Stable W isotope evidence for redistribution of homogeneous $^{182}$W anomalies in SW Greenland

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Abstract

We present the first high precision stable tungsten isotope data for a comprehensive Eoarchean rock suite from the Isua region of SW Greenland with the aim to reconstruct the sources and processes that controlled the inventory of W in Eoarchean time and to place constraints on the origin of $^{182}$W anomalies in Eoarchean rocks. When compared to modern igneous rocks, the observed range of $\delta^{186/184}$W in the Eoarchean rocks is substantially larger, ranging from $-0.072$ to $+0.249$‰. But unlike in modern igneous rocks, we find no co-variation of $\delta^{186/184}$W with other geochemical parameters. Multiple stage mobilisation and re-enrichment of W by metasomatic fluids entirely obscured pristine geochemical signals. However, our results illustrate the potential of applying stable W isotopes as geochemical tracer for alteration effects on primary $^{182}$W signatures. Despite secondary alteration and the large variation in $\delta^{186/184}$W the excesses in $^{182}$W that were previously observed in the same rock samples appear to be unaffected by alteration arguing that the excesses were most likely initially uniform in the whole Eoarchean assemblage of SW Greenland.

Introduction

The early Earth differed significantly from its present day geological setting. Higher potential mantle temperatures but lower heat fluxes (Korenaga, 2003) affected most relevant geological processes such as partial mantle melting with higher melt proportions, the mode of fractional crystallisation, and global tectonics (e.g., de Wit et al., 1992; Van Kranendonk, 2010). For example, it remains controversial if modern style plate tectonics operated on a global or local scale or were even absent in Hadean and Eoarchean times (e.g., de Wit et al., 1992; Nutman et al., 1996; Van Kranendonk, 2010). Alternative models suggest vertical stagnant lid tectonics, where thickened and dense eclogitic crustal restites sink in sagduction regimes (e.g., Bédard, 2006). In the latter case, crustal recycling would have differed, also affecting the geochemical cycling of elements and thus, the geochemical composition of early crustal nuclei.

Stable W isotopes represent an emerging geochemical tool that might help to reconstruct the geologic and tectonic history of ancient rocks as well as the cycling of W through different geochemical reservoirs (Kurzweil et al., 2019; Münker et al., 2020). Distinct types of modern igneous rocks show resolvable variation in the stable W isotope compositions. For example, subduction related rocks that carry a significant subducted sediment component show isotopically heavy compositions for W. In contrast, isotopically lighter compositions were observed in back-arc lavas that formed above deeper subduction zone settings, more distant to the trench (Münker et al., 2020). Fractional crystallisation of olivine and pyroxene as well as partial melting of mantle peridotite, however, have limited and so far not resolvable effects on the stable W isotope composition of mafic and intermediate melts. Accordingly, plume related rocks from ocean island basalt settings and mid-ocean ridge basalts show limited variation in $\delta^{186/184}$W values (Eq. S-1), calling for a homogeneous modern mantle stable W isotope composition of $+0.085 \pm 0.019$‰. (Fig. 1; Kurzweil et al., 2019; Münker et al., 2020).

In this study, we present stable W isotope data for some of the Earth’s oldest rocks from the Isua Gneiss Complex, SW Greenland (IGC, 3620 to >3850 Ma; e.g., Nutman et al., 1996) including peridotites, tholeiitic metabasalts, boninite-like metabasalts, non-gneissic tonalite-trondhjemite-granodiorites (TTGs) and metasediments, with the aim to reconstruct the sources and processes that controlled the inventory of W in Eoarchean time. This region is of particular interest, because of widespread metasomatic alteration (Rosing et al., 1996) and a previously reported large scale mobility of W (Rizo et al., 2016; Tusch et al., 2019) that even led to ore grade enrichment of W at a local scale (Appel, 1986). Moreover, the IGC is one of the first localities on Earth, where significant $^{182}$W excesses were reported (e.g., Willbold et al., 2011); the excess of $^{182}$W is described by $\mu^{182}$W, which is defined in the SI, and stable W isotopes may aid to elucidate the significance of these isotope anomalies. We combine the stable W isotope data with previously published major and trace element concentration data.
as well as with $\mu^{182}$W data obtained for the same set of samples (Tusch et al., 2019) to place constraints on the geodynamic setting of the magmatic rocks, their relationship among each other and possible hydrothermal and metasomatic overprint.

