LUNAR ^{182}W AND THE AGE AND ORIGIN OF THE MOON.

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Introduction: The most widely accepted model for the formation of the Moon involves a giant impact onto proto-Earth near the end of Earth's accretion. Some of the most important constraints on lunar origin are provided by the similar O, Ti and W isotope compositions of the Earth and Moon, indicating that the Moon predominantly consists of material derived from the proto-Earth's mantle [1-3]. The most recent simulations of the Moon-forming impact are consistent with this [4-6]. The similar ^{182}W/^{184}W ratios of the bulk silicate Earth (BSE) and Moon are particularly important, because ^{182}W is the decay product of now-extinct ^{182}Hf. The ^{182}W/^{184}W of the bulk silicate portion of a planetary body mainly depends on the timescale and conditions of core formation, such that it is very unlikely that two distinct bodies have identical W isotope compositions. If the Moon contains a large fraction of impactor mantle material it would, therefore, be expected to have a ^{182}W/^{184}W different from that of the BSE.

Recently, small ^{182}W heterogeneities have been identified in the Earth's mantle. These have been interpreted to reflect the W isotope composition of Earth's mantle prior to addition of the late veneer [7] or to result from metal-silicate fractionation processes during accretion and differentiation of the Earth prior to the Moon-forming impact [8]. This raises the question as to whether the Moon has the same ^{182}W/^{184}W as the pre-late veneer BSE. Precisely constraining the ^{182}W/^{184}W of the Moon is difficult, however, due to cosmic-ray induced neutron capture (NC) reactions modifying ^{182}W abundances [9]. Here, we use non-radiogenic Hf isotopes as a neutron dosimeter for lunar samples [10] with the ultimate goal to identify samples devoid of NC effects. We use these samples to precisely determine the ^{182}W/^{184}W of the Moon and then use this value to constrain the age and origin of the Moon.

Samples and analytical methods: To identify samples devoid of significant neutron capture effects we investigated the non-radiogenic Hf isotope composition of 20 lunar samples including 6 KREEP-rich whole rocks, 8 low-Ti-, and 6 high-Ti mare basalts. Methods for sample dissolution and ion exchange chromatography followed [10]. Isotope analyses were conducted on the Neptune *Plus* MC-ICPMS at the University of Münster. Replicate analyses yielded 95% confidence intervals of better than 11 and 20 ppm for ^{178}Hf/^{177}Hf and ^{180}Hf/^{177}Hf (all $n \geq 5$) The ^{180}Hf/^{177}Hf and ^{178}Hf/^{177}Hf are reported as ppm deviations (µ-values) from terrestrial Hf.

Results: Most of the investigated samples show well resolved, coupled µ^{178}Hf and µ^{180}Hf variations up to +510 and -820 ppm that are typical for NC-induced effects (Fig. 1). However, four samples do not have resolved NC effects and display terrestrial µ^{178}Hf and µ^{180}Hf. The same samples also show no resolvable ^{149}Sm anomalies [10]. In these samples NC-induced effects, therefore, seem to be largely absent, making them ideal targets for determining the ^{182}W/^{184}W of the Moon.

Tungsten isotope data are available for metals of most of the investigated samples [1]. The metals contain virtually no Ta and hence no Ta-derived cosmogenic ^{182}W. In samples with significant fluence of secondary neutrons, the ^{182}W/^{184}W of the metals can nevertheless be modified by neutron capture on W isotopes themselves. This is illustrated in Fig. 1, where ε^{182}W of the metals is plotted against μ^{180}Hf of the corresponding whole-rock. There is a slight inverse correlation between ε^{182}W and μ^{180}Hf, demonstrating that samples with significant NC-induced variations in Hf isotopes tend to have slightly lower measured ε^{182}W compared to samples having terrestrial μ^{180}Hf. The largest offset is observed for KREEP-rich sample 65015, which exhibits a large NC-induced ^{180}Hf shift and a low measured ε^{182}W of *ca.* –0.9. It is noteworthy that even samples with only modest NC-induced Hf isotope variations (i.e., μ^{180}Hf<100) tend to have slightly lower ε^{182}W than samples devoid of any NC-induced isotope shifts (Fig. 1).

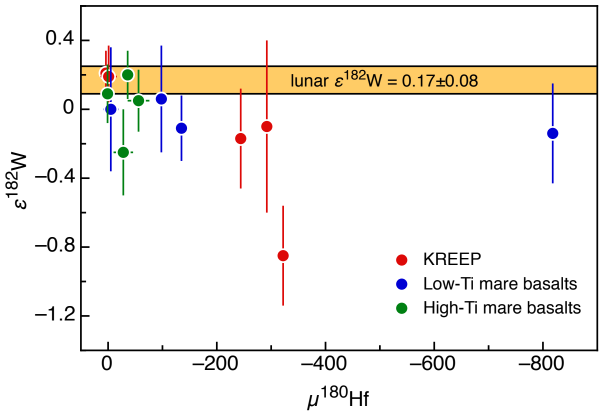

Figure 1. ε^{182}W *vs.* μ^{180}Hf for lunar samples. The lunar ε^{182}W is the mean of the four samples having no NC-induced ^{180}Hf anomalies.

