MOLYBDENUM–RUTHENIUM ISOTOPIC EVIDENCE FOR HETEROGENEOUS ACCRETION OF EARTH.

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Introduction: Dynamical models of planetary accretion predict that Earth's building blocks derived from a wide area of the protoplanetary disk, including some carbonaceous chondrite-like material from the outer Solar System [*e.g.*, 1]. Consistent with this, chemical models of core-mantle differentiation show that Earth most likely formed from a heterogeneous assemblage of bodies, which became increasingly oxidized and volatile-rich towards the later stages of accretion [2–4]. Until now, however, these heterogeneous accretion models have been difficult to reconcile with the isotopic record of Earth's accretion.

The bulk silicate Earth (BSE) is isotopically most similar to enstatite chondrites (EC) [5], which has led to the idea that Earth predominantly accreted from a homogeneous inner disk region with an EC-like isotopic composition [6]. This interpretation is supported by the observation that the BSE and bulk meteorites appear to plot on a single 'cosmic' Mo-Ru isotope correlation [7,8]. This is because these two elements recorded distinct phases of Earth's accretion: While the (highly siderophile) Ru in the BSE derives solely from the late veneer (*i.e.*, the last ~0.5% of material added to the mantle after cessation of core formation), the BSE's budget of (moderately siderophile) Mo was established during the last ~15% of accretion and thus predominantly represents the Moon-forming giant impactor (GI) and the late veneer (LV) [5,9]. Hence, the observed Mo-Ru correlation implies that the genetic characteristics of Earth's accretionary assemblage did not change (at least) during the final ~15% of Earth's growth history.

To investigate these apparent discrepancies between chemical/dynamical models and isotopic observations, we obtained Mo and Ru isotope data for several previously uninvestigated meteorite groups. Combined with recent literature data [8–11], this allows to re-evaluate the Mo-Ru isotope correlation in the light of the fundamental dichotomy between carbonaceous (CC) and non-carbonaceous (NC) meteorites [*e.g.*, 9], which provides important constraints on the late-stage accretionary assemblage of the Earth.

Samples and methods: We have obtained high-precision Mo and Ru isotope data (generally on the same powder) for acapulcoites/lodranites, winonaites, brachinites, ureilites, mesosiderites, aubrites, and several ungrouped achondrites. Additionally, the Ru isotope composition of an acid leachate (step 'L2', [9]) from the unequilibrated ordinary chondrite (OC) NWA 2458 was analyzed. Digestion, ion exchange chromatography, and isotope composition measurements using the Neptune *Plus* MC-ICP-MS at Münster followed our established procedures [9–11].

Results: Most analyzed samples show resolved nucleosynthetic Mo and Ru isotope anomalies, predominantly reflecting deficits in *s*-process nuclides. The observed range of anomalies is generally consistent with previously reported data; except for the acid leachate 'L2', which is characterized by much larger anomalies than observed for bulk meteorites (Fig. 1). Moreover, the brachinites stand out by showing indistinguishable Mo but variable Ru isotope anomalies. Of note, for the first time positive ε^{100}Ru anomalies (of up to 0.25ε) have been measured for two of the brachinites, corresponding to an excess of *s*-process Ru nuclides in these samples.

In a diagram of ε^{95}Mo *vs.* ε^{94}Mo, most investigated meteorites plot on the NC-line as defined by [9] and, therefore, belong to the non-carbonaceous meteorites. In contrast, two ungrouped achondrites (NWA 8548, NWA 6926) plot on the CC-line and are thus genetically linked to the carbonaceous chondrites.

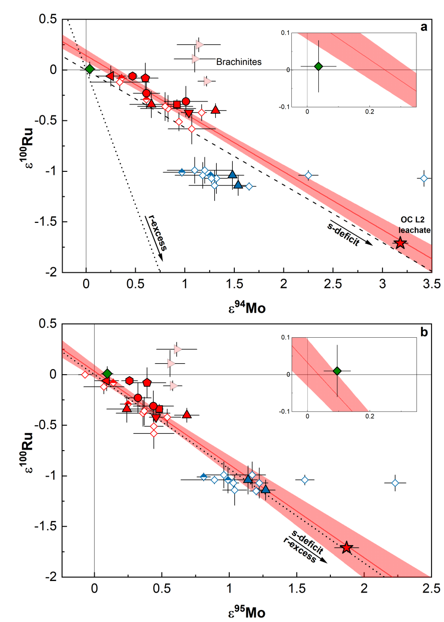

Fig. 1. NC meteorites (red) plot on a single (*s*-process) correlation line in ε^{100}Ru–ε^{i}Mo space, in excellent agreement with presolar SiC data (dashed lines, [15,16]). In diagrams that can resolve *s*- and *r*-process variations (**a**), CC meteorites (blue) and BSE (green) deviate towards an *r*-process-enriched composition.

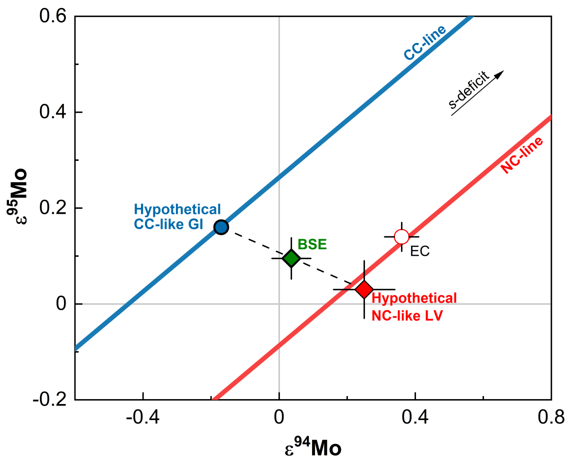

Fig. 2. Diagram of ε^{95}Mo *vs.* ε^{94}Mo illustrating a potential mixing scenario for reproducing the BSE's Mo isotope composition (green), involving an NC-like LV (red) and a CC-like GI (blue). Modified from [9].