**Results**

A detailed description of the sample material, the geological setting and the analytical procedure can be found in the SI. The peridotite samples show extreme variations in W concentrations between 59 and 4380 ng/g, corresponding to W/Th between 0.02 and 143. Their stable W isotope compositions range from +0.008 to +0.134 ‰ in $\delta^{186/184}$W (Table S-1, Fig. 1). Tholeiitic metabasalts show similarly variable W concentrations between 117 and 1835 ng/g (W/Th from 0.2 to 2.3) and an even larger range in $\delta^{186/184}$W (~0.072 to +0.136 ‰), clearly outside the range predicted for igneous processes (Kurzweil et al., 2019; Mazza et al., 2020). In contrast, the boninite-like metabasalts are more depleted in W with concentrations between 14 and 100 ng/g. These rocks show elevated $\delta^{186/184}$W values between +0.069 and +0.249 ‰. Non-gneissic TTGs range in W concentrations between 29 and 430 ng/g (W/Th between 0.01 and 0.35). The stable W isotope compositions vary between +0.016 and +0.179 ‰ in $\delta^{186/184}$W, thus showing a similar range as most mafic and ultramafic rocks (Table S-1, Fig. 1). In contrast, metasediments that are relatively rich in W (928 to 1547 ng/g) exhibit a smaller range in $\delta^{186/184}$W between +0.050 and +0.077 ‰.

In the complete dataset we observe no clear co-variation of $\delta^{186/184}$W values with any other geochemical parameters (Fig. 2), neither with major or trace element concentrations nor with element concentration ratios. The variability in $\delta^{186/184}$W values is independent of the geographic position, the age, and the rock type of the sample. Similarly, W concentrations show no co-variation with other element concentrations or with element concentration ratios (Fig. S-1).

**Discussion**

The major and trace element composition of tholeiitic and boninite-like metabasalts from the IGC is mainly controlled by fractional crystallisation of olivine and pyroxene (Polat and Hofmann, 2003), whereby the boninite-like melts originate from an already depleted, more harzburgitic mantle source. The peridotites of this study represent relict mantle rocks (van de Locht et al., 2018), and the TTGs likely formed by partial melting of hydrated mafic crust (e.g., Hoffmann et al., 2014; SI). The close genetic relationship of the rock suites analysed here might explain the observed tight co-variations between various compatible and incompatible elements (Table S-2, Fig. S-1; Tusch et al., 2019). Most elements that behave incompatibly during partial melting and fractional crystallisation of olivine and pyroxene (Zr, Th, Ba, Pb) show expected enrichments in more
differentiated rocks, whereas compatible elements such as Mg, Ni and Co are more depleted (Fig. S-1). These differentiation trends are even preserved for some fluid mobile elements (Ba, Pb), which is noteworthy, considering the complex geologic history of igneous rocks from the IGC that experienced several high grade metamorphic, hydrothermal and metasomatic events (Nuttman et al., 1996; Rosing et al., 1996). Partial recrystallisation during amphibolite facies grade metamorphism (e.g., the formation of secondary amphibole, feldspar and biotite) apparently changed the mineralogy without significantly changing the overall bulk geochemical composition for most elements. However, the incompatible and fluid mobile element W shows no co-variation with any other element (Fig. S-1), indicating that its budget was severely affected during metamorphism, metasomatism and hydrothermalism. Extreme W concentrations in peridotites up to 4380 ng/g (more than 100 fold compared to 12 ng/g of the modern mantle; König et al., 2011) and W/Th (0.02–143) that are, with the exception of sample 10–12A, highly elevated compared to the canonical value defined by modern igneous rocks and clearly indicate secondary enrichment of W (Rizo et al., 2016; Tusch et al., 2019). Primary hosts for secondary W enrichments by metasomatic fluids are minor mineral phases such as serpentine, Ti-rich mineral phases, phlogopite and sulfide or grain boundary assemblages (Liu et al., 2018). Indeed, fine serpentine veinlets as well as small metasomatic sulfides have been reported for most peridotites investigated here (van de Locht et al., 2018, 2020). Consistent with a previous study (Rizo et al., 2016), we thus suggest that W was strongly mobilised by metasomatic fluids. This secondary disturbance of W probably increased the variation in δ186/184W beyond the range that is expected for unaltered igneous rocks (Kurzweil et al., 2019; Mazza et al., 2020). Therefore, our data provides no straightforward insight into tectono-magmatic processes active during the formation of the IGC.

