1 **Open-system** ¹⁸²W–¹⁴²Nd isotope evolution of the early Earth

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2 Seema Kumari<sup>1,2</sup>, Andreas Stracke<sup>2*</sup>, Debajyoti Paul<sup>1</sup>
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4 ¹ Department of Earth Sciences, Indian Institute of Technology Kanpur, Kanpur 208016, Uttar

- 5 Pradesh, India
- 6 ² Westfälische Wilhelms Universität, Institut für Mineralogie, Corrensstr. 24, 48149 Münster,
- 7 Germany.
- 8
- 9

10 *Corresponding author

11 Email: astra_01@uni-muenster.de (Andreas Stracke)

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- 13 Abstract

We present a five-reservoir open-system model for the ¹⁸²Hf-¹⁸²W and ¹⁴⁶Sm-¹⁴²Nd 14 isotope evolution of the Earth to constrain early mantle-crust exchange and late accretion 15 processes. In the presented model, core formation is complete within 30–100 Myr after solar 16 17 system formation. The complementary bulk silicate Earth (BSE) differentiates to form a continental crust (CC), an incompatible element depleted upper mantle (UM), an initially 18 19 primitive but continuously evolving lower mantle (LM), and an isolated reservoir (IR) where 20 the recycled crust is stored for 1 Gyr before mixing into the LM. Late accretion adds bulk 21 Earth-like material to the mantle after core formation, concurrent to progressive silicate differentiation. The ¹⁸²W and ¹⁴²Nd isotope evolution in each reservoir is calculated with a 22 23 series of differential equations that compute the changing abundance of each isotope from the 24 start of solar system evolution (t = 4.56 Ga) to the present (t = 0 Ga). Core formation until at least 45–60 Myr after solar system initial is most compatible with the modeled ¹⁸²W evolution 25 of the silicate Earth, which limits the amount of late accreted material to about 1.0-0.5%. 26 However, the pre-late accretion μ^{182} W and Hf/W (or W) of the BSE depend strongly on the 27 28 rate and duration of core formation and determine the amount of late accreted material necessary to evolve to the present $\mu^{182}W_{BSE} \sim 0$. The interdependency of these parameters is 29 30 key for evaluating the variable influence of late accretion and early mantle-crust interaction on 31 the Hf-W evolution of the BSE. Nevertheless, heterogeneous distribution of the late accreted 32 material to the mantle, in combination with Hadean crust formation and recycling is required to form a mantle reservoir with a small range of ¹⁸²W excesses between 10–15 ppm throughout 33 the Archean, as observed in most Archean rocks. Reproducing the observed ¹⁴²Nd and ¹⁸²W 34 35 signatures in Hadean-Eoarchean mantle-derived rocks with our model further requires that 36 continental crust starts to form within the first ~ 50 Myr after core formation. Continuous 37 exchange between the crust and the different mantle reservoirs in our model leads to post-Archean homogenization of early-formed ¹⁸²W and ¹⁴²Nd heterogeneities and development of 38 39 present bulk silicate earth values in all silicate reservoirs. But if part of the recycled CC in our model is isolated from further exchange with other crustal and mantle reservoirs, the average 40 LM reservoir in the presented model maintains slightly negative μ^{182} W since late accretion, 41 which provides a possible explanation for the observed ¹⁸²W deficits in some young ocean 42 island lavas. 43

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45 **Keywords:** Hf-W isotope system, ¹⁴²Nd, open system evolution, late accretion, core formation,

46 early earth

47 1. INTRODUCTION

48 Owing to the limited rock record of Hadean and Archean rocks, our understanding of the geodynamic processes during Earth's earliest evolutionary phase remains rudimentary. The 49 ¹⁸²Hf-¹⁸²W systematics of meteoritic and planetary samples have shown that terrestrial core 50 51 formation occurred within the first 30-100 Myr of solar system formation (e.g., Lee and 52 Halliday, 1995; Harper and Jacobsen, 1996; Kleine et al., 2002; 2009; Yin et al., 2002; Halliday 53 and Wood, 2009). Continued accretion after core formation added further material, which 54 determined the mantle abundances of the highly siderophile elements (HSE: Re, Os, Ir, Ru, Pt, Rh, Pd, and Au) and influenced Earth's ¹⁸²W isotope evolution (Kimura et al., 1974; Kleine, 55 56 2011). It remains debated when core formation ceased, and thus when late accretion began, how long the late accretion phase lasted, and if dispersal of late-accreted material created 57 transient, but variably long-lived HSE and ¹⁸²W isotope heterogeneities in the Earth's mantle. 58 59 Van de Löcht et al. (2018), for example, argued that mantle rocks younger than 3.8 Ga have 60 HSE abundances similar to the modern mantle, suggesting termination of late accretion and 61 complete homogenization of the accreted material at ~3.8 Ga. Others argue for longer 62 homogenization timescales based on lower than present HSE abundances in komatiites older 63 than ~3.0 Ga (Maier et al., 2009). Concurrent to late accretion, Earth's earliest crust started to form (e.g., Wilde et al., 2001; Harrison et al., 2008), which initiated the progressive 64 65 compositional differentiation of the silicate Earth.

The short-lived radioactive decay systems 182 Hf $^{-182}$ W ($t_{1/2} = 8.9$ Myr) and 146 Sm $^{-142}$ Nd ($t_{1/2}$ 66 67 = 103 Myr) are variably sensitive to the different geodynamic processes during Earth's earliest 68 evolutionary phase (e.g., Kleine et al., 2002; Boyet and Carlson, 2005; Caro, 2011; Kleine, 69 2011; Kleine and Walker, 2017; Rizo et al., 2016; Rosas and Korenaga, 2018; Carlson et al., 2019). Owing to the moderately siderophile behavior of W under highly reducing conditions, 70 the ¹⁸²Hf-¹⁸²W decay system is mostly sensitive to metal-silicate fractionation during core 71 formation or early magma ocean crystallization (e.g., Kleine et al., 2009). However, under 72 73 more oxidizing conditions typical of silicate differentiation processes after core formation, W 74 is lithophile and more incompatible than Hf (Newsom et al., 1996; Righter and Shearer, 2003; 75 Arevalo and McDonough, 2008). Early crust formation and concurrent mantle depletion 76 therefore also influence the ¹⁸²W evolution of the silicate Earth, if they start within the lifetime of ¹⁸²Hf. On the other hand, because Sm and Nd are refractory lithophile elements (Nd is more 77 incompatible than Sm), the ¹⁴⁶Sm-¹⁴²Nd decay system is controlled exclusively by the timing 78 79 and nature of silicate differentiation within the first ~500 Myr of Earth's history (e.g., Jacobsen and Harper, 1996; Boyet and Carlson, 2005, Caro et al., 2006; Roth et al., 2013). 80

81 Most mantle-derived rocks older than 2.4 Ga have non-zero μ^{182} W within a narrow range 82 of about +10 to +15 (μ^{182} W is the ppm deviation in 182 W/ 184 W relative to the present terrestrial 83 standard), which are variably attributed to core formation, non-uniform distribution of late 84 accreted material within the mantle, and silicate melt-crystal or metal-silicate fractionation in 85 an early magma ocean (e.g., Willbold et al., 2011; Touboul et al., 2012; Touboul et al., 2014; 86 Liu et al., 2016; Puchtel et al., 2016; Puchtel et al., 2018; Archer et al., 2019; Tusch et al., 87 2019). Despite μ^{182} W within a narrow range of +10 to +15, μ^{142} Nd in Archean mantle-derived

rocks vary from positive to negative values ($\mu^{142}Nd$ is the ppm deviation in $^{142}Nd/^{144}Nd$ relative 88 89 to the present terrestrial standard), indicating that chemically distinct crustal and mantle 90 reservoirs started to form within the first ~500 Myr of Earth's history (e.g., Bennett et al., 2007; Rizo et al., 2011; O'Neil et al., 2016). The 3.8–3.3 Ga old rocks from the Isua Supracrustal 91 Belt, Greenland, for example, have $\mu^{182}W > 0$ and $\mu^{142}Nd > 0$ (Willbold et al., 2011; Rizo et al., 92 93 2016). On the other hand, ~3.5–3.3 Ga old rocks from the Pilbara Craton, Western Australia, 94 have $\mu^{182}W > 0$ but $\mu^{142}Nd \sim 0$ (Archer et al., 2019), and the ~4.0–3.6 Ga old rocks from the Acasta Gneiss Complex, Canada have $\mu^{182}W > 0$ and $\mu^{142}Nd < 0$ (e.g., Roth et al., 2014; 95 Willbold et al., 2015; Reimink et al., 2018). With $\mu^{182}W < 0$ and $\mu^{142}Nd < 0$, the ~3.5 Ga old 96 Schapenburg komatiites are an exception (Puchtel et al., 2016). Variable ¹⁴²Nd excesses and 97 98 deficits coupled with excess ¹⁸²W of similar magnitude in most Archean mantle-derived rocks 99 imply that heterogeneous early-formed mantle and crustal components are part of their mantle 100 source(s). In contrast, post-Archean rocks are generally similar to the modern accessible mantle with μ^{182} W ~0 and μ^{142} Nd ~0 (Rizo et al., 2013; Mundl et al., 2018; Rizo et al., 2019), 101 indicating progressive homogenization of Hadean and early Archean ¹⁸²W and ¹⁴²Nd 102 heterogeneities. However, some young ocean island basalts (OIB) have $\mu^{182}W$ <0, which 103 require either the preservation of ¹⁸²W deficits produced during the life-time of ¹⁸²Hf or 104 incorporation of core material with μ^{182} W ~ -200 (Mundl et al., 2017; Mundl-Petermeier et al., 105 106 2020; Rizo et al., 2019).

107 Here, we present an open system model for the isotopic evolution of Earth's major 108 reservoirs, which is adapted from the model presented by Kumari et al. (2016, 2019) by incorporating the ¹⁴⁶Sm-¹⁴²Nd and ¹⁸²Hf-¹⁸²W isotope systematics, and by implementing an 109 110 additional core reservoir within a five-reservoir model of Earth's isotopic evolution. The model quantitatively evaluates how (i) the duration and rate of core formation influence the pre-late 111 accretion μ^{182} W, W concentration and Hf/W ratio of the bulk silicate earth and how the 112 113 interdependency with (ii) the amount, rate, and style of late accretion, and (iii) the timing and nature of silicate differentiation (i.e., crust formation and crust-mantle interaction) affects the 114 115 ¹⁸²W and ¹⁴²Nd isotope evolution of the evolving silicate Earth.

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117 2. METHODS: OPEN SYSTEM EVOLUTION OF THE EARTH

118 **2.1. General model set-up**

119 The model presented here is an extended version of the model presented by Kumari et al. (2016, 2019), which uses the long-lived U-Th-Pb, Rb-Sr, Sm-Nd, and Lu-Hf isotope 120 systematics to quantify mass fluxes between a bulk continental crustal reservoir (CC), and two 121 122 different mantle reservoirs to simulate the geochemical evolution of the silicate Earth. The 123 modeled mantle reservoirs consist of an incompatible element depleted, so-called upper mantle 124 (UM), and a non-primitive lower mantle (LM). In addition, there is an isolated reservoir (IR), where recycled continental crust is stored before being transferred into the LM. In this open 125 126 system, or "box modeling" approach, radiogenic isotope ratios in a reservoir are functions of 127 the parent-daughter ratios in each reservoir as well as the fluxes into and out of the reservoirs 128 (e.g., Paul et al., 2002; Kumari et al., 2016).

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129 Here, we extend the open system model of Kumari et al. (2016, 2019) by including an 130 additional core reservoir. Starting with the elemental inventory of bulk earth, the core forms in different time periods, by mass and species (i.e., the moderately siderophile element W) 131 132 exchange between core and mantle until the core has reached its present mass (see Fig. 1, 133 section 2.3 and the supplementary material for equations describing the rate of mass and species 134 exchange between core and mantle). Core formation results in formation of a complementary silicate reservoir, the bulk silicate earth (BSE), with initial μ^{182} W, W concentration and Hf/W 135 determined by the duration and rate of core formation (section 2.3). After core formation, late 136 137 accretion of bulk Earth-like material and concurrent silicate differentiation into bulk crust and different mantle reservoirs regulate the ¹⁸²Hf-¹⁸²W and ¹⁴⁶Sm-¹⁴²Nd isotope evolution in this 138 five-reservoir model of Earth's isotopic evolution. 139

140 Specifically, the CC grows by mass fluxes from the LM and UM reservoirs and shrinks by 141 recycling into the mantle (Fig. 1). One fraction of the recycled crustal material goes into the 142 UM, which can be varied with the model parameter f_R (f_R has a default value of 0.4, Kumari et al., 2016). The remainder, $1-f_R$, is stored in the IR before being transferred to the LM. The 143 144 default storage time in the IR is 1 Gyr, but shorter and longer residence times are also explored. 145 Long residence times (>4.5 Ga), for example, simulate formation of an early reservoir that 146 remains isolated for the rest of Earth's history (e.g., Boyet and Carlson, 2005). The outgoing 147 flux into the CC and the influxes from the CC, LM, and late accreted material determine the 148 evolution of the UM (Fig. 1). The LM evolves by the initial influx from late accreted material, 149 and the continuous influx of recycled CC after transient storage in the IR, and the outgoing 150 fluxes into the UM and CC (Fig. 1).

