

### Uranium and thorium partitioning in the bulk silicate Earth and the oxygen content of Earth's core

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1	Uranium and thorium partitioning in the bulk silicate Earth and the oxygen
2	content of Earth's core
3	
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10	
11	Abstract
12	This study investigates the partitioning of U and Th between molten metal and
13	silicate liquid ( $D_U$ and $D_{Th}$ ) during Earth's core-mantle differentiation. We report new Th
14	partition coefficients between chondritic silicate melt and various Fe-rich alloys in the
15	system Fe-Ni-C-S-Si as determined by experiments in a multi-anvil apparatus at 3–8 GPa,
16	2073–2373 K, and oxygen fugacities from 1.5 to 5 log units below the iron-wüstite (IW)
17	buffer. By compiling all existing data on molten metal-silicate liquid partitioning of U
18	and Th, we develop global models of U and Th partitioning between the mantle and core
19	throughout Earth's accretion. The calculated concentrations in the Bulk Silicate Earth
20	(BSE) are in agreement with previous studies (U_{BSE} = $11.42 \pm 0.45$ ppb and Th_{BSE} = $43.20$
21	$\pm$ 1.73 ppb), whereas the contents of these radioactive elements in the Earth's core remain
22	negligible. Compared to recent geochemical estimations, the calculated (Th/U)BSE
23	supports EL rather than EH enstatite chondrites as the reduced building blocks of the
24	Earth. Furthermore, we demonstrate that Th is much more sensitive than U to the oxygen
25	content of the metallic phase. To reproduce the Th/U ratio of the BSE within its
26	uncertainties, the oxygen content of the Earth's core must be lower than 4.0 wt%. By

27	combining other existing constraints, this suggests that the core contains 2.0–4.0 wt% O.
28	The calculations of U and Th concentrations and Th/U in the BSE developed herein can
29	be used as new constraints for determining the concentrations of other refractory
30	lithophile elements in the BSE as soon as their metal-silicate partition coefficients are
31	well constrained over the conditions of core segregation.

#### 32 **1. Introduction**

33 Uranium and thorium are refractory elements that condensed from the solar nebula 34 at high temperatures (>1400 K). One would thus assume that the Th/U ratio in the bulk 35 silicate Earth (BSE) should be equal (to the first order) to that of chondrites if these 36 elements were not fractionated during Earth's core formation. However, existing 37 geochemical models show some discrepancies between the U and Th concentrations and 38 Th/U ratio of the BSE compared to those of chondrites, as well as large uncertainties. For 39 instance, Lyubetskaya and Korenaga (2007) show a relative depletion of refractory 40 lithophile elements compared to previous estimates (e.g., McDonough and Sun, 1995; 41 Palme and O'Neill, 2003). The BSE composition can be constructed using a geochemical 42 approach based on mantle peridotite samples, which originate at depths shallower than 43 the transition zone. In addition, model of the primitive mantle based on petrological data 44 assumes global-scale homogeneity of the Earth's mantle. Moreover, the Th/U ratio of the 45 upper mantle may have evolved with time due to changes in surface redox conditions. 46 The recycling of U from the surface into Earth's interior differs from that of Th because U exists in two valence states (4+ and 6+), and highly soluble  $U^{6+}$  dominates under 47 48 oxidized surface conditions. The terrestrial upper mantle sampled by mid-ocean ridge 49 basalts shows a low Th/U ratio relative to that estimated from chondrites (Jenner and 50 O'Neill, 2012; Gale et al., 2013). Indeed, the significant addition of recycled uranium into the upper mantle has been confirmed by high-precision <sup>238</sup>U/<sup>235</sup>U measurements 51 52 (Andersen et al., 2015).

53 The partitioning of radioactive elements between different Earth reservoirs is a 54 topic of much debate since they play a major role in the thermal evolution of the Earth

and its mantle dynamics. Indeed, some amount of radioactive heating is necessary to drive the early geodynamo. Moreover, several studies have recently proposed that U and Th become more siderophile and/or chalcophile under reducing conditions, and consequently could have been sequestered in non-negligible amounts (up to 10 ppb U and 21 ppb Th) in the Earth's core (*e.g.*, McCubbin et al., 2012; Blanchard et al., 2017; Chidester et al., 2017; Wohlers and Wood, 2015, 2017, and references therein). It is thus essential to determine the budget of heat-producing elements in different planetary reservoirs.

62 In the present study, we present experimentally determined Th metal-silicate 63 partitioning data at up to 8 GPa, 2373 K, and over a wide range of oxygen fugacity 64 conditions and chemical compositions of the silicate and metallic phases, based on new 65 chemical analyses of the experimental products reported in Bouhifd et al. (2013). The 66 metal-silicate partitioning of Th has been the subject of very few experimental studies, 67 and the only existing data were obtained at 1.5 GPa using mainly sulfide liquids (Murrell 68 and Burnett, 1986; Wohlers and Wood, 2015, 2017). Then, we compiled all published experimental results on metal-silicate partitioning of these elements  $D_{\rm M} = \frac{X_{\rm M}^{\rm met}}{X_{\rm M}^{\rm sil}}$  (where 69  $X_{\rm M}^{\rm met}$  and  $X_{\rm M}^{\rm sil}$  are the wt% concentrations of element M in the metal and silicate phases, 70 71 respectively). It is then possible to regress these data to better constrain the influence of 72 physical parameters (pressure, temperature, oxygen fugacity) and the chemical 73 compositions of the studied phases on D<sub>U</sub> and D<sub>Th</sub>. These models were subsequently used 74 to derive the U and Th concentrations in the BSE and the core as well as the Th/U ratio of the BSE, and our results are consistent with previous results (e.g., Allègre et al., 2001; 75 76 Kargel and Lewis, 1993; Lyubetskaya and Korenaga, 2007; and references therein). We 77 combined our results with recent lead isotopic analyses (Wipperfurth et al., 2018) to

discriminate between different scenarios regarding Earth's building blocks. Furthermore,
our models show also that the concentrations of U and Th in the Earth's core are less than
1.5 ppb and 5 ppb, respectively. Finally, the calculations performed herein provide new
constraints on the oxygen content of the core, which cannot exceed 4 wt%.

82

#### 83

#### 2. Experimental methods

The run-products used in the present study are those described and analysed in Bouhifd *et al.* (2013). Here, we report new chemical analyses of thorium in the silicate and metallic phases and of oxygen in the Fe-rich alloys. In the following, we briefly summarize the experimental procedure and fully describe the analytical methods used to derive our new results.

89

#### 90 2.1. Starting materials

91 Silicate starting materials consisted of a C1-chondrite model composition 92 containing 49.6 wt% SiO<sub>2</sub>, 35.1 wt% MgO, 8.5 wt% FeO, 3.5 wt% Al<sub>2</sub>O<sub>3</sub>, and 3.3% CaO 93 (Wasson and Kallemeyn, 1988). This silicate composition is similar to that used to 94 determine the effect of water on the behavior of siderophile elements during core 95 formation (e.g., Clesi et al., 2016). Doping was achieved with mixtures of U and Th 96 dissolved in 0.5 M nitric acid (AAS standard solutions), which was denitrified in air at 97 1100 K for 4 h. The doping mixtures were added to the silicate starting material to achieve 98 concentrations of 1000 to about 4000 ppm per element. Fe-rich alloy powders in the Fe-99 Ni–Si–S system were added to the silicate starting material in 50:50 proportions by weight 100 to obtain several starting compositions. Oxygen fugacity ( $fO_2$ ) was varied between IW –

2 and IW –5 by adding metallic Si to the starting material. Each starting composition was
then mixed and ground under ethanol, and dried at ~400 K for at least 24 h.

103

#### 104 **2.2. High-pressure and high-temperature syntheses**

105 The high-pressure and high-temperature experiments were performed by Bouhifd 106 et al. (2013) using the French national 1000-ton and 1500-ton multi-anvil facilities in 107 Clermont-Ferrand, France. Briefly, the pressure assembly consisted of Cr-doped MgO 108 octahedra (18 or 14 mm edge length) containing a LaCrO<sub>3</sub> heater. The octahedra were 109 compressed using 32 mm tungsten carbide anvils with truncation edge lengths of 11 and 110 8 mm for the 18 and 14 mm octahedra, respectively, and pyrophyllite gaskets. Samples 111 were contained in either graphite or MgO single-crystal capsules in order to test the 112 impact of the capsule material on the measured metal-silicate partition coefficients. The 113 samples were first compressed to the desired pressure at room temperature (for instance 114 for 5 GPa experiments, we use about 100 tons on a 14/8 assembly) and then heated to the 115 target temperature for run durations of 1 to 2 min. These durations are sufficient to 116 achieve equilibrium between silicate melt and metallic liquid as found for many other 117 studies (e.g., Corgne et al. 2008; Cartier et al., 2014; Bouhifd et al., 2015; Clesi et al., 118 2018; and references therein) and short enough to prevent excessive reaction between the 119 capsule and the silicate or metallic phases. Temperatures were monitored with a thin axial 120 W<sub>5</sub>Re/W<sub>26</sub>Re thermocouple whose junction was in direct contact with the top of the 121 capsule. The thermocouples presented no difference of behavior when using either 122 graphite or MgO single crystal capsule, showing the non-contamination of thermocouple 123 during graphite experiments. The pressure and temperature uncertainties are estimated to be  $\pm 1$  GPa and  $\pm 100$  K, respectively. The samples were quenched by shutting off the power, which resulted in an initial quench rate of approximately 800 K/s. The samples were then decompressed over about 12 h. After the completion of each experiment, the run product was mounted in epoxy, polished, and carbon coated for chemical analyses.

128

#### 129 **2.3. Electron Microprobe**

130 The major and minor element compositions of the metal and silicate phases were 131 analyzed with a CAMECA SX100 electron microprobe with a 20 kV accelerating voltage 132 at the Laboratoire Magmas et Volcans (LMV, Clermont-Ferrand, France). Major element analyses in silicate phases were performed at 50 nA with a 10-20 µm defocused beam, 133 134 with on-peak counting times ranging from 5 to 80 s depending on element concentrations 135 and detection limit requirements (e.g. Bouhifd et al., 2013). Wollastonite was used as a 136 standard for Si and Ca, and MgO, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> for Mg, Al, and Fe, respectively. To 137 analyze K and S, we used natural KAlSi<sub>3</sub>O<sub>8</sub> and ZnS as standards, respectively. For 138 metallic phase analyses, we used a defocused beam (10–20  $\mu$ m), beam currents of 15 nA 139 for major elements (Fe, Ni, and Si) or 150 nA for trace elements, and on-peak counting 140 times ranging from 5 to 60 s. Pure Ni, Si, and Fe metals were used as standards. For 141 samples embedded in graphite capsules, we estimated the carbon content of the Fe-alloys 142 from the deviation of the analytical totals from 100%.

In the present study, we essentially focused our chemical analyses to determine the concentrations of Th in the silicate phase and oxygen contents in the metal phases. To analyze Th in the silicate, thorianite (ThO<sub>2</sub>) was used as standard. For metal analyses, pure Ni, Si, and Fe (NIST 665) metals were used as standards. To analyze oxygen in

147 metallic phases, NIST 665 and  $Fe_2O_3$  were used as standards. Prior to analyses, the 148 samples and standards were polished and carbon coated in the same way, then kept under 149 vacuum until analysis. Analyses were performed using 20 kV accelerating voltage, a 150 beam current of 15 nA, and a defocused beam of 30 µm, and the detection limit for oxygen 151 in the metals was 550 ppm.