The chemical composition of metasomatic fluids in the Izua region was shown to be variable on local to regional scales depending on the ambient rock assemblage (Rosing et al., 1996). This local heterogeneity probably also accounts for heterogeneous W concentrations and stable W isotope compositions of the ambient fluids and for the decoupling of W that is typically dissolved as an oxanion, which can be complexed with cationic ligands such as K⁺ or H⁺, from other nominally fluid mobile elements such as Ba or Pb that are transported as metal cations, which are complexed with anionic ligands such as Cl⁻ (Wood and Samson, 2000). The observed variability in δ186/184W values, which is not correlated with W concentrations (Fig. 1), argues against a single, regionally homogenous metasomatising fluid that overprinted primary stable W isotope compositions of IGC rocks to the same extent. The large variation of δ186/184W within different rock types rather calls for the involvement of different metasomatic fluids with locally (and temporally) variable stable W isotope compositions. To explain this local and temporal variability in δ186/184W, stable W isotope fractionation at various geologic conditions is required.

In general, the magnitude of equilibrium isotope fractionation of W is highly dependent on the geologic environment and the depth of oxidation. The oxidation state of W controls the bonding environments such as high oxidation states and low coordination numbers. Stable W isotope fractionation caused by redox changes in terrestrial igneous environments is not expected (Kurzweil et al., 2019), because the oxidised W⁶⁺ species is predominant in these settings (Forseca et al., 2014). However, during metasomatic alteration the preferential leaching of isotopically heavy W, which is mainly abundant as a tetrahedrally coordinated anion [WO₄]²⁻ in fluids, is expected, similar as in modern fluid-dominated subduction zone settings (Mazza et al., 2020). Moreover, octahedral coordination is preferred in hexagonally close packed mineral structures (e.g., wolframite), whereas the complex remains in tetrahedral coordination in cubic closed packed minerals (e.g., scheelite; Kuzmin and Purans, 2001). As such W-rich minerals are reported in the IGC (Appel, 1986), we speculate that the local mobilisation of W by metasomatic and hydrothermal fluids (and possibly seawater) as well as the formation of secondary W-rich mineral phases caused mass dependent stable W isotope fractionation in different directions due to localised changes in coordination.

