New insights into the Hadean mantle revealed by $^{182}$W and highly siderophile element abundances of supracrustal rocks from the Nuvvuagittuq Greenstone Belt, Quebec, Canada

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Tungsten concentration and isotopic data, coupled with highly siderophile element (HSE) concentration and Os isotopic data for ≥3.66 billion year-old ultramafic, mafic, and felsic supracrustal rocks from the Nuvvuagittuq Greenstone Belt, were investigated to place additional constraints on the nature and origin of $^{182}$W heterogeneities in the early Earth. The absolute and relative abundances of HSE in the mafic and ultramafic rocks are generally similar to those in modern rocks with comparable MgO contents. Further, most samples plot close to 3.8 to 4.4 Ga reference lines on a $^{187}$Re–$^{187}$Os isochron diagram, indicating that HSE abundances in most Nuvvuagittuq samples remained undisturbed by post-Eoarchean metamorphic events. All Nuvvuagittuq samples analyzed show well-resolved $^{182}$W excesses, ranging from +6 to +17 ppm, compared with the modern isotopic composition of W. The observed level of HSE abundances, coupled with the $^{182}$W enrichments of these rocks are seemingly inconsistent with their derivation from mantle that was isolated from a HSE-rich and $^{182}$W-depleted late accretionary component. However, the absence of correlation between W and MgO contents, as well as variable W enrichment relative to elements with similar incompatibilities suggest that the W in the Nuvvuagittuq samples involved fluid transport of the W in either the crust or the mantle, and that it has little genetic relationship with the HSE. Given the lack of evidence for extensive redistribution of W in the crust, the HSE and W elemental and isotopic systematics of the Nuvvuagittuq rocks may be explained by a model whereby peridotitic mantle, with modern-like HSE abundances, was metasomatized by fluids derived from a $^{182}$W-rich crustal component that had been recycled into the mantle via subduction or delamination. The source of the $^{182}$W excess carried by this crustal component remains enigmatic. It was most likely inherited from either pre-late accretionary, or early-depleted parental mantle reservoirs.

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1. Introduction

The lack of a substantive geological record for the Hadean eon has limited the knowledge of geological processes involved during the formative stages of Earth’s history. Nevertheless, a picture of the earliest portion of Earth history is gradually beginning to emerge from the study of Hadean and younger materials. Chemical and isotopic compositions of detrital zircons as old as ca. 4.38 Ga from the Jack Hills conglomerates, Narryer Gneiss Complex of Western Australia, have provided compelling evidence for the early generation of evolved, felsic crust, perhaps driven by or accompanied by some form of plate tectonics (Froude et al., 1983; Compston and Pidgeon, 1986; Trail et al., 2007; Harrison et al., 2008, 2009; Holden et al., 2009). Variations in $^{142}$Nd/$^{144}$Nd observed among Archean rocks (Boyet et al., 2003; Caro et al., 2003, 2006; Bennett et al., 2007; Rizo et al., 2012) can only have been generated by mantle differentiation processes that occurred prior to ca. 4.2 Ga, due to the rapid decay of $^{146}$Sm ($t_{1/2} = 68$ Myr; Kinoshita et al., 2012). Resolved anomalies in $^{142}$Nd/$^{144}$Nd have been found in rocks as young as 2.7 Ga from the Abitibi Greenstone Belt, Ontario, Canada, suggesting that at least some early-formed mantle heterogeneities were preserved for more than 1.8 Gyr (Debaille et al., 2013). Collectively, these studies indicate the early formation and long-term preservation of sizable, chemically fractionated reservoirs within the Hadean mantle, and implicate subsequent sluggish mixing of the mantle during both the Hadean and Archean, despite a presumably higher geothermal gradient than today.

Recently, the $^{182}$Hf–$^{182}$W isotopic system has shown promise for exploring additional processes involved in the formation and early
chemical evolution of the Earth's mantle. For this system, \(^{182}\text{Hf}\) decays to \(^{182}\text{W}\), with a half-life of 8.9 Myr (Vockenhuber et al., 2004). Significant radiogenic vari-ations in \(^{182}\text{W}/^{184}\text{W}\) can only have been produced during the first ~50 Myr of solar system history, while \(^{182}\text{Hf}\) was still ex-tant. The time window for generating currently resolvable isotopic anomalies for this system is therefore, much narrower than that for the \(^{146}\text{Sm}/^{144}\text{Nd}\) system. All terrestrial rocks analyzed to date for W iso-topes are characterized by \(^{182}\text{W}/^{184}\text{W}\) ratios that are ~200 ppm more radiogenic than those in chondrites (Kleine et al., 2002; Schoenberg et al., 2002; Yin et al., 2002). This requires that a major portion of Earth's W was removed to the core during the lifetime of \(^{182}\text{Hf}\), resulting in the generation of suprachondritic W/Fe in the mantle, and leading in turn to enrichment of the mantle in \(^{182}\text{W}/^{184}\text{W}\), relative to the chondritic ratio. In addition to core formation, early Hf/Fe fractionations could also have occurred in the mantle as a result of magma ocean crystallization and/or mantle overturn, as well as more localized processes, such as partial melting and melt removal (Newson and Palme, 1984; Newson et al., 1986, 1996; Sims et al., 1990; Righter and Shearer, 2003). Further, because mass balance arguments require the \(^{182}\text{W}/^{184}\text{W}\) of the core to be ~200 ppm lower than in the silicate Earth, isotopic anomalies char-acterized by depletion in \(^{182}\text{W}\) could result from core–mantle exchange at any time in Earth's history.

Although several studies have searched for W isotopic heterogene-ities in rocks derived from the modern and ancient mantle (e.g., Schoenberg et al., 2002; Schersten et al., 2004; Iizuka et al., 2010; Moynier et al., 2010), well resolved isotopic enrichments have only recently been reported, and these have so far been restricted to Archean rocks. Willbold et al. (2011) reported a uniform – 13 ppm enrichment in \(^{182}\text{W}/^{184}\text{W}\) in 3.6 to 3.8 Ga supracrustal rocks from the Isua Greenstone Belt, Greenland. Similarly, Touboul et al. (2012) reported ~15 ppm enrich-ment in 2.8 Ga komatitites from the Kostomuksha Greenstone Belt in Fennoscandia. Willbold et al. (2011) noted that the magnitude of enrichment in the Isua rocks is broadly consistent with estimates for the mantle prior to a putative, final addition of ~0.3 to 0.8 wt.% of Earth's mass by late accretion (Chou, 1978; Morgan et al., 2001). Conse-quently, they proposed that the mantle precursor to the Isua rocks was a reservoir that formed prior to substantial late accretion had occurred, and remained isolated, at least until it contributed to the Isua suite at 3.6–3.8 Ga.

