THE MOLYBDENUM-RUTHENIUM COSMIC CORRELATION REVISITED: NEW CONSTRAINTS ON EARTH'S LATE ACCRETIONARY HISTORY

T. Hopp[1], G. Budde[1] and T. Kleine[1], [1]Institut für Planetologie, University of Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany; (timo.hopp@wwu.de)

Introduction: Most bulk meteorites exhibit nucleosynthetic Mo and Ru isotope anomalies, and for many of them these anomalies are correlated in a manner that is consistent with variable depletion in an *s*-process component [e.g., 1-4]. The bulk silicate Earth (BSE) lies at one end of the Mo-Ru cosmic correlation, which has been interpreted to indicate that the genetic heritage of Earth's late-stage building blocks did not change [e.g., 5,6]. Specifically, Mo as a moderately siderophile element likely records the last ~10–20% of Earth's accretion, whereas Ru, as a highly siderophile element, predominately represents the last ~0.5% of accretion (i.e., the 'late veneer') [7]. Because the BSE seems to fall on the Mo-Ru cosmic correlation, prior studies have therefore argued that the final 10–20% of Earth's mass derives from a homogeneous feeding zone with a common genetic heritage and an isotopic composition similar to those of enstatite chondrites and IAB iron meteorites [6,7]. Recent work has identified a dichotomy of Mo isotope compositions between '*non-carbonaceous'* (NC) and '*carbonaceous*' (CC) meteorites, most likely representing material from inside and outside the orbit of Jupiter, respectively [8,9]. Of note, the Mo-Ru correlation only seems to hold for NC but not for CC meteorites [10]. Moreover, the BSE's Mo isotopic composition lies between those of the NC and CC reservoirs, indicating that some of the BSE's Mo derives from the CC reservoir [8,11]. Combined, these observations suggest that, contrary to observations from previous studies [e.g., 5–7], the BSE should *not* plot on the Mo-Ru correlation.

Here we address this issue by assessing the position of the BSE with respect to the Mo-Ru correlation line. We present combined Ru–Mo isotopic data for a large set of meteorites that have not been investigated so far. These include several groups of primitive achondrites, as well as mesosiderites. In addition, an acid leachate of a primitive ordinary chondrite was investigated. Combined, these data make it possible to precisely define the Mo-Ru correlation and to assess whether or not the BSE plots on the Mo-Ru correlation defined by NC meteorites. As such, our results have important implications for understanding the late stages of Earth's accretion.

Samples and methods: We have obtained Ru and Mo isotope data for ureilites, acapulcoite-lodranites, mesosiderites, aubrites, winonaites, and four ungrouped achondrites. The Ru and Mo isotopic data were either obtained on splits from the same homogeneous powder (~2-3 g), or were separated from the same digestion. The acid leachate was prepared from ~6 g of an ordinary chondrite powder using ~40 ml of ~5 M HNO_3 at room temperature for 5 days [12]. Ruthenium and Mo were separated from the sample matrix using our established ion exchange procedures [8,13]. The Mo and Ru isotope compositions were measured using the Neptune *Plus* MC-ICP-MS at Münster, using our established protocols [4,8], and are reported in ε-units as the parts-per-ten-thousand deviations from terrestrial standard compositions. The Mo isotopic data for most of the samples are reported in [11,12].

Results: The new Ru isotopic data for primitive achondrites and mesosiderites display variable ε^{100}Ru from *ca.* -0.06 to -1.10 (Fig. 1). Of these, winonaites, aubrites, and an enstatite achondrite show only small isotope anomalies and have Ru isotopic compositions similar to that of enstatite chondrites. By contrast, ureilites, mesosiderites, acapulcoite-lodranites, and two ungrouped achondrites have Ru isotope anomalies that are similar to those of ordinary chondrites and some NC iron meteorites. Two other ungrouped achondrites, which based on their Mo isotopic composition belong to the CC group, have distinctively larger isotope anomalies of ε^{100}Ru ≈–1, similar to Ru isotope anomalies observed for most CC iron meteorites [4,6,10].

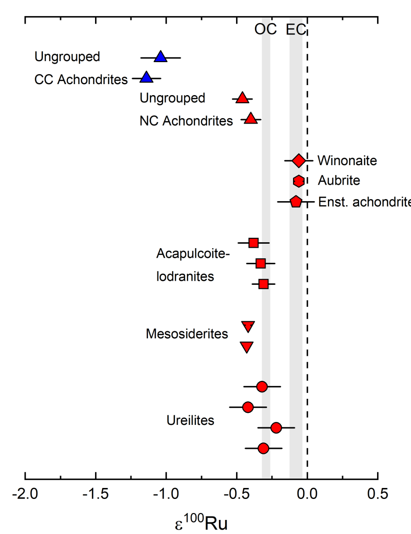

Fig. 1. Diagram of ε^{100}Ru for primitive achondrites. Thick grey lines indicate compositions of ordinary (OC) and enstatite (EC) chondrites for comparison [4,14].

The non-carbonaceous Mo-Ru correlation: Discriminating between an NC and CC heritage in Mo-Ru isotope space is only possible when Mo isotopes with a *p*-process contribution (^{92}Mo, ^{94}Mo) are used. For these, *r*- and *s*-process variations result in distinct isotope anomalies, as is evident for instance from distinct slopes of the *s*- and *r*-process mixing lines in plots of ε^{100}Ru versus ε^{92}Mo or ε^{94}Mo (Fig. 2a). This makes it possible to distinguish between CC material with its constant *r*-process excess and NC material. By contrast, if ε^{95}Mo, ε^{97}Mo, or ε^{100}Mo are used instead, the *s*- and *r*-process mixing lines are indistinguishable, and the difference between NC and CC meteorites cannot be resolved, because in plots of ε^{100}Ru versus ε^{95}Mo (or ε^{97}Mo and ε^{100}Mo), NC and CC meteorites plot on a single *s*-process mixing line (Fig. 2b). Thus, for distinguishing between an NC and CC heritage for Earth's late-stage accretionary material, the ε^{100}Ru versus ε^{92}Mo or ε^{94}Mo plots are most useful.

