Preservation of Earth-forming events in the W isotopic composition of modern flood basalts

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Abstract: How much of Earth's compositional variation dates to processes occurring during planet formation remains an unanswered question. High precision W isotopic data for rocks from two large igneous provinces, the North Atlantic Igneous Province and the Ontong Java Plateau, reveal preservation to the Phanerozoic of W isotopic heterogeneities in the mantle. These heterogeneities, caused by the decay of ^{182}Hf in high Hf/W ratio mantle domains, were created during the first ~50 Ma of Solar System history, and imply that portions of the mantle that formed during Earth's primary accretionary period have survived to the present.

Main text:

Four and a half billion years of geologic activity has overprinted much of the evidence for processes involved in Earth's formation and initial chemical differentiation. High-precision isotopic measurements, however, now allow the use of the variety of short-lived radionuclides that were present when Earth formed to provide a clearer view of events occurring during the first tens to hundreds of million years (Ma) of Earth history. Evidence from both the ^{146}Sm-^{142}Nd ($t_{1/2}$ = 103 Ma) and ^{129}I-^{129}Xe ($t_{1/2}$ = 15.7 Ma) systems show the importance of early mantle differentiation and outgassing events, but provide conflicting evidence on the preservation of early-formed mantle reservoirs to the present day (1-4). Of these short-lived systems, the ^{182}Hf-^{182}W ($t_{1/2}$= 8.9 Ma) system is uniquely sensitive to metal-silicate separation, and has been used effectively to trace the timing and processes of core formation (e.g. 5), arguably the most important chemical differentiation event to occur on a rocky planet. Only recently, however, have measurement techniques improved to the point of resolving $^{182}W/^{184}W$ variability in ancient (>2.7 Ga) terrestrial rocks, that reflects preservation of compositionally distinct domains in Earth's interior that were likely created during Earth formation (6-10). Young mantle-derived rocks examined to date have shown neither ^{142}Nd nor ^{182}W isotopic heterogeneity, suggesting that the early-formed compositional domains in Earth's interior were largely destroyed by mantle mixing processes acting during the first half of Earth history (1-4, 6-10). Here we report $^{182}W/^{184}W$ ratios in Phanerozoic flood basalts from Baffin Bay and the Ontong Java Plateau, some of which range to the highest ever measured in terrestrial rocks. These results document the preservation of regions within Earth's interior whose compositions were established by events occurring within the first ~ 50 Ma of Solar System history. This study, consequently, provides new insights into the processes at work during planet formation, the chemical structure of Earth's interior, and the interior dynamics that allowed preservation of chemical heterogeneities for 4.5 billion years.

Flood basalts are the largest volcanic eruptions identified in the geological record. These types of eruptions created both the North Atlantic Igneous Province, which hosts the Baffin Bay locale (11), and the Ontong Java Plateau, western Pacific Ocean (12). We have studied pillow lavas with high MgO, picritic compositions (Tab. S1) from Padloping Island, Baffin Bay (Pi-23 and Pd-2). We targeted these rocks because some Baffin Bay lavas contain the highest $^{3}He/^{4}He$ ratios ever measured (e.g. 13), along with Pb isotopic compositions (14) and D/H ratios (15) that indicate that their mantle source was relatively primitive and undegassed, consistent with isolation since shortly after Earth formation. Ontong Java is Earth's largest known volcanic province, and shares chemical and isotopic similarities with the Baffin Bay lavas, consistent with a primitive mantle source (16). The Ontong Java sample (192-1187A-009R-04R) is a basalt (Table S1) collected from the plateau's eastern flank by Ocean Drilling Project Leg 192.

