TIME CONSTRAINTS ON LATE ACCRETION TO THE EARTH AND MOON, AND NEW EVIDENCE FOR EARLY MANTLE DIFFERENTIATION DERIVED FROM COUPLED INVESTIGATIONS OF W AND OS ISOTOPE COMPOSITIONS. M. Touboul[1*], J. G. Liu[1], J. O'Neil[2], I. S. Puchtel[1] and R. J. Walker[1], [1]Department of Geology, University of Maryland, College Park, MD 20742, USA. [2]Observatoire de Physique du Glode de Clermont-Ferrand, Laboratoire Magmas et Volcans, Clermont-Ferrand, France.*corresponding author, mtouboul@umd.edu

Introduction: Improvements to analytical precision on $^{182}W/^{184}W$ ratios (~5 ppm) have revealed the existence of subtle isotopic anomalies in Archean rocks [1, 2]. The proccesses responsible for these W isotopic heterogeneities, however, have not yet been clearly identified. Willbold et al. [1] argued that a +13 ppm enrichment in ^{182}W in a suite of 3.8 Ga rocks from Isua, Greenland corresponds to the isotopic signature of the Earth's mantle prior to a final stage of late accretion to the Earth and Moon, termed late heavy bombardment [3]. Some have interpreted this event to have occurred between 3.9 and 3.8 Ga, based on ages of lunar impact melt rocks [4]. Indeed, late accretion of extraterrestrial materials with chondritic W concentrations and isotopic compositions, should have lowered the $^{182}W/^{184}W$ ratio of the Earth's mantle by ~20 ppm down to its present-day value ($\mu^{182}W$ = 0, where μ is the deviation in ppm from terrestrial reference standards). This conclusion is based on the assumption that late accretion added ~0.5 % of total mass of the mantle to Earth, as is necessary to account for the observed high absolute and chondritic relative abundances of highly siderophile elements (HSE) in the mantle. This interpretation, however, can not explain similar ^{182}W anomalies of +15 ppm observed in the 2.8 Ga Kostomuksha komatiites, Baltic Shield [2]. These rocks are characterized by extrapolated HSE source contents only ~20% lower than those present in the modern ambient mantle [5,6], which is difficult to reconcile with a mantle source that escaped incorporation of HSE-rich extraterrestrial materials. The ^{182}W excess present in the mantle source of the Kostomuksha komatiites is accompanied by ^{186}Os and ^{187}Os enrichments, which most likely reflect the presence of a primordial component, characterized by high Hf/W, as well as high Pt/Os and Re/Os ratios. The lack of a ^{142}Nd anomaly, however, means that whatever process was involved, it did not strongly fractionate Sm/Nd. This mantle reservoir would have to have been isolated from the convecting mantle less than 60 m.y. (and likely less than 30 m.y.) after CAI formation, and could represent a by-product of either metal-silicate equilibration at high pressure and temperature or differentiation of a magma ocean.

Here, we present new high-precision W isotope data for rocks from the Nuvvuagittuq greenstone belt of northern Quebec, Canada, which are coupled with HSE abundances, and Os isotope compositions, as well as published ^{142}Nd data. Some of these rocks are characterized by negative ^{142}Nd anolmalies and a correlation between their $^{142}Nd/^{144}Nd$ and their Sm/Nd ratios, suggesting that they were formed at 4.28 Ga, while ^{146}Sm was actively decaying [7]. The other petrogenetic model that could account for the ^{142}Nd /^{144}Nd vs. Sm/Nd correlation in the Nuvvuagittuq rocks would be a mixing between the depleted mantle and an early enriched mantle reservoir, in which case the 4.28 Ga age would provide a minimum age for the time of separation of the early enriched reservoir and the depleted mantle. Therefore, these rocks, or at least their mantle source, predate the late heavy bombardment. Their W isotope compositions may therefore provide further constraints on early processes involved in the generation of W isotopic heterogeneities within the Earth's mantle.

Analytical methods: Sample preparation, W chemical separation by ion exchange chromatography, and W high-precision isotope measurement by negative ion thermal ionization mass spectrometry (N-TIMS) are described in detail in [8]. One to 4 g aliquots of sample powders were processed to obtain the 1-1.5 μg of W necessary for each individual analysis. Tungsten and HSE abundances, determined by isotope dilution, and Os isotope compositions were measured on aliquots of the same batches of sample powders that were used for W isotope analysis.

Results: The 3.66 Ga Nuvvuagittuq tonalites have the highest W contents (~2.5 ppm) of the suite analyzed. Rocks with presumed ultramafic precursors, as well as rocks from the Ujaraaluk unit, have highly variable W contents ranging from 0.1 to 1.2 ppm and from 0.04 to 2 ppm respectively. Six Nuvvuagittuq rocks including 3 cummingtonite-amphibolites (PC129, PC132 and PC425), 2 ultramafic rocks (PC092, PC128) and 1 tonalite (PC286) have been measured for W isotopic composition (Fig. 1). Both ultramafic rocks and two of the cummingtonite-amphibolites show well-resolved positive ^{182}W anomalies of ~ +16 ppm. In contrast, the W isotopic compostion of the cummingtonite-amphibolite rock PC425 has a composition that is identical to that of terrestrial standards and modern terrestrial rocks. The tonalite appears to show a small

^{182}W anomaly of ~+5 ppm, but this will need to be confirmed by repeated measurements. Osmium concentrations range from 2.49 to 0.182 ppb, and are well correlated with MgO, consistent with HSE behavior during differentiation of terrestrial volcanic rocks. Additional HSE abundances and Os isotope compositions are currently being determined for this suite.

