**MOLYBDENUM ISOTOPES AND THE BUILDING BLOCKS OF THE EARTH.** J. Render, M. Fischer-Gödde, C. Burkhardt and T. Kleine, Institut für Planetologie, University of Münster, Wilhelm-Klemm Str. 10, 48149 Münster, Germany (jan.render@wwu.de).

**Introduction:** Chondritic meteorites are generally assumed to represent the building blocks of the Earth (and other terrestrial planets). However, which group of chondrites, or mix of chondrite groups, best represents the composition of the Earth is a matter of debate [1]. For example, while based on compositional arguments it was proposed that the Earth is best represented by carbonaceous chondrites [2], the indistinguishable O isotopic compositions of enstatite chondrites and the Earth's mantle was used to argue for the formation of the Earth from enstatite chondrites [3]. The idea of an enstatite chondritic Earth has gained significant momentum in recent years, due to the discovery of planetary-scale nucleosynthetic isotope anomalies for a variety of elements (Ca, Ti, Cr, Ni, Mo, Ru, Nd), all of which imply a very close genetic relationships between the Earth and enstatite chondrites [4-10].

While the isotopic similarity of the Earth and enstatite chondrites is undeniable, it is less clear as to whether enstatite chondrites represent the building blocks of the Earth. Mass-dependent Si isotope variations as well as differences in bulk Mg/Si between enstatite chondrites and the accessible silicate Earth seem to argue against an enstatite chondrite Earth [11-12], but these observations have less weight than the nucleosynthetic anomalies, which cannot be modified by secondary processes like core formation or mantle differentiation. Thus, definitive evidence against an enstatite chondritic Earth would come from the discovery of nucleosynthetic anomalies in enstatite chondrites relative to Earth. Hints for such anomalies can be found for Ti, where enstatite chondrites seem to show small $^{50}$Ti deficits compared to the Earth [13]. However, these small deficits can easily be balanced by addition of a small fraction of carbonaceous chondritic material, which is characterized by large $^{50}$Ti excesses [5,13]. Thus, the Ti isotope data would still permit the Earth to largely consist of enstatite chondritic material.

Significant Mo isotope anomalies in enstatite chondrites were reported by [8], however, this finding is based on only two samples and contrasts with earlier work [7]. Nevertheless, the Mo isotope anomalies in enstatite chondrites, if they exist, would effectively rule out an enstatite chondrite Earth, because all other meteorites analyzed so far are characterized by a deficit in *s*-process Mo relative to the modern terrestrial mantle. Thus, if enstatite chondrites also show an *s*-deficit, then the Earth can neither be made of enstatite chondrites nor of any combination of known chondrites. To address this issue and test the model of an enstatite chondrite Earth, we obtained high-precision Mo isotopic data for eight enstatite chondrites and three ordinary chondrites.

**Analytical methods:** Bulk pieces (>1g) of chondrites were carefully cleaned by abrasion with SiC paper and ultrasonication in Milli-Q water, before they were ground to fine powders in an agate mortar. All samples were digested in Savillex beakers on a hotplate using HF-$HNO_3$-$HClO_4$ (180°C, 7 days). Molybdenum was separated from the sample matrix using a three-stage ion exchange procedure [8]. The Mo isotope measurements were performed using the ThermoScientific Neptune *Plus* MC-ICP-MS at Münster, which is equipped with a Cetac Aridus II desolvating system. Instrumental mass bias was corrected using the exponential law and internal normalization to $^{98}$Mo/$^{96}$Mo = 1.453171 [14]. Potential isobaric interferences from Zr and Ru were quantified by monitoring $^{91}$Zr and $^{99}$Ru. Total procedural blanks were <1 ng and negligible for all samples.

