



HAL
open science

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

Hanika Rizo, Denis Andrault, N.R. Bennett, M. Humayun, A. Brandon, Ivan Vlastélic, Bertrand Moine, A. Poirier, Mohamed Ali Bouhifd, D.T. Murphy

► **To cite this version:**

Hanika Rizo, Denis Andrault, N.R. Bennett, M. Humayun, A. Brandon, et al.. 182W evidence for core-mantle interaction in the source of mantle plumes. *Geochemical Perspectives Letters*, 2019, 11, pp.6-11. <10.7185/geochemlet.1917>. <hal-02283763>

HAL Id: hal-02283763

<https://uca.hal.science/hal-02283763v1>

Submitted on 27 Apr 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons CC BY-NC-ND 4.0 - Attribution - Non-commercial use - No Derivative Works - International License

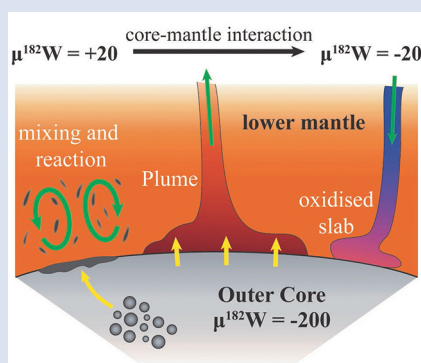
^{182}W evidence for core-mantle interaction in the source of mantle plumes

H. Rizo^{1*}, D. Andrault², N.R. Bennett³, M. Humayun⁴, A. Brandon⁵,
I. Vlastelic², B. Moine⁶, A. Poirier⁷, M.A. Bouhifd², D.T. Murphy⁸



doi: 10.7185/geochemlet.1917

Abstract



Tungsten isotopes are the ideal tracers of core-mantle chemical interaction. Given that W is moderately siderophile, it preferentially partitions 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 Paleoproterozoic 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.

Received 1 April 2019 | Accepted 17 May 2019 | Published 20 June 2019

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 $^{182}\text{W}/^{184}\text{W}$ 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 $^{182}\text{W}/^{184}\text{W}$ 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 $\mu^{182}\text{W}$ values in Table 1 and Figure 1, which are deviations in ppm from the W isotopic composition of the terrestrial standard

1. Department of Earth Sciences, Carleton University, Ottawa-Carleton Geoscience Centre, Ottawa, ON, K1S 5B6, Canada
 2. Laboratoire Magmas et Volcans, Université Clermont-Auvergne, CNRS, IRD, OPGC, Clermont-Ferrand, France
 3. Department of Earth and Planetary Sciences, University of California, Davis, CA 95616, USA
 4. Department of Earth, Ocean and Atmospheric Science, and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, USA
 5. Department of Earth and Atmospheric Sciences, University of Houston, Houston, TX 77204, USA
 6. Université Lyon, UJM Saint-Etienne, UCA, IRD, CNRS, Laboratoire Magmas et Volcans UMR 6524, Saint Etienne, France
 7. Département des Sciences de la Terre et de l'atmosphère, Geotop-Université du Québec à Montréal, Montreal, QC, H2X 3Y7, Canada
 8. Queensland University of Technology, Brisbane, Queensland, Australia
- * Corresponding author (e-mail: Hanika.Rizo@carleton.ca)



(assumed $\mu^{182}\text{W} = 0$). All plume-related samples analysed here yield negative $\mu^{182}\text{W}$ values ranging from -5.2 ± 3.7 to -20.2 ± 5.1 , including BHVO-2, which yields an average $\mu^{182}\text{W}$ 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 $\mu^{182}\text{W}$ values of $+15.3 \pm 4.6$ and $+13.1 \pm 4.1$, in the same range as most Hadean and Eoarchean mantle-derived rocks. Deviations measured in $\mu^{182}\text{W}$ are not associated with deviations in $\mu^{183}\text{W}$, confirming that ^{182}W variability is not the result of nuclear field shift effects (Figs. S-1 and S-2).