152 During the oxygen analyses, we found that the nominally oxygen-free standards 153 contained about  $0.21 \pm 0.02$  wt% O at 20 kV accelerating voltage; this value was 154 consistent among the standards. We additionally observed that the measured oxygen 155 contents of the standards decreased with increasing voltage from 7 to 15 kV before 156 reaching a plateau between 15 and 25 kV (the maximum voltage tested). We concluded 157 that the measured oxygen contents in the O-free standards were the result of rapid 158 adsorption of oxygen onto the surface of the standards. Therefore, we subtracted the value 159 obtained from the standards at 20 kV from every analysis of our run-products. The 160 corrected concentrations are presented in Tables A1 and A2. The reported oxygen 161 analyses are in good agreement with the recent parameterization for metal-silicate oxygen 162 partitioning reported by Fischer et al. (2015).

163

#### 164 **2.4. LA-ICP-MS**

U and Th concentrations in both metal and silicate phases were analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at LMV. We used a quadrupole ICP-MS (Agilent 7500-cs, Agilent Technologies) coupled with a 193 nm ArF excimer-type laser (Resonetics M-50). The laser was fired on selected sample regions

at a repetition rate of 3 Hz with 8 mJ output and a spot size of 15–44 µm. Pit depths were
roughly equivalent to the spot size.

- 171 During LA-ICP-MS analyses, the Ca signal was monitored during metal analyses 172 and the Fe and Ni signals during silicate analyses. Any sudden variation of their contents 173 was indicative of phase contamination (i.e., metal contamination during silicate phase 174 analysis or vice versa). Ablation was performed under a pure He flow for durations of 175 about 80 s (blank count rates were measured for 20 s prior to 60 s of ablation). The analyte 176 was carried to the ICP torch by a gas mixture in which  $N_2$  + Ar gases were added to the 177 pure He gas. Reference glasses NIST SRM 610, NIST 612, and BCR2-G were used for external calibration (Gagnon et al., 2008), and <sup>29</sup>Si, <sup>57</sup>Fe, and <sup>60</sup>Ni were used for internal 178 179 calibration. All data were processed using the GLITTER software package (Achterberg 180 et al., 2001). Detection limits calculated for U and Th were below 1 ppm.
- 181

#### **3. Results**

183 The experimental conditions and calculated U and Th partition coefficients ( $D_{\rm U}$  and 184  $D_{\rm Th}$ , respectively) are summarized in Table 1, and the chemical compositions of the 185 quenched silicate and metallic melts are reported in Tables A1 and A2. Typical run 186 products contained two immiscible phases: silicate glass and Fe-rich alloy (Fig. 1). 187 Microstructures of the run products showed that both phases were fully molten during the 188 experiments. In some cases, we observed dendritic microstructures in the silicate. When 189 dendritic microstructures were present within the region of interest, LA-ICP-MS analyses 190 were performed using a 44 µm spot size to average the heterogeneous quenched texture. 191 Several criteria indicate the attainment of thermodynamic equilibrium in these

experimental samples: (i) multiple analyses in the silicate phase show that it is
homogeneous with no evidence of chemical zoning, and (ii) all metal blobs embedded in
the silicate matrix are of similar composition.

195 A critical parameter during metal-silicate partitioning using the multi-anvil 196 technique is the nature of the capsule, because no material can be completely inert to both 197 silicate and metal liquids. Here we used two different capsules: MgO single-crystal and graphite capsules. Using graphite capsules, we usually observed low analytical totals for 198 199 the metallic phase, *i.e.*, between 93 and 98.9 wt% (Table A1), indicating significant 200 amounts of carbon dissolved in the Fe-rich alloy. However, we did not observe any effect 201 of the capsule material on  $D_{\rm U}$  or  $D_{\rm Th}$  considering analytical errors over the range of P-T 202 conditions explored in this study (Fig. 2). Similar behavior has been observed for the 203 metal-silicate partition coefficients of U and other lithophile elements (Bouhifd et al., 204 2013; 2015; and references therein). Finally, our experimental results showed that varying 205 the concentrations of U and Th in the starting materials had no effect on the resulting 206 metal-silicate partition coefficients (Tables A1 and A2).

207

#### 208 **3.1 Oxygen fugacity**

The prevailing oxygen fugacities in our experiments were calculated based on the Fe and FeO contents of the quenched metal and silicate phases, respectively, by considering the equilibrium reaction between Fe metal and Fe oxide:

212 
$$\operatorname{Fe}^{\operatorname{metal}} + \frac{1}{2} \operatorname{O}_2 \leftrightarrow \operatorname{FeO}^{\operatorname{silicate}}$$
 (1)

The  $fO_2$  can thus be estimated relative to the Iron-Wüstite buffer (IW) from the activities of Fe in the metal and FeO in the silicate following the equation:

215 
$$\log fO_2(\Delta IW) = 2 \times \log \left(\frac{a_{\rm Fe0}^{\rm sil}}{a_{\rm Fe}^{\rm met}}\right),$$
 (2)

216 where  $a_{FeO}^{sil} = \gamma_{FeO}^{sil} \times X_{FeO}^{sil}$  and  $a_{Fe}^{met} = \gamma_{Fe}^{met} \times X_{Fe}^{met}$  represent the activities of FeO in the 217 silicate liquid and Fe in the metal, respectively,  $\gamma_{FeO}^{sil}$  and  $\gamma_{Fe}^{met}$  are their respective activity 218 coefficients, and  $X_{FeO}^{sil}$  and  $X_{Fe}^{met}$  their respective mole fractions.

We calculated the activity coefficient of Fe in the Fe-rich alloys based on the formula of Ma (2001) using the interaction parameters  $\varepsilon$  defined in the Steelmaking Data Sourcebook (1988) (see also Wade and Wood, 2005; Siebert *et al.*, 2011) by the following formula for metallic solutions containing *N* components (six in our study: Fe, Ni, O, S, C and Si):

224 
$$\ln \gamma_{Fe} = \sum_{i=1}^{N-1} \varepsilon_i^i (\chi_i + \ln(1-\chi_i))$$

225 
$$-\sum_{j=1}^{N-2}\sum_{k=j+1}^{N-1}\varepsilon_{j}^{k}\chi_{j}\chi_{k}\left(1+\frac{\ln(1-\chi_{j})}{\chi_{j}}+\frac{\ln(1-\chi_{k})}{\chi_{k}}\right)$$

226 
$$+ \sum_{i=1}^{N-1} \sum_{k=1(k\neq 1)}^{N-1} \varepsilon_i^k \chi_i \chi_k \left( 1 + \frac{\ln(1-\chi_k)}{\chi_k} - \frac{1}{1-\chi_i} \right)$$

227 
$$+\frac{1}{2}\sum_{j=1}^{N-2}\sum_{k=j+1}^{N-1}\varepsilon_{j}^{k}\chi_{j}^{2}\chi_{k}^{2}\left(\frac{1}{1-\chi_{j}}+\frac{1}{1-\chi_{k}-1}-1\right)$$

228 
$$-\sum_{i=1}^{N-1}\sum_{k=1(k\neq i)}^{N-1}\varepsilon_{i}^{k}\chi_{i}^{2}\chi_{k}^{2}\left(\frac{1}{1-\chi_{i}}+\frac{1}{1-\chi_{k}}+\frac{\chi_{i}}{2(1-\chi_{k})^{2}}-1\right)$$
(3)

229 This treatment is available using the activity calculator
230 (<u>http://www.earth.ox.ac.uk/~expet/metalact/</u>) provided by the university of Oxford

(Wade and Wood, 2005). No pressure correction is made in our calculations due to thelack of reliable data for all elements.

To determine  $\gamma_{Fe0}^{sil}$  for all silicate melt compositions, we used the average value 233  $(\gamma_{\rm Fe0}^{\rm sil} = 1.5 \pm 0.5)$  derived from studies at 1 bar by O'Neill and Eggins (2002) for 234 several melt compositions in the CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system, and by Holzheid et al., 235 236 (1997) for melts in the anorthite-diopside system and komatiitic basalt, assuming no 237 pressure effect (Toplis, 2004). The calculated  $fO_2$  of our experiments ranged from IW -5 238 to IW -1. Values determined for each experiment are reported in Tables A1 and A2. For comparison, we also report the value of  $fO_2$  calculated assuming ideality ( $\gamma_{FeO}^{sil} = \gamma_{Fe}^{met} =$ 239 240 1), and the difference between the two values is within the uncertainties of the calculations. Thus, in the following, we use the fO<sub>2</sub> values calculated for the non-ideal 241 242 system.

243

#### 244 **3.2.** Parameterizations of the result

As reported in previous studies (*e.g.*, Righter *et al.*, 1997), the metal-silicate partition coefficient of element M  $(D_{\rm M}^{\rm met/sil})$  is linked to the free energy of the reaction, and can be related to *T*, *P*, and *f*O<sub>2</sub> by the following equation, to which we have added three terms to account for the metal composition (here, the silicate composition was kept constant, reflecting the early mantle during core formation):

250

251 
$$\log(D_{\rm M}^{\rm met/sil}) = a \log(fO_2) + b \frac{1}{T} + c \frac{P}{T} + d \log(1 - X_{\rm S}^{\rm met})$$

252 
$$+ e \log(1 - X_{\text{Si}}^{\text{met}}) + f \log(1 - X_{0}^{\text{met}}) + cst,$$
 (4)

where *a* is related to the valence of element M in the silicate melt, and *b* and *c* are related to the enthalpy  $\left(\frac{\Delta H^{\circ}}{RT}\right)$  and volume  $\left(\frac{P\Delta V^{\circ}}{RT}\right)$  of the system, respectively. Parameters *d*, *e*, and *f* are constants related to the chemical composition of the metallic phase. The term *cst* includes the effect of the entropy of the system  $\left(\frac{\Delta S^{\circ}}{R}\right)$ .

258 Using all existing data (presented here along with published data) for molten 259 metal-silicate liquid partitioning of U (63 data points) and Th (32 data points) for which 260 the T, P,  $fO_2$ , and silicate and metal compositions are all well characterized, we refined 261 the coefficients in equation (4) by multiple linear regression following a previously 262 validated approach (Bouhifd et al., 2013; Righter and Drake, 2003; Righter et al., 2010). 263 Data available in the literature come from a variety of sources (detailed in Appendix B) 264 using a variety of synthesis techniques presenting consistent results: piston-cylinder, 265 multi-anvil cell as well as diamond anvil cell. In order to obtain the best-fit 266 parametrizations, we excluded experiments with high uncertainties (>75% of the reported 267 partition coefficients), and data involving liquid metal-solid silicate equilibrium 268 considered as irrelevant to magma ocean conditions. For consistency, the literature values 269 for fO<sub>2</sub> and partition exchange coefficients were recalculated using the reported 270 concentrations of each element.

To determine the best-fit solutions for U and Th using equation (4), we performed several tests to establish the robustness of these parameterizations (Appendix C). The resulting parametrizations succeed in reproducing the experimental partition coefficients for a given set P, T,  $fO_2$  and chemical composition (Fig. 3a, b), and will thus be used to discuss the behavior of U and Th as a function of P, T,  $fO_2$ , and the chemical composition of the core.