Most of the newly investigated meteorites belong to the NC group of meteorites (Fig. 1) and, as such, make it possible to define the Mo-Ru correlation for NC meteorites more precisely (Fig. 2). This correlation line defines an *x*-axis intercept that is resolvable from the BSE, meaning that the BSE does not lie on the extent of the Mo-Ru correlation line defined by the best fit of the NC meteorites (Fig. 2a).

Implications for Earth's late-stage accretion: A key observation from the new data is that the BSE plots to the left (and hence the *r*-process enriched side) of the Mo-Ru correlation of NC meteorites. This is consistent with the contribution of a CC component to the BSE's Mo-Ru isotope inventory. Thus, both Mo isotopes alone [11,12] and the combined Mo-Ru isotope systematics can reveal the accretion of CC material to Earth during the late stages of its growth. One possibility is that the material added to the Earth during the last ~10-20% of accretion, including the late veneer, was comprised of a constant mixture of NC and CC material. Another possibility is that the late veneer is the sole host of the CC material, but this is difficult to reconcile with the large Ru isotope anomalies observed for CC meteorites, indicating that the late veneer contained a large fraction of NC material [14]. Finally, the CC material may derive from a few large impactors added during the late-stages of Earth's accretion but before the late veneer [11]. Either way, the contribution of CC bodies to Earth's late-stage accretionary assemblage can most readily be linked to the evolution of the gas giant planets, including their growth and early migration, resulting in an inward scattering of CC bodies, and a later orbital instability, which likely led to destabilization of the CC bodies' orbits and their collision with the growing Earth [15,16].

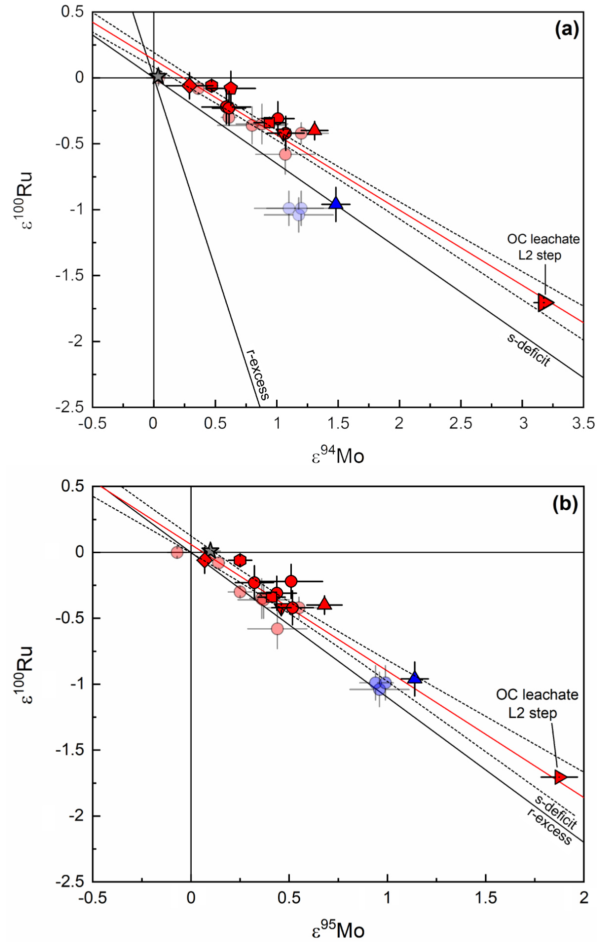

Fig. 2. Diagram of **(a)** ε^{100}Ru vs. ε^{94}Mo and **(b)** ε^{100}Ru vs. ε^{95}Mo. Red and blue symbols indicate NC and CC meteorites. Symbols of primitive achondrites according to Fig. 1. Transparent circles are chondrite and iron meteorite data [4,6,14,17]. The grey star represents the BSE [6,11]. Solid black lines are modelled s- and r-process mixing lines [18]. The solid red line represents best fits of the NC data with the 95% c.i. represented by dashed black lines.

References: [1] Dauphas N. et al. 2002. *Astrophys. J.* 565, 640-644. [2] Burkhardt C. et al. 2011. *EPSL* 312, 390-400. [3] Chen J.H. et al. 2010. *GCA* 74, 3851-3862. [4] Fischer-Gödde M. et al. 2015. *GCA* 168, 151-171. [5] Dauphas N. et al. 2004. *EPSL* 226, 465-475. [6] Bermingham K. et al. 2018. *EPSL* 487, 221-229. [7] Dauphas N. 2017. *Nature* 541, 521-524. [8] Budde G. et al. 2016. *EPSL* 454, 293-303. [9] Kruijer T. S. et al. 2017. *PNAS* 114, 6712-6716. [10] Worsham E. A. et al. (2018) *LPSC*, abstr. 2720. [11] Budde G. et al. 2018. *LPSC*, abstr. 2253. [12] Budde et al. 2019. *LPSC*, this meeting. [13] Hopp T. and Kleine T. 2018. *EPSL* 494, 50-59. [14] Fischer-Gödde M. and Kleine T. 2017. *Nature* 541, 525-527. [15] O'Brien et al. 2014. *Icarus* 239, 74-84. [16] O'Brien et al. 2014. *Icarus* 184, 39-58. [17] Render et al. 2017. *GPL* 3, 170-178. [18] Savina et al. 2004. *Science* 303, 649-652.