REFINING THE Mo-Ru COSMIC CORRELATION. K. R. Bermingham[1], E. A. Worsham[1], R. J. Walker[1], [1]Department of Geology, University of Maryland, College Park, Maryland, 20742, USA (kberming@umd.edu).

Introduction: Recent studies have highlighted the correlation between the Mo and Ru isotope compositions of some meteorite groups [1-3]. This correlation, termed the Mo-Ru cosmic correlation, is consistent with predictions from *s*-process nucleosynthetic theory [4]. As a result, the Mo-Ru cosmic correlation has been used to support the hypothesis that nucleosynthetic isotope anomalies in Mo and Ru are a result of the heterogeneous distribution of *s*-process-rich materials in the solar nebula [1-3,5]. The cause of isotopic variability remains debated, but it may be a product of selective thermal processing or incomplete mixing of presolar grains in the solar nebula [3,5]. The linear nature of the correlation, however, requires that the nucleosynthetic component hosts for these two cosmochemically dissimilar elements were somehow processed and mixed in the solar nebula in the same manner.

The compositional estimate of the bulk silicate Earth (BSE) lies at one end of this cosmic correlation (Fig 1). This is noteworthy because the Mo and Ru budgets of the BSE were likely established during different stages of planetary accretion [1]. A significant portion of the budget of Mo, a moderately siderophile element (MSE), was likely set through high pressure metal-silicate partitioning during the final ~10% of terrestrial accretion [1,6-8]. By contrast, the Ru budget in the terrestrial mantle (along with the other highly siderophile elements) was likely set after cessation of core segregation, perhaps as a result of several large impacts during the final ~0.5% of Earth's accretion [6,9]. If the relative timing of the establishment of the Mo and Ru budgets of the BSE were offset in this manner, then the fact the BSE lies on the Mo-Ru correlation suggests that there was no significant change in the composition of accreting material during the final 10% of accretion [1].

There are, however, issues with the construction of the current Mo-Ru cosmic correlation: (1) It comprises a limited number of meteorite groups and very few meteorites from less well-sampled groups and ungrouped meteorites; (2) a significant number of the data which have been used in the generation of the trend have not been coupled with monitors of cosmic ray exposure effects; (3) and, many of the Mo and Ru isotope data have not been obtained for the same or neighboring pieces of meteorite. Points (2) and (3) can potentially lead to unaccounted for, within-group heterogeneities. Such heterogeneities are known to result from uncorrected cosmic ray exposure effects [3] or incomplete homogenization of a presolar component on the < 0.8 g sample scale [10].

Here we attempt to systematically address these issues. To limit within-group heterogeneities, we have collected Mo and Ru isotopic data from the same meteorite piece and digestion solution. From these solutions, we also collected aliquots for Os isotope analysis to monitor and correct for CRE effects. Importantly, we have continued to refine our high precision analytical methods using negative thermal ionization mass spectrometry (N-TIMS). We have achieved ≤6 ppm (2SD external precision of standards) for both Ru [11] and Mo isotope systems [12].

Methods: Pieces of grouped and ungrouped iron meteorites and chips of ordinary chondrites and enstatite chondrites were provided from the Smithsonian Institution, National Museum of Natural History. Iron meteorites were digested in 8M HCl. Complete dissolution of iron meteorites was achieved after 48 hrs. Ordinary and enstatite chondrites were digested for 52 hrs using concentrated HF-HNO_3 solutions after which a slurry of silicate material remained. Incomplete digestion is not considered problematic because the metal phases which carry Mo, Ru, and Os were dissolved, and high metamorphic grade chondrites were targeted for this study. After dissolution and centrifugation, the solutions were divided into aliquots for Mo, Ru, and Os isolation and purification. Molybdenum, Ru, and Os isolation and purification chemistries were based on [11-13]. Importantly, all Mo, Ru, and Os data reported here were collected from the same fraction of dissolved sample.

The Mo and Ru isotope compositions were measured using a *Thermo Fisher Triton Plus* TIMS operated in negative mode at the Department of Geology, University of Maryland. Oxygen isotope compositions were measured *in situ* using a 10^{12} ohm resistor in one amplifier, enabling accurate corrections for in-run oxygen isotope variations and oxide interferences. This correction is critical because significant variations in O isotopic composition from run to run, and during the course of a run can adversely affect analytical precision of the Mo and Ru isotopes of interest [2,11]. Replicate analyses of *Alfa Aesar* standards indicate an external precision of ±6 ppm (2σ SD) for $^{100}Ru/^{101}Ru$ (n=18); ±5 ppm (2σ SD) for $^{97}Mo/^{96}Mo$ (n=13); and, ±5 ppm (2σ SD) for $^{189}Os/^{188}Os$ (n=16). Data are corrected for instrumental mass fractionation using the

exponential law and $^{98}Mo/^{96}Mo$, $^{99}Ru/^{101}Ru$, or $^{192}Os/^{188}Os$ as the relevant normalizing ratio.

Results: We report the $\mu^{97}Mo$ and $\mu^{100}Ru$ isotope composition of meteorites from the IAB, IIAB, IIIAB, IVA, IVB, IC, 3 ungrouped iron meteorites, and an enstatite chondrite (where the μ-notation represents the deviation in ppm from terrestrial standards).

