Coupled ^{182}W-^{142}Nd constraint for early Earth differentiation

Frederic Moynier[a,b,1], Qing-Zhu Yin[a], Keita Irisawa[a,c], Maud Boyet[d], Benjamin Jacobsen[a], and Minik T. Rosing[e]

[a]Department of Geology, University of California, One Shields Avenue, Davis, CA 95616; [b]Department of Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University in St. Louis, One Brookings Drive, St. Louis, MO 63130; [c]Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo, 152-8551, Japan; [d]Laboratoire Magmas et Volcans, Unité Mixte de Recherche Centre National de la Recherche Scientifique 6524, Université Blaise Pascal, 5 rue Kessler, 63038 Clermont-Ferrand Cedex, France; and [e]Nordic Center for Earth Evolution, University of Copenhagen, Øster Voldgade 5-7, 1350 Copenhagen, Denmark

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Recent high precision ^{142}Nd isotope measurements showed that global silicate differentiation may have occurred as early as 30–75 Myr after the Solar System formation [Bennett V, et al. (2007) *Science* 318:1907–1910]. This time scale is almost contemporaneous with Earth's core formation at ∼30 Myr [Yin Q, et al. (2002) *Nature* 418:949–952]. The ^{182}Hf-^{182}W system provides a powerful complement to the ^{142}Nd results for early silicate differentiation, because both core formation and silicate differentiation fractionate Hf from W. Here we show that eleven terrestrial samples from diverse tectonic settings, including five early Archean samples from Isua, Greenland, of which three have been previously shown with ^{142}Nd anomalies, all have a homogeneous W isotopic composition, which is ∼2ε-unit more radiogenic than the chondritic value. By using a 3-stage model calculation that describes the isotopic evolution in chondritic reservoir and core segregation, as well as silicate differentiation, we show that the W isotopic composition of terrestrial samples provides the most stringent time constraint for early core formation (27.5–38 Myr) followed by early terrestrial silicate differentiation (38–75 Myr) that is consistent with the terrestrial ^{142}Nd anomalies.

hafnium | tungsten | hidden reservoir | Hawaii | Iceland

Short-lived chronometers provide evidence for the rapid differentiation of planet Earth. In particular, ^{182}Hf-^{182}W ($T_{1/2}$ = 8.9 Myr) and ^{146}Sm-^{142}Nd ($T_{1/2}$ = 103 Myr) have been used to constrain the age of core formation (1, 2) and of silicate differentiation (3–7), respectively. All terrestrial rocks analyzed so far are characterized by $^{182}W/^{184}W$ ratios that are ∼2ε-unit (see Table 1 caption for definition) higher than those of chondrites, which is commonly interpreted as evidence for early metal-silicate segregation and core formation (1, 2). Terrestrial rocks are also characterized by ∼0.2ε excess of $^{142}Nd/^{144}Nd$ relative to chondrites (3). This excess has been interpreted as evidence for early global differentiation of the silicate Earth during the first 30–75 Myr of the Solar System, where the resulting enriched silicate reservoir is permanently stored at the base of the lowermost mantle (3), Hadean crust (8), or in the roots of cratons (9) (see *SI Text* for comments on alternative theories).

Whereas tungsten is a moderately siderophile element, it is also highly incompatible during silicate partial melting; in fact, W, U, and Th all have similar partition coefficients (10, 11). In contrast, Hf, which is a lithophile element, is only moderately incompatible during silicate partial melting (11). Consequently, W is strongly fractionated from Hf during silicate melting events (12), resulting in oceanic and continental crust that is enriched in W (∼400 and ∼1,000 ppb, respectively) relative to the mantle (∼16 ppb) (12, 13). Therefore, mantle differentiation/melting events that occurred early enough in Earth's history (35–70 Myr), as constrained by ^{142}Nd data, should fractionate Hf/W ratios and result in ε^{182}W anomalies with time. The ∼2ε^{182}W anomalies observed between terrestrial rocks and chondrites (refs. 1 and 2 and this work) should, therefore, be attributed to the collective effects of both silicate melting (crust/mantle differentiation), as well as silicate/metal fractionation (core/mantle differentiation), and not solely because of the silicate/metal fractionation as previously thought (1, 2). Consequently, it is important to reevaluate the evolution of ^{182}W anomalies in the context of early silicate differentiation as constrained by ^{142}Nd anomalies, when ^{182}Hf was still extant.

