Early Earth Differentiation Investigated Through ^{142}Nd , ^{182}W , and Highly Siderophile Element Abundances in Samples From Isua, Greenland

H. Rizo^{*1,2,3}, R.J. Walker³, R.W. Carlson², M. Touboul⁴, M.F. Horan², I.S. Puchtel³, M. Boyet⁵, M.T. Rosing⁶

¹GEOTOP, Université du Québec à Montréal, Montréal, Québec H3C 3P8, Canada

²Department of Terrestrial Magnetism, Carnegie Institution for Science, Washington DC 20015, USA

³Department of Geology, University of Maryland, College Park, MD 20742, USA

⁴Laboratoire de Géologie de Lyon, Ecole Normale Supérieure de Lyon, 69007 Lyon, France

⁵Laboratoire Magmas et Volcans, Université Blaise Pascal-CNRS-IRD-OPGC, 5 rue Kessler, 63038 Clermont-Ferrand, France

⁶University of Copenhagen, DK-1350 København K2, Denmark

*** Corresponding author at:** GEOTOP, Université du Québec à Montréal, Montréal, Québec H3C 3P8, Canada. E-mail address: hanika.rizo@uqam.ca

Submitted: June 26th 2015

Revised: November 25th, 2015

Abstract

We report new data for W concentrations, stable W isotopic compositions, high-precision $^{182}\text{W}/^{184}\text{W}$ ratios, highly siderophile element (HSE) abundances and ^{187}Re - ^{187}Os isotopic systematics in a suite of 3.8 Ga to 3.3 Ga mafic and ultramafic rocks from the Isua supracrustal belt, and the Paleoarchean terrane in the northwestern part of the belt. These data are compared with published data for ^{146}Sm - ^{142}Nd systematics in the same samples. The samples from the Isua supracrustal belt show well resolved excesses of $^{182}\text{W}/^{184}\text{W}$ of up to ~21 ppm, consistent with previous W isotopic data reported by Willbold et al. (2011). While there is abundant evidence that W was mobilized in the crust accessed by the Isua supracrustal suite, the isotopic anomalies are interpreted to primarily reflect processes that affected the mantle precursors to these rocks. The origin of the ^{182}W excesses in these rocks remains uncertain. The Isua mantle source could represent a portion of the post-core-formation mantle that was isolated from late accretionary additions (e.g., Willbold et al., 2011). However, the combined ^{182}W , Re-Os isotopic systematics, and HSE abundances estimated for the source of the Isua basalts are difficult to reconcile with this interpretation. The W isotope variations were more likely produced as a result of fractionation of the Hf/W ratio in the mantle during the lifetime of ^{182}Hf , i.e., during the first 50 Ma of Solar System history. This could have occurred as a result of differentiation in an early magma ocean. The Isua suite examined is also characterized by variable $^{142}\text{Nd}/^{144}\text{Nd}$, but the variations do not correlate with the variations in $^{182}\text{W}/^{184}\text{W}$. Further, samples with ages between 3.8 Ga and 3.3 Ga show gradual diminution of ^{142}Nd anomalies until these are no longer resolved from the modern mantle isotopic composition. By contrast, there is no diminishment of ^{182}W variability with time, suggesting different mechanisms of origin and retention of isotopic variations for these two extinct-radionuclide isotope systems. The presence of ^{182}W isotopic anomalies in rocks as young as 3.3 Ga, implies that early-formed, high Hf/W domains survived for more than 1 Ga in the convective mantle.

Keywords: Isua supracrustal belt, early Earth differentiation, ^{182}W , ^{142}Nd , highly siderophile elements

1. Introduction

The earliest history of the Earth is veiled in mystery due to the scarcity and degree of reworking of early Archean and especially Hadean rocks and minerals. Nevertheless, short-lived isotope systems can provide important information about Earth's primary differentiation and early chemical evolution. The Hf-W isotope system ($^{182}\text{Hf} \rightarrow ^{182}\text{W}$, $t_{1/2} = 8.9$ Ma, Vockenhuber et al., 2004) is particularly valuable for studying events that occurred during the first ~50 Ma of Solar System history. This system is an ideal tracer of metal-silicate segregation, because W is moderately siderophile, while Hf is strongly lithophile. The Hf-W system has been commonly applied to study core formation processes, where core formation led to the creation of high (bulk silicate Earth) and low (core) Hf/W ratio domains within the Earth. Comparing the $^{182}\text{W}/^{184}\text{W}$ ratio of Earth's mantle to that of chondritic meteorites can therefore provide important information about the timing of the formation of Earth's core. The observation that the $^{182}\text{W}/^{184}\text{W}$ ratio of Earth's mantle is on average ~200 ppm higher than that of chondrites has been attributed to primary core-mantle segregation during the first ~30 million years of Solar System history (Yin et al., 2002; Kleine et al., 2002; Kleine et al., 2009; Schoenberg et al., 2002). Tungsten is also more incompatible than Hf in most silicate minerals, so major variations in Hf/W ratios also likely resulted from crystal-liquid fractionation processes occurring in the silicate Earth (e.g., Righter and Shearer, 2003; Brown et al., 2014). If fractionation between W and Hf occurred while ^{182}Hf was extant, W isotopic heterogeneities in the mantle should have been created.

Eoarchean rocks from both the Isua supracrustal belt (southwest Greenland) and the Acasta gneisses (Northwest Territories, Canada) were among the first terrestrial rocks to be analyzed for W isotopic composition (Moynier et al., 2010; Iizuka et al., 2010). The $^{182}\text{W}/^{184}\text{W}$ ratios measured in these rocks, with the ± 20 -30 ppm uncertainty typical of these studies, were indistinguishable from the modern mantle. Recent improvements in analytical techniques have pushed the precision of $^{182}\text{W}/^{184}\text{W}$ ratio measurements below ± 5 ppm (Willbold et al., 2011; Touboul and Walker, 2012). Measurements made by these high-precision techniques have revealed that ancient rocks from the Isua supracrustal belt, the Acasta gneisses, the Nuvvuagittuq greenstone belt, as well as late Archean komatiites from Kostomuksha, have ^{182}W excesses of 5 to 15 ppm compared to the modern mantle (Willbold et al., 2011; Touboul et al., 2012; Touboul et al., 2014; Willbold et al., 2015). The causes of the ^{182}W enrichments are still debated, but

currently center on two possibilities. One is that these samples were derived from portions of the mantle that, following completion of core segregation, remained isolated from late accretionary additions of materials with chondritic W isotopic compositions (Willbold et al., 2011). The addition of ~0.5 wt.% of chondritic material to the silicate portion of the Earth following cessation of core formation has frequently been called on for establishment of chondritic relative abundances of the highly siderophile elements (HSE) in the mantle (Chou et al., 1983; Kimura et al., 1974). This process is commonly termed *late accretion*. Because the $^{182}\text{W}/^{184}\text{W}$ ratio of chondrites is ~200 ppm lower than Earth's modern accessible mantle, this amount of late addition of chondritic materials would have lowered the $^{182}\text{W}/^{184}\text{W}$ ratio of the bulk mantle by ~10-20 ppm. Consequently, mantle sources isolated from these late additions would be enriched in ^{182}W by that amount, compared to the mantle that fully incorporated late accretionary components. In addition to a more radiogenic W isotopic composition, these isolated mantle sources would also be depleted in HSE. The only published data for which ^{182}W excesses and HSE abundances have been measured are those from Kostomuksha and Nuvvuagittuq, yet these rocks do not appear to be derived from mantle sources that were significantly depleted in HSE relative to the modern mantle (Puchtel and Humayun, 2005; Touboul et al., 2012; Touboul et al., 2014).

Another possible cause for terrestrial ^{182}W anomalies is fractionation of the Hf/W ratio in the mantle as a result of crystal-liquid differentiation in a terrestrial magma ocean, while ^{182}Hf was still extant. This possibility was proposed to explain ^{182}W enrichment in the 2.8 Ga Kostomuksha komatiites (Touboul et al., 2012). For this scenario, the differentiation must take place within ~30 Ma of the formation of the Solar System in order to result in the observed enrichment in ^{182}W . Touboul et al. (2012) considered both metal-silicate partitioning in a lower mantle magma ocean, and silicate solid-liquid partitioning in a whole mantle magma ocean, to create isotopically enriched mantle domains that could be tapped at a later time. In the case of the Kostomuksha komatiites, the resulting high $^{182}\text{W}/^{184}\text{W}$ domain must have survived for at least ~1.7 Ga, in order to be sampled at 2.8 Ga.

If terrestrial W isotopic variability is due to early magma ocean differentiation, then a correlation between $^{182}\text{W}/^{184}\text{W}$ and $^{142}\text{Nd}/^{144}\text{Nd}$ ratios might be expected. The abundance of ^{142}Nd was enhanced through the short-lived decay of ^{146}Sm ($t_{1/2} = 103$ Ma). Magma ocean differentiation will fractionate the Sm/Nd ratio in the same way as the Hf/W ratio. If the fractionation occurred during the lifetime of ^{182}Hf , it also occurred during the lifetime of ^{146}Sm .

In comparison to the ^{182}Hf - ^{182}W system, the ^{146}Sm - ^{142}Nd system involves two lithophile elements, and therefore, is only sensitive to silicate differentiation events. The excesses and deficits in ^{142}Nd relative to modern terrestrial Nd standards detected in Archean rocks from southwest Greenland (Bennett et al., 2007; Boyet et al., 2006; Caro et al., 2006; Rizo et al., 2011; Rizo et al., 2012; Rizo et al., 2013), suggest that these samples were derived from incompatible element enriched and depleted portions of the mantle that were differentiated in the Hadean. Further, the Sm-Nd systematics of the Isua supracrustal belt rocks suggest that early-formed chemical heterogeneities in the mantle source(s) of these rocks were mixed away by ~ 3.3 Ga (Rizo et al., 2013). If both $^{182}\text{W}/^{184}\text{W}$ and $^{142}\text{Nd}/^{144}\text{Nd}$ ratios reflect differentiation of an early terrestrial magma ocean, then variability of $^{182}\text{W}/^{184}\text{W}$ ratios from the rocks of the Isua supracrustal belt should also diminish with time.

A third possibility to explain variation in $^{182}\text{W}/^{184}\text{W}$ ratios that has not yet been considered stems from the possibility of coupled geochemical reactions and analytical artifacts. Geochemical reactions during metamorphic mobilization of W can potentially cause mass dependent fractionation of W isotope ratios. Instrumental mass fractionation during a mass spectrometric measurement is normally corrected assuming an exponential mass dependence to the fractionation. If a sufficiently large natural mass fractionation occurred that followed another mass dependent fractionation law (e.g., linear, equilibrium, Rayleigh), the exponential correction of the measured W ratios could potentially produce apparent $^{182}\text{W}/^{184}\text{W}$ variations that would reflect an analytical artifact, rather than a geologically meaningful relation to ^{182}Hf decay. In contrast to Nd, there are an insufficient number of isotopes of W to assess this possibility by examining other W isotopic ratios, so it is necessary to assess the magnitude of mass dependent fractionation of W in samples.

Here, we report W concentrations, stable W isotope compositions, high-precision $^{182}\text{W}/^{184}\text{W}$ ratios, and HSE abundances, including ^{187}Re - ^{187}Os isotopic systematics, in a suite of 3.8 Ga to 3.3 Ga mafic and ultramafic rocks from the Isua supracrustal belt, and the Paleoarchean terrane in the northwestern part of the belt. All of the mafic samples investigated here have been previously analyzed for ^{146}Sm - ^{142}Nd systematics (Rizo et al., 2011; Rizo et al., 2012; Rizo et al., 2013).

