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1 Rare Earth Element Partitioning Between  
2 Sulphides and Melt: Evidence for Yb<sup>2+</sup> and  
3 Sm<sup>2+</sup> in EH Chondrites

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18 **Abstract**

19 We present the first complete dataset of partition coefficients of Rare Earth Elements (REE)  
20 between oldhamites or molten FeS and silicate melts. Values have been determined at 1300  
21 and 1400°C from experiments on mixtures of a natural enstatite chondrite and sulphides  
22 powders (FeS or CaS) performed in evacuated silica tubes for different  $f_{O_2}$  conditions (from  
23 IW-6.9 to IW-4.1). Obtained REE partitioning values are between 0.5 and 5 for oldhamites and  
24 between 0.001 and 1 for FeS. In both sulphides, Eu and Yb are preferentially incorporated  
25 compared to neighbouring REE. X-ray Absorption Near Edge Structure measurements on Yb  
26 and Sm demonstrate the partial reduction to 2+ valence state for both elements, Yb reduction  
27 being more pronounced. Therefore, the Yb anomaly in the sulphides is interpreted to be an  
28 effect of the presence of Yb<sup>2+</sup> in the system and the amplitude of the anomaly increases with  
29 decreasing oxygen fugacity. The obtained oldhamite/silicate melt partition coefficients patterns  
30 are unlike any of the observed data in natural oldhamites from enstatite chondrites and  
31 achondrites. In particular, the low values do not explain the observed enrichments in oldhamite  
32 crystals. However, positive Eu and Yb anomalies are observed in some oldhamites from EH  
33 chondrites and aubrites. We attribute these anomalies found in meteorites to the sole  
34 oldhamite control on REE budget. We conclude that the presence of positive Eu and Yb  
35 anomalies in oldhamites is a good indicator of their primordial character and that these  
36 oldhamites carry a condensation signature from a highly reduced nebular gas.

## 37 1. Introduction

38 Enstatite chondrites form a group of meteorites that have been considered as a potential  
39 representative primitive material for the Earth (Javoy, 1995, 2010; Boyet et al., 2018). This  
40 is because they display isotope similarities with Earth for many elements, such as O, N,  
41 Ca, Ti, Cr, Ni, Mo, Ru, Os (Clayton, 1993; Javoy et al., 1984; Trinquier et al., 2007, 2009;  
42 Meisel et al., 1996; Dauphas et al., 2004; Fischer-Gödde and Kleine, 2017). Recently  
43 Dauphas (2017) proposed that enstatite chondrite type material represents at least 70 %  
44 of the Earth's building blocks. On the basis of FeO content of the present-day mantle Clesi  
45 et al. (2016) proposed that the Earth could have been accreted from 85 to 90% of material  
46 similar to EH chondrite. The redox conditions of formation of these meteorites have been  
47 estimated by using Si content of the metal phase (Larimer and Buseck, 1974) as well as  
48 by electrochemical methods (Brett and Sato, 1984). All studies concluded that equilibrium  
49 conditions are very reducing, at least below IW-3 (IW refers to iron-wüstite equilibrium (Fe-  
50 FeO equilibrium)). Under these particular conditions, elements that are lithophile in the  
51 Earth mantle conditions tend to be siderophile and/or chalcophile (Lodders and Fegley,  
52 1993; Gannoun et al., 2011). This is attested by the presence of various unusual sulphide  
53 phases in these rocks. Among these sulphides, oldhamites (CaS) contain large  
54 concentrations of actinides and lanthanides, resulting in about half the budget of Rare Earth  
55 Elements (REE) of these meteorites being in oldhamites (Crozas and Lundberg, 1995;  
56 Gannoun et al., 2011; Barrat et al. 2011).

57 Enstatite chondrites are also considered as an analogue of bulk Mercury or at least a good  
58 sample of the feeding zone of Mercury (Lewis, 1972; Wasson, 1988; Malavergne et al.,  
59 2010; Ebel and Alexander, 2011; Ebel, 2017). This is because of the low FeO surface  
60 content of Mercury determined by spectroscopy or by the MESSENGER mission (Sprague  
61 and Roush, 1998; Robinson and Taylor, 2001; Warrel and Blewett, 2004; Murchie et al.,  
62 2015), its high Fe/Si ratio, the presence of Ca and Mg sulphides at its surface (Nittler et al.,  
63 2011; Weider et al., 2012; Zolotov et al., 2013), the similar volatiles abundance as in EC

64 (Evans et al., 2015; Ebel, 2017) and the C abundance at its surface (Peplowski 2016). All  
65 those features are attribute to the highly reducing conditions for the formation of Mercury  
66 (McCubbin et al., 2012; Namur et al., 2016).

67 The REE distribution in enstatite chondrites has been studied in order to discuss the  
68 processes of formation of these meteorites. On the basis of the high melting temperature  
69 of CaS ( $2450\pm 50^\circ\text{C}$  for pure oldhamite, Medvedev et al., 1979) and the similarities of REE  
70 patterns measured in oldhamites of enstatite chondrites and aubrites (reduced  
71 achondrites), several authors suggested that the oldhamites were relicts of solar nebula  
72 condensation that survived igneous processes (Kurat et al., 1992; Floss and Crozaz 1993;  
73 Lodders et al., 1993; Lodders, 1995, 1996b). On the other hand, textural evidences and  
74 some REE patterns in natural CaS crystals are in favour of an igneous origin (Floss and  
75 Crozaz, 1993; Piani, 2016; Wheelock, 1994).

76 Previous experimental studies have addressed the REE partitioning between sulphide  
77 phases (CaS or FeS, crystalline or molten) and silicate melt (Jones and Boynton, 1983;  
78 Lodders and Palme, 1989, 1990; Lodders et al., 1990; Lodders, 1995, 1996 a, b; Dickinson  
79 et al., 1990 a, b, c, 1991; Dickinson and McCoy, 1997; Wohlers and Wood, 2015; 2017).  
80 The obtained partition coefficients could not reproduce the high enrichment (100 to 1000  
81 times CI) found in natural oldhamites from enstatite chondrites and achondrites (Wheelock  
82 et al., 1994, Larimer and Ganapathy, 1987; Lundberg and Crozaz, 1988; Crozaz and  
83 Lundberg, 1995; Hsu, 1998). In addition, none of these studies provided a complete  
84 dataset on REE partitioning. In order to gain further insight into REE behaviour at very  
85 reduced conditions we have determined sulphide/silicate partitioning for oxygen fugacities  
86 between IW-5 and IW-7. We report the first complete experimental determination of molten  
87 FeS/silicate melt and oldhamite/silicate melt REE partition coefficients. The newly obtained  
88 D values are used to discuss the REE budget in reduced meteorites (enstatite chondrites  
89 and aubrites). In addition, some samples have been studied using X-ray Absorption Near

90 Edge Structure (XANES) in order to determine the valence states of Yb and Sm at reducing  
91 conditions.

92

## 93 **2. Methods**

### 94 **2.1 Experiments**

95 Starting material was a natural equilibrated Enstatite Chondrite (Hvittis, EL6, composition given  
96 by Rubin, 1984). Fragments of Hvittis were ground in ethanol and doped with between 250  
97 and 1000 ppm of the 14 REE. Doping was achieved with REE oxides dissolved in nitric acid.  
98 Firstly, the REE solution was evaporated. The solid residue was then mixed with the Hvittis  
99 powder in ethanol. The obtained powders were dried and mixed in ethanol with either CaS or  
100 FeS powders. The final mixture contained 50 wt.% of the doped chondrite and 50 wt.% of the  
101 sulphide.

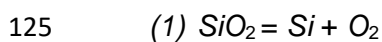
102 All the powders were loaded in graphite crucibles that were placed in pure silica tubes of 10  
103 centimetres length. The tubes were evacuated at between  $10^{-2}$  and  $10^{-4}$  mbar and heated at  
104 200°C before and during pumping to evacuate adsorbed volatile elements. The powders were  
105 equilibrated at 1300°C or 1400°C from 1 to 160 hours in a vertical furnace with MoSi heating  
106 components. The zone of the tube containing the sample was placed in the hotspot of the  
107 furnace (about 3 cm long). The temperature at the top of the tube was 200°C below the  
108 temperature at the hotspot. The temperature values were chosen following McCoy et al. (1997;  
109 1999), who showed that 1400°C is the optimal temperature for formation of large oldhamite  
110 grains for the analyses. These temperatures are close to those of the previous experimental  
111 studies from the literature. The experiments ended by quenching the tubes in air. Quenching  
112 in water was avoided in order to prevent tube breakage and potential sample dissolution. The  
113 graphite crucibles were extracted from the tube, mounted in resin and polished to  $\frac{1}{4}$   $\mu\text{m}$  grit  
114 using diamond suspension. In order to avoid sulphide loss during polishing, water was avoided  
115 and ethanol was used as a lubricant. Lubricant was used since dry polishing could have been

116 destructive by plucking out the sulphides. Details on the experiments are presented in Table  
117 1. The pressure values presented in the table are the initial pressures during sealing of the  
118 tubes. Gas formation during heating resulted in pressure increase but it was not possible to  
119 estimate its value.