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#### **3.2.1.** Effects of pressure and temperature on $D_U$ and $D_{Th}$

279 The first test of our parameterizations of the metal-silicate partitioning of U and Th 280 show that, within the range of experimental conditions investigated, the pressure has only 281 negligible effects on  $D_{\rm U}$  and  $D_{\rm Th}$ . For instance, at  $\Delta IW - 2$  and constant chemical 282 composition of the metallic phase (79.5 wt% Fe, 10 wt% Ni, 6 wt% Si, 2.5 wt% O, 2 wt% 283 S), the effect of pressure on  $D_{\rm U}$  is relatively small. Varying the pressure from 10 to 50 GPa (at 3500 K) lead to a small variation of  $D_U$  from about  $5 \times 10^{-3}$  to  $8 \times 10^{-3}$ . However, 284 285 data for Th are only available up to 8 GPa. By plotting the  $D_{Th}/D_U$  ratio versus pressure 286 (Fig. 4), we found that this ratio is constant within uncertainties. So we set the parameter 287 c (related to the pressure in equation (4)) to zero. By doing so, we found that the quality 288 of subsequent parameterizations with c = 0 is unchanged (Appendix C).

At constant pressure (between 5 and 50 GPa), a temperature increase from 2500 to 3500 K induces an increase of  $D_U$  and  $D_{Th}$  of about one order of magnitude. This suggests that, of the two parameters, temperature is the factor that most strongly influences the molten metal-silicate liquid partitioning of U and Th, consistent with results for U reported by Chidester *et al.* (2017).

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#### **3.2.2.** Oxidation state of U and Th at reducing conditions

296 Metal-silicate partitioning experiments can be used to estimate the valence of any 297 metallic element M in a silicate liquid as function of  $fO_2$ . The partitioning of an element M between silicate and metal involves an exchange reaction between its oxidized form (MO<sub>n/2</sub>) in the silicate melt and its reduced form in the metal (M), which depend on  $fO_2$ and the valence *n* of the element in the silicate as reported in the following reaction:

301 
$$MO_{n/2} \leftrightarrow \frac{n}{4}O_2 + M$$
 (5)

It is therefore possible to interpret the parameter a of our multi parameter linear 302 regression as equal to  $-\frac{n}{4}$  for each element. From equation (4), we determined that 303 304 parameter a for thorium is  $-0.95 \pm 0.25$ , consistent with its valence of 4+ in silicate melts 305 at reducing conditions from  $\Delta IW$  –5 to  $\Delta IW$  –1. However, for uranium, we determined parameter a to be  $-0.73 \pm 0.09$ , indicating a more complicated exchange reaction than for 306 307 Th. Previous studies have proposed that the valence of U in silicate melts under reducing 308 conditions can be 4+, as suggested by low pressure (<20 GPa) metal-silicate partitioning 309 experiments (e.g. Malavergne et al., 2007; Bouhifd et al., 2013; Wohlers and Wood, 310 2017), or 2+ (e.g. Chidester et al., 2017; Blanchard et al., 2017; Boujibar et al., 2019). 311 The parameterization performed herein shows that the parameter a for U does not 312 correspond to any single valence state (4+ or 2+). By fixing the parameter a to -1 or to -1313 0.5, reflecting a valence of 4+ or 2+ for uranium in silicate melts at reducing conditions, 314 the quality of our parameterizations remains the same as for a = -0.73. So we decided to 315 keep this parameter equals to  $-0.73 \pm 0.09$  avoiding any supplementary hypothesis on the 316 parameterizations. In fact, when we report the uranium partition coefficients as a function 317 of oxygen fugacity for experiments where the S content is low ( $X_S < 2 \text{ wt\%}$ ), we could see a change of the valence of U in silicate melt from 4+ to 2+ around  $\Delta IW$  -2 (Fig. 5). 318 319 This behavior is consistent with the change of the oxidation state of Nb and Ta in silicate 320 melts at reducing conditions (Cartier et al., 2014). However, further experiments and X-

321 ray absorption near edge structure analyses are required to confirm and better characterize

322 the valence of uranium in silicate melts at the conditions of Earth's core formation.

- 323
- 324

#### **3.2.3.** Effects of silicate and metal compositions on $D_{\rm U}$ and $D_{\rm Th}$

The existing data on molten metal-silicate liquid partitioning of uranium show disagreement about the effect of silicate composition on  $D_U$ . Chidester *et al.* (2017) proposed that the SiO<sub>2</sub> content of the silicate has a measurable effect on  $D_U$ . However, Blanchard *et al.* (2017) found that there is no effect of the SiO<sub>2</sub> content nor the degree of polymerization of the silicate melt on  $D_U$ . By combining all existing data on molten metal - silicate liquid partitioning of U and Th we found that the effect of SiO<sub>2</sub> has no significant impact on the partitioning of Th and U (see Appendix C).

The effect of carbon dissolved in the metallic phase on  $D_U$  and  $D_{Th}$  is estimated by 332 333 comparing C-bearing and C-free experiments. As reported in Tables A1 and A2, the 334 presence of carbon in the metallic phase has only a negligible impact on  $D_{\rm U}$  and  $D_{\rm Th}$  (Fig. 335 2). This is in good agreement with the C-U interaction parameter in a C-saturated iron 336 alloy, listed as 0 at temperatures around 1600-1700 K in the Steelmaking Data 337 Sourcebook (1988). Thus, since we do not observe any significant impact of carbon (up 338 to 4.8 wt%) on  $D_U$  and  $D_{Th}$  (Fig. 2), we do thus not include a parameter for C in our 339 parameterizations for U and Th.

We also found that varying the Si content of the metallic phase did not lead to significant variations of the Th/U ratio of the BSE nor concentrations of U and Th in the different reservoirs. For example, an accretion scenario with a Si-free core and a scenario using the parametrization taken from Fischer *et al.* (2015) (which propose a core with 8.5 344 wt% Si) lead to a 1% variation of the Th/U ratio of the silicate reservoir when all other 345 parameters are kept constant. So, we do not include a parameter for Si in our 346 parameterizations.

The effect of sulfur in the metallic phase on  $D_U$  and  $D_{Th}$  seems to depend on S 347 348 concentration and experimental pressure. For instance, we noticed a small dependence of 349  $D_{\rm U}$  and  $D_{\rm Th}$  on S content for concentrations <10 ± 2 wt%;  $D_{\rm U}$  and  $D_{\rm Th}$  increase by less 350 than half an order of magnitude when the S content is increased from 2 to 10 wt%, 351 consistent with low-pressure (Fig. 6) and high-pressure experimental data (e.g. Bouhifd 352 et al., 2013; Blanchard et al., 2017; Chidester et al., 2017). However, we observed a 353 strong dependence of  $D_{\rm U}$  and  $D_{\rm Th}$  on S concentrations at >20 wt% S. At low pressures 354 (<20 GPa) and  $\Delta IW$  –2, increasing the sulfur content from 2 to 35 wt% (corresponding to the FeS composition) results in an increase of  $D_U$  from  $8.4 \times 10^{-4}$  to  $4.4 \times 10^{-1}$  (roughly 355 356 three orders of magnitude), and  $D_{\rm Th}$  shows a smaller variation from  $8.4 \times 10^{-4}$  to  $8.3 \times 10^{-1}$ 357 <sup>2</sup>. At higher pressures (around 50 GPa), 3000 K, and  $\Delta IW$  –2, increasing the S content from 2 to 35 wt% led to an increase of  $D_{\rm U}$  from about 4.6×10<sup>-3</sup> to 2.4, making U a slightly 358 359 siderophile element at these extreme conditions. At the same conditions, the same increase in S content increases  $D_{\text{Th}}$  from 6.2×10<sup>-3</sup> to 0.6; Th thus remains a lithophile 360 361 element at all investigated P, T, and  $fO_2$  conditions and chemical compositions. We note 362 that for sulfide-silicate partitioning at  $\Delta IW - 2$ ,  $D_U$  is ~10 times higher than  $D_{Th}$ . Similar conclusions were made by Wohlers and Wood (2017) from low-pressure and low-363 364 temperature data. However, at lower oxygen fugacities around IW -5, they differ by only 365 a factor of 2.

18

366 By performing the parameterizations presented herein, we found the oxygen content 367 of the metallic phase to exert the strongest influence on metal-silicate U and Th 368 partitioning.  $D_{\rm Th}$  is more sensitive than  $D_{\rm U}$  to the oxygen content of the metal. For 369 instance, at similar P-T conditions and  $\Delta IW$  –2, an increase in the oxygen content of the metal from 2 to 5 wt% increases  $D_{\rm U}$  by less than one order of magnitude (from ~5×10<sup>-4</sup> 370 to  $3 \times 10^{-3}$ ) but  $D_{\rm Th}$  by about two orders of magnitude (from  $\sim 2 \times 10^{-4}$  to  $1.7 \times 10^{-2}$ ). This 371 372 difference will provide strong constraint on the composition of the Earth's core, as 373 discussed in section 4.2.

374 Finally, we note that we were able to separate the effects of oxygen and sulfur on  $D_{\rm U}$  and  $D_{\rm Th}$  by compiling all existing data from S-rich systems at low pressures to S-free 375 376 systems at high pressures, as S-rich and S-free metals are known to incorporate oxygen 377 at low and high pressure, respectively. For example, whereas Blanchard et al. (2017) used 378 only high-pressure experiments to constrain the impact of O on metal-silicate U 379 partitioning, our parameterization incorporates data from S-rich experiments at low 380 pressure (Wohlers and Wood, 2015, 2017) and S-free to S-rich experiments at high 381 pressure (Blanchard et al., 2017; Chidester et al., 2017).

By taking into account all the features discussed above, the best-fit solutions of our parameterizations for molten metal – silicate liquid partitioning of uranium and thorium are reported in equations (6) and (7). These equations will be used to discuss the behavior of U and Th during the Earth's core segregation.

387 
$$\log \left( D_{\text{U}}^{\text{met/sil}} \right) = (-0.72 \pm 0.07) \times \log(fO_2) + (-8346 \pm 1804) \times \frac{1}{T} + (-15.33 \pm 1.13) \times \log(1 - X_{\text{S}}^{\text{met}}) + (-51.55 \pm 7.86) \times \log(1 - X_{0}^{\text{met}}) + (-1.52 \pm 0.52)$$
(6)

389

390 
$$\log \left( D_{\text{Th}}^{\text{met/sil}} \right) = (-0.96 \pm 0.10) \times \log(fO_2) + (-9967 \pm 2618) \times \frac{1}{T} + (-13.76 \pm 1.40) \times \log(1 - X_{\text{S}}^{\text{met}}) + (-137.82 \pm 26.63) \times \log(1 - X_{0}^{\text{met}}) + (0.77 \pm 1.12) (7)$$

392

Where  $D_{\rm U}^{\rm met/sil}$  and  $D_{\rm Th}^{\rm met/sil}$  are molten metal – silicate liquid partition coefficients of uranium and thorium (on weight basis), respectively;  $f_{\rm O2}$  is the oxygen fugacity relative to the iron-wüstite buffer; T is the temperature in K;  $X_{\rm S}^{\rm met}$  and  $X_{\rm O}^{\rm met}$  are the wt% contents of S and O in the metallic phase, respectively.

- 397
- **4. Discussion**
- 399

#### 400 **4.1.** U and Th concentrations and the Th/U ratio of the bulk silicate Earth

401 The U and Th contents of the BSE depend on the total amounts of both elements on 402 Earth, which are directly connected to the nature of Earth's building blocks and their 403 partitioning between silicate and metal reservoirs. Geochemical data from chondrites 404 show that absolute U and Th concentrations both vary by about 23% among the different 405 chondrite groups, whereas the Th/U ratio is relatively constant, varying by only 7% 406 (Wasson and Kallemeyn, 1988). To reproduce the present-day mantle FeO content of about 8 wt%, the Earth must have been accreted from a large fraction (80-90%) of 407 408 reduced bodies (EH or EL enstatite chondrites) with 10 to 20% of Earth's mass likely accreted from more oxidized bodies (e.g., Clesi et al., 2016; Rubie et al., 2015). 409 Furthermore, Dauphas et al. (2014) showed that the terrestrial <sup>17</sup>O, <sup>48</sup>Ca, <sup>50</sup>Ti, <sup>62</sup>Ni, and 410 <sup>92</sup>Mo isotopic compositions can be reproduced by a mixture of 91% enstatite, 7% 411

412 ordinary, and 2% carbonaceous chondrites. Indeed, this chondritic composition can
413 explain the subchondritic Nb/Ta ratio of the BSE (Cartier *et al.*, 2014).