2. Geological setting

The samples studied here come from the 3.3 to 3.8 Ga mafic and ultramafic units from the Isua area of southwest Greenland. Additionally, one scheelite (CaWO_4) sample from the same area was studied. The mafic samples are the same as discussed in Rizo et al. (2011; 2012; 2013). Consequently, only a brief description of the geological setting for the samples is given here. More details can be found in Nutman and Friend (2009), where complete geological descriptions of all lithologies of the Isua supracrustal belt and associated gneisses are given.

The Isua supracrustal belt is located in the Nuuk region of southwest Greenland, and is composed of metamorphosed mafic, ultramafic, and felsic igneous rocks and sedimentary units. The Amitsoq gneisses that intruded the belt at ~3.7 Ga (Baadsgaard et al., 1986) provide a minimum age for the supracrustal rocks. The precursors to the mafic units (now amphibolites) have been characterized petrologically and geochemically as boninites, tholeiites and picrites (Gill et al., 1981; Polat et al., 2002; Rosing et al., 1996; Polat and Hofmann, 2003). The ~ 3.7-3.8 Ga spatially, and presumably temporally, associated ultramafic units have been suggested to represent mantle residues (Friend and Nutman, 2011). A recent study, however, suggested that the protoliths of these rocks were instead igneous cumulates, formed by accumulation of olivine, spinel, plagioclase and orthopyroxene from tholeiitic and boninitic magmas (Szilas et al., 2014). The mafic Ameralik dykes intruded both the supracrustal rocks and the Amisoq gneisses at ~ 3.4 Ga. A Paleoarchean terrane devoid of Ameralik dykes, and composed of mafic rocks and felsic gneisses, is juxtaposed to the northwest fringe of the Isua supracrustal belt. Mafic rocks from this terrane have been geochemically characterized as tholeiites. While the intrusion of ~ 3.1 Ga felsic sheets (Nutman and Friend, 2009) constrains the minimum age for these rocks, Sm-Nd and Lu-Hf isochrons for these rocks suggest an age of ~ 3.3 Ga for their emplacement (Rizo et al., 2013).

3. Analytical techniques

3.1. Tungsten concentrations

Tungsten concentrations of the mafic and ultramafic samples and the scheelite from the Isua supracrustal belt, as well as of the basalt standard BIR-1, the MORB glass standard VE-32, and the Hawaiian basalt standard BHVO-1, were determined by isotope dilution. A calibrated tracer solution containing highly enriched ^{186}W was added to the sample powders (~200 mg) at the outset of the digestion procedure. Separate aliquots of sample powder were used for the isotope dilution and isotope composition measurements. Sample dissolution and sample-spike equilibration were achieved in *Savillex* vials with a 5:1 mixture of concentrated $\text{HF}:\text{HNO}_3$, on a hotplate at ~120°C for three days. Samples were then dried down twice and re-dissolved in 2 ml of concentrated HNO_3 , followed by two successive dry downs and re-dissolutions in 5 ml of 6M HCl . All the samples were completely dissolved, except for the scheelite sample. After the dissolution, a white precipitate was observed in the scheelite sample. This residue was probably tungstic acid (H_2WO_4), which is a common precipitate observed during conventional acid digestion of scheelites (Chu et al., 2012). Chu et al. (2012) concluded that formation of this precipitate does not cause mass fractionation of Nd, so we consider it unlikely that W isotope ratios were modified by these processes.

The W fraction was separated using an anion-exchange column filled with 1 ml of AG1-X8 resin. Total blanks were between 0.3 to 0.4 ng, which represent a maximum of 5% for the samples with the lowest W concentrations. Tungsten concentrations were determined using the *Thermo iCap Q* ICP-MS at the Department of Terrestrial Magnetism (DTM) of the Carnegie Institution for Science. Instrumental mass bias effects on W were corrected through sample-standard bracketing with an *Alfa Aesar* W standard and using an exponential law and a value for $^{186}\text{W}/^{184}\text{W}$ of 0.92767.

The accuracy of the W concentration measurements was monitored via analysis of the standards BIR-1, VE-32, and BHVO-1 (**Table 1**). The BIR-1 mean W concentration for 3 different dissolutions of 6.9 ± 1.7 ppb ($2\sigma_m$, $n=3$) is consistent with the mean values of 6.0 ppb and 6.1 ppb of Babechuk et al. (2010), and 7.2 ppb of König et al. (2011). The VE-32 W concentration was measured at 56.0 ± 4.0 ppb ($2\sigma_m$, $n=2$), consistent with the value of 56.8 ppb of Arevalo and McDonough (2008). BHVO-1 gave a mean value of 274 ± 7 ppb, which is identical within errors to the compiled value of 270 ppb reported in Govindaraju (1994). External precision as determined from multiple measurements of the same sample is typically better than $\pm 10\%$ (2 r.s.d.).

3.2. Tungsten stable isotopic compositions

The stable isotope compositions of W in six Isua mafic samples (00-007, 00-010, 00-029, 00-039, 00-042 and 460257, **Table 2**) were measured using the *Nu Plasma HR* at DTM. Tungsten solutions from samples and the *Alfa Aesar* standard were prepared in 0.4 M HNO₃ acid to each have ~200 ppb W. Solutions were aspirated into the plasma using an MCN 6000 desolvating nebulizer. Instrumental mass fractionation was monitored using the *Alfa Aesar* W standard solution, which was analyzed before and after each sample. Fractionation of the standard over the total course of these measurements (7.5 hours) was 0.2‰ per AMU. No instrumental fractionation correction was applied to the samples or the standards. Internal precision of the analyses was, on average, 0.02, 0.1 and 0.02 ‰ (2σ) on the ¹⁸²W/¹⁸⁴W, ¹⁸³W/¹⁸⁴W and ¹⁸⁶W/¹⁸⁴W ratios, respectively.

3.3. Re-Os isotopic compositions and highly siderophile element abundances

Enriched tracer solutions of ¹⁸⁵Re, ¹⁹⁰Os, and mixed ¹⁹¹Ir-⁹⁹Ru-¹⁹⁴Pt-¹⁰⁵Pd spikes and ~1g of sample powder were sealed in borosilicate Carius tubes with 4ml of concentrated HCl and 5ml of concentrated HNO₃. The Carius tubes were placed in an oven at 270°C for four days. Osmium was extracted from the acid solution into carbon tetrachloride (Cohen and Waters, 1996), then back-extracted into 4ml of concentrated HBr, and further purified using a micro-distillation technique (Birck et al., 1997). Rhenium, Ir, Ru, Pt and Pd were separated and purified using anion exchange column chromatography (Rehkämper and Halliday, 1998).

Osmium isotope analyses of the ultramafic samples were performed at DTM on a *Thermo Fisher Triton* thermal-ionization mass spectrometer (TIMS) using OsO₃⁻ ions. Ion beams were quantified via peak hopping using a single electron multiplier. Typical ion intensities for ¹⁹²OsO₃⁻ were ~ 200,000 cps. Instrumental mass bias effects on Os were corrected using an exponential law and a value for ¹⁹²Os/¹⁸⁸Os of 3.083. The internal precision for ¹⁸⁷Os/¹⁸⁸Os of all analyses was better than ±0.5% (2 s.d.). The Os blank contribution was between 1.2 and 2.0 pg. Possible ¹⁸⁵Re was monitored at mass 233 during each analysis. The signal at this mass never exceeded 5 cps and no corrections on mass 235 (¹⁸⁷OsO₃⁻) were made. Two sessions of analyses gave values

for $^{187}\text{Os}/^{188}\text{Os}$ of the DTM internal J-M Os standard of 0.17374 ± 4 and 0.17399 ± 6 , which are in good agreement with the previous published value of 0.173927 ± 5 measured on Faraday cups (e.g. Luguet et al., 2008). Concentrations of Os were determined with an uncertainty better than 0.3% (2 r.s.d.). Osmium isotopic compositions of the mafic samples were measured at the University of Maryland (UMd) using a *NBS* mass spectrometer. Run conditions were identical to those described above for the *Triton* analyses. For this instrument, two analyses of 150 pg of the UMd Os standard gave values for $^{187}\text{Os}/^{188}\text{Os}$ of 0.1139 ± 2 and 0.1140 ± 2 , which are both consistent with the accepted value of 0.11376 ± 11 (e.g. Puchtel et al., 2014).

Rhenium, Ir, Ru, Pt and Pd concentrations were determined on either a *Thermo iCap Q* ICP-MS at DTM or a *Nu Plasma* instrument with a triple electron multiplier configuration in a static mode at the UMd. The concentrations for all the HSE using the *iCap Q* were determined with < 5% (2 r.s.d.) uncertainties, except for Re of samples 050004 and 879300, which were determined with a precision of 16% and 15%, respectively. The instrumental mass fractionation of these analyses was corrected using the standard-sample bracketing method (one standard measured before and after every sample). Highly siderophile element concentrations were determined with $\pm 2\%$ of uncertainty on the *Nu Plasma* for Ru, Pt, and Pd, and $\pm 0.5\%$ for Re and Ir. The accuracy of the data on this instrument was assessed by comparing the results for the reference materials UB-N and GP-13 obtained during the ongoing analytical campaign (Puchtel et al., 2014). Concentrations of all HSE and Os isotopic compositions obtained at the UMd were in good agreement with the data for these standards reported by other laboratories (Puchtel et al., 2014). Diluted spiked aliquots of iron meteorites were run during each analytical session as secondary standards. The results from these runs agreed within 0.5% for Re and Ir, and within 2% for Ru, Pt, and Pd, with fractionation-corrected values obtained from measurements of undiluted iron meteorites using Faraday cups of the same instrument with a signal of >100 mV for the minor isotopes.

Total analytical blank determined during the course of the analytical campaign averaged (pg, 2σ): 2 ± 1.5 (Re), 1.6 ± 0.5 (Ir), 56 ± 10 (Ru), 47 ± 5 (Pt), 4 ± 0.5 (Pd). These correspond to blank contributions of less than 0.7%, except for Re (< 7% for all samples, except for samples 050004 and 879300 which have less than 9 pg Re, and for which blank contributions were ~25% and ~22%, respectively).

3.4. Tungsten isotopic composition

Sample dissolution and chemical separation protocols followed for W isotopic measurements are described in detail in Touboul and Walker (2012). Appropriate amounts of sample powder sufficient to extract $\sim 1.5 \mu\text{g}$ of W (1.5 to 7g) were digested in a 5:1 mixture of concentrated HF:HNO₃ in *Savillex* vials placed on a hotplate at 120°C for four days. After evaporation to dryness, the samples were taken up in $\sim 10\text{ml}$ of concentrated HNO₃ and dried down. This step was repeated twice. The samples were then re-dissolved in $\sim 20\text{ml}$ of 6M HCl and placed in a closed *Teflon* vessel on a hotplate at 120°C overnight. If undissolved sample was visible, the residue was re-dissolved in concentrated HF:HNO₃. Once clear sample solutions were obtained, they were evaporated to dryness. Tungsten was then separated from the bulk rock by first using cation exchange chromatography, followed by a three-step anion exchange separation procedure. Tungsten yields for each sample were assessed at the end of the chemical purification. A small aliquot of each purified sample was taken and their W concentrations determined using the *Thermo iCap Q* ICP-MS by comparison of signal intensity to a W standard solution of known concentration. Yields were always better than 80%. Total blanks were measured systematically and never exceeded 10 ng, representing less than 1% of the total amount of W processed for each sample, and were therefore negligible.