In this study, we present ^{182}W data for the following samples: (*i*) Five Isua Supracrustal Belt samples, of which three have ^{142}Nd anomalies (14, 15). The location of the Isua's samples is shown in ref. 15. The age of the Isua Supracrustal Belt ranges from 3.71 to 3.81 Gyr (14–19); (*ii*) two basalts from Loihi Seamount, Hawaii, which is located 30 km south of Kilauea volcano; (*iii*) one Icelandic picrite from the neovolcanic zone of Theistareykir (Storaviti N65°88′, W16°85′) located in the northeastern part of Iceland; (*iv*) three kimberlites from Safartoq, S.W. Greenland (see ref. 20 for details of sample location) and one Allende carbonaceous chondrite (Table 1). All the terrestrial samples analyzed in this study have already been described and their Nd isotopic compositions have been measured (3, 14, 15, 21). We then evaluate the results by comparing a simple 3-stage model of the evolution of ^{182}W anomalies as a function of the Hf/W fractionation produced by both silicate/metal segregation and silicate solid/liquid fractionation with a 2-stage model for ^{142}Nd evolution, where Sm/Nd fractionation is only affected by silicate fractionation because of the lithophile nature of Sm and Nd. In this study, we use ε notation relative to terrestrial standards to describe isotopic variation of samples and to compare with literature values, and we use $\Delta\varepsilon$ notation relative to chondritic compositions for modeling purposes (see Table 1 and figure captions for the definitions of ε- and $\Delta\varepsilon$-units).

Results and Discussion

As shown in Table 1 and Fig. 1, all of the terrestrial samples analyzed in this study have uniform ^{182}W excesses, relative to chondrites. The unweighted mean of $\Delta\varepsilon^{182}$W values for all the samples analyzed in the present study is 1.99 ± 0.31 (2σ) relative to the chondrite average (1, 2). Our results are entirely consistent with recent data reported on a suite of terrestrial rocks, including Isua samples (22).

Three scenarios could potentially account for the homogeneous ∼2ε ^{182}W excesses relative to chondrites measured in the Isua samples:

i. The differentiation of the source reservoir of Isua rocks occurred after ^{182}Hf was extinct. In that case our results give a lower limit to the differentiation of the source reservoir

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[1]To whom correspondence should be addressed. E-mail: moynier@levee.wustl.edu.

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Table 1. W and Nd isotopic compositions of selected terrestrial rocks and meteorite

