SIDEROPHILE GENETICS OF LATE-STAGE TERRESTRIAL ACCRETION: NEW CONSTRAINTS ON THE COMPOSITION OF EARTH'S BUILDING BLOCKS. K.R. Bermingham[1,2,a], H.A. Tornabene[1,2], B.S. Meyer[3], A. Patel[1], S.J. Mojzsis[4], R.J. Walker[2]. [1]Department of Earth and Planetary Sciences, Rutgers University, Piscataway, NJ 08854 USA. [2]Department of Geology, University of Maryland, College Park, MD 20742 USA. [3]Department of Physics and Astronomy, Clemson University, Clemson NC 29631 USA. [4]Origins Research Institute, Research Centre for Astronomy and Earth Sciences, Budapest 1121 Hungary. [a]katherine.bermingham@rutgers.edu

Introduction: Earth formed from the sequential addition of Solar System-derived bodies sourced from various heliocentric distances [1,2]. Understanding the origin of Earth, therefore, requires knowledge of when and from where in the Solar System Earth's building blocks accreted. The silicate Earth, however, has been mixed for over 4.5 billion years, owing to geodynamical processes such as differentiation and convective stirring. These processes would undoubtedly have led to the attenuation of any original discrete chemical fingerprints that may have been inherited from the building blocks. Nevertheless, mass independent nucleosynthetic (i.e., *genetic*) isotope variations that are well documented in bulk meteorites, may serve as sensitive tracers to identify specific types of building blocks which may have left a record in the mantle.

For example, the isotopic compositions (e.g., Cr, Ti, and Ni) of bulk meteorites have been applied to uniquely characterize the genetics of their parent bodies. The parent bodies of meteorites, in turn, acquired their genetic isotopic compositions as a result of the imperfect mixing of presolar grains in the protoplanetary disk [e.g., 3]. Genetic tracers further distinguish non-carbonaceous (NC) from carbonaceous chondrite (CC) materials, which may reflect formation inboard and outboard of Jupiter, respectively [4].

For several reasons, the siderophile elements Mo and Ru are particularly well suited to investigating the genetics of the building blocks participating in the latter stages of Earth's accretion. First, they are commonly used genetic tracers to discriminate among NC and CC origins of meteorites. Second, the Mo and Ru isotopic compositions of most meteorites are correlated, indicating that their genetic isotope variations are likely caused by heterogeneous distribution of the same carriers [5,6]. Third, most of the Mo and Ru present in the bulk silicate Earth (BSE) was likely added during two *different* stages of Earth's accretion, providing complementary genetic information of participating building blocks [5,7]. The dominant proportion of Mo in the BSE was likely established during the final 10 to 20 % of Earth's accretion, possibly coincident with closing stages of core segregation [5,7]. Contrariwise, Ru was likely predominantly set during the final 0.5 to 1% of Earth's accretion (i.e., *late accretion*) [7-10].

It was recently shown that Eoarchean rocks from Isua, West Greenland record mass independent enrichments in ^{100}Ru/^{101}Ru and ^{102}Ru/^{101}Ru [11], relative to estimates for the BSE [12]. Enrichments of this nature are not observed in any known bulk meteorites. That study [11] linked the anomalous Ru isotopic composition to the genetic signature of a building block component that preceded late accretion. The authors concluded that Ru added by a CC-dominated component during late accretion lowered the ^{100}Ru/^{101}Ru and ^{100}Ru/^{101}Ru to the present compositions recorded by the BSE estimate.

Determination of the mass independent Mo isotopic composition of materials similar to those characterized by Ru isotopic anomalies, as well as more precisely constraining the present BSE composition, is critical to assessing the nature of the pre-late accretion component. Molybdenum is only moderately siderophile, compared to the highly siderophile nature of Ru. Thus, late accretion likely did not modify the BSE Mo composition as much as it did Ru in the BSE.

For this study, we repeatedly analyzed a molybdenite (MoS_2) from the central Isua Supracrustal Belt (ISB) for comparison to the Ru results. This sample either formed during the Eoarchean, or later via remobilization of Mo from the surrounding Eoarchean rocks. Furthermore, we analyzed the Mo isotopic compositions of younger molybdenites from Ivigtut Greenland, Highland Valley Canada, Komaki Japan, and Bushveld South Africa.

Methods: Samples were chemically processed following [6,13]. Isotopic compositions were determined using a *Thermo Scientific Triton* thermal ionization mass spectrometer. For this study we developed a new, 3-step multi-dynamic method to improve analytical precision over our prior studies. Repeated, long-term analysis of an *Alfa Aesar* Mo standard yielded precision as shown in **Fig. 1**.

