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P. Faure, M. Boyet, Mohamed Ali M.A. Bouhifd, Geeth Manthilake, T. Hammouda, J.-L. Devidal

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1 **Determination of the refractory enrichment factor of the bulk silicate Earth from**  
2 **metal-silicate experiments on Rare Earth Elements**

3  
4 P. Faure<sup>1</sup>, M. Boyet<sup>1\*</sup>, M.A. Bouhifd<sup>1</sup>, G. Manthilake<sup>1</sup>,  
5 T. Hammouda<sup>1</sup> and J.-L. Devidal<sup>1</sup>

6 <sup>1</sup>Laboratoire Magmas et Volcans, Université Clermont Auvergne, CNRS UMR 6524,  
7 OPGC-IRD, F-63000 Clermont-Ferrand, France

8 \*Corresponding authors: [maud.boyet@uca.fr](mailto:maud.boyet@uca.fr)

9  
10  
11 **Abstract**

12 This study investigates the partitioning of rare earth elements (REE) from La to Gd  
13 between molten metal and silicate to evaluate potential fractionation occurring during  
14 core-mantle differentiation. We report molten metal-silicate liquid partition coefficients  
15 from 24 multi-anvil experiments, extending the range of pressure, previously ranging  
16 from 1 to 8 GPa, up to 14 GPa. Experiments were performed at temperatures of between  
17 2300 and 2560 K, and for oxygen fugacities ranging from the IW (Iron-Wüstite buffer)  
18 to IW -4. Metal-silicate partition coefficients for the studied REE vary with the oxygen  
19 fugacity and S concentration in the metallic phase of the system. These elements were  
20 all lithophile during the Earth's accretion. By compiling all existing data on molten  
21 metal-silicate liquid partitioning, REE partitioning between the mantle and core during  
22 the Earth's accretion can be determined for a wide range of P, T and  $f_{O_2}$  conditions  
23 representing the early evolution of planetary bodies from planetesimals to planets. REE  
24 concentrations of the bulk silicate Earth (BSE) are calculated from accretion scenarios  
25 using varying proportions and compositions of chondritic building blocks. The models

26 selected are those that reproduce the Earth's nucleosynthetic isotope signature and the  
27 Ni/Co, Th/U and Nb/Ta ratios of the BSE. The BSE refractory element enrichment  
28 factor determined from REE data is equal to 2.88 (relative to CI chondrites). This  
29 calculation takes into account the depletion in volatile elements in the Earth compared  
30 to chondrites. This new estimate is in good agreement with previous determinations  
31 based on analysis of the upper mantle rocks, which supports the idea of a chemically  
32 homogeneous mantle. We also confirm that the formation of the core, with or without  
33 segregation of a sulfide phase, does not fractionate Sm/Nd and cannot be responsible for  
34 the  $^{142}\text{Nd}$  excess measured in modern terrestrial samples relative to chondrites.

## 35 **1. Introduction**

36 The planets of our Solar System result from the accretion of smaller objects including  
37 differentiated protoplanetary bodies and primitive objects formed in the early Sun's  
38 protoplanetary disk. The bulk chemical compositions of differentiated objects, which  
39 are composed of a metallic core surrounded by a silicate reservoir, are difficult to  
40 estimate because we do not have access to all the different reservoirs. Core-mantle  
41 differentiation processes concentrate chemical elements in the different reservoirs  
42 according to their partition coefficients. Siderophile elements are preferentially drawn  
43 into the metallic core whereas lithophile elements remain in the silicate portion.  
44 Chondrites, which escaped planetary differentiation, are commonly used as a reference  
45 for elements characterized by a high condensation temperature called refractory  
46 elements. Unlike volatile elements, they must not have been partially lost during the  
47 accretion stage. Then planetary bodies should retain chondritic ratios of refractory  
48 lithophile elements (RLE) in their silicate parts. Ratios of two elements characterized by  
49 a high condensation temperature (e.g. Ca, Al, rare earth elements) are similar in the  
50 different chondrite groups (Wasson and Kallemeyn, 1988). This observation forms the  
51 basis for many geochemical models used for reconstructing the composition of the bulk  
52 silicate Earth (BSE). Proposed BSE compositions have chondritic RLE ratios, and the  
53 absolute concentrations in the BSE for these elements are commonly expressed in the  
54 literature using the enrichment factor (EF), which is the BSE to CI concentration ratio  
55 ( $EF = [RLE]_{BSE} / [RLE]_{CI}$ ). This enrichment factor is usually determined from the  
56 concentrations measured for highly refractory elements (e.g. Al, Ti) in the most fertile  
57 upper mantle rocks. Once determined, it is applied to all RLE to calculate the BSE  
58 composition. Enrichment factors are in the range of 1.7 to 2.8 in the literature

59 explaining the differences in published BSE compositions (Lyubetskaya and Korenaga,  
60 2007; McDonough and Sun, 1995; Palme and O'Neill, 2014). Concentrations in heat-  
61 producing elements vary by ~20% in the different BSE models with important  
62 implications on the geodynamics and habitability of Earth (Jellinek and Jackson 2015).

63

64 The absence of RLE fractionation during the early phase of the Earth's evolution has  
65 been challenged, due to the presence of small  $^{142}\text{Nd}/^{144}\text{Nd}$  excesses in modern terrestrial  
66 samples relative to chondrites (up to 30 parts per million in the  $^{142}\text{Nd}/^{144}\text{Nd}$  ratio  
67 depending of the chondrite group; Boyet and Carlson, 2005). Since  $^{142}\text{Nd}$  is a radiogenic  
68 isotope partly produced by the decay of  $^{146}\text{Sm}$  ( $T_{1/2}=103$  Ma), a very early  
69 differentiation event of the silicate Earth had been proposed to explain this offset (Boyet  
70 and Carlson, 2005). Variation in the  $^{142}\text{Nd}/^{144}\text{Nd}$  ratio measured between the different  
71 groups of chondrites reflects nucleosynthetic heterogeneities in the protoplanetary disk  
72 during the accretion stage (Boyet et al., 2018). However, variations in mass-independent  
73 stable isotope ratios for Nd ( $^{145}\text{Nd}/^{144}\text{Nd}$ ,  $^{148}\text{Nd}/^{144}\text{Nd}$  and  $^{150}\text{Nd}/^{144}\text{Nd}$ ) are too small to  
74 be clearly resolved, with the exception of carbonaceous chondrites (Saji et al., 2016).  
75 The smallest difference in  $^{142}\text{Nd}$  between chondrite and terrestrial samples is for the  
76 enstatite chondrite group (average value -10 ppm, Boyet et al., 2018). Enstatite  
77 chondrites (EC) display nucleosynthetic isotope signature similar to BSE for a large  
78 number of isotope systematics suggesting that they represent a large fraction of the  
79 material accreted to form the Earth (e.g. Dauphas 2017). Because the analytical  
80 precision is not sufficient to detect significant variations in other Nd isotope ratios in  
81 EC relative to the terrestrial reference, a radiogenic origin of the  $^{142}\text{Nd}$  excess measured  
82 in modern terrestrial samples cannot be totally disproved. In this case the small excess

83 of  $^{142}\text{Nd}$  in modern terrestrial samples relative to chondrites could be the result of  
84 Sm/Nd fractionation produced during the lifetime of the parent isotope, i.e. during the  
85 first 500 Ma of Solar System history.

86

87 The Earth's core was proposed by Andreasen et al. (2008) as a potential enriched  
88 reservoir (early-formed low Sm/Nd reservoir characterized by deficit in  $^{142}\text{Nd}$ ), even  
89 though no REE partition coefficients were available then for core-forming conditions.

90 While experimental data suggest that Sm and Nd remain lithophile and behave in a  
91 similar fashion during liquid metal – liquid silicate partitioning (Bouhifd et al., 2015), it  
92 has been proposed that the addition of a significant amount of S into the core would  
93 fractionate Sm and Nd enough to explain the small  $^{142}\text{Nd}$  excess in modern terrestrial  
94 samples relative to chondrites (Wohlert and Wood, 2015). A small number of recent  
95 experiments performed at higher temperature (2100°C), more compatible with core  
96 formation conditions, seems to rebut elemental fractionation between Sm and Nd in a  
97 sulfur-rich environment (Wohlert and Wood, 2017). To further constrain the behaviour  
98 of REE during core-mantle differentiation processes, we report molten metal-silicate  
99 liquid partition coefficients (D) determined from 24 multi-anvil experiments. We  
100 extended the range of pressure to 14 GPa, as previous measurements had only been  
101 carried out between 1.5 and 8 GPa. Experiments were performed from 2300 to 2560 K,  
102 and for oxygen fugacity conditions ranging from IW (Iron-Wüstite buffer) to IW-4.  
103 Partition coefficients were determined for REE from La to Gd in a liquid metal-liquid  
104 silicate system with various amounts of S. Our new data set, combined with all existing  
105 experimental results, give a consistent parameterisation of the behaviour of these  
106 elements during magma ocean episodes for planetary bodies of different sizes

107 (planetesimals to planets) and for compositions representing the diversity found in the  
108 inner Solar System.

109

## 110 **2. Experimental methods**

### 111 **2.1. Starting materials**

112 The starting material for the silicate consisted of a natural equilibrated EC from the EL6  
113 subgroup (Hvittis, composition given by Rubin, 1983). Once finely ground, the powder  
114 was doped with the studied elements, at a level ranging from 1500 ppm to 1 wt% per  
115 REE. Since the field of application of Henry's law is not well defined for REE, we  
116 decided to split the studied REE into two different doping solutions, synthesized from  
117 AAS standard solutions, in order to minimize the amount of trace elements in the  
118 starting materials. Type A solution contained La, Ce, Pr, Nd and Sm, while type B  
119 solution contained Nd, Sm, Eu and Gd. For sulfur-rich experiments, a type C solution  
120 containing all 7 REE from La to Gd at a level of 1500 ppm each was synthesized. All  
121 solutions contained Nd and Sm in order to compare our experiments with previous  
122 studies (Bouhifd et al., 2015; Wohlers and Wood, 2017).

123

124 Various amounts of Fe-rich alloys (in the Fe–Ni–Si–S system) were then added in a  
125 weight proportion of 50:50. Control of the  $f_{O_2}$  between IW to IW-4 was obtained by  
126 addition of metallic Si to the starting material, resulting in the reduction of the FeO  
127 present in the silicate phase from about 20 wt% to ~0.2 wt% in some run-products. Each  
128 composition was mixed and ground in ethanol, before being dried and stored in a  
129 vacuum sealed dessicator for at least 48 h.

130

## 131 **2.2. High-pressure and high-temperature syntheses**

132 High-pressure and high-temperature experiments were carried out using the 1000-ton  
133 and 1500-ton multi-anvil apparatuses installed at the French National High-Pressure  
134 facility of Laboratoire Magmas et Volcans (LMV) in Clermont-Ferrand. Experimental  
135 conditions are summarised in Table 1, based on pressure calibrations similar to those  
136 already described in Boujibar et al., (2014) and Hammouda (2003). The pressure  
137 assemblies consisted of Cr-doped MgO octahedra, 18 or 14 mm edge length, containing  
138 a stepped graphite or LaCrO<sub>3</sub> heater, respectively. Octahedra were compressed using 32  
139 mm tungsten carbide anvils with truncation edge lengths of 11 and 8 mm (with 18 and  
140 14 mm octahedra, respectively) and pyrophyllite gaskets. The samples were contained  
141 either in graphite for 6 GPa experiments or in MgO single crystal capsules for 14 GPa  
142 experiments. The assembled octahedra were dried in an oven at 500 K overnight before  
143 each experiment. The samples were first compressed to the target pressure at room  
144 temperature and then heated to the desired temperature (between 2300 and 2560 K) for  
145 durations of 2 to 4 min. These durations are sufficient to achieve equilibrium between  
146 silicate melt and metallic liquid (e.g. Boujibar et al., 2014; Faure et al., 2020; Siebert et  
147 al., 2011) while preventing excessive reaction between the capsule and the silicate or  
148 metallic phases. Textural and chemical evidences (uniformed quenched silicate melts,  
149 well-formed metal blobs, chemically homogeneous metallic and silicate phases)  
150 confirmed that equilibrium was achieved in the sample. Temperatures were monitored  
151 with a thin axial W<sub>5</sub>Re/W<sub>26</sub>Re thermocouple whose junction was in direct contact with  
152 the top of the capsule. In the event that the thermocouple was lost, the temperature was  
153 determined using the power/temperature relation determined in previous experiments.  
154 The pressure and temperature uncertainties are estimated to be  $\pm 1$  GPa and  $\pm 100$  K



155 respectively, since no pressure correction was made for the emf of the thermocouple  
156 (e.g. Li et al., 2003). The samples were quenched by shutting off the power, which  
157 resulted in a quench rate of approximately 800 K/s. The samples were then  
158 decompressed over a period of about 12h. After the experiment, the run-product was  
159 mounted in epoxy, polished and carbon coated for the chemical analyses.

160

### 161 **2.3. Electron Microprobe**

162 Major and minor elements in the metal and silicate phases were analyzed using the  
163 LMV CAMECA SX100 electron microprobe using a 20 kV accelerating voltage. Major  
164 elements analyses in the silicate phase were performed at 50 nA with a 5-20  $\mu\text{m}$   
165 defocused beam, counting times on the peak ranging from 5 to 80 seconds depending on  
166 element concentrations and detection limit requirements. The standards for silicates  
167 were natural minerals and synthetic oxides (Si, Ca: wollastonite; Mg: forsterite; Al:  
168  $\text{Al}_2\text{O}_3$ ; Fe: fayalite; Na: albite; K: orthoclase; Ti, Mn:  $\text{MnTiO}_3$ ; Cr:  $\text{Cr}_2\text{O}_3$ ; Ni: NiO). For  
169 metallic and sulfide phase analyses, we used a defocused beam (10–20  $\mu\text{m}$ ), beam  
170 currents of 15 nA for the major elements (Fe, Ni, S and Si) and 150 nA for the trace  
171 elements, and counting times on the peak ranging from 5 to 60 s. Standards were pyrite  
172 for Fe and S in sulfides, and pure metal (Fe, Mn, Si, Mg, Ni, Cr) for metallic alloys. For  
173 samples embedded in graphite capsules, the carbon content in Fe-alloys was estimated  
174 from the deviation of the analyses totals from 100%.

175

### 176 **2.4. Laser Ablation ICP-MS**

177 Trace element concentrations were determined using the LMV Elements XR laser-  
178 induced coupled plasma-mass spectrometer (LA ICP-MS) coupled with a 193 nm ArF

179 excimer type laser (Resonetics M-50). The laser was fired at selected sample regions at  
 180 a repetition rate of 2 to 4 Hz with 4 mJ output energy beam, with a spot size diameter of  
 181 15–44  $\mu\text{m}$  in the silicate, and 80-130  $\mu\text{m}$  in the metal. Ablation duration lasted usually  
 182 around 80 s and was done in a pure He atmosphere. Reference material glasses NIST  
 183 SRM 610, NIST 612 and BCR2-G were used for external calibration (Gagnon et al.,  
 184 2008), and  $^{29}\text{Si}$ ,  $^{57}\text{Fe}$  and  $^{60}\text{Ni}$  were used as internal calibrators. All data were processed  
 185 using the GLITTER software package (Achterberg et al., 2001). Ca signal was  
 186 monitored during metal analyses and Fe and Ni signals during silicate analyses. Any  
 187 sudden variation in their content was considered as indicative of phase contamination  
 188 (metal contamination during the silicate phase analysis, or vice versa) and the  
 189 corresponding analyses were rejected.

190

## 191 **2.5 Oxygen fugacity determination**

192 Oxygen fugacity was calculated using the Fe and FeO contents of the metal and silicate  
 193 quenched phases, using the equilibrium reaction:



195 The  $f_{\text{O}_2}$  was estimated relative to the Iron-Wüstite buffer (IW) from the activities of Fe  
 196 and FeO in the metal and silicate following the equation:

$$197 \log f_{\text{O}_2}(\Delta\text{IW}) = 2 \times \log \left( \frac{a_{\text{FeO}}^{\text{sil}}}{a_{\text{Fe}}^{\text{met}}} \right) \quad (2)$$

198 where  $a_{\text{FeO}}^{\text{sil}} = \gamma_{\text{FeO}}^{\text{sil}} \times X_{\text{FeO}}^{\text{sil}}$  and  $a_{\text{Fe}}^{\text{met}} = \gamma_{\text{Fe}}^{\text{met}} \times X_{\text{Fe}}^{\text{met}}$  represent the activity of FeO in the  
 199 silicate liquid and Fe in the metal phase, respectively.  $X_{\text{Fe}}^{\text{met}}$  and  $X_{\text{FeO}}^{\text{sil}}$  are the molar  
 200 fractions of Fe in the metallic phase and FeO in the silicate liquid.  $\gamma_{\text{FeO}}^{\text{sil}}$  and

201  $\gamma_{Fe}^{met}$  represent the activity coefficient of FeO in the silicate liquid, and the activity of Fe  
202 in the metallic phase, respectively.

203 The Fe activity coefficient in Fe-rich alloys was calculated from the formula of Ma  
204 (2001), using the interaction parameters  $\epsilon$  provided Wade and Wood (2005) and the  
205 activity calculator (<http://www.earth.ox.ac.uk/~expet/metalact/>) provided by the  
206 University of Oxford.

207 We used the average gamma value derived from studies at 1 bar by O'Neill and Eggins  
208 (2002) for several melt compositions in the CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system, and by  
209 Holzheid et al. (1997) for melts in the anorthite-diopside system and komatiitic basalt,  
210 assuming no pressure effect on the activity coefficients in silicate melts (Toplis, 2004).

