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^{182}W evidence for core-mantle interaction in the source of mantle plumes

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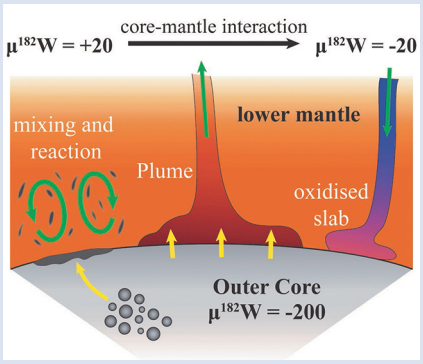
Abstract



Tungsten isotopes are the ideal tracers of core-mantle chemical interaction. Given that W is moderately siderophile, it preferentially partitioned into the Earth's core during its segregation, leaving the mantle depleted in this element. In contrast, Hf is lithophile, and its short-lived radioactive isotope ^{182}Hf decayed entirely to ^{182}W in the mantle after metal-silicate segregation. Therefore, the ^{182}W isotopic composition of the Earth's mantle and its core are expected to differ by about 200 ppm. Here, we report new high precision W isotope data for mantle-derived rock samples from the Paleoarchean Pilbara Craton, and the Réunion Island and the Kerguelen Archipelago hotspots. Together with other available data, they reveal a temporal shift in the ^{182}W isotopic composition of the mantle that is best explained by core-mantle chemical interaction. Core-mantle exchange might be facilitated by diffusive isotope exchange at the core-mantle boundary, or the exsolution of W-rich, Si-Mg-Fe oxides from the core into the mantle. Tungsten-182 isotope compositions of mantle-derived magmas are similar from 4.3 to 2.7 Ga and decrease afterwards. This change could be related to the onset of the crystallisation of the inner core or to the initiation of post-Archean deep slab subduction that more efficiently mixed the mantle.

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Letter

Deep-rooted upwelling mantle plumes are potential candidates for carrying geochemical evidence of chemical interaction between the liquid outer core and the base of the mantle. Ocean island basalts (OIB), erupted at hotspots, are the surface expression of these mantle plumes. While the He and Os isotope compositions and Fe/Mn ratios of these magmas have been interpreted as possible evidence for core-mantle exchange (*e.g.*, Walker *et al.*, 1995; Brandon *et al.*, 1998; Porcelli and Halliday, 2001; Humayun *et al.*, 2004; Bouhifd *et al.*, 2013), other interpretations have also been invoked (*e.g.*, Sobolev *et al.*, 2007; Lassiter, 2006; Luguet *et al.*, 2008).

Strong evidence for core-mantle interaction may come from the short-lived ^{182}Hf-^{182}W system. With a half-life of 8.9 Ma (Vockenhuber *et al.*, 2004), ^{182}Hf decayed into ^{182}W during the first ~50 Myr of the solar system's history. Since Hf is a lithophile element, it is concentrated in the silicate portion of the Earth. In contrast, W partitions preferentially into metal, and mass balance calculations suggest that ~90 % of the Earth's W resides in the core (McDonough, 2003). The difference in the W isotopic composition of the Earth's mantle and chondritic meteorites implies that the W-rich core has a ^{182}W/^{184}W ratio ~200 ppm lower than the mantle (*e.g.*, Kleine *et al.*, 2009). Therefore, chemical exchange between the core and the source of mantle plumes could be detectable in the ^{182}W/^{184}W ratio of OIB.

The samples studied here are plume-related volcanic rocks from the Réunion Island and the Kerguelen Archipelago hotspots, the certified reference material Hawaiian basalt BHVO-2, as well as samples from the ~3.475 Ga Mount Ada Basalts of the Pilbara Craton (samples and analytical methods are described in the Supplementary Information). The ^{182}W isotope compositions of these samples are presented as μ^{182}W values in Table 1 and Figure 1, which are deviations in ppm from the W isotopic composition of the terrestrial standard