414 Similarly, we present here models of planetary accretion focusing on the evolution 415 of the U and Th contents and the Th/U ratio of the BSE. We adopted continuous core 416 formation models similar to those reported by Rubie et al. (2015) and Clesi et al. (2016). 417 In our models, the Earth accreted from impactors of a given chemical composition, which 418 then equilibrated (fully or partially) with the magma ocean of the proto-Earth until the 419 planet obtained its final mass  $(M_{\rm E})$ . We assume that impactors were already differentiated 420 into silicate mantles and metallic cores (Taylor and Norman, 1990). This differentiation 421 is defined by a pressure and temperature of equilibrium, leading to the partitioning of 422 their bulk compositions coherent with their masses  $M_{\rm I}$  (from 0.01  $M_{\rm E}$  to 0.1  $M_{\rm E}$ ). This 423 assumption only affects the results when the cores of impactors fail to completely 424 equilibrate with the terrestrial magma ocean, which is predicted to have occurred only 425 during the final few relatively large impacts (e.g. Deguen et al., 2014) (see below).

426 At each step of accretion (1%  $M_{\rm E}$ ), the impactor's metal and silicate equilibrate 427 within the proto-mantle, which accounts for 68% of the planet's mass. We tested various 428 increments of accretion (0.1%, 1%, and 10%  $M_{\rm E}$ ) and observed no impact on the final 429 result as long as the ratio  $M_{\rm I}/M_{\rm E}$  is maintained. We set the equilibration pressure to 50% 430 of the core-mantle boundary pressure at each step. This fraction is derived from previous 431 studies on the partitioning of siderophile elements sensitive to pressure (e.g., Boujibar et 432 al., 2014; Fischer et al., 2015), leading to a final pressure of equilibration of 60 GPa 433 (Siebert et al., 2012). Temperature is fixed at the liquidus of chondritic melts (Andrault 434 et al., 2011), which evolved from 1900 K at 1% accretion to 3500 K during the final stage 435 of accretion. Oxygen fugacity is constrained by the building block composition and the 436 amount of reduced / oxidized building block along accretion. Since a large amount of 437 reduced bodies is required to meet Earth's isotopic composition (Dauphas et al., 2014; 438 Dauphas, 2017; Javoy, 2010; Boyet et al., 2018), this model follows the fO<sub>2</sub> paths defined 439 in Clesi et al. (2016), i.e., ranging from IW -5 to IW -2. However, The fO<sub>2</sub> path of Earth 440 accretion has a negligible effect on the resulting (Th/U)<sub>BSE</sub> which vary by less than 0.7% 441 when considering an accretion at constant  $fO_2$  (IW-2 throughout accretion) instead of a 442 reduced to oxidized accretion scenario. The  $fO_2$  path mainly affects the content of the metallic phase in light elements (see below). Partitioning is determined using our 443 444 parameterizations for U and Th (Table 2). Following the approach of Deguen et al. 445 (2014), we take into account the effect of partial metal-silicate equilibration on elemental 446 partitioning, which mainly affects the last 40% of Earth's accretion. We consider that 447 equilibration between the proto-Earth's mantle and the metal of the impactors becomes 448 less efficient as accretion progresses (e.g., Deguen et al., 2014; Rubie et al., 2015). For 449 the last giant impact that formed the Moon ( $M_{\rm I} = 0.1 M_{\rm E}$ ), we find that the impactor's core 450 merges almost completely with the Earth's proto-core, with less than 5% of its mass 451 equilibrating with the silicate mantle. However, we find that the impact of this 452 equilibration on our parameterization is very limited, in agreement with Rudge et al. 453 (2010). Since we consider two mostly lithophile elements, disequilibrium models are as 454 compatible with the geochemical observations as equilibrium models, and the elemental 455 concentrations of the BSE remain within uncertainties in either case.

456 At each step of accretion, the O, Si, and Ni content of the metallic core is calculated 457 using the parameterization of Fischer *et al.* (2015). The C content of the core remains 458 constant at 0.2 wt% during accretion (Wood et al., 2006), and a late addition of sulfur-459 rich material increases the S content of the core to 2 wt% to fit geophysical, geochemical, 460 and experimental estimates (e.g., Allègre et al., 1995; Boujibar et al., 2014; Dreibus and 461 Palme, 1996; Palme and O'Neill, 2003). Variations of the O and Si contents in the metal 462 are related to the proportion of reduced and oxidized building blocks, which influence the 463  $fO_2$  path. At the end of accretion model in which Earth is built from a major proportion (80%) of reduced materials, the Earth's core contains 0.2 wt% C, 2 wt% S,  $6.75 \pm 0.75$ 464 465 wt% Si, and  $2.8 \pm 0.7$  wt% O. On the other hand, models in which Earth is built from 466 more oxidized materials (following an accretion with constant fO<sub>2</sub> at IW-2, Fischer et al. (2015) and references therein) propose Earth's core concentrations up to 5.85 wt% O and 467 468 2.04 wt% Si. To determine the viability of any accretion scenarios and the resulting U and Th concentrations in the different reservoirs, we also studied the evolution of Ni, Co, 469 470 Nb, and Ta, elements that have well-constrained metal-silicate partitioning behavior in 471 the literature. The parameterizations used to constrain the behaviors of these elements are 472 those of Fischer et al. (2015) for Ni and Co and Cartier et al. (2014) for Nb and Ta. As a 473 first test of validity, any accretion scenarios studied herein must reproduce the Ni/Co and 474 Nb/Ta elemental ratios in the present-day mantle.

A major contribution of enstatite chondrites during Earth's accretion is supported by the strong similarities between mass-independent isotopic ratios measured in enstatite chondrite and terrestrial samples (*e.g.*, Javoy, 1995; Dauphas, 2017; Boyet *et al.*, 2018). However, the most recently published trace element measurements of enstatite chondrites (Barrat *et al.*, 2014; Dauphas and Pourmand, 2015) reveal variable U and Th concentrations and significant differences relative to the compilation published by

481 Wasson and Kallaymen (1988). As U and Th concentrations are low in enstatite 482 chondrites, obtaining accurate measurements remains challenging. Thus, in our model, 483 we consider the enstatite chondrite U and Th concentrations of Barrat et al. (2014) and 484 Dauphas and Pourmand (2015) to represent the reduced end-members. We note here the 485 significant effect of weathering on the Th/U ratios of samples reported in these studies. 486 Under oxidizing surface conditions, these elements show contrasting behavior, with U 487 behaving as a water-soluble hexavalent species, whereas Th remains in a tetravalent state 488 (Kramers and Tolstikhin, 1997). Prolonged exposure to atmospheric conditions would 489 therefore raise the Th/U ratio of extraterrestrial samples. For instance, the average Th/U 490 ratios of enstatite chondrites (falls and finds) are  $4.23 \pm 0.81$  for EL chondrites and 3.59 491  $\pm$  0.52 for EH chondrites (1 $\sigma$  uncertainties), but these ratios are lowered to (Th/U)<sub>EL</sub> = 492  $3.85 \pm 0.52$  and  $(Th/U)_{EH} = 3.24 \pm 0.21$  when only chondrite falls are included. Therefore, 493 we only took into account concentrations measured in chondrites fall (Table 3). Results 494 published by Barrat et al. (2014) and Dauphas and Pourmand (2015) were obtained using 495 classical ICPMS technique and isotope dilution by MC-ICPMS, respectively. Three 496 samples (2 EL and 1 EH) are significantly different from the average Th/U values and 497 have been removed from the dataset (see Appendix D). The average values are 4.39±0.52 498 and 3.24±0.17 for EL and EH groups, respectively. Identical values are obtained when 499 only concentrations obtained by isotope dilution technique are considered.

500

501 We tested several scenarios involving different carbonaceous chondrites as the 502 oxidized building blocks of the Earth. Scenarios 2, 6, 7, and 8 (Table 4) which involve 503 different type of carbonaceous chondrites, show no significant differences in the final 504 concentrations of the modeled reservoirs. Therefore, we henceforth use CI chondrite falls 505 (Table 3) as a proxy for the oxidized building blocks as they have the most precisely 506 analyzed trace element concentrations (Barrat *et al.*, 2012).

Table 4 summarize the results of several scenarios of Earth accretion involving various building block mixing. All these scenarios reproduce the Nb/Ta and Ni/Co elemental ratios of the BSE, within uncertainties, as shown in Table 4. Our calculations produce a BSE with  $11.77 \pm 0.45$  ppb U,  $40.42 \pm 1.62$  ppb Th, and Th/U =  $3.43 \pm 0.13$ when using only EH chondrites as the reduced material (scenario 1, Table 4), and  $11.42\pm0.45$  ppb U,  $43.20\pm1.73$  ppb Th, and Th/U =  $3.78 \pm 0.15$  when using only EL chondrites as the reduced material (scenarios 2, Table 4).

514 The same calculations show the Earth's core to contain about 1.28 ppb U and 4.80 ppb Th using EH chondrites (scenario 1) or 1.24 ppb U and 5.22 ppb Th using EL 515 516 chondrites (scenario 2). Such U and Th concentrations would produce much less than 1 517 TW of energy due to radioactive decay, compared to the estimated 5-15 TW heat flux 518 escaping the core (Lay *et al.*, 2008). Thus, even for the highest  $D_{\rm U}$  and  $D_{\rm Th}$  values, the U 519 and Th contents of the Earth's core represent a negligible contribution to the heat flow 520 from the core to the mantle. These results are marginally affected by increasing the 521 amount of the reduced materials from 80 to 90% (scenarios 1, 2 and 9, Table 4).

522 Our results are also in agreement, within uncertainties, with the Th/U 523 concentrations reported by several authors (*e.g.*, Allègre *et al.*, 2001; McDonough and 524 Sun, 1995; Kargel and Lewis, 1993; Lyubetskaya and Korenaga, 2007, and references 525 therein). However, given the large uncertainties on the published Th/U value of the BSE 526 (up to 35% of the reported value), it is not possible to discriminate between the different 527 scenarios proposed here. Nevertheless, Wipperfurth et al. (2018) recently proposed Th/U =  $3.776^{+0.122}_{-0.075}$  for the BSE, derived from the <sup>208</sup>Pb\*/<sup>206</sup>Pb\* ratios (where the 528 asterisks denote the radiogenic component) of various terrestrial rocks compared to the 529 chondritic <sup>208</sup>Pb\*/<sup>206</sup>Pb\* value (Blichert-Toft et al., 2010). Considering the errors on their 530 531 result, our results using EL chondrites match the BSE Th/U value, whereas models using 532 EH chondrites produce Th/U ratios significantly different (at 95% confidence) from the 533 estimated BSE value (Fig. 7). Although combinations of EL and EH chondrites are 534 possible scenarios for Earth's accretion (scenarios 3, 4, and 5, Table 4), EL chondrites 535 must represent the main portion of the mixture. This observation supports the notion that 536 EL rather than EH chondrites represent the dominant fraction of Earth's building blocks 537 (Boyet et al., 2018).