211

## 212 **3. Results**

### 213 **3.1. Phase assemblages and compositions**

214 Typical run products consisted of quenched silicate melts and liquid metal blobs (Figure  
215 1). Measured chemical compositions of the quenched silicate and metallic melts are  
216 reported in Appendix A. The run-product microstructures show that both phases became  
217 fully molten during the high pressure and high temperature experiments. The metallic  
218 phase generally forms a large “core” located at the center or to one side of the capsule  
219 or, less frequently, large drops distributed throughout the sample. In some cases,  
220 dendritic microstructures are observed in the silicate, requiring a defocused beam for  
221 chemical analyses to average the heterogeneous quenched textures. Several criteria are  
222 used to demonstrate the thermodynamic equilibrium of these experimental samples: (i)  
223 multiple analyses in the silicate phase show that it is homogeneous with no evidence of

224 chemical zoning, and (ii) all metal blobs embedded in the silicate matrix have identical  
225 composition within uncertainties.

226

227         In the present study we also tested the effect of the nature of the capsule (graphite  
228 vs. MgO single crystal) on REE partitioning. Using graphite capsules, analytical totals  
229 for the metallic phases indicate some amount of C dissolved in the metal (from 0.21 to  
230 4.99 wt%, see Appendix A1). More details about the dissolution of C into the metallic  
231 phases are reported in Appendix A2. On the other hand, the MgO single crystal capsule  
232 tends to saturate the silicate phase in MgO, leading to the formation of olivine quenched  
233 crystals instead of enstatite in these samples. Previous studies based on multi-anvil and  
234 piston-cylinder experiments (Bouhifd et al., 2015; Wohlers and Wood, 2017) showed  
235 that these interactions do not have a significant effect on the partitioning of REE. In  
236 addition, we observed no noticeable difference in REE molten metal-silicate liquid  
237 partition coefficients between 14 GPa (MgO single crystal capsule) and 6 GPa (graphite  
238 capsule) experiments for a similar range of temperature,  $f_{O_2}$  and chemical composition,  
239 showing no significant impact of the nature of the capsule or pressure in our  
240 experiments (Appendix B).

241

### 242 **3.2. Experimental partition coefficients**

243 Overall, 24 experiments were performed, resulting in 24 new partition coefficients for  
244 Sm and Nd and 15 for La, Ce, Pr, Eu and Gd (Table 1). Molten metal – silicate liquid  
245 partitioning are always low, ranging from  $10^{-3}$  to  $10^{-6}$ , in agreement with results  
246 obtained in previous studies for experiments performed at similar conditions (see  
247 Appendix C). The two main parameters influencing liquid metal - liquid silicate

248 partition coefficients are the oxygen fugacity and the sulfur content of the metallic  
249 phase. Changing the oxygen fugacity conditions from IW-4 to IW-1 leads to a decrease  
250 in the partition coefficient by two to three orders of magnitude (Figure 2 and Appendix  
251 D.1). On the other hand, the transition from pure Fe metal to pure FeS increases the  
252 partition coefficient of all studied REE by up to three orders of magnitude (Figure 3 and  
253 Appendix D.2).

254

255 Europium behaves slightly differently to other studied REE in our experimental  
256 conditions (Figures 2-4). Around the Iron-Wüstite buffer, more than 50 % Eu is divalent  
257 in a basaltic melt (Burnham et al., 2015). Thus, in the redox conditions of the present  
258 study, Eu is mainly in a +2 valence state.  $\text{Eu}^{2+}$  is more stable in a sulfide phase than all  
259 the other trivalent REE, as shown in all the FeS-bearing experiments in this study  
260 (Figure 4). In all sulfur-rich samples, the sulfide phase is enriched in Eu, leading to a  
261 mean  $D_{\text{Eu}}$  2.5 times higher than the partition coefficients for the other REE. Values from  
262 the literature are also plotted in Figure 4. Results obtained from experiments performed  
263 in evacuated silica tubes at temperatures of between 1200 and 1400 °C (Ingrao et al.,  
264 2019; Lodders, 1996) are in agreement with our results. These similarities strongly  
265 suggest that pressure and temperature have a negligible effect on molten Fe-rich alloy –  
266 silicate liquid partitioning of the studied REE ( $D_{\text{REE}}$ ). That  $D_{\text{REE}}$  is little dependent on  
267 temperature can be shown by the fact that the free energy of the exchange  
268 reactions for REE are not sensitive to the variation of the temperature in the likely range  
269 during core formation (details are reported in Appendix D.3).

270

271 By including experiments from previous studies, it is also possible to analyze the impact  
 272 of the nature of the silicate phase on the behavior of the studied REE. The NBO/T  
 273 (Non-Bridging Oxygen per Tetrahedral cations) value is an indicator of melt  
 274 polymerization, with zero corresponding to a completely polymerized melt (SiO<sub>2</sub> melt)  
 275 and a value of 4 corresponding to a completely depolymerized melt (Mg<sub>2</sub>SiO<sub>4</sub> melt). For  
 276 roughly similar experimental conditions and metallic compositions, and for a large  
 277 difference in silicate composition (NBO/T from 0.5 to 3.7, see Appendix A and C), the  
 278  $D_{\text{REE}}$  coefficients are similar within the analytical uncertainties. Furthermore, besides  
 279 FeO that is directly related to the oxygen fugacity of experiments, we find no significant  
 280 impact of any of the major oxides that compose the silicate phase on the partition  
 281 coefficient of the studied REE, for the available dataset. Therefore, data suggest that the  
 282 silicate melt composition has no significant influence on the REE metal-silicate  
 283 partition coefficients.

284

### 285 **3.3. Parameterisation of the results**

286 Partitioning of an element between metal and silicate phases can be considered as an  
 287 exchange reaction involving Fe, FeO and the oxidized and reduced components of  
 288 element M, of valence  $n$ :



290 By considering the equilibrium for this exchange reaction, it is possible to write the  
 291 following relationship between  $\log(D_M)$  and  $\log(f_{\text{O}_2})$  (Righter et al., 2010):

$$292 \quad \log(D_M) = a \log(f_{\text{O}_2}) + b \frac{1}{T} + c \frac{P}{T} + d \log(1 - X_{S \text{ metal}}) + e \quad (5)$$

293 The  $a$ ,  $b$ ,  $c$ , and  $e$  terms relate to valence  $n$  ( $a = -\frac{n}{4}$ ), enthalpy ( $\frac{\Delta H^\circ}{RT}$ ), volume ( $\frac{P\Delta V^\circ}{RT}$ ),  
294 and entropy ( $\frac{\Delta S^\circ}{R}$ ), respectively. The empirical term  $d$  takes into account the effect of  
295 sulfur in a metallic liquid ( $X_{S_{metal}}$  is the wt.% of S into the metallic phase), as discussed  
296 previously.

297

298 In order to refine the values of  $a$  and  $d$  for La, Ce, Nd, Sm, Eu, and Gd, we used all  
299 existing data sets for which the partitioning behavior, phase compositions and  
300 experimental conditions (temperature, pressure, oxygen fugacity) had been accurately  
301 determined. We considered solid silicate for experiments performed at  $T <$  melting  
302 temperature of the silicate phase (liquidus). The references as well as the conditions (P,  
303 T,  $f_{O_2}$ ) available for each experiment are listed in Appendices A and C. We used a  
304 multiple linear regression (approach used by Bouhifd et al., 2015; Faure et al., 2020;  
305 Righter et al., 2010) for each element of interest. For every regression, the robustness of  
306 each overall model significance was determined using a Fisher-Snedecor test, and a  
307 Student test was run to assess the significance of every variable. Results of the two-  
308 variable parameterisation for La, Ce, Pr, Nd, Sm, Eu and Gd are summarized in Table 2  
309 with their respective standard deviations and determination coefficients. The p-values  
310 determined for each variable are also reported. As seen above, only  $a$  and  $d$  are relevant  
311 to REE partitioning behavior. The parameters  $b$  and  $c$ , corresponding respectively to the  
312 effect of T and P are found here of no statistical significance, and are therefore set equal  
313 to 0. This result reflects the negligible impact that T and P have on  $D_{REE}$  (Appendix B),  
314 in comparison to the effect displayed by  $X_{S_{metal}}$  and  $f_{O_2}$ , within a dataset containing  
315 experiments performed up to 14 GPa and 2560 K. While this observation is in  
316 agreement and validate previous studies based on a smaller range of P and T (Bouhifd et

317 al., 2015; Wohlers and Wood, 2017), a dependence on pressure or temperature might be  
318 resolved when data obtained from higher pressure experiments will be collected.

319

320 The value of parameter  $a$  being proportional to the valence of one element (equations 5  
321 and 6), the parameterisations proposed here are consistent with all REE being in a +3  
322 valence state within the studied range of oxygen fugacity conditions, with the exception  
323 of Eu, which is essentially +2 below the IW buffer. In an S-free system, an oxygen  
324 fugacity from IW-5 to IW-2 will lead to a decrease in  $D_{Nd}$  from  $2.32 \times 10^{-3}$  to  $3.76 \times 10^{-5}$   
325 and a decrease in  $D_{Eu}$  from  $3.71 \times 10^{-4}$  to  $2.34 \times 10^{-5}$  (Figure 2). The effect of the sulfur  
326 content of the metal is also noticeable in our parameterisation, leading to an increase of  
327 all REE partition coefficients by about three orders of magnitude when the S content in  
328 the metallic phase increases from 0 to ~35 wt% at constant oxygen fugacity. For  
329 example, at IW-2,  $D_{Eu}$  increases from  $2.34 \times 10^{-5}$  to  $2.45 \times 10^{-2}$  and  $D_{Nd}$  increases from  
330  $3.31 \times 10^{-5}$  to  $2.56 \times 10^{-2}$  (Figure 3). No noticeable difference is found between Eu and the  
331 other REE with respect to the effect of the sulfur content in metal. In the discussion, we  
332 will use parameterisations obtained in the range of conditions of the available dataset, in  
333 order to establish the partitioning of REE in the conditions of Earth's core formation.

334

## 335 **4. Discussion**

### 336 **4.1. Absence of Sm-Nd fractionation during planetary core formation**

337 Previous high pressure – high temperature experiments led to different conclusions  
338 concerning the role of core formation on the Sm/Nd ratio of the BSE. Elemental  
339 fractionation between Sm and Nd was reported from sulfide-silicate partitioning data in  
340 experiments performed at 1.5 GPa and temperatures between 1400 and 1650°C



341 (Wohlbers and Wood, 2015). However, when both phases are molten, this fractionation is  
342 no longer observed. This is shown in our study and from published high pressure – high  
343 temperature experiment datasets (Figure 5, Bouhifd et al., 2015; Wohlbers and Wood,  
344 2017). Sulfide-silicate and metal-silicate partition coefficients for Sm and Nd vary with  
345 two parameters:  $f_{O_2}$  conditions and sulfur content. They must be taken into account  
346 when calculating Sm and Nd concentrations in bulk planetary silicate reservoirs. A late  
347 addition of sulfide (FeS) to the segregating core, as proposed by Wohlbers and Wood  
348 (2015), would change the final Sm and Nd concentrations of the BSE since the partition  
349 coefficients increase by three orders of magnitude from pure Fe metal to pure FeS.  
350 However, Sm and Nd cannot be fractionated during core formation in a Solar System  
351 planetary body of any size.

352

#### 353 **4.2. Refractory Lithophile Element enrichment factor for the Earth calculated** 354 **from metal/silicate partitioning experiments**

355 Concentrations of refractory lithophile elements in the BSE are conventionally  
356 estimated by comparing the chemical composition of the most pristine peridotites  
357 (xenoliths and peridotite massifs) representative of the upper mantle and that of  
358 chondrites. The traditional Earth composition models have been based on CI chondrites  
359 because their bulk composition closely matches the composition of the solar  
360 photosphere, except for the most volatile elements. REE concentrations in the BSE are  
361 commonly defined using the RLE enrichment factor (EF), which is applied to all  
362 refractory lithophile elements considered to be present in the BSE (similar to primitive  
363 mantle) in chondritic proportions. When expressed relative to the concentration  
364 measured in CI chondrites, this RLE factor lies within the range of 1.7 to 2.8 (Table 3).

365 The determination of this EF is a key feature of most BSE model since non-refractory  
366 and non-lithophile element concentrations in the BSE are determined via their observed  
367 mantle ratio with RLE. Therefore, the enrichment of the BSE in RLE will dictate the  
368 concentration of the BSE in all elements.

369 Here we propose a new approach where the RLE enrichment factor is calculated from  
370 the experimental molten metal – silicate liquid REE partitioning results. We have  
371 developed a model of planetary accretion focusing on the partitioning of REE between  
372 the mantle and the core throughout Earth's formation. In this model, the Earth accreted  
373 from impactors with a given chemical composition, which then equilibrate (fully or  
374 partially) with the magma ocean of the proto-Earth, until the planet obtains its final  
375 mass ( $M_E = 5.97 \cdot 10^{24}$  kg). All the scenarios result in a fully formed Earth, with a  
376 primitive mantle representing 68% of its mass, the core representing the last 32%. The  
377 model takes into account the composition of various building blocks potentially  
378 involved over the entire history of the Earth's accretion and metal/silicate partitioning  
379 data which evolve with core formation conditions ( $fO_2$ , pressure, temperature,  
380 composition). The accretion model is described in detail in Appendix E.

381

382 The measurement of small variations in mass-independent stable isotope ratios for a  
383 large number of elements, also called nucleosynthetic anomalies, provides a real  
384 opportunity to investigate the genetic relationship between the different planetesimals  
385 and planets. Several mixtures of different building blocks (which differ in nature and  
386 proportions) have been proposed in previous studies to match the terrestrial isotopic  
387 signature (e.g. Dauphas et al., 2014; Lodders, 2000). Results vary mainly because  
388 different studies focused on different elements. However, most of the studies which

389 integrate a large database of isotopic ratios agree on a major contribution of enstatite  
390 chondrites in the mixture with a smaller contribution of carbonaceous chondrites and/or  
391 ordinary chondrites (Warren, 2011; Dauphas 2017; Liebske and Khan, 2019). We  
392 assume that Earth accreted materials with bulk chondrite composition from known type  
393 of meteorites and potential effects of collisional erosion on the chemical composition  
394 are not considered (see Palme and O'Neill, 2014).

395

396 Among the available models, only those with a mixture of different building blocks (of  
397 chondritic composition) that succeed in reproducing the Earth's isotopic signature are  
398 considered (e.g. Dauphas, 2017; Warren, 2011). In order to further test the validity of  
399 the accretion scenarios, we also studied the evolution of certain element ratios whose  
400 molten metal-silicate liquid partitioning behaviour is well constrained in the literature:  
401 Ni/Co, Nb/Ta, and Th/U. Accretion scenarios must be able to reproduced these  
402 elementary ratios already well established for the BSE (Nb/Ta =  $14.0 \pm 0.60$ ; Th/U =  
403  $3.78 \pm 0.12$ ; Ni/Co =  $18.90 \pm 0.30$ , Munker, 2003; Palme and O'Neill, 2014; Wipperfurth  
404 et al., 2018). The parameterisations used to constrain the behavior of these elements  
405 during metal-silicate partitioning are taken from Fischer et al. (2015) for Ni and Co,  
406 Cartier et al. (2014) for Nb and Ta and Faure et al., (2020) for U and Th. Of all the  
407 accretion scenarios tested, only those reproducing (within  $2\sigma$  uncertainties) the BSE  
408 elemental ratios are considered in the following discussion (Dauphas, 2017; Dauphas et  
409 al., 2014; Lodders, 2000; Warren, 2011). These four accepted scenarios contain for the  
410 building blocks between 70 and 91% of EC, the rest being made more oxidized (CC or  
411 OC) materials (Table 4). Several models involving different building blocks mixture fail

412 at reproducing the BSE elementary ratios (Javoy, 1995; Burbine and O'Brien, 2004;  
413 Javoy et al., 2010; Fitoussi and Bourdon, 2012).

414

415 Rare earth element concentrations in the BSE for these four accepted scenarios are  
416 reported in Table 4. Enrichment factors (EF) can be calculated from the comparison of  
417 these BSE compositions with CI chondrites concentrations. However, it must be noted  
418 that none of the measured chondrite compositions have so far succeeded in reproducing  
419 the Earth's depletion in volatile elements compared to CI, as the Earth is more depleted  
420 in those elements than any known chondrite (Allègre et al., 2001; Braukmüller et al.,  
421 2019; Wang et al., 2016). While it has been suggested that the Earth's depletion in  
422 volatile elements could be the result of erosion following a giant impact during late  
423 accretion (Halliday, 2004; Hubbard and Ebel, 2014), it has also been proposed that this  
424 depletion pattern was already present in the Earth's building blocks (Birck et al., 1999;  
425 Siebert et al., 2018, and references therein). The depletion of the Earth in volatiles  
426 elements, no matter its occurrence in the planet history, would have a direct impact on  
427 the concentration of RLE within the BSE. In order to take the impact of volatile  
428 depletion on RLE concentrations in the resulting BSE into account, the concentration of  
429 volatile elements in chondrites has been recalculated in order to fit the Earth's volatile-  
430 element depletion pattern. This concerns volatile and moderately volatile elements, i.e.  
431 those with 50% condensation temperatures below 1230 K (Lodders, 2003). The  
432 composition of non-refractory elements for each chondrite group has been recalculated,  
433 by applying the primitive mantle (BSE) ratios when normalized to Mg (Lyubetskaya  
434 and Korenaga, 2007; Palme and O'Neill, 2014). Then, concentrations of all elements  
435 were recalculated to reach 100% weight total. The resulting compositions are found to

436 be enriched in RLE compared to measured chondrite compositions by a factor  $f_{dry}$   
437 ranging from 1.6 for EH chondrites, to 2.0 for CM chondrites (Appendix E). A  
438 weighted average of these  $f_{dry}$  factors, depending on the respective proportion of each  
439 chondrite composition in the Earth's building blocks (Table 4), was applied to our  
440 calculations.