The interpretation favored by Willbold et al. (2011) for the Isua rocks, however, cannot be used to explain the positive \(^{182}\text{W}\) isotopic anomalies present in the Kostomuksha komatitites. One expected col-latereal effect of sampling mantle that is missing a major proportion of late accreted materials is that derivative rocks should be char-acterized by lower abundances of highly siderophile elements (HSE; including Os, Ir, Ru, Pt, Pd and Re) relative to those present in the modern mantle. This is because late accretion may be responsible for the addition of ~95% of the HSE now present in the silicate portion of the Earth (Chou, 1978; Walker, 2009), compared to only ~10% for moderately siderophile elements, such as W. To achieve the \(^{182}\text{W}\) isotopic composition observed in the Kostomuksha komatitites via the model of Willbold et al. (2011), the mantle source of the komatitites would be expected to be significantly depleted in HSE. The Kostomuksha komatitites, however, appear to be derived from mantle with a nearly full complement of HSE, compared with the modern mantle (Puchtel and Humayun, 2005). Touboul et al. (2012) attributed the Kostomuksha W anomalies, as well as accompa-nying enrichments in initial \(^{186}\text{Os}/^{184}\text{Os}\) and \(^{187}\text{Os}/^{184}\text{Os}\) (Puchtel et al., 2005), to either metal–silicate fractionation processes occurring in a deep, lower mantle magma ocean, or silicate fractionation processes occurring during the crystallization of a large, upper man-tle magma ocean. For either scenario, the mantle reservoir from which the komatitites were at least in part derived, would need to have been isolated from the convective mantle less than 50 Myr after the formation of the solar system, then survive for more than 1.7 Gyr until formation of the Kostomuksha komatitites.

Here, we investigate the pre-3.6 Ga rocks from the Nuvvuagittuq Greenstone Belt, Quebec, Canada. We report new W isotopic data, along with \(^{187}\text{Re}/^{187}\text{Os}\) isotopic systematics, and HSE abundance data for several chemically-diverse rock types. These data, combined with other chemical data and published \(^{142}\text{Nd}\) data, are used to provide further constraints on processes involved in the generation of W isotopic heterogeneities early Earth history.

2. Overview of the Nuvvuagittuq Greenstone Belt and samples

The Nuvvuagittuq Greenstone Belt is located in the Northeastern Superior Province, Canada within the Hudson Bay terrane defined by Boily et al. (2009). This highly–metamorphosed area of ~10 km² is dom-inated by a mafic lithology called the Ujaraaluk unit, ranging in composi-tion from basaltic to basaltic andesite (O'Neil et al., 2011). The Ujaraaluk unit includes co-genetic ultramafic rocks interpreted to be cu-mulates from mafic magmas (O'Neil et al., 2007, 2011, 2012). The Nuvvuagittuq Greenstone Belt is surrounded and intruded by multiple generations of rocks from the tonalite–trondhjemite–granodiorite se ries (TTG) dated at ~3.76 Ga, ~3.66 Ga, 3.50 Ga and 3.35 Ga (David et al., 2009; Cates and Mojzsis, 2007, 2009; O'Neil et al., 2013; Darling et al., 2013).

The mafic and ultramafic rocks from the Ujaraaluk unit are divided into three geochemically distinct groups mainly based on their Al/Ti ra-tios and rare earth element (REE) patterns (O'Neil et al., 2011). The base of the sequence is composed of high-Ti mafic rocks with relatively flat, primitive mantle-normalized incompatible lithophile trace element profiles. By contrast, the upper portion of the sequence consists of low-Ti rocks, ranging from basalts to andesites. The low-Ti group has been further subdivided into incompatible element enriched and in-compatible element depleted rocks. The Ujaraaluk unit was interpreted by O'Neil et al. (2011) to represent mafic volcanic rocks erupted in a submarine environment and affected by variable degrees of hydrother-mal alteration. Compositional evolution from the high-Ti group to the low-Ti groups reflects a transition from rocks with tholeiitic affinities to rocks with boninitic and calc-alkaline affinities, similar to what is ob-served in modern suprasubduction settings (O'Neil et al., 2011; Turner et al., 2014).

The age of the rocks of the Nuvvuagittuq Greenstone Belt has been debated. The oldest U–Pb ages on zircons obtained in the Nuvvuagittuq Greenstone Belt are ~3.8 Ga (e.g., Cates and Mojzsis, 2007; David et al., 2009). These zircons, however, are from thin trondhjemite intrusions, and provide only a minimum age constraint for the mafic rocks. Gates et al. (2013) proposed a maximum age of 3.78 Ga based on the oldest \(^{207}\text{Pb}/^{206}\text{Pb}\) age on zircon from a putative detrital felsic quartzite. Darling et al. (2013), however suggested a metasomatically altered felsic orthogneiss origin for the felsic quartzite, in which case it cannot be used to place a maximum age constraint on the supracrustal rocks of the Nuvvuagittuq Greenstone Belt.

Mafic rocks and co-genetic ultramafic cumulates from the Ujaraaluk unit show a large variation in \(^{142}\text{Nd}\) (~18 to –8 ppm compared to terrestrial Nd standard) and are characterized by a correlation between \(^{142}\text{Nd}/^{144}\text{Nd}\) and Sm/Nd ratios. O'Neil et al. (2008, 2012) interpreted this correlation as representing an isochron, and evidence that the rocks formed at ~4.39 Ga, while \(^{146}\text{Sm}\) was still extant. It has alter-na-tively been proposed that the correlation represents a mixing line be-tween a Hadean enriched reservoir and the ambient convective mantle (Roth et al., 2013, Guitreau et al., 2013). The ultramafic cumu-lates systematically exhibit higher \(^{142}\text{Nd}/^{144}\text{Nd}\) and Sm/Nd compared to their mafic counterparts. O'Neil et al. (2012) interpreted this correla-tion between the ultramafic cumulates and the mafic rocks as evidence for igneous magmatic fractionation of the Ujaraaluk unit prior to 4 Ga. Massive gabbro sills intruding the Ujaraaluk unit yielded a \(^{143}\text{Sm}/^{144}\text{Nd}\) isochron age of 4115 ± 100 Ma, consistent with a Hadean age for the belt.
For the present study, we analyzed three ultramafic and three mafic samples from each of the three different geochemical Ujaraaluk groups identified by O’Neil et al. (2011). In addition, data for TTG sample PC039 and PC286 were also collected. Both of these rocks have been interpreted to be derived by re-melting of the Nuvvuagittuq Greenstone Belt mafic crust. Sample PC039 is a tonalite from the ≤3.66 Ga-old TTG formation, whereas PC286 has U–Pb zircon ages of 3.781 ± 11 Ga (Darling et al., 2013) and 3.756 ± 4 Ga (O’Neil et al., 2013). The Hf isotopic compositions of zircons from the ≤3.66 Ga Nuvvuagittuq TTGs are consistent with their derivation from a Hadean, Ujaraaluk-like mafic precursor (O’Neil et al., 2013). In contrast, the ca. 3.76 Ga TTG series, including the trondhjemitic sample PC286, appear to have been derived from a different mafic source, possibly similar to the intruding gabbro sills (O’Neil et al., 2013).