We present data from the short-lived ^{182}Hf-^{182}W and ^{146}Sm-^{142}Nd systems because these two systems are variably sensitive to the core formation and mantle differentiation processes that occurred early in Earth history. We compare these data with data from the long-lived U-Th-He, ^{147}Sm-^{143}Nd and ^{187}Re-^{187}Os isotope systems, together with W and highly siderophile element (HSE: Re, Os, Ir, Ru, Pt, Pd) concentrations, to better discern early differentiation events from those occurring over all of Earth history. Glassy rim and core pieces of sample Pi-23 (Pi-23a and Pi-23b, respectively), a bulk sample of Pd-2, and a bulk sample of 192-1187A-009R-04R are characterized by high $^{182}W/^{184}W$ ratios that are well resolved from standards, with $\mu^{182}W$ values ranging from +10 to +48 (where $\mu^{182}W = [(^{182}W/^{184}W)_{sample}/(^{182}W/^{184}W)_{standard} - 1] \times 10^6$) (Fig. 1 and Table 1, ref. 17). The $\mu^{182}W$ values for sample Pi-23a and Pi-23b are in good agreement. This rules out the role of stable W isotope fractionation through interaction of seawater with the pillow rim in creating the measured ^{182}W values (17). Samples 192-1187A-009R-04R and Pd-2 are characterized by the lowest W concentrations and the highest $\mu^{182}W$ values (Table 1). The W concentrations of these two samples (23 and 26 ppb, respectively) are broadly consistent with magmas derived by 15-20% partial melting of a mantle source with ~5 ppb W, consistent with a primitive source free of W-rich recycled crust (17, Fig. S2). The geological reference materials VE-32 (mid-ocean ridge glass) and BHVO-1 (Hawaiian basalt) were measured at the same time as the Baffin Bay and Ontong Java samples, and yielded $\mu^{182}W$ values of -0.8 ± 4.5 and -2.3 ± 7.7, respectively (Table 1). These $\mu^{182}W$ values are indistinguishable from the terrestrial *Alfa Aesar* W standard ($\mu^{182}W = 0$) and other modern rocks (6-10). The $^3He/^4He$ ratio measured in olivines of the Baffin Bay samples (Table S3, 17) yielded values up to 48.4 R_A (R_A being the $^3He/^4He$ ratio normalized to the atmospheric ratio of 1.39×10^{-6}) which are in agreement of previous findings (13) and indicate that the source of these lavas is relatively undegassed, and possibly isolated since Earth formation. The Baffin Bay and Ontong Java Plateau samples have HSE abundances and initial $^{187}Os/^{188}Os$ ratios (providing a record of long-term Re/Os ratio) that are indistiguishable from other modern mantle-derived lavas with similar MgO abundances that do not show elevated $\mu^{182}W$ (Figure 2, Table S4, 18).

Variability in $^{182}W/^{184}W$ ratios reflects Hf/W fractionation while ^{182}Hf was extant. Fractionations in Hf/W are observed in early Solar System materials (e.g. 5), so variable tungsten isotopic compostions in terrestrial samples can reflect the imperfect mixing of late additions of such materials (6, 9). The $\mu^{182}W$ value of +48 for Baffin Bay sample Pd-2, however, is larger than can be accounted for by this process, and so this possibility is discounted (see Supplementary Text). Fractionation of Hf/W can also have occurred as the result of endogenous Earth differentiation processes such as magma ocean crystallization (7) and core formation (9). Silicate fractionation processes, however, cannot be responsible for the generation of the anomalous ^{182}W in the sources of Baffin Bay and Ontong Java lavas. If the high $\mu^{182}W$ was due to silicate fractionation in a magma ocean while ^{182}Hf was extant, then $\mu^{182}W$ should positively correlate with $\mu^{142}Nd$, the decay product of the short-lived ^{146}Sm ($t_{½}$ = 103 Ma) isotope system. Instead, the $\mu^{142}Nd$ values of the samples are indistinguishable from all other modern basalts so far measured (Fig. S3, Table S5, 17).

This leaves fractionation of Hf/W as a result of metal-silicate segregation accompanying core formation as the probable cause of the observed anomalies in the Phanerozoic samples. Metal-silicate segregation is the most effective process capable of fractionating Hf/W ratios, because Hf is a strongly lithophile trace element, while W is moderately siderophile. The low W concentrations estimated for the mantle source of the flood basalts studied here are consistent with mantle domains that experienced metal-silicate segregation (Table 1, Supplementary Text). Repeated metal-silicate segregation events during planet formation (19) could create one or more mantle domains with distinct $\mu^{182}W$ without affecting the Sm-Nd system. Such events would result in variable $\mu^{182}W$ due to different times of the metal-silicate segregation events (Figure 3), or different Hf/W ratios in the resulting mantle reservoirs that reflect differing oxidation states, and hence, differing W partitioning into metal (Supplementary Text). The key observation, which is also seen in the results reported here, is that terrestrial samples with ^{182}W excesses do not seem to derive from sources depleted in HSE (Figure 2, 6-10). Highly siderophile elements have partition coefficients between metal and silicate of $>10^4$ (20), thus, their concentrations in metal-depleted mantle domains are expected to be very low. Evolving oxidation states during Earth accretion might explain the decoupling of ^{182}W and HSE, because while W becomes less siderophile under oxidizing conditions, the HSE, even at high oxidation states, are not soluble in silicates (20). This type of model, however, requires subsequent late accreted HSE to be mixed into different mantle domains without the mixing away of tungsten isotopic heterogeneity. Alternatively, the observed decoupling could be explained if some metal from the core of the Moon-forming giant impactor was retained in the mantle, followed by a minor amount of late accretion (9). This type of model requires that a substantial mass of high density metal be retained in the Earth' mantle following the impact, when the mantle was partially or wholly molten, and that the retained metal contained chondritic relative abundances of the HSE. These models and others have been presented to try to explain the apparent decoupling of W isotopic compositions and HSE abundance variations. These models are summarized in the Supplementary Text along with a few additional suggestions.