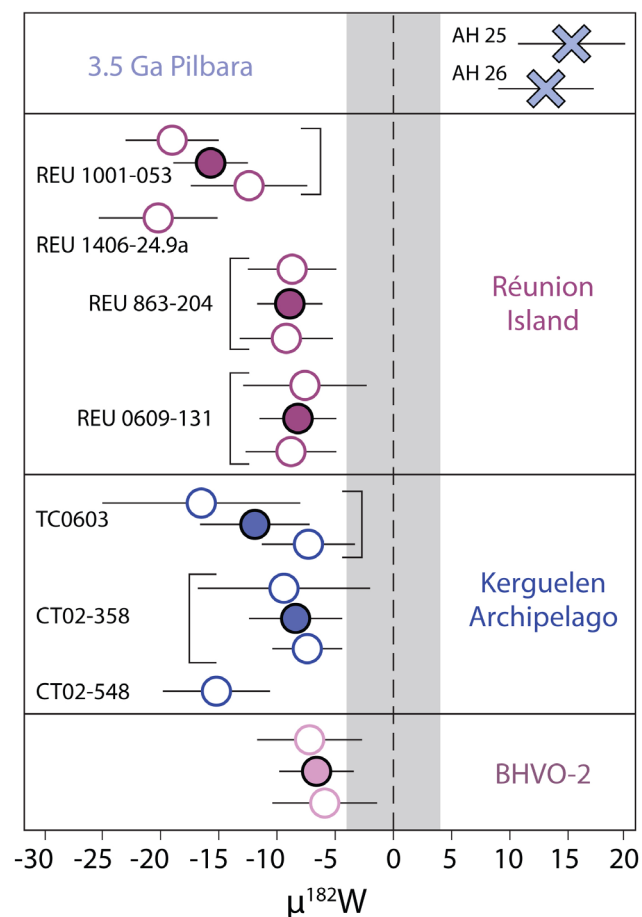


Figure 1 $^{182}\text{W}/^{184}\text{W}$ data obtained in this study shown as $\mu^{182}\text{W}$ values. Open symbols are individual analysis of samples and filled symbols show the average of the different duplicates. Errors on individual measurements shown are 2 standard error (2 s.e.) and propagated 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 $\mu^{182}\text{W} \sim -200$, and its gradual homogenisation into the mantle would have decreased its $\mu^{182}\text{W}$ 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 $^3\text{He}/^4\text{He}$ 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 $\mu^{182}\text{W}$ value of +20, was subject to core addition that created domains with $\mu^{182}\text{W}$ values as low as -20. The most negative $\mu^{182}\text{W}$ values measured in OIB constrain the maximum core contribution to their sources to ~ 0.8 wt. %, calculated by mass balance assuming a core $\mu^{182}\text{W}$ 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 $\mu^{182}\text{W}$ and HSE abundances in mantle-derived rocks. As discussed above, mantle-derived rocks with negative $\mu^{182}\text{W}$ values do not possess HSE enrichments,