151 A series of first-order differential equations, describing the changing abundance of each 152 isotope species in each reservoir, is solved numerically using the fourth-order Runge-Kutta 153 method at 1 Myr time steps from 4.56 Ga to the present (see supplementary material of Kumari 154 et al., 2016 for details and also supplementary material of this study for additional equations 155 constraining the core-mantle mass and species exchange). The set of fixed and variable model 156 parameters (Tables S1-S3) are discussed in detail in Kumari et al. (2016, 2019). These include 157 reservoir masses (M), the residence or isolation time (IT) of the recycled CC material in the IR, 158 and bulk mass or elemental transfer factors (D_i) between the different reservoirs, which are constrained by simultaneously reproducing the estimated present-day average elemental 159 160 abundances and isotope ratios of each reservoir (Tables 1-3). These present terrestrial reservoir 161 compositions are constrained by global data of mid-ocean ridge basalts (MORB, UM), plumederived ocean island basalts (OIB, LM), and the continental crust (CC) (see details in Kumari 162 163 et al., 2016, 2019). The composition of the additional core reservoir in the model presented here (Table 2) is taken from estimates of Arevalo and McDonough (2008) and McDonough 164 165 (2014).

Note that the mass transfer factor D_i in our model is *NOT* a bulk solid-melt partition coefficient, but rather a parameter that represents the combined mass transfer for each element *i* between the different reservoirs (Paul et al., 2002). Mass transfer could result from several processes such as one or more melting events, potential fluid transport, etc. A value of $D_i > 1$ enriches, and a value of $D_i < 1$ depletes a given reservoir in the element *i*. Based on constraints

- 171 from the long-lived radioactive decay systems (Rb-Sr, Sm-Nd, Lu-Hf, U-Pb, Kumari et al., 2016 and 2019), our model assumes exponential crustal growth with 90% of the flux coming 172 from the UM and the remainder from the LM, resulting in a present mass fraction of the UM 173 174 reservoir ($m_{\rm UM} = M_{\rm UM}/M_{\rm M}$) of ~0.5–0.6. Because the majority of the CC is thus formed from the UM, the model parameter $m_{\rm UM}$ effectively controls the concentration of each element in the 175 UM ($C^{i}_{UM} = M^{i}_{UM}/(M_{M} \times m_{UM})$; where C^{i}_{UM} is the concentration of element *i* in the UM, M^{i}_{UM} 176 177 is the mass of element *i* in the UM, and $M_{\rm M}$ is the total mantle mass). We have also performed 178 model simulations by varying the parameters $m_{\rm UM}$, $f_{\rm R}$, D_i , and the residence time of recycled 179 crust in the IR to explore different scenarios that satisfy the observational constraints from the ¹⁸²W and ¹⁴²Nd data in Archean rocks. 180
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182 **2.2. Initial state of the model**

The initial bulk Earth abundances of ¹⁴⁶Sm, ¹⁸²Hf, and ¹⁸²W were calculated using the solar system initial isotope ratios of ¹⁴⁶Sm/¹⁴⁴Sm = 0.0085 (Boyet et al., 2010), ¹⁸²Hf/¹⁸⁰Hf = 1.018×10⁻⁴ (Burkhardt et al., 2008), and ¹⁸²W/¹⁸⁴W = 0.864598 (Kleine and Walker, 2017), and the present abundances of the stable isotopes ¹⁴⁴Sm, ¹⁸⁰Hf, and ¹⁸⁴W. The abundances of the stable isotopes (¹⁴⁴Sm, ¹⁸⁰Hf, ¹⁸⁴W) are calculated using their present relative abundances and concentrations of Sm, Hf, and W in the bulk Earth (Table 1). The solar system initial ¹⁴²Nd/¹⁴⁴Nd_i is calculated using the following equation:

190 ${}^{142}\text{Nd}/{}^{144}\text{Nd}_t = {}^{142}\text{Nd}/{}^{144}\text{Nd}_i + ({}^{146}\text{Sm}/{}^{144}\text{Sm})_I({}^{144}\text{Sm})_P({}^{147}\text{Sm}/{}^{144}\text{Nd})_P(1-e^{-\lambda I46 \times t})$ (1) 191 where *t* is the time from the origin of the solar system to the present. Further, the (${}^{147}\text{Sm}/{}^{144}\text{Nd})_P$ 192 and (${}^{144}\text{Sm}/{}^{147}\text{Sm})_P$ are calculated using the present abundances of isotopes and concentrations 193 of Sm and Nd in the bulk Earth (Table 1). The calculated initial abundances of all modeled 194 radioactive parents, radiogenic daughters, and stable isotopes in the bulk Earth are given in the 195 supplementary material (Table S4).

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197 **2.3. Core formation**

In our model, core formation begins at t = 4.56 Ga (the start of solar system condensation) and starts with the mass $(5.94 \times 10^{24} \text{ kg})$ and elementary inventory (Sm, Nd, Hf, W) of the bulk Earth (Table 1). In the default model set-up, the core grows linearly to its present mass of 1.883 $\times 10^{24}$ kg for periods of 30, 45, 60, or 100 Myr. The 30 Myr core formation period is one endmember case, constrained by single-stage instantaneous 182 Hf $-{}^{182}$ W core growth models (Kleine et al., 2009). For the 100 Myr end-member, 182 Hf is almost completely extinct at the end of core formation.

In each increment of core formation, W goes into the core, but Hf, Sm, and Nd stay in the complementary silicate reservoir, the bulk silicate earth (BSE). The BSE thus maintains chondritic Sm/Nd and μ^{142} Nd values until the end of core formation, but evolves to progressively lower W concentrations (W_{BSE}) and higher Hf/W_{BSE} and μ^{182} W_{BSE} values. The latter are determined by the rate and overall magnitude of the W flux to the core, which in our model, is controlled by the bulk silicate-metal transfer factor, $D_{W,silicate-metal}$. The Hf/W_{BSE} (W_{BSE}) and μ^{182} W_{BSE} values at the end of core formation define the subsequent ¹⁸²W evolution

- 212 of the BSE, but unfortunately remain unknown (Kruijer et al., 2015, Touboul et al., 2015). We therefore use the present $\mu^{182}W_{BSE}$ to constrain the ¹⁸²W evolution of the BSE. The present 213 μ^{182} W_{BSE} is 0 by definition, but has been lowered by continued accretion after core formation, 214 215 during the so-called 'late accretion' phase. Recent estimates of the present, pre-late-accretion $\mu^{182}W_{BSE}$ range from +10 and +40 (Kruijer et al., 2015; Touboul et al., 2015). We use a 216 μ^{182} W_{BSE} target value in the middle of this estimated range, and adjust $D_{W,silicate-metal}$ for each 217 given core formation period such that the BSE evolves to $\mu^{182}W = +25$ at the present day, 218 219 without adding any late accreted material.
- This strategy allows exploring how different rates of core formation, simulated by varying $D_{W,silicate-metal}$, influence the modeled W_{BSE} , Hf/ W_{BSE} , and $\mu^{182}W_{BSE}$ values at the end of core formation, and how these different starting values change the ¹⁸²W evolution of the evolving crust and mantle reservoirs during subsequent late accretion and silicate differentiation processes (see detailed discussion in sections 3.1, 4.1).
- 225 An alternative strategy would be to assume that the present pre-late accretion $\mu^{182}W_{BSE}$ value (+25) is equivalent to the $\mu^{182}W_{BSE}$ value at the end of core formation. But this 226 assumption inherently implies that there is no contribution of radiogenic ¹⁸²W to the ¹⁸²W 227 budget of the BSE after core formation ended, that is, late accretion started after ¹⁸²Hf became 228 extinct (>80-100 Myr). Although this may be a viable assumption (e.g., Maurice et al., 2020), 229 230 the duration of core formation remains unknown (e.g., Rudge et al., 2010). Moreover, despite the short ca. 8.9 Myr half-life of ¹⁸²Hf, radiogenic ¹⁸²W contributes significantly to the ¹⁸²W 231 232 budget of the BSE, if core formation is shorter than ~80 Myr (Fig. 2). Hence to allow for 233 different core formation periods, and thus starting times of late accretion, we used the core growth model described above, and discussed in more detail in section 3.1, to constrain the 234 $\mu^{182}W_{BSE}$ and Hf/W_{BSE} (W_{BSE}) at the end of core formation. 235
- Any deviations from the default linear core formation model, for example a large mass and thus W flux to the core early or late during core formation (e.g., by a giant impact), influence the initial μ^{182} W_{BSE}, W_{BSE} and Hf/W_{BSE} at the start of late accretion, and thus the subsequent ¹⁸²W evolution of all silicate reservoirs (Fig. 3). Different, non-linear core formation scenarios are therefore also explored, and discussed in more detail in sections 3.1 and 4.1.
- In addition, the comparatively large uncertainty of the present, pre-late accretion $\mu^{182}W_{BSE}$ 241 target value, with a possible range of values between +10 and +40, affects the modeled 242 $\mu^{182}W_{BSE}$ evolution. This uncertainty is caused by the large uncertainty of the parameters 243 required to make this estimate (Kruijer et al., 2015; Touboul et al., 2015). Namely, the amount 244 245 and type of late accreted material, which is derived from the HSE concentrations of the BSE, 246 but especially the W_{BSE} (13 ± 10 ppb, 2SD, Arevalo and McDonough, 2008). The chosen target value in our model, $\mu^{182}W_{BSE} = +25$, is therefore by no means a robust constraint. How these 247 imposed uncertainties on the $\mu^{182}W_{BSE}$ evolution influence other model-derived constraints, 248 249 e.g., the mass of late accreted material, is discussed in detail in sections 3.2 and 4.2.

251 2.4. Late accretion

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Late accretion is the addition of extra-terrestrial material to Earth after the end of core formation (Chou, 1978; Walker, 2009). In our model, late accretion thus starts with the end of 254 core formation at 30, 45, 60 or 100 Myr after solar system formation (4.56 Ga) and ends at 3.8 Ga. Addition of late accreted material until 3.8 Ga marks the end of the so-called 'lunar 255 256 cataclysm' (Tera et al., 1974), which is often considered as the end of the late accretion period 257 (e.g., Maier et al., 2009; van de Löcht et al., 2018). The late accreted material (also termed 'late 258 veneer') used in this study has Hf and W abundances similar to estimates for bulk Earth (C_W = 180 ppb, $C_{\text{Hf}} = 197$ ppb; Table 1; McDonough, 2014) and a μ^{182} W of -190 ± 10 (Kleine et al. 259 2004). The late accreted material (LAM) is added until the BSE has a $\mu^{182}W \sim 0$ at 3.8 Ga 260 261 similar to its present value. The target for the evolution of the UM reservoir is the narrow range of μ^{182} W values between +10 and +15 that is observed in most mantle-derived Archean rocks 262 263 (4.0–2.5 Ga), and the μ^{182} W ~0 for post-Archean basalts (e.g., Mundl et al., 2018; Rizo et al., 2019). 264

265 We investigate different styles of late accretion. During uniform, or homogeneous late accretion, the fraction of LAM going to the UM and LM is proportional to the mass of these 266 267 mantle reservoirs (section 3.4.1). Non-uniform or heterogeneous late accretion is when the UM 268 reservoir receives a smaller relative fraction of the incoming material than the LM reservoir (section 3.4.2). Note that although we use the terminology of upper and lower mantle (UM and 269 270 LM), there is no spatial connotation implied. Rather, these two boxes in our model should simply be perceived as two different mantle reservoirs that can receive different amounts of 271 272 LAM (and have different in-and outgoing fluxes from and to the crust).

We also simulate different rates of late accretion, for example adding a significant fraction of the material at the beginning or end of the late accretion period, which simulates sudden addition of large single bodies versus addition of a fixed amount per time interval (linear flux rate). How the different rates, but also composition of the late accreted materials (e.g., differentiated vs. undifferentiated objects) affect the μ^{182} W evolution of the different silicate reservoirs, as well as the geodynamic implications of the different late accretion scenarios will be discussed in detail in sections 3.3 and 4.2.

280281 **3. RESULTS**

282 **3.1. Effect of core formation on the pre-late accretion W**_{BSE}, Hf/W_{BSE}, and μ¹⁸²W_{BSE}

The evolution of $\mu^{182}W_{BSE}$ for core formation periods of 30, 45, 60 and 100 Myr is shown in Fig. 4. In each case, $\mu^{182}W_{BSE}$ evolves to the chosen present target value of +25 without late accretion (Kruijer et al., 2015; Touboul et al. 2015; Kruijer and Kleine, 2017).

Notably, even for a core formation period of 60 Myr, when ¹⁸²Hf is nearly extinct, a minute amount ¹⁸²Hf is left over in the BSE (¹⁸²Hf/¹⁸⁰Hf_{BSE} >0, Fig. 2), which leads to a subsequent increase of $\mu^{182}W_{BSE}$, if not counteracted by the addition of late accreted material (Fig. 4). Hence, for core formation times, *t*_{CF}, less than ~80 Myr (Figs. 2 and 4), the duration of core formation influences $\mu^{182}W_{BSE}$ considerably and, depending on Hf/W_{BSE} at *t*_{CF}, determines how much radiogenic ¹⁸²W is produced in the BSE after core formation.