Tungsten isotopic compositions were analyzed as W oxide (WO⁻³) using the *Thermo-Fisher Triton* thermal-ionization mass spectrometer at DTM. Samples were loaded onto zone-refined Re filaments, previously outgassed at $\sim 2\text{A}$ under a vacuum. Each measurement consisted of data acquisition for 42 blocks of 30 ratios each (8s integration time), while using amplifier rotation. Baselines were measured every block by beam deflection for 30 cycles (each of 1.05 s). Measurements were performed using 2 steps of static acquisition, where Faraday cups were set for peak coincidence with a first step having ¹⁸³W in the axial cup, and then the zoom lens was adjusted to achieve peak-cup coincidence for the second step that placed ¹⁸⁵W in the axial cup. During measurements, isobaric interferences for W were always monitored and were below detection limit for Ta, and never exceeded 0.25 for the ¹⁸⁵Re/¹⁸²W ratio and 0.007 for ¹⁸⁸Os/¹⁸²W. Tungsten isotope ratios were corrected for instrumental mass fractionation using an exponential law and ¹⁸⁶WO₃/¹⁸³WO₃=1.994902 as normalizing ratio (oxide ratio calculated from metal ratios from Lee and Halliday, 1997, using an oxygen isotopic composition of ¹⁷O/¹⁶O = 0.0003749 and

$^{18}\text{O}/^{16}\text{O} = 0.0020439$ (Nier, 1950). After this correction, the $^{182}\text{W}/^{184}\text{W}$ vs. $^{183}\text{W}/^{184}\text{W}$ ratios of the samples and the standards showed a positive correlation ($R^2=0.9875$ and $R^2=0.9917$, respectively, Figure S1, Supplementary material), with slopes that are identical within errors (2.225 ± 0.077 (2σ) and 2.238 ± 0.078 (2σ), respectively). This observation is consistent with Touboul and Walker (2012). They suggested that this correlation results from the effects of mass dependent oxygen isotope fractionation on the W ratios. The second-order correction for oxygen isotope fractionation was performed using the slope resulting from the $^{182}\text{W}/^{184}\text{W}$ vs. $^{183}\text{W}/^{184}\text{W}$ correlation of the standards (2.238) and a ratio of $^{183}\text{W}/^{184}\text{W} = 0.416729$. More details of the correction method can be found in Touboul and Walker (2012). The *Alfa Aesar* W standard was measured on a regular basis during the different analytical sessions and gave an average value for the $^{182}\text{W}/^{184}\text{W}$ ratio of 0.864766 ± 0.000004 (± 4.6 ppm, 2σ , $n=6$) for session B494, 0.864767 ± 0.000003 (± 3.5 ppm, 2σ , $n=4$) for session B504, 0.864771 ± 0.000004 (± 5 ppm, 2σ , $n=3$) for session B530 and 0.864770 ± 0.000004 (4.8 ppm, 2σ , $n=9$) for session B554. The ^{182}W isotope ratios are hereafter expressed in μ -units and calculated relative to the average value obtained for each session of the *Alfa Aesar* W standard ($\mu^{182}\text{W} = (^{182}\text{W}/^{184}\text{W})_{\text{sample}} / (^{182}\text{W}/^{184}\text{W})_{\text{standard}} - 1 \times 10^6$).

4. Results

4.1. Re-Os and HSE abundances

Rhenium-osmium isotopic data for the mafic and ultramafic samples are provided in **Table 3** and shown in **Figure 1**. On the Re-Os isochron diagram the data for most mafic samples plot between the 3.3 Ga and 3.8 Ga reference isochrons (**Figure 1A**), except for mafic sample 00-007, which plots well above these reference isochrons. All mafic rocks combined, excluding 00-007, define a trend with a positive slope corresponding to an age of 3.85 ± 0.27 Ga and an initial $^{187}\text{Os}/^{188}\text{Os} = 0.1\pm1.7$ (MSWD = 354). The large uncertainty on the initial Os isotopic composition reflects the high Re/Os ratios of the mafic samples and the scatter about the regression line. Although there is considerable scatter, these data suggest that the Re-Os isotopic systematics of most of these rocks have been generally closed since the Eoarchean. Given that Re is typically the most mobile of the HSE, these results also suggest that the abundances of the other HSE present in these rocks have been little affected by post Eoarchean processes.

By contrast, the ultramafic samples do not plot within uncertainties of the 3.3-3.8 Ga reference isochrons (**Figure 1B**), despite the fact that they likely formed within that time interval. These samples define a scattered correlation on the Re-Os isochron diagram corresponding to an age of 2.82 ± 0.33 Ga, an initial $^{187}\text{Os}/^{188}\text{Os}$ of 0.1011 ± 0.0023 , and an MSWD = 256. The scatter is reduced somewhat if the data for sample 879375a is excluded from the regression (MSWD=32) but the age (2.80 ± 0.16 Ga) and initial $^{187}\text{Os}/^{188}\text{Os}$ (0.1007 ± 0.0011) are not significantly different from those determined using the data for all ultramafic samples. The age of ~ 2.8-2.9 Ga corresponds to a well-known metamorphic episode within the Isua supracrustal belt (Blichert-Toft and Frei, 2001; Frei et al., 2001; Gruau et al., 1996; Rollinson, 2009; Rizo et al., 2011), suggesting that the Re-Os systematics in the ultramafic rocks were affected by this metamorphic event. Nevertheless, the initial $^{187}\text{Os}/^{188}\text{Os}$ of the isochrons for the ultramafic rocks of 0.1007 ± 0.0011 is similar, within errors, to the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of olivine and spinel separates from ~3.8 Ga peridotites from southwest Greenland (0.1021 ± 0.0002 and 0.1009 ± 0.0002 , respectively, Bennett et al., 2002). These $^{187}\text{Os}/^{188}\text{Os}$ ratios are also identical within errors to the chondritic $^{187}\text{Os}/^{188}\text{Os}$ ratio at 3.7-3.8 Ga. As with the mafic rocks, the HSE abundances of the ultramafic rocks may primarily reflect their Eoarchean abundances, but the evidence of open-system behavior of the Re-Os systematics requires some level of caution in interpreting these concentrations.

Abundances of the HSE in whole rock mafic and ultramafic samples from the Isua supracrustal belt are reported in **Table 3** and presented in **Figure 2**. The mafic rocks show strong depletions in the Ir-group platinum-group elements (IPGE: Os, Ir, Ru), and relative enrichments in the Pt group PGE (PPGE: Pt, Pd), as well as Re. Most of the ultramafic samples show positively sloped HSE patterns with slight enrichment in the more incompatible HSE (Pt, Pd), although with significant depletions in Re. Two samples, S33 and 050004, show more irregular patterns, with relative enrichments in Ru, and strong depletions in Pt.

4.2. Tungsten concentrations and isotopic compositions

The W concentrations for the mafic, ultramafic and scheelite samples from the Isua supracrustal belt, and the standards BIR-1, BHVO-1 and VE-32 are presented in **Table 1**. Collectively, mafic and ultramafic samples from Isua have W concentrations that range from 123

to 943 ppb, except for mafic samples 460217 and 460219 that have much higher concentrations of 2.6 ppm and 3.1 ppm, respectively. The measured W concentration in the scheelite was 190 ppm, but this concentration is likely not representative of the material because of the strong possibility that considerable W was removed into the precipitate following the digestion.

The W isotopic data for the mafic, ultramafic and scheelite samples from the Isua supracrustal belt, the BHVO-1 rock standard and the *Alfa Aesar* W standard solution are presented in **Table 4** and **Figure 3**. Tungsten ratios were acquired using one to three measurements from a single filament loading. The external reproducibility for the $^{182}\text{W}/^{184}\text{W}$ mean of the single filament loadings of the samples was, in general, better than ± 5 ppm (2SD), which is similar to the external reproducibility of the standard. The measured $^{182}\text{W}/^{184}\text{W}$ ratio in the BHVO-1 standard is identical to the mean value of the *Alfa Aesar* standard within error ($\mu^{182}\text{W}=0$). Most of the ~ 3.3 Ga (n=4), ~ 3.4 Ga (n=2), ~ 3.7 Ga (n=5) and ~ 3.8 Ga (n=2) mafic samples, as well as the scheelite and three ultramafic samples, show well resolved excesses of ^{182}W , compared to the standard. The samples with the poorest external reproducibility were samples 00-039 and 00-044, which yielded $\mu^{182}\text{W} = +23 \pm 11$ ppm and 14 ± 9 ppm, respectively. The resolvable positive $\mu^{182}\text{W}$ anomalies for the different age groups range from +7 to +21 ppm (**Fig. 3**). The results for three samples (00-007, 00-010 and 00-042) were duplicated, and processed via two separate digestions each. Tungsten from these duplicated dissolutions gave $\mu^{182}\text{W}$ values that were indistinguishable within ± 5 ppm. The $\mu^{182}\text{W}$ results for most samples are in good agreement with previously reported excesses of +9 to +15 ppm for 7 samples from the Amitsoq gneiss complex, where W isotope data were obtained by MC-ICP MS (Willbold et al., 2011). Samples 460217, 460219 (3.8 Ga amphibolites), and S31 and S33 (ultramafic rocks), however, have W isotopic compositions that are indistinguishable from the standard. Overall, there appears to be no diminution in the magnitude of ^{182}W enrichment with decreasing age (**Fig. 4**), in contrast to published data for ^{142}Nd (Rizo et al., 2013).

5. Discussion

5.1. Natural mass fractionation and the genesis of ^{182}W anomalies

Mass-dependent isotope fractionation can be caused by equilibrium and kinetic chemical reactions. This fractionation is important to consider when attempting to measure very small differences in non-mass dependent isotopic ratios, such as $^{182}\text{W}/^{184}\text{W}$. Mass independent anomalies are normally calculated after correction for instrumental mass fractionation during analysis, on the assumption that the mass dependency of the instrumental fractionation follows an exponential law (e.g., Russell et al., 1978; Hart and Zindler, 1989). By contrast, there is no reason to believe that chemically induced mass fractionation follows the same laws (Russell et al., 1978). Application of exponential mass fractionation corrections to samples that are initially fractionated following some other mass dependency can create apparent anomalies that deviate in magnitude away from the isotope pair used for mass fractionation correction (e.g., Hart and Zindler, 1989; Upadhyay et al., 2008; Andreasen and Sharma, 2009; Carlson, 2014).

The magnitude of isotope fractionation for high atomic number elements, such as W, is expected to be limited due to the small relative mass differences between the W isotopes. Nevertheless, Irisawa and Hirata (2006) showed that, while igneous samples displayed no mass dependent fractionation of W isotopes, mass dependent fractionations of 0.05 and 0.15 per mil per amu were observed in an ore and a sediment sample, respectively. They also showed mass dependent fractionation of W isotopes resulting from ion exchange chromatography when recovery was less than 70%. They suggested that low temperature precipitation and/or evaporation-condensation processes during sample formation could cause the observed fractionations. Such processes must be considered possible for the rocks from the Isua supracrustal belt, especially given the presence of scheelite in the vicinity of some of the rocks studied.