Semi-cosmic Mo-Ru isotope correlation: Except for brachinite-like achondrites, whose Mo-Ru systematics seem to be disturbed by parent body processes, all NC meteorites (chondrites, iron meteorites, achondrites) plot on a single *s*-process correlation line in diagrams of ε^{100}Ru *vs.* ε^{i}Mo, in excellent agreement with Mo-Ru isotope systematics of presolar SiC grains and the OC leachate 'L2' (Fig. 1). Bulk CC meteorites generally follow the same trends; however, they show systematic differences in diagrams of ε^{100}Ru *vs.* $\varepsilon^{92,94}$Mo [11], in which (due to the *p*-process contribution to ^{92}Mo and ^{94}Mo) *s*- and *r*-process variations follow distinct slopes. In these diagrams (Fig. 1a), CC meteorites deviate significantly from the correlation line (defined by NC meteorites) towards an *r*-process-enriched composition. As such, the Mo-Ru isotope correlation holds only for NC meteorites, representing bodies that formed in the inner Solar System [*e.g.*, 9].

Heterogeneous late-stage accretion of Earth: Unlike previous studies, we find that (analogue to CC meteorites, albeit to a smaller degree) the BSE deviates from the NC correlation line in diagrams of ε^{100}Ru *vs.* $\varepsilon^{92,94}$Mo, while it does not in ε^{100}Ru *vs.* $\varepsilon^{95,97,100}$Mo (Fig. 1). This observation indicates the contribution of *r*-process-enriched CC-like material to the Mo budget of the BSE, as inferred previously solely based on Mo isotopes [9].

As the BSE's Mo and Ru recorded only the last ~15% of Earth's growth history, the combined Mo-Ru isotope data require that the GI or the LV had a significant contribution from CC-like material. As discussed in [9], one plausible scenario is that the LV had a pure NC-like composition, while the GI had a pure CC-like composition. In this case, the Mo isotope signature of the LV can be deduced from the *x*-axis intercepts (*i.e.*, ε^{100}Ru=0) of the NC ε^{100}Ru–ε^{i}Mo correlation lines (Fig. 1). As expected, this hypothetical composition plots on the NC-line in the ε^{95}Mo–ε^{94}Mo space, close to that of EC (Fig. 2). In this case, Earth's building material largely consisted of EC-like bodies, while some CC-like material was only added through the GI at the end of Earth's main accretion phase. Note that the BSE composition can only be reproduced if the GI had (in addition to a CC-like *r*-excess) a small *s*-excess, but was overall relatively similar to Earth's (NC-like) main building material (Fig. 2).

In an alternative scenario [9], the GI as well as the LV had mixed CC/NC compositions, meaning that these components both represent mixtures of genetically distinct materials. Such a heterogeneous LV, consisting of CC and NC materials, may resolve the apparent discrepancy between refractory and volatile (highly) siderophile elements, which suggest an NC-like or a CC-like LV, respectively [10,12–14]. In this case, refractory elements (*e.g.*, Ru, Os) would largely reflect the volatile-poor NC component, whereas volatile elements (*e.g.*, Se, Te) would predominantly derive from the volatile-rich CC component of the LV.

Conclusions: The refined Mo-Ru isotope systematics of meteorites reveal that the final stages of Earth's accretion were heterogeneous and consisted of a mixture of NC and CC materials. This observation is consistent with chemical models of core-mantle differentiation, which argue for heterogeneous accretion and the addition of more oxidized and volatile-rich material towards the end of Earth's formation [2–4]. As such, this study resolves the inconsistencies between homogeneous accretion models inferred from prior interpretations of the Mo-Ru isotope correlation, and the chemical evidence for a heterogeneous accretion of the Earth.

References: [1] O'Brien D. P. et al. (2014) *Icarus*, 239, 74-84. [2] Wade J. and Wood B.J. (2005) *EPSL*, 236, 78-95. [3] Rubie D.C. et al (2015) *Icarus*, 248, 89-108. [4] Grewal D.S. et al. (2019) *Science Advances*, 5, 1-12. [5] Dauphas N. (2017) *Nature*, 541, 521-524. [6] Dauphas N. (2014) *RSTA*, 372, 20130244. [7] Dauphas N. et al. (2004) *EPSL*, 226, 465-475. [8] Bermingham K.R. et al. (2018) *EPSL*, 487, 221-229. [9] Budde G. et al. (2019) *Nature Astronomy*, 3, 736-741. [10] Fischer-Gödde M. and Kleine T. (2017) *Nature*, 541, 525-527. [11] Worsham E. et al. (2019) *EPSL*, 521, 103-112. [12] Meisel T. et al. (1996) *Nature*, 383, 517-520. [13] Wang Z. and Becker H. (2013) *Nature*, 499, 328-331. [14] Varas-Reus M.I. et al. (2019) *Nature Geoscience*, 12, 779-782. [15] Savina M. et al. (2004) *Science*, 303, 649-652. [16] Stephan T. et al. (2019) *ApJ*, 877, 101.