292 Different $\mu^{182}W_{BSE}$ and Hf/W_{BSE} (180 Hf/ $^{184}W_{BSE t=0}$) at t_{CF} for different rates and durations 293 of core formation (Figs. 3 and 4) result from different mass and associated W flux rates required 294 to accumulate the total mass of the core over different core formation periods. The W flux rate 295 to the core is controlled by the silicate-metal transfer factor $D_{W,silicate-metal}$ in our model (section 2.3). Different $D_{W,silicate-metal}$ values lead to different W_{BSE} and W_{core} at t_{CF} (Table 4). Because Hf remains entirely in the evolving BSE, the different Hf/W_{BSE} at t_{CF} thus result solely from the different W_{BSE} values at t_{CF} . Hence the $D_{W,silicate-metal}$ is set such that the Hf/W_{BSE} and $\mu^{182}W_{BSE}$ at t_{CF} lead to the present pre-late accretion target value $\mu^{182}W_{BSE}$ of +25 (Table 4; Fig. 4, eqn 2), which is calculated by:

 $^{182}W/^{184}W_{BSE t=0} = ^{182}W/^{184}W_{BSE tCF} + [^{182}Hf/^{180}Hf_{tCF} \times ^{180}Hf/^{184}W_{BSE t=0}]$ 301 (2)For our default linear core formation model, the $\mu^{182}W_{BSE}$ at t_{CF} ($^{182}W/^{184}W_{BSE tCF}$) decreases 302 for shorter core formation periods, t_{CF} (Table 4; Fig. 4). But because 182 Hf/ 180 Hf_{tCF} increases 303 exponentially with shorter t_{CF} during the lifetime of ¹⁸²Hf, Hf/W_{BSE} (¹⁸⁰Hf/¹⁸⁴W_{BSE,t=0}) also has 304 to decrease to evolve to a fixed present $\mu^{182}W_{BSE}$ ($^{182}W/^{184}W_{BSE,t=0}$, Table 4). Shorter core 305 formation periods during the lifetime of ¹⁸²Hf therefore lead to lower $\mu^{182}W_{BSE}$, but also require 306 lower Hf/W_{BSE} at t_{CF} to evolve to the same present pre-late accretion $\mu^{182}W_{BSE}$ of +25 (Table 307 308 4; Figs. 3 and 4). The low Hf/W_{BSE} values at t_{CF} for short core formation times are due to high 309 W_{BSE} values caused by low $D_{W,silicate-metal}$ values (Table 4).

310 Any deviations from the default linear core formation model, for example a large mass and 311 thus W flux to the core early or late during a given core formation period, influence the μ^{182} W_{BSE}, Hf/W_{BSE} (W_{BSE}) values at the end of core formation, t_{CF} (Table 4; Fig. 3). For fast 312 core growth rates early during a given core formation period, $\mu^{182}W_{BSE}$ at t_{CF} increases 313 compared to the linear core growth model (Table 4; Fig. 3). As the value of $(^{182}Hf/^{180}Hf)_{tCF}$ is 314 only a function of t_{CF} , higher $\mu^{182}W_{BSE}$ at t_{CF} in response to fast early core growth rates during 315 a given core formation period therefore require lower Hf/W_{BSE} to get the same present $\mu^{182}W_{BSE}$ 316 317 (+25, Fig. 3).

Hence, different rates and durations of core formation cause variable $\mu^{182}W_{BSE}$, Hf/W_{BSE}, and W_{BSE} at the end of core formation or start of the late accretion period (Figs. 3 and 4). Ultimately, these different BSE starting values determine the subsequent ¹⁸²W isotope evolution of the BSE, and influence other model-derived constraints, foremost the amount of late accreted material required to evolve to $\mu^{182}W_{BSE} = 0$ at the end of the late accretion period, as discussed in the following.

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5 **3.2** The relation between the rates of core growth and the amount of late accretion

326 The amount of late accreted material (LAM) and the rate and duration of core formation are interdependent parameters, because the different $\mu^{182}W_{BSE}$ and Hf/W_{BSE} (W_{BSE}) values in 327 response to different rates and durations of core growth determine how much LAM is required 328 329 to evolve to $\mu^{182}W_{BSE} = 0$ at the end of the late accretion period (3.8 Ga). In our default linear 330 core growth model, the amount of LAM varies from 1.9% to 0.07% relative to the bulk Earth 331 mass for core formation periods between 30 and 100 Myr, and is largest for short core formation periods (Table 4; Fig. 4). Longer core formation periods require less LAM, mainly 332 because W_{BSE} at t_{CF} is lower, and although Hf/W_{BSE} and $\mu^{182}W_{BSE}$ are higher compared to 333 334 shorter core formation periods (Table 4; Fig. 4; section 3.1).

Any deviations from the linear core formation model, for example rapid early or late core growth, and thereby a large W flux to the core early or late in the pre-late accretion period (e.g., following the moon-forming impact), considerably influence the $\mu^{182}W_{BSE}$ and W_{BSE} (or 338 Hf/W_{BSE}) at the start of the late accretion period, and thus also the amount of LAM required to evolve to $\mu^{182}W_{BSE} \sim 0$ at the end of late accretion (Fig. 3 shows results for $t_{CF} = 45$ Myr, Table 339 4). Rapid early core growth leads to higher $\mu^{182}W_{BSE}$ and ${}^{182}W_{BSE}$ (lower Hf/W_{BSE}) immediately 340 341 after core formation and require a larger mass of LAM compared to linear core growth (Fig. 3; Table 4). A rapid rate of core growth late during the core formation period, for example by a 342 giant impact, leads to lower $\mu^{182}W_{BSE}$ and W_{BSE} (higher Hf/W_{BSE}) immediately after core 343 formation and requires a smaller mass of LAM compared to linear core growth (Fig. 3; Table 344 4). The rate and duration of core formation thus have a large influence on the μ^{182} W and W 345 concentration (Hf/W) of the BSE and thus also the amount of LAM inferred from the ¹⁸²W 346 systematics. Similar effects are also observed for other core formation periods of 30, 60, and 347 100 Myr (Figs. S1-S3; Table 4). 348

The amount of LAM is most sensitive to W_{BSE} at the end of core formation (Table 4; Fig. 349 5). This is because late accretion essentially compensates for the excess 182 W that leads to the 350 assumed $\mu^{182}W_{BSE} = +25$ without late accretion, compared to $\mu^{182}W_{BSE} = 0$ including LAM. 351 This small amount of excess ¹⁸²W depends on the values of $\mu^{182}W_{BSE}$. Hf/W_{BSE} (W_{BSE}) and 352 353 ¹⁸²Hf/¹⁸⁰Hf at the end of core formation (eqn. 2), and is therefore set entirely by the pre-late accretion processes (core formation rate in our model, see detailed discussion in sections 3.1 354 and 4.2). Because the absolute amount of excess ^{182}W scales with W_{BSE} , the amount of late 355 accreted material needed to develop to $\mu^{182}W_{BSE} = 0$ is most sensitive to W_{BSE} at t_{CF} . The lower 356 W_{BSE} at t_{CF} , the smaller is the absolute amount of excess ¹⁸²W, and the smaller is the amount 357 LAM required to develop to $\mu^{182}W_{BSE} = 0$ at the end of late accretion (Table 4; Fig. 3). 358

Other than W_{BSE} , the composition of the LAM has an effect on the required amount of LAM. But since variable rates and duration of core formation result in highly variable W_{BSE} (Table 4), and if the variation in $\mu^{182}W$ of possible late accreted materials is comparatively small (Kleine et al., 2009; see further discussion in section 4.2), the composition of the LAM has a subordinate effect on the amount of LAM compared to the value of W_{BSE} , which is set by core formation (and early accretion, see further discussion in section 4.2).

365

366 **3.3**¹⁸²W isotope evolution of the BSE: influence of variable rates of late accretion

The shape of the $\mu^{182}W_{BSE}$ evolution curve during the late accretion phase depends strongly 367 on the amount of LAM per time interval, that is, the rate of late accretion. The constant 368 369 composition and amount of LAM per time interval in our default model (linear late accretion rate, Fig. 6a-b and section 2.4) leads to a linear decrease of $\mu^{182}W_{BSE}$ shortly after the end of 370 core formation until $\mu^{182}W_{BSE} = 0$ at the end of late accretion at 3.8 Ga. In contrast, adding 90% 371 372 of the total amount of LAM to the mantle in the initial 100 Myr of late accretion (rapid late accretion scenario) leads to a rapid decrease of $\mu^{182}W_{BSE}$ in this time interval (Fig. 6a-b). When 373 90% of the total amount of LAM is added in the last 100 Myr of late accretion time (delayed 374 late accretion scenario) the BSE maintains high $\mu^{182}W_{BSE}$ values, depending on the initial 375 μ^{182} W_{BSE}, and Hf/W_{BSE} at the start of late accretion (i.e., the rate and duration of core formation, 376 section 3.1). Thereafter, $\mu^{182}W_{BSE}$ rapidly drops to 0 during this final late accretion phase (Fig. 377 378 6b).

379 Note, however, that the BSE evolution shown in Fig. 6b and d is essentially a theoretical reservoir evolution, because mantle-crust differentiation starts concurrent to late accretion, and 380 thus the BSE reservoir ceases to exist with the start of late accretion. The subsequent silicate 381 382 Earth evolution is effectively captured by the evolving mantle and crust reservoirs (UM, LM, IR, CC) in our model. The ¹⁸²W evolution of the evolving mantle and crustal reservoirs is 383 influenced by several parameters. These are how the LAM is distributed between the different 384 385 mantle reservoirs (UM and LM), and how the distribution of W between the evolving mantle 386 and crustal reservoirs affects the W concentrations (and Hf/W) and thus the proportion of W 387 from the LAM to the amount of W in each reservoir. The latter essentially regulates how 388 sensitive each reservoir reacts to the incoming late accretion flux. Starting with the simplest 389 case of uniform distribution of the LAM to the UM and LM (homogeneous late accretion) in 390 the following (section 3.4.1), it will be discussed how the variable distribution of the LAM 391 between the UM and LM (heterogeneous late accretion, section 3.4.2), and variable rates of 392 late accretion affect their ¹⁸²W evolution (section 3.4.3).

393

394 **3.4 Crust-mantle** ¹⁸²W isotope evolution

395 3.4.1 Homogeneous late accretion

Figure 7 shows model results for uniform or homogeneous addition of the LAM to both the evolving UM and LM reservoir until 3.8 Ga for core formation periods of 30, 45, 60, and 100 Myr, using the set of model parameters listed in Table S2. For transfer from mantle to crust, the default bulk elemental enrichment factor for W between mantle and crust (D_W), is set equal to that of Th and U (~200) as used by Kumari et al. (2016) based on the assumption that W is similarly incompatible during silicate differentiation as U and Th (Righter and Shearer, 2003; Arevalo and McDonough, 2008).

403 In Fig. 7, all silicate reservoirs initially develop $\mu^{182}W > 0$ due to decay of left-over ¹⁸²Hf, which then variably decreases due to the addition of LAM with $\mu^{182}W = -190$. Notably, the 404 405 LM is the largest silicate reservoir in our model, but the bulk of the CC is formed by the mass 406 flux from the UM (section 2.1, Kumari et al., 2016, 2019). This means there is only a small outgoing flux from the LM to the CC. The return-flux of the CC goes into the UM and IR (Figs. 407 408 1 and 7). Because the isolation time of the recycled material in the IR is ~1 Gyr before mixing into the LM, there is effectively no incoming flux of recycled CC into the LM until 1 Gyr after 409 core formation (~3.5 Ga). Even thereafter, the effect on $\mu^{182}W_{LM}$ is minimal owing to the small 410 411 amount of W in the recycled crust relative to the large amount of W in the LM. Hence, the LM 412 maintains a 'near-primitive' composition and thus evolves similarly to the BSE until the end of the late accretion period (3.8 Ga), and subsequently maintains a μ^{182} W ~0 (for all four core 413 414 formation periods).

415 The CC is formed mostly by the mass flux from the UM (Fig. 1, section 2.1), and thus only 416 little W is left in the UM leading to high Hf/W_{UM} values ($D_W > D_{Hf}$). Consequently, the UM is 417 very sensitive to the addition of LAM, which changes its $\mu^{182}W_{UM}$ more easily than that of any 418 other reservoir. In fact, the UM retains so little W after the core formation that the addition of 419 small amounts of LAM overwhelm the otherwise increasing $\mu^{182}W_{UM}$ due its high Hf/W_{UM}, 420 resulting in $\mu^{182}W_{UM} < 0$ in the Archean (Fig. 7).