Sample ID	Sample description	Location	$\varepsilon^{182}W$	$\Delta\varepsilon^{182}W$	2σ	$\varepsilon^{186}W$	2σ	$\varepsilon^{142}Nd$	$\Delta\varepsilon^{142}Nd$	2σ
93(07)81	Picrite	Iceland	−0.39	1.58	0.52	0.23	0.62	−0.07 (ref. 21)	0.11	0.14
LO 158-4	Basanoid	Loihi, Hawaii	0.11	2.08	0.28	−0.59	0.42	0.01 (ref. 21)	0.19	0.12
LO 1802-4b	Alkaline basalt	Loihi, Hawaii	0.06	2.03	0.29	−0.33	0.38	−0.08 (ref. 21)	0.10	0.10
Kim 2	Kimberlite	Safartoq, Greenland	0.06	2.03	0.50	−0.41	0.62			
Kim 5	Kimberlite	Safartoq, Greenland	−0.15	1.82	0.29	−0.67	0.50	0.00 (ref. 15)	0.18	0.03
Kim15	Kimberlite	Safartoq, Greenland	−0.08	1.89	0.27	−0.33	0.33	0.03 (ref. 15)	0.21	0.02
00-001	Metapillow	Isua, Greenland	0.00	1.97	0.23	0.20	0.44			
00 013b	Metagabbro	Isua, Greenland	0.09	2.06	0.24	−0.04	0.37	0.13 (ref. 14)	0.31	0.05
Replicate*	Metagabbro	Isua, Greenland	0.11	2.08	0.34	0.15	0.48	0.13 (ref. 15)	0.31	0.05
00-022	Metapillow	Isua, Greenland	−0.02	1.95	0.19	0.32	0.22	0.15 (ref. 15)	0.33	0.06
Replicate*	Metapillow	Isua, Greenland	−0.07	1.90	0.35	0.29	0.35	0.15 (ref. 15)	0.33	0.06
Replicate*	Metapillow	Isua, Greenland	0.19	2.16	0.26	−0.30	0.32	0.15 (ref. 15)	0.33	0.06
46-0242	Metapillow	Isua, Greenland	0.04	2.01	0.27	0.05	0.25	−0.01 (ref. 14)	0.17	0.13
46-0257	Metapillow	Isua, Greenland	0.15	2.12	0.37	−0.42	0.39	0.32 (ref. 14)	0.50	0.20
Replicate*	Metapillow	Isua, Greenland	0.22	2.19	0.41	0.18	0.40	0.32 (ref. 14)	0.50	0.20
Allende	CV chondrite	Asteroid belt	−1.73	0.22	0.29	0.39	0.20	−0.31 (ref. 3)	−0.13	0.03

*Two separate sample digestions, each followed by independent chemical separation.
For this study, the ε unit and $\Delta\varepsilon$ unit are defined as: $\varepsilon^{182}W = [(^{182}W/^{184}W)_{sample}/(^{182}W/^{184}W)_{reference}-1] \times 10{,}000$ and $\varepsilon^{186}W = [(^{186}W/^{184}W)_{sample}/(^{186}W/^{184}W)_{reference}-1] \times 10{,}000$, respectively.
The W reference used in this study is a terrestrial standard Alfa Aesar (stock no. 35770, lot no. 233665H).
$\Delta\varepsilon^{182}W = \varepsilon^{182}W_{sample}-\varepsilon^{182}W_{CHUR}$ with $\varepsilon^{182}W_{CHUR} = -1.97 \pm 0.13$ (refs. 1 and 2).
^{142}Nd are referenced to La Jolla terrestrial standard and $\Delta\varepsilon^{142}Nd = \varepsilon^{142}Nd_{sample}-\varepsilon^{142}Nd_{ordinary\ chondrites}$ with $\varepsilon^{142}Nd_{ordinary\ chondrites} = -0.18$ (ref. 42).

(>90 Myr). This scenario is unlikely, however, because Bennett et al. (7) measured coupled ^{142}Nd-^{143}Nd excesses in 3.85-Gyr-old rocks from West Greenland and calculated, with no free parameters (5), a tightly constrained range between 30 and 75 Myr of the silicate differentiation for source reservoir of these rocks.

ii. The differentiation of the source reservoir of Isua rocks occurred during the first 90 Myr, but the two reservoirs have since been partially remixed. The nature and timing of the homogenization was such that analytically resolvable ^{142}Nd anomalies ($>0.03\varepsilon$) were preserved but ^{182}W anomalies were not ($<0.3\varepsilon$). There is indeed evidence to support partial remixing. Most terrestrial samples have $\varepsilon^{142}Nd$ values that are around $\sim 0.00 \pm 0.03\varepsilon$ (4, 8, 9, 15); however, some Isua samples have $\varepsilon^{142}Nd$ excesses that are even larger [up to 0.20ε (4, 7, 14)], whereas some rocks from the Nuvvuagittuq greenstone belt in northern Quebec, Canada (8) and lithospheric mantle-derived alkaline rocks from the Khariar alkaline complex in southeastern India (9) show lower $\varepsilon^{142}Nd$ ratios by -0.07 to -0.15ε, and -0.08 to -0.13ε, respectively. This range of $\varepsilon^{142}Nd$ values implies the existence and mixing of the depleted and enriched reservoirs in the first ∼300 Myr of Earth's history (7–9, 14).

