

HIGH-PRECISION W ISOTOPE COMPOSITION OF THE MOON FOR CONSTRAINING LATE ACCRETION AND LUNAR FORMATION. M. T. Touboul¹, R. J. Walker¹, I. S. Puchtel¹, ¹Departement of Geology, University of Maryland, MD 20740, USA (mtouboul@umd.edu).

Introduction: Discovery of small enrichments in $^{182}\text{W}/^{184}\text{W}$ in some Archean rocks, relative to modern mantle [1,2], suggests both exogeneous and endogenous modifications to highly siderophile element and moderately siderophile element abundances in the terrestrial mantle. Collectively these isotopic enrichments suggest the formation of chemically fractionated reservoirs in the terrestrial mantle that survived the putative Moon-forming giant impact, and also provide support for the late accretion hypothesis. The lunar mantle sources of volcanic glasses and basalts were depleted in highly siderophile elements (HSE) relative to the terrestrial mantle by at least a factor of 20 [3]. The most likely explanations for the disparity between the Earth and Moon are either that the Moon received a disproportionately lower share of late accreted materials than Earth, such as may have resulted from stochastic late accretion, or the major phase of late accretion occurred prior to the Moon-forming event, and the putative giant impact led to little drawdown of HSE to the Earth's core.

Day et al. [3] have proposed that late accretion of materials with chondritic bulk compositions added ~0.4 to 0.8 wt. % of mass to the Earth, and ~0.05 wt. % mass to the Moon. If this is true, and if late accretion to the mantles of the Earth and Moon largely postdated the formation of the Moon, then mass balance calculations predict that the W isotopic composition of the lunar mantle should be more radiogenic than the Earth by ~10 to 30 ppm, as the higher proportion of late accreted materials added to Earth would have lowered the $^{182}\text{W}/^{184}\text{W}$ of the terrestrial mantle towards the isotopic composition of chondrites (~ -200 ppm relative to present Earth) more than for the lunar mantle. The mass balance arguments to arrive at this conclusion are very similar to those used by Willbold et al. [1] to account for the W isotopic compositions of Isua rocks.

Accurate and precise measurement of the $^{182}\text{W}/^{184}\text{W}$ of the lunar mantle is critical to test this prediction. Because of the effects of cosmic rays on ^{182}W , particularly production resulting from cosmic ray interactions with ^{181}Ta [4], most studies of the W isotopic composition of the lunar mantle have focused on Ta-free metal, separated from impact melt rocks and basalts [e.g., 5]. Most recently, Touboul et al. [6] analyzed separated metal from a suite of diverse lunar basalts and KREEP-rich impact melt rocks. That study reported isotopic homogeneity among the different metals measured, and reported a group average

$^{182}\text{W}/^{184}\text{W}$ that is 9 ± 10 ppm higher than terrestrial standards (based on the 2 standard error of 15 measurements)(Fig. 1). Touboul et al. [6] interpreted the W data to mean that the Moon formed ≥ 52 Myr after formation of the solar system, and also that the lunar magma ocean crystallized after ^{182}Hf was no longer extant, ≥ 60 Myr after solar system formation.

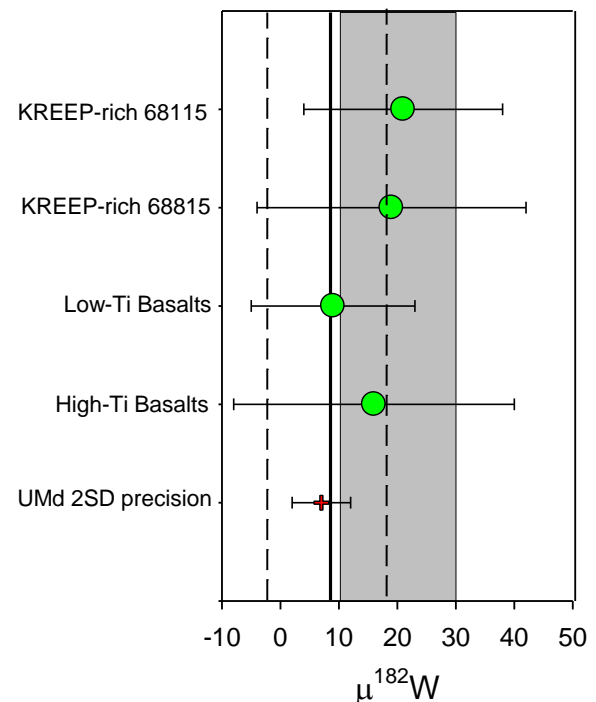


Fig. 1: $\mu^{182}\text{W}$ (the deviation in parts per million of the $^{182}\text{W}/^{184}\text{W}$ of a sample compared to terrestrial standards and modern terrestrial rocks) for metal separated from lunar basalts and melt rocks (68815 and 68815) from [6]. Error bars represent the reported 2 sigma standard errors of results for multiple analyses of individual rocks (68815 and 68815) and 2 sigma weighted averages of data for multiple samples of low-Ti mare basalts and high-Ti mare basalts. The solid line and dashed lines represent the collective average and 2 standard error of analyses, respectively, of 15 samples [6]. The shaded gray field represents the range of isotopic compositions predicted for the differential late accretion model discussed in the text. Also shown for comparison is the current level of resolution (2 standard deviation) for $\mu^{182}\text{W}$ at the University of Maryland using the methods of Touboul and Walker [7].