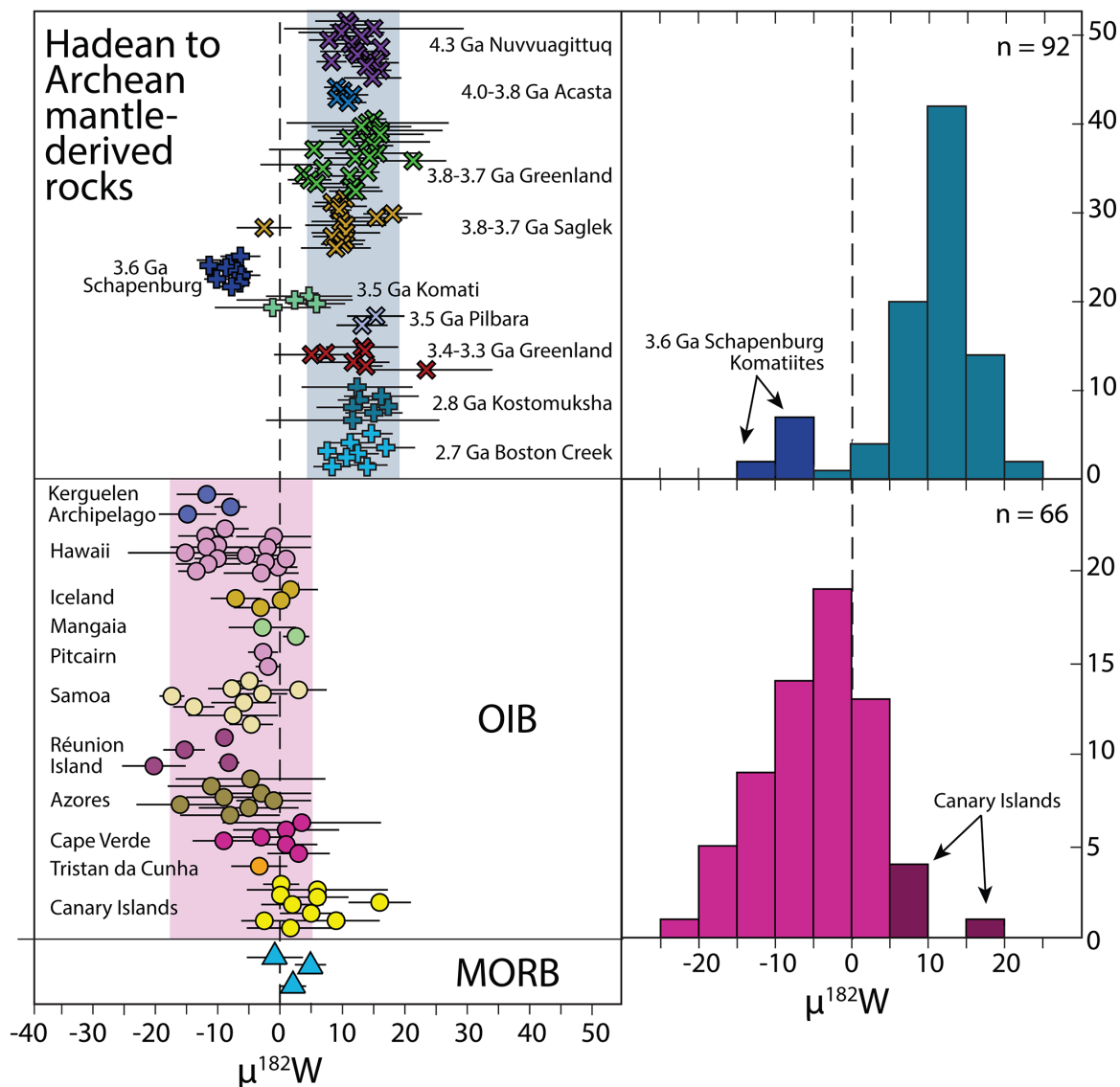


Figure 2 Compilation of all existing $^{182}\text{W}/^{184}\text{W}$ data shown as $\mu^{182}\text{W}$ values. Hadean and Archean mantle-derived rocks are organised in order of their age, with the oldest at the top and the youngest at the bottom. Shaded areas show the average $\mu^{182}\text{W}$ values \pm 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 $\mu^{182}\text{W}$ values, which have decreased in the modern mantle (Fig. 2). This broad distinction in $\mu^{182}\text{W}$ 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 $f\text{O}_2$ (van der Hilst and Kárason, 1999). Since W adopts a high valence (4+ to 6+) in silicates, increasing the $f\text{O}_2$ 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 $\mu^{182}\text{W}$ values in the post-Archean 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 $\mu^{182}\text{W}$ signature of deep mantle plumes are related to the onset of inner core segregation, $\mu^{182}\text{W}$ could be used as an alternative tool to study this process.