To understand the metasomatic processes in more detail the separate consideration of distinct rock types and their specific petrographic properties is necessary. For example, TTGs with sub-canonical W/Th show low δ186/184W, whereas TTGs with canonical or supra-canonical W/Th show higher δ186/184W (Fig. 2b). A similar relationship is observed for peridotites. Most peridotite samples show strong W enrichment (high W/Th) and relatively high δ186/184W. The only peridotite with sub-canonical W/Th was also hydrated most strongly (10–12A; van de Locht et al., 2020) and shows the lowest δ186/184W of all peridotites. These relationships indicate the preferential mobilisation of isotopically heavy W by metasomatic fluids, leaving behind W depleted rocks that are isotopically lighter (Fig. 2b). The apparently higher number of W-rich peridotites with high δ186/184W might reflect sampling bias, as strongly altered samples such as 10–12A are usually excluded. Thus, strong W enrichments in peridotites do not necessarily require external sources of W but could also relate to very local W redistribution within single rock types. Importantly, W-rich peridotites in SW Greenland were metasomatised by chemically different fluids (H₂–rich vs. CO₂–rich; Rosing et al., 1996) as also indicated by crosscutting fine serpentine veins (SOISB1 and NUB peridotites) and carbonate veins (sample 10–34, respectively (van de Locht et al., 2020). Generally high W/Th in these samples indicate that both fluids were rich in W but it seems that W concentrations were higher and δ186/184W slightly lower in CO₂-rich fluids that percolated the carbonate bearing peridotite 10–34 (Fig. 2b). These relationships clearly suggest that the source of W in metasomatic fluids was heterogeneous and of different isotopic polarity.

Compared to modern igneous rocks, samples from the IGC show uniform excesses in the radiogenic isotope 182W. This excess was explained by either a missing late veneer component that was depleted in 182W (Willbold et al., 2011; Dale et al., 2017), or by early silicate differentiation during the lifetime of short lived 182Hf and the respective formation of 182W-enriched and 182W-depleted silicate reservoirs, respectively (Rizo et al., 2016; Tusch et al., 2019). In all these studies, mass dependent isotope fractionation that occurred during the chemical separation of W and the measurement of W isotope abundances is corrected assuming the exponential mass fractionation law and a given reference value of the 184W/182W ratio. However, natural mass dependent isotope fractionation during fluid controlled processes might have followed a different mass fractionation law (e.g., Hart and Zindler, 1989; SI). The application of inappropriate mass fractionation laws may therefore theoretically create apparent mass independent isotope effects in 186W (Hart and Zindler, 1989; SI). Assuming the equilibrium mass fractionation law during natural stable W isotope fractionation, however, the observed range in δ186/184W can maximally account for 182W excesses that are smaller than 2 ppm in 184W (Fig. S-2, Table S-3) a similar range that was also previously predicted by stable W isotope data of lower precision (Rizo et al., 2016). Moreover, we observe no co-variation of μW and δ186/184W values (Fig. 3). Thus, 182W excesses of around
Figure 3  Despite variable δ186/184W, the excess of 182W is homogeneously distributed in igneous rocks from the IGC (Tusch et al., 2019). We hypothesise that mass dependent stable W isotope fractionation during multi-stage metasomatic redistribution of W caused locally variable δ186/184W without affecting the regionally homogeneous mass independent excesses of 182W.

Acknowledgements

This study is part of the “Infant Earth” project that has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No 669666). We thank Austin Boyd and Minik Rosing for providing sample material. Helen Williams is acknowledged for editorial handling. Constructive comments raised by two anonymous reviewers and Helen Williams helped to improve the quality of the article.

Editor: Helen Williams

Additional Information

Supplementary Information accompanies this article at http://www.geochemicalperspectivesletters.org/article/2024.

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Stable W isotope evidence for redistribution of homogeneous $^{182\text{W}}$ anomalies in SW Greenland

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Supplementary Information

The Supplementary Information includes:
- Geological Setting and Sample Material
- Methods, Analytical Precision and Accuracy
- The Influence of Different Mass Fractionation Laws on $\mu^{182\text{W}}$
- Figures S-1 and S-2
- Tables S-1 to S-3
- Supplementary Information References