538

#### 539 4.2. Th/U ratio of the BSE and the oxygen content of Earth's core

540 As discussed in section 3.2.3, our parameterizations of  $D_{\rm U}$  and  $D_{\rm Th}$  show that the 541 oxygen content of the Earth's core had a major impact on the fractionation of Th and U 542 during core segregation. Indeed, the most recent accretion models and high-pressure and 543 high-temperature studies suggest that Earth's core contains at least some amount of 544 oxygen (e.g., Bouhifd and Jephcoat, 2011; Tsuno et al., 2013; Siebert et al., 2012; Badro 545 et al., 2014; Fischer et al., 2015; Rubie et al., 2015; and references therein). Existing 546 models propose a large range of plausible oxygen contents in the Earth's core. Based on 547 geochemical arguments, Allègre *et al.* (2001) concluded that the core contains  $5.0 \pm 0.5$ 548 wt% O, whereas Javoy et al. (2010) reported  $2.55 \pm 1.39$  wt% O. By coupling 549 geochemical and geophysical constraints, Badro et al. (2014; 2015) concluded that the core contains 2.7 to 5 wt% O. Fischer *et al.* (2015) estimated the oxygen content of the core by following similar accretion scenarios and found that the Earth's core contains 2.1–2.6 wt% O. Finally, to fit the present-day mantle concentrations of some moderately siderophile elements (Cr, V, and Mn), Siebert *et al.* (2013) suggested that the core should contain 2 to 5.5 wt% O. A general consensus of the literature can be found on a minimum content of oxygen in the core of 2 wt% O.

556 By tracing the evolution of the Th/U ratio of the BSE versus the oxygen content of 557 the core (Fig. 8) using our parameterizations of  $D_{\rm U}$  and  $D_{\rm Th}$  (Eq. 4, Table 2), at 4.0 wt% O in the core, our modeled Th/U ratio of the BSE is beyond the 95% confidence level 558 559  $(2\sigma)$  of the BSE value. In this model, we equilibrate a CI-like chondritic composition with 560 a proto-Earth (Barrat et al., 2012), simulating the last stages of core segregation when the 561 most oxygen was incorporated into the metallic phase. For these calculations, we use the BSE Th/U value  $(3.776^{+0.122}_{-0.075})$  given by Wipperfurth *et al.* (2018), which is in good 562 563 agreement with several other studies (e.g., Allègre et al., 1995; Kargel and Lewis, 1993). 564 By combining the geophysical and geochemical constraints reported above with the 565 added constraint of the Th/U ratio of the BSE, the core must contain 2 to 4 wt% O.

566

#### 567 **4.3 Impact of a late sulfide addition on U and Th partitioning**

Another process that could have fractionated the Th/U ratio of the BSE is the late addition of sulfide (FeS) to the segregating core (*e.g.*, Wohlers and Wood, 2017). The S content of the Earth's core is about 2 wt% (*e.g.*, Allègre *et al.*, 1995; Badro *et al.*, 2014; Boujibar *et al.*, 2014; Dreibus and Palme, 1996; Palme and O'Neill, 2003, and references therein), and different scenarios exist to explain how the Earth acquired sulfur during core 573 segregation. If S was added throughout Earth's accretion, we find that the U and Th 574 contents of the core and the BSE would have barely been affected. If S was added 575 exclusively in the last 10-20% of Earth's accretion (e.g. Wood and Halliday, 2005), our 576 continuous core formation calculations show that the U and Th concentrations of the BSE 577 would be lowered by 3%, whereas the variation of the Th/U ratio of the BSE would be 578 negligible. Furthermore, our parameterizations (Eq. 4, Table 2) suggest that the late 579 addition of sulfur-rich bodies would have increased the U and Th concentrations in the 580 core by less than 6%. Thus, the late addition of sulfide (10–20%) to the Earth should not 581 have drastically affected the U and Th contents of the BSE and the core, which contribute no more than 1 TW of the energy required to sustain the geodynamo. Finally, the addition 582 583 of sulfide to the core, at any time during Earth's accretion, would not be observable based 584 on the Th/U ratio of the BSE.

585

586 **5.** Conclusion

In the present study, we presented new metal – silicate partition coefficients of Th in a fully liquid environment. Combined with literature data from previous studies, we developed new parametrizations of the behavior of U and Th in the context of a magma ocean, that demonstrate the dependence of  $D_U$  and  $D_{Th}$  on the metallic melt composition and the temperature.

592 The new parameterizations are then used to better constrain the conditions of core 593 formation and the composition of the core, in a multi-stage core growth models, by 594 comparing the resulting  $(Th/U)_{BSE}$  to the latest result by Wipperfurth *et al.* (2018). When 595 considering building block mixing that reproduce the major isotopic and elementary

596 features of the BSE, the calculated concentrations ( $U_{BSE} = 11.42 \pm 0.45$  ppb and  $Th_{BSE} =$ 597  $43.20 \pm 1.73$  ppb) best reproduce (Th/U)<sub>BSE</sub> when using reduced building blocks with an 598 EL chondrites type composition rather than EH. This support the idea that EL chondrites 599 (rather than EH) constitute a major part of Earth's reduced building blocks. In the 600 meantime, the contents U and Th in the Earth's core remain negligible, and cannot be significantly affected by the addition of sulphur. Finally, we show that, in order to 601 602 reproduce the latest Th/U ratio of the BSE within its uncertainties (Wipperfurth et al., 603 2018), the oxygen content of the Earth's core cannot exceed 4wt%.

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#### 813 Figure Captions

814	Figure 1. Backscattered electron image of sample #979 in its graphite capsule after
815	polishing. This sample was prepared from a C1 chondrite model composition + FeNi as
816	the starting material, and was recovered from 6 GPa and 2173 K.
817	

Figure 2. Effect of the nature of the capsule (C or MgO) on U and Th partition coefficients. The experiments were performed at exactly the same conditions (~2073 K and 4 GPa or 2173 K and 6 GPa at IW –2), and we changed only the nature of the capsule. Runs 975 (4 GPa) and 1022 (6 GPa) were performed in graphite capsules, and runs 979 (4 GPa) and 986 (6 GPa) in MgO single-crystal capsules (Table 1).

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Figure 3. Comparison between (a) U and (b) Th metal-silicate partition coefficients
(D<sub>U</sub> and D<sub>Th</sub>, respectively) determined experimentally and predicted by multi-variable
linear regressions (Eqs. 6 and 7). Solid and dotted lines represent the 1:1 correspondence
and 1\sigma errors on our regression (\sigma_U = 0.69, \sigma_{Th} = 0.85), respectively. R<sup>2</sup> is 0.85 for U and
0.82 for Th. Data references are reported in Appendix B.
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829

830 **Figure 4.** Evolution of  $D_{Th}/D_U$  as a function of pressure in S-free metal-silicate 831 partitioning experiments of this study and Wohlers & Wood (2017).

832

Figure 5. Molten metal – silicate liquid partition coefficients as a function of
oxygen fugacity. The experimental data are taken from Blanchard *et al.* (2017); Bouhifd *et al.* (2013); Chidester *et al.* (2017); Malavergne *et al.* (2007); Wheeler *et al.*, (2006);

Wohlers & Wood (2017). These experimental data are corrected from the effect of *T* and oxygen content of the metallic phase using the equations (6) and (7). In the present plot we excluded data involving sulfide liquids, and only consider partitioning data between silicate melt (with S content < 5 wt%) and Fe-rich alloys. The solid lines of slope -1 or -0.5 represent uranium in valence 4+ or 2+, respectively.

841

Figure 6. Evolution of (a) U and (b) Th partition coefficients with the concentration
of S in the metallic phase for experiments performed below 10 GPa, between 2050 and
2350 K, and at around IW –2.

845

846 Figure 7. Compilation of Th/U ratios estimated for the BSE compared with the results of this study. The grey line indicates the average BSE value of all studies shown 847 848 (Th/U = 3.70). All error bars are  $1\sigma$ , except data from Wipperfurth et al. (2018) and this 849 study, for which error bars represent  $2\sigma$  error propagations. Although our EL and EH 850 scenarios match the global geochemical models within  $1\sigma$  uncertainties, only our EL 851 chondrite-based model is in agreement with the recent isotopic lead analysis of the BSE 852 Th/U value (Wipperfurth et al., 2018), suggesting EL chondrites as one of Earth's main 853 building blocks.

854

Figure 8. Evolution of the Th/U ratio of the BSE with the O content of the Earth's core (black solid line). The calculations were made at 60 GPa and 3500 K. The grey solid line represents the Th/U ratio observed in the BSE (Wipperfurth et al., 2018). The black and grey dashed lines represent  $2\sigma$  errors on the model and the observed BSE Th/U value,

- 859 respectively. The shaded area corresponds to unrealistic oxygen concentrations in the 860 metallic phase, based on previous studies (see text for references). The maximum value 861 of 3.95 wt% O varies little with modification of the final parameters of the model such as
- 862 *P*, *T*, and the chemical composition of the building blocks.

## Figure 1.



# Figure 2.



### Figure 3a.



Figure 3b.



# Figure 4.



Figure 5.



# Figure 6a.



Figure 6b.



## Figure 7.



## Figure 8.



Sample	Capsule	P (Gpa)	<b>T</b> (K)	$\log fO_2$ ( $\Delta IW$ )	$\mathbf{D}_{\mathrm{U}}^{*}$	D <sub>Th</sub>
#969	Graphite	4	2128	-1.43	5.65×10 <sup>-5</sup>	3.86×10 <sup>-5</sup>
#975	Graphite	4	2073	-1.56	4.51×10 <sup>-5</sup>	1.26×10 <sup>-5</sup>
#1026	Graphite	5	2273	-0.82	1.64×10 <sup>-3</sup>	1.14×10 <sup>-3</sup>
#1027	Graphite	5	2273	-4.42	3.73×10 <sup>-3</sup>	1.34×10 <sup>-3</sup>
#1022	Graphite	6	2173	-1.74	2.30×10 <sup>-5</sup>	
#979	MgO	4	2075	-1.70	2.07×10 <sup>-5</sup>	2.02×10 <sup>-5</sup>
#986	MgO	6	2173	-1.64	1.76×10 <sup>-4</sup>	8.22×10 <sup>-5</sup>
#1021	MgO	6	2173	-1.44	1.54×10 <sup>-3</sup>	9.92×10 <sup>-5</sup>
#1028	MgO	8	2373	-1.45	1.71×10 <sup>-3</sup>	1.89×10 <sup>-4</sup>
#1029	MgO	8	2373	-4.67	1.64×10 <sup>-2</sup>	4.00×10 <sup>-3</sup>

**Table 1**. Experimental conditions (P, T,  $f_{O_2}$ ) and metal - silicate partitioning coefficients of U and Th for the different samples.

\* The partition coefficient values of U are taken from Bouhifd et al., 2013.

Elements	Nº.	$R^{2}$	а	b	d	f	cst
	74	0.95	-0.72	-8346	-15.33	-51.55	-1.53
	74	0.85	$\pm0.07$	$\pm$ 1103	$\pm$ 1.13	± 7.86	$\pm0.52$
ть	4.4	0.92	-0.96	-9967	-13.76	-137.82	0.77
	44	0.82	$\pm0.10$	$\pm2618$	$\pm$ 1.40	$\pm26.63$	$\pm$ 1.12

**Table 2.** Results of the multi-variable linear regression based on Equation 4 using our experimental data together with those listed in Appendix B.

 $N^{\circ}$ .: number of experiments;  $R^{2}$ : correlation coefficient.