iii. Isua's samples analyzed here are amphibolites that have been subjected to multiple metamorphic episodes and have experienced trace element alteration (23). Such alteration may have affected the ^{182}Hf-^{182}W systematic, because W is somewhat hydrophilic (24). W occurs as scheelite ($Ca(W,Mo)O_4$) in skarn deposits in contact metamorphism or as wolframite ($(Fe,Mn)WO_4$) in vein systems related to granite intrusions. The tungstate ion is soluble in hydrous fluids even at low temperatures, so in the absence of high Ca activities (i.e., skarn environments) or high Fe^{+2} fluids, W is expected to move around relatively freely during amphibolite facies metamorphism. Neodymium, on the other hand, is not very fluid-mobile and is therefore less likely to be affected by these processes. Thus small ^{182}W anomalies may be rehomogenized, whereas ^{142}Nd will not.

We now discuss first the significance of $\sim 2\varepsilon$ ^{182}W anomalies of terrestrial rocks in comparison to chondrites as the consequence of both silicate differentiation and core formation, followed by combined modeling of $\varepsilon^{142}Nd$ evolution as a result of silicate differentiation. We model the $\varepsilon^{182}W$ effect by using a 3-stage model in which the first stage is the evolution of a homogenous chondritic uniform reservoir (CHUR) formed at time T_1 [4,568 Myr (25, 26)], the second stage is metal/silicate differentiation, which occurs at time T_2, and the third stage is silicate differentiation, which starts at T_3, by using the following equation:

$$\begin{aligned}\Delta\varepsilon^{182}W_{MR} &= Q_{182} f^{Hf/W}_{BSE}\left(\frac{^{182}Hf}{^{180}Hf}\right)_{T_1}\left(e^{-\lambda_{182}(T_1-T_2)} - e^{-\lambda_{182}(T_1-T_3)}\right)\\ &\quad + Q_{182} f^{Hf/W}_{EDR}\left(\frac{^{182}Hf}{^{180}Hf}\right)_{T_1} e^{-\lambda_{182}(T_1-T_3)}\\ &= Q_{182} f^{Hf/W}_{BSE}\left(\frac{^{182}Hf}{^{180}Hf}\right)_{T_1} e^{-\lambda_{182}(T_1-T_2)}\\ &\quad + Q_{182}\left[f^{Hf/W}_{EDR} - f^{Hf/W}_{BSE}\right]\left(\frac{^{182}Hf}{^{180}Hf}\right)_{T_1} e^{-\lambda_{182}(T_1-T_3)}. \end{aligned} \quad [1]$$