Geological Setting and Sample Material

The Itsaq Gneiss Complex (IGC) in SW Greenland consists of up to 80% of granitoids of the tonalite, trondhjemite-granodiorite (TTG) suite associated with complex assemblages of amphibolites, chemical and clastic sediments as well as felsic- to ultramafic units. (Moorbath et al., 1973; Nutman et al., 1996). Based on separate metamorphic histories it is subdivided into the Isukasia terrane (ISB and SOISB samples, Table S-1) and the Færingeshavn terrane (NUK samples, Table S-1; Nutman et al., 1996). Part of the Isukasia terrane is the Isua supracrustal belt (ISB), which is further divided into a 3.7 Ga old northern terrane and a 3.8 Ga old southern terrane (Nutman and Friend, 2009). Supracrustal rock assemblages and metatonalitic orthogneisses from the Northern- and Southern terrane are crosscut by the ~3.45-3.55 Ga old noritic Ameralik dykes. Juxtaposition of both terranes was dated to 3.68 Ga on a sedimentary mylonitic unit that separates both terranes (Nutman and Friend, 2009). Most rocks of the IGC were metamorphosed to amphibolite grade during at least two major metamorphic events at 3.61 Ga and 3.55 Ga (Blicher-Toft and Frei, 2001; Nutman et al., 2002; Crowley, 2003). Furthermore, the IGC region experienced several phases of metasomatic alteration by fluids of locally variable composition (carbonate- and H$_2$O-rich; Rose et al., 1996; Rosing et al., 1996). The stage of deformation also varies locally including high- and low strain domains (Nutman et al., 1996; Nutman and Friend, 2009).

Supracrustal rock assemblages of the IGC mainly consist of amphibolites with island arc tholeiitic geochemical affinity (herein called tholeiitic metabasalts; Polat et al., 2002; Jenner et al., 2009; Nutman and Friend, 2009; Hoffmann et al., 2010). In the ISB typical pillow structures are locally preserved indicating low grades of deformation (Nutman and Friend, 2009). Abundant quartz globules and quartz veins contain unstrained quartz that pre-dates metamorphic fabrics. These globules and veins were interpreted to reflect chemical precipitates from circulating ocean-floor-type hydrothermal fluids (Appel et al., 2001). The Northern terrane of the ISB also includes amphibolites with boninitic character that are petrogenetically unrelated to amphibolites with island arc tholeiitic affinity (Polat et al., 2002; Polat and Hofmann, 2003). In contrast to the tholeiitic basalts, the boninite-like metabasalts formed by partial melting of a depleted harzburgitic mantle source, which was poor in clinopyroxene due to its progressive extraction during earlier melting events (Green, 1976; Tatsumi, 1989; van der Laan et al., 1989). Boninite-like metabasalts of this study originate from the
eastern limb of the Isua Greenstone belt. Their original mineralogical composition was replaced during metamorphism by amphibole, plagioclase, chlorite, epidote, titanite and quartz (Polat et al., 2002). A more detailed description of tholeiitic and boninite-like metabasalts that have been analysed for this study can be found in Polat et al. (2002), Hoffmann et al. (2010) and Tuscher et al. (2019). In the western part of the ISB a mingling association of felsic and mafic magma was recently discovered (Boyd, 2018). The mafic unit is of tholeiitic composition. The felsic magma derived from partial melting of gabbro, which was previously altered by hydrothermal fluids (Boyd, 2018). The felsic unit shows a petrogenetic relationship to the massive felsic unit in the centre of the ISB thus not representing a late addition to the ISB (Boyd, 2018). The mingling association preserved primary magmatic structures that rather indicate the coeval eruption of felsic and mafic units, which was dated to 3808.0 ± 1.2 Ma (Boyd, 2018). Samples analysed for this study include a granular felsic rock, as well as a mafic and a leucosome enclave close to the mafic felsic contact. A more detailed description of this association can be found in Boyd (2018) and Tuscher et al. (2019).

