HIGH-PRECISION ^{182}W MEASUREMENTS ON MARE BASALTS: CONSTRAINTS ON THE ORIGIN AND DIFFERENTIATION OF THE MOON. T.S. Kruijer & T. Kleine. Institut für Planetologie, University of Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany (thomas.kruijer@wwu.de).

Introduction: The Moon likely formed from hot debris produced in a giant impact on the proto-Earth [e.g., 1]. After this event, the Moon underwent large-scale differentiation, which probably involved the crystallisation of a lunar magma ocean [e.g., 2,3]. These processes can be very well studied using the short-lived ^{182}Hf-^{182}W system ($t_{1/2}$= 8.9 Myr), because (i) the Moon may exhibit an ^{182}W anomaly inherited from the impactor, and (ii) and early crystallisation of the lunar magma ocean would have led to ^{182}W heterogeneities within the Moon [e.g., 5-8]. However, precisely determining ^{182}W compositions of lunar samples is severely complicated by cosmic ray–induced neutron capture on Ta, leading to the production of ^{182}W and large cosmogenic ^{182}W variations among lunar samples [e.g., 9]. Two recent studies have precisely determined the pre-exposure ^{182}W value of KREEP-rich samples by analysing specimens devoid of neutron capture effects. These studies have shown that KREEP has a 27±4 ppm ^{182}W excess over the modern bulk silicate Earth (BSE) [7,8]. This finding raises the question as to whether other lunar reservoirs—such as the mare basalt sources—exhibit similar or larger ^{182}W excesses. Addressing this question is important not only for deducing the timescales of lunar differentiation but also for precisely determining the ^{182}W value of the bulk Moon.

Determining the ^{182}W signatures of mare basalts is challenging, because due to their high Ta/W, neutron capture effects may be significant even for weakly irradiated samples. One way to overcome this problem would be to analyse metal samples [5,6], but given the low abundance of metals in mare basalts, very large sample masses must be processed to obtain sufficient W for precise isotope analysis. Here we use a different approach and utilize high-precision Hf isotope and Ta/W ratio measurements to empirically quantify the effects of secondary neutron capture on measured ^{182}W compositions. We report results for low-Ti mare basalt 12004, high-Ti mare basalt 74255, and lunar meteorite Kalahari 009; the analyses of additional mare basalts and determination of the Ta/W ratios are underway.

Methods: After digestion of the lunar samples (~0.5 g) in HF-HNO_3 (2:1), and taking aliquots determining Ta/W ratios, Hf and W were separated by ion exchange chromatography [7]. The Hf and W isotope compositions were measured on a ThermoScientific Neptune *Plus* MC-ICPMS at Münster [7], and reported in ε-units as the parts per 10^4 deviation from terrestrial standard values. For quantifying the neutron fluence of samples with high Ta/W, obtaining precise Hf isotope data (~5 ppm, 95% conf.) was essential. This was achieved using longer measurements (200 cycles of 4.2s) and by measuring each sample ≥5 times.

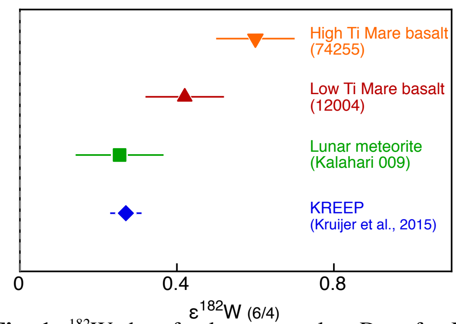

Fig. 1: ^{182}W data for lunar samples. Data for KREEP are from [7].

Results: All investigated samples exhibit $\varepsilon^{182}W$ distinctly higher than the terrestrial value (Fig. 1,2), consistent with [7,8]. In agreement with its very low exposure age (~230 yr) [10], Kalahari 009 shows no resolvable Hf isotope anomaly, and its $\varepsilon^{182}W$ is in excellent agreement with the value previously obtained for KREEP [7,8]. The low- (12004) and high-Ti (74255) mare basalts both have slightly elevated $\varepsilon^{182}W$ (Fig. 1), but also show small Hf isotope anomalies, indicative of small neutron capture effects (Fig. 2).