$\Delta\varepsilon^{182}W_{MR}$ is the difference between the present-day $\varepsilon^{182}W$ of mantle reservoirs (MR) and the $\varepsilon^{182}W$ of CHUR ($\varepsilon^{182}W_{CHUR} = -1.97 \pm 0.13$ (1, 2). It is assumed that the source of MR is the Early Depleted Reservoir (EDR) (3). Q_{182} is $10^4 \times (^{182}Hf/^{182}W)_{CHUR} = 15{,}500$ (27); $((^{182}Hf/^{180}Hf)_{T_1} = 1 \times 10^{-4}$ (1, 2). $f_{Hf/W}(BSE)$, the fractionation factor of Hf/W ratios between bulk silicate Earth (BSE) and CHUR, is defined as $f_{Hf/W}(BSE) = (^{180}Hf/^{184}W)_{BSE}/(^{180}Hf/^{184}W)_{CHUR} - 1$. We use the $(Hf/W)_{BSE}$ ratio of 17 ± 5 (28) and $(Hf/W)_{CHUR} = 1.1$ (29), and therefore $f_{Hf/W}(BSE)$ varies from 10 to 19. Likewise, $f_{Hf/W}(EDR)$ is the fractionation factor of the Hf/W ratio between EDR and CHUR. Mass balance between the depleted mantle and the continental crust, as described in detail in ref. 3, is used to estimate the concentration of Hf and W in EDR by varying sizes for its complement, the Early Enriched Reservoir (EER), which we assume is the size of either the D″ layer [in which case $f_{Hf/W}(EDR) = 17$–22)] or the entire lower mantle [$f_{Hf/W}(EDR) = 16$–21]. For this calculation, the concentration of Hf and W in the continental crust, depleted mantle, and CHUR are compiled from the literature (13, 29–41). We explore the full range of Hf/W ratios estimated for BSE (28) because these values are the main source of uncertainty for our model. Compared to the earlier core-formation model (1, 2), the third term with $f_{Hf/W}(EDR)$ in Eq. **1** is newly added to describe ^{182}W growth because of silicate differentiation (see *SI Text* for further details).

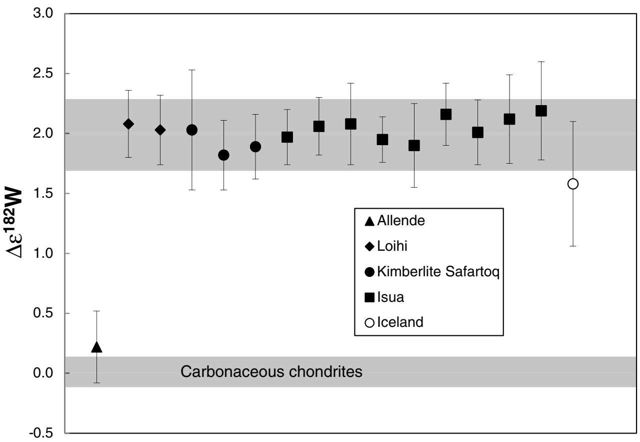

Fig. 1. Plot of $\Delta\varepsilon^{182}W = \varepsilon^{182}W_{sample}$-$\varepsilon^{182}W_{CHUR}$ for terrestrial rocks measured in this study compared to carbonaceous chondrite Allende (this study) and literature average (1, 2).

The evolution of the W isotopic composition of the silicate mantle reservoir ($\Delta\varepsilon^{182}W_{MR}$) as a function of the time of silicate differentiation (varying T_3) for different ages of core formation ($T_1 - T_2 = 20, 28, 30$ Myr, etc.) is shown in Fig. 2. The $\Delta\varepsilon^{182}W_{MR} = +1.97 \pm 0.13$ in this case reflects the collective effects from both rapid growth because of core formation as well as further accelerated growth because of preferential extraction of W into the EER, or early continental crust extraction, leading to a higher Hf/W ratio in the resulting EDR. The ^{182}W isotopic composition of rocks from all tectonic settings rules out a core-formation time (T_1-T_2) earlier than ~28 Myr under the parameter space considered in the simple model, because $\Delta\varepsilon^{182}W_{MR}$ will always be higher than the measured difference between terrestrial rocks and CHUR. If the core formation occurred significantly later (e.g., T_1-$T_2 > 35$ Myr), the model shows that the silicate differentiation would occur before core formation, an unlikely scenario (the lower gray curves in Fig. 2). If one assumes that core formation is contemporaneous with or precedes silicate differentiation, then ^{182}W isotopes require core formation at ~30 Myr and silicate differentiation to occur at 43 ± 4 Myr, respectively.