**Table 3.** U and Th abundances (in ppb) for CI and EC chondrites used in this work. Only samples which fall where observed have been selected here, taken from the most recent published trace element measurements on chondrites. The n value represents the number of samples the U and Th concentration are based on.

	n	U	1 <b>σ</b>	Th	1 <b>σ</b>	Th/U	1 <b>σ</b>	references
CI chondrites	7	7.72	0.23	28.30	1.42	3.66	0.11	Barrat et al, 2012
EL chondrites	8	6.60	1.00	28.70	3.11	4.39	0.52	Barrat et al, 2014; Dauphas and Pourmand
EH chondrites	7	8.33	0.69	26.95	1.51	3.24	0.17	2015

**Table 4.** Different scenarios of Earth's accretion involving reducing chondrites (EH or EL type) and more oxidized ones (CI, CO, CV or CM) in various proportions. CI, EH and EL concentrations are presented in Table 3. Other chondrite compositions are taken from Wasson and Kallemeyn (1988), but scenarios 5,6 and 7 show that recent CI chondrites U and Th concentrations can be used as a proxy for carbonaceous chondrites. The uncertainties presented here are all  $2\sigma$ . Nb/Ta and Ni/Co ratios of the resulting BSE as well as the Si and O content of the associated core are calculated for each scenario. Each scenario presented here reproduce, within 2  $\sigma$  uncertainties, the Nb/Ta and Ni/Co of the BSE, presented for comparison in the last row of this table. Nb/Ta, Ni/Co and Th/U of the BSE, are taken from Münker et al. (2003), Lyubetskaya and Korenaga (2007) and Wipperfurth et al. (2018), respectively. Scenarios 9 and 10 are building block mixing proposed by Dauphas et al. (2014) and Dauphas, (2017), respectively. For these scenarios, since no precision is given considering the EC type used in these scenarios, we used the average of the EH and EL values given in Table 3, CI chondrites were considered as representative of carbonaceous chondrites (CC) chondrites and ordinary chondrites (OC) concentrations is an average of L LL and H chondrites concentration taken from Wasson and Kallemeyn (1988).

Saamaria	Reduced material %		Reduced material % Oxidized material %				Core (ppb)				
Scenario					Nb/Ta	Ni/Co	U	Th	Th/U	U (ppm)	Th (ppm)
1	EH	80	CI	20	13.75 ±0.55	19.1 ±0.80	11.77 ±0.45	40.42 ±1.62	3.43 ±0.13	1.28 ±0.05	4.80 ±0.20
2	EL	80	CI	20	14.68 ±0.59	18.7 ±0.76	11.42 ±0.48	$43.20\pm1.73$	$3.78\pm\!0.15$	1.24 ±0.07	5.22 ±0.21
3	EH-EL	40-40	CI	20	13.76 ±0.56	19.1 ±0.78	11.61 ±0.46	$41.88 \pm 1.67$	$3.60\pm0.14$	1.24 ±0.05	4.82 ±0.20
4	EH-EL	20-60	CI	20	$14.03 \pm 0.57$	19.1 ±0.77	11.51 ±0.46	$42.52\pm\!\!l.70$	$3.69\pm\!0.15$	1.25 ±0.06	5.05 ±0.20
5	EH-EL	60-20	CI	20	13.75 ±0.56	19.1 ±0.79	11.68 ±0.47	41.16 ± <i>1.64</i>	$3.52 \pm 0.14$	$1.28 \pm 0.05$	4.83 ±0.20
6	EL	80	СМ	20	$13.08 \pm 0.60$	19.45 ±0.81	11.49 ±0.46	$43.20 \pm 2.20$	3.76 ±0.25	1.24 ±0.12	5.23 ±0.42
7	EL	80	CO	20	$14.46\pm\!0.55$	19.23 ±0.84	11.46 ±0.63	$42.40 \pm 2.06$	3.70 ±0.23	1.24 ±0.11	5.23 ±0.41
8	EL	80	CV	20	13.88 ±0.54	$19.27 \pm 0.82$	11.40 ±0.72	42.18 ±2.51	$3.70\pm\!\!0.30$	1.25 ±0.16	$5.24 \pm 0.56$
9	EC	91	OC-CC	7-2	11.28 ±0.66	$18.75 \pm 0.89$	11.39 ±0.85	42.82 ±2.02	$3.76 \pm 0.32$	1.25 ±0.13	$5.29 \pm 0.51$
10	EC	71	OC-CO	5-24	12.23 ±0.61	19.73 ±0.88	11.80 ±0.83	43.66 ±2.06	3.70 ±0.32	1.20 ±0.13	5.15 ±0.50
BSE					14.00 ±0.60	18.90 ±0.32			3.78 ±0.24		

	i analysis of th	e run produce.	s using gruph	ne eupsuies.	
$P (GPa)^1$	4	4	5	5	6
$T (K)^{2}$	2128	2073	2273	2273	2173
Run	969	975	1026	1027	1022
<b>Silicate</b> EPMA (wt%)					
$SiO_2$	$48.93 \pm 0.57$	48.20±0.43	$43.00{\pm}0.89$	$54.05 \pm 0.39$	$50.37 \pm 0.42$
Al <sub>2</sub> O <sub>3</sub>	4.33±0.31	$3.72 \pm 0.22$	$3.59{\pm}0.42$	$3.83 \pm 0.10$	$2.60{\pm}0.12$
FeO	$8.44 \pm 0.13$	7.54±0.17	$13.83{\pm}0.63$	$0.32 \pm 0.04$	$7.50{\pm}0.45$
MgO	33.29±0.77	$36.39 \pm 0.55$	$33.93{\pm}0.82$	$35.76 \pm 0.49$	34.86±0.53
CaO	$2.87 \pm 0.11$	2.77±0.13	$2.60{\pm}0.21$	$3.05 \pm 0.05$	$2.88 \pm 0.12$
K <sub>2</sub> O	$0.47 \pm 0.02$	$0.44{\pm}0.03$	$2.25 \pm 0.22$	$2.47 \pm 0.03$	$0.30{\pm}0.03$
NiO	$0.13 \pm 0.01$	$0.19{\pm}0.02$	$0.14{\pm}0.02$	n.d.	0.13±0.02
PbO	0.16±0.01	$0.14 \pm 0.01$	n.d.	n.d.	$0.09 \pm 0.01$
UO <sub>2</sub>	0.54±0.03	$0.52{\pm}0.03$	0.21±0.02	0.17±0.01	$0.48 \pm 0.03$
Total	99.16	99.91	99.56	100.13	99.21
LA-ICP-MS (ppm)					
U	3896±100	3769±156	905±108	1126±22	4353±220
Th	3881±72	3957±163	879±71	1100±12	4120±140
<b>Metal</b> EPMA (wt%)					
Fe	58.73±0.59	61.03±1.10	54.01±1.20	83.30±0.32	74.61±0.68
Ni	36.55±0.76	35.42±0.99	19.60±1.10	$0.07 \pm 0.04$	20.25±0.69
S			23.28±0.82		
Si				15.76±0.65	
Pb	0.73±0.10	0.33±0.14	$0.11 \pm 0.01$	n.d.	$0.10{\pm}0.02$
<sup>3</sup> O	$0.03 \pm 0.01$	$0.05 \pm 0.04$	$0.75 \pm 0.13$	$0.16 \pm 0.02$	$0.03{\pm}0.02$
Fotal	96.32	97.06	97.86	99.51	95.20
LA-ICP-MS (ppm)					
U	0.22±0.10	0.17±0.10	$1.48 \pm 0.60$	4.2±0.96	0.10±0.06
Th	0.15±0.04	0.05±0.01	$1.00{\pm}0.30$	1.47±0.15	n.d.
$^{3}\log f_{02}$ ( $\Delta IW$ )	-1.81	-1.95	-1.25	-4.95	-2.07
$^{4}\log f_{02}$ ( $\Delta IW$ )	-1.43	-1.56	-0.82	-4.42	-1.74
$D_{\mathrm{U}}$	5.6 ×10 <sup>-5</sup>	4.5 ×10 <sup>-5</sup>	$1.6 \times 10^{-3}$	3.7 ×10 <sup>-3</sup>	2.3 ×10 <sup>-5</sup>
_ 3	$\pm 2.7 \times 10^{-5}$	$\pm 2.8 \times 10^{-5}$	$\pm 0.8 \times 10^{-3}$	$\pm 0.9 \times 10^{-3}$	$\pm 1.5 \times 10^{-5}$
$D_{ m Th}$	3.9 ×10 <sup>-5</sup>	$1.3 \times 10^{-5}$	$1.1 \times 10^{-3}$	$1.3 \times 10^{-3}$	
- 11	$+1.1 \times 10^{-5}$	$+0.3 \times 10^{-5}$	$+0.4 \times 10^{-3}$	$+0.15 \times 10^{-3}$	

Appendix A. Chemical analysis of all the run products. Table A1. Chemical analysis of the run products using graphite capsules.

$P (GPa)^1$	4	6	6	8	8
T (K) <sup>2</sup>	2075	2173	2173	2373	2373
Run	979	986	1021	1028	<sup>4</sup> 1029
Silicate EPMA (wt%)					
SiO <sub>2</sub>	48.20±0.85	$47.00 \pm 0.76$	49.75±1.20	$47.84 \pm 0.82$	47.41±0.71
Al <sub>2</sub> O <sub>3</sub>	$4.14 \pm 0.46$	$5.80 \pm 0.42$	$2.60 \pm 0.25$	4.06±0.39	4.31±0.24
FeO	$8.86 \pm 0.55$	$8.00{\pm}0.51$	$9.50 \pm 0.62$	9.12±0.53	$0.31 \pm 0.02$
MgO	35.41±0.77	$34.45 \pm 0.85$	33.86±0.85	$34.41 \pm 0.78$	37.73±0.95
CaO	$2.57 \pm 0.38$	$2.55 \pm 0.32$	$1.90\pm0.21$	$2.45 \pm 0.24$	2.55±0.15
K <sub>2</sub> O	$0.35 \pm 0.02$	$0.37 \pm 0.03$	$0.18{\pm}0.04$	$1.25 \pm 0.46$	3.15±0.17
NiO	$0.14{\pm}0.01$	$0.14 \pm 0.01$	$0.13 \pm 0.01$	$0.10{\pm}0.01$	n.d.
РЬО	$0.05 \pm 0.02$	n.d.	n.d.	n.d.	$0.10{\pm}0.01$
$UO_2$	$0.36 \pm 0.05$	$0.35 \pm 0.05$	$0.11 \pm 0.01$	$0.10\pm0.02$	$0.28 \pm 0.02$
Total	100.08	98.66	98.03	99.33	95.84
LA-ICPMS (ppm)					
U	3858±478	3300±424	846±76	850±130	859±51
Th	3969±491	3162±67	$1008 \pm 95$	899±190	851±41
Metal EPMA (wt%)					
Fe	66.91±0.54	56.11±0.90	61.39±1.53	$60.34 \pm 0.9$	84.64±0.59
Ni	$30.02 \pm 0.22$	$40.52 \pm 0.58$	$17.97 \pm 0.81$	$18.24 \pm 0.57$	$0.26 \pm 0.07$
S			$20.03 \pm 0.82$	19.69±0.33	
Si					13.81±0.31
Pb	$0.38 \pm 0.06$	$0.23 \pm 0.03$	$0.12 \pm 0.01$	$0.19{\pm}0.02$	0.27±0.10
<sup>3</sup> O	$0.05 \pm 0.02$	$0.06 \pm 0.02$	$0.33 \pm 0.04$	$0.42 \pm 0.04$	$0.05 \pm 0.03$
Total	97.57	97.12	99.94	98.9	99.24
LA-ICPMS (ppm)					
U	$0.08 \pm 0.04$	$0.58{\pm}0.15$	$1.30\pm0.16$	$1.45 \pm 0.36$	14.1±3.5
Th	$0.08 \pm 0.04$	0.26±0.05	0.10±0.01	$0.17 \pm 0.05$	3.4±0.3
$^{5}\log f_{\rm O2}$ ( $\Delta \rm IW$ )	-2.05	-1.99	-1.76	-1.80	-5.02
$^{6}\log f_{\rm O2}$ ( $\Delta {\rm IW}$ )	-1.70	-1.64	-1.44	-1.45	-4.67
$D_{ m U}$	2.1 ×10 <sup>-5</sup>	$1.8 \times 10^{-4}$	1.5 ×10 <sup>-3</sup>	1.7 ×10 <sup>-3</sup>	1.6 ×10 <sup>-2</sup>
	$\pm 1.3 \times 10^{-5}$	$\pm 0.7 \times 10^{-4}$	$\pm 0.3 \times 10^{-3}$	$\pm 0.7 \times 10^{-3}$	±0.5 ×10 <sup>-2</sup>
$D_{ m Th}$	6.05 ×10 <sup>-5</sup>	8.2 ×10 <sup>-5</sup>	9.9 ×10 <sup>-5</sup>	1.9 ×10 <sup>-4</sup>	4.0 ×10 <sup>-3</sup>
	±2.00 ×10 <sup>-5</sup>	±1.8 ×10 <sup>-5</sup>	±1.9 ×10 <sup>-5</sup>	$\pm 1.0 \times 10^{-4}$	±0.5 ×10 <sup>-3</sup>

 Table A2. Chemical analyses of run products using MgO-single crystal capsules (wt%).

n.d. not analysed.

