle by definition lies at the origin, which happens to be on the cosmic correlation. Dynamical modelling suggests that the Earth accreted from materials originating from a wide variety of heliocentric distances [40–42]. The fact that the Earth's mantle lies on the molybdenum–ruthenium cosmic correlation supports the idea that, on average, the composition of the material accreted by the Earth did not change before and after core formation. Note, however, that CI and EH-EL chondrites may both be close to the origin [5,31] and the Mo–Ru correlation alone does not alleviate all ambiguities in the accretion history of the Earth.

5. Conclusions

Planetary-scale nucleosynthetic anomalies bear important information on how the protosolar nebula formed and evolved. The molybdenum anomalies observed by Dauphas et al. [4,5] correlate between the various isotopes (Figs. 1, 2). These molybdenum anomalies also correlate with isotopic anomalies in ruthenium (Fig. 3), recently measured at JPL-Caltech [12,13]. Furthermore, these correlations lie along lines that pass through terrestrial composition and pure s -process molybdenum and ruthenium, calculated from s -process nucleosynthetic theory (Fig. 4). The most likely host phases of these anomalies are presolar silicon carbide grains condensed in the envelopes of low-mass AGB stars.

Molybdenum is moderately siderophile while ruthenium is highly siderophile. Thus, mantle molybdenum was predominantly accreted during the main stage of planetary growth while the ruthenium now present in the mantle was delivered as part of a late veneer. The isotopic compositions of mantle molybdenum and ruthenium therefore record the accretion of the Earth at different times, before and after the completion of core formation, which is thought to have occurred within a few tens of million years of solar system formation [31,37–39]. The fact that the Earth's mantle lies on the cosmic Mo–Ru correlation

may imply that the feeding zone of the Earth did not change drastically with time. The same rationale could be applied to other terrestrial planets and their satellites, including Mars and the Moon, if the molybdenum and ruthenium isotopic compositions of the silicate portions of these objects were known.

Part of the motivation for heterogeneous accretion models was to deliver the oceans and overlying atmosphere as part of a late oxidizing veneer. Recent dynamical [41] and geochemical [43] evidence support the idea that the Earth accreted wet, thus removing any requirement for a drastic change in the nature of the material accreted by our planet.

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Appendix A

A.1. Uncertainty calculations

After purification, molybdenum was analyzed by MC-ICPMS. Each sample (n measurements) was analyzed sequentially with a concentration-matched reference solution of pure Mo (m measurements),

$$Y_1 Y_2 Y_3 Y_4 Y_5 x_1 Y_6 \dots Y x Y x Y \dots Y_{m-5} x_n \\ \times Y_{m-4} Y_{m-3} Y_{m-2} Y_{m-1} Y_m, \quad (\text{A1})$$

where the Y and x denote reference and sample isotopic ratios corrected for mass fractionation by internal normalization. The average Mo isotopic composition of the sample was normalized to that of the reference solution,

$$\varepsilon = (\bar{x}/\bar{Y} - 1) \times 10^4. \quad (\text{A2})$$

The standard deviation (σ_Y) of the reference isotopic ratio was calculated based on the m repli-

cates. It was assumed to be equal to the standard deviation of the sample ratio. The standard deviations of the averages \bar{Y} and \bar{x} are therefore σ_Y/\sqrt{m} and σ_Y/\sqrt{n} , respectively. These uncertainties can then be propagated in the calculation of ε by linearization of the functional relationship [44],

$$\sigma_\varepsilon = \sqrt{1/m + 1/n} \frac{\sigma_Y}{\bar{Y}} \times 10^4 \quad (\text{A3})$$

This value takes into account uncertainties on both sample and standard ratios. As the number m of standard measurements increases, the contribution of the reference value to the total uncertainty decreases.

A.2. Demonstration of Eq. (1)

The abundance of any isotope i is the sum (subscript t for total) of the terrestrial composition (\oplus) and some excess or deficit in s -process (s),

$${}^i\text{Mo}_t = {}^i\text{Mo}_\oplus + {}^i\text{Mo}_s. \quad (\text{A4})$$

Combining this general equation with that applied to ${}^{96}\text{Mo}$, one gets,

$${}^{96}\text{Mo}_t \left[({}^i\text{Mo}/{}^{96}\text{Mo})_t - ({}^i\text{Mo}/{}^{96}\text{Mo})_\oplus \right] = {}^{96}\text{Mo}_s \left[({}^i\text{Mo}/{}^{96}\text{Mo})_s - ({}^i\text{Mo}/{}^{96}\text{Mo})_\oplus \right]. \quad (\text{A5})$$

Using the notation introduced in the caption to Fig. 1 and Eq. (2) for ρ_{Mo}^i and $\varepsilon_{\text{Mo}}^{i*}$ (where the asterisk indicates that it has not been corrected for natural and instrumental mass fractionation) the previous equation can be rewritten as,

$${}^{96}\text{Mo}_t \varepsilon_{\text{Mo}}^{i*} \times 10^{-4} = {}^{96}\text{Mo}_s \rho_{\text{Mo}}^i. \quad (\text{A6})$$