Metatonalitic orthogneisses and non-gneissic TTGs from the IGC represent some of the oldest fragments of continental crust (Nutmans et al., 1996). They formed either by melting of subducted mafic crust at high pressures (Defant and Drummond, 1990; Rapp et al., 2003) or by melting of thickened island-arc crust at relatively lower pressures (Smithies, 2000; Hoffmann et al., 2011; Nagel et al., 2012). These felsic melts likely originated from partial melting of above mentioned tholeiites (Hoffmann et al., 2011, 2014). TTGs intruded slightly older ultramafic supracrustal rock assemblages that were already deformed and metamorphosed prior to the intrusion (Nutmans and Friend, 2009; Hoffmann et al., 2011). Within this study non-gneissic TTGs from the ISB and a low strain area south of the ISB were also analysed. These samples consist of plagioclase, quartz, hornblende, biotite, apatite and titanite. More details can be found in Hoffmann et al. (2014).

The area south of the ISB also comprises ultramafic lenses that are tectonically intercalated in tonalitic gneisses and TTGs (Nutmans et al., 1996). In contrast to supracrustal amphibolites, these dunitic and harzburgitic enclaves might either reflect their derivative cumulates (Szilas et al., 2015) or relics of Eoarchean mantle rocks (e.g. van de Locht et al., 2018, 2020). Szilas et al. (2015) observed ultramafic units in the ISB further to the north with olivine crystals that are enclosed by serpentine. These authors interpreted the olivine to be of metamorphic origin that formed during dehydration of serpentinitized rocks. The ultramafic rocks from south of the ISB analysed for this study contain olivine, orthopyroxene and amphibole with minor amounts of serpentine, biotite, chlorite and sulphides, the latter minerals being mainly linked to small veinlets (van de Locht et al., 2018, 2020). Despite the limited stability of olivine at hydrous low pressure conditions, mantle-like PGE patterns and the chemical composition of the olivines both indicate that these ultramafic units reflect mantle residues instead of cumulates (van de Locht et al., 2018). A more detailed description of our ultramafic samples can be found in Friend et al. (2002), van de Locht et al. (2018) and Tuscher et al. (2019).

The sediment unit that separates the Northern and the Southern terrane of the ISB mainly consists of metamorphosed and metasomatized cherts, siliciclastic turbidites, carbonates and banded iron formations. Metasediments analysed for this study are from the Garbenschiefer Formation in the western limb of the ISB having an approximate age of 3.72 Ga (Rosing, 1999; Kamber et al., 1998). The mineralogical composition of these sediments comprises quartz, mica, chlorite, chalcopyrite and graphite (more details in Rosing, 1999 and Hoffmann et al., 2010).

Methods, Analytical Precision and Accuracy

Short summaries of the chemical separation procedure and measurement parameters are presented in Tables S-3 and S-4. The stable W isotope composition of pure W cuts was measured using a ThermoFisher Scientific® NeptunePlus MC-ICP-MS at the University of Cologne. Details of the measurement setup parameters are provided in Kurzweil et al., (2018). The iterative solution of Compston and Oversby (1969) was applied for the data reduction of individual measurement cycles assuming that the instrumental mass bias follows the exponential law. To correct for the isobaric interferences of $^{186}$Hf, $^{180}$Ta, $^{180}$Os, and $^{186}$Os we simultaneously measured $^{177}$Hf, $^{182}$Ta and $^{186}$Os and assumed the same instrumental mass bias for these elements as for W. We present our data in the $\delta$-notation and relative to NIST SRM 3163 in $\%_{\text{std}}$.

$$\delta^{186/184}\text{W} = \left(\frac{\frac{^{186}}{^{184}}\text{W}_{\text{Sample}}}{^{186/184}\text{W}_{\text{NIST SRM 3163}}} - 1\right) \times 1000$$  \text{Eq. S-1}