441

442 Calculated enrichment factors are reported in Table 4 for the four accepted scenarios  
443 corresponding to those proposed by Dauphas, (2017), Dauphas et al., (2014), Lodders,  
444 (2000) and Warren, (2011). Values are identical within error and the average  $EF_{dry}$   
445 value is 2.88 (Figure 6). The effect of volatile depletion shown in the figure is  
446 significant, increasing the enrichment factor by a value of about 1. Compared to the  
447 concentrations given by previous authors (Table 3, Figure 6), our results are in  
448 agreement with BSE composition models based on a geo-petrological approach,  
449 showing high RLE concentrations (McDonough and Sun, 1995; Palme and O'Neill,  
450 2014). McDonough and Sun (1995) use plots of Ca/Yb, Sc/Yb and Sm/Yb of fertile  
451 lherzolites ( $MgO \leq 40.5wt\%$ ) against a  $TiO_2$  content of the BSE set at 0.2 wt. % to  
452 estimate the absolute proportions ( $EF=2.75$ ). Palme and O'Neill (2014) use a mass  
453 balance approach to calculate the primitive mantle composition. By first estimating the  
454 major oxide concentrations in the primitive mantle (MgO,  $SiO_2$  and FeO), they deduce  
455 the amount of the two RLE oxides, CaO and  $Al_2O_3$ , using their chondritic ratios. They  
456 obtain an RLE enrichment factor of  $2.83 \pm 0.23$ . The two other BSE models presented in  
457 Figure 6 yield lower enrichment factors. Lyubetskaya and Korenaga, (2007), by  
458 reassessing the peridotite database from McDonough and Sun (1995), obtain an RLE  
459 enrichment factor of the BSE of  $2.16 \pm 0.37$ . This value overlaps with the  $EF_{dry}$  factor

460 obtained following the model proposed by Dauphas et al. (2014) (Figure 6). The  
461 difference with McDonough and Sun, (1995)'s results is due to the statistical treatment  
462 of the database, specifically the selection criteria of pristine samples (metasomatism,  
463 melt extraction) and the statistical data filtering

464

465 In the model proposed by Allègre et al. (2001), concentrations of refractory elements in  
466 the BSE are significantly lower and the calculated enrichment factor is within the range  
467 of those calculated from models that do not consider the volatility trend of the BSE  
468 (open circles in Figure 6). Allègre et al. (2001) use Mg/Si and Al/Mg ratios for the least  
469 differentiated sample of Earth's mantle of 0.945 and 0.095, respectively, taken from  
470 Hart and Zindler, (1986). Trace element concentrations are then calculated based on the  
471 cosmochemical trend shown by carbonaceous chondrites (and sometime other chondrite  
472 groups) in a trace element ratio plot. This model requires very few assumptions and  
473 succeeds in reproducing the depletion trend of the Earth's volatile elements. However,  
474 when estimating the Earth's RLE concentrations using the ratio trends of these elements  
475 in chondrites, this method fails to take into account the relative enrichment in refractory  
476 elements of the BSE compared to chondrites due to volatile element loss. Thus they  
477 obtain a BSE composition enriched in REE by an average of  $1.70 \pm 0.24$  compared to  
478 CI.

479

#### 480 **4.3. Generalisation of the enrichment factor to all RLE?**

481 Most BSE models assume fixed chondrite-normalized RLE ratios. While we show that  
482 this hypothesis is relevant for REE from La to Gd (except Eu under specific conditions),  
483 some elements usually classified as RLE may change their behavior at core-forming

484 conditions ( $P$ ,  $T$ ,  $f_{O_2}$ ). For example, Nb and Ta are both siderophile elements in reduced  
485 conditions. Heterogeneous accretion models in which conditions evolve from reduced to  
486 oxidized during the Earth's accretion explain the superchondritic Nb/Ta ratio of the  
487 BSE (Cartier et al., 2014). Therefore, the RLE enrichment factor presented here should  
488 only be used to calculate the abundances of elements that are known to remain  
489 lithophile under Earth accretion conditions. Within the REE group, two elements are  
490 likely to behave differently: Eu and Yb. Data on heavy REE are available in the study of  
491 Ingrao et al. (2019) and Wohlers and Wood (2017). In a similar fashion to Eu in a sulfur  
492 rich environment, Yb fractionation occurs in very reduced conditions (IW -5 to -7) and  
493 the partial reduction to a +2 valence state has been identified using X-ray Absorption  
494 Near Edge Structure measurements (Ingrao et al., 2019). However, since Eu is more  
495 sensitive than Yb to a valence change under reduced conditions, and no significant  
496 fractionation between Eu and other studied REE is observed, we do not anticipate that  
497 core formation would cause an Yb anomaly in the calculated BSE REE pattern.  
498 Furthermore, the S content of the Earth's core is considered to be about 2 wt% from  
499 geophysical, geochemical and cosmochemical constraints (e.g. (Allègre et al., 2001;  
500 Boujibar et al., 2014). There is still debate as to whether the Earth's core acquired its  
501 sulfur signature over the entire accretion history, or exclusively in the last 10-20 % of  
502 the Earth's accretion (e.g. Wood and Halliday, 2005). In order to consider the impact of  
503 the accretion of sulfur-rich bodies on the concentration of REE in the different  
504 reservoirs, we ran models representing several scenarios involving impactors containing  
505 iron sulfide instead of metallic iron, in various proportions (up to 20% of the Earth's  
506 mass). No significant variation in REE concentrations or ratios within the BSE is

507 observed. The addition of sulfide to the Earth's core, at any time during the Earth's  
508 accretion, leaves no noticeable trace on the resulting REE concentrations of the BSE.

509

#### 510 **4.4. Chemical uniformity of present day mantle?**

511 BSE composition models based on the analysis of the upper mantle rocks consider  
512 samples from the upper mantle to be chemically representative of the mantle as a whole.

513 However, it has been proposed that a substantial difference exists between a pyrolitic

514 upper mantle and the lower mantle, below the 660 km seismic discontinuity, particularly

515 in terms of Mg/Si and Mg/Fe (Ringwood, 1989). Various evidences have been used to

516 infer a lower mantle chemically distinct from the upper mantle in terms of major and

517 trace elements. Among them, the isotopic and chemical heterogeneities measured in

518 mantle-derived basalts. Measured isotopic ratios support the existence of early-formed

519 chemical heterogeneities that could be preserved in the deepest part of the mantle.

520 Furthermore, the apparent mismatch between laboratory-measured properties in upper

521 mantle composition assemblage and the seismic and other geophysical properties

522 observed in the lower mantle, coupled with the identification of a global seismic

523 discontinuity at 660 km depth and early interpretations of the density of the lower

524 mantle led to the design of a two chemically distinct layers model of Earth's mantle (see

525 Hofmann, 2014 for a review).

526

527 However, one compelling observation in favor of a homogeneous mantle is tomographic

528 images showing slabs of oceanic lithosphere descending through the lower mantle

529 (Fukao and Obayashi, 2013). Furthermore, recent studies combining mineral physics

530 data with seismological constraints support the idea that the lower mantle is most likely



531 pyrolytic and that there is no need for a chemically stratified mantle (Hyung et al., 2016;  
532 Zhang et al., 2013). While it has been suggested that the Earth's layers could affect just  
533 the bulk mantle trace element budget (Campbell and O'Neill, 2012), our models show  
534 that REE abundances estimated for upper mantle samples are well reproduced by the  
535 resulting BSE using accretion models with isotopically-supported building block  
536 mixing. This supports the argument in favor of a chemically uniform mantle.

537

## 538 **5. Conclusion**

539 Molten metal – silicate liquid partitioning data have been obtained from 24 multi-anvil  
540 experiments on rare earth elements from La to Gd. These elements are lithophile under  
541 the conditions of Earth accretion, with molten metal – silicate liquid partition  
542 coefficients ranging from  $10^{-2}$  to  $10^{-6}$ . Their partitioning behaviour is mainly constrained  
543 by the oxygen fugacity and the S concentration in the metallic phase of the system.  
544 Using our data, together with previously published results, we obtain a two-variable  
545 parameterisation for these elements. They are trivalent during the Earth's accretion,  
546 even at low oxygen fugacity conditions, with the exception of Eu, which is divalent.  
547 Our results show that Sm and Nd are not significantly fractionated by core formation  
548 processes over a large range of  $f_{O_2}$  conditions, even in the presence of a large quantity of  
549 sulfur. The main impact of core formation is to concentrate the REE within the BSE.  
550 The absolute REE concentration in the BSE depends on the nature of the building  
551 blocks involved in the accretion scenario. Accretion scenarios using mixtures of  
552 chondrites that match the nucleosynthetic signature of the Earth give an average  
553 enrichment factor of 2.88 relative to CI. This result takes into account the RLE  
554 enrichment of the BSE due to the Earth's depletion in volatile elements compared to

555 chondrites. Our estimate is in good agreement with those of McDonough and Sun  
556 (1995) and Palme and O'Neill, (2014), and in favor of a chemically homogeneous  
557 present day mantle. This enrichment factor can be extended to other elements which  
558 remain strictly lithophile during Earth core formation. The formation of the core, with  
559 or without segregation of a sulfide phase, cannot be responsible for the small  $^{142}\text{Nd}$   
560 excess measured in modern terrestrial samples relative to chondrites.

561

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572

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726

727 **Figure Captions**

728

729 **Figure 1.** Backscattered electron image of the sample #1322, recovered from a 6 GPa  
730 and 2503 K experiment in a graphite capsule.

731

732 **Figure 2.** Evolution of metal-silicate partition coefficients for neodymium and europium  
733 ( $D_{Nd}$  and  $D_{Eu}$ ) with  $\log fO_2$ . Datapoints are from this study (Appendix A) and from the  
734 literature (Appendix B). Data are corrected for the effect of metallic sulfur using the  
735 parametrization presented in equation 6 and Table 2. Similar binary plots for other  
736 studied REE are given in Appendix D.1. Dashed line represents fitted linear regression,  
737 in agreement with equation 6 and parameters values displayed in Table 2.

738

739 **Figure 3.** Evolution of metal-silicate partition coefficients for neodymium and  
740 europium ( $D_{Nd}$  and  $D_{Eu}$ ) with the S concentration in the metal. Datapoints are from this  
741 study (Appendix A) and from the literature (Appendix C). Data are corrected for the  
742 effect of oxygen fugacity using the parametrization presented in equation 6 and Table 2.  
743 Similar binary plots for other studied REE are given in Appendix D.1. Dashed line  
744 represents fitted linear regression, in agreement with equation 6 and parameters values  
745 displayed in Table 2.

746

747 **Figure 4.** Sulfur-silicate partition coefficients for REE (normalized to  $D_{Nd}$ ) determined  
748 in all S-rich experiments ( $X_S$  from 25.3 to 35.2 wt. %). The average sulfur-silicate  
749 partition coefficients from Ingrao et al. (2019), Lodders (1996) and Wohlers and Wood  
750 (2017) are also plotted. Error bars are not shown for clarity, but  $D_{Eu}$  values are

751 significantly distinct from those of other REE (with the exception of experiment #509  
752 and Wohlers and Wood, 2017).

753

754 **Figure 5.** Ratio of metal-silicate partition coefficients determined for Sm and Nd  
755 ( $D_{\text{Sm}}/D_{\text{Nd}}$ ) as a function of oxygen fugacity. Data presented are from this study as well  
756 as those from the literature for experiments performed over the chondritic liquidus.  
757 Error bars display the  $1\sigma$  uncertainties on original data. These samples present S  
758 contents in the metallic phase ranging from 0 to 35 wt.%.

759

760 **Figure 6.** RLE enrichment factors of the BSE calculated from accretion scenarios using  
761 mixtures of different chondritic building blocks, compared with published BSE  
762 composition models. Open circles represent RLE enrichment factors determined from  
763 our accretion model in the BSE using measured chondrite compositions. Higher values  
764 of RLE enrichment factors (noted  $EF_{\text{dry}}$  in Table 4) are obtained when the volatile  
765 depletion is taken into account. BSE enrichment factors in RLE ( $EF_{\text{dry}}$ ) are well  
766 reproduced by BSE composition from McDonough and Sun, (1995) and Palme and  
767 O'Neill, (2014).

**Table 1.** Experimental conditions (P, T,  $f_{O_2}$ ) and metal-silicate partition coefficients of REE (La to Gd) for the different samples. Given uncertainties are 1 sigma. For this work, different doping solutions were synthesized. Type A solution contained La, Ce, Pr, Nd and Sm, while type B solution contained Nd, Sm, Eu and Gd. For sulphur-rich experiments, a type C solution containing all 7 REE from La to Gd was prepared. \*Temperature determined using the power/temperature relation deduced from previous experiments.