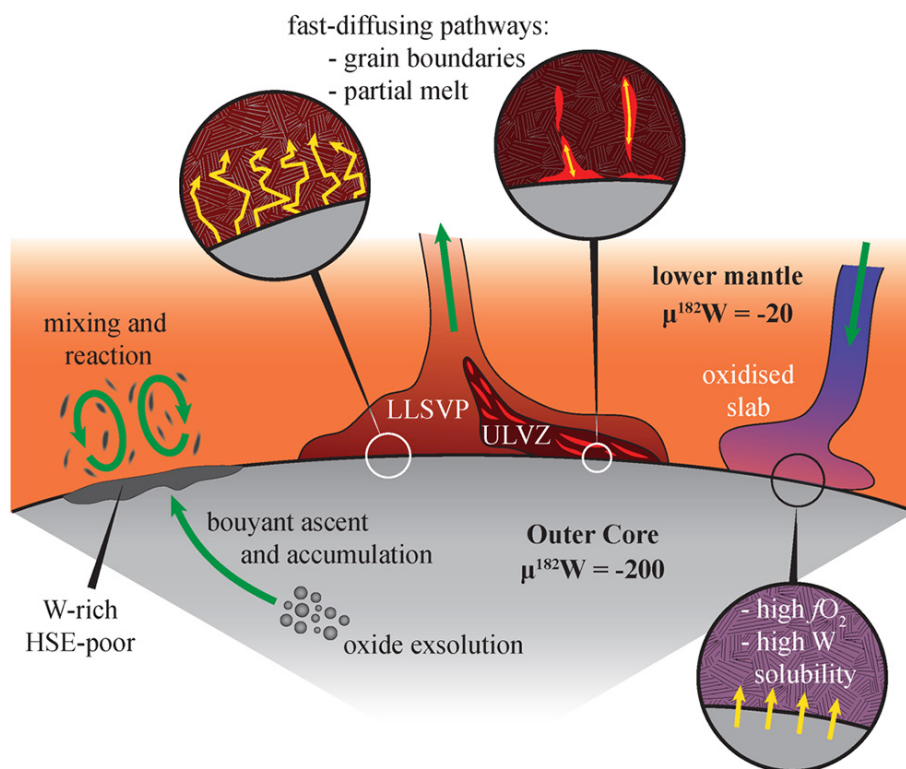


Figure 3 Schematic cartoon showing possible processes for core-mantle chemical interaction.

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	$\mu^{182}\text{W}$	$\mu^{183}\text{W}$
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

$\mu^X\text{W}$ values ($\mu^X\text{W} = ((^{X}\text{W}/^{184}\text{W})_{\text{sample}} / (^{X}\text{W}/^{184}\text{W})_{\text{standard}} - 1) \times 10^6$) 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 $^{182}\text{W}/^{184}\text{W}$ 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.

Acknowledgements

This manuscript was improved after insightful comments from G. Pearson and four anonymous reviewers and the editor, A. Luguet. We appreciate helpful discussions with R.W. Carlson, R. Walker and J. O'Neil, and discussions related to analytical protocols with G. Quitté, G. Archer and J. Blenkinsop. We thank L. Bouvier for her participation in the beginning of this project, and S. Zhang for assistance with TIMS, and N. DeSilva and S. Mohanty for assistance with ICP-MS facilities. We also thank the Geological Survey of Western Australia and R. Hepple for assistance with collection of the Pilbara Craton samples. This research was supported by a Natural Sciences and Engineering Research Council of Canada (NSERC) Discovery grant to H. Rizo (RGPIN-2015-03982), and by the Fonds de Recherche Nature et Technologies (FRQNT) start up programme for new university researchers.

