

APPLICATION OF THE ^{182}Hf - ^{182}W ISOTOPE SYSTEM TO CONSTRAINING THE TIMING OF LATE ACCRETION TO THE EARTH AND MOON. R. J. Walker¹, M. Touboul¹ and I. S. Puchtel¹, ¹Department of Geology, University of Maryland, College Park, MD 20742 USA (rjwalker@umd.edu).

Introduction: Over the past two decades, the short-lived ^{182}Hf - ^{182}W isotopic system ($^{182}\text{Hf} \rightarrow ^{182}\text{W} + \beta^-$ where $t_{1/2} = 8.9$ Myr) has been widely used for dating early solar system processes, due to the unique geochemical properties of the system [1-2]. As a moderately siderophile element (MSE), W is largely, but not completely, extracted from the silicate mantles of planetary bodies during segregation of metallic cores [e.g., 3]. Hafnium, in contrast, is lithophile and is essentially wholly retained in the silicate portions of planetary bodies. Therefore, determination of the abundance of the daughter nuclide ^{182}W , relative to other stable, non-radiogenic isotopes (e.g., ^{184}W), is of special interest for constraining the timing of planetary core formation. For example, the higher than chondritic $^{182}\text{W}/^{184}\text{W}$ ratio of the terrestrial mantle has been interpreted to reflect core segregation and generation of supra-chondritic Hf/W in the mantle during the first ~30 Myr of solar system history, while ^{182}Hf was extant [4-5].

Following the cessation of significant core segregation, the Hf/W ratio of the Earth's mantle would likely have been further modified by post-core-formation events, such as the crystallization of transient magma oceans, partial melting of the mantle, or subsequent crystal-liquid fractionation processes [3]. If such events occurred before ^{182}Hf became extinct, additional ^{182}W isotopic variations would have been generated in the mantle. It is even likely that ^{182}W isotopic heterogeneities were created in the mantle after ^{182}Hf was no longer extant. The term "late accretion" is used to describe the process of mass addition to the Earth by continued accretion subsequent to cessation of core formation. It is a process that has been commonly invoked to account for the relatively high abundances of the highly siderophile elements (HSE; including Os, Ir, Pt and Re) present in the mantle [6,7]. Late accretion equivalent to 0.3 to 0.8% of the total mass of the mantle, the amount necessary to account for the observed mantle abundances of HSE [8], would have lowered the $^{182}\text{W}/^{184}\text{W}$ of the mantle by 10 to 30 ppm, as materials with comparatively ^{182}W -depleted compositions, such as planetesimals with bulk chondritic compositions, were accreted to Earth.

Willbold et al. [9] recently reported $\sim 13 \pm 4$ ppm ^{182}W enrichments, relative to younger terrestrial rocks and standards, in 3.8 Ga rocks from the Isua greenstone belt, Greenland. This study provided the first evidence for W isotopic heterogeneity in terrestrial materials. Willbold et al. [9] concluded that the ^{182}W rich isotopic composition of the Isua suite preserves

the composition of the mantle prior to a final stage of late accretion to the Earth and Moon, termed the terminal bombardment, that has been previously hypothesized, based on common 3.8 to 3.9 Gyr ages for lunar impact melt rocks associated with the major impact basins [10-11]. Willbold et al. [9] argued that the addition of materials of chondritic bulk composition ($\mu^{182}\text{W} = -200$) that were rich in W, as well as HSE, would have lowered the W isotopic composition of the bulk mantle from an older, more radiogenic composition. They posited that the Isua rocks are remnants of the prior, primordial mantle. This hypothesis is consistent with that of Maier et al. [12] in which it was concluded that a gradual increase in the abundances of HSE is recorded in mantle sources of Archean komatiites formed between ~3.5 and 2.9 Ga rocks, and that this reflects a downward mixing of the HSE into the deep mantle sources of the komatiites.