3. Analytical methods

Before chemical processing, 5 to 30 g aliquots of all samples were crushed in a jaw crusher and then powdered in an alumina shutter box. Two different powders were prepared for each sample to investigate potential sample heterogeneity with regard to W concentrations. Chemical and analytical procedure for determination of W and HSE abundances decrease regularly from the ultramafic suite, whereas it increases with the IPGE alloys, as previously proposed for some komatiitic and basaltic rocks, to the maﬁc rocks, to the tonalites. Consequently, the abundances of these elements are broadly, positively correlated with common indices of magmatic differentiation, such as MgO (Fig. 2a–c). These positive trends on MgO variation diagrams are consistent with the typically compatible behavior of IPGE during magmatic differentiation (Barnes et al., 1985). Of greatest note, the IPGE are well correlated with Cr (Fig. A.1), suggesting that their abundances were primarily controlled by chromite-associated IPGE alloys, as previously proposed for some komatiitic and basaltic lavas (e.g., Rehkämper et al., 1999; Puchtel and Humayun, 2001).

Ultramafic rocks from the low-Ti and high-Ti groups show distinct trends on a plot of MgO vs. Cr (Fig. A.1). Chromium decreases with decreasing MgO for the low-Ti ultramafic suite, whereas it increases within the high-Ti ultramafic suite (O’Neil et al., 2011). This suggests fractionation of the high-Ti and low-Ti cumulates under different

Table 1

<table>
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<th>Samples</th>
<th>Lithology</th>
<th>Os</th>
<th>Ir</th>
<th>Ru</th>
<th>Pt</th>
<th>Pd</th>
<th>Re</th>
<th>186Re/180Os</th>
<th>187Os/186Os</th>
<th>≤20</th>
<th>TRD</th>
<th>TMA</th>
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<td>0.01</td>
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<td>7.4</td>
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<td>0.23</td>
<td>0.01</td>
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<td>9.73</td>
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<td>0.90</td>
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<td>0.0022</td>
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<td>0.0011</td>
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Note: The parameters used in model age calculation are: λm = 1.666 × 10−11 year, (186Re/180Os)TRD = 0.402, (187Os/186Os)TMA = 0.1270 (Shirley and Walker, 1998).
oxidizing conditions and water contents. Similar trends may be observed for the IPGE (Fig. 2a, b and c) where the high-Ti ultramafic samples have lower IPGE content, although analysis of additional samples with >25 wt.% MgO would be required to confirm this trend.

The abundances of the PPGE present in the Ujaraluit ultramafic and mafic rocks are characterized by generally negative correlations with MgO. This is consistent with the typically moderately to strongly incompatible behavior common for these elements during mantle melting and magmatic differentiation involving mafic liquidus phases (Barnes et al., 1985; Brügmann et al., 1987; Rehkämper et al., 1999). For example, in the Pd versus MgO diagram (Fig. 2d), the mafic and ultramafic rocks all plot within a negatively sloping field. In general, the Pt contents of Nuvvuagittuq ultramafic and mafic rocks are also negatively correlated with MgO (Fig. 2e), however, two ultramafic samples, PC094 and PC213, have anomalously high Pt abundances of 19 and 21 ppb, respectively. This may reflect late-stage addition of Pt-rich sulfides, which have previously been proposed to explain high Pt contents measured in some ophiolite samples (Luguet et al., 2007; Schulte et al., 2009). The Pt and Pd abundances for the two TTG samples plot far off of the negatively sloping trends defined by the ultramafic rocks and the Urajaaluk mafic rocks in the MgO variation diagram (Fig. 2da and d.e).

In contrast to other HSE, Re shows no well-defined correlations with either the MgO (Fig. 2f) or Cr contents (Fig. A.1). Some Nuvvuagittuq samples are characterized by anomalously high or low Re abundances. For example, mafic sample PC275 has a Re content of 2.3 ppb, whereas compositionally similar samples PC227, PC410, and PC425 have Re...
concentrations of <0.02 ppb. The other mafic samples all have Re abundances between 0.2 and 0.5 ppb. The Re concentrations of 0.7 and 0.9 ppb for two ultramafic rock samples, PC128 and PC213, respectively, are much higher than those of the other ultramafic rocks, which range from 0.01 to 0.2 ppb. The Re–Os isotopic results presented below suggest that these anomalous concentrations are most likely the result of recent Re gain/loss. After excluding the samples with anomalous Re contents, the mafic rocks show higher overall Re concentrations than the ultramafic rocks, consistent with the incompatible behavior of Re during magmatic differentiation.

4.2. Re–Os isotopic systematics

The Nuvvuagittuq rocks are characterized by a relatively large range in $^{187}$Os/$^{188}$Os and $^{187}$Re/$^{188}$Os (Table 1). In the ultramafic rocks, $^{187}$Os/$^{188}$Os and $^{187}$Re/$^{188}$Os range from 0.1036 to 0.2188, and 0.024 to 2.33, respectively. By contrast, the mafic rocks are characterized by much larger variations in $^{187}$Os/$^{188}$Os and $^{187}$Re/$^{188}$Os ratios ranging from 0.302 to 5.80, and 0.161 to 323, respectively. The sample with the lowest $^{187}$Os/$^{188}$Os among the entire Nuvvuagittuq suite (ultramafic rock PC18) has a $T_{\text{Ma}}$ Re–Os model age as defined by Shirey and Walker (1998) of 3.92 Ga. No meaningful isochron is observed, even when each geochemical

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![Fig. 2. Variations of HSE abundances (in ppb) versus MgO (in wt.%) in the Nuvvuagittuq suite. The symbols are the same as those used in Fig. 1. Open diamonds indicate the composition of the primitive mantle (PM) (from Becker et al., 2006).](Fig2)

![Fig. 3. Plot of $^{187}$Re/$^{188}$Os versus $^{187}$Os/$^{188}$Os isochron diagram for the Nuvvuagittuq samples. Symbols are the same as those used in Fig. 1. Uncertainties on $^{187}$Os/$^{188}$Os and $^{187}$Re/$^{188}$Os ratios are smaller than symbols. Dotted lines correspond to reference lines for samples formed from a parental reservoir with chondritic isotopic composition at 2.7, 3.8 and 4.4 Ga. With a very high $^{187}$Re/$^{188}$Os ratio of ~170, coupled with a $^{187}$Os/$^{188}$Os of ~4.6, low-Ti enriched group sample PC 275 plots well below the 2.7 Ga reference isochron and is not shown.](Fig3)
group (low-Ti enriched, low Ti depleted and high-Ti samples) is considered individually. However, most Nuvvuagittuq rocks plot near or between 3.8 and 4.4 Ga reference lines on the $^{187}\text{Re}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ diagram (Fig. 3). The mafic rocks with anomalously low Re contents (PC227, PC410 and PC425) are characterized by slightly sub-chondritic $^{187}\text{Re}/^{188}\text{Os}$, but retain relatively high $^{187}\text{Os}/^{188}\text{Os}$ of 0.212 to 0.573, resulting in their plotting far above the 3.8 and 4.4 Ga reference lines (Fig. 3). This is most likely due to a recent Re loss in these samples. By contrast, the samples with anomalously high Re (PC128, PC213, and PC275) are characterized by relatively high $^{187}\text{Re}/^{188}\text{Os}$ but generally low $^{187}\text{Os}/^{188}\text{Os}$, and consequently plot significantly below these reference lines. These samples probably experienced open system behavior of Re and/or Os long after formation, with the most likely explanation for these characteristics being recent Re addition.