Regardless of the origin of the ^{182}W variability, arguably more surprising than the fact that Earth experienced such early differentiation events, is that reservoirs formed by these early processes remain in the mantle today. This conclusion is now supported by data from both W and Xe (1, 22) isotopic variability, but not ^{142}Nd, where the evidence suggests that the observed heterogeneity in ^{142}Nd/^{144}Nd ratio was reduced to an unobservable level by the end of the Archean, likely though the mixing caused by mantle convection. Perhaps a key to reconcile these observations is that the ^{129}I-^{129}Xe system primarily reflects mantle outgassing, and the ^{182}Hf-^{182}W system metal-silicate separation, whereas the ^{146}Sm-^{142}Nd system is controlled by internal mantle differentiation. For both W and Xe, one component of the complementary chemical differentiation, the core for W, and the atmosphere for Xe, may not be available for effective recycling and mixing in the mantle (23). By contrast, for Nd, the main reservoirs created during early Earth differentiation may have been in a portion of the mantle that has been effectively mixed by mantle circulation. Estimates for how much of the mantle can remain unmixed depend on the rheological properties assigned to the various materials involved. Some models (e.g. 24) show that as much as 20% of the mantle may remain isolated as distributed masses in the mantle. An important aspect of the results presented here is that both ^{182}W anomalies and elevated ^{3}He/^{4}He (Table S3) appear in at least two major flood basalts. These events produce huge volumes of magma that must be derived by melting large volumes of mantle during unusual thermal events in the history of mantle circulation. The large size and sporadic nature of flood basalts is perhaps more indicative of a layer in the mantle that has an appropriate density or rheological properties to keep it from effectively mixing with the rest of the mantle. One candidate for such a reservoir is the large low seismic shear velocity provinces (LLSVP) imaged at the base of the mantle (25). These regions appear to be warmer and compositionally different from surrounding mantle. Estimates of their volume range to as high as 7% of the mantle, or of order 6 x 10^{10} km^3. If the LLSVP are remnants of early differentiation events on Earth, they must have a delicately balanced density contrast compared to the surrounding mantle to allow their survival through 4.5 billion years of dynamic Earth history.

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Figure 1. μ^{182}W values measured for Baffin Bay and Ontong Java Plateau samples, the geological reference materials VE-32 and BHVO-1 and the *Alfa Aesar* W standard. The values are expressed as parts in 10^6 or ppm deviations from the average measured from the W standard. The grey shaded area represents the 2 standard deviation (2σ) for the W standard measurements. Errors for each data point are 2σ.

Figure 2. Highly siderophile element abundances (HSE) for the Baffin Bay and Ontong Java Plateau samples. Abundances are normalized to the HSE of carbonaceous chondrites (CI) of ref. 26. Grey shaded area shows the range of HSE abundances for type-2 Hawaiian picrites (ref. 27).

Figure 3. **Model for the creation of distinct W isotopic mantle reservoirs.** (**A**) Early core formation leaves the proto-Earth's mantle with a high Hf/W ratio that, with time, evolves to a high μ^{182}W value (i). (**B**) The impact of a large body affects the Hf/W ratio and W isotopic composition of a portion of the proto-Earth's mantle. (**C**) Evolution of the portion of the mantle (ii) affected by the impact of a large body, involving some degree of isotopic equilibration between impactor materials and mantle. The core of the impactor subsequently merges with the core of the proto-Earth. (**D**) Possible scenario after isostatic adjustment (e.g. 28), and creation of

a mantle with heterogeneous $\mu^{182}W$ through impacts of large bodies. Mantle domains affected by impacts that occur after the extinction of ^{182}Hf, will no longer generate radiogenic ^{182}W, so their $^{182}W/^{184}W$ ratios will change only by mixing with other terrestrial reservoirs or with late-accreted chondritic material. (**E**) Late accretion representing ~ 0.5% of Earth's mass decreases the $^{182}W/^{184}W$ ratio of all the earlier formed reservoirs by ~ 15 ppm. This last accretion is responsible for endowing the modern mantle with chondritic relative abundances of the HSE.