120

## 121 **2.2 Determination of oxygen fugacity**

122 For most of the samples, the intrinsic  $f_{O_2}$  values were determined using Si content of the metal  
123 phase in equilibrium with the silicate assemblage, taking in consideration the following  
124 equilibrium:



126 At equilibrium we have

$$127 \quad (2) \Delta G = 0 = \Delta G^\circ + RT \cdot \ln K_{eq}$$

128 with

$$129 \quad (3) K_{eq} = \frac{a_{Si} \cdot f_{O_2}}{a_{SiO_2}}$$

130 yielding

$$131 \quad (4) \Delta G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = -RT \ln \frac{a_{Si} \cdot f_{O_2}}{a_{SiO_2}},$$

132 where  $\Delta G^\circ$  is the free energy change for the reaction,  $R$  the gas constant,  $T$  the temperature  
133 (in K),  $\Delta_r H^\circ$  the enthalpy changes of the reaction,  $\Delta_r S^\circ$  the entropy changes and the  $^\circ$  represents  
134 the standard state.

135 Silicon activity in the metallic phase is calculated with:

$$136 \quad (5) a_{Si} = X_{Si} \cdot \gamma_{Si}$$

137  $X_{Si}$  is the Si molar content of the metal and  $\gamma_{Si}$  its activity coefficient. We used coefficients in  
138 the Fe-Si system given by Yang et al. (2014) in order to calculate Si activities.

139 The samples containing enstatite and in some case silica, we considered that all experiments  
140 were close to silica saturation. Then we set  $a_{SiO_2} \approx 1$  in the calculations.

141 The pressure effect on  $\Delta G^\circ$  is considered negligible.

142 We calculated  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  using the compilation of Robie and Hemmingway (1979). Then  
143 we calculated oxygen fugacity of the system as follows:

$$144 \quad (6) \quad f_{O_2} = e^{\frac{\Delta G^\circ}{RT}} \cdot \frac{a_{SiO_2}}{a_{Si}}$$

145 We express the oxygen fugacity relative to iron-wüstite (IW) buffer.

146 For that we calculate  $f_{O_2} - f_{O_2(IW)}$  at the same temperature:

$$147 \quad (7) \quad \log f_{O_2}(\text{sample}) = \log f_{O_2}(IW) + \Delta IW$$

148 with

$$149 \quad (8) \quad \log f_{O_2}(IW) = 6.57 - \frac{27215}{T} + 0.055 \times (-1)/T$$

150 after Huebner (1971).

151 Calculated  $f_{O_2}$  values are presented in Table 1.

## 152 **2.3 Major element analysis**

153 Quantitative analyses of major elements have been obtained with a CAMECA SX100 electron  
154 microprobe. A 15 kV accelerating voltage and a beam current of 15 nA were used. A focused  
155 beam was used on crystals and metals whereas the beam was defocused to 10 $\mu$ m for the  
156 glasses. In silicates, oxygen was always estimated according to oxide stoichiometry. The  
157 standards were natural minerals or synthetic oxides for silicates, pyrite for Fe and S in  
158 sulphides and pure metals (Fe, Mn, Si, Mg, Ni, Cr) for metallic alloys. Carbon content in the



159 metal phase was calculated by deficit of the sum of the analysed elements to 100%. We found  
160 that the difference to 100% was close to C saturation in iron-nickel alloys (Paek and Pak,  
161 2014), which is expected from experiments performed in graphite crucibles. For some  
162 experiments, we also determined C content by electron microprobe, as indicated in Table 2  
163 and 3.

## 164 **2.4 Trace element analysis**

165 An Agilent 7500-cs induced coupled plasma spectrometer (ICP-MS) coupled with a Resonetics  
166 M-50 laser was used to determine trace element concentrations in the different phases. The  
167 laser was operated at 193 nm wavelength with a 2mJ energy, and 2Hz pulse frequency for  
168 samples with CaS and 4 Hz for samples with FeS. Laser spot size was between 12 and 33  $\mu\text{m}$   
169 depending on the nature of the phase and the sample. Ablation was done in pure He  
170 atmosphere for duration ranging between 40 and 60 seconds. Signal calibration was done with  
171 a NIST 610 glass standard (Gagnon et al., 2008). Different internal standards were used: Fe  
172 for the FeS and metals and Ca for the oldhamites and silicate glasses. To check accuracy  
173 NIST 612 and BCR glasses were used as secondary standards. These analyses were  
174 compared to reference values (Gagnon et al, 2008). Our measurements are in good agreement  
175 with Gagnon et al values with always less than 20% deviation (see supplementary material).  
176 The GLITTER software (Van Achetberg et al., 2001) was used for the trace-element data  
177 reduction. Detection limit was <1ppm for all elements, as determined from counting statistics  
178 on the samples. In the study of Gannoun et al. (2011), LA-ICPMS and SIMS methods were  
179 compared and it was found by repeated measurements that the two methods agreed within  
180 6% for light REE and between 4% and 16% for heavy REE.

181

182

## 183 **2.5 X-Ray Absorption Near Edge Spectroscopy (XANES)**

184 X-Ray Absorption Near Edge Spectroscopy (XANES) was used to determine Ytterbium and  
185 Samarium valence states in the experiments with CaS, only. Ytterbium L3-edge absorption  
186 data were collected on the BM 23 beamline at European Synchrotron Radiation Facility (ESRF)  
187 using the microbeam setup ( $5\mu\text{m} \times 5\mu\text{m}$ ) in reflection mode (Cartier et al. 2015). The energy  
188 was scanned between 8.85 keV and 9.05 keV. For Yb absorption energy calibration we used  
189 Yb metal foil (Goodfellow),  $\text{YbI}_2$  commercial powder (Sigma Aldrich) for the divalent state and  
190  $\text{Yb}_2\text{O}_3$  (Sigma Aldrich) for the trivalent state. We also analysed a natural apatite crystal. Across  
191 the scanned energy range, we also observed the Ho L2-edge absorption line at 8.919 keV.

192 Samarium L3-edge absorption data were collected on the CRG BM 16 FAME-UHD Beamline,  
193 also at ESRF. On this beamline the beam size is  $100\ \mu\text{m} \times 300\ \mu\text{m}$  (HxV, Full Width Half  
194 Maximum values) therefore it was not possible to analyse the phases (sulphide; glass)  
195 separately (crystal typical size of the order of  $30\ \mu\text{m}$ ) and the analyses represent averages of  
196 the phases present in the samples. However, on BM 16, analysing crystals allow for scanning  
197 the fluorescent X-ray wavelengths, yielding very high spectral resolution for the XANES data  
198 (high-energy-resolution fluorescence detection or HERFD-XANES, Hazemann (2009); Proux  
199 (2017)), the energy bandwidth of the fluorescence detection (measured around 1.1eV) being  
200 smaller than the energy bandwidths of the electronic level involved in the absorption process.  
201 Moreover, this narrow energy bandwidth of the fluorescence detection system allows also to  
202 have Sm L3-edge spectra ( $\approx 6.716\text{keV}$ ) free from the Nd L1-edge contribution ( $\approx 6.722\text{keV}$ ),  
203 even if the Sm  $\text{L}\alpha_1$  fluorescence line selected (at  $5.636\text{keV}$ ) is close to the Nd fluorescence  
204 lines characteristic of the L1-edge (mainly  $\text{L}\beta_3$  at  $5.829\text{keV}$  and  $\text{L}\beta_4$  at  $5.723\text{keV}$ ). The incident  
205 energy ranged between 6.70 keV and 6.74 keV and no other absorption line than that of Sm  
206 was observed. For Sm L3-edge absorption energy calibration we used Sm metal foils  
207 (Goodfellow): energy position of the first maximum of the first derivative Sm metal foil spectrum  
208 was set to 6.616 keV.  $\text{SmI}_2$  commercial powder (Sigma Aldrich) for the divalent state and  
209  $\text{Sm}_2\text{O}_3$  (Sigma Aldrich) for the trivalent state were also studied as reference spectra.

210 Figure 1 presents standards analysis for Yb and Sm sessions. For both Yb and Sm, the  
211 standard analyses were performed on pellets composed of a mixture of BN and the standard  
212 using the transmission mode. For both elements the pellets contained 20 times more BN than  
213 standard powders. For the samples, measurements were performed on polished resin mounts  
214 in fluorescence mode. Before absorption data acquisition, X-Ray fluorescence maps were  
215 acquired (Figure 2) in order to locate the phases in the sample.