Run	Capsule	Doping solution	P (GPa)	T (K)	log $f_{O_2}$ ( $\Delta$ IW)	$D_{La}$	$D_{Ce}$	$D_{Pr}$	$D_{Nd}$	$D_{Sm}$	$D_{Eu}$	$D_{Gd}$
509	Graphite	C	6	2361	-0.60	$6.19 \times 10^{-4}$ $\pm 1.63 \times 10^{-4}$	$1.01 \times 10^{-3}$ $\pm 1.33 \times 10^{-4}$	$9.28 \times 10^{-4}$ $\pm 1.23 \times 10^{-4}$	$9.98 \times 10^{-4}$ $\pm 1.67 \times 10^{-4}$	$9.49 \times 10^{-4}$ $\pm 1.88 \times 10^{-4}$	$1.31 \times 10^{-3}$ $\pm 1.86 \times 10^{-4}$	$7.16 \times 10^{-4}$ $\pm 2.09 \times 10^{-4}$
536	Graphite	C	6	2386	-0.47	$1.40 \times 10^{-3}$ $\pm 8.24 \times 10^{-5}$	$2.35 \times 10^{-3}$ $\pm 3.70 \times 10^{-4}$	$1.98 \times 10^{-3}$ $\pm 1.55 \times 10^{-4}$	$1.86 \times 10^{-3}$ $\pm 5.95 \times 10^{-5}$	$1.49 \times 10^{-3}$ $\pm 1.85 \times 10^{-4}$	$4.95 \times 10^{-3}$ $\pm 3.14 \times 10^{-4}$	$8.33 \times 10^{-4}$ $\pm 5.88 \times 10^{-5}$
581	Graphite	C	6	2563*	-0.86	$4.24 \times 10^{-4}$ $\pm 8.44 \times 10^{-5}$	$5.86 \times 10^{-4}$ $\pm 1.16 \times 10^{-4}$	$5.41 \times 10^{-4}$ $\pm 8.95 \times 10^{-5}$	$4.81 \times 10^{-4}$ $\pm 9.93 \times 10^{-5}$	$3.56 \times 10^{-4}$ $\pm 5.16 \times 10^{-5}$	$1.01 \times 10^{-3}$ $\pm 1.44 \times 10^{-4}$	$2.10 \times 10^{-4}$ $\pm 2.16 \times 10^{-4}$
594	Graphite	B	6	2388	-3.18				$1.76 \times 10^{-4}$ $\pm 1.48 \times 10^{-5}$	$1.40 \times 10^{-4}$ $\pm 1.99 \times 10^{-5}$	$2.19 \times 10^{-4}$ $\pm 1.77 \times 10^{-5}$	$1.00 \times 10^{-4}$ $\pm 6.96 \times 10^{-6}$
596	Graphite	B	6	2499	-3.40				$3.38 \times 10^{-5}$ $\pm 1.04 \times 10^{-5}$	$3.50 \times 10^{-5}$ $\pm 5.11 \times 10^{-7}$	$2.46 \times 10^{-5}$ $\pm 5.02 \times 10^{-7}$	$2.61 \times 10^{-5}$ $\pm 9.61 \times 10^{-7}$
598	Graphite	A	6	2543	-1.47	$1.92 \times 10^{-5}$ $\pm 4.96 \times 10^{-6}$	$1.79 \times 10^{-5}$ $\pm 1.71 \times 10^{-6}$	$1.11 \times 10^{-5}$ $\pm 4.01 \times 10^{-6}$	$1.10 \times 10^{-5}$ $\pm 1.77 \times 10^{-6}$	$1.07 \times 10^{-5}$ $\pm 1.55 \times 10^{-6}$		
599	Graphite	A	6	2532	-3.26	$5.99 \times 10^{-5}$ $\pm 2.89 \times 10^{-5}$	$8.24 \times 10^{-5}$ $\pm 1.42 \times 10^{-6}$	$5.97 \times 10^{-5}$ $\pm 3.95 \times 10^{-6}$	$6.76 \times 10^{-5}$ $\pm 5.17 \times 10^{-6}$	$7.22 \times 10^{-5}$ $\pm 1.66 \times 10^{-5}$		
600	Graphite	A	6	2536	-2.81	$1.25 \times 10^{-5}$ $\pm 9.85 \times 10^{-6}$	$2.22 \times 10^{-5}$ $\pm 9.56 \times 10^{-6}$	$1.39 \times 10^{-5}$ $\pm 3.47 \times 10^{-6}$	$2.09 \times 10^{-5}$ $\pm 4.65 \times 10^{-6}$	$1.94 \times 10^{-5}$ $\pm 1.53 \times 10^{-6}$		
601	Graphite	A	6	2517	-3.58	$2.19 \times 10^{-5}$ $\pm 1.44 \times 10^{-5}$	$4.87 \times 10^{-5}$ $\pm 1.82 \times 10^{-5}$	$4.40 \times 10^{-5}$ $\pm 1.23 \times 10^{-5}$	$5.00 \times 10^{-5}$ $\pm 1.70 \times 10^{-5}$	$6.96 \times 10^{-5}$ $\pm 1.43 \times 10^{-5}$		
603	Graphite	B	6	2500	-3.48				$2.66 \times 10^{-5}$ $\pm 4.41 \times 10^{-6}$	$2.62 \times 10^{-5}$ $\pm 2.69 \times 10^{-6}$	$2.21 \times 10^{-5}$ $\pm 3.12 \times 10^{-6}$	$1.61 \times 10^{-5}$ $\pm 2.22 \times 10^{-6}$
685	Graphite	C	6	2529*	-0.68	$1.02 \times 10^{-3}$ $\pm 3.73 \times 10^{-4}$	$1.42 \times 10^{-3}$ $\pm 5.23 \times 10^{-4}$	$1.33 \times 10^{-3}$ $\pm 4.68 \times 10^{-4}$	$1.21 \times 10^{-3}$ $\pm 4.54 \times 10^{-4}$	$1.02 \times 10^{-3}$ $\pm 4.01 \times 10^{-4}$	$2.30 \times 10^{-3}$ $\pm 7.54 \times 10^{-4}$	$6.40 \times 10^{-4}$ $\pm 2.70 \times 10^{-4}$
693	MgO single crystal	B	14	2560	-1.51				$1.25 \times 10^{-5}$ $\pm 5.70 \times 10^{-6}$	$1.18 \times 10^{-5}$ $\pm 2.64 \times 10^{-6}$	$1.34 \times 10^{-5}$ $\pm 5.31 \times 10^{-6}$	$8.47 \times 10^{-6}$ $\pm 3.43 \times 10^{-6}$
694	Graphite	B	6	2365	-0.59				$1.83 \times 10^{-5}$ $\pm 2.35 \times 10^{-6}$	$1.77 \times 10^{-5}$ $\pm 2.22 \times 10^{-6}$	$1.29 \times 10^{-5}$ $\pm 6.03 \times 10^{-6}$	$4.59 \times 10^{-5}$ $\pm 3.79 \times 10^{-5}$
696	MgO single crystal	A	14	2560*	-1.51	$2.61 \times 10^{-6}$ $\pm 1.26 \times 10^{-6}$	$6.30 \times 10^{-6}$ $\pm 2.91 \times 10^{-6}$	$4.88 \times 10^{-6}$ $\pm 2.17 \times 10^{-6}$	$5.36 \times 10^{-6}$ $\pm 1.84 \times 10^{-6}$	$6.17 \times 10^{-6}$ $\pm 2.57 \times 10^{-6}$		
698	Graphite	C	6	2429	-0.63	$2.74 \times 10^{-3}$ $\pm 5.05 \times 10^{-4}$	$3.44 \times 10^{-3}$ $\pm 5.44 \times 10^{-4}$	$3.24 \times 10^{-3}$ $\pm 4.87 \times 10^{-4}$	$3.04 \times 10^{-3}$ $\pm 3.76 \times 10^{-4}$	$2.74 \times 10^{-3}$ $\pm 3.12 \times 10^{-4}$	$5.21 \times 10^{-3}$ $\pm 6.54 \times 10^{-4}$	$2.06 \times 10^{-3}$ $\pm 2.80 \times 10^{-4}$
699	Graphite	C	6	2439	-0.20	$4.01 \times 10^{-3}$ $\pm 3.42 \times 10^{-4}$	$4.85 \times 10^{-3}$ $\pm 4.24 \times 10^{-4}$	$4.93 \times 10^{-3}$ $\pm 4.49 \times 10^{-4}$	$4.46 \times 10^{-3}$ $\pm 3.34 \times 10^{-4}$	$4.15 \times 10^{-3}$ $\pm 3.69 \times 10^{-4}$	$7.75 \times 10^{-3}$ $\pm 1.28 \times 10^{-3}$	$3.27 \times 10^{-3}$ $\pm 4.72 \times 10^{-4}$
1320	Graphite	A	6	2450	-1.38	$8.09 \times 10^{-5}$ $\pm 1.12 \times 10^{-4}$	$1.89 \times 10^{-5}$ $\pm 9.66 \times 10^{-6}$	$1.31 \times 10^{-5}$ $\pm 3.09 \times 10^{-6}$	$9.36 \times 10^{-6}$ $\pm 1.85 \times 10^{-6}$	$2.31 \times 10^{-5}$ $\pm 3.75 \times 10^{-6}$		
1321	Graphite	A	6	2543*	-2.67	$1.56 \times 10^{-4}$ $\pm 4.82 \times 10^{-6}$	$2.21 \times 10^{-4}$ $\pm 7.30 \times 10^{-6}$	$2.24 \times 10^{-4}$ $\pm 8.93 \times 10^{-6}$	$2.29 \times 10^{-4}$ $\pm 1.25 \times 10^{-5}$	$2.98 \times 10^{-4}$ $\pm 1.47 \times 10^{-5}$		
1322	Graphite	A	6	2486*	-3.16	$1.71 \times 10^{-4}$ $\pm 3.98 \times 10^{-6}$	$3.10 \times 10^{-4}$ $\pm 3.33 \times 10^{-6}$	$3.26 \times 10^{-4}$ $\pm 4.45 \times 10^{-6}$	$3.54 \times 10^{-4}$ $\pm 5.58 \times 10^{-6}$	$4.70 \times 10^{-4}$ $\pm 9.25 \times 10^{-6}$		
1323	Graphite	A	6	2503	-3.42	$3.27 \times 10^{-4}$ $\pm 1.15 \times 10^{-4}$	$5.11 \times 10^{-4}$ $\pm 1.09 \times 10^{-4}$	$6.04 \times 10^{-4}$ $\pm 1.03 \times 10^{-4}$	$6.55 \times 10^{-4}$ $\pm 8.62 \times 10^{-5}$	$7.65 \times 10^{-4}$ $\pm 1.22 \times 10^{-4}$		
1324	Graphite	B	6	2499*	-0.82				$4.86 \times 10^{-5}$ $\pm 3.71 \times 10^{-5}$	$7.60 \times 10^{-5}$ $\pm 4.17 \times 10^{-5}$	$7.45 \times 10^{-5}$ $\pm 5.94 \times 10^{-5}$	$6.97 \times 10^{-5}$ $\pm 2.12 \times 10^{-5}$
1325	Graphite	B	6	2517	-3.11				$2.80 \times 10^{-5}$ $\pm 9.16 \times 10^{-6}$	$4.42 \times 10^{-5}$ $\pm 1.22 \times 10^{-5}$	$5.54 \times 10^{-5}$ $\pm 1.07 \times 10^{-5}$	$4.34 \times 10^{-5}$ $\pm 3.68 \times 10^{-5}$
1326	Graphite	B	6	2536	-3.95				$1.10 \times 10^{-3}$ $\pm 5.73 \times 10^{-5}$	$1.37 \times 10^{-3}$ $\pm 1.12 \times 10^{-4}$	$8.30 \times 10^{-4}$ $\pm 5.95 \times 10^{-5}$	$1.02 \times 10^{-3}$ $\pm 1.37 \times 10^{-4}$
1327	Graphite	B	6	2519	-3.46				$1.88 \times 10^{-4}$ $\pm 1.73 \times 10^{-4}$	$2.96 \times 10^{-4}$ $\pm 1.51 \times 10^{-4}$	$1.71 \times 10^{-4}$ $\pm 1.27 \times 10^{-4}$	$3.21 \times 10^{-4}$ $\pm 4.06 \times 10^{-6}$

**Table 2.** Results of the multi-variable linear regression based on Equation 6 using experimental data from this study and those from literature listed in Appendix B. Two-variable parametrizations regressed the variables related to  $\log f_{O_2}$  ( $a$ ), the metallic concentration of S ( $d$ ), along with the equation constant ( $e$ ). The p-value for each variable used is also shown, with a significance level of 5%.

<i>Element</i>	<i>N°</i>	<i>R<sup>2</sup></i>	<i>a</i>	<i>p-value</i>	<i>d</i>	<i>p-value</i>	<i>e</i>	<i>p-value</i>
<b>La</b>	25	<b>0.86</b>	-0.61 ±0.12	1.90 .10 <sup>-5</sup>	-14.20 ±1.5	3.41 .10 <sup>-9</sup>	-5.34 ±0.27	2.90 .10 <sup>-15</sup>
<b>Ce</b>	24	<b>0.87</b>	-0.60 ±0.10	6.66 .10 <sup>-5</sup>	-13.45 ±1.40	4.23 .10 <sup>-9</sup>	-5.23 ±0.26	4.37 .10 <sup>-15</sup>
<b>Pr</b>	21	<b>0.88</b>	-0.61 ±0.08	6.50 .10 <sup>-5</sup>	-12.65 ±1.30	1.31 .10 <sup>-8</sup>	-5.24 ±0.23	1.63 .10 <sup>-14</sup>
<b>Nd</b>	42	<b>0.81</b>	-0.62 ±0.09	7.00 .10 <sup>-8</sup>	-12.45 ±1.16	2.47 .10 <sup>-13</sup>	-5.19 ±0.21	5.17 .10 <sup>-26</sup>
<b>Sm</b>	42	<b>0.8</b>	-0.61 ±0.08	5.14 .10 <sup>-8</sup>	-11.91 ±1.17	1.01 .10 <sup>-12</sup>	-5.13 ±0.21	9.24 .10 <sup>-26</sup>
<b>Eu</b>	25	<b>0.9</b>	-0.40 ±0.11	9.64 .10 <sup>-5</sup>	-15.12 ±1.24	3.02 .10 <sup>-11</sup>	-5.10 ±0.23	1.30 .10 <sup>-16</sup>
<b>Gd</b>	20	<b>0.89</b>	-0.63 ±0.14	3.82 .10 <sup>-5</sup>	-11.59 ±1.17	1.07 .10 <sup>-8</sup>	-5.24 ±0.21	2.43 .10 <sup>-15</sup>

**Table 3.** Concentration of REE (La to Gd), in ppb, along with the enrichment factor (EF) in RLE compared to CI for the BSE proposed in the literature, based on cosmochemical and/or petrological approaches. All EF are taken from the original papers, with the exception of Allègre et al. (2001), for which the EF is calculated using REE concentrations in the BSE normalized to CI chondrite concentrations given by Barrat et al. (2012). Uncertainties on EF presented here are taken from the original papers for Palme and O'Neill (2014) and Lyubetskaya and Korenaga (2007), and extrapolated from the uncertainties on the REE concentrations given in the BSE in Allègre et al. (2001) and McDonough and Sun (1995). Uncertainty ( $1\sigma$ ) on the enrichment factor takes into account the uncertainties on the BSE and the CI compositions.

	<b>La</b>	<b>Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>EF compared to CI</b>
Palme and O'Neill, 2014	683 $\pm$ 68	1753 $\pm$ 175	265 $\pm$ 39	1341 $\pm$ 134	434 $\pm$ 43	166 $\pm$ 17	585 $\pm$ 29	<b>2.83 <math>\pm</math> 0.23</b>
Lyubetskaya and Korenaga, 2007	508 $\pm$ 87	1340 $\pm$ 230	203 $\pm$ 35	994 $\pm$ 170	324 $\pm$ 55	123 $\pm$ 21	432 $\pm$ 74	<b>2.16 <math>\pm</math> 0.37</b>
Allègre et al., 2001	415 $\pm$ 42	1088 $\pm$ 218	165 $\pm$ 8	814 $\pm$ 81	259 $\pm$ 8	97.9 $\pm$ 3	348 $\pm$ 28	<b>1.70 <math>\pm</math> 0.24</b>
McDonough and Sun, 1995	648 $\pm$ 65	1675 $\pm$ 168	254 $\pm$ 25	1250 $\pm$ 125	406 $\pm$ 41	154 $\pm$ 15	544 $\pm$ 54	<b>2.75 <math>\pm</math> 0.27</b>

**Table 4.** Presentation of the accretion models considered in this study. a) Building block mixing proposed by several authors (in %) in order to create the BSE nucleosynthetic composition, which also reproduce several elemental ratios of the BSE (see text for details). b) Resulting REE concentrations (ppb) in the BSE, along with their 1 sigma uncertainty. Where no precision relative to the chondritic subgroup is given, an average concentration of every subgroup is used to define the building block compositions. Concentrations used for chondrites are reported in Appendix E. Two enrichment factors based on these REE concentrations are reported for each model. EF is obtained using the measured composition of chondrites, whereas  $EF_{dry}$  is based on chondritic compositions depleted in volatile elements to match the terrestrial depletion (see text for more details). The resulting enrichment factors are calculated for each REE based on the composition of CI chondrite given by Barrat et al. (2012). Uncertainty ( $1\sigma$ ) on the enrichment factor takes into account the uncertainties on the calculated BSE and the CI composition.

a)	Enstatite Chondrites		Carbonaceous Chondrites				Ordinary Chondrites		
	EH	EL	CI	CV	CO	CM	H	L	LL
Dauphas, 2017	71				24		5		
Dauphas et al., 2014	91		2				7		
Warren, 2011	76		24						
Lodders, 2000	70		4	5			21		
<b>b)</b>									
	Resulting BSE composition							EF	$EF_{dry}$
	<i>La</i>	<i>Ce</i>	<i>Pr</i>	<i>Nd</i>	<i>Sm</i>	<i>Eu</i>	<i>Gd</i>		
Dauphas et al., 2017	442 ±31	1156 ±69	179 ±11	919 ±74	299 ±27	108 ±10	423 ±38	1.80± 0.24	2.94± 0.24
Dauphas et al., 2014	405 ±36	1061 ±85	162 ±11	829 ±50	270 ±16	96 ±8	380 ±30	1.65 ± 0.26	2.69± 0.26
Warren et al., 2011	402 ±32	1047 ±73	160 ±10	814 ±58	262 ±24	98 ±6	369 ±30	1.76± 0.23	2.87± 0.23
Lodders, 2000	425 ±30	1074 ±86	162 ±11	807 ±57	255 ±18	95 ±8	352 ±32	1.86± 0.24	3.05± 0.24

Figure 1 .

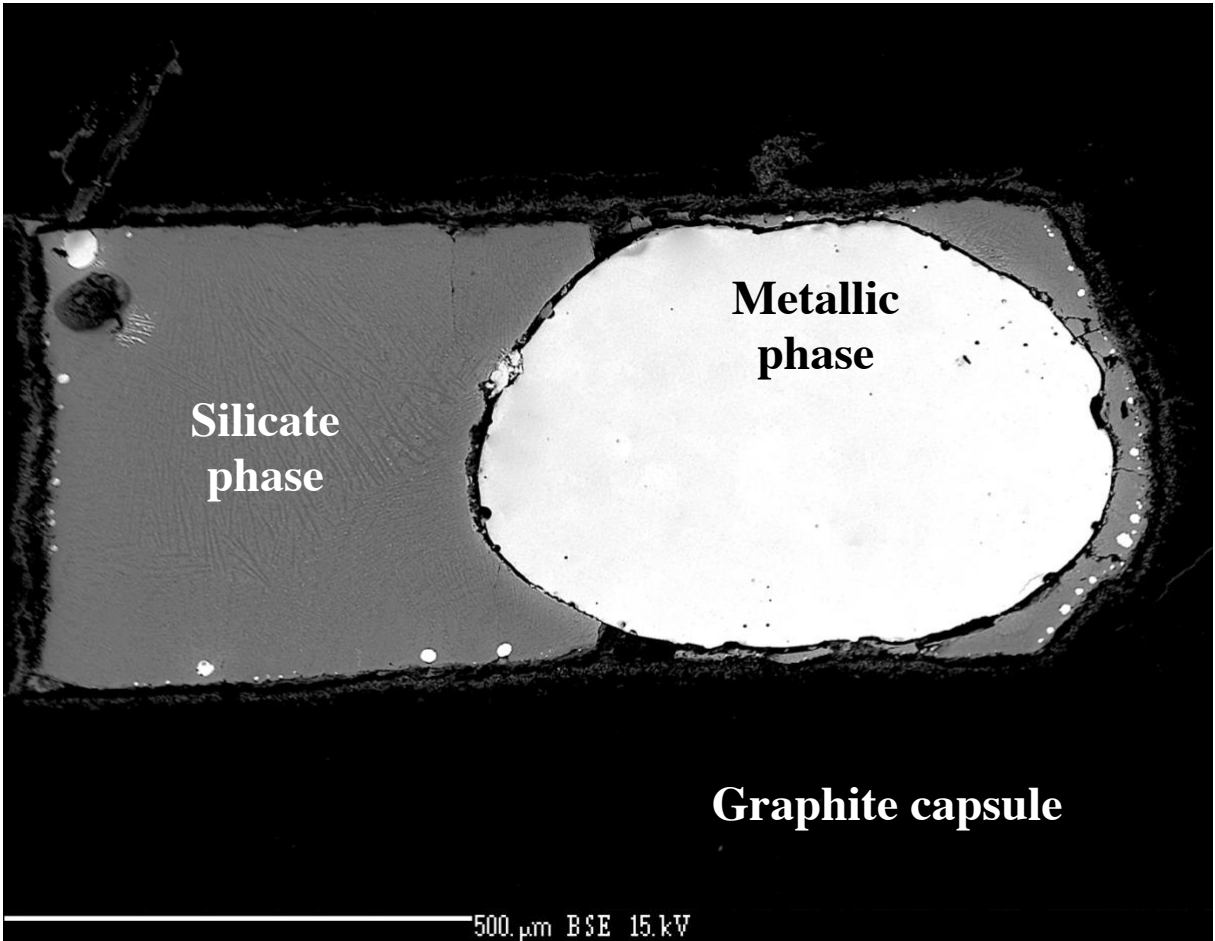




Figure 2.