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(assumed $\mu^{182}W = 0$). All plume-related samples analysed here yield negative $\mu^{182}W$ values ranging from -5.2 ± 3.7 to -20.2 ± 5.1, including BHVO-2, which yields an average $\mu^{182}W$ of -6.6 ± 1.9, consistent with previous reports (Willbold *et al.*, 2011; Mundl *et al.*, 2017; Kruijer and Kleine, 2018; Mei *et al.*, 2018). In contrast, the ~3.475 Ga Mt. Ada Basalts samples yield positive $\mu^{182}W$ values of +15.3 ± 4.6 and +13.1 ± 4.1, in the same range as most Hadean and Eoarchean mantle-derived rocks. Deviations measured in $\mu^{182}W$ are not associated with deviations in $\mu^{183}W$, confirming that ^{182}W variability is not the result of nuclear field shift effects (Figs. S-1 and S-2).

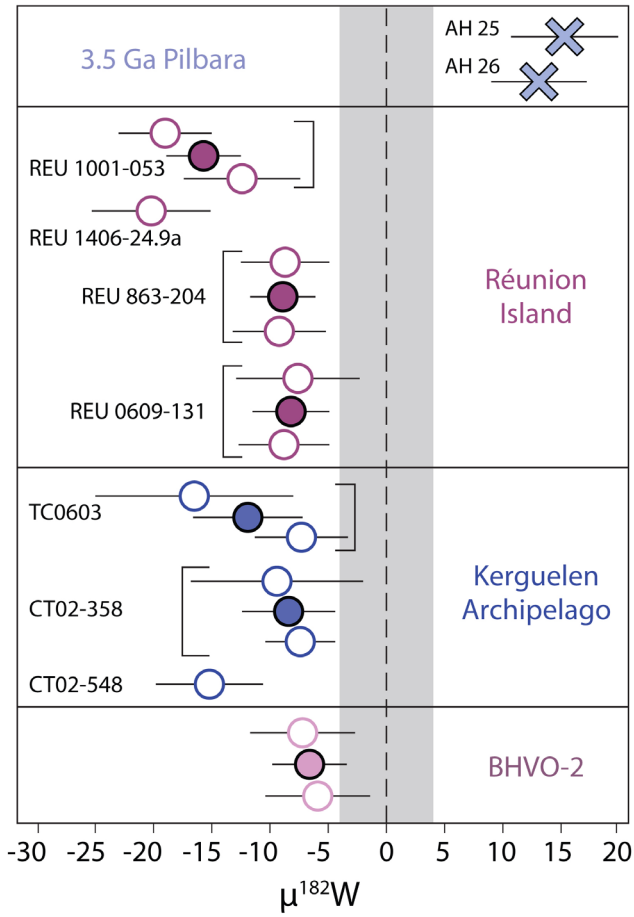

Figure 1 $^{182}W/^{184}W$ data obtained in this study shown as $\mu^{182}W$ values. Open symbols are individual analysis of samples and filled symbols show the average of the different duplicates. Errors on individual measurements shown are 2 standard error (2 s.e.) and propagated uncertainties are shown for averages. The shaded area represents the reproducibility obtained (2 s.d.) on repeated measurements of the Alfa Aesar W standard.

Coupled with other high precision W isotope studies of mantle-derived rocks, the data reveal that the ^{182}W isotopic composition in the Hadean-Archaean mantle was different from the modern mantle (Fig. 2). With the exception of the ~3.55 Ga Schapenburg komatiites, Hadean to Archean volcanism sampled a mantle characterised by ^{182}W excesses of +5 to +20 ppm. In contrast, the mantle accessed by modern mantle-plume magmatism is characterised by ^{182}W anomalies from +5 to -20 ppm. The lavas from the Canary Islands are the only OIB to display resolvable ^{182}W excesses, however, this hotspot seems to originate at shallower depths (King and Ritsema, 2000; Courtillot *et al.*, 2003) and various geochemical tracers suggest these magmas were contaminated by the ancient continental root (*e.g.*, Thirlwall *et al.*, 1997).