The results from Touboul et al. [6] provided a hint that the lunar mantle may be enriched in ^{182}W , relative to the modern terrestrial mantle, and within the predicted level of enrichment (Fig. 1). However, with uncertainties for individual measurements exceeding 10 ppm in that study, precision was insufficient to definitively test the prediction. Now that precision of individual measurements can be <5 ppm, it is necessary to re-measure the isotopic compositions of W in metals extracted from a similar set of lunar volcanic rocks as examined by Touboul et al. [6]. A uniform positive offset of 10 to 30 ppm, relative to the present terrestrial mantle, could be interpreted as evidence for the hypothesized proportional disparity in late accretion to the Earth and Moon. It will also be important to reassess whether there is resolvable W isotopic heterogeneity among the mantle reservoirs sampled by lunar basalt. Small, but analytically resolved heterogeneity could be interpreted as evidence for uneven mixing of late accreted materials into different portions of the lunar mantle, or for very minor, variable ingrowth of ^{182}W while ^{182}Hf was still live. These possibilities may be discriminated based on the nature of the hypothetical variations and how they may correlate with estimates of HSE abundances, or projections for Hf/W fractionations in the sources of the diverse lunar volcanic rock suite.

It is also possible that high precision measurements of lunar metals will reveal that there is no W isotopic difference between the Earth and Moon above the 5 ppm level. If this is the case, it may be cause for a reconsideration of the late accretion hypothesis altogether.

Here we will present new W isotope data for metals separated from the KREEP-rich Apollo sample 68115 obtained using our new high precision analytical method by TIMS [7], to more precisely assess the W isotope composition of the lunar mantle, which can help to resolve these issues.

Methods: 3.5 g of the sample 68115 was allocated to us. Based on metal content (9 mg/g) and to the W abundance in its metal grains (26 ppm), metals separated from such sample amount should provide more than the 500 ng of W necessary for high precision isotope measurement.

The sample was crushed in an agate mortar and separated into several size fractions using nylon sieves. Magnetic fractions have been separated using a hand-magnet, and further purified by repeated grinding, magnetic separation and ultrasonication in distilled ethanol. The purity of the metal separates will be checked to be free of visible silicate or oxide grains under the binocular microscope. The subsequent analytical procedure is slightly modified from Touboul et

al. [6]. The metal separates will be dissolved in 6 M HCl in 15 ml Savillex vials at 120 °C on a hotplate, such that most of the potentially present silicate and oxide impurities should not dissolve. After metal dissolution, a $\sim 0.5\%$ aliquot of the sample will be spiked with both ^{179}Hf and ^{182}W tracers for determination of Hf and W concentrations and the remaining $\sim 99.5\%$ solution will be dried. After repeated re-dissolutions in 14M HNO_3 with minor H_2O_2 , and subsequent dry downs, samples were converted into the chloride form via dissolution and drying down in 6M HCl. After dry-down, the sample will be finally dissolved in 0.5M HCl-0.5 M HF and loaded onto pre-cleaned anion exchange columns (2ml of BioRad AG1X8, 100-200 mesh). The sample matrix will be eluted using 0.5M HCl-0.5 M HF and 1M HF. Tungsten will be then collected using 6 M HCl-1 M HF. After dry-down and redissolution in 0.5M HCl-0.5M HF, the W cut will be further purified using an identical chemical procedure onto a 140 μl anion exchange columns. Collected W will be dried, then repeatedly redissolved in HNO_3 - H_2O_2 and dried-down to eliminate Os and potential organic components. Total procedural blanks using this method were commonly ~ 100 pg and therefore will be negligible.

Tungsten will be loaded in 1M HNO_3 onto a single Re filament together with $5\mu\text{g}$ of Gd and La. W isotope composition will be measured at the <5 ppm precision level on a *Thermo Triton* TIMS at UMD following the analytical procedure of Touboul and Walker [7].

Spiked aliquots will be processed using classical chemical procedure for isotope dilution and measured on a Nu MC-ICP-MS at UMD as described in [6]. Hf/W ratio will be used to quantitatively constrain potential contribution of W derived from silicate and oxide impurities in the final metal separate.

References: [1] Willbold M. et al. (2011) *Nature* 477, 195-198. [2] Touboul M. et al. (2012) *Science* 335, 1065-1069. [3] Day et al., *Science* 315, 217-219. [4] Leya et al. (2000) *EPSL* 175, 1-12. [5] Kleine et al. (2005) *Science* 310, 1671-1674 [6] Touboul et al. (2007) *Nature* 450, 1206-1210. [7] Touboul M. and Walker R.J. (2012) *IJMS* 309, 109-117.

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