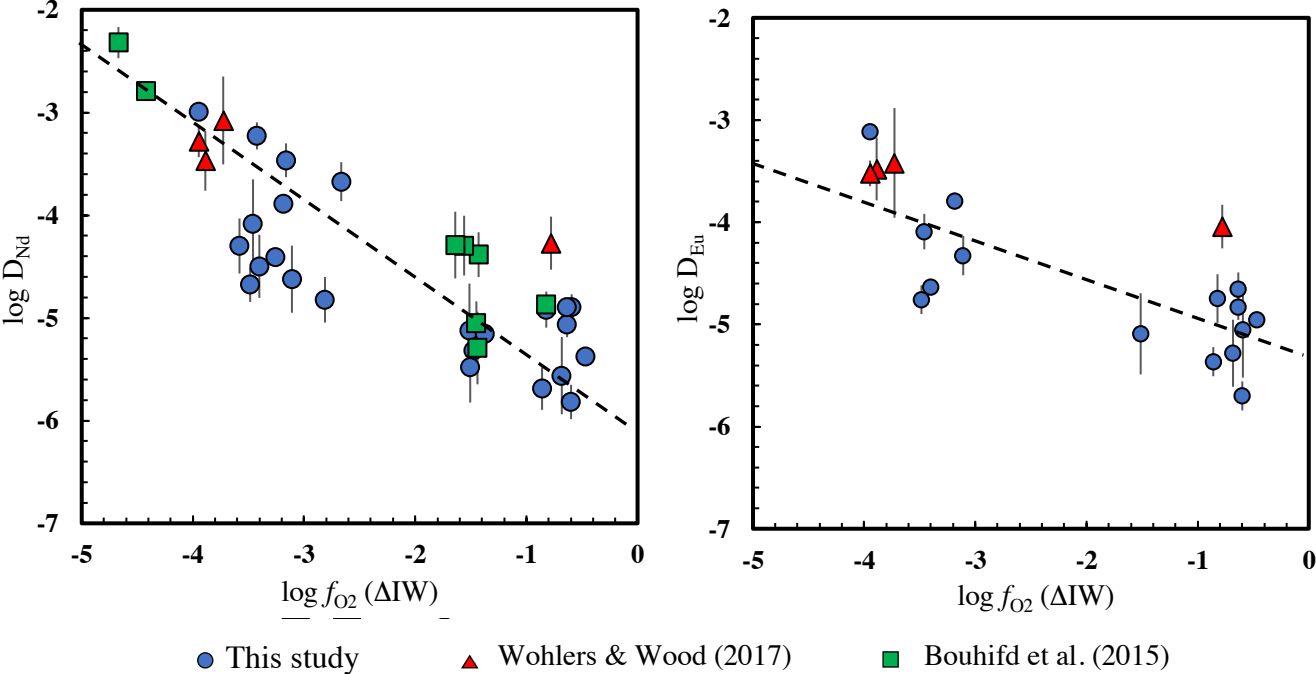


Figure 3.

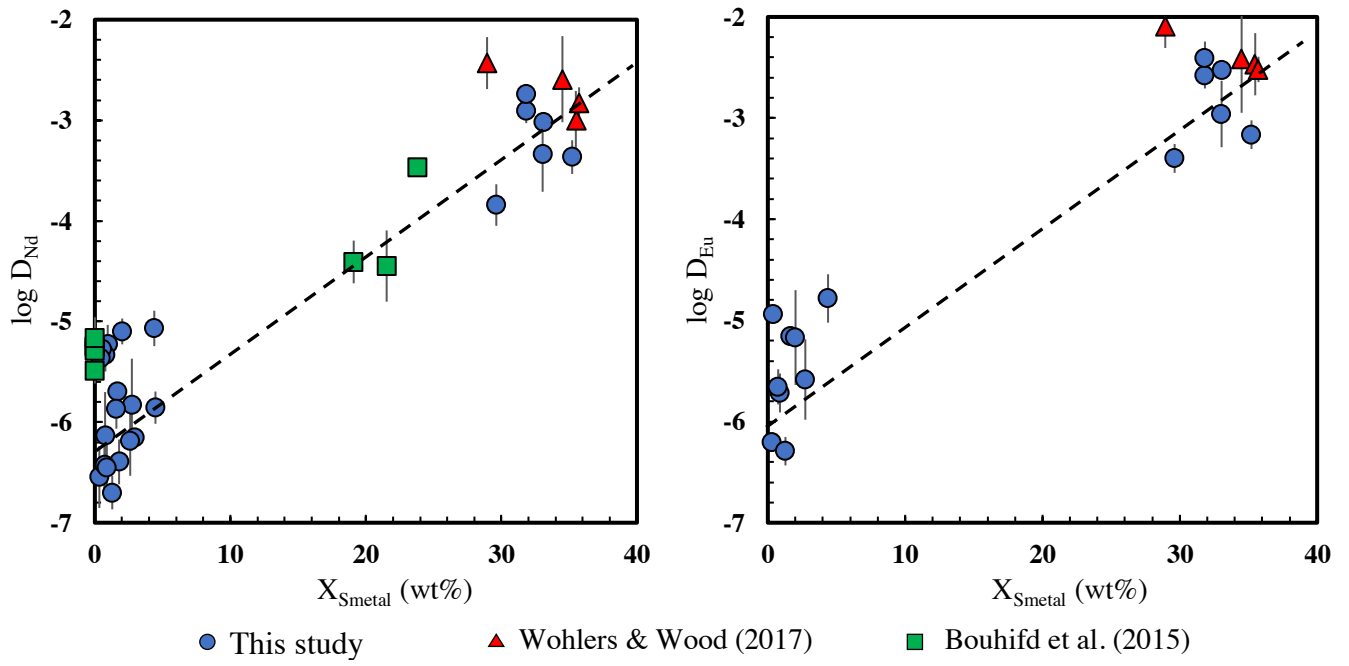


Figure 4.

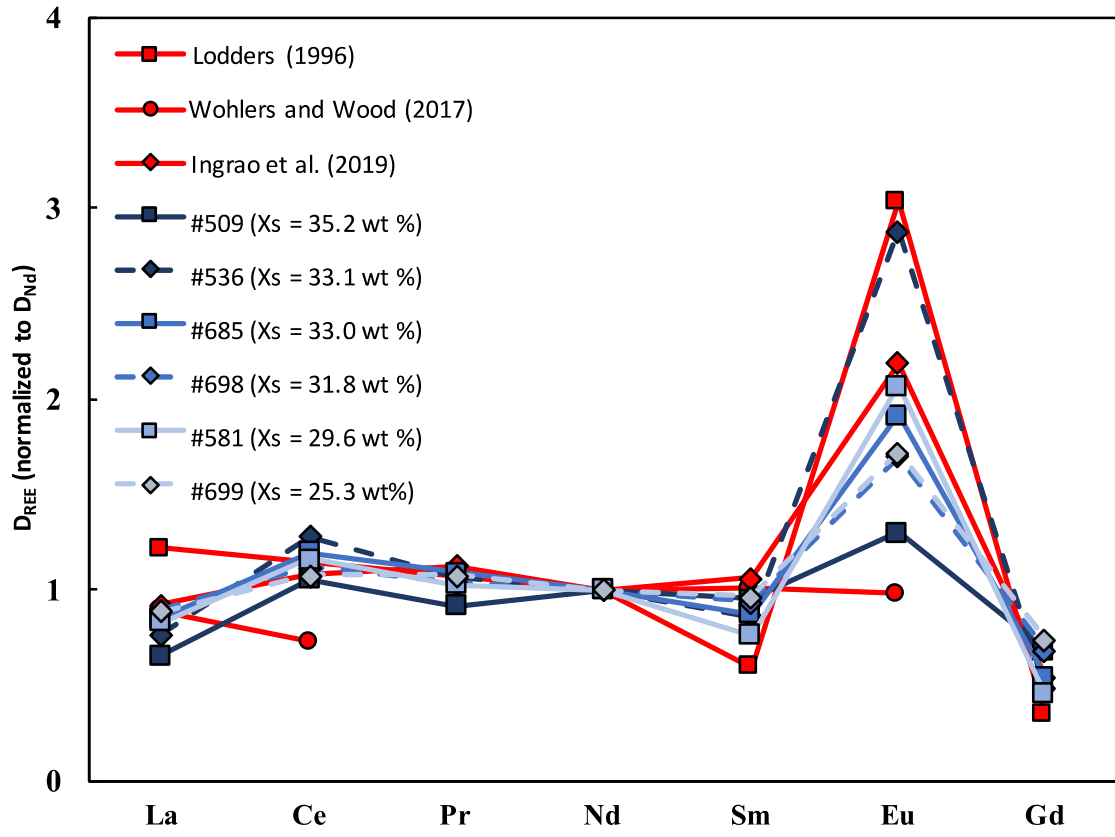


Figure 5.

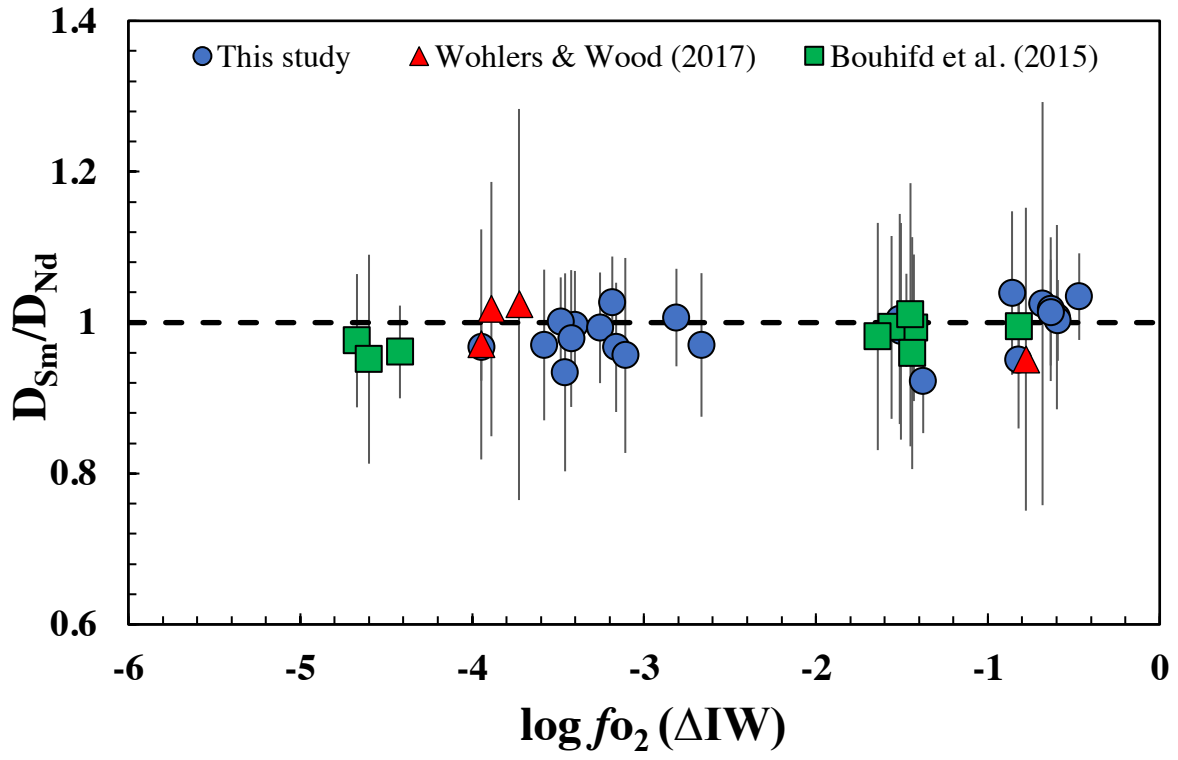
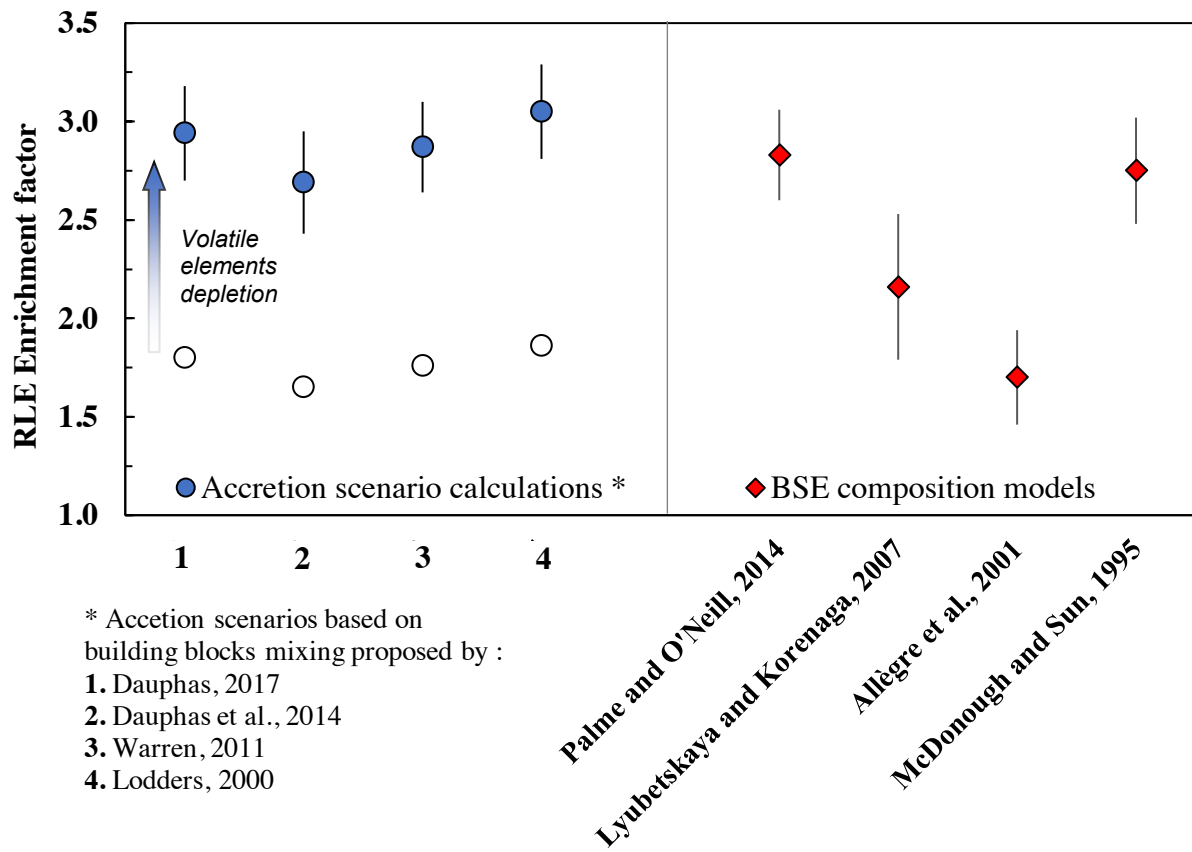


Figure 6.