<sup>1</sup>*Pressure uncertainties are estimated to be*  $\pm$  0.5 *GPa of the reported values.* 

<sup>2</sup>*Temperature uncertainties are within*  $\pm$  100 K.

<sup>3</sup>Oxygene concentration in metal is the result of microprobe analysis in samples subtracted of the concentration analyzed in pure Fe sample Nist665 ( $Xo_{Nist665}=0.21\pm0.01$  wt%).

<sup>4</sup>*For the run #1029, total of about 1.5 wt% of trace elements in the silicate are not reported.* 

<sup>5</sup>Oxygen fugacities relative to Iron-Wüstite buffer assuming that the activities of Fe and FeO were equal to their mole fraction.

<sup>6</sup>Oxygen fugacities relative to Iron-Wüstite buffer assuming that  $\gamma_{FeO} = 1.5$ . and  $\gamma_{Fe}$  is calculated using the formula of Ma, 2001.

$D_U$	D <sub>Th</sub>	$\frac{\log(f_{O2})}{(\Delta IW)}$	<i>P</i> (Gpa)	<i>T</i> (K)	$\frac{X_{S metal}}{(\text{wt.\%})}$	$X_{c metal}$ (wt.%)	X <sub>Si metal</sub> (wt.%)	X <sub>O metal</sub> (wt.%)
	This	work (*D	ata present	ted in Bo	ouhifd et a	el, 2013)		
*2.30×10 <sup>-5</sup>		-1.74	6	2173	0.00	4.8	0.00	0.03
*4.51×10 <sup>-5</sup>	1.26×10 <sup>-5</sup>	-1.56	4	2073	0.00	2.94	0.00	0.05
*2.07×10 <sup>-5</sup>	2.02×10 <sup>-5</sup>	-1.70	4	2075	0.00	0.00	0.00	0.05
*1.64×10 <sup>-3</sup>	4.00×10 <sup>-3</sup>	-0.82	5	2273	23.28	2.14	0.00	0.75
*5.65×10 <sup>-5</sup>	3.86×10 <sup>-5</sup>	-1.43	4	2128	0.00	3.68	0.00	0.03
*1.76×10 <sup>-4</sup>	8.22×10 <sup>-5</sup>	-1.64	6	2173	0.00	0.00	0.00	0.06
*1.64×10 <sup>-2</sup>	1.14×10 <sup>-3</sup>	-4.67	8	2373	0.00	0.00	13.81	0.05
*1.71×10 <sup>-3</sup>	1.89×10 <sup>-4</sup>	-1.45	8	2373	19.69	0.00	0.00	0.42
*3.73×10 <sup>-3</sup>	1.34×10 <sup>-3</sup>	-4.42	5	2273	0.00	0.49	15.76	0.16
*1.54×10 <sup>-3</sup>	9.92×10 <sup>-5</sup>	-1.44	6	2173	20.03	0.00	0.00	0.33
1.0 1 10	,,,_ 10	N	Malavergne	et al., 2	007	0100		
4.70×10 <sup>-2</sup>		-4.80	20	2673	33.30	0.00	1.50	0.00
4.30×10 <sup>-2</sup>		-5.40	5	2173	0.00	0.00	9.10	0.00
8.65×10 <sup>-3</sup>		-4.80	20	2673	2.30	2.10	26.60	0.00
			Wheeler e	t al., 200	)6			
3.30×10 <sup>-5</sup>		-2.06	2	2373	2.40	0.00	0.00	0.00
1.70×10 <sup>-5</sup>		-2.02	2	2123	0.10	0.00	0.00	0.00
4.10×10 <sup>-4</sup>		-2.23	2	2123	21.40	0.00	0.00	0.00
2.40×10 <sup>-5</sup>		-2.31	3	2123	9.30	0.00	0.00	0.00
1.20×10 <sup>-3</sup>		-1.92	10	2273	28.80	0.00	0.00	0.00
8.70×10 <sup>-4</sup>		-1.80	10	2123	29.30	0.00	0.00	0.00
1.90×10 <sup>-5</sup>		-1.98	10	2223	6.80	0.00	0.00	0.00
8.20×10 <sup>-4</sup>		-1.83	10	2073	27.70	0.00	0.00	0.00

**Appendix B.** Compilation of the experimental data used to derive the coefficients of Equation (4) for U and Th. The uncertainties on the reported data can be found in the original papers.

1.14×10 <sup>-2</sup>	3.88×10 <sup>-4</sup>	-2.57	2	1673	36.85	0.00	0.00	0.92
2.05×10 <sup>-2</sup>	7.24×10 <sup>-4</sup>	-3.42	2	1673	36.00	0.00	0.00	0.36
1.13×10 <sup>-1</sup>	3.15×10 <sup>-3</sup>	-4.09	2	1673	36.86	0.00	0.00	0.21
$1.53 \times 10^{+1}$	7.29×10 <sup>-1</sup>	-4.19	2	1673	35.63	0.00	0.00	0.20
1.79×10 <sup>-2</sup>	3.69×10 <sup>-3</sup>	-1.16	2	1673	33.24	0.00	0.00	3.06
4.45×10 <sup>-2</sup>	2.55×10 <sup>-3</sup>	-2.99	2	1923	36.68	0.00	0.00	0.37
5.52×10 <sup>-1</sup>	2.52×10 <sup>-2</sup>	-4.03	2	1923	35.55	0.00	0.00	0.21
5.83	2.58×10 <sup>-1</sup>	-4.20	2	1923	32.92	0.00	0.00	0.21
7.05	2.44×10 <sup>-1</sup>	-4.24	2	1923	33.82	0.00	0.00	0.16
8.86×10 <sup>-2</sup>	2.74×10 <sup>-3</sup>	-4.03	2	1773	33.89	0.00	0.00	0.24
3.17	1.28×10 <sup>-1</sup>	-4.39	2	1773	32.18	0.00	0.00	0.51
1.64×10 <sup>-2</sup>	1.07×10 <sup>-3</sup>	-1.81	2	1773	35.46	0.00	0.00	1.98
2.03×10 <sup>-2</sup>	3.03×10 <sup>-3</sup>	-1.45	2	1773	33.40	0.00	0.00	3.18
		We	ohlers and	d Wood, 2	2017			
3.46×10 <sup>-2</sup>	4.26×10 <sup>-4</sup>	-4.07	2	1908	29.31	2.45	0.00	0.15
1.13×10 <sup>-1</sup>	3.57×10 <sup>-3</sup>	-4.15	2	1908	32.17	2.44	0.02	0.07
5.67×10 <sup>-1</sup>	3.10×10 <sup>-2</sup>	-4.20	2	1908	32.83	2.92	0.02	0.14
4.83×10 <sup>-1</sup>	2.76×10 <sup>-2</sup>	-4.21	2	1908	32.56	4.28	0.02	0.39
1.04	6.97×10 <sup>-2</sup>	-4.27	2	1908	34.23	3.90	0.01	0.18
4.42×10 <sup>-1</sup>	1.25×10 <sup>-1</sup>	-3.93	2	2373	35.49	2.51	0.01	0.01
3.57×10 <sup>-3</sup>	1.95×10 <sup>-1</sup>	-3.98	2	2373	35.73	2.87	0.01	0.05
1.42	3.41×10 <sup>-1</sup>	-3.83	2	2373	34.50	2.96	0.80	0.47
4.63×10 <sup>-2</sup>	5.14×10 <sup>-3</sup>	-0.78	2	2373	28.94	1.62	0.08	3.91
7.12×10 <sup>-5</sup>	6.92×10 <sup>-5</sup>	-4.62	2	1923	0.00	0.00	1.79	0.00
1.11×10 <sup>-4</sup>	4.47×10 <sup>-6</sup>	-4.96	2	1923	0.00	0.00	3.42	0.00
2.02×10 <sup>-4</sup>	9.82×10 <sup>-6</sup>	-5.41	2	1923	0.00	0.00	8.25	0.00
2.11×10 <sup>-4</sup>	8.31×10 <sup>-5</sup>	-5.66	2	1923	0.00	0.00	10.94	0.00
3.04×10 <sup>-4</sup>	7.69×10 <sup>-5</sup>	-4.60	2	1923	0.00	4.43	2.61	0.03
1.59×10 <sup>-4</sup>	7.84×10 <sup>-4</sup>	-4.97	2	1923	0.00	4.43	6.08	0.09

#### Wohlers and Wood, 2015

8.41×10 <sup>-4</sup>	8.53×10 <sup>-5</sup>	-5.01	2	1923	0.00	4.43	4.32	0.08
4.63×10 <sup>-4</sup>	0.00	-5.39	2	1923	0.00	4.43	9.39	0.03
2.44×10 <sup>-3</sup>	1.63×10 <sup>-4</sup>	-5.53	2	1923	0.00	4.43	11.31	0.01
			Chidester	et al., 20	17			
1.08×10 <sup>-1</sup>		-2.91	67	4700	0.00	0.00	20.25	2.90
1.49×10 <sup>-1</sup>		-3.46	61	5000	0.00	0.00	27.54	3.19
7.02×10 <sup>-2</sup>		-2.44	57	3800	0.00	0.00	29.91	2.01
9.74×10 <sup>-1</sup>		-1.63	55	5400	15.01	0.00	12.14	8.03
2.66×10 <sup>-1</sup>		-3.31	57	4800	0.00	0.00	23.29	0.91
5.82×10 <sup>-2</sup>		-3.25	41	4000	0.00	0.00	31.50	0.73
2.87×10 <sup>-1</sup>		-2.08	54	4400	2.74	0.00	5.13	6.86
			Blanchard	l et al., 20	17			
2.27×10 <sup>-1</sup>		-0.66	62	3600	8.76	0.00	1.43	10.17
1.10×10 <sup>-1</sup>		-0.84	49	3500	4.13	0.00	1.10	6.79
2.99×10 <sup>-1</sup>		-0.66	70	3700	8.08	0.00	1.23	10.41
3.18×10 <sup>-1</sup>		-0.74	81	4000	10.39	0.00	2.71	12.11
2.34×10 <sup>-1</sup>		-0.96	49	3700	0.00	0.00	5.78	9.14
3.20×10 <sup>-1</sup>		-0.95	71	4000	4.12	0.00	1.60	9.20
1.34×10 <sup>-1</sup>		-0.83	54	4000	5.19	0.00	1.74	7.73
4.84×10 <sup>-1</sup>		-0.93	60	3800	0.00	0.00	3.12	10.54
3.25×10 <sup>-1</sup>		-0.85	71	4100	0.00	0.00	3.45	12.38
			Boujibar	et al 201	9			
3.09×10 <sup>-5</sup>	1.02×10 <sup>-5</sup>	-2.58	1	1973	0.61	4.09	2.91	0.12
8.91×10 <sup>-5</sup>	2.40×10 <sup>-5</sup>	-2.65	1	1853	3.21	0.76	3.79	0.23
2.95×10 <sup>-4</sup>	1.70×10 <sup>-4</sup>	-2.80	1	1823	2.31	0.62	4.20	0.19
5.25×10 <sup>-4</sup>	7.08×10 <sup>-5</sup>	-3.16	1	1973	0.50	1.88	12.02	0.06
2.09	1.48×10 <sup>-1</sup>	-3.16	1	1973	32.79	1.77	0.16	0.46
6.92×10 <sup>-5</sup>	9.77×10 <sup>-5</sup>	-3.20	1	1773	2.08	0.74	4.00	0.25
3.31×10 <sup>-5</sup>	8.32×10 <sup>-6</sup>	-3.59	1	1973	0.50	1.61	11.56	0.11
2.09	1.38×10 <sup>-1</sup>	-3.59	1	1973	33.32	1.82	0.13	0.16