Results: The 2SE values of repeated analyses (n=6) of the Isua molybdenite are characterized by well resolved negative deviations in ^{94}Mo/^{96}Mo and ^{100}Mo/^{96}Mo, and a positive deviation in ^{97}Mo/^{96}Mo, from the 2SE of ratios for repeated analyses of the *Alfa Aesar* standard (**Fig. 1**). The ^{95}Mo/^{96}Mo is also marginally lower.

All other (younger) samples plot within their measurement uncertainties of the 2SE uncertainty of the standard (**Fig. 1**). Thus, as with Ru, the Isua Mo isotopic composition is characterized by an anomalous isotopic composition compared to younger materials.

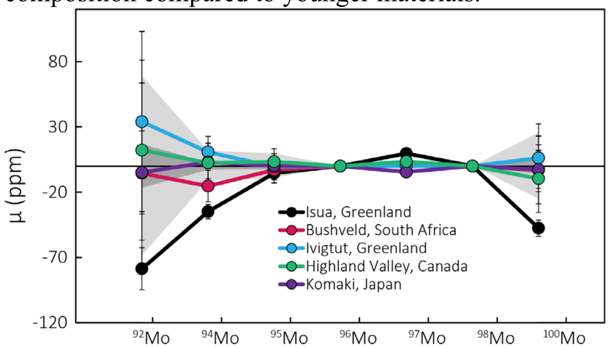

***Fig. 1.** Molybdenum isotopic compositions of Eoarchean molybdenite from Isua Greenland, and younger molybdenites from Ivigtut Greenland, Highland Valley Canada, Komaki Japan, and Bushveld South Africa. Ratios are reported in µ-notation, which is the ppm deviation relative to the Alfa Aesar Mo standard. The grey fields represent the 2SD (light) and 2SE (dark) of repeated analyses of the Mo standard.*

In a plot of μ^{94}Mo *vs.* μ^{95}Mo (**Fig. 2**), the Isua molybdenite plots within the error envelop of the CC regression line, where the NC (red) and CC (blue) lines and error envelopes were calculated using *Isoplot* and data from a compilation of bulk meteorites [e.g., 14]. Of note, the Isua molybdenite plots at substantially lower μ^{94}Mo and μ^{95}Mo than any known bulk meteorites with CC genetics. Hence, similar to the Isua Ru isotopic composition, it has an isotopic composition with currently no known cosmochemical analog.

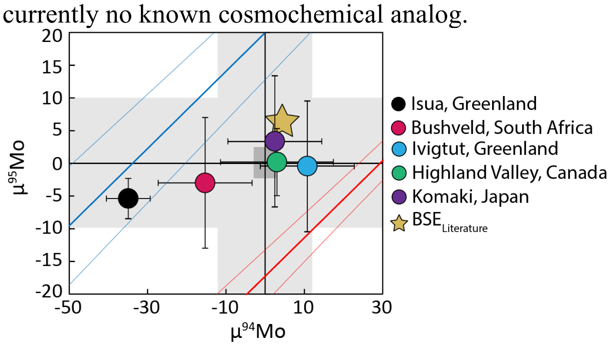

***Fig. 2.** Mo isotopic composition of molybdenites from Isua, Greenland, and younger molybdenites. The star is the estimated BSE composition compiled from literature data. Samples are reported in ppm, relative to the Alfa Aesar standard which is defined as zero. The grey fields represent the 2SD (light) and 2SE (dark) of repeat analyses of the standard.*

As noted by [15] the estimated Mo isotopic composition for the BSE, as well as these new data for the younger molybdenites, plot between the NC and CC lines (**Fig. 2**). This indicates that Earth's building blocks comprised a mix of CC and NC bodies.

Discussion: Models utilizing mixing equations were derived to determine if the Mo isotopic composition of the Isua molybdenite could be a consequence imparted by the accretion of one or more *s*-process enriched building blocks. Pure *s*-process compositions defined by presolar grains or nucleosynthesis models were used instead of reported bulk meteorite compositions, given the lack of any known meteorite with comparable Mo isotopic compositions. Heterogeneous distribution of presolar grains in the protoplanetary disk was modeled by incorporating Mo isotopic compositions of reported presolar SiC grains [5]. The Isua Mo isotopic composition can be reproduced by mixing 0.001% to 0.003% pure *s*-process material with a proto-Earth composition, and possibly a small *r*-process or currently unidentified nucleosynthetic component.

The anomalous Mo isotopic signature of the Isua molybdenite compared with the BSE indicates that Earth's building blocks, as with Ru, exhibited a range of genetic isotope compositions towards the latter stages of accretion. The apparent disappearance of an isotopically anomalous Ru signature subsequent to the Eoarchean has been attributed to late accretion of a dominantly CC component [11]. A similar explanation for the disappearance of Mo anomalies seems unlikely, given the only minor proportion of Mo added to the mantle by late accretion. An alternative explanation for one or both elements may be required.

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