## Appendix A1. Chemical analysis of all run products

Run	509	536	581	594	596	598	599	600	601	603	685	693	694	696	698	699	1320	1321	1322	1323	1324	1325	1326	1327	
Capsule	Gr	Gr	Gr	Gr	Gr	Gr	Gr	Gr	Gr	Gr	Gr	MgO	Gr	MgO	Gr	Gr	Gr	Gr	Gr	Gr	Gr	Gr	Gr	Gr	Gr
P (GPa)	6	6	6	6	6	6	6	6	6	6	6	14	6	14	6	6	6	6	6	6	6	6	6	6	6
T (K)	2361	2386	2563	2388	2499	2543	2532	2536	2517	2500	2529	2560	2365	2560	2429	2439	2450	2543	2486	2503	2499	2517	2536	2519	
NBO/T	2.19	2.07	2.29	1.21	1.46	1.81	1.56	1.42	1.26	1.20	1.34	3.66	2.28	3.66	2.41	2.78	1.93	1.81	1.77	1.46	1.46	1.26	1.42	1.69	
Doping solution	C	C	C	B	B	A	A	A	A	B	C	B	B	A	C	C	A	A	A	A	B	B	B	B	
<b>Silicate major elements (wt%)</b>																									
SiO <sub>2</sub>	43.15 ±0.81	38.59 ±2.94	44.83 ±4.01	64.22 ±0.53	65.66 ±0.73	55.91 ±0.37	62.52 ±0.44	66.54 ±0.34	64.42 ±0.65	63.72 ±0.84	46.31 ±1.19	40.50 ±0.76	46.33 ±0.52	40.73 ±0.93	45.95 ±1.44	39.77 ±0.54	55.24 ±0.67	62.45 ±0.54	58.28 ±1.32	63.06 ±0.47	50.13 ±0.61	64.58 ±0.4	64.93 ±0.52	62.22 ±0.27	
Al <sub>2</sub> O <sub>3</sub>	2.10 ±0.06	1.63 ±0.78	3.08 ±1.80	4.93 ±0.09	2.84 ±0.07	2.30 ±0.07	2.23 ±0.08	2.32 ±0.11	2.37 ±0.23	2.56 ±0.20	2.02 ±0.05	0.69 ±0.25	2.01 ±0.09	0.86 ±0.23	2.05 ±0.23	1.93 ±0.09	1.8 ±0.15	2.02 ±0.05	4.07 ±0.86	2.07 ±0.06	2.12 ±0.08	2.55 ±0.05	2.61 ±0.05	1.84 ±0.02	
FeO	29.60 ±0.62	33.79 ±5.14	24.20 ±3.61	0.93 ±0.60	0.43 ±0.36	6.05 ±0.30	0.89 ±0.13	1.31 ±0.68	0.41 ±0.12	0.64 ±0.08	21.16 ±1.62	7.77 ±0.57	20.39 ±0.6	7.92 ±0.77	22.98 ±1.89	31.25 ±0.63	8.08 ±0.8	1.77 ±0.85	0.96 ±0.33	0.60 ±0.34	13.60 ±0.93	1.03 ±0.1	0.28 ±0.12	0.59 ±0.1	
MnO	0.14 ±0.01	0.20 ±0.06	0.19 ±0.01	0.17 ±0.03	0.06 ±0.04	0.27 ±0.02	0.12 ±0.01	0.06 ±0.02	0.09 ±0.04	0.04 ±0.04	0.18 ±0.02	0.04 ±0.02	0.12 ±0.03	0.01 ±0.01	0.18 ±0.03	0.16 ±0.02	0.10 ±0.03	0.02 ±0.02	0.03 ±0.01	0.03 ±0.02	0.03 ±0.05	0.08 ±0.02	0.02 ±0.02	0.04 ±0.03	0.06 ±0.03
MgO	23.82 ±0.61	24.27 ±1.92	20.89 ±6.35	23.89 ±0.32	31.11 ±0.68	30.22 ±0.46	31.52 ±0.44	25.92 ±1.75	31.46 ±1.87	24.16 ±2.02	24.59 ±0.48	45.67 ±2.04	23.87 ±0.32	45.37 ±1.84	23.78 ±0.52	19.99 ±0.65	30.93 ±1.01	29.08 ±0.15	34.37 ±0.34	29.62 ±0.34	27.77 ±0.17	25.67 ±0.4	29.47 ±0.34	34.3 ±0.20	
CaO	1.18 ±0.11	1.40 ±0.69	2.20 ±1.94	2.85 ±0.09	1.71 ±0.14	1.63 ±0.06	1.74 ±0.08	1.31 ±0.3	1.35 ±0.14	1.97 ±0.17	1.46 ±0.19	1.02 ±0.45	1.55 ±0.09	1.51 ±0.58	1.60 ±0.25	1.28 ±0.11	1.37 ±0.11	1.59 ±0.04	1.19 ±0.08	1.68 ±0.05	1.74 ±0.08	1.87 ±0.02	2.35 ±0.12	1.44 ±0.07	
NiO	0.01 ±0.01	0.13 ±0.07	0.03 ±0.04	0.05 ±0.03	0.01 ±0.02	0.11 ±0.09	0 ±0	0.03 ±0.04	0.01 ±0.01	0.10 ±0.04	0.02 ±0.02	0.12 ±0.02	0.05 ±0.03	0.11 ±0.03	0.03 ±0.04	0.02 ±0.03	0.03 ±0.03	0.00 ±0.00	0.01 ±0.02	0.00 ±0.00	0.09 ±0.02	0.06 ±0.02	0.03 ±0.02	0.01 ±0.02	
S	0.44 ±0.17	0.41 ±0.42	0.39 ±0.34	0.85 ±0.02	2.35 ±0.18	0.09 ±0.01	0.58 ±0.05	0.69 ±0.09	1.88 ±0.35	0.52 ±0.12	0.58 ±0.23	0.02 ±0.02	0.06 ±0.02	0.04 ±0.03	0.46 ±0.10	0.32 ±0.04	0.12 ±0.03	0.58 ±0.03	0.40 ±0.04	0.69 ±0.01	0.08 ±0.02	0.91 ±0.04	1.74 ±0.07	0.82 ±0.04	
Total	100 ±0.41	100 ±0.25	95.41 ±3.60	97.05 ±0.23	101.81 ±0.58	96.48 ±0.60	99.02 ±0.96	97.49 ±0.96	100.1 ±0.56	93.21 ±1.57	95.75 ±1.11	95.81 ±1.17	94.32 ±0.23	96.51 ±0.7	95.87 ±0.76	94.98 ±0.62	97.55 ±0.86	96.94 ±0.39	98.92 ±0.93	97.06 ±0.82	95.53 ±0.49	95.79 ±0.63	99.71 ±0.85	100.5 ±0.28	
<b>Silicate trace elements (ppm)</b>																									
La	1488.76 ±162.88	1115.2 ±15.96	2210.36 ±160.5	n.d.	n.d.	1683.49 ±59.41	1773.03 ±11.19	1825.08 ±120.95	904.13 ±56.85	n.d.	1432.74 ±52.85	n.d.	n.d.	5573.63 ±703.63	1438.02 ±60.84	1440.28 ±60.84	2950.63 ±382.65	4099 ±126.62	1728.8 ±40.32	3501.33 ±42.93	n.d.	n.d.	n.d.	n.d.	
Ce	1466.95 ±158.71	1116.8 ±32.4	2241.21 ±134.72	n.d.	n.d.	1935.38 ±64.47	1817.6 ±14.27	1922.86 ±158.84	960.16 ±68.11	n.d.	1442.32 ±34.31	n.d.	n.d.	5000.36 ±569.46	1438.83 ±69	1440.22 ±69	3207.3 ±437.94	4060.12 ±133.97	1847.67 ±19.85	3590.89 ±29.12	n.d.	n.d.	n.d.	n.d.	
Pr	1380.46 ±152.28	1092.65 ±8.24	2142.67 ±133.15	n.d.	n.d.	1969.17 ±94.86	1818.56 ±16.18	1885.15 ±134.56	951.79 ±78.97	n.d.	1400.6 ±29.99	n.d.	n.d.	5023.98 ±488.6	1413.92 ±72.87	1410.02 ±72.87	3106.54 ±435.34	3912.61 ±155.66	1824.01 ±24.87	3486.91 ±17.36	n.d.	n.d.	n.d.	n.d.	
Nd	1397.98 ±162.8	1106.2 ±1.24	2341.73 ±129.97	4846.55 ±167.12	1306.93 ±12.94	1939.57 ±31.71	1778.71 ±16.68	1883.78 ±138	946.77 ±71.77	11009.18 ±529.81	1414.77 ±35.77	4097.52 ±319.91	6795.43 ±70.15	5190.93 ±494.6	1456.72 ±66.23	1459.12 ±66.23	3171.43 ±476.81	4157.83 ±227.23	1803.75 ±28.45	3662.92 ±12.08	5352.93 ±481.7	8585.13 ±85.86	3676.36 ±37.35	543.56 ±5.34	
Sm	1398.14 ±169.83	1180.27 ±20.09	2423.93 ±137.62	5176.65 ±136.5	1377.22 ±12.02	2386.39 ±29.39	1811.96 ±3.45	1976.1 ±147.96	1006.88 ±75.83	10715.86 ±584.18	1466.95 ±28.22	4246.38 ±196.01	6734.14 ±43.76	5368.81 ±422.37	1505.86 ±65.63	1503.46 ±65.63	3598.06 ±466.16	3999.4 ±197.66	1840.75 ±36.19	3700.39 ±7.89	5416.94 ±447.91	8424.43 ±54.29	3858.79 ±31.17	578.14 ±3.3	
Eu	1385.91 ±162.88	1193.66 ±16.81	2310.67 ±146.24	5243.2 ±106.64	1404.41 ±11.38	n.d.	n.d.	n.d.	n.d.	9923.99 ±390.9	1428.49 ±25.6	4074.99 ±232.15	6628.3 ±136.34	n.d.	1441.67 ±57.45	1439.66 ±57.45	n.d.	n.d.	n.d.	n.d.	5086.39 ±164.41	7756.16 ±65.18	4041.3 ±42.66	587.45 ±5.23	
Gd	1342.66 ±157.84	1183.04 ±2.91	2409.34 ±109.5	5283.7 ±126.88	1375.12 ±10.02	n.d.	n.d.	n.d.	n.d.	10643.77 ±587.79	1460.09 ±33.86	3976.81 ±238.12	6550.85 ±68.65	n.d.	1469.82 ±69.6	1472.12 ±69.6	n.d.	n.d.	n.d.	n.d.	5418.7 ±438.92	8404.09 ±65.13	3976.29 ±26.77	585.48 ±7.41	

## Appendix A1. (continued)

Run	509	536	581	594	596	598	599	600	601	603	685	693	694	696	698	699	1320	1321	1322	1323	1324	1325	1326	1327	
<b>Metal Major elements (wt%)</b>																									
Fe	61.48 ±0.51	61.97 ±0.23	63.13 ±0.51	87.04 ±0.42	75.98 ±0.49	76.09 ±0.85	86.63 ±1.49	84.87 ±0.56	78.47 ±0.31	87.92 ±0.46	61.73 ±0.3	79.11 ±0.74	91.4 ±0.26	79.5 ±0.75	62.75 ±0.22	67.94 ±1.62	83.97 ±0.35	88.28 ±0.33	85.25 ±0.38	82.93 ±0.31	77.89 ±0.78	88.88 ±0.97	80.39 ±0.24	81.64 ±0.27	
Ni	1.26 ±0.09	1.47 ±0.1	2.84 ±0.37	1.5 ±0.05	1.12 ±0.08	14.09 ±0.28	2.3 ±0.11	2.18 ±0.1	1.79 ±0.05	1.79 ±0.05	15.1 ±0.05	1.47 ±0.05	14.83 ±0.25	2.24 ±0.76	4.46 ±1.34	9.41 ±0.24	1.73 ±0.08	4.13 ±0.13	2.8 ±0.07	14.07 ±1.32	0.68 ±0.04	0.72 ±0.05	3.92 ±0.06		
S	35.22 ±1.75	33.09 ±0.16	29.62 ±1.39	1.65 ±0.05	0.33 ±0.07	4.47 ±0.26	2.95 ±1.78	1.79 ±0.77	0.7 ±0.35	1.28 ±0.41	33.04 ±0.51	2.73 ±0.27	2.02 ±0.18	2.61 ±0.62	31.83 ±1.09	25.3 ±2.23	1.59 ±0.15	0.95 ±0.06	0.77 ±0.03	0.55 ±0.06	4.38 ±1.23	0.88 ±0.22	0.43 ±0.1	0.76 ±0.16	
Si	0.05 ±0.03	0.01 ±0	0.03 ±0.01	6.6 ±0.1	22.52 ±0.46	0.03 ±0.02	4.82 ±0.24	8.76 ±0.21	18.69 ±0.06	5.62 ±0.09	0.08 ±0.04	0.05 ±0.01	0.07 ±0.01	0.03 ±0.01	0.06 ±0.02	0.1 ±0.03	0.11 ±0.03	6.46 ±0.12	7.35 ±0.37	12.92 ±0.13	0.02 ±0.01	6.82 ±0.1	16.65 ±0.63	12.4 ±0.34	
Cr	0.09 ±0.01	0.11 ±0.01	0.04 ±0.03	0.16 ±0.01	0.13 ±0.01	0.15 ±0.02	0.21 ±0.09	0.15 ±0.05	0.14 ±0.04	0.13 ±0.02	0.13 ±0.02	0.02 ±0.02	0.05 ±0.02	0.04 ±0.06	0.08 ±0.02	0.02 ±0.01	0.12 ±0.01	0.1 ±0.01	0.06 ±0.01	0.07 ±0.01	0.04 ±0.01	0.12 ±0.04	0.08 ±0.01	0.09 ±0.02	
Mn	0.02 ±0	0.04 ±0.01	0.02 ±0.01	0 ±0.01	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0	0 ±0
Total	98.04	96.69	95.67	96.95	99.94	94.82	96.91	97.76	99.79	96.66	96.79	97.01	95.01	97.04	96.97	97.82	95.19	97.52	97.57	99.28	96.41	97.39	98.28	98.8	
C*	1.96 ±1.36	3.31 ±0.39	4.33 ±0	3.05 ±0.01	0.06 ±0.13	5.18 ±0.63	3.09 ±0.21	2.24 ±0.3	0.21 ±0.06	3.34 ±0.25	3.21 ±0.48	4.99 ±0.28			3.03 ±0.39	2.18 ±0.35	4.81 ±0.11	2.48 ±0.3	2.43 ±0.22	0.72 ±0.34	3.59 ±0.32	2.61 ±0.85	1.72 ±0.63	1.2 ±0.38	
<b>Metal trace elements (ppm)</b>																									
La	0.92 ±0.14	1.57 ±0.07	0.94 ±0.12	n.d.	n.d.	0.03 ±0.01	0.11 ±0.05	0.02 ±0.02	0.02 ±0.01	n.d.	1.46 ±0.48	n.d.	n.d.	0.01 ±0.01	3.95 ±0.56	5.77 ±0.25	0.24 ±0.3	0.64 ±0	0.3 ±0	1.15 ±0.39	n.d.	n.d.	n.d.	n.d.	
Ce	1.48 ±0.03	2.62 ±0.34	1.31 ±0.18	n.d.	n.d.	0.03 ±0	0.15 ±0	0.04 ±0.01	0.05 ±0.01	n.d.	2.04 ±0.71	n.d.	n.d.	0.03 ±0.01	4.96 ±0.54	6.98 ±0.28	0.06 ±0.02	0.9 ±0	0.57 ±0	1.84 ±0.38	n.d.	n.d.	n.d.	n.d.	
Pr	1.28 ±0.03	2.17 ±0.15	1.16 ±0.12	n.d.	n.d.	0.02 ±0.01	0.11 ±0.01	0.03 ±0	0.04 ±0.01	n.d.	1.86 ±0.62	n.d.	n.d.	0.02 ±0.01	4.58 ±0.45	6.97 ±0.28	0.04 ±0	0.88 ±0	0.6 ±0	2.11 ±0.35	n.d.	n.d.	n.d.	n.d.	
Nd	1.4 ±0.07	2.05 ±0.06	1.13 ±0.17	0.85 ±0.04	0.04 ±0.01	0.02 ±0	0.12 ±0.01	0.04 ±0.01	0.05 ±0.01	0.29 ±0.03	1.71 ±0.6	0.05 ±0.02	0.12 ±0.01	0.03 ±0.01	4.43 ±0.35	6.5 ±0.19	0.03 ±0	0.95 ±0	0.64 ±0	2.4 ±0.31	0.26 ±0.18	0.24 ±0.08	4.04 ±0.17	0.1 ±0.09	
Sm	1.33 ±0.1	1.76 ±0.19	0.86 ±0.08	0.72 ±0.08	0.05 ±0	0.03 ±0	0.13 ±0.03	0.07 ±0.04	0.07 ±0.01	0.28 ±0.01	1.49 ±0.56	0.05 ±0.01	0.12 ±0.01	0.03 ±0.01	4.13 ±0.29	6.25 ±0.28	0.08 ±0	1.19 ±0	0.87 ±0	2.83 ±0.45	0.41 ±0.19	0.37 ±0.1	5.29 ±0.39	0.17 ±0.09	
Eu	1.82 ±0.04	5.91 ±0.29	2.34 ±0.19	1.15 ±0.07	0.03 ±0	n.d.	n.d.	n.d.	n.d.	0.22 ±0.02	3.28 ±1.02	0.05 ±0.02	0.09 ±0.04	n.d.	7.51 ±0.64	11.18 ±1.41	n.d.	n.d.	n.d.	n.d.	0.38 ±0.29	0.43 ±0.08	3.36 ±0.21	0.1 ±0.07	
Gd	0.96 ±0.17	0.99 ±0.07	0.51 ±0.03	0.53 ±0.02	0.04 ±0	n.d.	n.d.	n.d.	n.d.	0.17 ±0.01	0.93 ±0.37	0.03 ±0.01	0.3 ±0.25	n.d.	3.03 ±0.27	4.81 ±0.47	n.d.	n.d.	n.d.	n.d.	0.38 ±0.08	0.37 ±0.31	4.08 ±0.52	0.19 ±0.1	
log ( $f_{O_2}$ ) ( $\Delta IW$ )	-0.6	-0.47	-0.86	-3.18	-3.4	-1.47	-3.26	-2.81	-3.58	-3.48	-0.68	-1.51	-0.59	-1.51	-0.63	-0.2	-1.38	-2.67	-3.16	-3.42	-0.82	-3.11	-3.95	-3.46	

**Table S1.** Chemical analysis of the run products. Totals in silicate consider only major oxides, and only S-rich phase for the metallic phase when demixion in the Fe–S–Ni–C system occurs (see Appendix A2).

All the reported experiments were performed using the Hvittis based composition. Pressure uncertainties are estimated to be  $\pm 0.5$  GPa of the reported values and temperature uncertainties are within  $\pm 100$  K. Oxygen fugacities relative to Iron–Wüstite buffer assuming that  $\gamma_{FeO} = 1.5$ , and  $\gamma_{Fe}$  is calculated using the interaction parameters approach.

Gr: Graphite; MgO: MgO single crystal.

\* For samples embedded in graphite capsules, the maximum C contents in Fe-alloys is estimated from the deviation of the analyses totals from 100%.