4.3. Tungsten abundances and isotopic compositions

Whole rock W abundances and isotopic compositions of Nuvvuagittuq samples are reported in Table 2. The ultramafic rocks and mafic rocks have highly variable W concentrations ranging from 0.1 to 1.4 ppm and from 0.04 to 2.3 ppm, respectively. The Nuvvuagittuq tonalites have the highest W contents of the suite analyzed (~2.5 ppm). The variations in absolute abundance of W are not correlated with the MgO content (Fig. 4).

All Nuvvuagittuq rocks show well resolved, positive $^{182}\text{W}$ anomalies (Fig. 5) relative to modern samples investigated to-date (Willbold et al., 2011; Touboul et al., 2012). Collectively, the mafic and ultramafic rocks have $^{182}\text{W}$ excesses, averaging a $\mu^{182}\text{W}$ value (where $\mu^{182}\text{W}$ is a part per million the deviation of the $^{182}\text{W}/^{184}\text{W}$ ratio of a sample relative to the terrestrial reference standard) of $+13.3 \pm 5.8$ ppm ($n = 27, 2\sigma$ SD). There is no statistical difference between the average values for mafic and ultramafic rocks at our ± 5 ppm ($2\sigma$ SD) level of analytical precision. Further, average $\mu^{182}\text{W}$ values of high-Ti, low-Ti enriched, and low-Ti depleted samples are $+14.7 \pm 4.8$ ($n = 14, 2\sigma$ SD), $+12.6 \pm 6.3$ ($n = 6, 2\sigma$ SD), and $+10.9 \pm 4.0$ ($n = 7, 2\sigma$ SD), respectively, so no resolvable $^{182}\text{W}$ variation is observed among the different geochemical subgroups.

In contrast to the mafic and ultramafic rocks, the tonalites show significant variations in W isotope compositions. Sample PC309 has a positive $^{182}\text{W}$ anomaly of $+14.8 \pm 3.8$ ($n = 3, 2\sigma$ SD), which is identical within the uncertainty to the average $\mu^{182}\text{W}$ values of the mafic and ultramafic rocks. Sample PC286, however, is characterized by a significantly lower $\mu^{182}\text{W}$ value of $6.8 \pm 2.2$ ($n = 3, 2\sigma$ SD).

5. Discussion

5.1. HSE systematics and mantle source characteristics

The mantle abundances of HSE may be a direct reflection of the proportion of late accreted materials to the Earth (e.g., Chou, 1978), so constraining the concentrations of the HSE present in the mantle precursors to the Nuvvuagittuq sample suite may be critical to interpreting their $^{182}\text{W}$ isotopic enrichments. As noted above, Willbold et al. (2011) concluded that similarly $^{182}\text{W}$-enriched rocks from Isua, Greenland were ultimately derived from mantle that either formed prior to the major phase of late accretion, or that late accreted materials had not yet been mixed into that source domain. The Willbold et al. (2011) study did not report HSE abundances for the Isua rocks studied, so it remains unknown whether the HSE abundances present in the rocks examined are consistent with the prediction for low HSE abundances present in the precursor mantle.
Before attempting to estimate the abundances of the HSE in the mantle source of the Nuvvuagittuq rocks, it is important to first ensure that the abundances of these elements present in the rocks today reflect their abundances at the time when the rocks formed. Since rocks from the Nuvvuagittuq Greenstone Belt have undergone multiple phases of deformation and high-grade metamorphism (O’Neil et al., 2007; Cates and Mojzsis, 2009), it is critical to assess chemical changes to the HSE that may have resulted from this complex history.

One important indication of mobility of at least one HSE in some of the Nuvvuagittuq rocks is provided by the Re–Os isotopic data. As noted above, some samples plot either well below or well above the 3.8 and 4.4 Ga reference isochrons (Fig. 3). Collectively, these observations most likely reflect modest, post formation Re and/or Os loss or addition, such as may have been caused by thermal metamorphism during a well-documented 2.7 Ga metamorphic event that affected these rocks (O’Neil et al., 2007; Cates and Mojzsis, 2009), or as a result of recent alteration (suspected is a well-documented 2.7 Ga metamorphic event that affected these rocks or as a result of recent alteration). Moreover, the correlations of IPGE and PPGE with MgO within the mafic and ultramafic suites are broadly consistent with the respective behavior of these elements commonly observed during magmatic differentiation of mafic systems (e.g., Pitcher et al., 2009). Collectively, these observations suggest that the HSE abundances of Nuvvuagittuq samples have not been strongly modified by post-Eoarchean processes, and can be used to infer HSE abundances of their mantle source.

Determining the abundances of HSE in the mantle sources of mafic supracrustal rocks is challenging. The relatively low extents of partial melting of the mantle usually presumed for mafic systems may lead to incomplete removal of HSE-rich, low-T sulfides from the mantle residue. Further, if the resulting melt was S-saturated, it is possible that HSE would be partially lost from the system via sulfide precipitation prior to arrival at the surface. Retention of some types of sulfides in mantle residues, and precipitation of sulfides prior to eruption are generally accepted as a reason for highly fractionated PM-normalized HSE patterns usually observed in mafic rocks (e.g., Bézos et al., 2005).

One method used in planetary studies to estimate the relative abundances of HSE in mantle sources of mafic rocks, is to compare Pt abundances in those rocks with averages for the global terrestrial Pt database for rocks with broadly similar MgO contents (e.g., Brandon et al., 2012). This approach may be viable for Nuvvuagittuq rocks because, at least for Earth, Pt is not strongly partitioned between mantle and mafic crust. This means that mantle–crust partitioning of Pt is not as sensitive to extents of partial melting and redox conditions as other HSE, such as Os and Ir. We have taken the same approach here. The average concentrations of Pt in the Nuvvuagittuq mafic and ultramafic rocks are 8.6 ± 7.9 (2σ SD) and 5.1 ± 4.5 ppb, respectively. In comparison, average Pt concentrations from the literature for mid-ocean ridge basalts (MORB), Hawaiian picrites, continental theolitea, and arc lavas, are 0.74 ± 1.7, 2.3 ± 2.5, 4.9 ± 1.9 and 4.8 ± 5.7 ppb, respectively (Rehkämper et al., 1999; Bézos et al., 2005; Dale et al., 2009; Bennett et al., 2000; Ireland et al., 2009; Rocha-Júnior et al., 2012; Woodland et al., 2002; Kepezhinskas et al., 2002). Thus, Pt concentrations in the Nuvvuagittuq mafic and ultramafic rocks are similar to or higher than in modern rocks with similar MgO contents. The results of this comparison suggest that the mantle sources of the Nuvvuagittuq mafic and ultramafic rocks had broadly similar Pt, and by inference other HSE abundances, compared to modern PM estimates. Although these are relatively crude estimates, we conclude that HSE abundances in the Nuvvuagittuq mantle source were similar to or above those in the modern PM estimates.

5.2. Tungsten elemental systematics

Before exploring possible causes for the $^{182}$W enrichments, it is important to consider the W concentration data for the Nuvvuagittuq samples. Tungsten normally behaves as a highly-incompatible trace element during mantle melting and silicate differentiation (Newsom and Palme, 1984; Newsom et al., 1986, 1996; Sims et al., 1990; Righer and Shearer, 2003). The W concentrations of the Nuvvuagittuq samples, however, show no correlations with chemical indicators of crystal–liquid fractionation, such as MgO, even if each geochemical subgroup is considered individually (Fig. 4). There are relatively high and low W concentrations for mafic and ultramafic rocks within each chemical group. For example, multiple aliquots of mafic samples PC–410 and PC–437, from the low-Ti depleted group, have similar concentrations that average at ~150 ppb. By contrast, sample PC–227, with a lower MgO, has a considerably lower W concentration, averaging ~15 ppb.