Cosmic ray exposure effects have been documented in some iron meteorites, where reactions occurring at epithermal energies (>0.5eV) are dominant [3,12]. In our study, these effects were monitored and corrected for using ^{189}Os. Osmium-189 isotopic anomalies were identified in the majority of iron meteorite samples, with $\mu^{189}Os$ values ranging from +3.7±5 to -107±5. For example, Deport (IAB) recorded the largest yet measured $\mu^{189}Os$ = -107±5, which is associated with a reported cosmic ray exposure age of 1150±70 Ma [15]. The corresponding $\mu^{100}Ru$ = +41 for Deport is significantly offset from other IAB meteorites (e.g., $\mu^{100}Ru$ = +8.7±6 and +5.7±6.5 for Bischtube and Toluca, respectively). This shift in $\mu^{100}Ru$ is consistent with that predicted due to neutron capture reactions on ^{99}Ru and ^{101}Ru, which are used for mass fractionation (e.g., $^{99}Ru(n,\gamma)^{100}Ru$ and $^{101}Ru(n,\gamma)^{102}Ru$; $^{99}Ru_{resonance\ integral}$ ~ 160±20 barn, $^{101}Ru_{resonance\ integral}$ ~100±20 barn [3,16]). The pre-exposure Ru isotope compositions for meteorite groups were calculated by taking the intercept at the origin of the $\mu^{189}Os$ vs. $\mu^{100}Ru$ correlations.

Cosmic ray exposure effects in most Mo isotopes are smaller than those found in Ru, by virtue of the lower resonance integral of the normalizing isotopes ^{96}Mo and ^{98}Mo ($^{96}Mo_{resonance\ integral}$ ~17±3 barn and $^{98}Mo_{resonance\ integral}$ ~6.9±0.3 barn [16]). Consequently, the $\mu^{97}Mo_{Deport}$=-8.6±8.7 is in agreement with other measured IABs ($\mu^{97}Mo_{Bischtube}$ = -3.9±6; $\mu^{97}Mo_{Toluca}$=0.7±6). Effects are evident in ^{95}Mo, however, consistent with predicted effects from neutron capture on ^{95}Mo (resonance integral ~111±5 barns), where $^{95}Mo(n,\gamma)^{96}Mo$ [12].

All CRE-corrected meteorites (except the enstatite chondrite and two samples from the IAB group) display resolved negative $\mu^{100}Ru$ isotope anomalies (**Fig. 1**). There are no well-resolved isotope variations from the *Alfa Aesar* Ru standard in $^{96}Ru/^{101}Ru$, $^{98}Ru/^{101}Ru$, and $^{102}Ru/^{101}Ru$ $^{104}Ru/^{101}Ru$. These Ru isotope compositions are in good agreement with [3,5], and, therefore, are interpreted to indicate a variable *s*-process deficit as the source of Ru isotope anomolies.

Molybdenum isotope compositional data for the same samples are reported here and show variations in ^{92}Mo, ^{94}Mo, ^{95}Mo, ^{97}Mo, and ^{100}Mo, when data are normalized to $^{98}Mo/^{96}Mo$. These results are in agreement with previously published data and have been interpreted to indicate *s*-process deficits, as in [7,8,14].

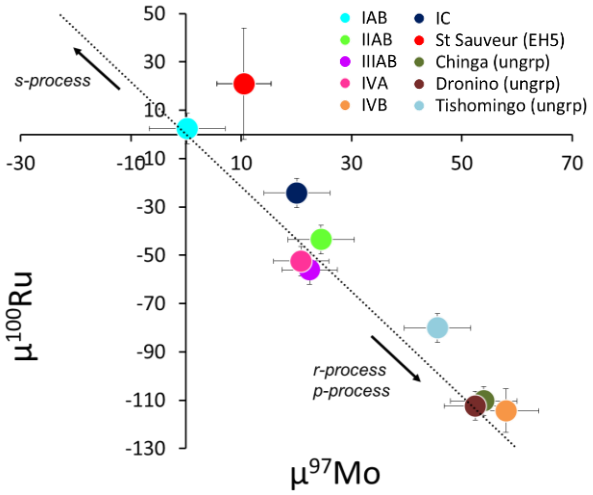

Fig. 1. The $\mu^{97}Mo$ and CRE corrected $\mu^{100}Ru$ for meteorite groups and individual meteorites from this study. The BSE value for each element is assumed to be 0. Dotted line represents a mixing line between s-process Mo and Ru [1]. Error bars represent the 2SD associated with the measurement campaign, or 2 s.e. internal error associated with a single measurement (whichever is larger).

Discussion: When combining the new $\mu^{97}Mo$ data with CRE corrected $\mu^{100}Ru$ data for grouped meteorites, the Mo-Ru correlation is retained (Fig. 1), though scatter around the correlation persists. A single line cannot be fitted through all data points. Of note, Tishomingo (ungrouped), Bendego (IC), and Saint-Sauveur (EH5) do not plot within uncertainties of the calculated s-process deficit line [1]. Deviations from linarity may be a result of the decoupling of Mo and Ru arising from either differential thermal processing the two elements in the early solar nebula by, or a modest, heterogeneous distribution of Mo and Ru (relative to each other) in the solar nebula. Finally, $\mu^{97}Mo$=10.1±4.6 of Saint-Sauveur is clearly resolved from the terrestrial standard composition. This indicates that EH chondrites likely cannot have been a dominant component of the last 10% of accreted material.

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