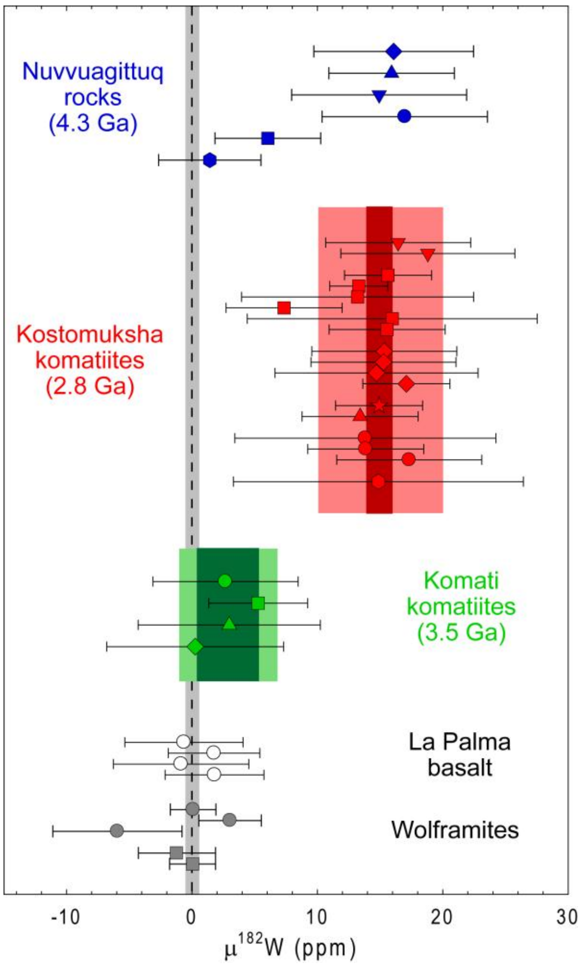

Figure 1. Tungsten isotopic compositions of Nuvvuagittuq rocks (this study) and Komati and Kostomuksha komatiites [2]. Data for the modern La Palma basalt, LP15, and two wolframites from Datovani (grey circles) and Masivni (grey squares), Czech Republic, are also shown for comparison. Each unique symbol corresponds to a distinct sample. Identical symbols show replicate measurements of the same sample. The gray area corresponds to the 2σ SE uncertainty for repeated analyses of the *Alfa Aesar* W standard (*n*=60).

Discussion: Tungsten concentrations show no correlation with chemical indicators of crystal-liquid fractionation, such as the MgO content, even when samples from the same lithology are considered. Potential open-system behaviour with regards to W in some Nuvvuagittuq rocks is, therefore, possible. Although no apparent correlation between W isotope compositions and W abundances is observed, less radiogenic $\mu^{182}W$ values for PC286 and PC132 may potentially reflect contamination with W having a 'normal' isotope composition, possibly reflecting post-eruption alteration or crustal assimilation.

The ultramafic sample PC092, characterized by high MgO content (32.7 %), has an Os abundance similar to the primitive upper mantle [9]. Assuming this high Os content can be directly linked to that in the source of the rock, this observation may indicate that the bulk of the late accreted materials had already been delivered to Earth and homogenized within the mantle by 4.3 Ga, and, hence, prior to the hypothesized late havy bombardement, in contrast to the earlier conclusions of [1] and [10].

As with the positive ^{182}W anomalies previously reported for the Kostomuksha komatiites, the anomalous isotope composition of some Nuvvuagittuq rocks, including sample PC092 ($\mu^{182}W$ = +16.1 ± 6.4), cannot simply reflect the isotopic signature of the Earth's mantle before late accretion, because of their relatively high HSE contents. Here also, the mechanisms able to produce a mantle domain with high Hf/W ratio while ^{182}Hf was still extant (<60 m.y. after CAI formation) must have controlled the processes necessary to produce these anomalies.

The ^{182}W excesses in both the Nuvvuaggituq samples and the Kostomuksha komatiites indicate differentiation of the Earth's mantle earlier than the giant impact and the formation of the Moon [11]. Early differentiation products must have been preserved during this cataclysmic event which, therefore, did not induce complete homogenization of the silicate Earth and, most likely, rules out complete melting of the Earth's mantle by this process.

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Acknowledgments: This work is supported by NSF-CSEDI grant 0757808 and NASA grant NNX07AM29G. James Day and Lukas Ackerman are thanked for providing the La Palma basalt and the two wolframites, respectively.