The standard NIST SRM 3163 as well as an Alfa Aesar reference solution were repeatedly measured during measurement sequences having a long-term reproducibility in $\delta^{186/184}\text{W}$ of 0.000 ± 0.012 $\%_{\text{std}}$ (n = 148) and +0.055 ± 0.016 $\%_{\text{std}}$ (n = 113), respectively. Between different measurement sessions (n = 13), the average isotopic difference between Alfa Aesar and NIST SRM 3163 was very constant with $\Delta^{186/184}\text{W} = 0.086 ± 0.010 \%_{\text{std}}$. Additionally, the reference materials AGV-2 and BCR-2 were measured repeatedly, also including individual processing through the complete chemical separation procedure. Results for the andesitic reference material
AGV-2 (+0.007 ± 0.013 ‰; 2 s.d.; n = 6) and the basalt BCR-2 (+0.064 ± 0.006 ‰; 2 s.d.; n = 5) are consistent with previously determined compositions (Krabbe et al., 2016; Kurzweil et al., 2018) and confirm the previously reported 2 SD external reproducibility of ±0.018 ‰ in δ186/184W.

The Influence of Different Mass Fractionation Laws on \( \mu^{182W} \)

Mass fractionation laws relate a mass dependent isotope fractionation that is observed for one isotope ratio \( R_A \) with \( R_A = N_A/N_i \) to a second isotope ratio \( R_b \) of the same element with \( R_b = N_b/N_i \), where \( N_i \) is the abundance of isotope \( i \) with mass \( m_i \). This relation can be expressed by the isotope fractionation factor \( \alpha_{i} = \alpha_{i}^{m} \). The exponent \( \beta \) is a function of the masses of the isotopes and can be calculated using different mass fractionation laws (Wombacher et al., 2003). For example:

\[
\begin{align*}
\text{Equilibrium law} & \quad \beta = (1/m_i - 1/m_2) / (1/m_1 - 1/m_2) \quad \text{Eq. S-2} \\
\text{Exponential (Kinetic) law} & \quad \beta = \ln(m_1/m_2) / \ln(m_1/m_3) \quad \text{Eq. S-3} \\
\text{Power law} & \quad \beta = (m_1 - m_2) / (m_1 - m_3) \quad \text{Eq. S-4}
\end{align*}
\]

The exponential and the power law represent empirical relationships to describe the instrumental mass bias during isotope measurements (Russell et al., 1978; Hart and Zindler, 1989; Maréchal et al., 1999). The equilibrium and the kinetic law describe theoretical considerations that follow equilibrium isotope exchange and kinetic isotope fractionation processes, respectively (Young et al., 2002). In most W isotope studies mass dependent isotope fractionation that occurred during the measurement of W isotope abundances is corrected assuming the exponential mass fractionation law using a given reference value of 186W/184W = 0.927670 (Völkening et al., 1991). However, stable W isotope fractionation during the chemical separation of W and metasomatic alteration prior to the separation and measurement of W isotopes might be better described by another mass fractionation law such as the equilibrium law. The inappropriate application of mass fractionation laws can create apparent anomalies in single isotope abundances (Hart and Zindle, 1989; Rizo et al., 2016), an effect that will be described in more detail below.