3.89×10 <sup>-5</sup>	1.02×10 <sup>-3</sup>	-3.90	5	2173	1.68	1.90	14.43	0.06
2.51	1.32×10 <sup>-1</sup>	-3.90	5	2173	31.53	0.00	1.54	4.85
6.17×10 <sup>-4</sup>	1.10×10 <sup>-4</sup>	-4.29	1	1973	0.12	2.70	10.33	0.02
5.01×10 <sup>-3</sup>	8.32×10 <sup>-6</sup>	-5.23	1	1973	0.04		25.42	0.55

#### Appendix C. Calculation of coefficients from equation 4 for U and Th.

To determine the best parameterization of the behavior of Uranium and Thorium considering the database available, we performed a stepwise regression to determine the most pertinent variables to include in our parameterization and their best-fit parameters.

We first listed all the variables with a potential influence on the U and Th partition coefficients. In addition to the variables present in the final parameterization (Table 2), we also tested the metallic C, Ni and Si concentration and the  $SiO_2$  concentration in the silicate. These parameters are available for all experiments in Appendix B.

Prior to each regression, we ran a correlation analysis to avoid using redundant variables. We calculated the Pearson correlation coefficient (r) for each pair of variables described here. The Pearson correlation coefficients of all variables used in the final parameterizations are listed in Table C.1. We also calculated the determination coefficient ( $\hat{r}$ ), presented in Table C.2, which quantify the proportion of linear variance of one variable that can be explained by the other variable. In our dataset, only a few noticeable correlations can be found between the variables used in the parameterizations. The most important correlation was found between SiO<sub>2</sub> in the silicate and Si in the metal (r = 0.82,  $\hat{r} = 0.67$ ). We therefore decided to test these variables in separate regressions. For the rest of the variables, the fact that no correlations were found in our database can be explain by the diversity of the experimental conditions (P, T,  $fO_2$ ) and the variety of starting compositions used by the different authors, which renders variables that are usually correlated in natural systems uncorrelated here.

	`
•	1
a	

log(D <sub>U</sub> )	log(fO <sub>2</sub> )	1/T	log(1-Xs)	log(1-X <sub>0</sub> )
log(fO <sub>2</sub> )	1.00			
1/T	-0.27	1.00		
log(1-X <sub>s</sub> )	0.38	-0.29	1.00	
log(1-X <sub>0</sub> )	-0.31	0.19	-0.29	1.00

b)

log(D <sub>Th</sub> )	log(fO <sub>2</sub> )	<i>1/T</i>	log(1-X <sub>s</sub> )	log(1-X <sub>0</sub> )
log(fO <sub>2</sub> )	1.00			
1/T	-0.29	1.00		
log(1-Xs)	0.29	-0.35	1.00	
log(1-X <sub>0</sub> )	-0.31	-0.04	0.30	1.00

**Table C.1.** Pearson correlation coefficients (*r*) for each pair of variables used in the final parameterization of a)  $D_{\rm U}$  and b)  $D_{\rm Th}$ .

	`
•	• •
a	

log(D <sub>U</sub> )	log(fO <sub>2</sub> )	<i>1/T</i>	log(1-Xs)	log(1-X <sub>0</sub> )
log(fO <sub>2</sub> )	1.00			
1/T	0.08	1.00		
log(1-Xs)	0.14	0.08	1.00	
log(1-X <sub>0</sub> )	0.09	0.04	0.08	1.00

b)

log(D <sub>Th</sub> )	log(fO <sub>2</sub> )	<i>1/T</i>	log(1-X <sub>s</sub> )	log(1-X <sub>0</sub> )
log(fO <sub>2</sub> )	1.00			
1/T	0.08	1.00		
log(1-X <sub>s</sub> )	0.09	0.13	1.00	
log(1-X <sub>0</sub> )	0.10	0.00	0.09	1.00

**Table C.2.** Determination coefficients  $(\hat{r})$  for each pair of variables used in the final regressions for a) U and b) Th.  $\hat{r}$  is the square product of the Pearson correlation coefficient, r, which quantifies the proportion of linear variance of one variable that is explained by the other variable. The low  $\hat{r}$  values presented here suggest the absence of multi-collinearity in our model.

Regressions were performed for every non-redundant variable. For each regression, the overall model significance was determined with a Fisher-Snedecor test (*F* value and associated *p*-value), and a Student's *t*-test was run for every single variable (*t*-stat and associated *p*-value). We used a significance level of  $\alpha = 5\%$ , meaning that any value associated with a *p*-value < 0.05 and a *t*-stat > 1.96 is considered to be of statistical significance, at the 95% confidence level. Every variable found to be statistically insignificant was set to 0 and the remaining variables were regressed another time. For each new regression, potential correlations of the remaining variables were checked before calculation. In the end, we obtained a regression with six statistically significant and uncorrelated variables (other than *cst*) to constrain the evolution of  $D_{\text{Th}}$  and  $D_{\text{U}}$ .

We first ruled out of the parameterization terms related to  $SiO_2$  in the silicate and Ni in the metal, which were found to be of no statistical significance. We then removed the variables related to C and Si in the metal from the regression process: although they are found to be significant variable while having a weak effect, we realized parameterization with and without these parameters and the overall model robustness increased for both U and Th parameterizations when these parameters are not taking into account. The coefficients of other variables remained unchanged. Furthermore, considering the absence of any major effect on samples within graphite capsules and our qualitative analyses of metallic C in samples (obtained from the deviation of microprobe totals from 100%), we removed C in the metal from the final parameterizations.

The effect of pressure on  $D_{\text{Th}}$  is poorly constrained by the available dataset ( $c_{Th} = 276 \pm 289$ , with a *p*-value of 0.54 and *t*-stat = 1.02 in the first parameterization), and, while the value of  $c_u$  is shown to be of statistical significance ( $c_U = 15.6 \pm 45.2$ , with a *p*-value of 0.04 and *t*-stat = -2.52) it remains fairly negligible and overlaps with 0, within the error bar. By plotting the  $D_{\text{Th}}/D_{\text{U}}$  ratio versus pressure (Fig. 4), we found that this ratio is constant within uncertainties. We therefore decided to fix the parameter  $c_{\text{Th}}$  and  $c_{\text{U}}$  equal to 0, reducing the number of variables in the two parameterizations (other than *cst*) to four, without any effect on the other variables.

The final parameterizations of log  $D_U$  and log  $D_{Th}$  present fairly robust overall model significance. 85% and 82% ( $R^2$ ) of the respective variations of log  $D_U$  and log  $D_{Th}$  observed within the data are accounted for by the variables included in the final parameterization. The Fisher-Snedecor test values of each model (96.76 for U and 35.65 for Th) associated to its *p*value (significance *F*) confirm the overall pertinence of these parameterizations. The significance of each variable used in these models is also confirmed by their calculated *p*values.

Final parame	terization of log <i>D</i> U				
Regression Sta	atistics				
Multiple R	0.92				
$R^2$	0.85				
Adjusted $R^2$	0.83				
Standard error	0.67				
Observations	74				
¥7 • A					
Variance Ana	ilysis				
	degrees of freedom	Square Sum	Mean Sum	F-value	Significance F
Regression	4	182.46	45.61	96.76	9.24 .10 <sup>-28</sup>
Residual	70	32.99	0.47		
Total	74	215.45			
	Coefficients	Standard errors	t-Stat	p-value	
cst	-1.52	0.05	-2.94	0.004	
a	-0.72	0.10	-9.69	1.44 .10 <sup>-14</sup>	
b	-8346	1103	-8.29	5.26 .10-12	
d	-15.3	1.10	-13.50	3.61 .10-21	
f	-51.5	7.80	-6.55	7.85.10-9	

terization of log <i>D</i> <sub>Th</sub>				
atistics				
0.88				
0.82				
0.76				
0.71				
44				
llysis				
degrees of freedom	Square Sum	Mean Sum	F-value	Significance F
4	72.87	18.21	35.65	1.53 .10-12
39	19.92	0.51		
43	92.79			
Coefficients	Standard errors	t-Stat	p-value	
0.77	1.10	0.24	0.80	
-0.96	0.10	-3.20	0.002	
-9967	2618	-5.01	7.22.10-6	
-13.7	1.40	-9.79	4.60.10-12	
	terization of logD <sub>Th</sub> ntistics 0.88 0.82 0.76 0.71 44 ilysis degrees of freedom 4 39 43 Coefficients 0.77 -0.96 -9967 -13.7	terization of logD <sub>Th</sub> ntistics         0.88         0.82         0.76         0.71         44         Ilysis         degrees of freedom         Square Sum         4         72.87         39       19.92         43       92.79         Coefficients       Standard errors         0.77       1.10         -0.96       0.10         -9967       2618         -13.7       1.40	terization of logD <sub>Th</sub> ntistics	terization of log $D_{Th}$ uistics

#### Appendix D. (Th/U) value in EH and EL Chondrites.



Figure S1: Th/U measured in fall EH and EL chondrites. Data from Dauphas and Pourmand (2015) (plain symbol) and Barrat et al. (2014) (open symbol). U and Th concentrations are obtained using isotope dilution measurements in Dauphas and Pourmand (2015) and classical ICPMS technique measurements in Barrat et al., (2012), with a precision on U/Th ratio of 2.4% and 7.15% (2stdev), respectively. To determine these errors, we have considered the replicate measurements published for chondrites using the same analytical techniques. Seven measurements of the carbonaceous chondrite Allende were published in Pourmand and Dauphas (2010). They obtain a precision of 2.4% (2stdev) on Th/U (3.77±0.09). Barrat et al. (2012) published 6 measurements on Orgueil (carbonaceous chondrite). They obtained precision of 7.15% (2stdev) on Th/U (3.57±0.25). These error bars are represented in the figure. They are always smaller than the symbol size for data published by Dauphas and Pourmand (2015). Among the data represented in this plot, 3 samples are significantly outside the error bar (dark blue and orange rectangle, for EH and EL chondrites, respectively), which have been removed from the dataset. The resulting Th/U average values are significantly different: (Th/U)<sub>EH</sub>=3.24±0.17 and (Th/U)<sub>EL</sub>=4.39±0.52 (light blue and orange fields, respectively).

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