HIGH-PRECISION ^{182}W COMPOSITION OF THE MOON: CONSTRAINTS ON LATE ACCRETION AND LUNAR FORMATION MODELS. T.S. Kruijer, T. Kleine, M. Fischer-Gödde, P. Sprung. Institut für Planetologie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Strasse 10, 48149 Münster, Germany (Correspondence: thomas.kruijer@wwu.de).

Introduction: By the most accepted theory of lunar origin, a giant impact on Earth led to the formation of the Moon, and also initiated the final stage of Earth's core segregation [1]. Core formation should have removed the highly siderophile elements (HSE) from the bulk silicate Earth (BSE), yet HSE abundances are higher than expected [2]. One explanation for this overabundance is that a 'late veneer' of primitive material was added to the BSE after the core formed. To test this hypothesis, W isotopes are useful because (1) the late veneer material had different ^{182}W/^{184}W than the BSE, and (2) proportionally more material was added to the Earth than the Moon [2]. Thus, if a late veneer occurred, the ^{182}W compositions of the BSE and Moon must be different. Moreover, the giant Moon-forming impact would have likely also created ^{182}W differences because impactor mantle and core material with distinct ^{182}W/^{184}W mixed with proto-Earth during the giant impact.

However, determining the lunar ^{182}W/^{184}W is complicated by cosmic ray–induced secondary neutron capture reactions. These reactions not only involve ^{182}W production via neutron capture on ^{181}Ta, but also neutron capture–induced burnout of ^{182}W. Hence, the previously measured ε^{182}W=0.09±0.10 (2 s.e.) (ε^{182}W is the parts per 10^4 deviation from the ^{182}W/^{184}W of the present-day BSE) for the Moon [3], which was based on Ta- and thus cosmogenic-^{182}W-free lunar metals, may have been lowered by ^{182}W-burnout, and therefore only provides a minimum estimate. Without a suitable neutron dosimeter, the previously measured ε^{182}W values of the lunar metals had been corrected using cosmic ray exposure ages, but these do not directly measure the neutron dose that affects W isotopes. Furthermore, the analytical precision of the previous studies was >10 ppm (2 s.e.) for individual samples, which is insufficient to resolve a small ^{182}W anomaly of the Moon. Consequently, it has been unclear until now whether the Moon and present-day BSE differ significantly in ε^{182}W.

To precisely determine the ε^{182}W of the Moon, we analyzed KREEP-rich samples using improved techniques for high-precision W isotope measurements by MC-ICPMS [4] combined with a new approach for quantifying cosmogenic ε^{182}W variations using Hf isotopes [5].

Results: The KREEP-rich samples exhibit a well-defined ε^{182}W–ε^{180}Hf correlation (Fig. 1), reflecting neutron capture-induced modifications of both Hf and W isotope compositions. The pre-exposure ε^{182}W (*i.e.*, unaffected by neutron capture) of KREEP is defined either by the intercept of the ε^{182}W–ε^{180}Hf correlation (Fig. 1) or by samples lacking significant ε^{180}Hf anomalies (14321, 68115, 68815) and is +0.28±0.04 (95% conf.). We interpret this value to represent that of the bulk silicate Moon, because lunar differentiation at ~4.4 Ga [6] postdates ^{182}Hf extinction. This is consistent with previously reported ε^{182}W values for non-irradiated mare basalts [3], which are indistinguishable from the KREEP value determined here.

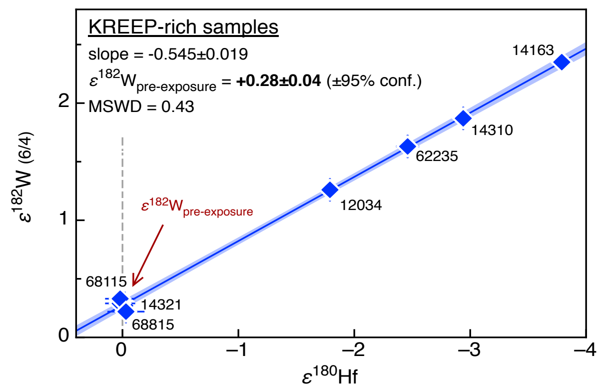

Fig. 1: ε^{182}W *vs.* ε^{180}Hf for KREEP-rich samples. Solid line shows a best-fit linear regression through the data points, which provides the pre-exposure ε^{182}W at ε^{180}Hf=0. Error bars indicate external uncertainties (95% conf. or 2 s.d.).