Several processes have been proposed to explain the cause of ^{182}W variability. None of these processes, however, seems to explain all geochemical observations satisfactorily. For example, excesses in ^{182}W observed in ancient rock samples could arise if they derived from mantle sources that remained partially isolated from the incorporation, after core formation, of meteoritic material (*e.g.*, Willbold *et al.*, 2011). This late-accreted material is assumed to possess $\mu^{182}W$ ~ -200, and its gradual homogenisation into the mantle would have decreased its $\mu^{182}W$ with time. Late accretion of ~0.5 wt. % of the Earth has also been invoked to explain the higher than expected highly siderophile element (HSE; Re, Os, Ir, Ru, Pt, Pd) abundances in Earth's mantle (*e.g.*, Chou *et al.*, 1978; Walker, 2009). Therefore, variability of ^{182}W is expected to correlate with HSE source abundances. Yet, it rarely does, and the HSE depleted Schapenburg samples even indicate the opposite relationship (Puchtel *et al.*, 2016). Estimating HSE abundances of mantle sources is, however, complicated since these elements are controlled by sulphides, whose partial melting behaviour is very complex.

Another proposed process is that early (<50 Ma) silicate differentiation, following crystallisation of a magma ocean, could have also created ^{182}W variability. Since W is more incompatible than Hf (Shearer and Righter, 2003), early differentiated reservoirs will be characterised by fractionated Hf/W ratios and develop excesses and deficits in ^{182}W. Silicate differentiation in the first 50 Ma of Earth's history should have also affected the short-lived ^{146}Sm-^{142}Nd isotope system ($t_{1/2}$ = 103 Ma; Marks *et al.*, 2014). Coupled ^{142}Nd and ^{182}W anomalies in the ancient rock record, however, are not ubiquitous and most modern mantle rocks measured so far exhibit ^{142}Nd variations that deviate by less than 5 ppm from the terrestrial standard (Fig. S-3).

While the scenarios discussed above might explain some of the ^{182}W anomalies detected in the rock record, the temporal shift observed in the W isotopic composition of the mantle seems to reflect one predominating process. Chemical interaction between the core and the mantle sources of plumes could be such a process. Core-mantle interaction does not affect lithophile elements such as Nd, and is thus compatible with the observed lack of coupling between ^{182}W and ^{142}Nd. Furthermore, the correlations between ^{182}W and $^{3}He/^{4}He$ ratios (Mundl *et al.*, 2017) and Fe/Mn ratios (Fig. S-4) could corroborate this process, since both He and Fe/Mn have also been proposed as tracers of core-mantle interaction (Porcelli and Halliday, 2001; Humayun *et al.*, 2004; Bouhifd *et al.*, 2013). In this scenario, the Earth's mantle, initially characterised by a maximum $\mu^{182}W$ value of +20, was subject to core addition that created domains with $\mu^{182}W$ values as low as -20. The most negative $\mu^{182}W$ values measured in OIB constrain the maximum core contribution to their sources to ~0.8 wt. %, calculated by mass balance assuming a core $\mu^{182}W$ value of -200 (Kleine *et al.*, 2009) and W concentration of ~500 ppb (McDonough, 2003).

Diffusive isotope exchange of W at the core-mantle boundary (CMB) is one of the plausible mechanisms of core-mantle interaction (Fig. 3). At CMB conditions, grain boundary diffusion experiments indicate W can diffuse over distances of 1-10 km in the mantle over 100 Myr (Hayden and Watson, 2007) and even higher diffusion rates may arise from the presence of partially molten silicates at the CMB (*e.g.*, Andrault *et al.*, 2014; Yuan and Romanowicz, 2017). Hayden and Watson (2007) also determined the grain boundary diffusivity of the HSE, and concluded that these elements are also susceptible to 'leaking' from the core over geological timescales. The high concentrations of HSE in the core relative to the mantle mean that even a small flux of HSEs from the core should result in coupling between $\mu^{182}W$ and HSE abundances in mantle-derived rocks. As discussed above, mantle-derived rocks with negative $\mu^{182}W$ values do not possess HSE enrichments,