- There are two ways to counteract the evolving $\mu^{182}W_{UM} < 0$ in our model: (1) adding less LAM and (2) recycling crust (CC) with $\mu^{182}W_{UM} > 0$. Increasing the recycling flux of the CC into the UM relative to the IR by varying the parameter f_R (from 0.1 to 0.9, section 2.1) results in a less negative $\mu^{182}W_{UM}$ in the Archean (Fig. 7). But the effect is limited due to the relatively small mass of the CC at this time, and thus the small amount of W recycled into the UM. Therefore, the only way to counteract the negative $\mu^{182}W_{UM}$ is by non-uniform addition of LAM to the UM and LM, that is, by heterogeneous addition of the LAM to Earth's mantle.
- 428

429 **3.4.2 Heterogeneous late accretion**

Figure 8 shows the ¹⁸²W evolution in the different modeled silicate reservoirs when the 430 LAM is added linearly, but non-uniformly, to both the UM and LM for a core formation period 431 432 of 45 Myr, and late accretion until 3.8 Ga (model results for core formation periods of 30, 60 433 and 100 Myr are shown in Figures S4-S7). Adding only a small fraction (2%) of the total amount of LAM to the UM (and the remainder to the LM) leads to positive $\mu^{182}W_{UM}$ values at 434 435 the beginning of the late accretion period (Figs. 8 and 9). Geodynamically, this corresponds to 436 a scenario where parts of a progressively depleting mantle (the modeled UM) receive less LAM than other parts of the mantle (e.g., the LM in our model). The scenario where the UM receives 437 only 2% of the total amount of LAM and the remaining 98% goes into the LM (Fig. 8) 438 successfully reproduces the $\mu^{182}W_{UM}$ target range, i.e., the observed range of $\mu^{182}W \sim +10-15$ 439 of most Archean rocks. 440

441 The key parameters for achieving a successful solution shown in Fig. 8 are the non-uniform mixing of LAM into the mantle, and the recycling of CC with $\mu^{182}W$ >0. Addition of recycled 442 crust with high μ^{182} W to the UM results in a significant increase in the μ^{182} W_{UM} in the Archean 443 (Fig. 8). The kink in the μ^{182} W_{UM} evolution observed immediately after the end of late accretion 444 445 at 3.8 Ga in Fig. 8 marks the effect of crustal recycling, which becomes more pronounced after the end of late accretion and protracts the time interval of $\mu^{182}W_{UM}$ ~+10–15 until the end of 446 Archean. Hence, a balance between the addition of LAM with $\mu^{182}W < 0$ (-190) and recycling 447 of CC with μ^{182} W >0 is essential for maintaining a near-constant μ^{182} W ~+10–15 in the UM 448 over the entire duration of the Archean. Progressive interaction of crust and mantle afterwards 449 slowly homogenizes μ^{182} W in the crust and mantle reservoirs resulting in a steady decrease of 450 μ^{182} W in the CC and UM (and increase in LM) from ~+10–15 since the Archean towards the 451 present $\mu^{182}W_{BSE} = 0$. 452

However, maintaining $\mu^{182}W_{UM}$ in the range of +10 to +15 requires that the total amount 453 of LAM added to the UM is comparatively small (2% of the total flux, Fig. 8). But even then, 454 455 $\mu^{182}W_{UM}$ is between +10 and +15 only for a short time-period between 3.8 and 3.5 Ga if the default mantle-crust transfer coefficient D_w of 200 is used (Fig. 9a). Prolonging the time 456 interval of $\mu^{182}W_{UM} \sim +10$ and +15 therefore also requires a higher W flux to the crust, resulting 457 in a higher Hf/W ratio in the UM, and consequently, an increased W flux with positive μ^{182} W 458 back into the UM. Such a higher W flux to the crust is simulated by increasing the mantle-crust 459 $D_{\rm W}$ from 200 (Fig. 9a) to ~400, and is used for the models shown in Figure 8 and 9b, which 460 reproduce the target range of $\mu^{182}W_{UM} \sim +10-15$ in the Archean. Similar ¹⁸²W evolution 461

462 patterns in mantle reservoirs are also observed for core formation periods of 30 Myr (Fig. S5),

463 60 Myr (Fig. S6), and 100 Myr (Fig. S7).

Adding a larger fraction of the total amount of LAM to the UM, for example 10%, leads to a steep decline from $\mu^{182}W_{UM} >+20$ at the beginning, to ~0 at the end of the late accretion period at 3.8 Ga, which is shown in Fig. 9a for a D_W of 200. Increasing the D_W from 200 to 400 in this case does not compensate for the $\mu^{182}W_{UM} \sim 0$ at the end of the late accretion period (not shown), and thus such a larger fraction of LAM to the UM cannot reproduce the target range of $\mu^{182}W \sim +10$ to +15 in the UM.

470

471 **3.4.3 Variable rates of late accretion**

472 Positive $\mu^{182}W_{UM}$ between ~+10 to +15 in Archean rocks require a mantle reservoir that 473 receives only a small fraction of the total LAM, which in our model is the UM. How the LAM 474 is distributed per time interval, i.e., the rate of late accretion, only has a second-order effect on 475 the $\mu^{182}W$ evolution of the UM.

476 Several different scenarios are explored (Fig. 6), for example a high flux initially or late, which simulates accretion of single large bodies. In case of a high flux early in the late accretion 477 period, 90% of the total amount of LAM is added non-uniformly to the mantle in the first 100 478 Myr after the core formation, whereas the remaining 10% is added to the mantle thereafter until 479 3.8 Ga (from the total, 2% added to UM and 98% to the LM as in Fig. 8). In this case, $\mu^{182}W_{UM}$ 480 decreases from values >+25 to values <+10 in the time interval between 4.0 and 2.5 Ga (Fig. 481 482 6c) and therefore does not reproduce the target range of +10 to +15 in this time-period. For 483 delayed late accretion or a high flux towards the end of the late accretion period, only 10% of 484 the total amount of LAM is added to the mantle until 3.9 Ga and the remaining 90% of the material is added in the last 100 Myr of the late accretion period between 3.9 and 3.8 Ga. In 485 486 this case, the $\mu^{182}W_{UM}$ suddenly decreases from +26 at 3.9 Ga to ~0 at 3.8 Ga (Fig. 6c), but thereafter increases towards a positive value due to addition of recycled crust with $\mu^{182}W > 0$, 487 488 and maintains $\mu^{182}W_{UM} \sim +10-15$ only for the second half of the late accretion period.

These results show that reproducing the observed excess ¹⁸²W in Archean rocks requires 489 490 uneven distribution of the LAM between different mantle reservoirs, that is, heterogeneous rather than homogeneous late accretion. Although the rate of late accretion also influences the 491 μ^{182} W evolution of the silicate reservoirs, the mass fluxes associated with concurrent crust 492 formation and recycling back into the mantle dominate the W distribution and therefore 493 determine how sensitive the ¹⁸²W isotope evolution of the crust and different mantle reservoirs 494 is to the amount of LAM in each time interval (Fig. 6). The most plausible $\mu^{182}W_{UM}$ evolution 495 that reproduces the observed $\mu^{182}W \sim +10-15$ from ca. 4.0 to 2.5 Ga in Archean rocks is for 496 497 addition of only ~2% of the total amount of LAM to the UM with a constant late accretion rate, 498 and the remainder going to the LM (Fig. 6).

499

500 **3.5** ¹⁴⁶Sm⁻¹⁴²Nd isotopic evolution

501 Samarium and Nd are lithophile elements, and thus the ¹⁴²Nd/¹⁴⁴Nd and ¹⁴³Nd/¹⁴⁴Nd isotope 502 evolution is not affected by core formation. The model results for various core formation 503 periods therefore represent the initiation of silicate differentiation at different times after solar

- 504 system initial (Fig. 10, Fig. S8). The μ^{142} Nd evolution in all the terrestrial reservoirs in our 505 model is also not affected by late accretion, because the Sm/Nd (146 Sm/ 144 Sm, 147 Sm/ 144 Sm, 506 and 147 Sm/ 144 Nd) of the late accreted material (Supplementary Table S4) and the mantle are 507 assumed to be chondritic and contribute only a negligible amount of the BSE's Sm-Nd budget. 508 Therefore, deviations from μ^{142} Nd $\neq 0$ in the presented model result from silicate differentiation 509 only, that is, incompatible element depletion and enrichment of the various mantle reservoirs 510 (UM, LM, IR) in response to formation and recycling of the CC.
- Assuming the same model parameters that reproduced the ¹⁸²W isotopic evolution in the 511 mantle (Fig. 8) and assuming the same D_{Sm} and D_{Nd} values adopted by Kumari et al. (2016 and 512 2019) that successfully reproduced the long-lived 147 Sm $-{}^{143}$ Nd systematics, the μ^{142} Nd of all 513 modeled mantle reservoirs remains within the range of the present BSE composition (Fig. 10a, 514 Fig. S8; μ^{142} Nd_{BSE} = 0 ± 5.6; e.g., Rizo et al., 2013). In contrast, μ^{142} Nd in mantle-derived 515 516 rocks reach a maximum value of +17.5 by the end of the Hadean (4.0 Ga, Rizo et al., 2013) and +11 by the end of the Eoarchean (3.6 Ga, Saji et al., 2018). These positive ¹⁴²Nd anomalies 517 in mantle-derived rocks generally disappear after ~ 2.5 Ga, suggesting homogenization of ¹⁴²Nd 518 signatures in Earth's mantle by the end of the Archean (e.g., Caro, 2011; Rizo et al. 2013, 519 520 Carlson et al., 2019), similar to what is observed for the ¹⁸²W evolution (Rizo et al., 2016; Mundl et al., 2018; Rizo et al., 2019). 521
- One way to achieve positive μ^{142} Nd values in the presented model, similar to what is 522 523 observed in Archean mantle-derived rocks, is to restrict the recycling flux from the CC to the UM. Less recycling of CC into the UM should lead to more positive $\mu^{142}Nd_{UM}$. However, 524 crustal recycling during the Hadean and Archean is essential for reproducing the ¹⁴³Nd isotopic 525 evolution in our previous studies (Kumari et al., 2016, 2019), in good agreement with the 526 527 results of Jones et al. (2019) and Rosas and Korenaga (2018). It is also required to maintain the $\mu^{182}W_{UM} \sim +10-15$ during the entire Archean (Section 3.2). Producing significantly positive 528 μ^{142} Nd_{UM} values by restricting the recycling flux to the mantle reservoirs in the model is 529 530 therefore problematic.
- 531 Another parameter that affects the extent of Nd depletion in the UM is its relative mass 532 ($m_{\rm UM}$). The mass of the UM in the presented model increases to ~60% of the entire mantle at present (i.e., $m_{\rm UM} = 0.6$). This is consistent with the mass-balance of heat producing elements 533 (Turcotte et al., 2001; Arevalo et al., 2013) and the mass flux from the LM to the UM in our 534 535 model, which is scaled to match the present plume flux (see Kumari et al., 2016, 2019 for a more detailed discussion of this aspect). The long-lived isotope systematics evaluated in our 536 earlier models (Kumari et al., 2016, 2019), however, allow for some flexibility in the present 537 538 value for the $m_{\rm UM}$. Decreasing the present $m_{\rm UM}$ value but maintaining the same rate of crustal growth (see section 2.1, Kumari et al., 2016, 2019) effectively leads to the extraction of the 539 540 same amount of CC from a relatively smaller fraction of the UM, and thus greater depletion of Nd in the UM. For example, decreasing $m_{\rm UM}$ from 0.6 to 0.4 considerably changes the evolution 541 of μ^{142} Nd and ϵ^{143} Nd in the UM, CC, and IR, but leads to a negligible change in the LM for 542 543 silicate differentiation starting 45 Myr after Earth formation (Fig. 10b and Fig. S9). Compared to $m_{\rm UM} = 0.6$, assuming $m_{\rm UM} = 0.5$ results in a $\mu^{142} \text{Nd}_{\rm UM}$ of +3.6, and a higher $\mu^{142} \text{Nd}_{\rm UM}$ of 544 +5.6 during the Hadean (Fig. 10b). Although μ^{142} Nd_{UM} of +11.5 is achieved in the Hadean for 545

546 $m_{\rm UM} = 0.4$, $m_{\rm UM} < 0.5$ cannot reproduce the ¹⁸²Hf–¹⁸²W systematics in our model, which limits 547 the plausible values for $m_{\rm UM}$. For $m_{\rm UM} = 0.5$, but slightly higher $D_{\rm Sm}$ and $D_{\rm Nd}$ values than 548 assumed by Kumari et al. (2016; Fig. 10a-b; Table 3 case I), our model generates a μ^{142} Nd_{UM} 549 of ~ +11 by the end of the Hadean and Eoarchean (Fig. 10c, Table 3 case II). The resulting 550 ϵ^{143} Nd evolution in the terrestrial reservoirs also satisfies the present constraints (Fig. S9; Table 551 3).

552 Interestingly, varying the residence time of recycled CC in the IR from 10 Myr to 5000 553 Myr, and therefore mimicking either complete mixing of the recycled crust with the LM or the formation of an isolated crustal reservoir, leads to no significant variation in the μ^{142} Nd of the 554 crust and mantle reservoirs, except for the latter case where the IR evolves to a present μ^{142} Nd 555 of ~ -10 (Fig. 10a). These results are in principal agreement with the mass balance discussed 556 557 by Boyet and Carlson (2005), who concluded that an early-formed, and subsequently isolated crustal reservoir must be much more incompatible element enriched than the current 558 559 continental crust (the CC reservoir in our model) or, almost the entire mantle must have been involved in Hadean crust formation to develop μ^{142} Nd $\neq 0$ of the accessible silicate Earth. 560

561

562 **4. DISCUSSION**

563 **4.1 Constraints on the rate of core formation**

In our model, different mass and associated W flux rates to the core are achieved by changing the bulk silicate-metal transfer factor, $D_{W,silicate-metal}$ (Table 4 and Table S5). These different W flux rates to the core determine the pre-late accretion $\mu^{182}W_{BSE}$, W_{BSE} , and Hf/ W_{BSE} values for different core formation periods and have the principal control on the amount of LAM necessary to evolve to $\mu^{182}W_{BSE} = 0$ (section 3.1).

569 In previous models (e.g., Halliday et al., 1996; Harper and Jacobsen, 1996; Kleine et al., 2004; Rudge et al., 2010; Fischer and Nimmo, 2018), the $\mu^{182}W_{BSE}$, W_{BSE} , and Hf/ W_{BSE} values 570 571 at the end of core formation are regulated by several parameters during early accretion and core 572 formation processes. Other than the duration of core formation, these are the rate of accretion, 573 the type of accreting material (differentiated or undifferentiated bodies), the extent of metal-574 silicate equilibration of the accreting (differentiated) material, and the partitioning of W 575 between metal and silicate. None of these parameters, however, is well constrained. A wide 576 range of underlying parameters (e.g., accretion rate, metal silicate equilibration rate, accretion 577 of differentiated or undifferentiated bodies), and thus early accretion and core formation 578 scenarios is therefore compatible with the isotopic constraints (Rudge et al., 2010). But any 579 combination of these diverse parameters effectively sets the W concentration (Hf/W ratio) and μ^{182} W of the BSE at the end of core formation. Although simplified, the same result is achieved 580 in our model by varying the bulk silicate-metal transfer factor for W ($D_{W,silicate-metal}$), which 581 582 effectively allows investigating a wide range of core formation scenarios.