Locality	Geodynamic context	Sample	$\mu^{182}W$ (ppm)	± 2σ (ppm)	W (ppb)
Baffin Bay	Flood basalt	Pi-23 a	11.9	5.9	62
Baffin Bay	Flood basalt	Pi-23 b	8.3	5.6	62
Baffin Bay	Flood basalt	Pd-2	48.4	4.6	26
Ontong Java Plateau	Flood basalt	192-1187A 009R 04R	23.9	5.3	23
East Pacific Rise	Mid-ocean ridge basalt	VE-32	-0.8	4.5	54
Hawaii	Ocean island basalt	BHVO-1	-2.3	7.7	274

Table 1. Tungsten concentrations and isotopic compositions measured for Baffin Bay samples Pi-23a, Pi-23b, Pd-2, the Ontong Java Plateau sample 192-1187A 009R 04R, the MORB glass sample VE-32, the BHVO-1 basalt standard. Uncertainties are 2σ. More details are given in ref. 17 and Table S2.

<u>Supplementary Materials:</u>

Materials and Methods

Figures S1-S7

Tables S1-S5

References (29-56)

Figures

Figure 1

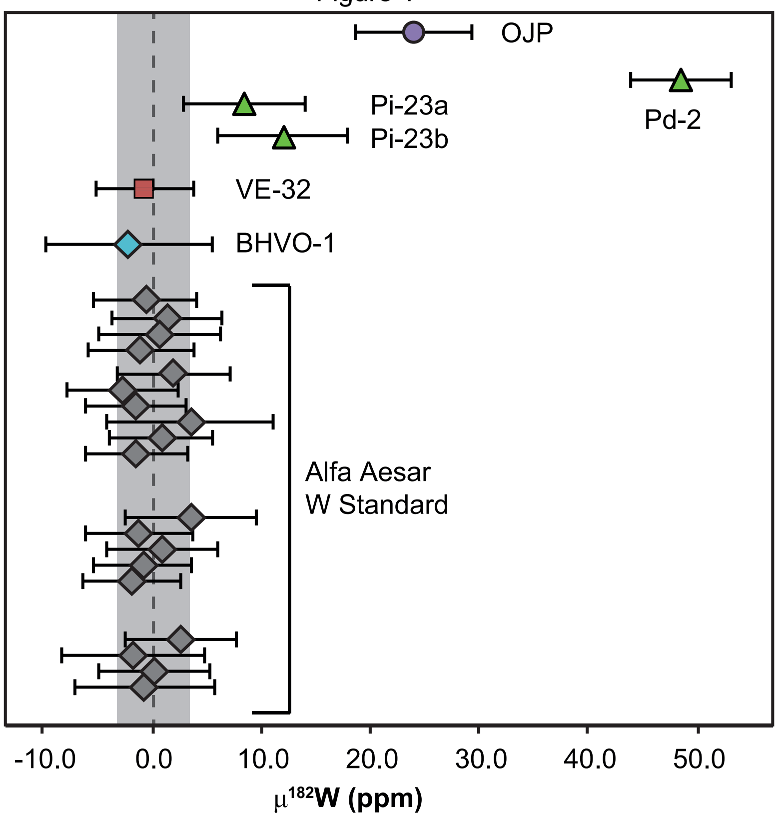

Figure 2

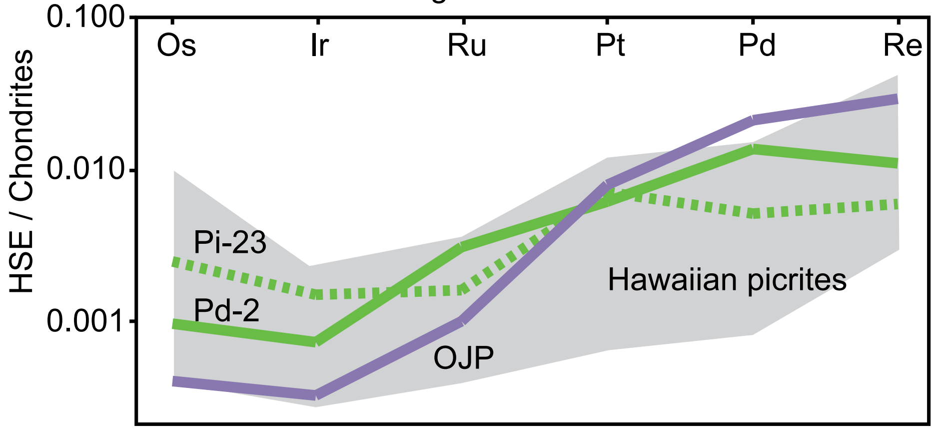

Figure 3