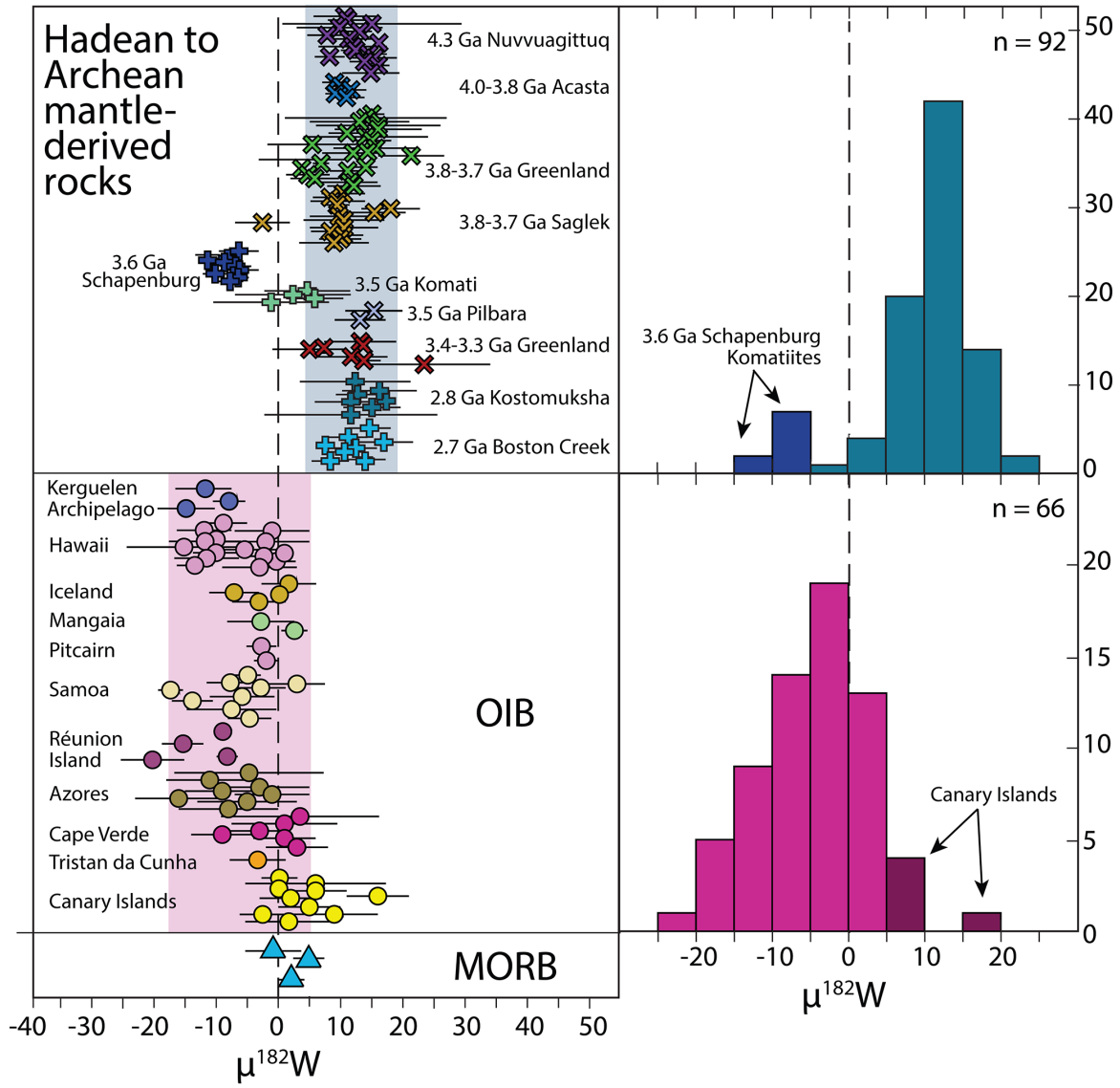

Figure 2 Compilation of all existing $^{182}W/^{184}W$ data shown as $\mu^{182}W$ values. Hadean and Archean mantle-derived rocks are organised in order of their age, with the oldest at the top and the youngest at the bottom. Shaded areas show the average $\mu^{182}W$ values ± 2 s.d. for Hadean-Archean and OIB samples. OIB: Ocean Island Basalts. MORB: Mid-Ocean Ridge Basalts. Data sources: Willbold *et al.*, 2011, 2015; Touboul *et al.*, 2012, 2014; Liu *et al.*, 2016; Puchtel *et al.*, 2016, 2018; Rizo *et al.*, 2016a,b; Dale *et al.*, 2017; Mundl *et al.*, 2017; Kruijer and Kleine, 2018; Mei *et al.*, 2018; Reimink *et al.*, 2018; and this study.

perhaps suggesting that this is not the primary mechanism of core-mantle interaction. However, relating HSE concentrations in mantle-derived rocks to the composition of their source regions is challenging and means we cannot rule out diffusion as a viable mechanism.