Discussion: *$^{182}W/^{184}W$ of the Moon.* As is evident from the ε^{182}W *vs.* μ^{180}Hf correlation (Fig. 1), the W isotope composition of the Moon can only be determined on samples devoid of any resolved NC-induced effects, even for lunar metals. On the basis of our non-radiogenic Hf isotope data we identified four such samples. For two of these samples—68115 and 68815— precise W isotope data are available, based on replicate analyses [1]. The mean ε^{182}W of these two samples is 0.20±0.08 (95% c.i., n=8). Mare basalts 12004 and 74255 also show no resolved NC-induced Hf isotope effects and their ε^{182}W is indistinguishable from albeit less precise than that of the two KREEP-rich samples [1]. Including the two mare basalts in the calculation of the mean results in ε^{182}W = +0.17±0.08 (95% c.i.), which we interpret as the current best estimate for the ε^{182}W value of the bulk silicate Moon.

Formation of the Moon from terrestrial mantle material. The ε^{182}W value of the bulk silicate Moon of +0.17±0.08 determined in the present study is in remarkable agreement with the small ^{182}W excesses identified in samples from the Isua supracrustal belt [7] and in some komatiites [8]. Willbold et al. [7] have argued that the elevated ε^{182}W of +0.13±0.04 they determined for Isua samples reflects the W isotope composition of the BSE before addition of the late veneer. That the bulk silicate Moon has the same ε^{182}W as the inferred pre-late veneer BSE supports this interpretation and suggests that the Moon almost entirely consists of material derived from the Earth's mantle.

Alternatively, ε^{182}W of the bulk silicate Moon is a residual signature of the W isotope composition of the impactor mantle. The composition of the impactor is not known, and so any such scenario is inherently difficult to test. However, it is highly unlikely that any impactor-dominated mixture with proto-Earth's mantle fortuitously results in the ε^{182}W of the Moon similar to that of the pre-late veneer BSE. This would require a W isotope composition of the impactor mantle very close to that of the proto-Earth's mantle, which is very unlikely given that these two bodies presumably had very different accretion and core formation histories [11].

The most straightforward interpretation of the similar ε^{182}W of the pre-late veneer BSE and the bulk silicate Moon is that the Moon almost entirely consists of terrestrial mantle material. This is consistent with the similar Ti and O isotope compositions of the Earth and Moon, but adds another dimension to the genetic link between the Earth and Moon. While the similarity in Ti and O isotope compositions could be accounted for if the impactor formed from the same type of nebular material and the same mix of nucleosynthetic components—as might have been the case if the impactor accreted at a similar heliocentric distance as the Earth—such a scenario cannot account for the similarity in ε^{182}W.

Age of the Moon. Touboul et al. [1] argued that the similar ε^{182}W of the BSE and bulk silicate Moon require formation of the Moon after extinction of ^{182}Hf, *i.e.*, >50 Ma after formation of the solar system. Later studies suggested that the ^{180}Hf/^{184}W ratios of the BSE and bulk silicate Moon are identical and that, therefore, the Moon may have formed 'early', at ~30 Ma after CAI formation [12, 13]. Here we argue that it is highly unlikely that the bulk silicate Moon has exactly the ε^{182}W of the pre-late veneer BSE, because lunar core formation had a significant effect on the Hf/W ratio of the bulk silicate Moon. It is now well established that the Moon has a small core. Simple mass balance indicates that the Hf/W ratio of the bulk Moon is about half that of the bulk silicate Moon [14]. Thus, making the Moon predominantly out of Earth's mantle material—as is required by the identical ε^{182}W values of the BSE and bulk silicate Moon—is difficult when at the same time the bulk Moon must have a Hf/W ratio only half that of the Earth's mantle. This would require mixing in some metal, presumably from the impactor core, but doing so would affect the W isotope composition of the Moon and move it away from the composition of the Earth's mantle. Thus, generating identical ε^{182}W and Hf/W values for the bulk silicate Moon and BSE is very difficult. The most straightforward interpretation, therefore, is that the Moon formed late, after extinction of ^{182}Hf, because then any Hf/W fractionation during lunar core formation would have had no effect on ε^{182}W.

References: [1] Touboul M. et al. (2007) *Nature*, *450*, 1206-1209. [2] Wiechert U. et al. (2001) *Science*, *294*, 345-348. [3] Zhang J.J. et al. (2012) *Nature Geoscience*, *5*, 251-255. [4] Canup R.M. (2012) *Science*, *338*, 1052-1055. [5] Cuk M. and Stewart S.T. (2012) *Science*, *338*, 1047-1052. [6] Reufer A. et al. (2012) *Icarus*, *221*, 296-299. [7] Willbold M. et al. (2011) *Nature*, *477*, 195-199. [8] Touboul M. et al. (2012) *Science*, *335*, 1065-1069. [9] Leya I. et al. (2000) *EPSL*, *175*, 1-12. [10] Sprung P. et al. (2013) *EPSL*, *380*, 77-87. [11] Nimmo F. et al. (2010) *EPSL*, *292*, 363-370. [12] Albarede F. (2009) *Nature*, *461*, 1227-1233. [13] Münker C. (2010) *GCA*, *74*, 7340-7361. [14] Rai N. and van Westrenen W. (2014) *EPSL*, *388*, 343-352.