Notably, the $D_{W,silicate-metal}$ used in our model is different from the W partition coefficient between metal and silicate ($K^d_{W,metal/silicate}$). However, our model-derived concentrations in the core and BSE (Table 2) can be used to calculate an effective $K^d_{W,metal/silicate}$ for variable core formation periods, and core formation scenarios. Assuming linear core growth, the calculated $K^d_{W,metal/silicate}$ is 11.5 for $t_{CF} = 30$ Myr, 23 for $t_{CF} = 45$ Myr, 46 for $t_{CF} = 60$ Myr, and 331 for

 $t_{\rm CF} = 100$ Myr (see supplementary material section 1). In comparison, the $K^d_{\rm W,metal/silicate}$ inferred 588 in previous studies ranges from ~17 to ~200 (Wade and Wood, 2005; Kleine and Walker, 589 2017). Therefore, although the $D_{W,silicate-metal}$ in our model is essentially a free parameter 590 591 allowing for a wide range of possible core formation scenarios, calculating $K^{d}_{W,metal/silicate}$ values from the W concentrations in the core and BSE at the end of core formation allows comparing 592 593 our model results to those of more complex core formation models, and thus narrowing down 594 the plausible range of scenarios. Assuming linear core growth, for example, the calculated $K^{d}_{W.metal/silicate}$ values are in good agreement with literature values (Wade and Wood, 2005; 595 Kleine and Walker, 2017) for $t_{CF} \sim 30-80$ Myr (see more detailed discussion in the 596 597 supplementary materials).

Hence, the key parameters that determine the $\mu^{182}W_{BSE}$, W_{BSE} , and Hf/ W_{BSE} values at the end of core formation in our, and previous more elaborate core formation models, are the timing and rate of core formation and associated W flux to the core (Table 4). The continuous, linear core formation rate used in our default model is considered a median case. In this case, core formation times between 40-60 Myr result in W_{BSE} and Hf/ W_{BSE} values within the estimated range ($W_{BSE} = 13 \pm 10$, Arevalo and McDonough, 2008; Hf/ $W_{BSE} = 17 \pm 5$, Kleine et al., 2009; Table 4, Fig. 11).

605 The W_{BSE} (Hf/W_{BSE}) at the end of core formation, however, depends more strongly on the 606 rate rather than the total duration of core formation (section 3.1 and 3.2; Fig. 11). The W_{BSE} (and $\mu^{182}W_{BSE}$) increase and the Hf/W_{BSE} decrease for progressively larger W flux rates to the 607 608 core early during a given core formation period (Fig. 3 and 11). Even for a core formation time 609 of 100 Myr, where the W_{BSE} is excessively low (and thus Hf/W_{BSE} unrealistically high) for a 610 linear core formation rate (Table 4; Fig. 11), W_{BSE} and Hf/W_{BSE} within the range of current 611 estimates can thus be found by varying the core formation rate. If more than 50% of the W is 612 transferred to the core within the first 30 Myr of the 100 Myr core formation period, for example, the resulting W_{BSE} and Hf/W_{BSE} are within the range of current estimates (Table S5; 613 614 Fig. 11). There is a limit, however, on the rate of early core formation. Models where 90% of the W goes into the core in the first 10 Myr of core formation all have very similar, but 615 616 excessively high W_{BSE} (low Hf/W_{BSE}) independent of the total duration of core formation 617 (Table 4; Fig. 11).

Overall, therefore, it is mostly the rate of core formation, rather than the total duration of 618 core formation that influences the $\mu^{182}W_{BSE}$, W_{BSE} , and Hf/W_{BSE} values at the end of core 619 formation. The W_{BSE} is very sensitive to this effect, and becomes much lower (Hf/W_{BSE} higher) 620 621 if a large fraction of the W is transferred to the core in the second half of a given core formation 622 period. Compare, for example, the W_{BSE} (Hf/W_{BSE}) for variable rates of core formation for t_{CF} 623 = 100 Myr in Table S5 and Fig. S3. Hence, single events, for example a giant impact, which cause large, sudden mass fluxes to the core also have a large influence on the $\mu^{182}W_{BSE}$, W_{BSE} , 624 and Hf/W_{BSE} values at the end of core formation. Such scenarios are captured by our models 625 626 where 90% of the W enters the core in the first or last 10 Myr of core formation (Table 4). Excessively high W_{BSE} (low Hf/W_{BSE}) result for rapid early core growth, and low W_{BSE} (high 627 Hf/W_{BSE}) for late core growth, independent of the duration of core formation. A giant impact 628

shortly before the end of a 100 Myr (or longer) core formation period, for example, is therefore
difficult to reconcile with current estimates of the W_{BSE} and Hf/W_{BSE} values (Table 4; Fig. S3).
Overall, the discussion above shows that more precise constraints on W_{BSE} would provide
tighter constraints on several key, but largely unconstrained processes, such as the duration and
rate of core formation, the timing of a giant, moon-forming impact during the pre-late accretion
phase, but also the amount of late accreted material, as discussed in the following.

635

636 **4.2 Constraints on the amount and type of late-accreted material**

Addition of variable amounts of LAM decreases the $\mu^{182}W_{BSE}$ to 0 by the end of the late 637 accretion period (3.8 Ga, Fig. 4). As discussed in sections 3.2 and 4.1 and shown in Figs. 3-5 638 639 (Table 4), the amount of LAM depends mostly on the W_{BSE} at the end of core formation. For the default linear core formation model, W_{BSE} at the end of core formation (38-1.5 ppb) and 640 641 the amount of LAM (1.9-0.07%) decreases with increasing duration of core formation (Figs. 3 and 4; Table 4). However, the rate of core formation has a large influence on the W_{BSE} 642 643 (Hf/W_{BSE} and μ^{182} W_{BSE}) at the end of core formation and thus also the amount of LAM inferred from the ¹⁸²W systematics. Consequently, an even larger range of W_{BSE} (68–0.09 ppb) and 644 645 amount of LAM (3.4-0.004%) results, even for a fixed duration of core formation (e.g., 100 646 Myr), but variable rates of core growth (or rate of W transfer to the core, Table 4, Table S5; 647 Fig. S3).

Nevertheless, the amount of LAM inferred from the ¹⁸²W isotope systematics in our model 648 649 (Table 4; Fig. 4) is generally in good agreement with HSE-based estimates. However, the rate of core formation and the amount of LAM are mutually dependent on W_{BSE}, that is, estimates 650 of the amount of LAM based on ¹⁸²W isotope constraints are only possible for a given rate and 651 overall duration of core formation. Because a wide range of (early accretion and) core 652 formation scenarios in our and previous models (e.g., Halliday et al., 1996; Harper and 653 Jacobsen, 1996; Kleine et al., 2004; Rudge et al., 2010; Fischer and Nimmo, 2018) are 654 655 compatible with current constraints on W_{BSE} (13 ± 10, Arevalo and McDonough, 2008) and Hf/W_{BSE} (17 \pm 5, Kleine et al., 2009), the ¹⁸²W isotope systematics alone do not allow tight 656 657 constraints on the amount of LAM (Fig. 5), until more precise estimates of the W_{BSE} become 658 available.

659 Notably, the amount of LAM inferred from our model (Table 4; Fig. 4) is derived for a 660 single composition of the LAM (section 2.4). Considering variability in the W concentration 661 and/or isotope composition of the late accreted material, for example by accreting differentiated 662 versus undifferentiated bodies, certainly influences the amount of LAM, but only within the 663 bounds set by the core formation (and early accretion) processes (section 3.2). Late accretion contributes only ~7-13% of the W budget of the BSE in our models (Table 4), which is 664 665 consistent with other estimates (e.g., Kleine and Walker, 2017). The present elemental and ¹⁸²W budget in the silicate Earth (W_{BSE} and $\mu^{182}W_{BSE}$) is therefore mostly set during the pre-666 late accretion phase. Considering variability in the type of LAM (e.g., differentiated vs. 667 undifferentiated bodies) is thus certainly important, especially for reconciling constraints on 668 the amount and type of LAM from the HSE budget and the ¹⁸²W isotope evolution, but is of 669

subordinate importance for constraining the amount of LAM from the ¹⁸²W isotope constraints
 alone.

The effect of differentiated (e.g., Marchi et al., 2018) versus undifferentiated (as assumed 672 673 in our modeling study) nature of late accreting bodies on the Hf-W isotopic evolution of Earth needs to be evaluated. In order to be compatible with the HSE, Re-Os, and moderately-volatile-674 675 chalcophile element (e.g., Se-Te) constraints, Kruijer et al. (2015) suggest a carbonaceouschondrite-like LAM composition with a minor fraction of iron-meteorite-like material. Note 676 that our bulk-Earth-like LAM μ^{182} W and W concentrations are similar to Kruijer et al. (2015). 677 Different chondrite groups have very similar μ^{182} W and W concentrations (e.g. Kleine et al., 678 679 2004) and chondrites constitute 80% of the mix of LAM favored by Kruijer et al. (2015). The 680 μ^{182} W and W concentrations of the LAM vary mainly by changing the proportion of chondrite to iron meteorite (IV A group has 10 times higher W and $\mu^{182}W = -350$). But because of the 681 682 fractionated HSE patterns of the iron meteorites, there is limited flexibility on the chondrite/iron meteorite ratio (Day et al., 2016; Walker et al., 2008; McCoy et al., 2011). 683 Therefore, the associated variation in bulk μ^{182} W and W compositions of the LAM is 684 comparatively small and has a second-order effect on the amount of LAM and thus the $\mu^{182}W$ 685 686 evolution of the silicate Earth during the late accretion phase.

However, if a large fraction of the LAM were differentiated material (Marchi et al., 2018), 687 the bulk μ^{182} W and W composition of the accreted differentiated material could change 688 689 significantly depending on how much of the impactor's core was retained in (or equilibrated 690 with) Earth's mantle. According to simulations by Marchi et al. (2018), ~20-70% of the impactor's core are retained in Earth's mantle depending on impactor's size, angle and velocity. 691 692 Taking μ^{182} W and W compositions of core and mantle of impacting differentiated body from Marchi et al. (2018), the bulk impactor composition changes considerably, ranging from $\mu^{182}W$ 693 = +26 and W = 45 ppb for retaining 20% of the impactor's core to $\mu^{182}W = -163$ and W = 120 694 ppb for retaining 70% of the impactor's core, the latter is similar to our LAM. Thus, depending 695 696 on the composition of impactors, its size, and impact conditions, late accretion of differentiated bodies may introduce much more heterogeneous material with respect to $\mu^{182}W$ and W 697 698 composition than accreting undifferentiated bodies. In this case the effect of late accretion on μ^{182} W and W composition of Earth is difficult to predict due to an enormous range of free 699 parameters (impactor's size, fraction core retained, impact conditions, etc.) and thus any 700 701 modeled scenario would be highly speculative. We did not include any specific model of 702 differentiated impactor for this reason. Moreover, metal distribution and/or metal-silicate 703 equilibration may be limited to localized domains (Marchi et al., 2018, Maas et al., 2021) and create considerable (transient?) heterogeneity in μ^{182} W with either higher or lower μ^{182} W than 704 705 the terrestrial mantle at the time of impact.

706

707 **4.3 Impact of present pre-late accretion** $\mu^{182}W_{BSE}$ on the amount of late-accreted material

Varying the assumed present, pre-late accretion value of $\mu^{182}W_{BSE} = +25$ influences the modeled $\mu^{182}W$ evolution of the BSE. This value is estimated by subtracting LAM from the present BSE with $\mu^{182}W_{BSE} = 0$ (e.g., Kruijer et al., 2015; Touboul et al., 2015). With a mass and composition of the LAM constrained by the HSE systematics (e.g., Day et al., 2007; Walker, 2009; Fischer-Gödde and Becker, 2012), and current estimates for the W_{BSE} (Arevalo and McDonough, 2008), the resulting present pre-late accretion $\mu^{182}W_{BSE}$ varies between +10 and +40 (Kruijer et al., 2015; Touboul et al., 2015).