As a test of the late stage, late accretion hypotheses to affect both W isotopes and HSE abundances, we report W isotope composition data for 3.47 Ga komatiites from the Komati Formation of the Barberton greenstone belt, South Africa [13], and 2.82 Ga komatiites from the Kostomuksha greenstone belt, Baltic Shield, Russia [14]. Puchtel and Walker [15] estimated that the Komati and Kostomuksha komatiite sources contained ~45 and ~75 %, respectively, of the late accretionary component now present in the modern mantle.

Analytical Methods: We recently developed a new technique to measure $^{182}\text{W}/^{184}\text{W}$ to a 2σ precision of ± 4.6 ppm using negative thermal ionization mass spectrometry [16]. After chemical purification of W through a four-step ion exchange chromatographic separation, the W isotopic composition is measured as WO_3^- by negative thermal ionization mass spectrometry using a *Thermo-Fisher Triton* instrument. Data are initially corrected for oxide interferences, assuming a predefined O isotope composition, and for mass fractionation, by normalization to $^{186}\text{W}/^{184}\text{W}$ or $^{186}\text{W}/^{183}\text{W}$, using an exponential law. A small second-order effect, likely reflecting a mass dependent change of O isotope composition in the measured W oxides, is corrected by normalization to $^{183}\text{W}/^{184}\text{W}$ using a linear law. Repeated analysis of both standard solutions and rocks demonstrate external reproducibility of $^{182}\text{W}/^{184}\text{W}$ within ± 4.5 ppm (2σ SD).

Results: The $\mu^{182}\text{W}$ values (where $\mu^{182}\text{W}$ values are the deviation in ppm from the terrestrial reference standard) for four Komati samples average $+2.6 \pm 4.1$

(2σ SD), and are indistinguishable from terrestrial standards and the modern La Palma basalt (Canary Islands) we repeatedly analyzed ($\mu^{182}\text{W} = +0.1 \pm 2.4$) (**Fig. 1**). In contrast, the eighteen Kostomuksha komatiite samples analyzed (including replicate digestions) have $\mu^{182}\text{W}$ values that average $+14.8 \pm 4.8$ (2σ SD), which is well-resolved from the terrestrial standard (**Fig. 1**).

Discussion: Although the 13 ppm enrichment in ^{182}W in rocks from Isua is similar in magnitude to that of the Kostomuksha komatiites, the interpretation that Willbold et al. [9] applied to the Isua rocks is problematic for the Kostomuksha rocks. To test a similar model for the Komati and Kostomuksha sources, we modeled mixing between a primordial, ^{182}W -enriched, yet HSE depleted reservoir, and a bulk chondritic composition (**Fig. 2**). Total HSE content is expressed as the percent deviation of content in the mantle source, relative to the concentration in the primordial mantle. The effects of contributions of late accreted materials ranging from 0.3 to 0.8% of the total mass of the mantle are calculated, assuming that the HSE present in the silicate Earth today were entirely derived from late accretion. Given the estimates that the Komati and Kostomuksha komatiite sources contained ~45 and ~75 %, respectively, of the late accretionary component now present in the modern mantle, the older Komati komatiites should show more radiogenic $\mu^{182}\text{W}$ (~9 ppm) than the Kostomuksha komatiites (~4 ppm). This is not observed and suggests that the Kostomuksha source cannot simply be primordial mantle that had been largely stripped of HSE by core formation. We also note that there is minimal overlap between uncertainties in the W isotopic composition of the Komati komatiites and the mantle mixing model of **Fig. 2**, suggesting that the downward mixing model of Maier et al. [12] is not viable for at least the Komati komatiites. We instead attribute the enrichment in the Kostomuksha komatiites to reflect preservation of an early Earth (within ~30 Myr of solar system formation) differentiation product.

Conclusions: If late accretion was responsible for establishing HSE abundances in the mantle following core formation, this process likely dominantly occurred prior to the postulated late heavy bombardment. Thus, W isotopes can be used to limit the proportion of mass added to the Earth and Moon during this event.