This equation can be written for any isotope, including the one used for internal normalization, ${}^{98}\text{Mo}$. Combining Eq. (A6) with the same equation applied to ${}^{98}\text{Mo}$, it follows that,

$$\varepsilon_{\text{Mo}}^{i*} / \varepsilon_{\text{Mo}}^{98*} = \rho_{\text{Mo}}^i / \rho_{\text{Mo}}^{98}. \quad (\text{A7})$$

During analysis, the isotopic composition is corrected for instrumental and natural mass fractionation. This is done by setting the ${}^{98}\text{Mo}$ ratio to a constant value ($\varepsilon_{\text{Mo}}^{98*} = 0$). This correction propagates to other isotopes through,

$$\varepsilon_{\text{Mo}}^i = \varepsilon_{\text{Mo}}^{i*} - \mu_{\text{Mo}}^i \varepsilon_{\text{Mo}}^{98*}, \quad (\text{A8})$$

where μ_{Mo}^i is the mass difference relative to the normalizing pair as introduced in Eq. (3). Combining Eqs. (A7) and (A8), it follows that,

$$\varepsilon_{\text{Mo}}^i = (\rho_{\text{Mo}}^i / \rho_{\text{Mo}}^{98} - \mu_{\text{Mo}}^i) \varepsilon_{\text{Mo}}^{98*}. \quad (\text{A9})$$

This equation can also be written for ${}^{92}\text{Mo}$. $\varepsilon_{\text{Mo}}^{98*}$ can then be eliminated, resulting in Eq. (1) of the text.

$$\varepsilon_{\text{Mo}}^i = \frac{\rho_{\text{Mo}}^i - \rho_{\text{Mo}}^{98} \mu_{\text{Mo}}^i}{\rho_{\text{Mo}}^{92} - \rho_{\text{Mo}}^{98} \mu_{\text{Mo}}^{92}} \times \varepsilon_{\text{Mo}}^{92}. \quad (\text{A10})$$

A.3. Demonstration of Eq. (4)

Mass balance equations similar to Eq. (A4) can be written for ${}^{96}\text{Mo}$, ${}^{98}\text{Mo}$, ${}^{99}\text{Ru}$ and ${}^{101}\text{Ru}$ (the normalizing pairs). After some rearrangement, it is straightforward to show that,

$$\begin{aligned} ({}^{98}\text{Mo}/{}^{96}\text{Mo})_t (y + 1) \\ = ({}^{98}\text{Mo}/{}^{96}\text{Mo})_s y + ({}^{98}\text{Mo}/{}^{96}\text{Mo})_\oplus \end{aligned} \quad (\text{A11})$$

and

$$\begin{aligned} ({}^{99}\text{Ru}/{}^{101}\text{Ru})_t (y + 1/c) \\ = ({}^{99}\text{Ru}/{}^{101}\text{Ru})_s y + ({}^{99}\text{Ru}/{}^{101}\text{Ru})_\oplus / c, \end{aligned} \quad (\text{A12})$$

where $y = {}^{96}\text{Mo}_s / {}^{96}\text{Mo}_\oplus$ quantifies the contribution of the s -process and c is the curvature coefficient [Eq. (5)]. Eliminating y from these two equations, it follows that,

$$(\varepsilon_{\text{Mo}}^{98*} - 10^4 \rho_{\text{Mo}}^{98}) / (\varepsilon_{\text{Ru}}^{99*} - 10^4 \rho_{\text{Ru}}^{99}) = c \times \varepsilon_{\text{Mo}}^{98*} / \varepsilon_{\text{Ru}}^{99*}. \quad (\text{A13})$$

See Fig. 1 caption and Eq. (6) for ρ_{Ru}^i and $\varepsilon_{\text{Ru}}^{i*}$ notations (the star indicates that it has not been corrected for natural and instrumental mass fractionation). The departure from terrestrial composition is small ($\varepsilon_{\text{Mo}}^{98*} < 10^4 \rho_{\text{Mo}}^{98}$ and $\varepsilon_{\text{Ru}}^{99*} < 10^4 \rho_{\text{Ru}}^{99}$), the previous equation can therefore be approximated to,

$$\varepsilon_{\text{Ru}}^{99*} = c \rho_{\text{Ru}}^{99} / \rho_{\text{Mo}}^{98} \times \varepsilon_{\text{Mo}}^{98*}. \quad (\text{A14})$$

Similarly to Eq. (A9), the ruthenium isotopic composition corrected for mass fractionation is,

$$\varepsilon_{\text{Ru}}^i = (\rho_{\text{Ru}}^i / \rho_{\text{Ru}}^{99} - \mu_{\text{Ru}}^i) \varepsilon_{\text{Ru}}^{99*}, \quad (\text{A15})$$

where μ_{Ru}^i is the mass difference relative to the normalizing pair as introduced in Eq. (7). Combining Eqs. (A9), (A14) and (A15) (applied to ^{100}Ru), it is then easy to show that Eq. (4) is valid,

$$\varepsilon_{\text{Ru}}^{100} = \frac{\rho_{\text{Ru}}^{100} - \rho_{\text{Ru}}^{99} \mu_{\text{Ru}}^{100}}{\rho_{\text{Mo}}^{92} - \rho_{\text{Mo}}^{92} \mu_{\text{Mo}}^{92}} c \times \varepsilon_{\text{Mo}}^{92}. \quad (\text{A16})$$

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