Fig. 5. $^{182}$W values for Nuvvuagittuq rocks. Each unique symbol corresponds to a distinct sample. Symbols are the same as those used in Fig. 1. Identical symbols show replicate measurements of the same sample. Symbols with cross correspond to the average of replicated measurements. The dark-gray area corresponds to the 2σ SE uncertainty for repeated analyses of the Alfa Aesar standard (n = 60). Each color indicates a distinct geochemical group: green = low-Ti depleted samples, blue = low-Ti enriched samples, red = high-Ti samples. Lighter-colored and dark-colored symbols correspond to metamorphic rocks from the Ujaraaluk formation with mafic and ultramafic affinities, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Although duplicate analyses of W typically vary by only a few percent, the duplicate measurements for PC-227 vary by nearly a factor of 3. This is the sample with the lowest abundance of W for the Nuvvuagittuq suite and we attribute that variability to the nugget effect that is also common for HSE.

Also of note, some of the ultramafic rocks have among the highest W concentrations of the suite. For example, samples PC-018 and PC-504 have W concentrations of ~1 ppm. It is difficult to envision attaining concentrations in the mafic and ultramafic rocks that are nearly 100 times higher than in the estimates for the PM, solely through melting and/or crystal–liquid fractionation processes, even given the very incompatible nature of W. For example, for 5% batch melting of the mantle and assuming a mantle-melt bulk distribution coefficient of 0.1, an enrichment factor for the melt of only ~7 can be achieved. The Nuvvuagittuq ultramafic rocks probably formed as cumulates from a mafic melt, so it is unlikely that an enrichment factor of >10, relative to the mantle starting composition could have resulted from magmatic processes. For comparison, modern Hawaiian picrites with MgO (and HSE) contents broadly similar to those of the Nuvvuagittuq ultramafic rocks, have average W concentrations of ~150 ppb (about a factor of 10 greater than estimates for their mantle sources), with all concentrations lower than 500 ppb [Ireland et al., 2009].

Given these observations, we conclude that the W concentrations present in the Nuvvuagittuq suite could not have been attained solely by melting of mantle with normal W abundances, followed by subsequent crystal–liquid fractionation. Thus, other processes must be considered. As noted above, all of the rocks are assumed to have been affected by variable, syn- or post-crystallization, hydrothermal alteration processes [O’Neil et al., 2011]. The possibility that W in some or all of the Nuvvuagittuq rocks experienced open-system behavior must be explored. For example, excess W (above the levels produced by magmatic differentiation) might have been variably introduced to the rocks via aqueous transport at some time after crystallization. One way to gauge the impact of secondary crustal processes, such as fluid alteration, on the Nuvvuagittuq rocks is to assess whether there are correlations between W concentrations and indices of alteration, or degree of metamorphism. Common indices of weathering include the Chemical Index of Alteration (CIA; Nesbitt and Young, 1982), or the empirical statistical index of chemical weathering (WI) developed by Ohta and Arai (2007) which, in contrast to CIA, is independent of the composition of the protolith. We find no apparent relationship between W abundances and chemical alteration indices (Fig. A.2) or W isotopic compositions (Fig. A.3). We also note that the metamorphic grade of the Nuvvuagittuq suite is relatively uniform (amphibolite facies: Majnoon, 2013), so no correlation between W abundance and metamorphic grade exists. Although we cannot rule out hydrothermal alteration as the major cause for the high W concentrations in some rocks, the lack of correlations between extents of alteration/metamorphism and W abundances, leads us to conclude that the variations in W abundances were not primarily established by secondary crustal processes.

Excluding both magmatic and post-crystallization modification processes as the primary causes for the observed W concentrations leads us next to consider processes that may have led to variable W enrichments in mantle source rocks prior to melting, such as fluid-induced metasomatism. For this, it is useful to consider W abundances in the context of behavior of other highly incompatible lithophile trace elements, particularly those that can reflect formation in specific tectonic environments.

5.3. A convergent margin origin?

There is a growing body of evidence indicating that some Archean basalts share geochemical similarities with modern arc basalts and boninites (e.g., Polat et al., 2002; Polat and Hofmann, 2003; Smithies et al., 2003, 2004; Jenner et al., 2009). Abundances of high field strength elements (HFSE) have been widely used to distinguish between arc and non-arc rocks (e.g., McCulloch and Gamble, 1991; Pearce and Peate, 1995; Condie, 2003) and, by comparison, constitute a powerful tool for investigating geological settings relevant for Archean rocks with presumed mafic and ultramafic precursors (Condie, 2005; Pearce, 2008; Furnes et al., 2009), although this has been recently questioned by Willbold et al. (2009).

One way to identify fluid transport processes in environments where crust is recycled back into the mantle is to consider Th–Nb variation diagrams. Thorium is more mobile and incompatible than Nb in subduction settings and tends to be transported by slab melts and fluids into the overlying mantle wedge (e.g., Bailey and Ragnarsson, 1994; Kelley et al., 2005). By contrast, Nb is preferentially retained by Ti-rich phases during melting of the subducting slab (Ryerson and Watson, 1987; Brenan et al., 1994; Stalder et al., 1998; Foley et al., 2000; Walker et al., 2001; Kalfoun et al., 2002; Schmidt et al., 2004) and is also especially immobile during slabs dehydration [Tatsukiji and Kogiso, 1997]. Thus, island-arc related basalts are normally characterized by low Nb/Th, and plot above the mantle array defined by MORB and ocean island basalts (OIB) in Th/Yb vs. Nb/Yb diagrams [Pearce, 2008]. The 3.8 Ga metabasalts of the Isua Greenstone Belt also plot above the mantle array, consistent with an origin as arc-related basalts, and, consequently, the enrichment of Th relative to Nb was interpreted as indicating a convergent margin setting for the generation of Isua Greenstone Belt metabasalts [Polat et al., 2002; Polat and Hofmann, 2003; Jenner et al., 2009]. The Nuvvuagittuq mafic and ultramafic samples are also characterized by lower Nb/Th ratios than modern OIB and MORB, and are displaced toward the low-Nb, high-Th side of the Th/Yb vs. Nb/Yb diagram (Fig. 6a; O’Neil et al., 2011). Thus, it may be useful to consider Nuvvuagittuq W in the context of origin in a convergent margin environment.

The strong incompatibility of W during mantle melting has commonly been broadly equated with such trace elements as U, Th, and Ta, regardless of tectonic environment of their formation (e.g., Newsom et al., 1986; Sims et al., 1990; Newsom et al., 1996; Noll et al., 1996; Arevalo and McDonough, 2008). Most recently, König et al. (2008, 2011) reported that in MORB, W/U, W/Th and W/Ta ratios are confined to restricted ranges of 0.1 to 0.7, 0.05 to 0.23, and 0.08 to 0.29, respectively. They noted that these ratios increase slightly with increasing W concentrations, indicating that, at least during the production of MORB, W is slightly more incompatible than U, Th, or Ta.