The Mo isotopic data are reported in $\varepsilon^i$Mo as the parts per $10^4$ deviations from terrestrial standard values and are calculated relative to the mean composition measured for an Alfa Aesar Mo standard during each session. The precision and accuracy of the Mo isotope measurements was evaluated by repeated measurements of the BHVO-2 basalt standard from five different digestions. For this sample we obtained $\varepsilon^i$Mo~0 for all Mo isotope ratios with the following external reproducibility (2 s.d.): ±0.38 $\varepsilon^{92}$Mo, ±0.27 $\varepsilon^{94}$Mo, ±0.16 $\varepsilon^{95}$-Mo, ±0.11 $\varepsilon^{97}$Mo and ±0.20 $\varepsilon^{100}$Mo.

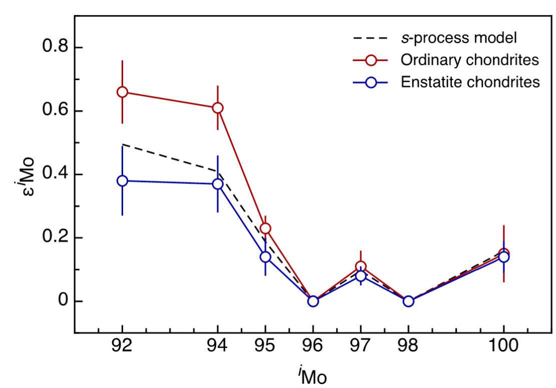


**Fig. 1.** $\varepsilon^i$Mo vs. $^i$Mo showing the average Mo isotopic compositions for enstatite and ordinary chondrites obtained in this study. Dashed line represents the expected composition for an *s*-deficit, calculated using the stellar model of [15].

**Results:** Enstatite and ordinary chondrites both display well resolved positive anomalies in $\varepsilon^{92}$Mo, $\varepsilon^{94}$Mo and $\varepsilon^{95}$Mo, while anomalies in $\varepsilon^{97}$Mo and $\varepsilon^{100}$Mo are less well resolved (Fig.1). The magnitude of the Mo isotope anomalies decreases in the order $\varepsilon^{92}$Mo >$\varepsilon^{94}$Mo >$\varepsilon^{95}$Mo >$\varepsilon^{100}$Mo >$\varepsilon^{97}$Mo and the resulting *w*-shaped pattern is characteristic for a deficit in *s*-process Mo relative to terrestrial Mo [8]. The average Mo isotope compositions of enstatite and ordinary chondrites are in excellent agreement with but more precise than previous results [8].

**Discussion:** To assess the origin of the Mo isotopic anomalies in the enstatite and ordinary chondrites it is useful to examine the data in a plot of $\varepsilon^{95}$Mo vs. $\varepsilon^{94}$Mo. In this plot, an *s*-deficit can readily be distinguished from an *r*-excess [8]. Fig. 2 shows that the Mo isotopic compositions of the enstatite and ordinary chondrites, like those of most other meteorites, are consistent with variable deficits in *s*-process Mo compared to terrestrial Mo.

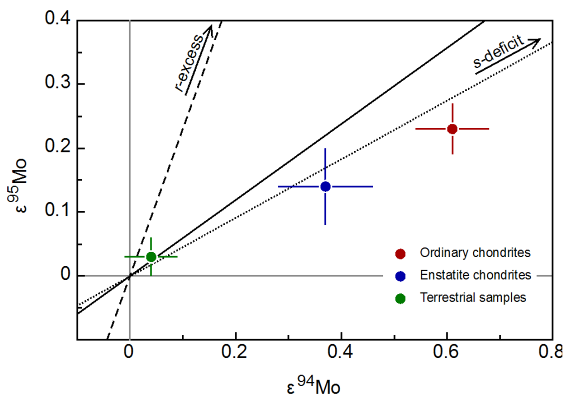


**Fig. 2.** $\varepsilon^{95}$Mo vs. $\varepsilon^{94}$Mo plot for enstatite and ordinary chondrites, and terrestrial samples analyzed in this study. Dashed line indicates expected isotope anomalies for an excess in *r*-process Mo, while the dotted line indicates an *s*-deficit. These two lines were calculated using the stellar model of [15]. Solid line represents mixing line between terrestrial Mo and *s*-process Mo as measured in SiC grains [16].

