

**THE DURATION OF MAGMA OCEAN CRYSTALLIZATION ON THE MOON – EVIDENCE FROM NEW W ISOTOPE DATA FOR METALS FROM HIGH- AND LOW-TI MARE BASALTS.** M. Touboul<sup>1</sup>, T. Kleine<sup>1</sup>, B. Bourdon<sup>1</sup>, H. Palme<sup>2</sup>, <sup>1</sup>Institut für Isotopengeologie und Mineralische Rohstoffe, Departement für Erdwissenschaften, ETH Zürich, Clausiusstrasse 25, 8092 Zürich, Switzerland ([touboul@erdw.ethz.ch](mailto:touboul@erdw.ethz.ch)), <sup>2</sup>Institut für Mineralogie und Geochemie, Universität zu Köln, Zùlpicherstr. 49b, 50674 Köln, Germany.

**Introduction:** The early chemical differentiation of the Moon was dominated by the crystallization of a magma ocean. Determining the crystallization age of the lunar magma ocean (LMO) is critical for understanding the timing of Moon formation, melting, and subsequent differentiation and cooling. The <sup>182</sup>Hf-<sup>182</sup>W decay scheme is well-suited for dating the crystallization of the LMO because the Hf/W ratios varied significantly between the different LMO reservoirs [1]. Thus, information on the early differentiation of the Moon should be preserved in the <sup>182</sup>W/<sup>184</sup>W of early-formed lunar reservoirs and is carried by lunar samples derived from any of these sources.

The chronological interpretation of W isotope ratios for lunar whole-rocks and minerals, however, has been hampered by the neutron-flux induced production of <sup>182</sup>W from <sup>181</sup>Ta caused by the intense cosmic irradiation of the lunar surface [2, 3]. To overcome this problem Kleine et al. [4] determined the W isotope composition of lunar metals because these do not contain any Ta that could have been converted to <sup>182</sup>W. Using this approach Kleine et al. found systematic variation in the W isotope composition of KREEP-rich samples (lowest <sup>182</sup>W/<sup>184</sup>W), low-Ti (intermediate <sup>182</sup>W/<sup>184</sup>W) and high-Ti mare basalts (highest <sup>182</sup>W/<sup>184</sup>W), indicating crystallization of the LMO as early as 30-50 Myr after start of the solar system. There are however only few W isotope data available for metals from low- and high-Ti mare basalts. To obtain a more comprehensive picture of the W isotope variations in the lunar mantle we obtained new W isotope data for metals from low- and high-Ti mare basalt. These data are used here to assess the duration of LMO crystallization and to address the issue why the Hf-W ages of the LMO (30-50 Myr) is inconsistent with its <sup>146</sup>Sm-<sup>142</sup>Nd age (~215 Myr) [5].

**Methods:** We separated metals from 3 high-Ti (70017, 70035, and 70215) and 3 low-Ti basalts (15058, 15499, and 15556). Between XX and XX mg of metal were obtained from ~4 g of sample. Samples were crushed in an agate mortar and sieved into several grain size fractions. Metals were then separated using a handmagnet and further purified by grinding and ultrasonication in distilled ethanol. The purity of the metal separates is checked under the binocular. The metals were dissolved in 6 M HCl-0.06 M HF and dried. Tungsten was separated from its sample matrix

using standard ion exchange techniques. All isotope measurements were performed using the Nu Plasma MC-ICPMS at ETH Zurich. The W isotope compositions of the samples are determined relative to an ALFA AESEAR standard solution and are expressed in  $\epsilon_W$ , which is the deviation of the <sup>182</sup>W/<sup>184</sup>W ratio of the sample from the terrestrial standard value. Instrumental mass bias is corrected by normalizing to <sup>186</sup>W/<sup>183</sup>W = 1.9859 and <sup>186</sup>W/<sup>184</sup>W = 0.92767 using the exponential law. Osmium interferences on masses 186 and 184 are corrected by monitoring <sup>188</sup>Os but corrections were found to be insignificant. <sup>183</sup>W/<sup>184</sup>W ratios were used as a monitor of accurate measurements. They agree for all samples analyzed here to within  $\pm 0.2\epsilon$  units with the terrestrial standard.

**Results:** The new W isotope data for lunar metals are summarized in Fig. 1. Also shown are previously published data for lunar metals [4] as well as selected W isotope data for lunar whole-rock samples and mineral separates that have been corrected for cosmogenic <sup>182</sup>W additions [3]. An important aspect of the new data is that in contrast to earlier reports we do not find variations in the W isotope composition of the metals separated from low- and high-Ti mare basalts. The W isotope composition of all samples analyzed here agree with each other and with the W isotope composition of metals from KREEP-rich samples reported by Kleine et al. [4]. All currently available data combined therefore suggest that most lunar samples have  $\epsilon_W \sim 0$  and that small positive <sup>182</sup>W anomalies have only been preserved in few samples.