## 216 **3. Results**

### 217 **3.1 Sample description**

218 The samples from experiments with CaS in the starting powders are composed by an  
219 amorphous silicate glass (45 to 53 vol%) containing oldhamite crystals (30 to 50  $\mu\text{m}$   
220 corresponding to 30 to 38 vol%) and iron-nickel metal phase (5 to 30  $\mu\text{m}$  corresponding to 14  
221 to 17 vol%). Run 1263 contains quartz crystals (30 to 50  $\mu\text{m}$  corresponding to 5 vol%). The  
222 samples from experiments with FeS in the starting powders are composed by an amorphous  
223 silicate matrix (7 to 11 vol%) containing molten FeS (37 to 47 vol%), an iron-nickel metal phase  
224 (5 to 30  $\mu\text{m}$  corresponding to 13 to 20 vol%) and enstatite crystals (28 to 36vol%). Some of the  
225 metal nuggets are enclosed within the iron sulphide phase. Typical sample textures are  
226 illustrated on Figure 3. Table 1 presents the phase fractions in each experiment. The  
227 proportions were estimated by coupling major element mass balance and image analysis using  
228 FOAMS program (Shea et al, 2010).

229

### 230 **3.2 Major element composition**

231 The phase compositions are given in Tables 2 and 3 for experiments containing CaS and FeS,  
232 respectively.

#### 233 **3.2.1 Experiments with CaS:**

234 The oldhamite phase is close to endmember composition with 91 to 94 wt.% CaS, 4 to 7 wt.%  
235 MgS and 3 wt.% FeS. The metal phase has an average composition of 82 wt.% of Fe, 4 to 7

236 wt.% of Ni and 3 to 12 wt.% of Si. The matrix is a quenched liquid silicate phase with CaO (20  
237 to 25 wt.%) and MgO (18 to 20 wt.%) being the main cations with Al<sub>2</sub>O<sub>3</sub> (3 wt.%) and S (2.08  
238 to 6.69 wt.%) and small amount of FeO (around 0.5 wt.%). With increasingly reducing  
239 conditions, S content in the melt decreases.

### 240 **3.2.2 Experiments with FeS**

241 The FeS phase is close to endmember composition with 99.5 wt.% FeS and 0.5 wt.% MgS.

242 The metal phase has an average composition of 80 to 91 wt.% of Fe, 1 to 3 wt.% of Ni and  
243 less than 1 wt.% of S and very small amount of Si (between 0.01 and 1 wt.%). For experiments  
244 with FeS the matrix contains CaO (5 to 12 wt.%), MgO (15 to 30 wt.%), Al<sub>2</sub>O<sub>3</sub> (7 to 15 wt.%),  
245 S (0.26 to 5.56 wt.%) and a small amount of FeO (around 1 wt.%).

246 With increasingly reducing conditions, S content in the metal decreases while Fe and Si  
247 contents increase.

248 The pyroxene composition is close to enstatite end member.

249

### 250 **3.3 Trace element composition**

251 Laser analyses were obtained for all 14 lanthanides. The results are presented in Table 4 and  
252 5 for CaS and FeS experiments, respectively. The average mass concentrations measured  
253 have been calculated for each element and each phase for the different samples. From these  
254 values the sulphide/silicate melt partition coefficients have been calculated for the samples.  
255 One sigma error is given in the tables for each series of values. Trace element Nernst partition  
256 coefficients ( $D = (\text{wt.\% element in the crystal}) / (\text{wt.\% element in the silicate melt})$ ) are given in  
257 Tables 4 and 5 for oldhamites and FeS, respectively. The reported errors on Nernst coefficient  
258 values were calculated as

$$259 \quad (9) \quad \sigma = \left( \sqrt{\frac{\sigma_{\text{sulfide}}^2}{\text{sulfide}} + \frac{\sigma_{\text{melt}}^2}{\text{melt}}} \right) \times D$$

260 Figures 4 and 5 present REE partitioning data for oldhamites and FeS, respectively. Elements  
261 have been sorted according to their atomic number.

262 In the oldhamite/silicate melt system, light-REE (LREE) and heavy-REE (HREE) are  
263 moderately incompatible, whereas middle-REE (Sm and Gd) are moderately compatible. For  
264 oldhamite/silicate melt coefficients we note two groups of spectra, one group of three spectra  
265 with  $La < 0.1$  and one group of five spectra with  $0.1 < La < 1$ . For FeS, all studied trace elements  
266 are incompatible in our experiments and FeS are depleted in HREE relative to LREE. We note  
267 positive anomalies for Eu and Yb partition coefficients in all experiments.

### 268 **3.4 Ytterbium and Samarium valence state**

269 XANES measurements at Yb and Sm L3-edge energy levels are presented in Figure 6.  
270 Measurements on the standards give the positions of the edges for 3+, 2+ and 0 valence  
271 states.

272 For Yb, oldhamites and glass show peaks corresponding to 3+ and 2+ valence states. The  
273 peak intensity for  $Yb^{2+}$  is higher for oldhamites than for glass, whereas the peak of  $Yb^{3+}$  is  
274 higher for the glass than for oldhamites, suggesting a preferential incorporation of  $Yb^{2+}$  in  
275 oldhamites compare to the glass.

276 As mentioned in the method section, for Sm the beam size was too large to analyse sulphide  
277 and the glass separately. Thus, the Sm L3-edge XANES spectra obtained are representative  
278 of the valence states of this element in the bulk sample with one small peak at the energy of  
279  $Sm^{2+}$  absorption and a larger peak at the energy of  $Sm^{3+}$ . Here we cannot document Sm  
280 valence distribution between oldhamites and silicate melt. However, the data show the  
281 presence of both  $Sm^{2+}$  and  $Sm^{3+}$  in the samples.

282

## 283 **4 Discussion**

284

#### 285 4.1 Origin of D value variation

286

287 As noted above, there is a clustering of oldhamite/melt partition coefficients with two sets of  
288 values. Three mixtures of the same composition were used for the experiments with CaS.  
289 Figure 7A shows the variation of the La D value for different samples as a function of the timing  
290 interval between the date of the powder preparation and the date of experiment for experiments  
291 containing CaS. We note that, for a given starting mixture, early experiments yield low D  
292 values, whereas subsequent experiments yield high values. Therefore, we attribute the  
293 clustering of the partition coefficient values to aging of the powders before loading in the silica  
294 tubes. Figure 7B also shows the La/Lu ratio as a function of the age of the powder for  
295 experiments with oldhamites. The  $D_{\text{oldhamite/melt}}(\text{La}) / D_{\text{oldhamite/melt}}(\text{Lu})$  does not vary with the age  
296 of the powders. The starting mixtures were analysed subsequently with a Thermo Scientific  
297 FLASH 2000 NC Analyzer to determine the carbon, hydrogen and nitrogen content. From  
298 hydrogen data we determined a water content of about 2 wt.% in the aged powder. Therefore,  
299 it appears that water favours REE incorporation in oldhamite. Consequently, the lower values  
300 are representative of the true values for REE partitioning between oldhamites and silicate melt.  
301 However, water presence does not affect the fractionation between REE and all experiments  
302 will be considered in the section below, dealing with anomalies.

303 In the case of FeS, we also note that D values increase with aging of the starting powders  
304 (Figure 7C) but the  $D_{\text{FeS/melt}}(\text{La}) / D_{\text{FeS/melt}}(\text{Lu})$  variation is more complex (Figure 7D). Overall  
305 there is a slight increase of the ratio with time for which there is no simple explanation but we  
306 note that the two most reduced experiments ( $f_{\text{O}_2}$  of IW-5.8) yield the highest  $D_{\text{FeS/melt}}(\text{La}) /$   
307  $D_{\text{FeS/melt}}(\text{Lu})$  ratios. The data of Lodders (1996) also show the same trend. Analyses show that  
308 the powder contains about 2 wt.% water so in the same manner as for oldhamite we attribute  
309 D (La) increase to water presence. Given the present data we cannot further discuss the effect  
310 of water on REE fractionation.

311

#### 312 **4.2 Comparison with previous experimental studies**

313 In Figure 8 we compare the newly obtained oldhamite/silicate melt and FeS/silicate melt  
314 partitioning coefficients with literature data. Jones and Boynton (1983) studied La, Gd and Lu  
315 partitioning between FeS, (Ca, Mg) S and a basaltic melt. Lodders (1996) study presents La,  
316 Nd, Sm, Eu, Gd, Yb and Lu partitioning between oldhamite or FeS and a silicate melt at 1300°C  
317 and reducing conditions ( $\log f_{O_2} = IW-3.97$ ). Dickinson et al. (1997) treated partitioning of La,  
318 Ce, Nd, Sm, Eu, Gd and Yb between (Ca, Mg) S melt and a silicate melt at 1200 and 1300°C.