Editor: Ambre Luguet

Additional Information

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



This work is distributed under the Creative Commons Attribution Non-Commercial No-Derivatives 4.0 License, which permits unre-

stricted distribution provided the original author and source are credited. The material may not be adapted (remixed, transformed or built upon) or used for commercial purposes without written permission from the author. Additional information is available at <http://www.geochemicalperspectivesletters.org/copyright-and-permissions>.

Cite this letter as: Rizo, H., Andrault, D., Bennett, N.R., Humayun, M., Brandon, A., Vlastelic, I., Moine, B., Poirier, A., Bouhifd, M.A., Murphy, D.T. (2019) ^{182}W evidence for core-mantle interaction in the source of mantle plumes. *Geochem. Persp. Let.* 11, 6–11.

References

- ALFÈ, D., PRICE, G.D., GILLAN, M.J. (2002) Iron under Earth's core conditions: Liquid-state thermodynamics and high-pressure melting curve from ab initio calculations. *Physical Review B* 65, 16511.
- ANDRAULT, D., PESCE, G., BOUHIFD, M.A., BOLFAN-CASANOVA, N., HÉNOT, J.M., MEZOUAR, M. (2014) Melting of subducted basalt at the core-mantle boundary. *Science* 344, 892-895.
- BADRO, J., SIEBERT, J., NIMMO, F. (2016) An early geodynamo driven by exsolution of mantle components from Earth's core. *Nature* 536, 326.
- BRANDON, A.D., WALKER, R.J., MORGAN, J.W., NORMAN, M.D., PRICHARD, H.M. (1998) Coupled ^{186}Os and ^{187}Os evidence for core-mantle interaction. *Science* 280, 1570-1573.
- BOUHIFD, M.A., JEPHCOAT, A.P., HEBER, V.S., KELLEY, S.P. (2013) Helium in an early Earth's core. *Nature Geoscience* 6, 982-986.
- CHOU, C.L. (1978) Fractionation of siderophile elements in the Earth's upper mantle. *Proceedings of the 9th Lunar and Planetary Science Conference* 1, 219-230.
- COURTILLOT, V., DAVAILLE, A., BESSE, J., STOCK, J. (2003) Three distinct types of hotspots in the Earth's mantle. *Earth and Planetary Science Letters* 205, 295-308.
- DALE, C.W., KRUIJER, T.S., BURTON, K.W. (2017) Highly siderophile element and ^{182}W evidence for a partial late veneer in the source of 3.8 Ga rocks from Isua, Greenland. *Earth and Planetary Science Letters* 458, 394-404.
- HAYDEN, L.A., WATSON, E.B. (2007) A diffusion mechanism for core-mantle interaction. *Nature* 450, 709.