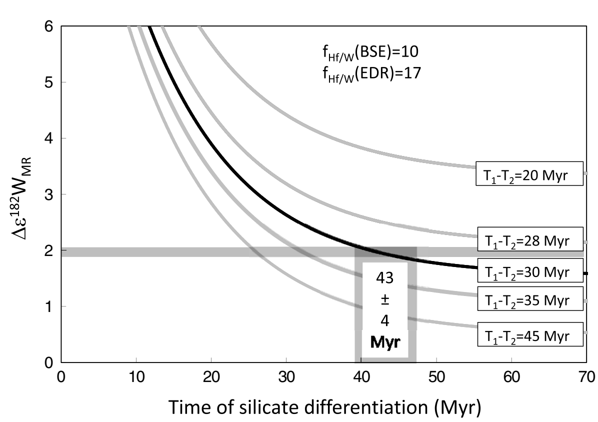

Fig. 2. W isotopic evolution by using a 3-stage model. The evolution of the $\Delta\varepsilon^{182}W_{MR} = \varepsilon^{182}W_{MR}$-$\varepsilon^{182}W_{CHUR}$ is plotted as a function of the time of the silicate differentiation for a series of fixed times for core formation (20, 28, 30, 35, and 45 Myr). MR refers to the mantle reservoir. EDR refers to early depleted reservoir, and BSE refers to bulk silicate earth. If the core formed too early (e.g., 28 Myr), then the $\Delta\varepsilon^{182}W_{MR} = +1.97$ reported in this work can never been reached. If the core formed too late (e.g., 40 and 45 Myr), it would imply that the silicate differentiation has occurred before core formation, which is unlikely. Only the black curve, T_1-$T_2 = 30$ Myr, is possible because the age of core formation constrains the time of silicate differentiation to be 43 ± 4 Myr.

Fig. 3 shows the evolution of the timing of silicate differentiation (T_1-T_3), as a function of the timing of core formation (T_1-T_2) for a fixed $\Delta\varepsilon^{182}W_{MR} = +1.97$. Two end member sizes are assumed for the EER: EER size equals that of the D″ layer (Fig. 3*A*) and the lower mantle (Fig. 3*B*). The effect of the full range of $f_{Hf/W}$(BSE) (10–19) (28) and the associated $f_{Hf/W}$(EDR) on the correlation between the time of silicate differentiation and the time of core formation is shown by the two curves in Fig. 3. Fig. 3 shows that the timing of silicate differentiation and core formation are strongly anticorrelated and asymptotically approach horizontal and vertical on the two ends. For core formation to occur after >38 Myr, the silicate differentiation would have to occur before core formation (i.e., before 38 Myr), which is unreasonable (marked as "forbidden zone" in Fig. 3). Thus our model results on the time scale of core formation are relatively insensitive to $f_{Hf/W}$(BSE), $f_{Hf/W}$(EDR), or the assumed size of the EER (Fig 3), within the range of silicate differentiation ages suggested by ^{142}Nd data. A silicate differentiation between 36 and 75 Myr implies the core formation occurred between 27.5 and 36 Myr. A large effect on the horizontal asymptote by the choice of $f_{Hf/W}$(BSE) is irrelevant as they are in the forbidden zone (silicate mantle differentiation before mantle is