319 Overall our results agree with data from the literature. Jones and Boynton (1983) and Lodders  
320 (1996) found that the partition coefficients increased from La to Lu for oldhamites while they  
321 decrease for FeS. Lodders (1996) also reported positive anomalies for Eu. The Yb anomaly in  
322 oldhamites that is observed in the present study has not been discussed by Lodders (1996)  
323 because the two neighbouring elements had not been measured (only Lu was measured).  
324 Dickinson et al. (1997) who studied oldhamite/silicate melt partitioning found two types of REE  
325 patterns in sulphides: patterns from “oldhamites with a high Ca” content have a positive Eu  
326 anomaly and those from “oldhamites with a low Ca” content have a negative Eu anomaly.

327 Wohlers and Wood (2015; 2017) studied the effect of  $f_{O_2}$  on U, Th and REE partitioning  
328 between silicate melt, and molten Fe-S alloys. Our partitioning data on FeS-bearing systems  
329 are consistent with the trend shown in their study. There is a sharp increase in D values as  
330 FeO content of the silicate melt drops below 1 mol%.

331

#### 332 **4.3 Ytterbium and Samarium valence change with redox conditions**

333 XANES measurements show unequivocally that Yb and Sm occur under both 3+ and 2+  
334 valence states in the experiments. For Yb, positive anomalies are always detected in  
335 sulphide/silicate melt partition coefficients.

336 In more detail, we modelled the ideal 3+ REE partition coefficients values. For this we used  
337 the lattice strain model (Blundy and Wood, 1994) for the substitution of cation according to its  
338 radius and charge in a given crystalline lattice. The data were modelled using a Quasi-  
339 Newtonian algorithm. For this we used measured data except for Eu, Yb and Sm. According  
340 to Papike (2005) and to XANES data, the three elements are present, at least partly, under the  
341 2+ valence state in the samples. The ionic radii used for the model calculations have been  
342 taken from Shannon (1976) database for 3+ cations with a coordination number of 6. The  
343 resulting model parameters are given in the supplementary material section We then calculated  
344 ideal partitioning data for 3+ elements for each experiment. These values are compared to  
345 measured data from experiment 1244 in Figure 9. The modelled values are the ideal  
346 partitioning coefficients called  $D^*$ .

347 For FeS, the lattice strain model is not relevant because the temperature of the experiments is  
348 higher than the FeS melting temperature. In the rest of this section, a qualitative estimation of  
349 the role of the  $fO_2$  on REE partitioning between oldhamite and silicate melt and valence change  
350 is presented. The objective here is to estimate what controls the behaviour of Yb and Sm in  
351 the studied system.

352 From the lattice strain modelling, we calculated the  $D/D^*$  ratios to model the magnitude of the  
353 anomalies. These values are presented in Table 6. Figure 10 shows the amplitude of the Yb  
354 and Sm oldhamite/silicate melt partitioning anomalies (expressed as  $D/D^*$ ) versus the oxygen  
355 fugacity.  $D/D^*$  value for Yb increases from 1.77 to 2.65 as oxygen fugacity decreases. For Sm  
356 the anomalies are smaller (from 1.04 to 1.09) and the correlation between  $D/D^*$  and  $fO_2$  less  
357 pronounced. However, we note the two most reduced experiments have the highest  $D/D^*$   
358 values. These observations suggest that the magnitude of the anomalies in Yb or Sm, could  
359 be a tool to estimate redox conditions for very reducing systems such as the enstatite  
360 chondrites environment.

361



#### 362 **4.4 On the origin of oldhamites in aubrites and enstatite chondrites**

363 The origin of oldhamites in enstatite chondrites and achondrites has been debated on the basis  
364 of several textural and chemical criteria. In order to discuss this origin, it is necessary to present  
365 the REE distribution in aubrites and enstatite chondrites. In both types of meteorites oldhamites  
366 are the principal carrier of REE with abundances around 100 times CI for enstatite chondrites  
367 and from 50 up to 1000 times CI for aubrites (Gannoun et al., 2011; Floss et Crozaz, 1993;  
368 Floss et al., 2001). In EH chondrites, enstatites are a secondary carrier of REE, with  
369 abundances between 1 and 10 times the CI of these elements, whereas other phases (such  
370 as niningerite, MgS) contain less than the CI abundances. In EL chondrites, the plagioclase is  
371 rich in Eu (up to 7 times CI) but not in the other REE (around 1 times CI or less), while the REE  
372 content of other phases is less than the CI abundances (Floss, 2001). In aubrites, alabandite  
373 and diopside both have up to 10 times the REE content of CI. The plagioclase is also a Eu  
374 carrier (6 to 10 times CI), whereas others REE are less abundant (Floss, 1993; Wheelock,  
375 1994). In aubrites, enstatite and forsterite have low REE abundances, with less than 0.2 times  
376 CI in the former and below detection limit in the latter (Floss, 1993; Wheelock, 1994).

377 On the basis of the general shape of the REE pattern as well as the presence of anomalies in  
378 some elements, 8 patterns have been identified in oldhamites from EH chondrites, 2 in  
379 oldhamites from EL chondrites and 10 in oldhamites from aubrites (Gannoun, 2011; Floss et  
380 Crozaz, 1993; Floss et al., 2001; Wheelock, 1994). Four of the patterns found in aubrites are  
381 also observed in EH and 2 of these 4 patterns are observed in EL. One type of pattern, convex  
382 upward, with only a negative Eu anomaly, is found in EH, EL and aubrites. It corresponds to  
383 the metamorphic type E described as clusters of anhedral oldhamite crystals accreted on  
384 kamacite-troilite clasts (Gannoun et al., 2011). The pattern associated to C-D types is also  
385 observed in aubrites but not in EL. It corresponds to single crystals of oldhamite intermingled  
386 in kamacite-troilite clasts and metal sulphide spherules or to oldhamite crystals covered with  
387 kamacite veneer. Figure 11 summarizes the REE pattern reported for oldhamites in enstatite  
388 chondrites and in aubrites.

389 Considering that all available experimentally determined oldhamite/silicate melt partition  
390 coefficients for the REE have values of 1 or less, it is clear that a simple oldhamite/silicate melt  
391 equilibrium cannot explain the high REE abundances found in oldhamite from enstatite  
392 chondrites and aubrites. Therefore, despite its refractory character, CaS cannot be a liquidus  
393 phase in natural complex systems. In addition, the presence of FeS results in CaS-FeS eutectic  
394 melting at about 1100 °C (Heumann, 1942). As discussed by previous authors, if oldhamite  
395 were of magmatic origin in enstatite chondrites and aubrites, it should result from a complex  
396 crystallisation history. Starting from a molten state with a chondritic REE abundance, enstatite  
397 would crystallise first. The resulting liquid would therefore become enriched in REE. Upon  
398 further cooling the sulphide phase (still molten) would be separated from the silicate phase.  
399 Given the overall sulphide/silicate partition coefficient values, the two melts would have similar  
400 concentrations for the light REE whereas the sulphide phase would be enriched in the heavy  
401 REE. Given the Fe/Ca ratio of the sulphide phase (of the order of 20; Rubin 1984) FeS would  
402 crystallise first according to the FeS-CaS phase diagram (Lodders 1996) and REE would stay  
403 in the sulphide liquid. Finally, CaS would crystallise last, concentrating all REE from the  
404 sulphide liquid. Given that oldhamite represents less than 1 wt% of enstatite chondrites,  
405 enrichment by a factor of 100 is expected.

406 As an alternative, some have suggested that oldhamites represent a relict of the primitive  
407 nebula and were not modified by interaction with other phases (Lodders, 1996; Dickinson and  
408 McCoy, 1997). However, such scenario should result in positive Eu and Yb anomalies (as  
409 discussed below), which are not commonly observed.

410 The present study provides the first analyses on Yb and Sm valence states in sulphides and  
411 silicates equilibrated under reducing conditions, such as those relevant to enstatite chondrites  
412 and aubrites. XANES analyses demonstrated the presence of Yb<sup>2+</sup> and Sm<sup>2+</sup>. Our results on  
413 Ho showed no presence of Ho<sup>2+</sup>. In the case of Yb, the micro-XANES data suggest preferential  
414 partitioning of Yb<sup>2+</sup> in the sulphide phase, compared to the silicate melt. We did not study Eu  
415 valence state specifically, but we anticipate all Eu to be present in 2+ state, according to

416 previous works (Papike, 2005). The positive europium and ytterbium anomalies observed in  
417 the present experimental work as well as in some of the naturally occurring oldhamites can  
418 thus be attributed to the preferential incorporation of these elements in their divalent state in  
419 the CaS crystals. Moreover, it is also possible that Sm anomalies observed by Gannoun et al.  
420 (2011) could be due to reduction to  $\text{Sm}^{2+}$ . Our results suggest that Eu and Yb (and possibly  
421 Sm) anomalies are observed when oldhamite is the only phase controlling REE budget.  
422 Lodders (1996) and Dickinson and McCoy (1997) suggested that Eu and Yb anomalies are  
423 attributed to preferential evaporation and condensation of these REE. Here we see that  
424 reduction can be at the origin of these anomalies. The diversity of REE patterns necessitate  
425 that other processes are implied during CaS crystallisation (Lodders, 1996; Dickinson, 1997).