- A different present pre-late accretion $\mu^{182}W_{BSE}$ leads to a different ¹⁸²W evolution of the 715 BSE. As discussed in detail in sections 3.1 and 3.2, the latter is controlled by the parameters 716 listed in equation (2). That is, the $\mu^{182}W_{BSE}$ at t_{CF} ($^{182}W/^{184}W_{BSE, tCF}$), as well as the Hf/W_{BSE} 717 and $^{182}\text{Hf}/^{180}\text{Hf}$ at t_{CF} . These parameters, and thus the present pre-late accretion value for 718 $\mu^{182}W_{BSE}$, are controlled by the rate and duration of core formation (and early accretion). The 719 ratio 182 Hf/ 180 Hf is entirely controlled by time, i.e., the duration of core formation (t_{CF}), whereas 720 the $\mu^{182}W_{BSE}$ and Hf/W_{BSE} at t_{CF} are mostly influenced by the rate of core formation. Because 721 722 Hf/W_{BSE} is determined by W_{BSE}, which is the main parameter that controls the amount of LAM, 723 a different ¹⁸²W evolution of the BSE also affects the amount of LAM (sections 3.1 and 3.2). Early rapid rates of core growth for a given t_{CF} , for example, lead to high $\mu^{182}W_{BSE}$ at t_{CF} , but 724 725 low Hf/W_{BSE} due to high W_{BSE} (Table 4). Achieving higher present, pre-late accretion μ^{182} W_{BSE} in this way therefore requires larger amounts of LAM to decrease μ^{182} W_{BSE} to 0 (and 726 727 vice versa). Several quantitative examples, showing to what extent the amount of LAM is affected by different ¹⁸²W_{BSE} evolution resulting from variable present pre-late accretion 728 μ^{182} W_{BSE} values are given in the supplementary material (Tables S6 and S7). These examples 729 show that the amount of LAM is affected considerably by assuming a different ¹⁸²W_{BSE} 730 evolution, but on a similar order as by varying the duration and rate of core formation. Hence, 731 the interdependency of $\mu^{182}W_{BSE}$ and Hf/W_{BSE} (W_{BSE}) at t_{CF} on the amount of LAM make it 732 impossible to constrain the amount of LAM from the ¹⁸²Hf-¹⁸²W isotope systematics alone 733 734 without constraining the duration and rate of core formation. Figure 12, for example, shows that even for a given amount of LAM, e.g., constrained by the HSE systematics, a given value 735 for W_{BSE} (Hf/W_{BSE}), as well as present pre-late accretion $\mu^{182}W_{BSE}$, the ${}^{182}Hf^{-182}W$ isotope 736 systematics are compatible with a range of $\mu^{182}W_{BSE}$ at t_{CF} , i.e., principally permit many 737 738 possible combinations of duration and rate of core formation (Fig. 12; Table 4; cf. Rudge et al., 2010). Notably, this large possible range of μ^{182} W_{BSE} at the end of core formation (cf. Halliday 739 740 et al., 1996; Harper and Jacobsen, 1996; Kleine et al., 2004) complicate constraining the ¹⁸²Hf-¹⁸²W evolution of the Earth-Moon system even for tight constraints on the initial lunar 741 742 μ^{182} W value (cf. Kruijer et al., 2015; Touboul et al., 2015; Kruijer and Kleine, 2017; Maurice 743 et al., 2020).
- 744 Owing to the interdependency and considerable uncertainty of the present pre-late accretion $\mu^{182}W_{BSE}$, W_{BSE} (Hf/W_{BSE}), and the amount of LAM (sections 3.1 and 3.2), the ¹⁸²Hf-¹⁸²W 745 evolution of the Earth-Moon system remains underdetermined. Reducing the uncertainty on 746 747 the present W_{BSE} (13 ± 10, 2SD; Arevalo and McDonough, 2008) however, would narrow down 748 the target range for W_{BSE} (Hf/W_{BSE}) of core formation models, and thus also the present, prelate accretion $\mu^{182}W_{BSE}$ value, and would also allow constraining the amount of LAM more 749 precisely. Deriving more precise constraints on the present W_{BSE} therefore, is key for improving 750 our understanding of core formation processes, and the ¹⁸²Hf-¹⁸²W evolution of the Earth-751 752 Moon system.

753 **4.4 The rate and style of late accretion and its admixing to the mantle**

Archean komatiites (4.0 to 2.4 Ga) with variable HSE abundances (~50-65%) relative to 754 the modern mantle have μ^{182} W roughly between +10 and +15 (Willbold et al., 2011, 2015; 755 756 Touboul et al., 2012; Rizo et al., 2016; Dale et al., 2017; van de Löcht et al., 2018). The 3.55 Ga Schapenburg komatiites are an exception with μ^{182} W of -8.4 ± 4.5 (2SD) and lower HSE 757 758 abundances than the modern mantle (Puchtel et al., 2016). Similarly, a recent study by Puchtel et al. (2020) reported a μ^{182} W of ~ -10 for the source of ~2.05 Ga old Jeesiörova and Kevitsa 759 komatiites from the Central Lapland Greenstone Belt, Finland, which seemingly derived from 760 761 a source containing $\sim 120 \pm 5\%$ of HSE budget of the present BSE. However, the long-lived 762 radiogenic isotope systematics of most Archean komatiites and post-Archean mantle-derived basalts generally indicate derivation from a variably incompatible element depleted mantle 763 (e.g., ε^{143} Nd ≥ 0), and thus our model simulations aimed for a range of μ^{182} W_{UM} of +10 and +15 764 765 between 4.0 and 2.5 Ga in the modeled UM reservoir (e.g., Fig. 8).

766 For homogeneous late accretion, none of the modeled mantle reservoirs achieve the target range of μ^{182} W ~+10 to +15 in the mantle between 4.0 and 2.5 Ga (section 3.2). Adding LAM 767 to both the UM and LM in the same relative proportions for a period of 760 Myr (until 3.8 Ga) 768 results in $\mu^{182}W_{UM} < 0$ throughout the Archean for core formation periods of 30–100 Myr (Fig. 769 770 7). This corresponds to a geodynamic scenario where the LAM was quickly distributed and homogenized throughout the entire mantle (uniform mixing) until the end of the abundant lunar 771 cratering period (e.g., Tera et al., 1974; Kring and Cohen, 2002). In this scenario, $\mu^{182}W_{UM} < 0$ 772 takes until after 2.0-1.5 Ga to dissipate and approach μ^{182} W ~0 (Fig. 7). In the LM reservoir, 773 μ^{182} W values >>15 result before 3.8 Ga and steeply decrease to ~0 in the early Archean, and 774 775 thereafter remain nearly constant until the present (Fig. 7). But the modeled LM retains μ^{142} Nd and ε^{143} Nd ~0 (Fig. 10 and Fig. S8 and S9), and thus could only explain Archean komatiites 776 with μ^{182} W >0, but μ^{142} Nd ~0 and ϵ^{143} Nd ~0 before ~3.5 Ga (e.g., Willbold et al., 2011, Rizo 777 et al., 2016; Archer et al., 2019) or μ^{182} W ~0 and μ^{142} Nd = ϵ^{143} Nd ~0 after ~2.5 Ga (Rizo et al., 778 779 2013; Mundl et al. 2018; Rizo et al., 2019).

Therefore, maintaining $\mu^{182}W_{UM}$ in the range of +10 to +15 requires that the total amount of LAM added to parts of the mantle, the UM in our model, is comparatively small (2% of the total late accretion flux, Fig. 8). This corresponds to a geodynamic scenario where the impactors are not efficiently homogenized within the entire mantle but are distributed and/or equilibrated with only parts of the mantle, similar to what has been suggested by ¹⁸²W studies of Archean rocks (Willbold et al., 2011; 2015; Dale et al., 2017; Archer et al. 2019).

Variable flux rates of LAM in different time intervals during the entire late accretion period 786 (early rapid, delayed or linear fluxes) also affect the evolution of $\mu^{182}W_{UM}$ (Fig. 6). A large flux 787 early in the late accretion period fails to produce the $\mu^{182}W_{UM}$ of +10 to +15 for a prolonged 788 789 time period, but either a delayed or linear late accretion model (or a constant flux of late accretion to mantle) successfully reproduce the $\mu^{182}W_{UM}$ of +10 to +15 from 4 to 2.5 Ga (Fig. 790 6c). Although the rate of late accretion therefore influences the μ^{182} W evolution of the silicate 791 792 reservoirs, the mass fluxes associated with concurrent crust formation and recycling back into 793 the mantle dominate the W distribution and thus the ¹⁸²W isotope evolution of the crust and 794 different mantle reservoirs (compare Fig. 6b, c and d).

795 **4.5 Timing of early silicate differentiation**

796 Observed μ^{142} Nd excesses in Archean komatiites are crucial evidence for the onset of mantle depletion in response to crust formation in the Hadean. The ubiquitous presence of 797 798 μ^{142} Nd excess (μ^{142} Nd ~+15) in 3.8–3.7 Ga old rocks from the Isua Supracrustal Belt suggests that the source mantle must have acquired this ¹⁴²Nd excess during the Hadean, implying 799 800 silicate differentiation starting ~4.5 Ga (Caro et al., 2006; Boyet and Carlson, 2006; Bennett et al., 2007; Rizo et al., 2011, 2013; Rizo et al. 2016; O'Neil et al., 2016; Saji et al., 2018). Similar 801 ¹⁴²Nd excess (μ^{142} Nd: +5 to +15) are also identified in other ancient terrains such as the Yilgarn 802 Craton in Western Australia (3.7 Ga; Bennett et al., 2007) and the Abitibi Greenstone Belt in 803 804 Canada (2.7 Ga; Debaille et al., 2013).

805 However, the model parameters that successfully reproduce the nearly constant target ¹⁸²W signatures in the UM do not result in significant μ^{142} Nd excesses in the modeled UM (Fig. 806 10a), which would be required to explain the combination of $\mu^{182}W \sim +10-15$ and $\mu^{142}Nd > 0$ 807 observed in many Archean komatiites (Willbold et al., 2011; Rizo et al., 2016). More positive 808 809 μ^{142} Nd of ~+11 by the end of Hadean can be achieved in the presented model in two ways: (1) increasing the elemental enrichment factors (D_{Sm} and D_{Nd}), thus more efficient transfer of Sm 810 811 and Nd from the UM to the CC and/or, (2) decreasing the fraction of present depleted mantle $(m_{\rm UM})$ from which 90% of the crust is being formed, thus effectively extracting the same 812 amount of CC from a smaller mass of UM. Both parameters are varied such that μ^{142} Nd of 813 ~+11 by the end of Hadean can be achieved. The required D_{Sm} and D_{Nd} (Table 3, case II) and 814 $m_{\rm UM} = 0.5$ are slightly different from the values assumed in Kumari et al. (2016, 2019), but 815 consistent with the ¹⁴³Nd and ¹⁸²W evolution in the crust-mantle system (Figs. 13 and S9). 816 Figure 13, for example, shows the effect of $m_{\rm UM}$ (0.6 \rightarrow 0.5) on the evolution of ¹⁸²W, where 817 the μ^{182} W_{UM} at the end of late accretion is slightly less positive due to addition of same amount 818 819 of LAM for a smaller relative UM mass, but the target +10 to +15 during the Archean is still reproduced (see Fig. S9 for the ¹⁴⁷Sm-¹⁴³Nd evolution). 820

Therefore, both the modeled ¹⁸²Hf-¹⁸²W systematics and ¹⁴²Nd (¹⁴³Nd) data on Archean 821 komatiites require that formation of differentiated crust (low Sm/Nd and Hf/W) and mantle 822 823 (high Sm/Nd and Hf/W) initiated soon after core formation. A delay in silicate differentiation, for example after the first 100 Myr, results in a maximum μ^{142} Nd_{UM} of ~+5 by the end of the 824 Hadean, similar to the present value. Delayed crust formation, particularly after the life-time 825 of ¹⁸²Hf, would also affect the $\mu^{182}W_{UM}$ evolution, because this would limit both the $\mu^{182}W_{CC}$ 826 to less positive values and the amount of crustal return flux into the UM, thus making it difficult 827 to protract the time interval of $\mu^{182}W_{UM} \sim +10$ to +15 for the entire Archean (4.0–2.5Ga). Our 828 model therefore suggests that a significant amount of early crust formation, within the life-time 829 of ¹⁸²Hf, and its subsequent recycling is essential for reproducing the variable, but often 830 decoupled μ^{182} W and μ^{142} Nd signatures in Archean rocks. 831

832 The box-model by Rosas and Korenaga (2018) also indicates rapid continental crust 833 formation in the early Hadean, creating as much as the present volume of continental crust by 834 the end of the Hadean. The extensive mantle depletion in the Hadean, in response to the massive 835 crustal growth in the model of Rosas and Korenaga (2018) produces an average μ^{142} Nd ~+15 in the upper mantle, close to the maximum value measured thus far in Archean rocks (μ^{142} Nd = +17.5; Rizo et al., 2013). If taken as the average of a distribution of values around the mean, the lower average μ^{142} Nd_{UM} ~+11 in our model is in principal agreement with the more positive μ^{142} Nd values observed on some of the Archean rocks, and permit more moderate crustal growth rates in the Hadean compared to the model by Rosas and Korenaga (2018).

841 In general, once the short-lived systems become extinct, recycling of crustal material and 842 its mixing in the convective mantle removes the early-formed isotopic anomalies by the end of 843 the Archean (for ¹⁴²Nd) and drives the ¹⁸²W–¹⁴²Nd isotopic compositions of the crust and 844 mantle reservoirs towards $\mu^{142}Nd_{BSE} \sim 0$ and $\mu^{182}W_{BSE} \sim 0$.

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846 **4.6 Implications for the μ¹⁸²W-μ¹⁴²Nd systematics in Archean rocks**

The reason for decoupling the μ^{182} W and μ^{142} Nd signatures in Archean rocks is that 847 although crust-mantle exchange affects both systems in the same sense, the ¹⁸²Hf-¹⁸²W isotope 848 849 evolution of the BSE is significantly affected by core formation and thereafter modified by late accretion, but the Sm-Nd system is not. In the presented model, the UM has positive values 850 for both μ^{182} W and μ^{142} Nd in the Archean (Fig. 8, Fig. 10c, see also Fig. S4 for core formation 851 times of 30, 60 and 100 Myr), in good agreement with what is observed for the 3.8–3.3 Ga old 852 rocks from the Isua Supracrustal Belt, Greenland (Willbold et al., 2011; Rizo et al., 2016). The 853 μ^{182} W >0 but μ^{142} Nd ≈ 0 for the 3.45–3.3 Ga rocks from Pilbara Craton, Western Australia 854 (Archer et al., 2019), can be explained by a more moderately depleted mantle, which still 855 preserves the positive μ^{182} W (Fig. 8), but develops no significant μ^{142} Nd anomalies (Fig. 10a). 856 A positive μ^{182} W and negative μ^{142} Nd is observed in the modeled CC (Figs. 8 and 10c), 857 suggesting that the μ^{182} W >0 and μ^{142} Nd <0 in the 4.0–3.6 Ga old rocks from the Acasta Gneiss 858 Complex, Canada (e.g., Roth et al., 2014; Willbold et al., 2015; Reimink et al., 2018) are 859 inherited crustal signatures. The coupling of negative $\mu^{142}Nd$ and $\mu^{182}W$ observed in the 3.55 860 Ga old Schapenburg komatiites (Puchtel et al., 2016), are more difficult to explain within the 861 context of the presented model, because no single reservoir has both μ^{142} Nd and μ^{182} W <0 at 862 863 any given time (Figs. 8 and 10). These rocks therefore likely have a more complex, multi-stage history, and perhaps acquired or inherited their μ^{142} Nd and μ^{182} W signatures during different 864 865 phases of their evolution (Puchtel et al., 2016).