References: [1] Lee D-C. and Halliday A.N. (1995) *Nature* **378**, 771. [2] Harper C.L. and Jacobsen S.B. (1996) *GCA* **60**, 1131. [3] Righter K. and Shearer C.K. (2003) *GCA* **67**, 2497. [4] Kleine et al. (2002) *Nature* **418**, 952. [5] Yin et al. (2002) *Nature* **418**, 949.

- [6] Chou C-L. (1978) *Proc. Lunar Planet. Sci. Conf.* **9th**, 219.
- [7] Morgan J.W. et al. (2001) *Meteor. & Planet. Sci.* **36**, 1257.
- [8] Walker R.J. (2009) *Chem. der Erde* **69**, 101
- [9] Willbold M. et al. (2011) *Nature* **477**, 195.
- [10] Terra F. et al. (1974) *EPSL* **22**, 1.
- [11] Dalrymple G.B. and Ryder G. (1996) *J. Geophys. Res.* **101**, 26069.
- [12] Maier W.D. et al. (2009) *Nature* **460**, 620.
- [13] Kröner A. et al. (1996) *Precam. Res.* **78**, 105.
- [14] Puchtel I.S. et al. (1998) *EPSL* **155**, 57.
- [15] Puchtel I.S. and Walker R.J. (2011) *2011 Goldschmidt Conf. abstr.*
- [16] Touboul M. & Walker R.J. (in press) *Intl. J. Mass Spectrom.*

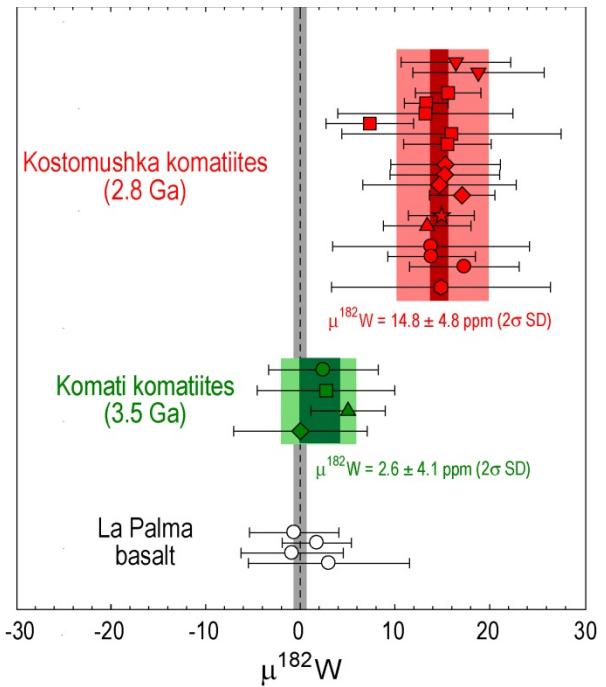


Figure 1. $\mu^{182}\text{W}$ values for Komati and Kostomuksha komatiites. Error bars represent 2σ SD.

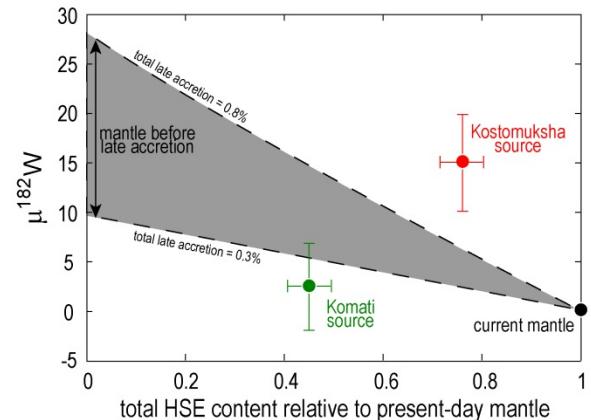


Figure 2. Plot of $\mu^{182}\text{W}$ versus total HSE content relative to present-day mantle (in %).