- HIROSE, K., MORARD, G., SINMYO, R., UMEMOTO, K., HERNLUND, J., HELFFRICH, G., LABROSSE, S. (2017) Crystallization of silicon dioxide and compositional evolution of the Earth's core. *Nature* 543, 99.
- HUMAYUN, M., QIN, L., NORMAN, M.D. (2004) Geochemical evidence for excess iron in the mantle beneath Hawaii. *Science* 306, 91-94.
- KLEINE, T., TOUBOUL, M., BOURDON, B., NIMMO, F., MEZGER, K., PALME, H., JACOBSEN, S.B., YIN, Q.-Z., HALLIDAY, A.N. (2009) Hf-W chronology of the accretion and early evolution of asteroids and terrestrial planets. *Geochimica et Cosmochimica Acta* 73, 5150-5188.
- KING, S.D., RITSEMA, J. (2000) African hot spot volcanism: small-scale convection in the upper mantle beneath cratons. *Science* 290, 1137-1140.
- KRUIJER, T.S., KLEINE, T. (2018) No ^{182}W excess in the Ontong Java Plateau source. *Chemical Geology* 485, 24-31.
- LASSITER, J.C. (2006) Constraints on the coupled thermal evolution of the Earth's core and mantle, the age of the inner core, and the origin of the $^{186}\text{Os}/^{188}\text{Os}$ "core signal" in plume-derived lavas. *Earth and Planetary Science Letters* 250, 306-317.
- LIU, J., TOUBOUL, M., ISHIKAWA, A., WALKER, R.J., PEARSON, D.G. (2016) Widespread tungsten isotope anomalies and W mobility in crustal and mantle rocks of the Eoarchean Saglek Block, northern Labrador, Canada: Implications for early Earth processes and W recycling. *Earth and Planetary Science Letters* 448, 13-23.
- LUGUET, A., PEARSON, D.G., NOWELL, G.M., DREHER, S.T., COGGON, J.A., SPETSIUS, Z.V., PARMAN, S. W. (2008) Enriched Pt-Re-Os isotope systematics in plume lavas explained by metasomatic sulfides. *Science* 319, 453-456.
- MARKS, N.E., BORG, L.E., HUTCHISON, I.D., JACOBSEN, B., CLAYTON, R.N. (2014) Samarium-neodymium chronology and rubidium-strontium systematics of an Allende calcium-aluminum-rich inclusion with implications for ^{146}Sm half-life. *Earth and Planetary Science Letters* 405, 15-24.
- MCDONOUGH, W.F. (2003) Compositional model for the Earth's core. *Treatise on geochemistry* 2, 568.
- MEI, Q.F., YANG, J.H., YANG, Y.H. (2018) An improved extraction chromatographic purification of tungsten from a silicate matrix for high precision isotopic measurements using MC-ICPMS. *Journal of Analytical Atomic Spectrometry* 33, 569-577.
- MUNDL, A., TOUBOUL, M., JACKSON, M.G., DAY, J.M., KURZ, M.D., LEKIC, V., HELZ, R.T., WALKER, R.J. (2017) Tungsten-182 heterogeneity in modern ocean island basalts. *Science* 356, 66-69.
- O'ROURKE, J.G., STEVENSON, D.J. (2016) Powering Earth's dynamo with magnesium precipitation from the core. *Nature* 529, 387.
- PORCELLI, D., HALLIDAY, A.N. (2001) The core as a possible source of mantle helium. *Earth and Planetary Science Letters* 192, 45-56.
- PUCHEL, I.S., BLICHERT TOFT, J., TOUBOUL, M., HORAN, M.F., WALKER, R.J. (2016) The coupled ^{182}W - ^{142}Nd record of early terrestrial mantle differentiation. *Geochemistry, Geophysics, Geosystems* 17, 2168-2193.
- PUCHEL, I.S., BLICHERT-TOFT, J., TOUBOUL, M., WALKER, R.J. (2018) ^{182}W and HSE constraints from 2.7 Ga komatiites on the heterogeneous nature of the Archean mantle. *Geochimica et Cosmochimica Acta* 228, 1-26.
- REIMINK, J.R., CHACKO, T., CARLSON, R.W., SHIREY, S.B., LIU, J., STERN, R.A., BAUER, A.M., PEARSON, D.G., HEAMAN, L.M. (2018) Petrogenesis and tectonics of the Acasta Gneiss Complex derived from integrated petrology and ^{142}Nd and ^{182}W extinct nuclide-geochemistry. *Earth and Planetary Science Letters* 494, 12-22.
- RIGHTER, K., GHIORSO, M.S. (2012) Redox systematics of a magma ocean with variable pressure-temperature gradients and composition. *Proceedings of the National Academy of Sciences* 109, 11955-11960.
- RIZO, H., WALKER, R.J., CARLSON, R.W., HORAN, M.F., MUKHOPADHYAY, S., MANTHOS, V., FRANCIS, D., JACKSON, M.G. (2016a) Preservation of Earth-forming events in the tungsten isotopic composition of modern flood basalts. *Science* 352, 809-812.
- RIZO, H., WALKER, R.J., CARLSON, R.W., TOUBOUL, M., HORAN, M.F., PUCHEL, I.S., BOYET, M., ROSING, M.T. (2016b) Early Earth differentiation investigated through ^{142}Nd , ^{182}W , and highly siderophile element abundances in samples from Isua, Greenland. *Geochimica et Cosmochimica Acta* 175, 319-336.
- SHEARER, C.K., RIGHTER, K. (2003) Behavior of tungsten and hafnium in silicates: a crystal chemical basis for understanding the early evolution of the terrestrial planets. *Geophysical Research Letters* 30, 7-1.
- SOBOLEV, A.V., HOFMANN, A.W., KUZMIN, D.V., YAXLEY, G.M., ARNDT, N.T., CHUNG, S.L., DANYUSHEVSKY, L.V., ELLIOTT, T., FREY, F.A., GARCIA, M.O., GURENKO, A.A., KAMENETSKY, V.S., KERR, A.C., KRIVOLUTSKAYA, N.A., MATVIENKOV, V.V., NIKOGOSIAN, I.K.,