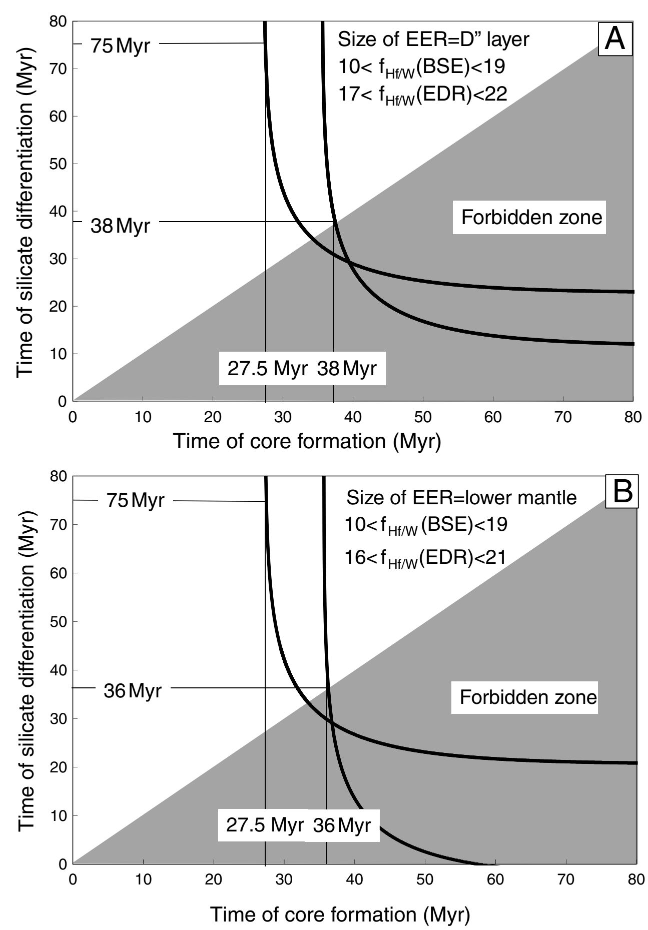

Fig. 3. The evolution of the time of silicate differentiation and the time of core formation are calculated for a fixed $\Delta\varepsilon^{182}W_{MR}$ value reported in this study for the two extreme sizes of the EER layer: (*A*) D″ layer and (*B*) lower mantle. The two curves represent the envelope of the error resulting from the uncertainty on $f_{Hf/W}$(BSE) and $f_{Hf/W}$(EDR). This plot shows if the silicate extraction occurred between 36 and 75 Myr after the formation of the Solar System, as suggested by ^{142}Nd data (3), the core must have been formed between 27.5 and 36 Myr. Note that the lower right half is a "forbidden zone" where silicate mantle differentiation precedes before core/mantle differentiation (extraction of melts from silicate mantle before mantle formation is an unlikely scenario).

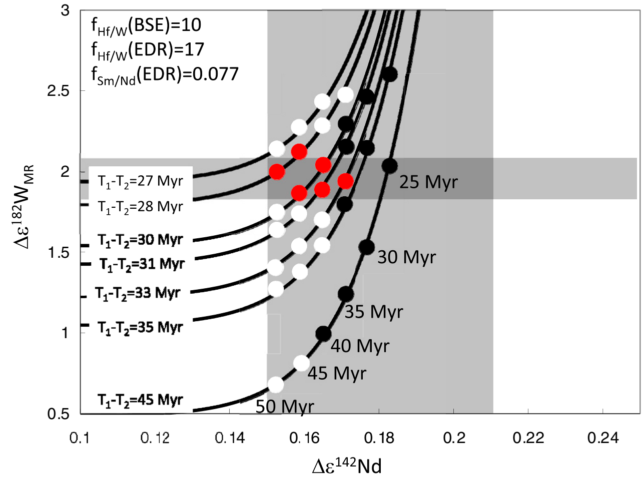

Fig. 4. $\Delta\varepsilon^{182}W_{MR}$ and $\Delta\varepsilon^{142}Nd$ evolution for a 3-stage model. $f_{Sm/Nd}(EDR)$ is assumed to be 0.077. The curves represent different times of core formation. The circles are the time of silicate differentiation. Vertical alignment of all circles reflects the fact that $\Delta\varepsilon^{142}Nd$ are not affected by core formation because of the lithophile nature of Sm and Nd. Because the time of core formation (T_2) has to proceed before the time of silicate differentiation (T_3), on each curve only the large circles (red or white) represent possible times for silicate differentiation. The gray bands represent the Nd and W isotope composition measured in modern terrestrial rocks, thus limiting further only the red circles to represent possible times of silicate differentiation and core formation.

segregated from the core). Thus, a tight constraint between the timing of core formation and silicate differentiation is not sensitive to the assumed value of $f_{Hf/W}(BSE)$ ranging from 10 to 19 (28).