Relative to a standard the isotope ratios \( R_a \) and \( R_b \) are expressed as δ-values with \( \delta_{A \text{ sample}} = (R_{A \text{ sample}} / R_{A \text{ Std}} - 1) \times 1000 \) and \( \delta_{B \text{ sample}} = (R_{B \text{ sample}} / R_{B \text{ Std}} - 1) \times 1000 \). Assuming no mass independent isotope fractionation, \( \delta_A \) and \( \delta_B \) are related by \( \delta_B = 1000 \times [(1 + \delta_A / 1000)^\beta - 1] \) (e.g. Farquhar et al., 2002). The larger the difference in \( \delta_A \), which is calculated as difference to an unfractionated modern mantle \( \delta_{186/184W} \) value of +0.085 ‰ with \( \delta_A = \delta_{A \text{ sample}} - \delta_{A \text{ modern mantle}} \) (Kurzweil et al., 2019), the larger is the difference between \( \delta_B \) that is calculated using the exponential law and \( \delta_B \) that is calculated using the equilibrium law. Accordingly, \( R_a \) ratios are also slightly different, which results in relative excesses/depletions of the isotope \( N_3 \). This excess/depletion can be estimated by \( \mu^{N3} = (R_{a \text{ law1}} / R_{a \text{ law2}} - 1) \times 10^6 \). For example, for \( N_1 = 184W, N_2 = 186W, N_3 = 182W \) we get \( R_a = 186W/184W \) and \( R_a = 182W/184W \). Relative to the modern upper mantle, samples from the IGC show a maximum in \( \delta^{186/184W} \) of +0.164 ‰ and a minimum in \( \delta^{186/184W} \) of -0.157 ‰, respectively. Using the \( \beta \) value of the equilibrium law (law1) and the exponential law (law2) and a 182W/184W ratio of 0.864780 (Völkening et al., 1991), the \( \mu^{182W}\text{Equilibrium} \) is then -1.8 ppm for the maximum \( \delta^{186/184W} \) value and +1.7 ppm for the minimum \( \delta^{186/184W} \) value (Fig. S-2; Table S-3). Using the \( \beta \) value of the power law (law1) and the exponential law (law2), the \( \mu^{182W}\text{Power} \) is +1.8 ppm for the maximum \( \delta^{186/184W} \) value and -1.7 ppm for the minimum \( \delta^{186/184W} \) value (Fig. S-2; Table S-3). Thus, the application of different mass fractionation laws can theoretically only account for apparent excesses in \( 182W \) that are smaller than 2 ppm (Fig. S-2; Table S-3).
Supplementary Figures

Figure S1  (a-f) Trace element variation diagrams illustrating that our samples exhibit linear co-variations between various compatible and incompatible element concentrations. Most incompatible elements (Zr, Th, Nb, Ba, Pb) show expected enrichments in more differentiated rocks (a-d, f), whereas compatible elements such as Mg, Ni are more depleted (b, e). These differentiation trends are also preserved for some fluid mobile elements such as Ba and Pb (c-f). However, the incompatible and fluid mobile element W shows no co-variation with any other parameter (g-i; red squares: Boninitic metabasalts, red diamonds: tholeiitic metabasalts, yellow diamonds: TTGs, black circles: mantle peridotite).
In most W isotope studies mass dependent isotope fractionation that occurred during the chemical separation of W and the measurement of W isotope abundances is corrected assuming the exponential mass fractionation law. However, natural stable W isotope fractionation prior to the separation and measurement of W isotopes might be better described by another mass fractionation law. This figure shows the apparent excesses/depletions in $^{182}$W that is generated by the exponential law although previous natural stable W isotope fractionation followed a different law. The larger the observed range in stable W isotope compositions relative to an unfractionated modern mantle $\delta^{186/184}$W value of +0.085 ‰ ($\delta^{186/184}$W_{sample} - $\delta^{186/184}$W_{modern mantle}), the larger is the relative apparent excess/depletion in $^{182}$W ($\mu^{182}$W = [(182W/184W)$_{sample}$ / (182W/184W)$_{SRM\ 3163}$] - 1) $\times$ 10$^6$, whereby isotope ratios were previously corrected for instrumental mass bias using the exponential law and a given $^{186}$W/$^{184}$W of 0.927672; Völkering et al., 1991). The green shaded area indicates the range observed for rocks of the IGC in SW Greenland relative to a modern mantle $\delta^{186/184}$W of +0.085 ‰. The excesses in $\mu^{182}$W of around +13 ppm that are observed in rocks of the IGC (Willbold et al., 2011; Rizo et al., 2016; Dale et al., 2017; Tusch et al., 2019) represent no analytical artefacts due to the application of inappropriate mass fractionation laws.

**Supplementary Tables**

Data Tables S-1 to S-3 are available to download from the online version of this article at http://www.geochemicalperspectivesletters.org/article2024.

**Table S-1** Tungsten concentration and stable isotope composition.

**Table S-2** Available literature data of the analysed sample set (references below).

**Table S-3** Calculation of apparent $^{182}$W anomalies due to the application of different mass fractionation laws.
Supplementary Information References