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867 **4.7 Implications for μ¹⁸²W deficits in modern OIBs**

Several studies have reported negative $\mu^{182}W$ (-5 to -23) in plume-derived ocean island 868 basalts (OIB, Mundl et al., 2017; Rizo et al., 2019; Mundl-Petermeier et al., 2020). This 869 870 observed ¹⁸²W-depletion in some modern OIBs can be explained within the framework of our model if part of the recycled CC remains isolated for most of Earth's history; see the evolution 871 872 of the IR for an isolation time of 5000 Myr in Fig. 8 and Fig. S4. The IR in our model is essentially a storage container for part of the recycled continental crust. As such, the IR could 873 874 either be perceived as an isolated part of the continental crust, or an isolated reservoir of 875 recycled CC in the mantle, although it is probably difficult to store low-density crust enriched

in incompatible and heat producing elements such as Th, U and K for sufficiently long timeperiods at a mantle boundary layer (e.g., the core-mantle boundary).

878 Nevertheless, for a residence time of the recycled CC in the IR of 5000 Myr, there is no material exchange between the IR and LM, allowing the LM to retain a ¹⁸²W-deficit acquired 879 during late accretion. Consequently, $\mu^{182}W_{LM}$ develops and maintains approximately constant 880 881 values of -6.9 ($t_{CF} = 30$ Myr) and -5.8 ($t_{CF} = 60$ Myr) from the end of late accretion to the 882 present (Figs. 8 and S4), despite significant mass transfer from the LM to the UM (and from 883 the CC to the UM and LM). Hence mantle plumes originating from a mantle reservoir that has 884 received (or equilibrated with) a certain flux of late accreted material but has never incorporated a recycled CC with μ^{182} W >0, could principally have small ¹⁸²W-deficits. Note that the LM in 885 our model represents most of the total mantle, especially in the early Archean. As mass fluxes 886 887 in our model are instantly homogenized within each reservoir, the value for each reservoir at 888 any time should be taken as the average of a distribution of values around the mean. Higher or 889 lower values are therefore implied for each reservoir. Moreover, smaller, natural mantle 890 reservoirs with similar evolution may develop more extreme values than the large reservoirs (or 'boxes') in our model, which may account for the larger range and overall more negative 891 892 μ^{182} W values in OIB compared to the modeled range of μ^{182} W_{LM} in the scenario discussed 893 above.

Alternatively, the ¹⁸²W deficit in young OIBs have been explained by core-mantle 894 895 exchange processes (Rizo et al., 2019; Mundl-Petermeier et al., 2020), which would not require preservation of early-formed ¹⁸²W anomalies in any mantle or crustal reservoir. For example, 896 897 Rizo et al. (2019) suggested that diffusive exchange at the core-mantle boundary or exsolution 898 of W-rich and HSE-poor Si-Mg-Fe oxides from the outer core to the mantle can modify the μ^{182} W of the mantle from +20 to about -20. But this would double the HSE abundances, which 899 900 is inconsistent with the low HSE abundances observed in most OIB with $\mu^{182}W < 0$ (Mundl et 901 al., 2017). Alternatively, Mundl-Petermeier et al. (2020) suggest that equilibration of a (partially) molten silicate layer with the Earth's core could explain the μ^{182} W deficits in OIB 902 903 without leading to strongly enriched HSE abundances. Although the exact mechanisms of core-904 mantle exchange processes remain ambiguous, core-mantle exchange is an attractive way to explain observed ¹⁸²W deficits in some OIB, because it alleviates the need for preserving early-905 formed ¹⁸²W anomalies, which according to the model presented here, is difficult and only 906 907 possible under special circumstances. Recently, Lesher et al. (2020) argued that thermo-908 diffusion could lead to iron isotope fractionation across the core-mantle boundary, causing 909 entrainment of fractionated core material into the convecting mantle. Because this scenario would also affect the mantle's μ^{182} W, it should lead to predictable μ^{182} W and stable Fe isotope 910 variations, and thus be a readily testable hypothesis. 911

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913 **5. CONCLUSIONS**

The presented five-reservoir open-system model (Fig. 1) investigates how the ¹⁴⁶Sm-¹⁴²Nd and ¹⁸²Hf-¹⁸²W isotope systematics of the silicate Earth are affected by late accretion, and progressive mantle-crust differentiation after core formation. Different rates and durations of core formation result in variable μ^{182} W, Hf/W, and W concentration of the bulk silicate earth

- 918 (BSE) at the start of late accretion. The initial $\mu^{182}W_{BSE}$, Hf/W_{BSE}, and W_{BSE} are interdependent
- 919 parameters and understanding the 182 Hf- 182 W evolution of the silicate earth therefore requires
- 920 detailed constraints on the timing and rate of core formation and the associated W flux to the
- 921 core, including the time, composition, and mass flux of a potential moon-forming giant impact.
- 922 But all these parameters remain major unknowns. It is clear, however, that the rate rather than
- 923 the total duration of core formation mainly controls the ¹⁸²Hf-¹⁸²W systematics, and thus more 924 precise constraints on the rate of early accretion and core formation, and the associated W
- 924 precise constraints on the rate of early accretion and core formation, and the associated W 925 distribution between silicate and metal are required to narrow down possible range of $\mu^{182}W_{BSE}$,
- 926 Hf/W_{BSE} , and W_{BSE} values at the start of late accretion.
- Ultimately, these different BSE starting values determine the amount of late accreted 927 material required to evolve to $\mu^{182}W_{BSE} = 0$ at the end of the late accretion period, and the ¹⁸²W 928 evolution of the evolving mantle and crustal reservoirs. The amount of late accreted material 929 930 is mainly determined by the pre-late accretion W_{BSE} value and thus most sensitive to core formation and early accretion processes. The¹⁸²W evolution of the evolving mantle and crustal 931 932 reservoirs is controlled by the proportion of W from the late accreted material to the amount of 933 W in each reservoir. The latter essentially regulates how sensitive each reservoir reacts to the 934 incoming late accretion flux. A progressively depleting mantle with low W concentration is very susceptible to addition of late accreted material with $\mu^{182}W < 0$ (-190), leading to $\mu^{182}W$ 935 936 deficits, which can only be avoided by limiting the amount of late accreted material. 937 Heterogeneous addition of the late accreted material to Earth's mantle is therefore required to 938 develop variably incompatible element depleted mantle with $\mu^{182}W \ge 0$, as observed in most Archean rocks. Maintaining the near-constant $\mu^{182}W \sim +10$ to +15 observed in mantle-derived 939 940 rocks throughout the Archean in a progressively more depleted mantle reservoir requires a balance between the addition of late accreted material with $\mu^{182}W < 0$ and recycling of crustal 941 material with μ^{182} W >0. Although the rate of late accretion also influences the μ^{182} W evolution 942 of the evolving mantle and crustal reservoirs, it is only a second-order effect, because the mass 943 944 fluxes between these reservoirs dominate their W concentrations, and because late accretion 945 only contributes ~7–13% of the BSE's W budget.
- Notably, reproducing the observed, and often decoupled ¹⁴²Nd and ¹⁸²W signatures in 946 Hadean-Eoarchean mantle-derived rocks requires the initiation of continental crust formation, 947 and recycling back into the mantle within the first ~ 50 Myr after core formation. Due to 948 continuous crust-mantle exchange, these early-formed ¹⁸²W and ¹⁴²Nd isotopic anomalies 949 generally disappear in the post-Archean in all silicate reservoirs. However, the recently 950 observed ¹⁸²W deficits in some young OIBs can be explained within the framework of the 951 presented model by mantle materials that never incorporated a recycled flux of early formed 952 crust with $\mu^{182}W > 0$, and can thus preserve $\mu^{182}W$ deficits acquired during late accretion. 953 Alternatively, the ¹⁸²W deficits in some young OIBs may result from core-mantle exchange, 954 which would obviate the need for preserving early-formed ¹⁸²W anomalies, but, of course has 955 956 very different geodynamic implications.
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- 1206 FIGURE CAPTIONS
- 1207

Fig. 1. Schematic representation of a five-reservoir open-system model of the Earth showing the mass fluxes between the reservoirs. The core and the silicate reservoirs exchange material only during core formation. Subsequently, late accreted material is added to the mantle reservoirs with concurrent silicate differentiation, that is, formation of continental crust and its recycling into the mantle.

Fig. 2. The calculated radiogenic contribution of ^{182W} from ¹⁸²Hf decay in a BSE-like reservoir, calculated by (¹⁸²Hf/¹⁸⁰Hf)*t*_{CF} x (¹⁸⁰Hf/¹⁸⁴W)_{BSE}; *t*_{CF} is the time after solar system initial (4.56 Ga) when core formation ended, and thus the starting point of the BSE evolution. For a BSElike reservoir with (¹⁸⁰Hf/¹⁸⁴W)_{BSE} = 25.4 (Kleine and Walker, 2017), the radiogenic contribution of ¹⁸²W from ¹⁸²Hf decay is analytically resolvable (i.e., >5 ppm) for core formation periods up to ~80 Myr, for (¹⁸²Hf/¹⁸⁰Hf)*t*_{CF} starting from a solar system initial (¹⁸²Hf/¹⁸⁰Hf)*i* = 1.018 × 10⁻⁴.

Fig. 3. Diagrams showing (a) three different core growth models for a total duration $t_{CF} = 45$ 1220 Myr, and (b) the corresponding evolution of $\mu^{182}W_{BSE}$ with (dashed lines) and without (solid 1221 lines) adding late accreted material (LAM) to achieve a present-day $\mu^{182}W_{BSE} = 0$. The black 1222 lines are for linear growth, the red curves show results for 90% of core growth within the first 1223 10 Myr and the blue curve for 90% of core growth within the last 10 Myr of the entire 45 Myr 1224 1225 core formation period. Also listed in panel (b) is the mass of LAM (relative to bulk Earth mass) and the $\mu^{182}W_{BSE}$ and W concentration (¹⁸²W_{BSE}) at the end of core formation (45 Myr) for 1226 each of the three scenarios. Similar plots for core formation periods of 30, 60, and 100 Myr are 1227 1228 provided in the supplementary materials (Fig. S1, S2, and S3). These results for each model 1229 are also listed in Table 4.

Fig. 4. Modeled $\mu^{182}W_{BSE}$ evolution with (green lines) and without late accretion (black lines) for four different core formation times ($_{tCF}$) of 30, 45, 60, and 100 Myr after solar system formation at 4.56 Ga. The green lines show the isotopic evolution of $\mu^{182}W_{BSE}$ after core formation to $\mu^{182}W_{BSE} = 0$ at 4.41 Ga by the addition of late accreted material of bulk Earthlike composition; the amount of late accreted material (LAM) for each t_{CF} is given in wt% of the bulk Earth mass. The end of late accretion at 4.41 Ga is chosen for illustrative purposes, i.e., to clearly resolve the differences between the individual model curves.

1237 Fig. 5. The diagram shows the amount of late accreted material (LAM) versus the W 1238 concentration in the bulk silicate earth (W_{BSE}) for different core formation periods (t_{CF}) and 1239 rates of core formation. Different colors represent variable core formation periods and different 1240 symbols represents variable core formation rates. The squares represents models where 90% 1241 of the core forms in the initial 10 Myr, the circle represents linear core formation models, and 1242 the triangle represents models where 90% of the core forms in the last 10 Myr of the core 1243 formation period. Results for $t_{CF} = 100$ Myr also include cases where 70% and 50% of the core 1244 formed by the initial 30 Myr, shown here with the + symbol. Data are from Table 4 and Table 1245 S5. Present-day $W_{BSE} = 13 \pm 10$ (2SD) is shown by the shaded gray box.

