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

F. Kurzweil, C. Münker, J.E. Hoffmann, J. Tusch, R. Schoenberg

Supplementary Information

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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 Færingehavn 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 (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 Tusch et al. (2019).

In the western part of the ISB a mingling association of felsic and mafic magmas was recently discovered (Boyd, 2018). The mafic unit is of tholeiitic composition. The felsic magma derived from partial melting of gabro, 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 Tusch et al. (2019).

Metatonalitic orthogneisses and non-gneissic TTGs from the IGC represent some of the oldest fragments of continental crust (Nutman et al., 1999). 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 (Nutman 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 (Nutman 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 Earthian 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 Tusch 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 $^{182}Hf$, $^{180}Ta$, $^{180}Os$, and $^{186}Os$ we simultaneously measured $^{176}Hf$, $^{181}Ta$, and $^{186}Os$ and assumed the same instrumental mass bias for these elements as for $W$. We present our data in the δ-notation and relative to NIST SRM 3163 in $\delta^{186}$/$^{184}$W = \left[\frac{\text{Sample}}{\text{NIST SRM 3163}}\right] - 1 \times 1000 \quad \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 $\delta^{186}$/$^{184}$W of 0.006 ± 0.012 ‰ (n = 148) and +0.055 ± 0.016 ‰ (n = 113), respectively. Between different measurement sessions (n = 13), the average isotopic difference between Alfa Aesar and NIST SRM 3163 was very constant with $\Delta^{186}$/$^{184}$W = 0.056 ± 0.010 ‰. 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
The Influence of Different Mass Fractionation Laws on $\mu^{182}W$

Mass fractionation laws relate a mass dependent isotope fractionation that is observed for one isotope ratio $R_A$ with $R_A = N_2/N_1$ to a second isotope ratio $R_B$ of the same element with $R_B = N_3/N_1$, where $N_i$ is the abundance of isotope $i$ with mass $m_i$. This relation can be expressed by the isotope fractionation factor $\alpha_2 = a \times \beta$. 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:

$$\beta = (m_1 - m_3) / (m_1 - m_2)$$  \hspace{1cm} \text{(Young et al., 2002)} \hspace{1cm} \text{Eq. S-2}

$$\beta = \ln(m_1/m_2) / \ln(m_1/m_3)$$  \hspace{1cm} \text{(Young et al., 2002)} \hspace{1cm} \text{Eq. S-3}

$$\beta = (1/m_1 - 1/m_2) / (1/m_1 - 1/m_3)$$  \hspace{1cm} \text{(Maréchal et al., 1999)} \hspace{1cm} \text{Eq. S-4}

The exponential and the power law represent empirical relationships to describe the instrumental mass bias during isotope measurements (Russel 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 $^{186}W/^{184}W = 0.927670$ (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 inappropiate application of mass fractionation laws can create apparent anomalies in single isotope abundances (Hart and Zindler, 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 $\delta$-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 unfractonated modern mantle $\delta^{186/184}W$ 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 $\delta_A$ 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 $\mu^{32} = (R_A \text{ law1} / R_A \text{ law2} - 1) \times 10^6$. For example, for $N_1 = ^{184}W$, $N_2 = ^{186}W$, $N_3 = ^{182}W$ we get $R_A = ^{186}W/^{184}W$ and $R_B = ^{182}W/^{184}W$. Relative to the modern upper mantle, samples from the IGC show a maximum in $\delta^{186/184}W$ of $+0.164$‰ and a minimum in $\delta^{186/184}W$ of $-0.157$‰, respectively. Using the $\beta$ value of the equilibrium law (law1) and the exponential law (law2) and a $^{182}W/^{184}W$ ratio of 0.864780 (Völkening et al., 1991), the $\mu^{182}W_{\text{Equilibrium}}$ is then $-1.8$ ppm for the maximum $\delta^{186/184}W$ value and $+1.7$ ppm for the minimum $\delta^{186/184}W$ value (Fig. S-2; Table S-3). Using the $\beta$ value of the power law (law1) and the exponential law (law2), the $\mu^{182}W_{\text{Power}}$ is $+1.8$ ppm for the maximum $\delta^{186/184}W$ value and $-1.7$ ppm for the minimum $\delta^{186/184}W$ value (Fig. S-2; Table S-3). Thus, the application of different mass fractionation laws can theoretically only account for apparent excesses in $^{182}W$ 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 excess/depletions in $^{182}\text{W}$ 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 $\delta^{186/184}\text{W}$ value of +0.085 ‰ ($\delta^{186}_{\text{W, modern mantle}} = \delta^{186}_{\text{W, sample}} - \delta^{186}_{\text{W, modern mantle}}$), the larger is the relative apparent excess/depletion in $^{182}\text{W}$ ($\mu^{182}_{\text{W}} = \left(\left(\frac{^{182}_{\text{W, sample}}}{^{184}_{\text{W, sample}}}\right) / \left(\frac{^{182}_{\text{W, SRM 3163}}}{^{184}_{\text{W, SRM 3163}}}\right)\right) - 1 \times 10^6$, whereby isotope ratios were previously corrected for instrumental mass bias using the exponential law and a given $^{186}_{\text{W, SRM 3163}}$ of 0.927672; Völkeninger et al., 1991). The green shaded area indicates the range observed for rocks of the IGC in SW Greenland relative to a modern mantle $\delta^{186/184}\text{W}$ of +0.085 ‰. The excesses in $\mu^{182}_{\text{W}}$ 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 $^{182}\text{W}$ anomalies due to the application of different mass fractionation laws.
Supplementary Information References