Core-mantle interaction could be also a consequence of Si-Mg-Fe oxide exsolutions from the core (Badro *et al.*, 2016; O'Rourke and Stevenson, 2016; Hirose *et al.*, 2017) (Fig. 3). Our experimental results show that these oxides can efficiently incorporate W in their structure without the accompanying HSE (Supplementary Information; Figs. S-5 and S-6). These exsolutions are expected to form by simple secular core cooling, since the solubility of oxides in liquid iron decreases with decreasing temperature (Badro *et al.*, 2016; O'Rourke and Stevenson, 2016; Hirose *et al.*, 2017). Additional to core cooling, the crystallisation of the inner core likely led to higher oxygen concentrations in the outer liquid core and increased Si-Mg-Fe oxide precipitation, since oxygen is not easily incorporated into solid iron (Alfè *et al.*, 2002). More oxidising conditions in the outer core decreases the affinity of W for the liquid metal (Righter and Ghiorso, 2012; Wade *et al.*, 2012), inducing the extraction of W from the core and its incorporation into the mantle.

Regardless of the exact mechanism of core-mantle interaction, a key observation to consider is that the mantle between 4.3 Ga and 2.7 Ga seems to be characterised by constant $\mu^{182}W$ values, which have decreased in the modern mantle (Fig. 2). This broad distinction in $\mu^{182}W$ *vs.* age could imply a change in mantle dynamics after the Archean. Slab subduction of oxidised material into the deep mantle might have induced W disequilibrium at the CMB by increasing its fO_2 (van der Hilst and Kárason, 1999). Since W adopts a high valence (4+ to 6+) in silicates, increasing the fO_2 at the CMB decreases its siderophile behaviour (*e.g.*, Righter and Ghiorso, 2012; Wade *et al.*, 2012), favouring its extraction from the core and incorporation in the lower mantle. Deep slab subduction might have also played a role in scavenging material from the CMB. Alternatively, the change of $\mu^{182}W$ values in the post-Archaean mantle could be related to the crystallisation of the inner core. Large experimental uncertainties on thermal conductivity values of liquid iron in the outer core limit our understanding of inner core crystallisation. If changes in the $\mu^{182}W$ signature of deep mantle plumes are related to the onset of inner core segregation, $\mu^{182}W$ could be used as an alternative tool to study this process.