The samples studied here have positive average $\mu^{182}\text{W}$ anomalies of +15 ppm. We have modeled the amount of mass dependent fractionation necessary to produce these $\mu^{182}\text{W}$ anomalies, using linear, power, Rayleigh and equilibrium mass fractionation laws. **Figure 5** shows W isotope anomalies created by an exponential correction of W that has been naturally fractionated through the different mass dependencies. This model indicates that a sample that has undergone a linear- or power-law mass dependent fractionation of 0.65 per mil per AMU will result in apparent $\mu^{182}\text{W}$ anomalies of +15 ppm, after the correction of the W ratios with the exponential law, as used for the TIMS measurements. By contrast, the model also shows that a

rock that has undergone mass dependent fractionation following Rayleigh or equilibrium laws will yield negative apparent $\mu^{182}\text{W}$ anomalies after exponential correction.

The results for the measured stable W isotopic composition by MC-ICPMS for 6 samples from the Isua supracrustal belt are shown in **Figure 6**. The absence of instrumental fractionation correction accounts for the observed correlation between the different W isotope ratios. Compared to the *Alfa Aesar* standard, the mean $\delta^{182}\text{W}$, $\delta^{183}\text{W}$ and $\delta^{184}\text{W}$ values (where δ is the per mil deviation of the isotopic ratio from the standard) for the 6 samples are 0.0 ± 0.1 . Thus, we conclude that the $\mu^{182}\text{W}$ anomalies measured by TIMS on the Isua samples are not due to mass dependent fractionation of W stable isotopes.

5.2. Tungsten concentrations and $^{182}\text{W}/^{184}\text{W}$

To constrain the $^{182}\text{W}/^{184}\text{W}$ ratio of the mantle source(s) of the mafic and ultramafic samples from the Isua supracrustal belt, we first consider whether the W now present in these rocks is representative of the W present in the rocks at the time their igneous protoliths formed. Experimental and empirical evidence indicates that W behaves as a highly incompatible element in silicate melts, closely following the behavior of U, Th and Nb (Arevalo and McDonough, 2008; König et al., 2011). However, for the mafic samples analyzed in this study, there is no correlation between W and U, Th, Nb or MgO concentrations, despite the fact that U is correlated with Th and with Nb (Fig. S2, **Supplementary material**). This observation suggests that the W concentrations of the Isua rocks do not follow a simple magmatic differentiation trend. Consistent with this, many of the mafic samples analyzed here have higher W concentrations than would be expected for basalts derived from a mantle source characterized by W concentrations similar to those estimated for the bulk silicate Earth (BSE: $\sim 12\text{-}13$ ppb; Arevalo and McDonough et al., 2008, König et al., 2011). The magnitude of W enrichments, compared to Th and Nb, are listed in **Table 1**. Partial melting and simple crystal-liquid fractionation calculations using a partition coefficient value for W of 0.02 (Shearer and Righter 2003), suggest that a magma generated by 10% partial melting of a source containing ~ 13 ppb of W would have ~ 100 ppb W. The W concentration of such a primitive magma could potentially increase, due to fractional crystallization, to as high as ~ 180 ppb for 40% fractional crystallization. Therefore, of the mafic

samples, only 460257, 460203, 00-014 and 00-015 have W concentrations within the range expected for typical melts of a mantle source with BSE-like W concentrations.

The ultramafic samples studied here have concentrations between ~150 and ~950 ppb, although five out of seven samples have concentrations <250 ppb. Regardless of the origin of these rocks (mantle residues or cumulates from ultramafic liquids), most of these concentrations are also too high to have been derived from normal mantle via common igneous fractionation processes. Comparably high W concentrations have been measured in some non-contaminated and highly melt-depleted upper mantle peridotites, suggesting that W can sometimes be retained in an Os-Ir-Ru alloy phase (Babechuk et al., 2010). Consistent with this, high concentrations of W have been documented for some Os-Ir-Ru alloys (Barkov et al., 2006), although, these alloys are interpreted to have formed during secondary metasomatic alteration. Other Os-Ir-Ru alloys that have been analyzed for W, however, have concentrations that are low (Walker et al., 2005).

The high concentrations of W present in many of the Isua samples suggest addition of W to mafic and ultramafic precursors from processes other than partial melting and/or fractional crystallization. One possible explanation for the higher than expected W concentrations in some of the supracrustal rocks is by fluid-rock interaction in the mantle source region, given that there is compelling evidence that W can be highly mobile under hydrous conditions (Seiler et al., 2005; Arnórsson and Ókarsson, 2007; König et al., 2008). For example, Touboul et al. (2014) proposed that high W concentrations in some Nuvvuagittuq supracrustal rocks were the result of the hydrous transfer of fluid mobile elements, including W and Ba, from recycled crust into the mantle sources of the rocks. For the Isua suite, however, there is a lack of correlation between W and other highly fluid-mobile elements, such as Ba or Rb (Fig. S2, Supplementary material).

Another possible explanation comes from the observation that certain Isua mafic rocks were metasomatised via LREE-enriched fluid phases expelled from the surrounding tonalities (Rizo et al., 2012). Tonalitic gneisses from the Gothabsfjord region were analyzed by Willbold et al. (2011) for W isotopic composition and they reported $\mu^{182}\text{W}$ values of +16 and +20 ppm. Therefore, the interaction of W-rich fluids, derived from tonalitic materials, with the mafic rocks would increase the W concentration of the mafic rocks and impart the W isotopic composition of the surrounding tonalites.

The mobility of W in the Isua region is also shown by the occurrences of scheelite in the southern part of the Isua supracrustal belt (Appel, 1986). The one scheelite sample analyzed here

(200645) has a $\mu^{182}\text{W}$ value of $+16 \pm 4$, which is the same within analytical uncertainty as the $\mu^{182}\text{W}$ value obtained for samples with the lowest W concentrations ($+14.0 \pm 1.9$ for mafic sample 460257, $+13 \pm 6$ for mafic sample 00-015, $+13 \pm 6$ for ultramafic sample 879251 and $+14 \pm 6$ for ultramafic sample 789371). This raises the possibility that the W that precipitated to form the scheelite was mobilized from either the tonalites or from the mafic and ultramafic rocks.

The Isua samples were subjected to a widely recognized, late-stage 2.8-2.9 Ga metamorphic event (Blichert-Toft and Frei, 2001; Frei et al., 2001; Gruau et al., 1996; Rizo et al., 2011; Rollison, 2003), and post-formation Ca-metasomatism particularly affected the ultramafic rocks (Rosing, 1989). As noted, the Re-Os systematics for the ultramafic samples yield a slope corresponding to an age of ~ 2.8 Ga, consistent with the age of this metamorphic event. Modification of W concentrations by fluids rich in W during these alteration episodes could be responsible for the unusually high W concentrations in some samples. These episodes could also have modified the $^{182}\text{W}/^{184}\text{W}$ ratios of the samples, if the fluids had different W isotopic compositions than the precursor igneous rocks. For example, samples S31 and S33 have the highest W concentrations among the ultramafic rocks (566 and 873 ppb, respectively), and are characterized by only modestly enriched $\mu^{182}\text{W}$ values of $+5.8$ and $+4.7$, respectively. Both samples also have the highest CaO contents (respectively, 3 and 8 wt.%, Table S1 Supplementary material), the origin of which could have been Ca-rich fluids percolating through the rocks. Further, samples 460217 and 460219, which have the highest W concentrations of the mafic suite examined here (2.6 ppm and 3.1 ppm, respectively), do not show any resolvable ^{182}W anomalies compared to the standard. Collectively, the weak trend in W isotopic composition vs. W concentration in the high W concentration samples suggests that the high W concentration in the mafic and ultramafic rocks could have been caused by interactions with W-rich fluids that had “normal” ($\mu^{182}\text{W}=0$) terrestrial W isotopic compositions. For the rest of the samples, however, there is no clear correlation between W concentration and $^{182}\text{W}/^{184}\text{W}$ ratios (Fig. S3, Supplementary material).

We conclude that there is ample evidence for mobilization of W-rich fluids in the rocks of the Isua Supracrustal Belt. The observations, however, are somewhat contradictory. Given the radiogenic nature of the scheelite, it appears that at least some fluids carried a ^{182}W -rich signature. The most likely source of the mobilized W was the tonalites, or the mafic and ultramafic rocks. The fact that some rocks, with W concentrations that can be attributed to their igneous precursors,

are characterized by the same isotopic composition suggests that this signature originated in the mantle. The mafic and ultramafic rocks characterized by high W concentrations, but low to normal $\mu^{182}\text{W}$ values, appear to have equilibrated with another fluid carrying a normal W isotopic composition. The origin of this fluid remains enigmatic, but could represent a crustal component that is not sampled by the suite examined.

5.3. Radiogenic decay of ^{182}Hf as the cause of ^{182}W anomalies

Elevated $^{182}\text{W}/^{184}\text{W}$ ratios have now been reported for the Kostomuksha komatiites (Touboul et al., 2012), the Nuvvuagittuq supracrustal rocks (Touboul et al., 2014), the Acasta gneisses (Willbold et al., 2015), and this study confirms the report by Willbold et al. (2011) of ^{182}W excesses in samples from the Isua supracrustal belt. These excesses could have been produced by exogenous additions to the Earth (Willbold et al., 2011, Willbold 2015), by endogenous ingrowth of ^{182}W in the silicate Earth (Touboul et al., 2012), or both. We consider both categories of processes that may have led to the ^{182}W excesses in the Isua suite, in conjunction with accompanying ^{142}Nd , ^{187}Re - ^{187}Os and HSE data.

5.3.1 Sluggish mixing of late accretionary additions into the mantle.

Willbold et al. (2011) concluded that the Isua rocks they examined were derived from a mantle source that was missing a substantial portion of its late accretionary component. They noted that removal of ~0.5 wt% (of Earth's total mass) of a chondritic component from the mantle would result in a W isotopic composition in the mantle that would be enriched in ^{182}W compared to the modern mantle to the approximate level observed in the Isua rocks (~ 15 ppm). Minor late accretionary additions to the mantle can have such an effect on its W isotopic composition because chondrites are characterized by W concentrations that are approximately a factor of 10 higher than the BSE, and the W isotopic composition of chondrites is highly-depleted, with $\mu^{182}\text{W}$ values of ~-200 (Kleine et al., 2002). Portions of the mantle lacking a major portion of the ~0.5 wt.% late addition would have HSE abundances that would be significantly lower compared to those found in the modern mantle. This interpretation is also generally consistent with a gradual downward mixing of late accreted materials into the mantle, as suggested by the

apparent increase in the concentrations of Pt in 3.5 to 2.9 Ga komatiites (Maier et al., 2009). This model predicts that there should be no correlation between $\mu^{182}\text{W}$ and $\mu^{142}\text{Nd}$ in the mantle source of the Isua rocks, because the Nd concentrations (~0.6 ppm and ~ 1 ppm, respectively) and isotopic compositions of chondrites and Earth are so similar, so the late accretionary addition would have negligible effect on ^{142}Nd .

By contrast, a model invoking the sluggish mixing of late accretionary additions within the mantle predicts that there should be a negative correlation between mantle source abundances of HSE and $\mu^{182}\text{W}$. Thus, if the positive $\mu^{182}\text{W}$ values of the Isua rocks reflect a deficit of the late accretionary component, the rocks should also be characterized by lower HSE contents compared to modern analogs.