Arc magmas are generated, on average, via higher degrees of mantle melting compared with MORB (e.g., Tatsukiji and Eggins, 1995). Given the slightly more incompatible nature of W, this difference in melting regime should translate to slightly lower W/U, W/Th and W/Ta in arc magmas, compared with MORB. However, arc magmas exhibit higher W/Ta than MORB, and many arc magmas are also characterized by higher W/U and W/Th (König et al., 2008, 2011). Further, these ratios are typically positively correlated with parameters that reflect higher fluid flux, such as Ce/Pb (Chauvel et al., 1995) or Sb/Ce (Jochum and Hofmann, 1997). These correlations suggest that W enrichments may be generated by selective mobilization of W via subduction-related fluids. Consistent with this, arc magmas presumed to be generated with only the limited influence of slab-derived fluid interactions have W/U and W/Th similar to, or lower than, MORB, but still show W enrichment relative to fluid immobile elements, such as the HFSE (König et al., 2011). Collectively, these studies suggest that W is a particularly fluid-mobile element in a subduction zone environment.

Nuvvuagittuq samples are characterized by large variations in their W/U, W/Th, and W/Ta, and, as with W concentrations, these ratios do not correlate with common proxies for magmatic differentiation (e.g, MgO contents, Fig. A.4). Of note, high–Ti samples show much higher W/U (1.5 to 4.5), W/Th (0.3 to 3.5), and W/Ta (1.3 to 7.5) than MORB (0.1 to 0.7, 0.05 to 0.23, and 0.08 to 0.35, respectively). Compared with high-Ti samples, low-Ti samples show less variable and lower W/U (0.19 to 1.1), W/Th (0.05 to 0.3) and W/Ta (0.15 to 2.7), which overlap with MORB, yet trend to higher ratios (Fig. 6b).
samples also have similar to or slightly higher absolute U, Th, and Ta concentrations, compared with MORB. Thus, the high W/U, W/Th, and W/Ta ratios may indicate that W was selectively enriched, relative to those elements, in the mantle sources of the Nuvvuagittuq rocks.

Arc and non-arc basalts can also be discriminated by using Ba/La vs. Ba/Nb diagrams (Carr et al., 1990; Lin et al., 1990; Leeman et al., 1994; Patino et al., 2000). Both MORB and OIB show minor variations in Ba/La and Ba/Nb. Barium is highly fluid-mobile compared to REE and HFSE. Consistent with this, modern arc-related rocks are characterized by more variable and generally higher Ba/La and Ba/Nb ratios, compared with MORB and OIB. These variations have been interpreted to reflect increasing proportions of slab-derived components to their mantle sources.

As a consequence of its high mobility in fluids, retention of meaningful Ba elemental systematics in ancient crustal rocks that have undergone moderate to severe metamorphism is unexpected. However, Jenner et al. (2009) reported arc-like Ba/La and Ba/Nb for relatively highly metamorphosed, early Archean basalts from Isua. Surprisingly, the Nuvvuagittuq samples systematically plot below the non-arc rocks in the Ba/La vs. Ba/Nb diagram, and are most comparable to the trend defined by modern arc-related lavas (Fig. 6c).

Barium is a potentially important element to compare to W because, in addition to being fluid mobile, Ba is only slightly less incompatible than W. As a consequence, W/Ba ratios of MORB are relatively constant (0.001 to 0.007), although they slightly increase with MgO. In contrast, arc basalts show much larger W/Ba variations (0.0002 to 0.2) than MORB, and negative correlations between W/Ba and Ba contents, which have been interpreted as reflecting the higher mobility of Ba, relative to W, in subduction zones (König et al., 2011). In the plot of W/Ba vs. Ba, the Nuvvuagittuq samples show similar features to arc basalts, with highly variable W/Ba ratios (0.0002 to 0.1), which are negatively correlated with Ba concentrations (Fig. 6d).

We conclude that compositional similarities, with respect to HFSE and fluid mobile elements, between Nuvvuagittuq mafic and ultramafic samples and modern convergent margin lavas, indicate that a fertile hydrous component may have played a role in the petrogenesis of the Nuvvuagittuq suite. Given the known mobility of W in such settings, we propose that the highly variable W concentrations in at least some samples from the suite reflect the introduction of W to the mantle source rocks via fluids. These fluids may have been derived from a subducting slab and subsequently transferred to the mantle wedge.

However, since there is little geological evidence for early Archean subduction, other alternatives to deliver crustal fluids and their W to mantle domains must also be considered here. For example, Bédard et al. (2013) proposed that a subduction-like trace-element signature in the mantle may also develop due to the introduction of fluids degassed during crustal delamination into lithospheric mantle keel of Archean cratons. In such a model, W would then be inherited from delaminated basaltic lower crust via fluid transfer.

If the interpretation that the W was introduced to the mantle source of the Nuvvuagittuq mafic and ultramafic rocks via fluid transfer from either a subducting slab or delaminated crust is correct, there are some important ramifications for the interpretation of the W isotopic systematics of the suite. First, the enriched $^{182}$W nature of the suite may have been predominantly derived from the subducted/ delaminated crust, rather than from the pre-metasomatized mantle source. Second, the uniformity of the $^{182}$W isotopic compositions of the Nuvvuagittuq mafic and ultramafic rocks requires that either the crustal fluids and mantle source were both characterized by similar W isotopic compositions, or the metasomatic event thoroughly modified the mantle source to a uniform isotopic composition, reflecting the isotopic composition of the slab. Finally, because the HSE in the pre-metasomatized mantle source would have been minimally affected by the putative metasomatic event, there would be little genetic relationship between the W isotopic and the HSE abundance systematics of the suite.

Although we currently favor a model in which W is added to the mantle source of the Nuvvuagittuq rocks by fluid transport in the mantle, not all geochemical aspects of the Nuvvuagittuq suite rocks are consistent with this model. While the geochemical characteristics of the
low-Ti Ujaraaluk rocks resemble modern supra-subduction related rocks, the high-Ti Ujaraaluk do not exhibit subduction-like signatures. The latter have tholeiitic affinities with flat PM-normalized trace element patterns, and compositions that are consistent with fractionation under low water pressure conditions (O’Neil et al., 2011). If the W isotopic composition of the Nuvvuagittuq rocks was dominated by the isotopic composition of a slab fluxing fluids through a mantle wedge of a significantly different isotopic composition, a different $^{182}\text{W}$ composition for the low-Ti and high-Ti Ujaraaluk might be expected.

5.4. Models for $^{182}\text{W}$ enrichment

In the framework of a model whereby some, or all of the Nuvvuagittuq $\text{W}$ was introduced to the mantle sources of these rocks from subducted/delaminated crust, as transported by metasomatic fluids, a mechanism for producing the $-15$ ppm positive $\text{W}$ isotopic anomaly in the subducted component is required. One simple scenario to consider is that the $^{182}\text{W}$ enrichment originated in the subducted/delaminated crust via in situ radioactive decay of $^{182}\text{Hf}$. However, $\text{W}$ is considerably more incompatible than $\text{Hf}$, so most crustal rocks are characterized by low $\text{Hf}/\text{W}$, relative to their source. A very early formed crustal reservoir produced within the lifetime of $^{182}\text{Hf}$ would, most likely, have developed a $^{182}\text{W}$ deficit, relative to the bulk silicate Earth, rather than enrichment.