Up to now, our discussion has been solely based on the $\Delta\varepsilon^{182}W \sim 2\varepsilon$ effect, with a silicate differentiation time scale built into the W isotope model. We have not yet considered the $\Delta\varepsilon^{142}Nd \sim 0.2\varepsilon$ effect observed in all terrestrial rocks (3). Fig. 4 models the simultaneous evolution of $\Delta\varepsilon^{182}W_{MR}$ and $\Delta\varepsilon^{142}Nd$. $\Delta\varepsilon^{182}W_{MR}$ is calculated as described above, whereas $\Delta\varepsilon^{142}Nd$ is calculated by using a 2-stage model (Eq **2**) because Sm/Nd are both lithophile elements and are not affected by (i.e., transparent to) core formation (5).

$$\Delta\varepsilon^{142}\mathrm{Nd} = Q_{142} f_{\mathrm{EDR}}^{\mathrm{Sm/Nd}} \left(\frac{^{146}\mathrm{Sm}}{^{144}\mathrm{Sm}}\right)_{T_1} \left(e^{-\lambda_{146}(T_1-T_3)} - e^{-\lambda_{146}(T_1-T_4)}\right), \qquad [2]$$

where $Q_{142} = 354$ (6), $(^{146}Sm/^{144}Sm)_{T1} = 0.008$, $\lambda_{146} = 6.73$ Ga^{-1}, and $T_4 = 0$ Ga, which is the present time. $f_{Sm/Nd}(EDR)$ is the fractionation factor for the Sm/Nd ratio between the EDR and the CHUR and is defined in the same way as for the Hf/W ratio. The model presented in Fig. 4 uses $f_{Sm/Nd}(EDR) = 0.077$. The dark gray areas in Fig. 4 correspond to the intersection of $\Delta\varepsilon^{182}W_{MR}$ and $\Delta\varepsilon^{142}Nd$ measurements in terrestrial rocks. This gray area intercepts the ^{142}Nd and ^{182}W isotopic evolution curves when both the times of core formation and silicate differentiation satisfy the observed ^{142}Nd and ^{182}W values. In order for core formation to precede silicate differentiation ($T_2 \leq T_3$) and to satisfy both $\Delta\varepsilon^{182}W = +1.97 \pm 0.13$ (3, 4) and $\Delta\varepsilon^{142}Nd = +0.18 \pm 3$ for all terrestrial rocks relative to ordinary chondrites weighted average (42), core/mantle differentiation has to occur between 28 and 33 Myr and silicate differentiation between 35 to 50 Myr (big red circles in Fig. 4). Therefore, modeling ^{146}Sm-^{182}Nd and ^{182}Hf-^{182}W systems together gives even tighter constraints on both core/mantle and silicate differentiation.

Materials and Methods

Details of the chemical separation and mass spectrometry techniques used in this work are described by Irisawa and Hirata (43). W is purified from the matrix by elution through anionic-exchange resins. The average sample yields are >90%. The W isotope compositions were measured by multiple-collector inductively coupled plasma mass spectrometry at University of California–Davis. An exponential law was used to correct for mass fractionation assuming $^{183}W/^{184}W = 0.46712$. The measured $^{182}W/^{184}W$ ratio is expressed as $\varepsilon^{182}W = [(^{182}W/^{184}W)_{sample}/(^{182}W/^{184}W)_{standard} - 1] \times 10{,}000$ by using the terrestrial standard Alfa Aesar (stock no. 35770, lot no. 233665H). Tests performed with terrestrial basalts from Loihi and Iceland and kimberlites from Safartoq demonstrate that anomalies of $>0.3\varepsilon$ can be clearly resolved. The procedural blank was <0.9 ng, which is negligible compared to the amount of W in the samples (~500 ng).

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