- ROCHOLL, A., SIGURDSSON, I.A., SUSHCHEVSKAYA, N.M., TEKLAY, M. (2007) The amount of recycled crust in sources of mantle-derived melts. *Science* 316, 412-417.
- THIRLWALL, M.F., JENKINS, C., VROON, P.Z., MATTEY, D.P. (1997) Crustal interaction during construction of ocean islands: Pb-Sr-Nd-O isotope geochemistry of the shield basalts of Gran Canaria, Canary Islands. *Chemical Geology* 135, 233-262.
- TOUBOUL, M., PUCHTEL, I.S., WALKER, R.J. (2012) ^{182}W evidence for long-term preservation of early mantle differentiation products. *Science* 335, 1065-1069.
- TOUBOUL, M., LIU, J., O'NEIL, J., PUCHTEL, I.S., WALKER, R.J. (2014) 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. *Chemical Geology* 383, 63-75.
- VAN DER HILST, R.D., KÁRASON, H. (1999) Compositional heterogeneity in the bottom 1000 kilometers of Earth's mantle: toward a hybrid convection model. *Science* 283, 1885-1888.
- VOCKENHUBER, C., OBERLI, F., BICHLER, M., AHMAD, I., QUITTÉ, G., MEIER, M., HALLIDAY, A.N., LEE, D.-C., KUTSCHERA, W., STEIER, P., GEHRKE, R.J., HELMER, R.G. (2004) New Half-Life Measurement of Hf-182: Improved Chronometer for the Early Solar System. *Physical Review Letters* 93, 172501.
- WALKER, R.J. (2009) Highly siderophile elements in the Earth, Moon and Mars: update and implications for planetary accretion and differentiation. *Chemie der Erde-Geochemistry* 69, 101-125.
- WALKER, R.J., MORGAN, J.W., HORAN, M.F. (1995) Osmium-187 enrichment in some plumes: evidence for core-mantle interaction?. *Science* 269, 819-822.
- WADE, J., WOOD, B.J., TUFF, J. (2012) Metal-silicate partitioning of Mo and W at high pressures and temperatures: evidence for late accretion of sulphur to the Earth. *Geochimica et Cosmochimica Acta* 85, 58-74.
- WILLBOLD, M., ELLIOTT, T., MOORBATH, S. (2011) The tungsten isotopic composition of the Earth's mantle before the terminal bombardment. *Nature* 477, 195.
- WILLBOLD, M., MOJZSIS, S.J., CHEN, H.W., ELLIOTT, T. (2015) Tungsten isotope composition of the Acasta Gneiss Complex. *Earth and Planetary Science Letters* 419, 168-177.
- YUAN, K., ROMANOWICZ, B. (2017) Seismic evidence for partial melting at the root of major hot spot plumes. *Science* 357, 393-397.