The behavior of HSE during mantle melting is strongly controlled by the mineralogy and oxygen fugacity of the source rocks, as well as the degree of crystallization (particularly of sulfides) *en route* to the surface. This makes it difficult to precisely estimate the HSE abundances in the sources of ancient, relatively evolved, mantle-derived rocks. One approach is to compare the total HSE abundances in the ancient samples to those of modern rocks with similar origin and similar degree of fractionation (e.g., similar MgO contents). A more quantitative approach is to compare Pt concentrations between the ancient rocks and their modern equivalents. Platinum is perhaps the most useful of the HSE with which to assess absolute mantle source concentrations because it has a distribution coefficient near one during partial melting of the mantle, as well as during crystal-liquid fractionation (e.g., Walker, 2014).

Absolute and relative abundances of the HSE in the Isua mafic rocks are similar to those in modern mid-ocean ridge basalts, oceanic island basalts, and continental flood basalts (e.g., Bézous et al., 2005; Rocha-Junior et al., 2012; Day, 2013)(**Fig. 2**). The Pt concentrations of the mafic rocks (excepting low Pt samples 00-038 and 00-039) range from 40 to 100% of the estimate for the Pt concentration of the modern BSE (7.6 ppb; Becker et al., 2006), with an average for the five samples of 70%. If the precursor rocks are assumed to have been basaltic, and Pt was slightly compatible during mantle melting, the mantle source concentration was likely to have been >70% of the modern bulk silicate Earth. For the mafic rocks, there is no correlation observed between the Pt abundance and age of these rocks.

The concentrations of the HSE in the ultramafic rocks are generally lower than typical mantle lherzolites. With the exception of the Re depletions, however, the HSE patterns of the

ultramafic rocks are broadly similar to some mantle harzburgites and dunites, as well as some early Archean komatiites (e.g., Büchl et al., 2002; O'Driscoll et al., 2012; Puchtel et al., 2014). Samples S33 and 050004 show more irregular patterns, with relative enrichments in Ru, and strong depletions in Pt that are similar to some modern harzburgites. These types of patterns have been interpreted to reflect either sulfide break down during emplacement, or late stage mobility of sulfide (Fischer-Gödde et al., 2011). Except for the latter two samples, the Pt concentrations in the ultramafic rocks range from 60 to 80% of the bulk silicate Earth estimate for Pt, and average 66% (n=5). As with the mafic rocks, this estimate represents the lower limit for the Pt concentrations in the source of the ultramafic rocks.

If the magmatic precursors to these Eoarchean rocks were produced by mantle melting processes similar to today, and their HSE abundances are reflective of the concentrations in the precursor rocks, then the HSE data for the mafic and ultramafic rocks appear to be broadly similar to possible modern analogs. Thus, the Isua suite does not appear to have been derived from a mantle source that was strongly depleted in HSE. Further, Re-Os systematics of the Isua ultramafic rocks are consistent with a source that incorporated a major complement of late accretionary component. Since the partition coefficient of Os between metal and silicate is higher than that for Re, the mantle following core formation but before the addition of late accreted materials would have evolved with a much higher Re/Os ratio than the mantle that incorporated these materials. A mantle source that differentiated at ~4.5 Ga that had not yet received its late accretionary component, and that is sampled at ~ 3.8 Ga, would be estimated to have a $^{187}\text{Os}/^{188}\text{Os}$ ratio of ~0.15 (Walker et al., 2009). The $^{187}\text{Os}/^{188}\text{Os}$ of the Isua ultramafic rock source is ~ 0.10 and overlaps with the chondritic value, suggesting that at least the source of the ultramafic Isua lavas was overprinted by chondritic material. Combined HSE abundances, Re-Os systematics and $\mu^{182}\text{W}$ values for the Isua suite are, therefore, difficult to reconcile with the model proposed by Willbold et al. (2011).

5.3.2 Multiple core formation events during Earth growth

An alternative explanation for Isua's elevated $^{182}\text{W}/^{184}\text{W}$ ratio is that its mantle source records an older age of core formation than does the average modern mantle. During Earth accretion, discrete mantle domains may have formed with different Hf/W ratios after each core-

forming event following an accretionary impact large enough to instigate an episode of metal-silicate separation. The siderophilic nature of W may have been affected differently in each of these events because of the different pressures, temperatures and possibly O fugacities involved (e.g. Wade and Wood, 2005). The variability in both Hf/W ratios and the timing of the multiple core-forming events in the heterogeneous mantle would have led to variations in $^{182}\text{W}/^{184}\text{W}$, if the domains were generated while ^{182}Hf was still extant. If late accretion then followed these primary accretionary events, HSE (and W with chondritic $\mu^{182}\text{W}$) would subsequently get mixed into this isotopically “grainy” mantle without mixing out all of the W isotopic heterogeneity. This alternative model allows the formation of mantle domains with broadly “normal” HSE abundances, but variable $\mu^{182}\text{W}$ values. As with the previous model discussed, this process would not be expected to produce a correlation between ^{182}W and ^{142}Nd .

This alternative model assumes that impact-related or convection-induced large scale mixing in the mantle did not erase the discrete events of metal-silicate separation that occurred as the Earth grew by accretion. The likelihood of survival of such heterogeneities is unknown, but the presence of short-lived isotopic anomalies in late Archean rocks suggests that such heterogeneities are not easily mixed away (Touboul et al., 2012, Debaille et al., 2012). This model also requires that some mantle domains evolved to $^{182}\text{W}/^{184}\text{W}$ ratios that were substantially higher than estimates for the BSE, prior to late accretion. **Figure 7** shows $\mu^{182}\text{W}$ versus the Ir contents of a high $^{182}\text{W}/^{184}\text{W}$ mantle domain, such as that of Isua, and the effects that late accretion would have had on this reservoir. For such a mantle reservoir to end up with modern mantle Ir abundances (3.5 ppb) through late accretion, its $\mu^{182}\text{W}$ would have to have been +23 to +31 ppm before the late accretionary component was added. These values are similar to the ^{182}W excesses of 20 to 25 ppm recently identified for the lunar mantle relative to the modern terrestrial mantle (Touboul et al., 2015; Kruijer et al., 2015).

5.3.3. Early silicate differentiation in the mantle

Another way to generate variable $^{182}\text{W}/^{184}\text{W}$ in the mantle is by silicate crystal-liquid fractionation during the lifetime of the parent isotope ^{182}Hf . In this case, the Hf/W and resulting

$^{182}\text{W}/^{184}\text{W}$ ratios in differentiated portions of the mantle may not be correlated with HSE abundances. An important distinction between this way of generating variations in $^{182}\text{W}/^{184}\text{W}$ compared with those induced by the sluggish mixing of late accretionary additions, is that silicate differentiation in the mantle would likely also have affected Sm/Nd, and with time the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio. When considering both isotopic systems collectively, the daughter elements, Nd and W, are more incompatible than the parent elements, Sm and Hf. Therefore, a positive correlation between $\mu^{182}\text{W}$ and $\mu^{142}\text{Nd}$ would be expected in the differentiated reservoirs, unless the systems were somehow decoupled by subsequent processes.

The 3.7-3.8 Ga Isua samples analyzed here show both ^{182}W and ^{142}Nd excesses of between +5 and +21 ppm and between +9 and +15 ppm, respectively (**Fig. 4**). This is consistent with the idea of coupled Hf/W and Sm/Nd fractionation. The $\mu^{182}\text{W}$ and $\mu^{142}\text{Nd}$ values in the Isua mantle source reflect the time of the fractionation event and the degree of Hf/W and Sm/Nd fractionation. **Figure 8** shows evolution curves of $\mu^{182}\text{W}$ and $\mu^{142}\text{Nd}$ values of a mantle residue that differentiates between 30 Ma to 70 Ma after Solar System formation, and after 10%, 30% and 40% of melt extraction. Because of the differences in partition coefficients (e.g., $D_{\text{Hf}/\text{W}} = \sim 4.2$ while $D_{\text{Sm}/\text{Nd}} = \sim 1.3$, Corgne et al., 2005), silicate differentiation events will fractionate the Hf/W ratio more strongly than that of Sm/Nd, leading to considerably higher $\mu^{182}\text{W}$ than $\mu^{142}\text{Nd}$ values in the fractionated reservoirs, if the fractionation occurred early, when ^{182}Hf was comparatively abundant. A mantle residue differentiated prior to ~60 Ma after Solar System formation would be expected to have much higher $^{182}\text{W}/^{184}\text{W}$ excesses compared to $^{142}\text{Nd}/^{144}\text{Nd}$. For example, a mantle residue differentiated 30 Ma after Solar System formation, would evolve to values of $\mu^{182}\text{W} = +57$ and +254 ppm and $\mu^{142}\text{Nd} = +8$ to 31 ppm, for 10% and 40% of melt extraction, respectively. By comparison, differentiation after ^{182}Hf is extinct will lead to an absence of W isotopic variation, although it could still create variability in ^{142}Nd , if the event occurred while ^{146}Sm remained extant. The source of the Isua samples is characterized by maximum $\mu^{182}\text{W}$ and $\mu^{142}\text{Nd}$ values of +21 ppm, and 15 ppm, respectively. A mantle residue after ~30% of melt extraction that occurred ~60 Ma after Solar System formation would result in a mantle reservoir that would evolve to W and Nd isotopic compositions similar to the most radiogenic values seen in the Isua samples.

Arguing against silicate crystal-liquid fractionation as the cause of the W anomalies is the observation that the Nd data show a decreasing excess in ^{142}Nd with time, whereas the W isotopic

data show no correlation with the age of the samples (**Fig. 4**). As a result, the data do not define the expected positive correlation between the Nd and W isotopic compositions. Most perplexing is the ~3.4 Ga Ameralik dyke sample 00-015 that is characterized by a negative $\mu^{142}\text{Nd}$ value of -10, yet by a positive $\mu^{182}\text{W}$ value of +13. The negative $\mu^{142}\text{Nd}$ value must reflect an ancient, incompatible element enriched source, yet the positive $\mu^{182}\text{W}$ value is suggestive of a high Hf/W ratio that may be reflective of incompatible element depleted melt residues or cumulates. This sample is also characterized by a relatively low W concentration of 175 ppb, consistent with a mantle composition with no overprinting via W-rich fluids.

The declining $^{142}\text{Nd}/^{144}\text{Nd}$ with time in Isua rocks has been interpreted as reflecting the mixing away of early-formed chemical heterogeneities in the SW Greenland mantle (Bennett et al., 2007; Rizo et al., 2013). Yet this process would seemingly also mix away W isotopic heterogeneity. One possible explanation for the lack of correlation between W and Nd isotopic compositions in the Isua samples may be different times of formation of their source regions in the mantle. Figure 9 shows a possible model for the evolution of the Isua mantle source. As discussed earlier, the Isua suite appears to have been derived from a mantle source that had similar HSE abundances to the modern mantle. For this observation to be in agreement with the variations that characterize the samples in $^{182}\text{W}/^{184}\text{W}$, the late accreted material that brought the HSE to the Isua mantle source had to arrive before the differentiation of this mantle (**Fig. 9A and B**). A first, large-scale differentiation event during the lifetimes of both ^{182}Hf and ^{146}Sm (< 60 Ma) would have produced incompatible element depleted mantle reservoirs with positive $\mu^{182}\text{W}$ and $\mu^{142}\text{Nd}$, as well as incompatible element enriched mantle reservoirs, with negative $\mu^{182}\text{W}$ and $\mu^{142}\text{Nd}$ (**Figure 9B**). If this occurred after substantial late accretion, the HSE abundances in both depleted and enriched reservoirs would have been broadly comparable to the modern mantle. A second differentiation event is envisioned to have affected only the depleted reservoir (**Figure 9C**). Coupled ^{147}Sm - ^{143}Nd and ^{146}Sm - ^{142}Nd systematics suggest that the source of Isua differentiated 100-150 Ma after Solar System formation (Bennett et al., 2007; Caro et al., 2006; Rizo et al., 2012). Given this time constraint, and the difference in half-lives of ^{182}Hf and ^{146}Sm , this second differentiation event would have occurred after ^{182}Hf was no longer extant, but while ^{146}Sm was still extant. This event would, therefore, be recorded in Nd isotopic composition, but not in W.