Discussion: *Homogeneous* $\varepsilon^{182}W$ *in the bulk silicate Moon*. As a result of neutron capture, lunar samples exhibit a positive correlation between $\varepsilon^{182}W$ and $\varepsilon^{180}Hf$ × (Ta/W). Samples having the same pre-exposure $\varepsilon^{182}W$ should then plot on one single correlation line, whose intercept defines the pre-exposure $\varepsilon^{182}W$ of this suite of samples. Fig. 2 shows that all investigated samples—including KREEP-rich samples, mare basalts and lunar meteorite Kalahari 009—plot on a single, well-defined $\varepsilon^{182}W$ and $\varepsilon^{180}Hf$ × (Ta/W) correlation. These samples are, therefore, characterised

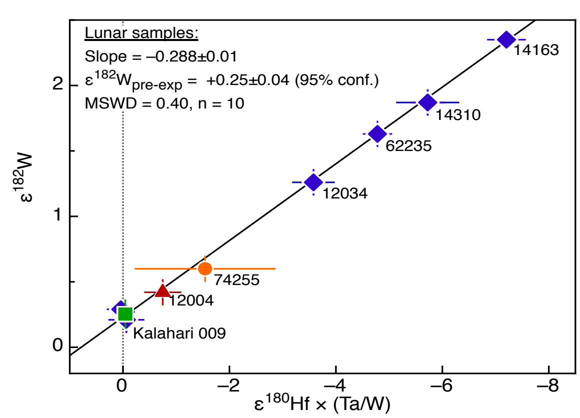

Fig. 2: $\varepsilon^{182}W$ *vs*. $\varepsilon^{180}Hf$ × (Ta/W) for lunar samples, with Ta/W ratios from [5,12].

by a common pre-exposure ε^{182}W of +0.25±0.04 (95% conf.) as obtained from the intercept of the correlation line. Thus, our data do not reveal a resolvable ^{182}W difference between lunar basalts and KREEP, suggesting that the ε^{182}W value of +0.25±0.04 is representative for the bulk silicate Moon.

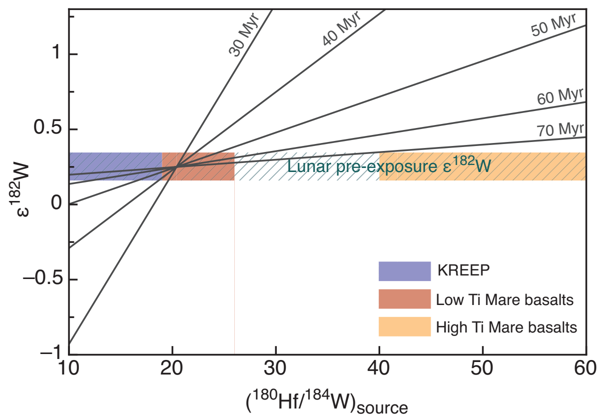

Fig. 3: ε^{182}W vs. the ^{180}Hf/^{184}W of lunar mantle sources. Shown are the pre-exposure ε^{182}W of the Moon from this study (*hashed area*), ranges in the Hf/W estimated for different lunar mantle reservoirs [5,6,11-13] (*shaded areas*), and reference isochrons for differentiation at different times after the start of the solar system (*solid lines*).

Timing of lunar magma ocean differentiation. Crystallisation of the lunar magma ocean generated mantle reservoirs with markedly distinct Hf/W [5,6,11-13]. Hence, if magma ocean crystallisation occurred within the lifetime of ^{182}Hf, then these reservoirs should have evolved to distinct ε^{182}W over time. However, our results demonstrate that, despite the variable Hf/W inferred for their sources [5,6,10-12], low-Ti and high-Ti mare basalts as well as KREEP have a homogeneous ε^{182}W (Fig. 3). Constraining the source Hf/W of Kalahari 009 is not straightforward, but its radiogenic initial Hf isotopic composition and old age of ~4.2 Ga [14] point to a mantle source that had undergone strong incompatible element depletion early in lunar history. Such a mantle source would likely have had a high Hf/W, but the ε^{182}W of Kalahari 009 is indistinguishable from KREEP, which is characterised by the lowest Hf/W among the lunar sample suite. Our results, therefore, demonstrate that the sources of KREEP, the mare basalts and Kalahari 009 must have been established after ^{182}Hf extinction, most likely later than ~70 Myr after solar system formation (Fig. 3). Such a 'late' time of magma ocean differentiation is consistent with the 'young' ages of ~4.4 Ga inferred for lunar mantle sources using other isotope systems [e.g., 15].