## Appendix A2.

### Role of graphite and MgO single-crystal capsules

For experiments with graphite capsules, and for S-rich experiments, we observed the coexistence of two immiscible liquids in the run products for the experimental conditions investigated here (see Figure below). For instance, the experiment performed at  $6\pm 1$  GPa (run #699) shows the coexistence of a S-rich liquid and a S-poor liquid. The chemical analyses of both phases are as following:

	<u>S-rich phase</u>	<u>S-poor phase</u>
Fe	$67.94 \pm 1.62$	$88.35 \pm 0.41$
Ni	$4.46 \pm 1.34$	$3.26 \pm 0.18$
S	$25.30 \pm 2.23$	$2.37 \pm 0.08$
Si	$0.10 \pm 0.03$	$0.06 \pm 0.02$
Cr	$0.02 \pm 0.01$	$0.03 \pm 0.01$
Total	$97.82 \pm 0.35$	$94.07 \pm 0.38$
Estimated C (wt%)	$2.18 \pm 0.35$	$5.93 \pm 0.38$

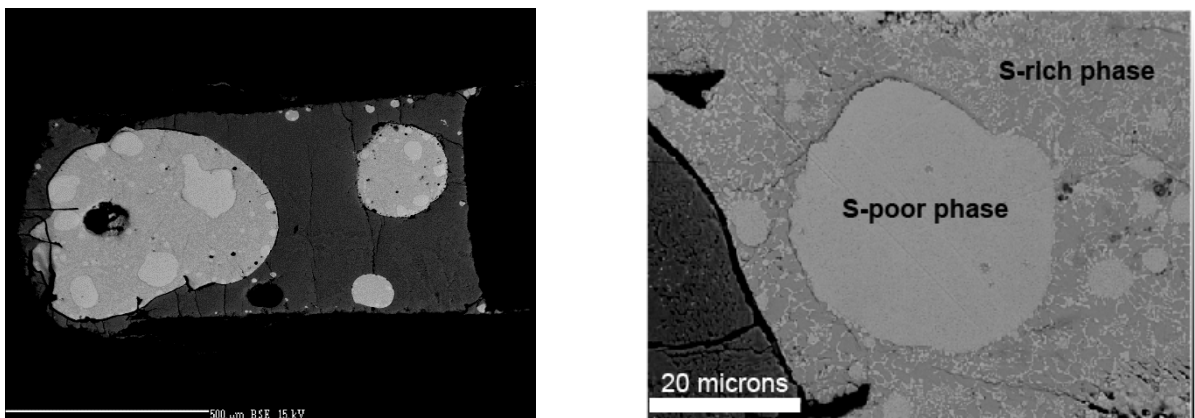


Figure A2-1. Back-scattered electron image of a run-product recovered from  $6\pm 1$  GPa and 2439 K showing a coexistence in the metallic phase of S-rich and S-poor molten alloys.

The presence of carbon into the metallic phase is due to C diffusion from the graphite capsule into the sample. Observations of a demixion in the Fe–S–Ni–C system are consistent with an immiscibility gap in the Fe–C–S system reported previously for pressures below 5.5 GPa (e.g. Corgne *et al.*, 2008; Dasgupta *et al.*, 2009).

By reporting the C content (for experiment with low Si content  $< 1$  wt%) versus the S content in the metallic phase for all the experiments in the present study (we estimated the C content as the deviation of the analyses totals from 100%). We found that our semi-quantitative C-analyses are compatible with a decrease of the C-solubility with increasing S-content in the metallic liquid.



Also C and Si contents of the metallic phase appear inversely correlated. These trends are consistent with previous experimental studies (Wang et al., 1991; Corgne et al., 2008; Dasgupta and Walker, 2008; Mann et al., 2009) and thermodynamic models at 1 bar (Bouchard and Bale, 1995).

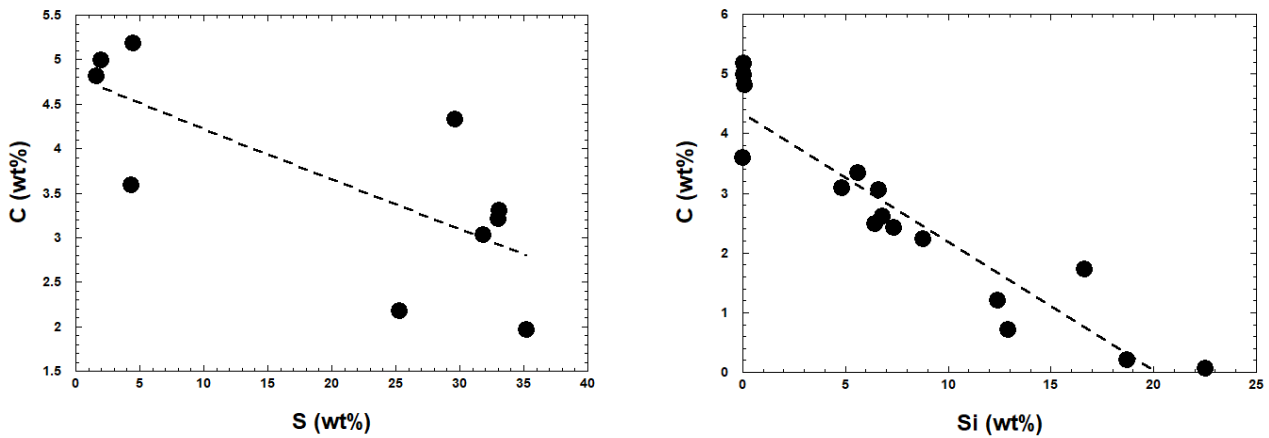


Figure A2-2. C (wt%) vs S (wt%) and C (wt%) vs Si (wt%) for run-products with low Si content, and with low S content, respectively.

### Low totals for the run-products with MgO single-crystal capsules

For two experiments with MgO capsules, we performed more than 20 chemical analyses and the Total in average is  $97.33 \pm 0.25$ . As reported in the back-scattered electron image below this is related to the state of the surface of the run-product that shows high level of porosity.

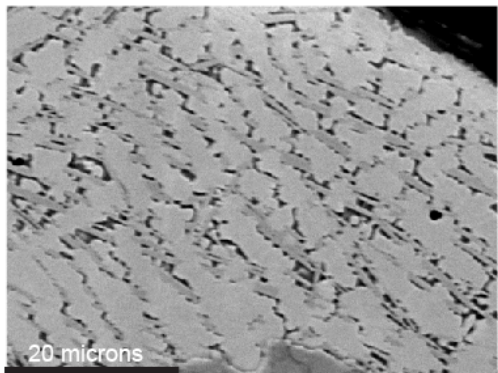
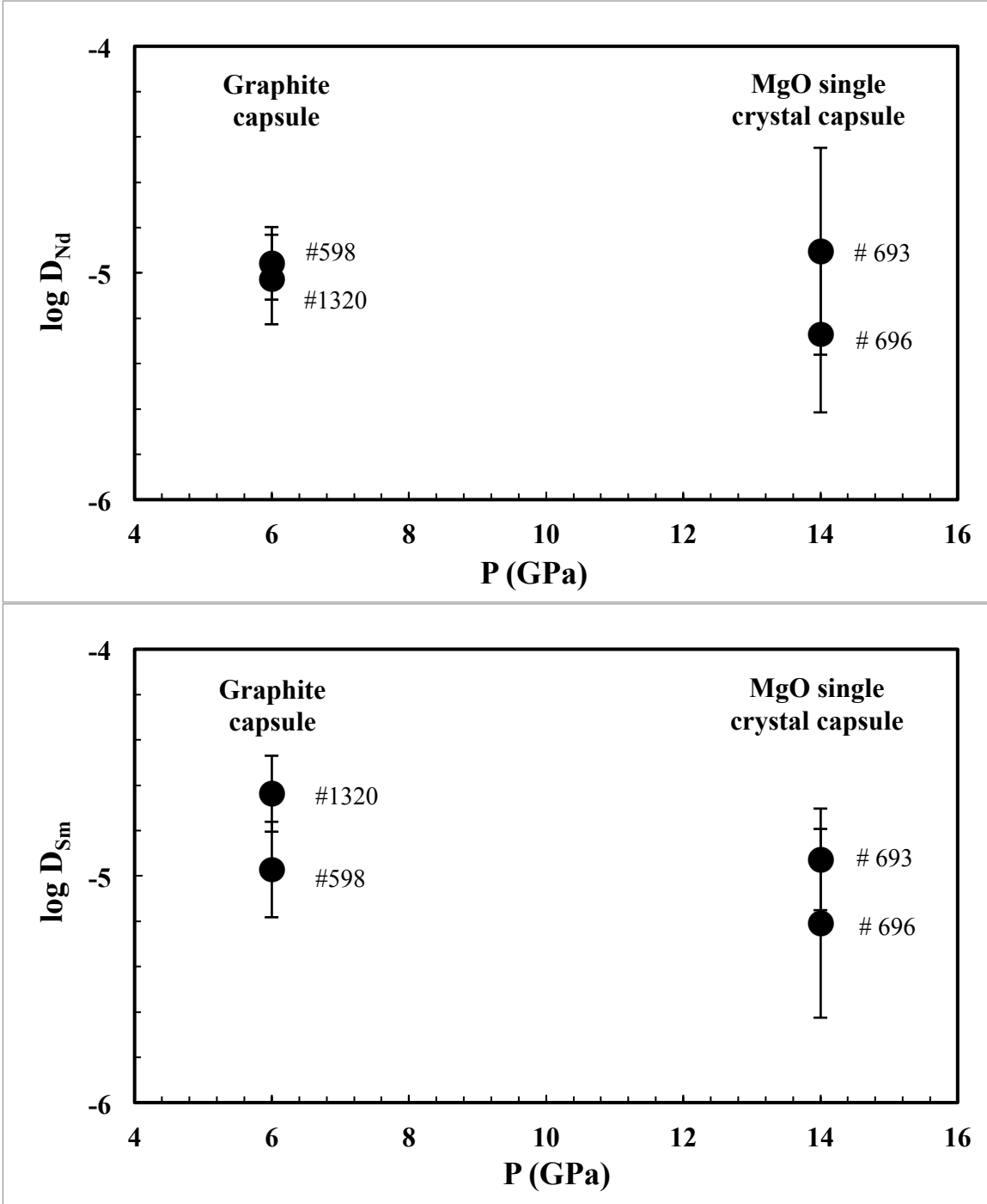


Figure A2-3. Back-scattered electron image of the metallic phase for a run-product recovered from  $14 \pm 1$  GPa, 2560 K, and using MgO as capsule.

**Appendix B.** Effect of the nature of the capsule (C or MgO) on Sm and Nd partition coefficients in our experiments. The experiments were performed in similar conditions (from 2450 to 2560 K, at  $\sim 1W-1.5$  in sulphur free environment), with the exception of pressure conditions. Error bars display 1 sigma uncertainties, showing no significant impact of the nature of the capsule or pressure on the resulting partition coefficients.



### Appendix C. Compilation of experimental data

<i>Run</i>	<i>Capsule</i>	<i>P (GPa)</i>	<i>T (K)</i>	$\log fO_2$ ( $\Delta IW$ )	<i>NBO/T</i>	$X_{S\ metal}$ (wt%)	$D_{La}$	$D_{Ce}$	$D_{Pr}$	$D_{Nd}$	$D_{Sm}$	$D_{Eu}$	$D_{Gd}$
Bouhifd et al., 2015													
969	Gr	4	2128	-1.43	3.61	0.00				$4.13 \times 10^{-5}$	$4.43 \times 10^{-5}$		
975	Gr	4	2073	-1.56	2.30	0.00				$5.05 \times 10^{-5}$	$5.38 \times 10^{-5}$		
1026	Gr	5	2273	-0.82	2.29	23.79				$1.08 \times 10^{-3}$	$1.12 \times 10^{-3}$		
1027	Gr	5	2273	-4.42	2.30	0.00				$1.60 \times 10^{-3}$	$2.06 \times 10^{-3}$		
986	MgO	6	2173	-1.64	2.08	0.00				$5.12 \times 10^{-5}$	$6.14 \times 10^{-5}$		
1021	MgO	6	2173	-1.44	2.35	21.53				$2.69 \times 10^{-4}$	$3.75 \times 10^{-4}$		
1028	MgO	8	2373	-1.45	2.16	19.10				$3.00 \times 10^{-4}$	$2.75 \times 10^{-4}$		
1029	MgO	8	2373	-4.67	2.14	0.00				$4.79 \times 10^{-3}$	$5.44 \times 10^{-3}$		
1082	Gr	5	2023	-4.60	0.52	0.00				$2.52 \times 10^{-2}$	$3.01 \times 10^{-2}$		
1137	Gr	5	1973	0.90	1.73	35.31				$1.18 \times 10^{-3}$	$7.73 \times 10^{-4}$		
Wohlers and Wood., 2017													
701	Gr	1.5	2373	-0.78	0.80	28.94	$1.06 \times 10^{-2}$			$1.10 \times 10^{-2}$	$9.92 \times 10^{-3}$	$1.87 \times 10^{-2}$	
700	Gr	1.5	2373	-3.73	0.24	34.50	$3.94 \times 10^{-1}$	$5.00 \times 10^{-1}$		$4.81 \times 10^{-1}$	$4.75 \times 10^{-1}$	$2.19 \times 10^{-1}$	
699	Gr	1.5	2373	-3.89	0.43	35.49	$2.02 \times 10^{-1}$	$1.43 \times 10^{-1}$		$2.35 \times 10^{-1}$	$2.45 \times 10^{-1}$	$2.29 \times 10^{-1}$	
697	Gr	1.5	2373	-3.95	0.25	35.73	$3.28 \times 10^{-1}$	$5.00 \times 10^{-1}$		$3.80 \times 10^{-1}$	$3.78 \times 10^{-1}$	$2.17 \times 10^{-1}$	
Ingrao et al., 2019													
1266		8.50E-06	1573	-4.10		36.88	$1.70 \times 10^{-2}$	$2.40 \times 10^{-2}$	$3.00 \times 10^{-2}$	$2.80 \times 10^{-2}$	$4.50 \times 10^{-2}$	$9.00 \times 10^{-2}$	$2.40 \times 10^{-2}$
1282		7.00E-08	1573	-4.50		36.56	$3.40 \times 10^{-2}$	$3.20 \times 10^{-2}$	$4.30 \times 10^{-2}$	$3.10 \times 10^{-2}$	$4.10 \times 10^{-2}$	$1.22 \times 10^{-1}$	$2.00 \times 10^{-2}$
1207		9.00E-07	1673	-4.80		38.23	$3.86 \times 10^{-1}$	$4.81 \times 10^{-1}$	$4.25 \times 10^{-1}$	$3.99 \times 10^{-1}$	$3.27 \times 10^{-1}$	$6.58 \times 10^{-1}$	$1.52 \times 10^{-1}$
1239		8.50E-07	1673	-4.80		36.48	$5.50 \times 10^{-2}$	$5.70 \times 10^{-2}$	$4.80 \times 10^{-2}$	$5.30 \times 10^{-2}$	$5.10 \times 10^{-2}$	$7.40 \times 10^{-2}$	$3.00 \times 10^{-2}$
1284		7.00E-08	1673	-5.80		36.66	$2.40 \times 10^{-2}$	$2.80 \times 10^{-2}$	$2.60 \times 10^{-2}$	$2.40 \times 10^{-2}$	$1.90 \times 10^{-2}$	$2.70 \times 10^{-2}$	$9.00 \times 10^{-3}$
1252		1.00E-06	1673	-5.80		36.56	$2.72 \times 10^{-1}$	$3.68 \times 10^{-1}$	$4.06 \times 10^{-1}$	$3.34 \times 10^{-1}$	$2.96 \times 10^{-1}$	$5.98 \times 10^{-1}$	$1.40 \times 10^{-1}$

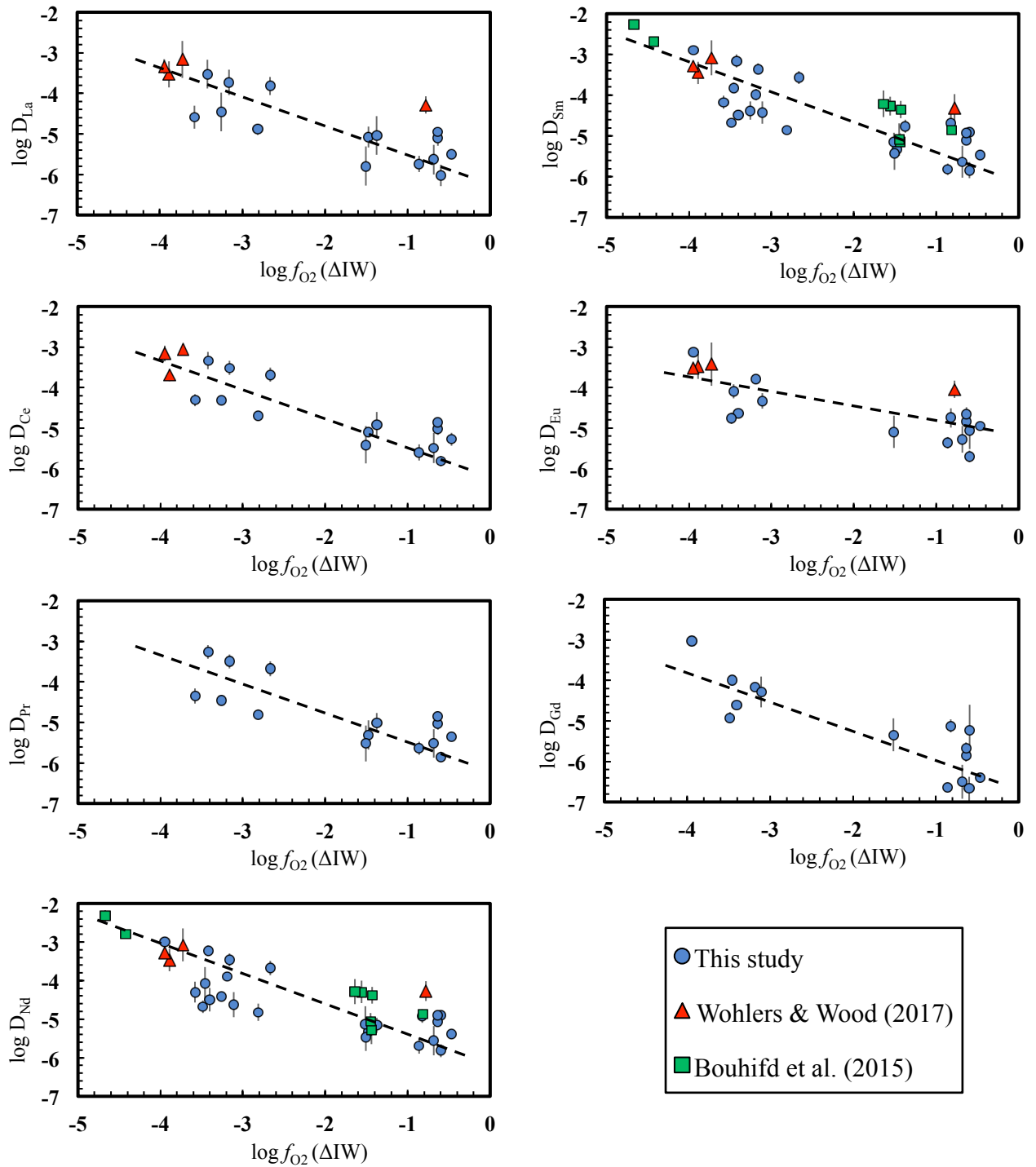
Appendix C. (continued)