426

## 427 **5 Conclusion**

428 The sulphide/silicate melt REE partition coefficients obtained in the present experimental study  
429 as well as in previous ones do not reproduce the observed abundances of REE in sulphides  
430 of reduced chondrites (enstatite chondrites) and achondrites (aubrites). This is true for  
431 oldhamites (measured oldhamites REE contents are higher than predicted ones) as well as for  
432 FeS (measured FeS REE contents are below detection limits). However, the present study  
433 does reproduce europium and ytterbium anomalies that are observed in a large population of  
434 oldhamites from reduced chondrites and achondrites. The positive Eu and Yb anomalies in  
435 oldhamites are attributed to the presence of  $\text{Eu}^{2+}$  and  $\text{Yb}^{2+}$  as identified for the latter using  
436 XANES measurements.

437 As to what oldhamites can tell us about REE budget during condensation of the solar system  
438 depends on its primordial character. Our results strongly suggest that, only in case of presence  
439 of Eu and Yb positive anomalies, REE budget is directly and only controlled by oldhamite.  
440 Other oldhamites types appear to have been affected by secondary processes that may be  
441 magmatic or metamorphic. Primitive oldhamite crystals, that is those displaying Eu and Yb

442 positive anomalies, are found only in EH chondrites and in aubrites. All oldhamites from EL  
443 chondrites appear to have a complex history. Since primitive oldhamites REE abundances do  
444 not match the oldhamite/silicate melt partition coefficients it seems that their REE signature  
445 has been acquired by interaction with the nebular gas. Those crystals may therefore provide  
446 us with information about the primordial environment of the solar system.

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460 **Table captions**

461 **Table 1:** Experimental conditions and run results.

462 **Table 2:** Major and minor electron microprobe composition of phases from experiments with  
463 CaS.

464 **Table 3:** Major and minor electron microprobe composition of phases from experiments with  
465 FeS.

466 **Table 4:** Minor and trace element concentrations in silicate melts and oldhamites in ppm from  
467 experiments with CaS powders and corresponding Nernst oldhamites/melt REE partition  
468 coefficients. All data were obtained by LA-ICP-MS.

469 **Table 5:** Minor and trace element concentrations in silicate melts and molten FeS in ppm from  
470 experiments with FeS powders and corresponding Nernst molten FeS/melt REE partition  
471 coefficients. All data were obtained by LA-ICP-MS.

472 **Table 6:** D/D\* ratios calculated for oldhamite/melt partitioning experiments.

473

474

475 **Figure captions**

476 **Fig. 1:** X-ray absorption near-edge spectroscopy spectra of the standards used. For  
477 ytterbium: results for Yb L3-edge obtained on BM23 beamline at ESRF, using the microbeam  
478 setup. Note that Ho L2-edge absorption line is also visible. For samarium: Results for Sm L3-  
479 edge obtained on BM16 FAME-UHD beamline of ESRF-CRG.

480 **Fig. 2:** Fluorescence maps obtained at ESRF on BM 23 line showing S, Ca and Fe  
481 abundance, for sample 1250. Regions rich in Ca and S (in red and orange on the maps on  
482 the left) are oldhamites. The red region in the right bottom angle of the third map  
483 corresponds to an iron-nickel bead. Regions poorer in the three elements (blue in the S and  
484 Fe map and green in the Ca map) represent the quenched glass. A SEM picture of the same  
485 area is compared to the maps in the fourth panel. Oldh. = oldhamite crystals; Metal = Fe-Ni  
486 alloy, Melt = quenched silicate melt.

487 **Fig. 3:** SEM pictures of four samples representative of the observed phases assemblage **A.**  
488 Hvittis + CaS starting powder at 1300°C. **B.** Hvittis + CaS starting powder at 1400°C. **C.**  
489 Hvittis + FeS starting powder at 1300°C. **D.** Hvittis + FeS starting powder at 1400°C. Oldh. =  
490 oldhamite crystals; Metal = Fe-Ni alloy, Melt = quenched silicate melt; Enst.=enstatites.

491 **Fig. 4:** Rare Earth Elements oldhamite/silicate melt partition coefficients for all the  
492 experiments with Hvittis + CaS mixture.

493 **Fig. 5:** Rare Earth Elements FeS/silicate melt partition coefficients for all the experiments  
494 with Hvittis + FeS mixture.

495 **Fig. 6:** XANES spectra determined from Hvittis + CaS samples. **A.** Yb L3-Edge measured in  
496 the oldhamite crystals. **B.** Yb L3-Edge measured in the glasses **C.** Sm L3-Edge on bulk  
497 samples. In A. and B. Ho absorption-edge is visible at 8.919keV. The patterns correspond to  
498 an average of the data for each sample, with 3 to 19 analyses by element on different spots.  
499 For the Yb analyses on the sample 1244 only one spot in both oldhamites and the glass  
500 were analysed.

501

502 **Fig. 7:** Sulphide/melt partition coefficient values obtained in the present study plotted as a  
503 function of the age of the powders used, expressed in days. The three mixtures used are  
504 represented in grey, open, and closed symbols for powders 1, 2, and 3, respectively. **A.** La  
505 for oldhamite/silicate melt partitioning. **B.** La/Lu partition coefficient ratio for oldhamite/silicate  
506 melt system. **C.** La for FeS/silicate melt partitioning. **D.** La/Lu partition coefficient ratio for  
507 FeS/silicate melt system. All REE present the same pattern as that of La shown in A and C.

508 **Fig. 8:** Comparison of the partition coefficients obtained in the present study with literature  
509 values (Lodders, 1996; Dickinson et al., 1997; Jones and Boynton, 1983). **A.**  
510 Oldhamite/silicate melt data. **B.** FeS/silicate melt data.

511 **Fig. 9:** Experimental values for oldhamite/silicate melt REE partition coefficients for  
512 experiment 1244, compared to values obtained using the lattice-strain model (Blundy and  
513 Wood, 1994) and considering all REE in the 3+ valence states with a coordination number of  
514 6.

515 **Fig. 10:** Intensities of the anomalies in Yb and Sm expressed as the ratio of measured and  
516 modelled partition coefficient ( $D/D^*$ ) plotted as a function of oxygen fugacity determined in  
517 the experiments.

518 **Fig. 11:** Various CaS REE patterns normalised to CI in aubrites and enstatite chondrites  
519 from the literature (Larimer and Ganapathy, 1987; Floss and Crozaz, 1993; Wheelock et al.,  
520 1994; Floss et al., 2001; Gannoun et al., 2011). Larimer and Ganapathy (1987) data shown  
521 as dashed line were obtained for 5 REE only. Other data cover all REE. See text for  
522 discussion and comparison with the present experimental data.

523

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**Table 1:** Experimental conditions and run results.

Run	Powder	P(bar)	T(C)	Duration(h)	$\Delta IW$	Result <sup>a</sup>
1250	EC + CaS	0.015	1300	10	-6.6	CaS (51). Met (15).Liq (34)
1263	EC + CaS	0.0075	1300	96	-6.5	CaS (52). Met (14).Liq (29).Qz(5)
1208	EC + CaS	0.009	1400	8	-6.9	CaS (46). Met (17).Liq (37)
1240	EC + CaS	0.0095	1400	10	-6.2	CaS (50). Met (15).Liq (35)
1246	EC + CaS	0.002	1400	48	-6.2	CaS (55). Met (15).Liq (30)
1305	EC + CaS	0.0034	1400	72	-6.1	CaS (51). Met (14).Liq (35)
1244	EC + CaS	0.009	1400	96	-5.8	CaS (46). Met (16).Liq (38)
1304	EC + CaS	0.0034	1400	160	-6.2	CaS (53). Met (14).Liq (33)
1266	EC + FeS	0.085	1300	1	-4.1	FeS (37). Met (20).Liq (7).Enst (36)
1282	EC + FeS	0.0007	1300	10	-4.5	FeS (45). Met (15).Liq (9).Enst (33)
1207	EC + FeS	0.009	1400	1	-4.8	FeS (45). Met (15).Liq (11).Enst (29)
1239	EC + FeS	0.0085	1400	1	-4.8	FeS (45). Met (14).Liq (13).Enst (28)
1284	EC + FeS	0.0007	1400	1	-5.8	FeS (47). Met (14).Liq (8).Enst (31)
1252	EC + FeS	0.01	1400	96	-5.8	FeS (47). Met (13).Liq (11).Enst (29)

Liq=Silicate melt ; Enst=Enstatite ; Met=Metallic Alloy ; CaS=Oldhamite ; FeS=molten FeS ;  
Qz=Quartz

<sup>a</sup> Phase proportions are expressed in volume percent

Table 2: Major and minor electron microprobe composition of phases from experiments with CaS.