Constraints on the origin of the Moon. Our results demonstrate that the Moon shows an excess in ε^{182}W of ~25±4 ppm over the modern BSE. This excess agrees with the predicted ^{182}W change resulting from disproportional late accretion to the Earth and Moon

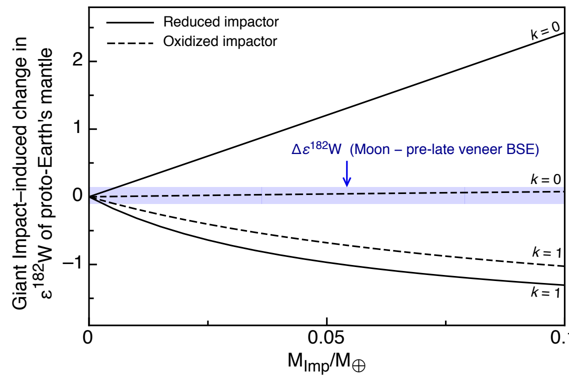

Fig. 4: Effect on the ε^{182}W of the proto-Earth after mixing variable amounts ($M_{Imp}/M_{\oplus}$) of impactor mantle and core material. The effects are shown for two impactor compositions and for no (k=0) or full (k=1) equilibration of the impactor core with the proto-Earth mantle.

after Earth's core had fully formed [7,8]. Hence, the pre-late-veneer BSE and the Moon were indistinguishable in ^{182}W. However, the giant impact itself should have caused a notable Earth–Moon ^{182}W difference by (1) changing the ε^{182}W of the proto-Earth mantle by adding impactor mantle and (partially) equilibrating impactor core material (Fig. 4), both carrying distinct ε^{182}W anomalies, and (2) by supplying W-rich but ^{182}W-depleted impactor core material into the lunar accretion disk. Thus, the Earth–Moon ^{182}W homogeneity is an unexpected outcome of the giant impact. Unlike for Ti and O isotopes, the ε^{182}W homogeneity is difficult to explain by accretion of impactor and proto-Earth from a homogeneous inner disk reservoir [16] or by making the Moon fully from proto-Earth mantle [17,18]. Thus, the ^{182}W results require a post–giant impact state that facilitated efficient isotopic equilibration of the BSE and the Moon.

Acknowledgement: We thank CAPTEM, NASA, and Ryan Zeigler for generously providing the Apollo lunar samples for this study.

References: [1] Canup RM & Asphaug E. (2001) *Nature* 412, 708–12. [2] Shearer C.K. & Papike J.J. (1999) *Am. Min.* 84, 1464-1494. [3] Wood J. A. et al. (1970) *Proc. Apollo 11 Lunar Sci. Conf.* 965–988. [4] Zhang J. et al. (2012) *Nature GeoSc.* 5, 251-255. [5] Kleine T. et al. (2005) *Science* 310, 1671-1673. [6] Touboul M. et al. (2007) *Nature* 450, 1206–1209. [7] Kruijer T.S. et al. (2015) *Nature* 520, 523-537. [8] Touboul M. et al. (2015) *Nature* 520, 530-533. [9] Leya I. et al. (2000) *EPSL* 175, 1-12. [10] Nishiizumi K. et al. (2005) MetSoc abstract #5270. [11] Righter K. &.Shearer C.K. (2003) *GCA* 67, 2497–2507. [12] Münker C. et al. (2010) *GCA* 74, 7340–7361 [13] Fonseca R.O.C. (2014) *EPSL* 404, 1-13. [14] Sokol A.K. et al. (2008) *GCA* 72, 4845-4873. [15] Gaffney A.M. & Borg L.E. (2014) *GCA* 140:227–240 [16] Dauphas N. et al. (2014) *Phil Trans R Soc A.,* 372. [17] Ćuk M. & Stewart S.T. (2012) *Science* 338, 1047–1052. [18] Canup R.M. (2012) *Science* 338, 1052–1055.