THE TUNGSTEN ISOTOPE COMPOSITION OF THE MOON: NEW CONSTRAINTS ON THE GIANT IMPACT. M. T. Touboul¹, I. S. Puchtel¹ and R. J. Walker¹, ¹Department of Geology, University of Maryland, MD 20742, USA (rjwalker@umd.edu).

Introduction: Discovery of small enrichments in $^{182}\mathrm{W}/^{184}\mathrm{W}$ in some Archean rocks, relative to the modern terrestrial mantle [1,2], suggests both exogeneous and endogenous modifications to highly siderophile element (HSE) and moderately siderophile element (MSE) abundances in the mantle. Collectively these isotopic enrichments indicate the formation of chemically fractionated reservoirs in the terrestrial mantle that survived the putative Moon-forming giant impact, and may also provide support for the late accretion hypothesis. The lunar mantle sources of volcanic glasses and basalts were depleted in 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 stochas-tic 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 already present in the mantle at that time.

Day et al. [3] 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. Consequently, if late accretion to the mantles of the Earth and Moon largely postdated the formation of the Moon, and the Moon formed with the same W isotopic composition as Earth, then mass balance calculations predict that the $^{182}W/^{184}W$ of the lunar mantle should now be higher than for the Earth by 10 to 30 ppm, as the greater proportion of late accreted materials added to Earth would have lowered the $^{182}W/^{184}W$ of the terrestrial mantle towards the isotopic composition of chondrites (~ -200 ppm relative to present Earth) more than for the lunar mantle.

Accurate and precise measurement of the $^{182}W/^{184}W$ of the lunar mantle is, therefore, 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 prior 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]. Touboul et al. [6] measured the W isotopic compositions of lunar basalts and impact melt rocks. Because of the terrestrial composition of W found in the lunar metals, separated from lunar basalts and impact melt rocks, that study interpreted the 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. However, the measurements for that study were made with with ± 25 -30 ppm precision, so the effects of disproportional late accretion could not be tested by it. In order to examine this issue further, we have applied our new measurement techniques, which provide W isotopic data with $\sim \pm 5$ precision (2σ SD) [7].

Methods: Apollo 16 KREEP-rich impact melt rocks 68115 and 68815 were chosen for study because they formed from target rocks with high W, and experienced only short-term exposure to cosmic rays. Given W concentrations typical of KREEP, together with typical contributions of siderophile elements to lunar impact melt rocks, we estimate the W present in the metal separates is >99% endogenous lunar W.

The samples were crushed in an agate mortar and separated into several size fractions using nylon sieves. Magnetic fractions were separated using a handmagnet, and further purified by repeated grinding, magnetic separation and ultrasonication in distilled ethanol. The purity of the metal separates were checked to be free of visible silicate or oxide grains under the binocular microscope. The subsequent analytical procedures used for W purification and isotopic analysis were reported in [7]. In brief, samples were processed through anion and cation exchange columns, and the highly-purified final W fractions were analyzed by negative thermal ionization mass spectrometry using the UMd *ThermoFisher Triton* mass spectrometer.

Metal separates from the impact melt rocks 68115,114, 68815,394 and 68815,396 have $\mu^{182}W$ values (where μ^{182} W is the deviation in ppm of the $^{182}W/^{184}W$ ratio of the sample from that of the modern terrestrial mantle) of $+23.3 \pm 3.8$ (n=3, 2σ SD), +18.1 ± 2.5 and $\pm 20.4 \pm 2.9$, respectively, which are identical within analytical uncertainty (Fig. 1). The average μ^{182} W value of +20.6 ± 5.1 (2 σ SD) for the three metal separates provides the current best estimate of the W isotopic composition of their parental KREEP reservoir, and most likely, the lunar mantle. These data are in good agreement with the previously published data for the same samples [6], but are considerably more precise. Of greatest note, the W isotopic compositions of the metals are now well resolved from the isotopic composition of the silicate portion of the modern Earth.

Discussion: The positive W isotopic offset between the Moon and silicate Earth can be attributed to one of

several possible causes, including: 1) cosmogenic exposure effects, 2) contribution of W from the basinforming impactor that created the melt rocks, 3) radiogenic ingrowth of ¹⁸²W in a high Hf/W domain within the lunar mantle while ¹⁸²Hf was extant, or 4) disproportional late accretion to Earth and Moon.

Possibilities 1 and 2 can be easily dismissed based on the measured, very low Ta/W of the metal separates, and based on mass balance estimates for W in KREEP-rich rocks, relative to possible impactors. Enrichment in ¹⁸²W as a result of radioactive decay can't be discounted at this time, although the magnitude of the offset is inconsistent with current estimates for the Hf/W of the bulk silicate Moon, and the mantle source of KREEP. We conclude that the most likely cause for the offset is disproportional late accretion to the Moon and Earth, especially given that it is an excellent match to the predicted offset [8].

If the W isotopic difference between the Moon and Earth really is the result of disproportional late accretion, then the results provide some important additional constraits on the nature of the putative giant impact that generated the Moon. First, an interpretation of disproportional late accretion requires the assumption that at the time of Moon formation, the Earth and Moon had the same W isotopic composition. This requirement follows other evidence for isotopic similarity between the Moon and Earth in elements such as O, Ti and Cr. One possible cause for this isotopic match is that the giant impactor happened to have been built from very similar building blocks as the Earth coincidentally winding up with essentially the same isotopic compositions for elements that show genetic variability in their isotopic compositions. The W isotopic composition of the silicate portion of the impactor, however, was an outcome of radiogenic decay of ¹⁸²Hf, coupled with the Hf/W history of its mantle. Consequently, it is exceptionally unlikely that the impactor would have evolved to the same W isotopic composition as Earth at the time of the impact. Thus, an interpretation of disproportional late accretion greatly favors giant impact scenarios that seek to explain the isotopic similarities between the Moon and Earth as a result of high temperature equilibration processes, rather than accretionary happenstance [e.g., 9].

An additional requirement for an interpretation of disproportional late accretion is that the late accretionary accumulation clocks for the Moon and Earth began at the time as the giant impact. Thus, the giant impact would have to have been a clearinghouse event for HSE that were present in the terrestrial mantle prior to the impact. This means that at least some of the metal from the core of the impactor efficiently extracted the HSE from the silicate Earth while transiting to merge with the core.



Figure 1: μ^{182} W of lunar metals separated from Apollo 16 KREEP-rich impact melt rocks 68115,114, 68815,394 and 68815,396. The gray vertical bar represents the composition of the bulk silicate Earth. The red circle corresponds to the average value of the 3 individual analyses of the metals (+20.6 ± 5.1 2 σ SD), which is our current best estimate for the W isotopic composition of the Moon.

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