More likely, the $^{182}\text{W}$ enrichment carried by a recycled component would have been a consequence of the anomalous isotopic composition of the mantle from which the crust was ultimately produced. Crust generated from such mantle more than $60$ Myr after solar system formation would not be subject to in situ radioactive decay of $^{182}\text{Hf}$. However, $\text{W}$ is more radiogenic. The model for the Isua rocks relies on internal differentiation processes. Post-$^{182}\text{Hf}$ generation of crust from mantle with a $-15$ ppm or greater $^{182}\text{W}$ excess, and later remobilization of this anomalous $\text{W}$ by metasomatic fluids could, therefore, account for the $\text{W}$ elemental and isotopic features of the Nuvvuagittuq rocks.

Willbold et al. (2011), Touboul et al. (2012) developed different models to account for $^{182}\text{W}$ enrichments in the mantle sources of Isua supracrustal rocks and Kostomuksha komatites, respectively. Both models could potentially have led to the production of a mantle reservoir characterized by an $-15$ ppm $^{182}\text{W}$ excess that subsequently could have melted to produce $^{182}\text{W}$-enriched crust. The model for the Kostomuksha komatites relies on internal differentiation processes within the mantle, while $^{182}\text{Hf}$ was extant. The model for the Isua rocks relies on a major change in the isotopic composition of $\text{W}$ in the mantle resulting from late accretion, most likely after $^{182}\text{Hf}$ was no longer extant. Both models are considered below.

First, we consider a model that involves processes of internal differentiation of the mantle. Fractionation mechanisms for $\text{Hf}/\text{W}$ were discussed by Touboul et al. (2012) for the Kostomuksha komatite source. In brief, a $-15$ ppm or greater $^{182}\text{W}$ excess can potentially be the result of indigenous $\text{Hf}/\text{W}$ fractionation reflecting either metal–silicate or silicate crystal–silicate liquid fractionation processes. For example, metal–silicate fractionation capable of generating such radiogenic compositions (or more radiogenic compositions) could occur in a basalt magma ocean through which late stage additions of metal to the core may sink and equilibrate with. Silicate crystal–liquid fractionation processes might occur as a result of the extraction of crust from the mantle, or as a consequence of crystalization or overturn of a magma ocean.

Chemical fractionations involving silicates in the mantle that would affect $\text{Hf}/\text{W}$, would also likely lead to collateral effects relating to the short-lived $^{146}\text{Sm}–^{142}\text{Nd}$ isotopic system. Both $\text{W}$ and $\text{Nd}$ are more incompatible than $\text{Hf}$ and $\text{Sm}$, respectively, so mantle differentiation by crustal extraction or magma ocean crystallization would likely have produced both a depleted reservoir with high both $\text{Hf}/\text{W}$ and $\text{Sm}/\text{Nd}$, and a complementary enriched reservoir with low both $\text{Hf}/\text{W}$ and $\text{Sm}/\text{Nd}$. If the $^{182}\text{W}$ excess in the Nuvvuagittuq suite reflects derivation from a mantle source domain affected by early melt depletion, while $^{182}\text{Hf}$ was still extant, there might also be expected a coupled $^{142}\text{Nd}$ enrichment. As noted above, however, there is no correlation between $^{142}\text{Nd}$ and $^{182}\text{W}$ for individual samples (Fig. 7a).

The $^{142}\text{Nd}/^{144}\text{Nd}$ variations in the mafic and ultramafic rocks from the Nuvvuagittuq suite correlate with $\text{Sm}/\text{Nd}$, which led to the interpretation of the data as an isochron with a slope corresponding to an age of $4388 \pm 125$ Ma (O’Neil et al., 2012). If the $^{142}\text{Nd}/^{144}\text{Nd}$ variations reflect in situ ingrowth, long after $^{182}\text{Hf}$ was no longer extant, then there is no reason to expect a correlation between $^{142}\text{Nd}$ and $^{182}\text{W}$ for individual samples. The extension of the isochron to a $\text{Sm}/\text{Nd} = 0$ yields an initial $^{142}\text{Nd}$ of $+4.3$ ppm at $4.39$ Ga, assuming that the accessible mantle has a $^{147}\text{Sm}/^{144}\text{Nd}$ of $0.2067$, the ratio needed to produce a $+18$ ppm $^{142}\text{Nd}$ enrichment in the mantle, compared to average chondrites, using the $^{146}\text{Sm}$ decay constant of Kinoshita et al. (2012). If this correlation represents a true isochron, then the initial $^{142}\text{Nd}$ value corresponds to the Nd

![Fig. 7.](a) $^{182}\text{W}$ versus measured $^{142}\text{Nd}$ for Nuvvuagittuq samples. Symbols are identical to Fig. 1. Neodymium isotopic data are from O’Neil et al. (2008, 2012). (b) $^{182}\text{W}$ versus $^{142}\text{Nd}$ for calculated Nuvvuagittuq mantle sources. The source $^{142}\text{Nd}$ correspond to the initial $^{142}\text{Nd}$ derived from $^{142}\text{Nd}$ versus $\text{Sm}/\text{Nd}$ correlation for each individual group (O’Neil et al., 2012), considered here as isochrons. The black curves correspond to products of different melting degree ($F$) from a source with same isotopic compositions than the modern mantle ($^{182}\text{W} = 0$ and $^{142}\text{Nd} = 0$). The blue dashed lines indicate loci of identical time for the formation of these reservoirs ($\Delta t_{\text{RSS}}$ = time interval relative to CAI formation). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
isotope composition of the mantle source at 4.39 Ga. In this case, the Nuvvuagittuq source would be characterized by both $^{142}$Nd and $^{182}$W excesses. This is broadly consistent with predictions for a very early depletion event that might have been responsible for both Sm–Nd and Hf–W fractionations (Fig. 7b).

Several factors, however, make it unlikely that the coupled Sm–Nd and Hf–W systems resulting from this scenario would be preserved within the framework of our model for the origin of the Nuvvuagittuq W involving mantle melting, production of crust, subduction/delamination of crust, and fluid transport of W, and possibly Nd. Although the generation of the crust is assumed to occur after $^{182}$W went extinct, $^{140}$Sm may have still been live. If so, the low expected Sm/Nd of the resulting crust would result in a $^{142}$Nd deficit relative to its mantle source. By contrast, the W isotopic composition of this material would remain unchanged. Second, in contrast to W, Nd is not a highly mobile mobile element. Hence, in a model where enriched W is transferred to the Nuvvuagittuq suite by metasomatic fluids, W and Nd would likely have had different origins. Therefore, neither of the prior disparate interpretations of the $^{142}$Nd/$^{144}$Nd variations among Nuvvuagittuq rocks, as either representative of an isochron (O’Neil et al., 2012), or a mixing line (Roth et al., 2013) precludes an interpretation of the $^{182}$W anomaly as being the product of an early mantle differentiation event. We conclude, therefore, that a terrestrial internal differentiation process to generate $^{182}$W enrichment in the ultimate source of the Nuvvuagittuq suite is a viable model, although one without strong supporting evidence. If this interpretation is correct, it implies that a mantle reservoir with a $^{182}$W value of $\sim+15$ was readily accessible for crust production over a considerable period of time, given that the Kostomuksha komatiites did not tap this source until 2.8 Ga.