**Discussion:** The new W isotope data for lunar metals presented here have far reaching implication for interpreting the Hf-W record of the lunar mantle. In contrast to earlier findings there is no systematic difference in  $\epsilon_W$  among KREEP-rich samples, low-Ti and high-Ti mare basalts. Instead, the majority of the low- and high-Ti mare basalts appear to have a W isotope compositions similar to that of KREEP. This suggest either that most <sup>182</sup>W anomalies resulting from an early differentiation of the Moon have been erased by later large-scale mixing within the lunar mantle or that the isolation of lunar reservoirs was delayed. Mixing as required in the former case could be related to late-stage cumulate overturn [7] but probably also requires that the LMO has not been completely solidified. The

new data therefore suggest that the crystallization of the LMO was more prolonged than estimated in earlier studies [4]

Given that most lunar samples appear to have  $\epsilon_W \sim 0$ , it seems reasonable to assume that the lunar mantle is characterized by this W isotope composition. This would imply that KREEP separated at a time when there was no sufficient amounts of  $^{182}\text{Hf}$  left to generate a  $^{182}\text{W}$  anomaly (i.e., later than  $\sim 60$  Myr). An alternative interpretation would be that an originally existing  $^{182}\text{W}$  anomaly in KREEP has been erased by later re-mixing with other LMO cumulates. This however seems unlikely, because the differentiation due to LMO crystallization has at least been partially preserved in the Moon. Furthermore, given that KREEP is strongly enriched in W compared to the other reservoirs in the lunar mantle, resetting the W isotope composition of KREEP would require substantial isotopic exchange between KREEP and the other reservoirs in the lunar mantle. It thus is more likely that KREEP preserved the W isotope composition acquired at the final stage of LMO crystallization.

The new W isotope data for lunar metals presented here therefore suggest a revision of the Hf-W chronology of the LMO. The data seem to require that the separation of KREEP and, hence, the final crystallization of the magma ocean, occurred *later* than  $\sim 60$  Myr after the solar system. This new age constraint could be consistent with the  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  model age of  $\sim 215$  Myr for the LMO [5]. However, the preservation of  $^{182}\text{W}$  anomalies in some lunar samples still requires that the Moon formed when  $^{182}\text{Hf}$  was still extant (i.e., earlier than 60 Myr).

Another important aspect of the new data is that the lunar and terrestrial mantles seem to have identical W isotope compositions. This is unexpected given that dynamical simulations of the Moon-forming impact indicate that the material that made the Moon is largely derived from the Impactor. The identical W isotope compositions of the lunar and terrestrial mantles therefore seem to require some kind of large-scale re-equilibration event associated with the giant impact. In spite of their identical  $\epsilon_W$  values the lunar and terrestrial mantles have slightly different Hf/W ratios (26.5 and 25, respectively), indicating either that the lunar and terrestrial mantles started off with different initial  $\epsilon_W$  values (but later evolved to similar  $\epsilon_W$  by coincidence), or that the giant impact occurred too late ( $> \sim 35$  Myr), such that resolvable  $\epsilon_W$  differences between the lunar and terrestrial mantles could not develop.

**Conclusions:** New Hf-W data for metals from low- and high-Ti mare basalts indicate that most lunar samples have identical W isotope compositions. Only in

few samples (4 out of 17) small  $^{182}\text{W}$  anomalies seem to have been preserved. The new data require a protracted crystallization of the LMO, which appears to be consistent with the  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  model age of the LMO.

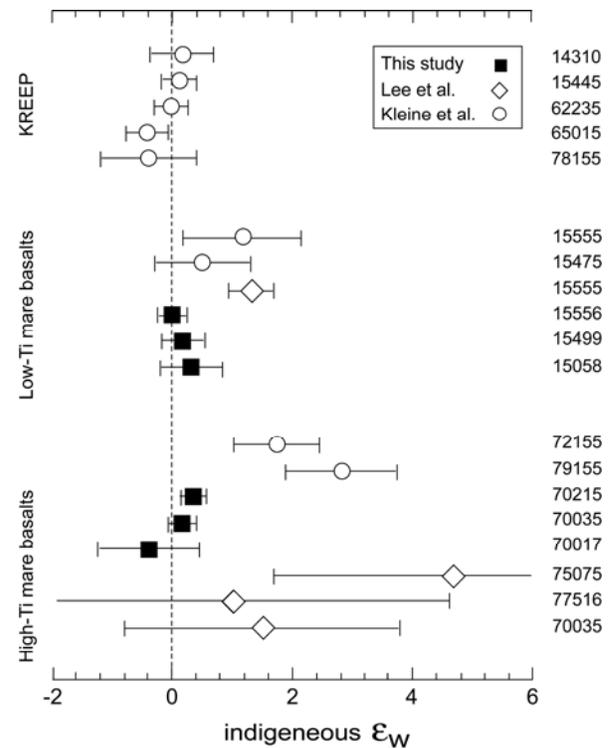


Fig. 1: indigenous  $\epsilon_W$  of lunar samples

**References:** [1] Shearer et al. (2000) *GCA* 64, 3599 [2] Leya et al. (2000) *EPSL* 175, 1. [3] Lee et al. (2002) *EPSL* 198, 267-274. [4] Kleine et al. (2005) *Science* 310, 1671-1674. [5] Nyquist et al. (1995) *GCA* 59, 2817. [6] Lee et al. (2002) *Science* 278, 1098. [7] Elkins-Tanton et al. (2002) *EPSL* 196, 239