<i>Run</i>	<i>Capsule</i>	<i>P (Gpa)</i>	<i>T (K)</i>	$\log fO_2$ ( $\Delta IW$ )	<i>NBO/T</i>	$X_{S\ metal}$ (wt%)	$D_{La}$	$D_{Ce}$	$D_{Pr}$	$D_{Nd}$	$D_{Sm}$	$D_{Eu}$	$D_{Gd}$
Lodders (1996)													
EQ6	Gr		1473	2.36		43.7	$1.00 \times 10^{-2}$		$1.00 \times 10^{-2}$		$9.00 \times 10^{-3}$	$6.50 \times 10^{-2}$	$5.00 \times 10^{-3}$
EQ1	Gr		1483	2.46		43.6	$9.00 \times 10^{-3}$		$9.00 \times 10^{-3}$	$7.50 \times 10^{-3}$	$5.50 \times 10^{-3}$	$4.40 \times 10^{-2}$	$5.80 \times 10^{-3}$
VQ1	Gr		1473	2.26		43.56	$1.50 \times 10^{-2}$		$1.60 \times 10^{-2}$	$1.70 \times 10^{-2}$	$1.40 \times 10^{-2}$	$6.60 \times 10^{-2}$	$1.40 \times 10^{-2}$
VQ2	Gr		1473	2.36		39.5	$5.60 \times 10^{-3}$		$6.00 \times 10^{-3}$	$8.00 \times 10^{-3}$	$4.60 \times 10^{-3}$	$3.90 \times 10^{-2}$	$3.00 \times 10^{-3}$
VQ4	Gr		1473	0.26		36	$4.10 \times 10^{-3}$		$3.50 \times 10^{-3}$		$3.70 \times 10^{-3}$	$6.00 \times 10^{-3}$	$2.80 \times 10^{-3}$
VQ3	Gr		1473	-1.44		33.6	$1.30 \times 10^{-3}$		$1.20 \times 10^{-3}$		$1.30 \times 10^{-3}$	$7.00 \times 10^{-3}$	
EQ9	Gr		1473	-2.74		37.65	$2.90 \times 10^{-1}$		$3.30 \times 10^{-1}$	$2.50 \times 10^{-1}$	$1.70 \times 10^{-1}$	$8.50 \times 10^{-1}$	$8.10 \times 10^{-2}$
EQ10	Gr		1473	-2.84		14.71	$4.80 \times 10^{-1}$		$5.10 \times 10^{-1}$	$3.80 \times 10^{-1}$	$2.00 \times 10^{-1}$	1.08	$1.40 \times 10^{-1}$
EQ4	Gr		1473	0		33.9	$1.40 \times 10^{-3}$		$1.00 \times 10^{-3}$		$7.00 \times 10^{-4}$	$3.50 \times 10^{-3}$	
EQ3	Gr		1473	-0.34		35	$6.00 \times 10^{-4}$					$3.00 \times 10^{-3}$	
QR1	Gr		1473	1.76		44.45	$3.10 \times 10^{-2}$				$1.60 \times 10^{-2}$	$1.15 \times 10^{-1}$	
QR2	Gr		1473	2.16		40.42	$3.80 \times 10^{-2}$				$2.50 \times 10^{-2}$	$1.64 \times 10^{-1}$	

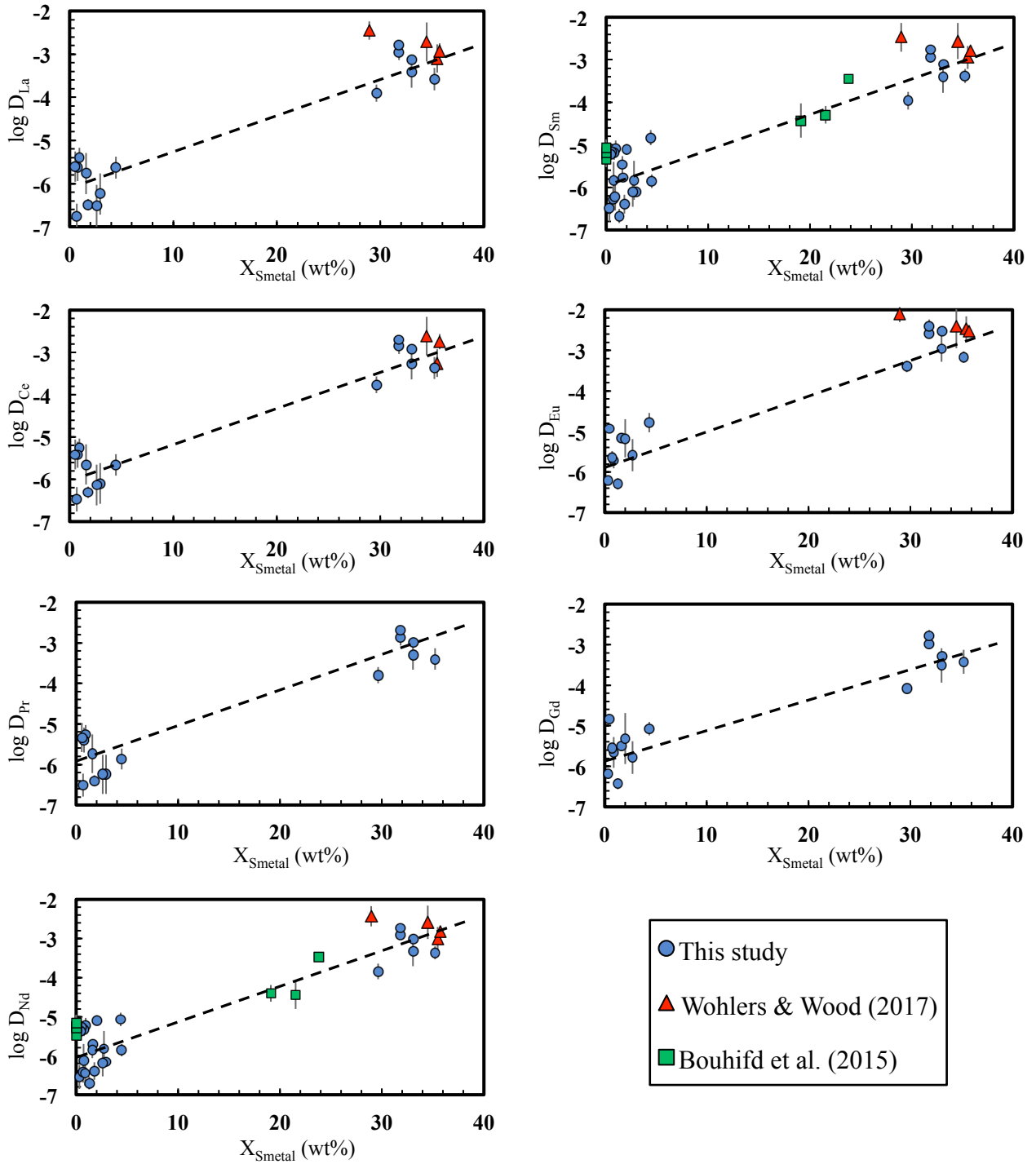
**Table S2.** Compilation of the experimental data used to derive the coefficients of equation (4) for all studied REE. The uncertainties on the reported data can be found in the original papers.

## Appendix D. Effect of experimental conditions on REE metal-silicate partition coefficients.

**D.1** Evolution of  $D_{\text{REE}}$  with  $\log f_{\text{O}_2}$ . Presented results are from this study (Appendix A) and from literature (Appendix B). Data are corrected from the effect of metallic sulphur, using the parametrization presented in equation 6 and Table 2.



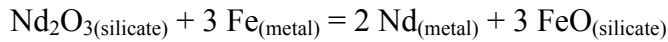
**Appendix D.2** Evolution of  $D_{REE}$  with the S concentration in the metal. Presented results are from this study (Appendix A) and from literature (Appendix B). Data are corrected for the effect of oxygen fugacity, using the parametrization presented in equation 6 and Table 2.



### Appendix D3. Effect of temperature on metal - silicate partitioning of REE

In the following, we will use Nd as an example to determine the effect of temperature on metal-silicate partitioning of the REE.

The metal - silicate partitioning of Nd is shown relative to that of Fe in terms of an exchange reaction:



The free energy of the reaction  $\Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T\Delta S_{\text{reaction}}$

where  $\Delta H_{\text{reaction}}$  and  $\Delta S_{\text{reaction}}$  are the enthalpy and the entropy of the reaction, respectively.

$$\Delta H_{\text{reaction}} = 3 H_{\text{formation}}(\text{FeO}) - H_{\text{formation}}(\text{Nd}_2\text{O}_3)$$

Using tabulated values of  $H_{\text{formation}}(\text{FeO})$  from Robie and Hemingway (1995); and those of Gschneidner et al. (1973) and Barin et al. (1989) for  $\text{Nd}_2\text{O}_3$ , a value of approximately 1000 kJ/mol is obtained for  $\Delta H_{\text{reaction}}$  at 2000 K.

$$\text{In addition, } \Delta S_{\text{reaction}} = 2 S(\text{Nd}) + 3 S(\text{FeO}) - S(\text{Nd}_2\text{O}_3) - 3 S(\text{Fe}).$$

Using tabulated values of Barin et al. (1989) for Nd, of Gschneidner et al. (1973) and Barin et al. (1989) for  $\text{Nd}_2\text{O}_3$ , and of Robie and Hemingway (1995) for Fe and FeO, a value of approximately 100 J/mol K is obtained for  $\Delta S_{\text{reaction}}$  at 2000 K.

Therefore, the term  $T\Delta S_{\text{reaction}}$  is about one order of magnitude lower than the term  $\Delta H_{\text{reaction}}$ .

Varying the temperature in the likely range during core formation (2500 to 3500 K), will result in a small change on  $\Delta G_{\text{reaction}}$ . From this, and considering that the effect of temperature on  $\Delta H_{\text{reaction}}$  is negligible, we conclude that temperature should not affect metal-silicate partitioning of Nd, and, by extension, all REE.

## Appendix E. Accretion model.

We present here models of planetary accretion focusing on the evolution of the REE (La to Gd) content of the different reservoirs (core, bulk silicate Earth) during metal-silicate differentiation.

At each step of accretion (1%  $M_E$ ), the impactor's metal and silicate equilibrate within the proto-mantle, which represents 68% of planet's mass throughout the entire accretion. Equilibration pressure is set at a pressure of 50% of the core-mantle boundary at each step. This fraction is derived from previous studies on the partitioning of siderophile elements sensitive to pressure (*e.g.* Boujibar et al., 2014; Fischer et al., 2015), leading to a final equilibration pressure set at 60 GPa (Siebert et al., 2012). Temperature is fixed at the liquidus of chondritic melts given in Andrault et al., (2011), evolving from 1900 K when the proto-Earth is at 1% of its final mass up to 3500 K in the final stage of accretion. The oxygen fugacity is constrained to the  $f_{O_2}$  paths defined in Clesi et al., (2016), into a range going from IW-5 to IW-2. All scenarios studied here reproduced within error, the Earth primitive mantle  $f_{O_2} \approx \Delta IW-2.3$ .

Each increment of the model represent the growth of the proto-Earth of 1% of its final mass, by the arrival of impactors already differentiated into silicate mantles and metallic cores (Taylor and Norman, 1990). The initial chemical compositions of impactors are those measured on various types of chondrites, depending of the studied scenarios chondrites mixtures (Wasson and Kallemeyn, 1988; see below for REE). The compositions of both metal and silicate reservoirs are calculated at 1 GPa and 2000 K for every element studied here, using their respective partition coefficients. The metal silicate equilibration takes place at  $f_{O_2}$  conditions coherent with the type of chondrites attributed to each accretion step, ranging from  $\sim IW -4$  to IW (Brett and Sato, 1984). In any way, the silicate reservoir of the impactor



contains the near total of all REE because the differentiation leads to a maximum of a few ppb of the studied REE in the metallic phase.

Partitioning is determined using our parameterizations from Table 2. Following the approach of Deguen et al. (2014), we take into account the effect of partial metal–silicate equilibration on element partitioning, which is mainly effective during the final 40% of Earth’s accretion. We apply here the method detailed in Rubie et al. (2011) in order to reproduce the metal–silicate partial equilibration by modeling an exponential decrease of the equilibration rates during the last stage of accretion (see equation 4 of Rubie et al., 2011). We consider that the equilibration between the proto-Earth’s mantle and the metal of the impactor becomes less efficient as the accretion progresses (e.g. Deguen et al., 2014; Rubie et al., 2015). For the last giant impact that formed the Moon ( $M_I=0.1M_E$ ), the impactor’s core merges almost completely with the Earth’s proto-core, with less than 5 % of its mass equilibrating with the silicate mantle. Due to the lithophile behavior of REE, the impact of equilibration on our results is very limited, in agreement with Rudge et al., (2010). At each step of accretion, the content of the metallic core in Ni, O and Si is defined using the parametrisations of Fischer et al. (2015). The C content of the core remains constant at 0.2 wt% during accretion (Wood et al., 2006), and a late addition of sulfur-rich material increases the S content of the core to 2 wt% to fit geophysical, geochemical, and experimental estimates (e.g., Allègre et al., 1995; Boujibar et al., 2014; Dreibus and Palme, 1996; Palme and O’Neill, 2003, Suer et al., 2017). Variations of the O and Si contents in the metal are related to the proportion of reduced and oxidized building blocks, which influence the  $f_{O_2}$  path. In models that consider a fully accreted Earth built from a major proportion (80%) of reduced materials, the Earth’s core contains 0.2 wt% C, 2 wt% S,  $6.75 \pm 0.75$  wt% Si, and  $2.8 \pm 0.7$  wt% O. However the incorporation of these light elements into the core lead to a negligible enrichment (no more than 1.3%) of the silicate reservoir in REE.

In order to use the most precise and up-to-date REE concentrations for the various types of chondrites proposed as building blocks for the Earth, we compiled data from the most recent publications. The lowest concentrations in REE among the different groups of chondrites are measured in CI and enstatite chondrites whereas the most enriched are those of the CV group (factor 2). For the EL subgroup, data on EL3 from Barrat et al. (2014) are considered. Most EL samples belong to the EL6 subgroup and show depletion in light REE relative to heavy REE due to melting and thermal metamorphism events (Barrat et al., 2014; Boyet et al., 2018; Rubin et al., 2009). Concentrations used in this model are presented in the table below (Table S3), along with the enrichment factor  $f_{dry}$  which is applied to the REE concentrations in order to take volatile depletion observed on Earth compared to chondrites into account (for details see text).

	<b>La</b>	<b>Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b><math>f_{dry}</math></b>	<b>references</b>
<b>EH</b>	222 ±17	575 ±35	86 ±5	433 ±21	138 ±6	52 ±2	194 ±12	<b>1.59</b>	<i>Barrat et al., 2014</i> <i>Dauphas and Pourmand 2015</i> <i>Boyet et al., 2018</i>
<b>EL</b>	250 ±53	650 ±120	100 ±18	509 ±87	166 ±31	59 ±7	235 ±33	<b>1.61</b>	
<b>CI</b>	248 ±26	637 ±58	98 ±42	496 ±35	161 ±10	61 ±4	221 ±16	<b>2.39</b>	<i>Barrat et al., 2012</i> <i>Braukmuller et al., 2018</i> <i>Pourmand and Dauphas., 2012</i> <i>Dauphas and Pourmand., 2015</i>
<b>CV</b>	475 ±45	1194 ±113	188 ±8	963 ±72	309 ±25	108 ±6	411 ±34	<b>1.69</b>	<i>Braukmuller et al., 2018</i> <i>Dauphas and Pourmand., 2015</i>
<b>CO</b>	363 ±104	949 ±242	151 ±27	784 ±105	255 ±29	96 ±12	362 ±9	<b>1.67</b>	
<b>CM</b>	294 ±33	772 ±79	122 ±12	620 ±61	203 ±19	77 ±7	315 ±51	<b>2.02</b>	<i>Dauphas and Pourmand., 2015</i>
<b>H</b>	397 ±146	957 ±229	142 ±32	700 ±135	216 ±32	81 ±6	289 ±37	<b>1.62</b>	
<b>L</b>	324 ±53	908 ±218	135 ±31	683 ±155	217 ±47	83 ±9	290 ±56	<b>1.69</b>	
<b>LL</b>	434 ±181	1134 ±476	168 ±69	844 ±338	265 ±102	91 ±9	352 ±130	<b>1.77</b>	

*Table S3. REE concentrations (in ppb) for chondrite groups used in our calculation, taken from the most recent published trace element measurements on chondrites.  $f_{dry}$  corresponds to the enrichment factor applied to concentrations of REE presented here in order to take the volatile depletion observed on Earth relative to chondrites into account.*

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