Discussion: The well-resolved ^{182}W excess of the Moon compared to the present-day BSE places important constraints on the occurrence of the late veneer as well as on its mass and timing. The mass and composition of the late veneer is constrained through absolute and relative HSE abundances and ratios of S, Se and Te in Earth's primitive mantle [2,7,8]. On this basis, the late veneer likely has a carbonaceous chondrite-like composition with a minor fraction of iron meteorite-like material [8], corresponding to ~0.35 % of Earth's mass. Mass balance considerations imply that the addition of a late veneer of this composition lowered the ε^{182}W of the BSE by ~0.15 to ~0.40 (Fig. 2). A late veneer composed exclusively of known groups of chondrites would have resulted in an only slightly smaller but still consistent shift of ~0.1 to ~0.3 ε^{182}W [9,10]. The corresponding effect of the late veneer on the lunar ε^{182}W is negligible, given that the mass fraction added to the lunar mantle was an order of magnitude smaller than that added to the Earth [2]. Therefore, the ε^{182}W difference between the Moon and the present-day BSE of +0.28±0.04 can be entirely accounted for by the addition of ^{182}W-depleted material to the BSE during late accretion, with a total mass consistent with that derived from the HSE abundances in Earth's mantle [2,8] (Fig. 2). This implies that previously accumulated HSEs in the Earth's mantle had been sequestered into Earth's core during the giant impact [2], demonstrating that the entire late veneer was added *after* the giant impact and the final stages of core segregation. These ^{182}W results, therefore, provide independent evidence for the late veneer hypothesis by demonstrating that the HSE abundances in the Earth's mantle were established by addition of primitive material after the Earth's core formed.

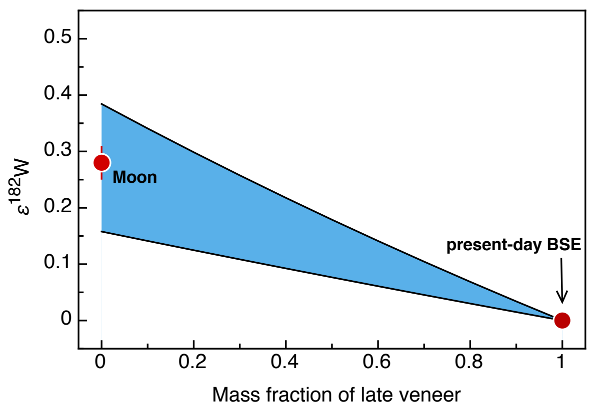

Fig. 2: ε^{182}W versus mass fraction of late-accreted material on Earth. The uncertainty on the pre-late veneer ε^{182}W of the BSE mainly results from the uncertainty on the W concentration of the BSE (13±5 ppb).

The above data suggest that the pre-late veneer BSE and the Moon have an indistinguishable ε^{182}W. This implies that there is no resolvable radiogenic ^{182}W difference between the Moon and the Earth, probably because the Moon formed late [3,6]—when ^{182}Hf was already extinct—or because the BSE and Moon have very similar Hf/W. In addition, the data suggest that the giant impact did not induce a ^{182}W anomaly in the Moon. This is not easily explained because the giant impact would have modified the ε^{182}W of proto-Earth's mantle (1) by adding impactor mantle material, which presumably had distinct ε^{182}W, and (2) through the (partial) equilibration of the impactor core with the proto-Earth's mantle. As such, the ε^{182}W of the proto-Earth's mantle before the giant impact was most likely different from its post-giant impact value (Fig. 3), meaning that the Moon and the post-giant impact Earth's mantle would probably not have a homogeneous ε^{182}W. Moreover, the lunar accretion disk would have contained W-rich but ^{182}W-depleted impactor core material, which consequently generated a significant shift in the W isotope composition of the proto-lunar material. Thus, while specific impactor and proto-Earth compositions and impact conditions that

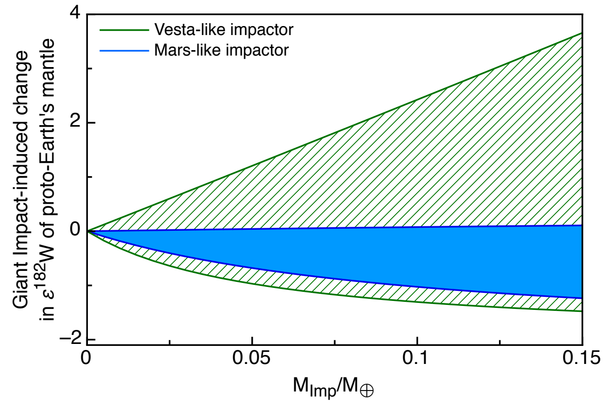

Fig. 3: Effect on the ε^{182}W of the proto-Earth after mixing variable amounts ($M_{Imp}/M_{\oplus}$) of impactor material (mantle and core) with the proto-Earth's mantle, *i.e.*, after the material forming the Moon had already been ejected.

match the ^{182}W compositions of the pre-late veneer BSE and the Moon can be identified [11], it is far more likely to produce significant Earth-Moon ε^{182}W differences, even if the Moon predominantly consists of proto-Earth material. Consequently, it would take extraordinary circumstances to generate the Earth-Moon ε^{182}W homogeneity through mixing of proto-Earth and impactor material during the giant impact.

The ε^{182}W homogeneity might be accounted for by post-giant impact equilibration between the lunar accretion disk and the Earth's mantle [12], but this would be difficult for a refractory element like W [13]. Other possibilities for the ε^{182}W homogeneity might be that the Moon was formed through impact-triggered fission from a fast-spinning proto-Earth [14] or that efficient equilibration occurred during the collision of two half-Earths [15]. However, in both scenarios it still has to be evaluated as to whether equilibration between impactor and proto-Earth would be possible prior to ejection of the proto-lunar material. Either way, the Earth–Moon ^{182}W homogeneity constitutes a fundamental constraint on any successful model of lunar origin.

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