Run	1250	Na 5	1263	Na 5	1208	Na 6	1240	Na 4	1246	Na 2	1305	Na 5	1244	Na 3	1304	Na 5
Oldhamite (wt%)	$1\sigma$		$1\sigma$		$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$
Si	0.07	0.02	0.07	0.03	0.07	0.06	0.43	0.52	0.02	0.01	0.01	0.01	0.05	0.02	0.02	0.01
Ti	0.01	0.01	0.01	0.01	2.24	0.06	0.00	0.00	0.01	0.01	0.02	0.02	0.00	0.00	0.01	0.02
Al	0.00	0.00	0.01	0.01	0.00	0.00	0.04	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.08	0.02	0.09	0.03	0.00	0.00	0.08	0.02	0.06	0.02	0.01	0.05	0.01	0.05	0.11	0.02
Fe	0.88	0.05	1.85	0.05	0.63	0.06	1.64	0.16	1.11	0.07	1.86	0.22	1.61	0.06	2.54	0.14
Mn	0.06	0.01	0.09	0.04	0.01	0.00	0.16	0.00	0.07	0.03	0.1	0.01	0.09	0.03	0.17	0.02
Mg	3.20	0.07	2.37	0.06	2.24	0.06	2.22	2.16	2.53	0.04	2.35	0.02	1.67	0.01	3.34	0.08
Ca	45.48	0.11	48.58	1.01	50.38	0.20	48.71	2.23	49.48	0.26	48.57	0.27	50.36	0.29	46.32	0.45
Na	0.05	0.02	0.02	0.01	0.02	0.02	0.07	0.11	0.01	0.01	0.01	0.01	0.00	0.01	0.00	0.00
Ni	0.01	0.01	0.03	0.02	0.09	0.01	0.00	0.00	0.02	0.03	0.02	0.01	0.02	0.02	0.01	0.02
S	50.16	0.16	43.46	0.46	44.21	0.13	41.73	2.57	43.84	0.14	43.72	1.3	43.4	0.15	42.96	0.12
Total	100.0		96.57		99.87		95.09		99.34		96.68		97.26		95.48	

Run	1250	Na 10	1263	Na 5	1208	Na 8	1240	Na 5	1246	Na 5	1305	Na 5	1244	Na 3	1304	Na 13
Metal (wt%)	$1\sigma$		$1\sigma$		$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$
Si	5.16	0.45	2.77	0.98	11.02	1.48	7.18	0.25	7.32	0.74	5.19	0.85	3.7	1.08	6.16	0.41
Al	0.00	0.00	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	0.00	0.00
Cr	0.25	0.18	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	0.03	0.03
Fe	84.62	0.73	85.58	2.48	79.99	2.74	83.88	1.38	82.33	5.59	85.44	2.82	83.02	1.93	86.18	1.24
Mn	0.01	0.02	0.02	0.02	0.01	0.02	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.02
Mg	0.01	0.01	0.00	0.00	n.a	n.a	0.01	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.00	0.01
Ca	0.35	0.11	0.24	0.18	n.a	n.a	n.a	0.00	0.00	0.00	n.a	n.a	n.a	0.35	0.11	
Ni	5.94	0.73	6.95	0.35	4.36	1.22	6.19	0.17	5.42	0.49	6.16	0.3	7.31	0.56	6.34	0.16
S	0.65	0.78	0.54	0.89	0.23	0.28	0.20	0.12	0.81	1.69	0.27	0.37	0.38	0.13	0.06	0.10
C	2.91	1.15	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	1.63	1.52
Total	99.88		96.1		95.61		97.48		95.92		97.07		94.41		100.76	
C <sup>a</sup>	3.01		3.90		4.39		2.52		4.08		2.93		5.59		0.87	

Run	1250	Na 9	1263	Na 5	1208	Na 5	1240	Na 2	1246	Na 5	1305	Na 5	1244	Na 3	1304	Na 9
Silicate melt (wt%)	$1\sigma$		$1\sigma$		$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$	$1\sigma$
SiO <sub>2</sub>	56.02	0.96	57.17	0.35	54.73	0.38	55.34	0.16	55.78	1.03	58.68	0.29	55.05	0.31	58.08	1.15
TiO <sub>2</sub>	0.17	0.03	0.13	0.02	0.11	0.02	0.12	0.08	0.20	0.03	0.25	0.02	0.13	0.03	0.16	0.03
Al <sub>2</sub> O <sub>3</sub>	3.01	0.16	2.17	0.02	2.85	0.1	2.52	0.09	2.53	0.07	3.43	0.07	2.43	0.09	2.44	0.21
FeO	0.28	0.05	0.47	0.08	0.28	0.05	0.53	0.05	0.44	0.13	0.22	0.03	0.56	0.16	0.34	0.59
MnO	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.02	0.01	0.01	0.01	0.01	0.02	0.01	0.01
MgO	17.95	0.65	19.24	0.27	16.73	0.37	15.39	0.19	18.98	0.28	19.85	0.21	14.29	0.33	25.37	2.28
CaO	18.85	0.41	23.43	0.57	21.56	0.77	22.47	0.73	18.76	0.77	15.8	0.3	24.15	0.27	12.01	2.35
Na <sub>2</sub> O	0.03	0.03	0.02	0.01	0.01	0.01	0.02	0.03	0.01	0.01	0.00	0.00	0.01	0.02	0.01	0.01
K <sub>2</sub> O	0.02	0.01	0.02	0.01	0.00	0.00	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.00	0.01
Ni <sub>2</sub> O <sub>3</sub>	0.01	0.01	0.01	0.01	0.01	0.01	0.04	0.02	0.02	0.02	0.01	0.02	0.00	0.01	0.00	0.01
S	3.22	1.29	2.33	0.23	3.41	0.58	5.73	0.06	5.08	0.80	1.97	0.59	6.69	0.38	2.08	0.97
Total	99.57		105.00		99.7		102.18		101.83		100.23		103.35		100.50	