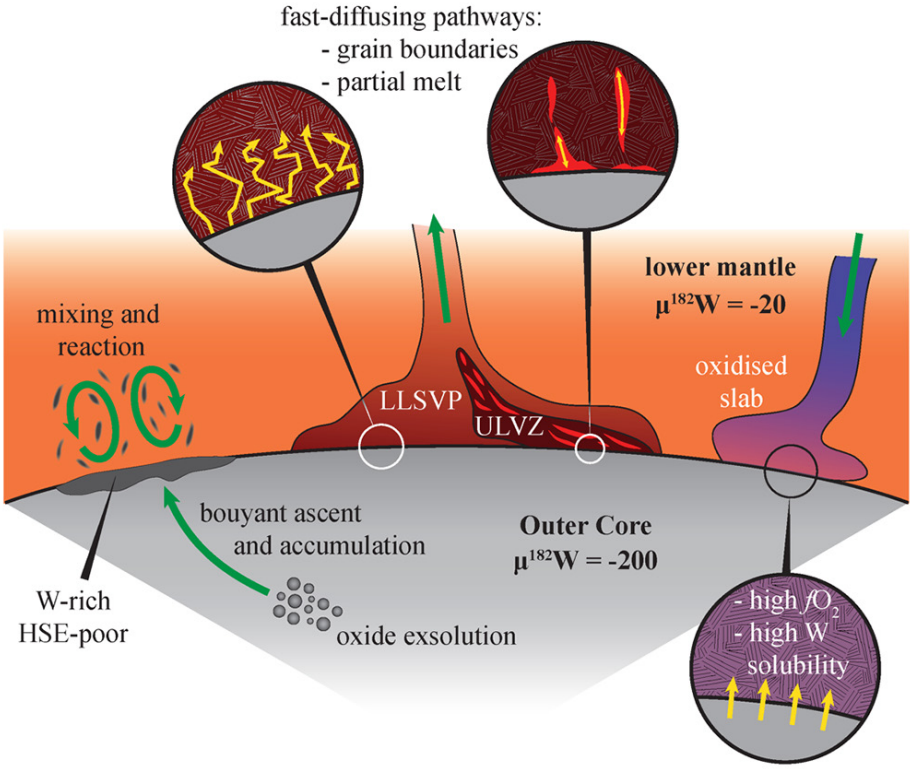

Figure 3 Schematic cartoon showing possible processes for core-mantle chemical interaction.

Table 1 Tungsten isotope results for rock samples from the Pilbara Craton, the Kerguelen Archipelago, Réunion Island and the Hawaiian basalt BHVO-2.

Location	Sample	$\mu^{182}W$	$\mu^{183}W$
Réunion Island	REU 1001-053	-19.0 ± 4.0	-3.3 ± 3.5
	REU 1001-053 duplicate	-12.4 ± 5.0	-1.6 ± 4.0
	REU 1001-053 average	-15.7 ± 3.2	-2.4 ± 2.7
	REU 1406-24.9a	-20.2 ± 5.1	-5.8 ± 4.7
	REU 863-204	-8.7 ± 3.8	0.7 ± 3.3
	REU 863-204 duplicate	-9.2 ± 4.0	-0.8 ± 3.4
	REU 863-204 average	-8.9 ± 2.8	-0.1 ± 2.4
	REU 0609-131	-7.6 ± 5.3	0.4 ± 4.7
	REU 0609-131 duplicate	-8.8 ± 3.9	4.0 ± 3.2
	REU 0609-131 average	-8.2 ± 3.3	2.2 ± 2.9
Kerguelen Plateau	TC0603	-16.5 ± 8.5	-3.1 ± 5.8
	TC0603 duplicate	-7.3 ± 4.0	2.1 ± 3.4
	TC0603 average	-11.9 ± 4.7	-0.5 ± 3.3
	CT02-358	-9.4 ± 7.4	-2.8 ± 7.2
	CT02-358 duplicate	-7.4 ± 3.0	1.9 ± 2.6
	CT02-358 average	-8.4 ± 4.0	-0.4 ± 3.8
	CT02-548	-15.2 ± 4.6	1.1 ± 3.7
Hawaii	BHVO-2	-7.2 ± 4.5	-0.9 ± 3.9
	BHVO-2 duplicate	-5.9 ± 4.5	4.3 ± 3.9
	BHVO-2 average	-6.6 ± 3.2	1.7 ± 2.8
Pilbara Craton	AH-25	15.3 ± 4.6	2.4 ± 3.7
	AH-26	13.1 ± 4.1	5.2 ± 3.5

$\mu^{X}W$ values ($\mu^{X}W = ([(^{X}W/^{184}W)_{sample}/(^{X}W/^{184}W)_{standard}]-1) \times 10^{6}$) are relative deviations of the W isotope composition of the samples from the Alfa Aesar W terrestrial standard in ppm. The standard was measured repeatedly between samples and yields a reproducibility on the $^{182}W/^{184}W$ ratio of 4.7 ppm (2 s.d., n = 11). Duplicates are measurements from different rock digestions. Errors on individual measurements are 2 standard error (2 s.e.) and averages show the propagated uncertainties on the average of multiple duplicates.

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Additional Information

Supplementary Information accompanies this letter at http://www.geochemicalperspectivesletters.org/article1917.

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