Possible differentiation mechanisms for this second event could include the formation of an early basaltic crust, which would be enriched in incompatible elements and would have had negative $\mu^{142}\text{Nd}$, but positive $\mu^{182}\text{W}$. The extraction of this crust would have left a depleted mantle with positive $\mu^{142}\text{Nd}$ and $\mu^{182}\text{W}$. Other possible mechanisms for the differentiation events invoked in the model shown in Figure 9 is differentiation resulting from melting, followed by crystal-liquid fractionation of the mantle after giant impacts. The high $^3\text{He}/^{22}\text{Ne}$ of the present-day mantle has been interpreted to reflect the outcome of multiple magma ocean events during the growth of Earth (Tucker and Mukhopadhyay, 2014).

The model presented in **Figure 9** can potentially explain why the early rock record of the Earth seems to be dominated by a component characterized by elevated $\mu^{182}\text{W}$. However, only a relatively small number of samples have been analyzed for both ^{142}Nd and ^{182}W , so conclusions based on the current available data must be considered tentative. All of the models described above would also imply that the major episodes of Earth formation and differentiation took more than 50 Ma to complete. For the model presented in **Figure 9**, the mantle at 3.8 Ga preserves a record of differentiation events that occurred both prior to 50 Ma after Solar System formation, affecting both W and Nd isotope compositions, and after 50 Ma, affecting only Nd isotope compositions. If multiple episodes of differentiation account for the lack of correlation between $^{182}\text{W}/^{184}\text{W}$ and $^{142}\text{Nd}/^{144}\text{Nd}$, then the Isua data show that these distinct reservoirs in the mantle were preserved until at least 3.8 Ga.

Acknowledgments

We thank T. Mock for assistance with the TIMS. B. Mhammed carried out the major element analyses. This article benefited from discussions with J. O'Neil and S. Shirey. We thank S. Shirey who provided sample VE-32. We thank J. Boyd who provided some of the ultramafic samples studied in this manuscript. We also thank the helpful comments and suggestions from two anonymous reviewers. This work was supported by NSF-CSEDI grant EAR1265169 to R.J. Walker.

Figure Captions

Figure 1. Re-Os isochron diagrams for Isua mafic (A) and ultramafic (B) whole rock samples. Error bars are smaller than the symbols. Regressions were calculated with Isoplot (version 3.41b, rev. 16 Nov 2005; Ludwig, 1991). The quoted errors on the ages are 2-sigma. Initial $^{187}\text{Os}/^{188}\text{Os}$ were calculated using the values for ordinary chondrites of Walker et al (2002) ($^{187}\text{Re}/^{188}\text{Os}$ of 0.421 and $^{187}\text{Os}/^{188}\text{Os}$ of 0.1283).

Figure 2. Highly siderophile element abundances (HSE) for the mafic (A) and ultramafic (B) samples of the Isua supracrustal belt, compared to those in modern basalts (Rocha-Junior et al., 2012) and modern peridotites (Fischer-Gödde et al., 2011). The HSE were normalized to the chondritic values of Horan et al. (2003). IAB: Island arc basalts, MORB: mid ocean ridge basalts.

Figure 3. $\mu^{182}\text{W}$ values measured for 14 mafic samples, 5 ultramafic samples and one scheelite from the Isua supracrustal belt, and the rock basalt standard BHVO-1. The values are expressed as parts in 1,000,000 or ppm deviations from the average measured from the Alfa Aesar standard (2σ , $n=22$). Smaller symbols are individual runs from the same sample dissolution; bigger symbols are the average of the runs. Errors for each data point are 2σ . The shaded area represents the external analytical error for the Alfa Aesar standard.

Figure 4. $\mu^{142}\text{Nd}$ vs. $\mu^{182}\text{W}$ for the mafic and ultramafic samples from Isua. Dark blue diamonds: 3.8 Ga mafic samples; green circles: 3.7 Ga mafic samples; brown triangles: 3.4 Ga mafic samples; light blue squares: 3.3 Ga mafic samples. $\mu^{142}\text{Nd}$ from Rizo et al., 2011, 2012 and 2013 and $\mu^{182}\text{W}$ values from this study. Grey squares: $\mu^{182}\text{W}$ Isua sample data from Willbold et al. (2011) with correspondent $\mu^{142}\text{Nd}$ from Caro et al. (2006). Insert in the top right: $\mu^{142}\text{Nd}$ and $\mu^{182}\text{W}$ for the same Isua samples vs. time.

Figure 5. Model for μW values obtained after correction with exponential law subsequent to natural fractionation of W stable isotopes following different mass dependencies.

Figure 6. Tungsten stable isotopic compositions for the mafic and ultramafic samples of the Isua supracrustal belt, and repeated measurements of the *Alfa Aesar* standard.

Figure 7. Model showing the $^{182}\text{W}/^{184}\text{W}$ vs. Ir content of a mantle source after core formation, prior to late accretion. If the Isua $\mu^{182}\text{W}$ of +15 ppm reflects a source that had already received its late accretion component, then mass balance constraints require that the mantle source prior to late accretion had a $\mu^{182}\text{W}$ between ~23 ppm and ~32 ppm. The late accretionary component taken in this model has chondritic $^{182}\text{W}/^{184}\text{W}$ ($\mu^{182}\text{W}=-190$ ppm), W concentrations between 100 and 200 ppb (range of concentrations measured for ordinary and carbonaceous chondrites, Wasson and Kallemeyn 1988; Anders and Grevesse, 1989; Newsom 1995, Kleine et al. 2004), and 609 ppb of Ir (chondritic average, Walker et al., 2009).

Figure 8. Evolution of $\mu^{142}\text{Nd}$ (solid curves) and $\mu^{182}\text{W}$ (dotted curves) through time of a residue after 10%, 30% and 40% of melt extraction. The different curves for each isotopic composition reflect different times of differentiation events ranging from 30 to 70 Ma after the 4568 Ma start of Solar System formation. The $\mu^{142}\text{Nd}$ and $\mu^{182}\text{W}$ values are calculated using half-lives of 103 Ma and 8.9 Ma for ^{146}Sm and ^{182}Hf , respectively. The chondritic values for W and Nd used are those of Kleine et al. (2009) and Boyet et al. (2010). Partition coefficients for Sm, Nd, Hf and W are those for a melt residue composed of 85% MgPv, 5% CaPv and 5% Mw (Corgne et al., 2005). More details on this model can be found in the Supplementary Material.

Figure 9. Model that satisfactorily explains the $\mu^{142}\text{Nd}$ and $\mu^{182}\text{W}$ values and HSE abundances of the Isua mantle source. A: metal-silicate segregation that results in a mantle with negligible HSE concentrations, high $\mu^{182}\text{W}$ and $\mu^{142}\text{Nd}=0$. B: first silicate differentiation occurring ~ 60 Ma, resulting in the creation of reservoirs with high $\mu^{182}\text{W}$ (+15 ppm) and $\mu^{142}\text{Nd}$, and low $\mu^{142}\text{Nd}$ and $\mu^{182}\text{W}$. Late accreted materials could be added to the mantle either in stage A or B of this model. C: second silicate differentiation happening between 100-150 Ma, and therefore after ^{182}Hf is no longer extant. This silicate differentiation creates only variations in $\mu^{142}\text{Nd}$ values, and could be the result of the crystal-liquid fractionation after a giant impact, or the extraction of a primitive crust.

References

- Arevalo, R.J., and McDonough, W.F., 2008. Tungsten geochemistry and implications for understanding the Earth's interior, *Earth Planet. Sci. Lett.*, 272, 656-665.
- Arnórsson S. and Ókarsson N., 2007. Molybdenum and tungsten in volcanic rocks and in surface and <100 °C ground waters in Iceland. *Geochim. Cosmochim. Acta* 71(2), 284–304.
- Baadsgaard, H., Nutman, A. P., and Bridgwater, D., 1986. Geochronology and isotopic variation of the early Archaean Amitsoq gneisses of the Isukasia area, southern West Greenland. *Geochim. Cosmochim. Acta* 50, 2173-2183.
- Babechuk, M., Kamber, B.S., Greig, A., Canil, D., Kodolányi, J., 2010. The behaviour of tungsten during mantle melting revisited with implications for planetary differentiation time scales. *Geochim. Cosmochim. Acta* 74, 1448-1470.
- Barkov A. Y., Fleet M. E., Martin R. F., Feinglos M. N. and Cannon B. (2006) Unique W-rich alloy of Os and Ir and associated Fe-rich alloy of Os, Ru, and Ir from California. *Am. Mineral.* 91, 191–195.
- Bennett, V.C., Brandon, A.D., and Nutman, A.P., 2007. Coupled ^{142}Nd - ^{143}Nd isotopic evidence for Hadean mantle dynamics, *Science*, 318, 1907-1910.
- Birck J. L., Roy-Barman M. & Capman F. Re-Os isotopic measurements at the femtomole level in natural samples. *Geostandards Newsletter* 20, 19-27 (1997).
- Blichert-Toft, J. and Frei, R., 2001. Complex Sm-Nd and Lu-Hf isotope systematics in metamorphic garnets from the Isua supracrustal belt, West Greenland. *Geochim. Cosmochim. Acta* 65, 3177-3189.
- Boyet, M., and Carlson, R.W., 2006. A new geochemical model for the Earth's mantle inferred from ^{146}Sm - ^{142}Nd systematics, *Earth Planet. Sci. Lett.*, 250, 254-268.
- Carlson, R.W. and Boyet, M., 2008. Composition of the Earth's interior : the importance of early events, *Phil. Trans. R. Soc. A* 366, 4077-4103.
- Carlson, R. W., Borg, L. E., Gaffney, A. M., and Boyet, M., 2014. Rb-Sr, Sm-Nd and Lu-Hf isotope systematics of the lunar Mg-suite: the age of the lunar crust and its relation to the time of Moon formation, *Philosophical Transactions Royal Society of London A* 372, 20130246.
- Caro, G., Bourdon, B., Birck, J.L. and Moor bath, S., 2006. High-precision $^{142}\text{Nd}/^{144}\text{Nd}$ measurements in terrestrial rocks: constraints on the early differentiation of the Earth's mantle, *Geochim. Cosmochim. Ac.*, 70, 164-191.