Na = Number of analyses

n.a. Not analysed

a. Maximum content calculated by difference from the total

O content in melt was estimated by stoichiometry

**Table 3:** Major and minor electron microprobe composition of phases from experiments with FeS.

Run	1266	Na 5	1282	Na 5	1207	Na 4	1239	Na 3	1284	Na 5	1252	Na 5
<b>Molten FeS (wt%)</b>		1 $\sigma$		1 $\sigma$		1 $\sigma$		1 $\sigma$		1 $\sigma$		1 $\sigma$
<b>Si</b>	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.05	0.02	0.01	0.01
<b>Ti</b>	0.19	0.12	0.19	0.14	0.23	0.10	0.43	0.46	0.15	0.15	0.19	0.14
<b>Al</b>	0.01	0.01	0.00	0.00	n.a		0.00	0.00	0.00	0.01	0.00	0.00
<b>Cr</b>	0.33	0.09	0.42	0.21	n.a		0.37	0.24	0.44	0.3	0.42	0.21
<b>Fe</b>	62.11	0.26	60.19	0.57	56.13	8.13	60.8	1.6	60.52	0.87	60.19	0.57
<b>Mn</b>	0.19	0.05	0.18	0.07	0.61	1.04	0.17	0.02	0.13	0.04	0.18	0.07
<b>Mg</b>	0.01	0.01	0.03	0.02	2.59	4.90	0.13	0.01	0.11	0.04	0.03	0.02
<b>Ca</b>	0.00	0.01	0.00	0.01	0.17	0.34	0.02	0.01	0.01	0.01	0.00	0.01
<b>Na</b>	0.01	0.02	0.03	0.02	n.a		0.01	0.01	0.05	0.04	0.03	0.02
<b>Ni</b>	0.41	0.03	0.47	0.04	0.25	0.15	0.45	0.03	0.61	0.07	0.47	0.04
<b>S</b>	36.88	0.26	36.56	0.23	38.23	2.36	36.48	0.01	36.66	0.22	36.56	0.23
<b>Total</b>	100.14		98.09		98.21		98.87		98.74		98.09	
Run	1266	Na 5	1282	Na 5	1207	Na 7	1239	Na 1	1284	Na 5	1252	Na 5
<b>Silicate (wt%)</b>		1 $\sigma$		1 $\sigma$		1 $\sigma$		1 $\sigma$		1 $\sigma$		1 $\sigma$
<b>SiO<sub>2</sub></b>	60.3	2.06	58.13	1.97	60.04	26.23	60.62	6.06	58.05	2.23	59.47	0.90
<b>TiO<sub>2</sub></b>	0.00	0.01	0.06	0.03	0.00	0.02	0.06	0.01	0.00	0.01	0.01	0.01
<b>Al<sub>2</sub>O<sub>3</sub></b>	0.29	0.15	0.5	0.25	0.11	0.01	0.26	0.03	1.07	1.78	0.22	0.04
<b>FeO</b>	0.59	0.20	0.28	0.10	0.19	53.18	0.30	0.03	0.64	0.24	0.10	0.02
<b>MnO</b>	0.02	0.02	0.01	0.01	0.02	0.01	0.00	0.00	0.01	0.01	0.01	0.01
<b>MgO</b>	39.18	1.57	37.38	1.64	40.00	0.02	39.92	3.99	36.69	4.27	38.8	0.96
<b>CaO</b>	0.92	0.06	0.31	0.11	0.09	0.03	0.15	0.01	0.61	0.99	0.09	0.03
<b>Na<sub>2</sub>O</b>	0.06	0.08	0.01	0.01	0.00	0.00	0.00	0.00	0.04	0.05	0.01	0.00
<b>K<sub>2</sub>O</b>	0.01	0.02	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.04	0.02	0.01
<b>Ni<sub>2</sub>O<sub>3</sub></b>	0.00	0.00	0.02	0.02	0.01	0.79	0.00	0.00	0.02	0.02	0.01	0.02
<b>SO<sub>2</sub></b>	0.02	0.03	0.04	0.05	0.01	0.01	0.00	0.00	1.00	2.16	0.01	0.00
<b>Total</b>	101.40		96.74		100.47		101.30		98.17		98.75	
Run	1266	Na 9	1282	Na 10	1207	Na 4	1239	Na 3	1284	Na 3	1252	Na 5
<b>Metal (wt%)</b>		1 $\sigma$		1 $\sigma$		1 $\sigma$		1 $\sigma$		1 $\sigma$		1 $\sigma$
<b>Si</b>	0.01	0.02	0.01	0.03	1.72	0.73	0.44	0.61	2.9	0.19	3.25	2.06
<b>Al</b>	n.a		n.a		n.a		n.a		n.a		n.a	
<b>Cr</b>	0.03	0.03	0.03	0.02	n.a		n.a		n.a		n.a	
<b>Fe</b>	82.45	7.52	85.91	5.07	91.33	2.14	89.32	9.07	89.04	0.22	90.43	1.31
<b>Mn</b>	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01
<b>Mg</b>	0.00	0.00	0.01	0.01	n.a		0.01	0.02	0.02	0.02	0.01	0.01
<b>Ca</b>	n.a		n.a		0.02	0.02	n.a		n.a		0.00	0.01
<b>Ni</b>	7.37	4.91	4.43	2.63	1.30	0.27	2.65	0.89	3.19	0.35	2.16	0.47
<b>S</b>	0.76	1.05	0.35	0.39	0.08	0.05	1.46	1.51	0.18	0.16	1.05	2.17
<b>C</b>	2.65	1.82	1.43	0.42	n.a		n.a		n.a		n.a	
<b>Total</b>	93.28		92.18		94.46		93.89		95.34		96.92	
<b>C<sup>a</sup></b>	9.37		9.25		5.54		6.11		4.66		3.08	
Run	1266	Na 10	1282	Na 9	1207	Na 3	1239	Na 2	1284	Na 7	1252	Na 5
<b>Silicate melt (wt%)</b>		1 $\sigma$		1 $\sigma$		1 $\sigma$		1 $\sigma$		1 $\sigma$		1 $\sigma$
<b>SiO<sub>2</sub></b>	64.82	1.84	57.53	0.16	53.10	0.56	49.62	1.47	55.14	1.38	51.2	0.35
<b>TiO<sub>2</sub></b>	0.02	0.02	0.05	0.03	0.02	0.02	0.00	0.00	0.03	0.03	0.02	0.02
<b>Al<sub>2</sub>O<sub>3</sub></b>	12.98	1.69	13.35	0.18	4.26	0.06	7.92	0.91	7.12	1.33	9.94	0.02
<b>FeO</b>	0.68	0.22	0.46	0.11	0.37	0.05	0.21	0.07	0.64	0.12	0.26	0.08
<b>MnO</b>	0.01	0.02	0.01	0.01	0.01	0.01	0.00	0.00	0.05	0.02	0.00	0.01
<b>MgO</b>	10.64	1.41	12.98	0.09	32.16	0.24	16.71	3.14	28.00	2.97	24.72	0.27
<b>CaO</b>	5.97	0.80	8.25	0.14	3.30	0.01	6.48	0.60	3.35	1.06	5.02	0.57
<b>Na<sub>2</sub>O</b>	0.58	0.11	0.01	0.02	0.00	0.00	0.06	0.00	0.05	0.07	0.03	0.01
<b>K<sub>2</sub>O</b>	0.10	0.04	0.00	0.01	0.00	0.00	0.00	0.00	0.03	0.03	0.02	0.01
<b>Ni<sub>2</sub>O<sub>3</sub></b>	0.01	0.01	0.02	0.03	0.01	0.01	0.01	0.01	0.04	0.03	0.02	0.01
<b>S</b>	0.26	0.03	0.88	0.08	5.17	0.08	4.25	0.69	5.61	0.62	5.56	0.23
<b>Total</b>	96.33		93.54		98.39		85.25		100.06		96.08	

Na = Number of analyses

n.a Not analysed

<sup>a</sup> Maximum content calculated by difference from the total<sup>O</sup> content in silicate and melt was estimated by stoichiometry

**Table 4:** Minor and traces LA-ICP-MS composition of silicate melts and sulphides in ppm from experiments with CaS powders and associated Nernst oldhamites/melt REE partition coefficients.

Run	1250 Silicate melt				D		1263 Silicate melt				D		1208 Silicate melt					
	Na 4	1 $\sigma$	CaS Na 3	1 $\sigma$	1 $\sigma$	1 $\sigma$	Na 5	1 $\sigma$	CaS Na 5	1 $\sigma$	1 $\sigma$	Na 6	1 $\sigma$	CaS Na 9	1 $\sigma$	D	1 $\sigma$	
<b>La</b>	282	11.2	75	2.8	0.27	0.05	986	61.5	45	2.6	0.05	0.00	270	12.6	54	2.4	0.20	0.01
<b>Ce</b>	225	8.8	113	4.2	0.50	0.00	836	42.3	71	3.3	0.08	0.01	204	11	67	3.4	0.33	0.02
<b>Pr</b>	188	6.6	138	4.7	0.73	0.04	706	26.1	84	3.0	0.12	0.01	162	7.6	76	3.4	0.47	0.03
<b>Nd</b>	169	6.8	159	6.1	0.94	0.09	641	33.1	100	4.9	0.16	0.01	144	11.5	85	6.2	0.59	0.06
<b>Sm</b>	147	5.8	187	7.1	1.27	0.00	591	19.3	119	4.0	0.20	0.01	122	7.4	96	5.5	0.79	0.07
<b>Eu</b>	67	2.3	293	9.8	4.37	0.09	304	22.9	186	12.7	0.61	0.06	65.7	5.7	127	9.8	1.93	0.22
<b>Gd</b>	157	5.3	186	6.3	1.18	0.09	585	33.8	116	6.2	0.20	0.02	124	8.8	95	6.2	0.76	0.07
<b>Tb</b>	155	5.9	181	6.4	1.17	0.07	582	35.4	114	6.4	0.20	0.02	128	11.5	95	7.7	0.74	0.09
<b>Dy</b>	170	6.7	187	7.0	1.10	0.06	642	40.7	120	7.0	0.19	0.02	137	17.8	93	10.8	0.68	0.12
<b>Ho</b>	178	6.1	182	6.1	1.02	0.04	680	46.1	116	7.1	0.17	0.02	145	16.0	93	9.4	0.64	0.10
<b>Er</b>	188	6.4	166	5.6	0.88	0.03	703	46.5	106	6.4	0.15	0.01	153	10.8	88	5.7	0.57	0.06
<b>Tm</b>	202	6.6	150	4.8	0.74	0.01	774	38.8	989	4.6	0.13	0.01	163	15.8	81	7.1	0.50	0.07
<b>Yb</b>	145	5.1	217	7.4	1.50	0.08	620	19.3	129	4.1	0.21	0.01	110	10.5	111	9.6	1.01	0.13
<b>Lu</b>	238	7.9	124	4.0	0.52	0.02	885	29.2	81	2.7	0.09	0.00	192	20.5	73	7.1	0.38	0.05