We next consider the possibility of an externally imposed change in the isotopic composition of the mantle as a means for the creation of the $^{182}$W enrichment. For example, Halliday (2008) reported an accretionary model for Earth in which the $^{182}$W of the bulk silicate Earth was as high as $\sim200$ prior to the putative giant impact that led to formation of the Moon. Addition of substantial impactor mass (\$10\%\$ of Earth) could have drawn down the W isotopic composition of the mantle close to 0. Survival of small portions of pre-giant impact mantle is a potential source of radiogenic W. On a smaller scale, late accretion of $\sim0.5\%$ mass to the mantle is a means to account for the high absolute and chondritic relative abundances of HSE in the modern mantle (Chou, 1978). As a MSE, W is mostly, but not entirely, extracted from the mantle into the core during core segregation. Consequently, the mantle now has a W concentration that is characterized by $\sim20$ times less W than in chondritic meteorites (Newsom et al., 1996). Addition of 0.5% of Earth’s mass of chondritic materials to the mantle via late accretion would result in a $\sim8\%$ increase in the W concentration in the mantle, but also in a decrease of the $^{182}$W of the mantle by $\sim10$ to 30 ppm. This is because chondrites are characterized by $^{182}$W values that are $\sim200$ ppm less radiogenic than the W isotopic composition of the present-day mantle. Therefore, the pre-late accretionary mantle should have been characterized by a $\sim10$ to 30 ppm $^{182}$W excess, relative to modern mantle (e.g., Willbold et al., 2011). The $^{182}$W enrichment in the Nuvvuagittuq samples, therefore, could reflect ultimate derivation of their W from mantle that had not yet received its full late accretionary complement. This model is similar to that proposed by Willbold et al. (2011) for Isua rocks. For our model, however, the Nuvvuagittuq rocks are not assumed to be directly derived from a pre-late accretionary mantle source, which would be inconsistent with their HSE abundances that are similar to modern mantle-derived rocks. Instead, the $^{182}$W excess of the pre-late accretionary mantle must first be transferred to a crustal reservoir whose ultimate subduction/delamination induces the release of W-rich metasomatic fluids with anomalous isotopic composition into the Nuvvuagittuq mantle source. This source is characterized by modern mantle-like HSE abundances and, hence, by a full complement of late accreted materials. Because the relative proportion of Nd added by late accretion would be very minor, late accretion would have had no effect on the Sm–Nd isotopic evolution of the source, and the isotopic systematics of $^{142}$Nd in the Nuvvuagittuq suite would be completely decoupled from the $^{182}$W systematics. As with the internal differentiation model, this model is permitted by the data, but because of the decoupling of HSE from W, also has no strong supporting evidence.

5.5. Implications

The evidence for W mobility in the pre-eruptive history of the Nuvvuagittuq suite is strongly suggestive of the involvement of W transfer from $^{182}$W-enriched slab to the mantle source of the Nuvvuagittuq rocks. This process likely led to decoupling of W isotopic systematics from HSE abundances and $^{146,147}$Sm–$^{182,184}$Nd systematics, making the determination of the specific cause of the $^{182}$W enrichment problematic.

The Nuvvuagittuq suite marks the third documented occurrence of $^{182}$W enriched terrestrial materials. All three enriched lithologic suites, the 3.8 Ga Isua supracrustals (Willbold et al., 2011), the 2.8 Ga Kostomuksha komatiites (Touboul et al., 2012), and now the either 4.3 or 3.8 Ga Nuvvuagittuq supracrustals, are characterized by similar $^{182}$W anomalies of +13 to +15 ppm. Although the data are still very limited, there appears to be no dissipation of the magnitude of this signal over the period of time represented by these suites. It is important to note, however, that the $^{182}$W-enriched signal is not common to all ancient rocks, as Touboul et al. (2012) reported essentially normal $^{182}$W isotopic compositions for the 3.5 Ga Komati komatiites.

Collectively, these results suggest that $^{182}$W-enriched reservoirs (mantle or crustal) were common during the first third of Earth history. If, as proposed by Willbold et al. (2011), one or more of the $^{182}$W enriched suites samples pre-late accretionary mantle, then it must be concluded that, at least with respect to siderophile elements, the Hadean and Archean mantle remained poorly mixed. A similar conclusion must be reached if, as proposed by Touboul et al. (2012), one or more of the enriched suites was derived from portions of Earth’s mantle that, through an unspecified fractionation process, generated excess $^{182}$W during the first 50 Myr of solar system history.

Combining published Nd isotopic data with the new HSE data for the Nuvvuagittuq suite provides some additional new insights into early Earth processes. If the $^{142}$Nd versus Sm/Nd linear trend defined by Nuvvuagittuq rocks is interpreted to be a ca. 4.4 Ga isochron, the fact that the rocks of the suite appear to have normal abundances of HSE means that appreciable quantities of late accreted materials were delivered to at least some portions of the mantle during the first ~200 Ma of Earth’s history. A similar conclusion can also be reached if, instead, the $^{142}$Nd versus Sm/Nd linear trend is interpreted to be a mixing line and that the Nuvvuagittuq rocks are 3.8 Ga-old. In order for this scenario to work, the $^{142}$Nd-enriched component would have to have been generated at $\geq4.4$ Ga ago. The HSE abundances in this component would have to have been near modern levels such that mixing with mantle with a normal Nd isotopic composition and HSE abundances would yield a mixing line with no apparent variation in HSE content from enriched to normal endmembers. Thus, either case suggests relatively early (~4.4 Ga) delivery of most late accreted materials to the mantle. A similar conclusion was reached by Puchtel et al. (2013, 2014) on the basis of their studies of HSE abundances and Sm–Nd, Lu–Hf and Pt–Re–Os systematics of early Archean komatiites from the Barberton Greenstone Belt.

6. Conclusions

All Nuvvuagittuq samples analyzed show well-resolved $^{182}$W excesses, ranging from +6 to +17 ppm. Tungsten abundances are not correlated with common indices of magmatic differentiation. The W elemental systematics of the Nuvvuagittuq rocks may best be explained by derivation from a mantle source that had been variably fertilized.
by W-rich fluids derived from a crustal component recycled by subduction or delamination. Given the 182W-enriched nature of all Nuvvuagittuq rocks, it is presumed that the fluids were derived from older crust characterized by 182W enrichment, which in turn was most likely inherited from its mantle source. The anomalous isotopic composition of such mantle reservoir could be the result of an early Hf/W fractionation during mantle differentiation, or an incomplete incorporation of late accreted materials. For either scenario the W isotopic systematics are decoupled from the HSE, so the models cannot be discriminated by using HSE abundances.

The normal HSE abundances in these rocks, coupled with the variability in 142Nd, suggest that HSE abundances in the sampled portion of the mantle were established by late accretion at or prior to 4.4 Ga, consistent with the delivery of most late accreted materials within the first 200 Myr of solar system history.

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Appendix A. Supplementary data

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References