- Chu, Z. Y., Guo, J. H., Yang, Y. H., Qi, L., Chen, L., Li, X. C., Gao, J. F., 2012. Evaluation of sample dissolution method for Sm-Nd isotopic analysis of scheelite. *J. of Anal. At. Spectrom.*, 27, 509-515.
- Chu, Z. Y., Li, C. F., Chen, Z., Xu, J. J., Di, Y. K., & Guo, J. H., 2015. High-precision measurement of $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$: isobaric oxide corrections with in-run measured oxygen isotope ratios, *Anal. Chem.*, 87, 8765-8771.
- Debaille, V., O'Neill, C., Brandon, A. D., Haenecour, P., Yin, Q. Z., Mattielli, N., & Treiman, A. H., 2013. Stagnant-lid tectonics in early Earth revealed by ^{142}Nd variations in late Archean rocks. *Earth Planet. Sci. Lett.*, 373, 83-92.
- Fischer-Gödde M, Becker H, Wombacher F. 2011. Rhodium, gold and other highly siderophile elements in orogenic peridotites and peridotite xenoliths. *Chem. Geol.* 280, 365–383.
- Frei, R., M.T., R., Waight, T., and Ulfbeck, D., 2001. Hydrothermal-metasomatic and tectono-metamorphic processes in the Isua supracrustal belt (West - Greenland): A multi - isotopic investigation of their effects on the Earth's oldest oceanic crustal sequence. *Geochim. Cosmochim. Acta* 66, 467-486.
- Friend, C. R. L. and Nutman, A. P., 2005. Complex 3670 - 3500 Ma orogenic episodes superimposed on juvenile crust accreted between 3850 - 3690 Ma, Itsaq Gneiss Complex, southern West Greenland. *Journal Geology* 113, 375 - 398.
- Gill, R. C. O., Bridgwater, D., and Allaart, J. H., 1981. The geochemistry of the earliest known basic metavolcanic rocks, West Greenland: A preliminary investigation. *Spec. Publ. Geol. Soc. Aust.* 7, 313-325.
- Govindaraju, K., 1994. Compilation of working values and sample description for 383 geostandards. *Geostandards Newsletter, The Journal of Geostandards and Geoanalysis* 18: 158.
- Gruau, G., Rosing, M., Bridgwater, D., and Gill, R. C. O., 1996. Resetting of Sm-Nd systematics during metamorphism of >3.7-Ga rocks: implications for isotopic models of early Earth differentiation. *Chem. Geol.* 133, 225-240.
- Hart, S.R. and Zindler, A., 1989. Isotope fractionation laws: a test using calcium. *Int. J. Mass Spectrom.* 89, 287-301.

- Iizuka, T., Nakai, S., Sahoo, Y.V., Takamasa, A., Hirata, T., Maruyama, S., 2010. The tungsten isotopic composition of Eoarchean rocks: Implications for early silicate differentiation and core-mantle interaction on Earth. *Earth Planet. Sci. Lett.* 291, 189-200.
- Irisawa, K. and Hirata, T., 2006. Tungsten isotopic analysis on six geochemical reference materials using multiple collector-ICP-mass spectrometry coupled with a rhenium-external correction technique. *J. Anal. At. Spectrom.*, 21, 1387-1395.
- Jacobson, S. A., Morbidelli, A., Raymond, S. N., O'Brien, D. P., Walsh, K. J. and Rubie, D. C. , 2014. Highly siderophile elements in Earth's mantle as a clock for the Moon-forming impact, *Nature*, 508, 84-87.
- Kleine, T., Munker, C., Mezger, K. and Palme, H., 2002. Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf-W chronometry, *Nature*, 418, 952-955.
- König, S., Münker, C., Hohl, S., Paulick, H., Barth, A.R., Lagos, M., Pfänder, J., Büchl., A., 2011. The Earth's tungsten budget during mantle melting and crust formation. *Geochim. Cosmochim. Acta* 75, 2119-2136.
- Lee, D.-C. and Halliday A.N., 1996. Core formation on Mars and differentiated asteroids. *Nature* 388, 854–857.
- Luguet, A., Nowell, G.M., Pearson, D.G., 2008. $^{184}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ measurements by Negative Thermal Ionisation Mass Spectrometry (N-TIMS): Effects of interfering element and mass fractionation corrections on data accuracy and precision, *Chem. Geol.*, 248, 342-262.
- Maier, W. D., Barnes, S. J., Campbell, I. H., Fiorentini, M. L., Peltonen, P., Barnes, S.-J. and R. H. Smithies, 2009. Progressive mixing of meteoritic veneer into the early Earth's deep mantle, *Nature*, 460, 620-623.
- Moynier, F., Yin, Q-Z., Irisawa, K., Boyet, M., Jacobsen, B., 2010. Coupled ^{182}W - ^{142}Nd constraint for early Earth differentiation. *Proc. Natl. Acad. Sci.* 107, 10810-10814.
- Nier, A.O., 1950. A redetermination of relative abundances of the isotopes of carbon, nitrogen, oxygen, argon, and potassium. *Physical Review* 77, 789-793).
- Nutman, A. P. and Friend, C. R. L., 2009. New 1:20,000 geological maps, synthesis and history of investigation of the Isua supracrustal belt and adjacent orthogneisses, southern West Greenland: a glimpse of Eoarchean crust formation and orogeny. *Precamb. Res.* 172, 189-211.

- Polat, A. and Hoffmann, A. W., 2003. Alteration and geochemical patterns in the 3.7-3.8 Ga Isua greenstone belt, West Greenland. *Precambrian Research* 126, 197-218.
- Polat, A., Hoffmann, A. W., and Rosing, M., 2002. Boninite-like volcanic rocks in the 3.7-3.8 Ga Isua greenstone belt, West Greenland: Geochemical evidence for intra-oceanic subduction zone processes in the early Earth. *Chem. Geol.* 184, 231-254.
- Puchtel, I.S., Walker, R.J., Touboul, M., Nisbet, E.G., Byerly, Gary R., 2014. Insights into early Earth from the Pt-Re-Os isotope and highly siderophile element abundance systematics of Barberton komatiites. *Geochim. Cosmochim. Acta* 125, 394-413.
- Rehkämper, M. and Halliday, A.N., 1998. Accuracy and long-term reproducibility of lead isotopic measurements by MC-ICPMS using an external method for the correction of mass discrimination. *Int. J. Mass Spectrom.*, 181, 123-133.
- Righter, K., and Shearer, C. K., 2003. Magmatic fractionation of Hf and W: constraints on the timing of core formation and differentiation in the Moon and Mars, *Geochim. Cosmochim. Ac.*, 67, 2497-2507.
- Rizo, H., Boyet, M., Blichert-Toft, J., and Rosing, M.T., 2011. Combined Nd and Hf isotope evidence for deep-seated source of Isua lavas, *Earth Planet. Sci. Lett.*, 312, 267-279.
- Rizo, H., Boyet, M., Blichert-Toft, J., and Rosing, M.T., 2013. Early mantle dynamics inferred from ^{142}Nd variations in Archean rocks from southwest Greenland, *Earth Planet. Sci. Lett.*, 377, 324-335.
- Rizo, H., Boyet, M., Blichert-Toft, J., O'Neil, J., Rosing, M.T., Paquette, J.L., 2012. The elusive Hadean enriched reservoir revealed by ^{142}Nd deficits in Isua Archean rocks, *Nature*, 491, 96-100.
- Rocha-Júnior, E. R.V., Puchtel, I.S., Marques, L.S., Walker, R.J., Machado, F.B., Nardy, A.J.R., Babinski, M., Figueiredo, A.M.G., 2012. Re-Os isotope and highly siderophile element systematics of the Paraná continental flood basalts (Brazil). *Earth Planet. Sci. Lett.*, 337-338, 164-173.
- Rollinson, H., 2003. Metamorphic history suggested by garnet-growth chronologies in the Isua Greenstone Belt, West Greenland. *Precambrian Research* 126, 181-196.
- Rosing, M. T., Rose, N. M., Bridgwater, D., and Thomsen, H. S., 1996. Earliest part of Earth's stratigraphic record: a reappraisal of the >3.7 Ga Isua (Greenland) supracrustal sequence. *Geology* 24, 43-46.

- Russell, W.A., Papanastassiou, D.A., Tombrello, T.A., 1978. Ca isotope fractionation on the Earth and other solar system materials. *Geochim. Cosmochim. Acta* 42, 1075-1090.
- Seiler R. L., Stollenwerk K. and Garbarino J. (2005) Factors controlling tungsten concentrations in ground water, Carson Desert, Nevada. *Appl. Geochem.* 20, 423–441.
- Szilas, K., Kelemen, P.B., Rosing, M.T., 2014. The petrogenesis of ultramafic rocks in the >3.7 Ga Isua supracrustal belt, southern West Greenland: Geochemical evidence for two distinct magmatic cumulate trends. *Gondwana Res.* In press.
- Touboul, M., Liu, J., O'Neil, J., Puchtel, I.S., Walker, R.J., 2014. New insights into the Hadean mantle revealed by ^{182}W and highly siderophile element abundances in supracrustal rocks from the Nuvvuagittuq greenstone belt, Quebec, Canada, *Chemical Geology* 383, 63-75.
- Touboul, M., Puchtel, I.S., Walker, R.J., 2012. ^{182}W evidence for long-term preservation of early mantle differentiation products, *Science*, 335, 1065-1069.
- Touboul, M., Walker, R.J. 2012. High precision tungsten isotope measurement by thermal ionization mass spectrometry, *Int. J. Mass Spectrom.*, 309, 109-117.
- Tucker, J. M., and Mukhopadhyay, S., 2014. Evidence for multiple magma ocean outgassing and atmospheric loss episodes from mantle noble gases, *Earth Planet. Sci. Lett.*, 393, 254-265.
- Upadhyay, D., Scherer, E., and Mezger, K., 2009. ^{142}Nd evidence for an enriched Hadean reservoir in cratonic roots. *Nature* 459, 1118-1120.
- Walker, R.J., Brandon, A.D., Bird, J.M., Piccoli, P.M., McDonough, W.F., Ash, R.D., 2005. ^{187}Os - ^{186}Os systematics of Os-Ir-Ru alloy grains from southwestern Oregon, *Earth Planet. Sci. Lett.*, 230, 211-226.
- Willbold, M., Elliott, T., Moorbath, S., 2011. The tungsten isotopic composition of the Earth's mantle before the terminal bombardment, *Nature*, 477, 195-198.
- Willbold, M., Mojzsis, S.J., Chen, H-W., Elliott, T., 2015. The tungsten isotope composition of the Acasta Gneiss Complex, *Earth Planet. Sci. Lett.*, 419, 168-177.

Table 1. Tungsten concentration data for the modern rock and glass standards BIR-1, BHVO-1 and VE-32, and mafic and ultramafic samples from the Isua supracrustal belt.