1246 Fig. 6. (a) Plots showing three different late accretion scenarios in which same amount of late 1247 accreted material (LAM) is added to the mantle after core formation. Core formation ends at 1248 45 Myr after solar system formation and late accretion ends at 3.8 Ga. The rate of accretion is 1249 varied by adding either 90% of total late accreted material to the mantle in the initial 100 Myr 1250 of total late accretion time period (rapid late accretion (LA) scenario) or 90% of total late 1251 accreted material to the mantle in the last 100 Myr of total late accretion time period (delayed 1252 late accretion scenario). Linear late accretion assumes a constant flux of late accreted material 1253 to the mantle in each time interval of late accretion. Panel (b) shows the modeled evolution of

- 1254 $\mu^{182}W_{BSE}$ for the three different late accretion scenarios, panel (c) the evolution of $\mu^{182}W$ for
- 1255 the modeled UM reservoir, and panel (d) the μ^{182} W evolution curves for all modeled reservoirs 1256 combined. The pink box shows the target range for $\mu^{182}W_{UM} = +10$ to +15 between 4.0 and 1257 2.5 Ga.
- Fig. 7. Plots showing the temporal evolution of μ^{182} W in all the silicate reservoirs with 1258 1259 concurrent silicate differentiation and late accretion. Late accretion (LA) to the mantle starts 1260 directly after core formation at (a) 30, (b) 45, (c) 60, and (d) 100 Ma and proceeds until 3.8 1261 Ga. Also shown are isotopic evolution curves for variable recycling fluxes to the UM, adjusted 1262 by the model parameter f_R , which is the fraction of recycled crust (CC) going to the UM (f_R = 0.1 to 0.9). The remainder of the crustal recycling flux $(1 - f_R)$ is stored in the IR reservoir for 1263 1 Gyr before being mixed with the LM. The present-day μ^{182} W of the terrestrial standard is 0 1264 The heading in 1265 \pm 3.9 (2SD). shown as a green box. each panel. e.g., " $t_{CF}_{45}Myr_{LA}_{760}Myr_{f_{R}}(0.1, 0.4, 0.9)$ IT 1000Myr" lists the model parameters used in 1266 each simulation. For example, t_{CF}_45Myr, means a 'core formation time' of 45 Ma after Earth 1267 1268 formation, LA_760Myr refers to a total 'late accretion' period of 760 Myr after Earth 1269 formation, $f_{\rm R}$ is the fraction of the recycling flux from the CC into the UM, and IT_1000Myr indicates that the recycled CC material that goes into the IR $(1 - f_R)$ is stored in the IR for 1000 1270 1271 Myr before being mixed to the LM. The same notation is used in the headings of all subsequent 1272 figures and summarizes the key model parameters of each simulation. More detailed model parameters are given in Supplementary Tables S1 and S2. 1273
- Fig. 8. Diagram showing the temporal evolution of μ^{182} W in all the silicate reservoirs for 1274 1275 concurrent silicate differentiation and late accretion (LA) after a core formation period of 45 1276 Myr. Here, late accreted material is added non-uniformly to the mantle for a total period of 1277 760 Myr after solar system initial with 2% being added to the UM and the remaining 98% to the LM. The $\mu^{182}W_{UM}$ evolution successfully reproduces the observed excess 182W (10–15 1278 1279 ppm) reported in Hadean-Archean rocks, which is shown by the pink shaded region. The kink 1280 in the $\mu^{182}W_{UM}$ evolution observed immediately after the end of late accretion at 3.8 Ga marks 1281 the effect of crustal recycling, which becomes more pronounced after the end of late accretion at 3.8 Ga and protracts the time interval of $\mu^{182}W_{UM} \sim +10-15$ until the end of Archean. The 1282 effect of variable isolation times (IT: 10, 1000, and 5000 Myr) of recycled material in the IR 1283 1284 on the evolution of μ^{182} W in all the reservoirs is also shown. For further details of the model see main text and Table S3 ($t_{CF} = 45$ Myr). The present-day $\mu^{182}W_{BSE} = 0 \pm 3.9$ (2SD) is shown 1285 by the green box. Results for core formation periods of 30, 60 and 100 Myr are shown in Fig. 1286 1287 S4.
- Fig. 9. Diagrams showing the μ^{182} W evolution in all modeled silicate reservoirs for a core formation time $t_{CF} = 45$ Myr with non-uniform mixing of late accreted material (LA) to the mantle until 760 Myr after Earth formation (3.8Ga). Comparison of isotopic evolutions for (a) addition of 2-10% of late accreted material to the UM and the remaining 90-98% to the LM using a W silicate-silicate transfer factor D_W of 200. Panel (b) shows results for addition of 2% of late accreted material to the UM and 98% to the LM, but using a higher a D_W of 300-400. The $D_W = 400$ case represents the successful solution also shown in Fig. 8.
- 1295 **Fig. 10.** (a) μ^{142} Nd evolution in silicate reservoirs for silicate differentiation (and simultaneous 1296 addition of late accreted material for 760 Myr) starting after core formation time (t_{CF}) of 45 1297 Myr; results for other core formation periods are shown in Fig. S8. Model parameters are as in 1298 Fig. 8. The green shaded region represents the present-day terrestrial average μ^{142} Nd = 0 ± 5.6
- 1299 (Rizo et al., 2013). (b) Temporal evolution of μ^{142} Nd in silicate reservoirs for $t_{CF} = 45$ Myr and
- 1300 a variable $m_{\rm UM}$ in the range 0.6–0.4. All other model parameters and conditions are the same
- 1301 as in (a). (c) Temporal evolution of μ^{142} Nd in silicate reservoirs for $t_{CF} = 45$ Myr and $m_{UM} =$

- 0.5. Solid lines represent μ^{142} Nd evolution with D_{Sm} and D_{Nd} used by Kumari et al. (2016, 1302 1303 2019), which are also used in modeling the results shown in (a) and (b). Dashed lines show isotopic evolution with higher $D_{\rm Sm}$ and $D_{\rm Nd}$ (Table 3 case II). Corresponding temporal 1304
- evolution of ε^{143} Nd for cases (b) and (c) are shown in Fig. S9. 1305
- Fig. 11. Diagram showing the effect of variable core formation periods (t_{CF}) and rates of core 1306 formation (early, linear or late, as given by the labels for each curve) on (Hf/W)_{BSE}. Gray bar 1307 1308 shows the range of Hf/W_{BSE} (17 ± 5 , Kleine et al., 2009). Data are from Table 4 and Table S5.

Fig. 12. Diagram of μ^{182} W_{BSE} versus W_{BSE} showing that the pre-late accretion μ^{182} W_{BSE} at t_{CF} 1309

- 1310 can be very variable and compatible with similar W_{BSE} and thus amounts of late accreted
- material (LAM = 0.82-1.1% in the examples shown above). Data are from Table 4 (for core 1311 formation periods of 30 and 45 Myr cases) and Table S5 (for core formation period of 100 1312
- Myr case). Note that the present-day pre-late accretion $\mu^{182}W_{BSE}$ is +25 in each case.
- 1313
- Fig. 13. μ^{182} W evolution in all the silicate reservoirs considering late accretion and 1314
- 1315 simultaneous silicate differentiation (same way as described in Fig. 8) after core formation
- ends at 45 Myr, for $m_{\rm UM}$ of 0.6 (solid lines) and 0.5 (dashed lines). The kink in the $\mu^{182}W_{\rm UM}$ 1316 evolution observed immediately after the end of late accretion at 3.8 Ga marks the effect of 1317
- 1318 crustal recycling, which becomes more pronounced after the end of late accretion and protracts
- the time interval of $\mu^{182}W_{UM} \sim +10-15$ until the end of Archean. Additional model parameters 1319
- and simulation conditions are provided in Table S3. Similar plots for core formation period of 1320
- 1321 30, 60, and 100 Myr are provided in Fig. S10.

Concentrations (ppm)	Bulk Earth	References
Hf	0.197	McDonough (2014)
W	0.180	"
Sm	0.27	"
Nd	0.84	"
SSI	Value	
$^{182}W/^{184}W$	0.864598	Calculated using terrestrial standard and $\mu^{182}W_{SSI}$ of -349 ± 0.07 (Kleine and Walker, 2017)
¹⁸² Hf/ ¹⁸⁰ Hf	$(1.018 \pm 0.043) \times 10^{-4}$	Kleine and Walker (2017); Burkhardt et al. (2008)
¹⁴² Nd/ ¹⁴⁴ Nd	1.141462	Calculated using the modified 142 Nd decay equation; see eqn (1) in section 2.2
146 Sm/ 144 Sm	0.0085 ± 0.0007	Boyet et al. (2010)
Terrestrial Standard	Value	
¹⁴² Nd/ ¹⁴⁴ Nd	1.141836	Roth et al. (2014)
$^{182}W/^{184}W$	0.864900	Kleine and Walker (2017)

Table 1. Present-day concentrations (ppm) in bulk Earth as well as the solar system initial (SSI) and present-day terrestrial standard isotopic ratios used in the model.

<u>1</u>	Core	BSE	LM	IR	UM	CC	mantle ⁺
Target W (ppb)	500±120 ¹	13±10 ¹			01/2	1000 ²	8.3±7.1 ¹
$t_{\rm CF} = 30 \rm Myr$							
W (ppb)	483	42.1	57.5	3010	2.04	2900	24.2
$\mu^{182}W$	-235	-0.1	-2.6	5.2	4.0	2.9	
$t_{\rm CF} = 45 \ {\rm Myr}$							
W (ppb)	521	22.9	31.5	1640	1.1	1580	13.3
$\mu^{182}W$	-216	0.2	-2.2	5.4	4.2	3.1	
$t_{\rm CF} = 60 \ {\rm Myr}$							
W (ppb)	543	11.8	12.2	940	0.53	750	5.2
$\mu^{182}W$	-207	0.7	-1.7	5.8	4.7	3.6	
$t_{\rm CF} = 100 \; \rm Myr$							
W (ppb)	562	1.7	2.3	120	0.08	120	1.0
$\mu^{182}W$	-199	0.03	-2.4	5.2	4.1	2.9	

Table 2. Model-derived present-day concentration of W (ppb) and μ^{182} W of core and silicate reservoirs for various core formation period (*t*_{CF}) of 30, 45, 60, and 100 Myr. Model parameters are given in Supplementary Table S3.

Note: ¹Arevalo and McDonough (2008) and McDonough (2014) with 2σ uncertainty; ²Rudnick and Gao (2014); ⁺ represents value for mean modern mantle, calculated as (W_{LM}×0.4 + W_{UM}×0.6).

Table 3. Model-derived present-day Sm and Nd concentrations (ppm) and isotopic ratios $(\mu^{142}\text{Nd} \text{ and } \epsilon^{143}\text{Nd})$ in UM and CC for $m_{\text{UM}} = 0.50$. Case I is for D_{Sm} and D_{Nd} adopted from Kumari et al. (2016, 2019) and Case II is for higher D_{Sm} and D_{Nd} .

	Target range	Case I	Case II
$D_{\text{Sm, UM} \rightarrow \text{CC}}$		8	12
$D_{\text{Sm, LM} \rightarrow \text{CC}}$		25	25
$D_{ m Nd,UM ightarrow CC}$		18	30
$D_{ m Nd, LM ightarrow CC}$		35	50
C _{Sm} , _{CC}	$3.5-6^{a}$	3.4	4.5
$C_{\rm Sm,UM}$	$0.58 - 0.71^{b}$	0.3	0.3
$C_{\rm Nd,CC}$	16–28 ^a	19.6	28.1
$C_{ m Nd,UM}$	$0.24 - 0.27^{b}$	0.9	0.8
ε ¹⁴³ Nd in CC	-10 to -25 ^c	-22.5	-22.9
ε ¹⁴³ Nd UM	8 to 12 ^c	9.2	16.4
μ^{142} Nd in CC	-5.6 to $+5.6^{d}$	-1.5	-0.9
μ^{142} Nd in UM	-5.6 to $+5.6^{d}$	1.2	1.7
μ^{142} Nd in UM (@ 4.0 Ga)	~11–17.5 ^d	~5.6	~10.6

Note: ^aRudnick and Gao (2014), Taylor and McLennan (1995), Taylor (1964); ^bWorkman and Hart (2005), Salters and Stracke (2004); ^cJacobsen and Wasserburg (1979); ^dRizo et al. (2013).

	Core formation model, $t_{\rm CF} = 30 \rm Myr$						Core formation model, $t_{\rm CF} = 45 \rm Myr$						
	90% in first 10 Myr		Linear		90% in last 10 Myr		90% in first 10 Myr		Linear		90% in last 10 Myr		
	no LAM	with LAM	no LAM	with LAM	no LAM	with LAM	no LAM	with LAM	no LAM	with LAM	no LAM	with LAM	
	at $t_{\rm CF} = 30$	at $t = 0$	at $t_{\rm CF} = 30$	at $t = 0$	at $t_{\rm CF} = 30$	at $t = 0$	at $t_{\rm CF} = 45$	at $t = 0$	at $t_{\rm CF} = 45$	at $t = 0$	at $t_{\rm CF} = 45$	at $t = 0$	
$D_{ m W}$,silicate-metal	3.40		5.05		6.54		3.45		6.67		9.55		
μ ¹⁸² wCore	-281	-281	-235	-235	-217	-217	-279	-279	-216	-216	-203	-203	
μ^{182W} BSE	-28.0	0.50	-75.3	-0.10	-152	-0.50	7.97	0.06	-32.9	0.50	-148	0.04	
W _{Core} (ppb)	410	410	483	483	519	519	413	413	521	521	551	551	
WBSE (ppb)	72	77	38	42	22	24	70	76	21	23	6.9	7.7	
Hf/W _{BSE}	3.8	3.6	7.1	6.5	13	11	3.9	3.6	13	12	39	35	
LAM		3.5%		1.9%		1.1%		3.4%		1.0%		0.34%	

Table 4. Model-derived result in the core and BSE, after complete core formation assuming three types of core growth, and with or without late accretion (LA) for core formation period (t_{CF}) of 30, 45, 60, and 100 Myr.

	Core formation model, $t_{\rm CF} = 60 \rm Myr$						Core formation model, $t_{\rm CF} = 100$ Myr					
	90% in first 10 Myr		Linear		90% in last 10 Myr		90% in first 10 Myr		Linear		90% in last 10 Myr	
	no LAM	with LAM	no LAM	with LAM	no LAM	with LAM	no LAM	with LAM	no LAM	with LAM	no LAM	with LAM
	at $t_{\rm CF} = 60$	at $t = 0$	at $t_{\rm CF} = 60$	at $t = 0$	at $t_{\rm CF} = 60$	at $t = 0$	at $t_{\rm CF} = 100$	at $t = 0$	at $t_{\rm CF} = 100$	at $t = 0$	at $t_{\rm CF} = 100$	at $t = 0$
Dw,silicate-metal	3.49		8.43		12.66		3.52		13.54		20.99	
μ ¹⁸² wCore	-277	-277	-207	-207	-199	-199	-276	-276	-199	-199	-197	-197
μ^{182W}_{BSE}	20.4	0.44	-9.92	-0.01	-152	0.73	24.8	-0.61	14.0	-0.04	-162	-0.01
W _{Core} (ppb)	416	416	543	543	561	561	417	417	562	562	565	565
W _{BSE} (ppb)	69	75	11	12	2.1	2.4	68	74	1.5	1.7	0.09	0.10
Hf/W _{BSE}	3.9	3.7	26	23	130	113	4.0	3.7	181	161	3048	2747
LAM		3.4%		0.52%		0.10%		3.4%		0.07%		0.004%

Figure 1



















Figure 10







