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 $\delta^{186/184}\text{W}$ 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 $\delta^{186/184}\text{W}$ 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 $\delta^{186/184}\text{W}$ 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.

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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; Mazza *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 (Mazza *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 $\delta^{186/184}\text{W}$ 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; Mazza *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 $\mu^{182}\text{W}$, 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

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Figure 1 Plot of stable W isotope compositions and W concentrations for Eoarchean rocks from the Itsaq Gneiss Complex. The observed range in $\delta^{186/184}\text{W}$ is even larger when compared to samples from modern OIBs, MORBs and arcs, and the variations are probably related to stable W isotope fractionation during local metasomatic processes.

as well as with $\mu^{182}\text{W}$ 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 $\delta^{186/184}\text{W}$ (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 $\delta^{186/184}\text{W}$ (−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 $\delta^{186/184}\text{W}$ 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 $\delta^{186/184}\text{W}$, 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 $\delta^{186/184}\text{W}$ between +0.050 and +0.077 ‰.

In the complete dataset we observe no clear co-variation of $\delta^{186/184}\text{W}$ values with any other geochemical parameters (Fig. 2), neither with major or trace element concentrations nor with element concentration ratios. The variability in $\delta^{186/184}\text{W}$ 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

Figure 2 Plots of measured W isotope compositions (a) versus MgO as an indicator for magmatic differentiation, (b) versus W/Th as an indicator for selective W mobility by metasomatic fluids and (c) versus Nb/Ta as an indicator for the presence of residual rutile during partial melting. We observe no co-variation of $\delta^{186/184}\text{W}$ values neither with any element concentration nor with any element ratio.

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 (Nutman *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 Löcht *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 $\delta^{186/184}\text{W}$ 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 Isua 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 oxyanion, 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 $\delta^{186/184}\text{W}$ values, which is not correlated with W concentrations (Fig. 1), argues against a single, regionally homogeneous metasomatising fluid that overprinted primary stable W isotope compositions of IGC rocks to the same extent. The large variation of $\delta^{186/184}\text{W}$ 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 $\delta^{186/184}\text{W}$, stable W isotope fractionation at various geologic conditions is required.

In general, the magnitude of equilibrium isotope fractionation in geological environments depends on differences in bond strengths, whereby heavy isotopes prefer stronger 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 W^{6+} species is predominant in these settings (Fonseca *et al.*, 2014). However, during metasomatic alteration the preferential leaching of isotopically heavy W, which is mainly abundant as a tetrahedrally coordinated anion $[\text{WO}_4]^{2-}$ 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 remobilisation 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 $\delta^{186/184}\text{W}$, whereas TTGs with canonical or supra-canonical W/Th show higher $\delta^{186/184}\text{W}$ (Fig. 2b). A similar relationship is observed for peridotites. Most peridotite samples show strong W enrichment (high W/Th) and relatively high $\delta^{186/184}\text{W}$. The only peridotite with sub-canonical W/Th was also hydrated most strongly (10–12A; van de Löcht *et al.*, 2020) and shows the lowest $\delta^{186/184}\text{W}$ 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 $\delta^{186/184}\text{W}$ 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 (H_2 -rich vs. CO_2 -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 Löcht *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 $\delta^{186/184}\text{W}$ slightly lower in CO_2 -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 ^{182}W . This excess was explained by either a missing late veneer component that was depleted in ^{182}W (Willbold *et al.*, 2011; Dale *et al.*, 2017), or by early silicate differentiation during the lifetime of short lived ^{182}Hf and the respective formation of ^{182}W -enriched and ^{182}W -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 $^{186}\text{W}/^{184}\text{W}$ 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 $\mu^{182}\text{W}$ (Hart and Zindler, 1989; SI). Assuming the equilibrium mass fractionation law during natural stable W isotope fractionation, however, the observed range in $\delta^{186/184}\text{W}$ can maximally account for ^{182}W excesses that are smaller than 2 ppm in $\mu^{182}\text{W}$ (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 $\mu^{182}\text{W}$ and $\delta^{186/184}\text{W}$ values (Fig. 3). Thus, ^{182}W excesses of around

Figure 3 Despite variable $\delta^{186/184}\text{W}$, the excess of ^{182}W 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 $\delta^{186/184}\text{W}$ without affecting the regionally homogeneous mass independent excesses of ^{182}W .

+13 ppm 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 caused by the application of inappropriate mass fractionation laws.

Despite variable secondary enrichment of W and heterogeneous $\delta^{186/184}\text{W}$ beyond the range observed in fresh igneous rocks, the excess of ^{182}W is homogeneously distributed in igneous rocks from the IGC (Tusch *et al.*, 2019). We therefore suggest that mass dependent stable W isotope fractionation during multi-stage metasomatic redistribution of W increased the variability in $\delta^{186/184}\text{W}$ on a local scale without affecting the mass independent excesses of ^{182}W . The sources of the metasomatic W likely tap different rock types as indicated by extremely variable W/Th and $\delta^{186/184}\text{W}$ in all analysed rock types. These observations argue against initially variable excesses in ^{182}W that were fully homogenised but are more consistent with an originally widespread and homogeneously distributed excess of ^{182}W within the Eoarchean assemblage of the IGC prior to the metasomatic redistribution of W. From a W perspective, this would permit combination with other geochemical parameters such as ^{142}Nd isotope or HSE signatures (e.g., Rizo *et al.*, 2016; Dale *et al.*, 2017; Saji *et al.*, 2018). In the light of coupled ^{182}W - ^{142}Nd anomalies (Rizo *et al.*, 2016) and recently reported Ru isotope data (Fischer-Gödde *et al.*, 2020), contributions from both missing late veneer and early silicate differentiation to the ^{182}W excesses now appear likely. For future ^{182}W isotope studies, the combination with stable W isotope analyses might represent an additional tool to assess the pristine character of W signatures.

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Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article2024>.

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