Sample	Rock	Lithology	Age (Ga)	W (ppb)	W/W*
BIR-1	Basalt		0	6.9	
VE-32	MORB glass		0	56	
BHVO-1	Basalt		0	274	
00-028	amphibolite	mafic	3.3	469	21
00-029	amphibolite	mafic	3.3	500	35
00-038	amphibolite	mafic	3.3	539	16
00-039	amphibolite	mafic	3.3	791	32
00-014	metadolerite dyke	mafic	3.4	70	2
00-015	metadolerite dyke	mafic	3.4	174	3
AM019	norite	noritic	3.4	352	
AM021	metadolerite dyke	mafic	3.4	37	1
00-007	amphibolite	mafic	3.7	394	3
00-008	amphibolite	mafic	3.7	250	2
00-010	amphibolite	mafic	3.7	356	1
00-042	amphibolite	mafic	3.7	442	16
00-044	amphibolite	mafic	3.7	317	2
460203	amphibolite	mafic	3.8	151	1
460217	amphibolite	mafic	3.8	2552	36
460219	amphibolite	mafic	3.8	3084	38
460257	amphibolite	mafic	3.8	123	2
879251a	serpentitnite	ultramafic	unknown	241	
879267a	serpentitnite	ultramafic	unknown	200	
879371a	serpentitnite	ultramafic	unknown	218	
879375a	serpentitnite	ultramafic	unknown	146	
879300a	serpentitnite	ultramafic	unknown	216	
050004a	peridotite	ultramafic	unknown	943	
S33a	peridotite	ultramafic	unknown	873	

W concentrations were determined by isotope dilution using an iCAP-Q ICP-MS for isotopic measurements

* is given for some of the mafic samples, and calculated using $W^* = (Th_N/Nt)$

Table 2. W stable isotope compositions of the mafic and ultramafic samples from the Isua supracrustal belt and the Alfa Aesar W standard

Sample	W Std	W Std	W Std	W Std	W Std	W Std	Std W	Std W	00-039	Std W	00-029	Std W	00-007	Std W	Std W	00-010	Std W	00-042	Std W	460257	Std W
¹⁸⁰ W/ ¹⁸⁴ W	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####
2σ	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####
¹⁸² W/ ¹⁸⁴ W	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####
2σ	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####
¹⁸³ W/ ¹⁸⁴ W	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####
2σ	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####
¹⁸⁶ W/ ¹⁸⁴ W	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####
2σ	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####	#####
Δ182 (‰)	-0.08	-0.09	-0.05	-0.04	-0.14	-0.13	-0.10	-0.08	0.10	-0.04	-0.03	0.05	-0.04	0.08	0.04	-0.11	-0.08	0.01	-0.19	0.04	-0.07
2σ	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.03	0.01	0.02	0.01	0.01	0.03	0.01	0.02	0.02	0.21	0.01
Δ183 (‰)	-0.05	-0.07	-0.03	-0.01	-0.08	-0.08	-0.07	-0.04	0.06	-0.03	0.02	0.00	-0.01	0.01	0.03	-0.11	0.00	-0.01	-0.07	0.07	-0.08
2σ	0.71	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.10	0.01
Δ186 (‰)	0.14	0.06	0.10	0.07	0.13	0.14	0.13	0.03	-0.09	0.02	-0.02	0.02	0.00	-0.07	-0.05	0.11	0.11	-0.02	0.12	-0.04	0.02
2σ	0.02	0.01	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.01	0.03	0.01	0.02	0.01	0.01	0.03	0.01	0.02	0.01	-0.06	0.01

W std : Alfa Aesar Tungsten standard solution

Table 3. Re-Os isotope data and highly siderophile element abundances for mafic and ultramafic samples from the Isua supracrustal belt

Sample	Lithology	Age	$^{87}\text{Re}/^{188}\text{Os}$	2σ	$^{37}\text{Os}/^{188}\text{Os}$	cor	2σ	$^{37}\text{Os}/^{188}\text{Os}$	($^{37}\text{Re}/^{188}\text{Os}$)	Re (ppb)	Os (ppb)	Ir (ppb)	Ru (ppb)	Pt (ppb)	Pd (ppb)
00-029	mafic	3.3	114	1	8.618	0.016	2.181	0.68	0.06	0.05	0.12	5.57	4.49		
00-038	mafic	3.3	667	7	45.40	0.13	7.678	0.96	0.04	0.01	0.04	0.47	0.45		
00-039	mafic	3.3	510	5	32.48	0.07	3.637	0.88	0.04	0.01	0.04	0.40	0.25		
00-007	mafic	3.7	760	8	63.44	0.18	15.11	0.51	0.02	0.08	0.02	3.15	2.43		
00-010	mafic	3.7	87.9	0.9	5.199	0.008	-0.387	0.73	0.07	0.19	0.16	7.79	7.10		
00-042	mafic	3.7	55.3	0.6	3.972	0.010	0.457	0.14	0.02	0.02	0.03	4.35	4.34		
460257	mafic	3.8	3.23	0.03	0.3867	0.0006	0.176	0.16	0.24	0.26	0.90	5.43	3.94		
879251a	ultramafic		0.645	###	0.13203	#####	0.090	0.18	1.35	1.82	4.84	6.36	7.25		
879267a	ultramafic		0.121	###	0.10599	#####	0.098	0.03	1.30	1.77	5.25	6.06	6.92		
879371a	ultramafic		0.205	###	0.11031	#####	0.097	0.05	1.10	1.64	4.76	5.52	5.70		
879375a	ultramafic		0.346	###	0.12054	#####	0.098	0.06	0.90	1.36	4.24	4.98	4.37		
879300a	ultramafic		0.042	###	0.10374	#####	0.101	0.01	1.01	1.72	4.70	5.94	7.79		
050004a	ultramafic		0.046	###	0.10245	#####	0.099	0.01	1.01	1.48	3.24	0.28	0.30		
S33a	ultramafic		0.707	###	0.13411	#####	0.088	0.09	0.64	0.42	2.92	0.41	0.73		
Blank ^a								0.2	0.2	0.2	5.6	47.1	0.4		
Blank ^a								0.5	1.2	0.7	7.5	28.1	18.5		

Re-Os isotopes measured on TIMS.

2σ errors for $^{187}\text{Re}/^{188}\text{Os}$ are < 1%, except for low Re/Os samples 050004a and 879300a, which errors are estimated ~ 15%

Uncertainties on Os isotope ratios reported are 2σ -mean and correspond to last significant figures

Initial $^{187}\text{Os}/^{188}\text{Os}$ values were calculated at the time of emplacement of the samples, using $\lambda^{187}\text{Re} = 1.666\text{e-}11$ (Smoliar et al., 1996) and the chondritic values of Meisel et al., 1996: $^{187}\text{Os}/^{188}\text{Os} = 0.1270$ and $^{187}\text{Re}/^{188}\text{Os} = 0.40186$

Abundances of HSE determined by isotope dilution, and re-calculated to anhydrous compositions

^a Blank reported as picograms.

Table 4. Tungsten isotopic compositions measured for mafic and ultramafic samples and one sheelite of the Isua supracrustal belt, the Alfa Aesar standard, and the BHVO-1 basalt standard.

Analytical session	Sample	Lithology	Age (Ga)	$^{182}\text{W}/^{184}\text{W}$ Mean dynamic	2σ	$\mu^{182}\text{W}$ (ppm)	2σ (ppm)
B554	BHVO	run#1		0.864761	0.000007	-2.3	7.7
B553	00-028	run#1	mafic	3.3	0.864770	0.000004	7.8
	00-028	run#2	mafic	3.3	0.864769	0.000005	6.7
	00-028	mean	mafic	3.3	0.864770	0.000001	7.3
B553	00-029	run#1	mafic	3.3	0.864776	0.000005	14.6
	00-029	run#2	mafic	3.3	0.864771	0.000004	8.8
	00-029	mean	mafic	3.3	0.864774	0.000005	11.7
B494	00-038	run#1	mafic	3.3	0.864769	0.000003	12.4
	00-038	run#2	mafic	3.3	0.864771	0.000002	15.1
	00-038	mean	mafic	3.3	0.864770	0.000002	13.7
B494	00-039	run#1	mafic	3.3	0.864774	0.000003	18.1
	00-039	run#2	mafic	3.3	0.864783	0.000005	28.7
	00-039	mean	mafic	3.3	0.864779	0.000009	23.4
B494	Am019	run#1	noritic	3.4	0.864770	0.000003	13.2
	Am019	run#2	noritic	3.4	0.864770	0.000003	14.0
	Am019	mean	noritic	3.4	0.864770	0.000001	13.6
B504	00-015	run#1	mafic	3.4	0.864771	0.000005	13.1
B494	00-007	run#1	mafic	3.7	0.864772	0.000003	16.1
B504	00-007	run#1	mafic	3.7	0.864771	0.000003	13.9
B530	00-008	run#1	mafic	3.7	0.864776	0.000004	10.3
	00-008	run#2	mafic	3.7	0.864769	0.000006	1.9
	00-008	run#3	mafic	3.7	0.864771	0.000003	4.0
	00-008	mean	mafic	3.7	0.864772	0.000006	5.4
B494	00-010	run#1	mafic	3.7	0.864770	0.000003	13.2
B504	00-010	run#1	mafic	3.7	0.864775	0.000002	18.0
B494	00-042	run#1	mafic	3.7	0.864771	0.000003	14.3
B504	00-042	run#1	mafic	3.7	0.864776	0.000003	18.5
	00-042	run#2	mafic	3.7	0.864768	0.000002	10.0
	00-042	mean	mafic	3.7	0.864770	0.000007	14.3
B553	00-044	run#1	mafic	3.7	0.864782	0.000005	21.3
B494	460217	run#1	mafic	3.8	0.864765	0.000004	7.2
	460217	run#2	mafic	3.8	0.864759	0.000003	0.3
	460217	mean	mafic	3.8	0.864770	0.000006	3.7
B494	460219	run#1	mafic	3.8	0.864764	0.000003	6.1
	460219	run#2	mafic	3.8	0.864765	0.000004	7.4
	460219	mean	mafic	3.8	0.864770	0.000001	6.8
B504	460257	run#1	mafic	3.8	0.864772	0.000003	15.0
	460257	run#2	mafic	3.8	0.864771	0.000003	13.0
	460257	mean	mafic	3.8	0.864770	0.000002	14.0
B554	S33	run#1	ultramafic	3.7-3.8	0.864769	0.000004	6.2
B587	S31	run#1	ultramafic	3.7-3.8	0.864760	0.000005	-2.2
	S31	run#2	ultramafic	3.7-3.8	0.864765	0.000004	4.0
	S31	mean	ultramafic	3.7-3.8	0.864770	0.000005	0.9
B586	879251	run#1	ultramafic	3.7-3.8	0.864773	0.000005	12.8
B586	879371	run#1	ultramafic	3.7-3.8	0.864774	0.000005	13.5
B554	50004	run#1	ultramafic	3.7-3.8	0.864775	0.000003	13.2
B554	200645	run#1	scheelite		0.864775	0.000003	13.7
	200645	run#2	scheelite		0.864778	0.000005	17.4
	200645	mean	scheelite		0.864777	0.000003	15.5

Uncertainties are 2 standard deviation (2 σ).

$^{182}\text{W}/^{184}\text{W}$ measurements are also expressed in $\mu^{182}\text{W}$ notation $[(^{182}\text{W}/^{184}\text{W})_{\text{sample}}/(^{182}\text{W}/^{184}\text{W})_{\text{standard}} - 1] \times 10^4$ to the W standard Alfa Aesar.

The $^{182}\text{W}/^{184}\text{W}$ of the Alfa Aesar standards gave for analytical session B494 0.864758 ± 0.000002 (2 σ , $n=6$), for B504 0.864759 ± 0.000004 (2 σ , $n=3$), for B530 0.864767 ± 0.000002 (2 σ , $n=2$), B554 0.864763 ± 0.000006 (2 σ , $n=11$), and for B587 0.864762 ± 0.000003 (2 σ , $n=5$).

Figure
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

- ~ 3.3 Ga samples
- ~ 3.7 Ga samples
- ~ 3.8 Ga samples
- Alfa Aesar W Std

★ Fractionation that would be necessary to explain $\mu^{182}\text{W}$ values of Isua samples

Figure 7

Figure 8

Figure 9