The well-resolved *s*-process Mo deficits of enstatite chondrites demonstrate that the Earth cannot be made of enstatite chondrites; the data also demonstrate that the Earth and enstatite chondrites also do not derive from a homogeneous inner disk reservoir. Instead the Earth is enriched in *s*-process matter compared to *all* chondrites (Fig. 3). Thus, no known group of chondrites, nor a combination thereof, can represent the building material of the Earth, because none of these combinations would yield the terrestrial Mo isotopic composition [8]. In fact, all meteorite classes (except IAB iron meteorites) show variable depletions in *s*-process Mo compared to terrestrial Mo (Fig. 3). This suggests that the building material of the Earth mostly derived from the inner solar system, whereas the meteorite parent bodies represent objects that always were in an orbit beyond Mars and as such contributed little material to the growing Earth. However, given that the *s*-process deficits increase in the order EC<OC<CC, there might have been radial zoning in the distribution of *s*-process matter in the solar protoplanetary disk. In this case the Earth may have been assembled from *s*-enriched material from the inner solar system mixed with chondritic material from greater heliocentric distances. Due to planetesimal scattering in the early solar system, some of this inner solar system material might have been transported into the asteroid belt; however, such material has yet to be identified. In either case, due to the *s*-process-enriched nature of the Earth compared to all groups of chondrites, caution must be exercised when using the isotopic composition of chondrites as a proxy for the isotopic composition of the Earth [10].

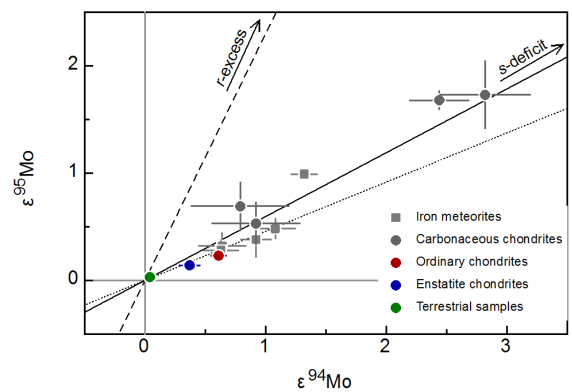


**Fig. 3.** $\varepsilon^{95}$Mo vs. $\varepsilon^{94}$Mo plot for meteorites. For definition of *r*-excess and *s*-deficit mixing lines see Fig. 2. Data for iron meteorites and carbonaceous chondrites from [8].

**References:** [1] Palme H. and O'Neill H.St.C. (2014) *Treat. Geochem. Vol. 2, 1-39*. [2] Allègre C.J. et al. (1995) *EPSL 134, 515-526*. [3] Javoy M. (1995) *Geophys. Res. Lett. 22, 2219-2222*. [4] Dauphas N. et al. (2014) *EPSL 407, 96-108*. [5] Trinquier A. et al. (2009) *Science 324, 374-376.* [6] Regelous M. et al. (2008) *EPSL 272, 330-338*. [7] Dauphas N. et al. (2002) *Geoph. Res. Lett. 29, 1084-1086*. [8] Burkhardt C. et al. (2011) *EPSL 312, 390-400*. [9] Fischer-Gödde M. et al. (2015) *GCA 168, 151-171*. [10] Burkhardt C. et al. *this conference.* [11] Fitoussi C. and Bourdon B. (2012) *Science 335, 1477-1480*. [12] Dauphas N. et al. (2015) *EPSL 427, 236-248*. [13] Zhang J. et al. (2012) *Nature Geosci. 5, 251-255*. [14] Lu Q. and Masuda A. (1994) *IJMS 130, 65-72*. [15] Arlandini C. et al. (1999) *ApJ 525, 886-900*. [16] Nicolussi G.K. et al. (1998) *GCA 62, 1093-1104*.