Run	1240 Silicate melt				D		1246 Silicate melt				D		1305 Silicate melt					
	Na 5	1 $\sigma$	CaS Na 6	1 $\sigma$	1 $\sigma$	1 $\sigma$	Na 6	1 $\sigma$	CaS Na 6	1 $\sigma$	1 $\sigma$	Na 6	1 $\sigma$	CaS Na 6	1 $\sigma$	D	1 $\sigma$	
<b>La</b>	531	21.0	37	1.4	0.07	0.00	413	36.5	101	6.2	0.24	0.03	526	23.5	112	4.7	0.21	0.01
<b>Ce</b>	379	12.7	44	1.5	0.12	0.01	317	27.6	126	8.1	0.40	0.05	441	18.6	165	6.5	0.37	0.02
<b>Pr</b>	299	9.9	50	1.7	0.17	0.01	275	28.7	145	11.5	0.53	0.07	379	19.7	200	9.4	0.53	0.04
<b>Nd</b>	265	10.4	58	2.3	0.22	0.01	254	27.1	166	13.5	0.65	0.09	340	17.4	230	10.6	0.68	0.05
<b>Sm</b>	233	10.7	65	2.8	0.28	0.02	225	24.2	190	16.1	0.84	0.12	330	15.9	300	13.2	0.91	0.06
<b>Eu</b>	134	5.5	83	3.2	0.62	0.03	126	14.6	257	24.7	2.04	0.44	169	9.3	347	17.0	2.05	0.15
<b>Gd</b>	219	8.7	62	2.4	0.28	0.02	232	25.9	196	17.0	0.84	0.13	294	15.6	269	12.9	0.91	0.07
<b>Tb</b>	224	7.7	62	2.1	0.28	0.01	231	28.1	190	18.1	0.82	0.14	294	15.8	263	12.7	0.89	0.06
<b>Dy</b>	244	8.9	66	2.4	0.27	0.01	248	30.3	195	18.8	0.79	0.12	317	19.4	269	14.6	0.85	0.07
<b>Ho</b>	260	9.6	64	2.3	0.24	0.01	257	31.2	188	17.9	0.73	0.12	330	19.2	264	13.6	0.80	0.06
<b>Er</b>	269	8.4	59	1.9	0.22	0.01	268	33	178	16.9	0.66	0.11	345	18.5	243	11.7	0.70	0.05
<b>Tm</b>	297	9.1	55	1.7	0.19	0.01	280	38	162	16.8	0.58	0.11	360	20.1	219	10.9	0.61	0.05
<b>Yb</b>	226	7.7	68	2.3	0.30	0.01	221	30.2	222	24.1	1.00	0.22	289	18.7	270	15.3	0.93	0.08
<b>Lu</b>	333	10.7	47	1.5	0.14	0.01	323	47.2	145	15.8	0.45	0.08	400	24.2	186	9.9	0.47	0.04

Run	1244 Silicate melt			D		1304 Silicate melt			D			
	Na 6	1 $\sigma$	CaS Na 5	1 $\sigma$	1 $\sigma$	Na 4	1 $\sigma$	CaS Na 4	1 $\sigma$	1 $\sigma$		
<b>La</b>	722	37.3	44	2.1	0.06	0.00	328	19.5	96	5.2	0.29	0.02
<b>Ce</b>	619	26.8	62	2.5	0.10	0.01	278	16.4	146	7.9	0.53	0.04
<b>Pr</b>	514	17.6	71	2.4	0.14	0.01	237	16.4	176	11.1	0.74	0.06
<b>Nd</b>	474	21.1	85	3.6	0.18	0.01	212	14.9	205	13.0	0.97	0.09
<b>Sm</b>	428	13.5	96	3.1	0.22	0.01	214	15.2	281	18.1	1.31	0.13
<b>Eu</b>	201	12.2	134	7.3	0.67	0.05	116	9.2	293	20.8	2.53	0.27
<b>Gd</b>	374	18.6	86	3.9	0.23	0.01	180	13.3	246	16.4	1.37	0.14
<b>Tb</b>	397	20	86	4.0	0.22	0.01	175	14.0	239	17.3	1.37	0.15
<b>Dy</b>	431	23.1	90	4.4	0.21	0.01	187	15.0	246	17.8	1.32	0.14
<b>Ho</b>	437	24.4	84	4.3	0.19	0.01	195	15.5	241	17.4	1.24	0.13
<b>Er</b>	471	25.7	80	4.0	0.17	0.01	202	16.3	225	16.4	1.11	0.12
<b>Tm</b>	506	22.0	74	3.0	0.15	0.01	212	18.6	206	16.3	0.97	0.12
<b>Yb</b>	407	12.8	98	3.1	0.24	0.01	176	15.7	245	19.7	1.39	0.17
<b>Lu</b>	538	17.6	57	1.8	0.11	0.00	241	22.8	178	15.1	0.74	0.09

Na = Number of analyses

**Table 5:** Minor and traces LA-ICP-MS composition of silicate melts and sulphide melts in ppm from experiments with FeS powders and associated Nernst molten FeS/silicate melt REE partition coefficients.

Run	1266				1282				1207									
	Silicate melt		Molten FeS		D		Silicate melt		Molten FeS		D		Silicate melt		Molten FeS		D	
	Na.2	1 $\sigma$	Na.3	1 $\sigma$	Na.3	1 $\sigma$	Na.3	1 $\sigma$	Na.4	1 $\sigma$	Na.4	1 $\sigma$	Na.3	1 $\sigma$	Na.2	1 $\sigma$	Na.3	1 $\sigma$
La	693	29.0	12	0.5	0.017	0.00	1848	80	63	2.0	0.034	0.00	1093	0.0	422	14.1	0.386	0.00
Ce	685	29.0	17	0.7	0.024	0.00	1778	105	56	1.8	0.032	0.00	1036	0.0	499	16.8	0.481	0.00
Pr	627	27.7	19	0.7	0.030	0.00	1679	119	73	2.3	0.043	0.00	1029	0.0	438	13.6	0.425	0.00
Nd	653	29.4	19	0.8	0.028	0.00	1798	145	56	2.0	0.031	0.00	1026	0.0	410	12.6	0.399	0.00
Sm	729	31.4	33	1.5	0.045	0.00	1924	144	78	2.6	0.041	0.00	1128	0.0	368	11.4	0.327	0.00
Eu	583	24.9	52	2.1	0.090	0.01	1122	104	137	4.3	0.122	0.01	905	0.0	596	18.6	0.658	0.00
Gd	927	44.4	23	1.0	0.024	0.00	2545	104	52	1.8	0.020	0.00	1319	0.0	200	6.2	0.152	0.00
Tb	947	45.2	27	1.1	0.029	0.00	2582	224	50	1.6	0.019	0.00	1475	0.0	142	4.4	0.097	0.00
Dy	1084	50.2	31	1.3	0.028	0.00	2813	238	52	1.7	0.018	0.00	1566	0.0	108	3.4	0.069	0.00
Ho	1117	53.8	27	1.0	0.024	0.00	2950	249	47	1.5	0.016	0.00	1718	0.0	68	2.1	0.039	0.00
Er	1116	50.9	23	1.0	0.021	0.00	3088	135	39	1.3	0.013	0.00	1717	0.0	43	1.4	0.025	0.00
Tm	1141	55.6	20	0.9	0.017	0.00	2936	176	30	1.0	0.010	0.00	1755	0.0	30	0.9	0.017	0.00
Yb	1096	51.5	39	1.6	0.036	0.00	2645	111	49	1.7	0.018	0.00	1678	0.0	83	2.6	0.050	0.00
Lu	1132	56.9	10	0.4	0.009	0.00	2859	113	18	0.6	0.006	0.00	1881	0.0	15	0.5	0.008	0.00

Run	1239				1284				1252									
	Silicate melt		Molten FeS		D		Silicate melt		Molten FeS		D		Silicate melt		Molten FeS		D	
	Na.3	1 $\sigma$	Na.3	1 $\sigma$	Na.3	1 $\sigma$	Na.5	1 $\sigma$	Na.6	1 $\sigma$	Na.6	1 $\sigma$	Na.5	1 $\sigma$	Na.4	1 $\sigma$	Na.4	1 $\sigma$
La	2527	92.2	139	91.4	0.055	0.04	599	21.3	14	0.5	0.024	0.00	768	30.9	209	110.0	0.272	0.14
Ce	2382	81.8	137	98.7	0.057	0.04	558	21.0	16	0.6	0.028	0.00	763	28.0	281	140.0	0.368	0.18
Pr	2300	75.7	111	95.2	0.048	0.04	499	20.5	13	0.6	0.026	0.00	729	25.0	296	150.0	0.406	0.21
Nd	2386	84.5	127	104.3	0.053	0.04	553	22.4	13	0.6	0.024	0.00	752	29.1	251	134.0	0.334	0.18
Sm	2636	88.0	133	111.5	0.051	0.04	598	24.5	12	0.5	0.019	0.00	825	29.0	244	129.0	0.296	0.16
Eu	1974	65.4	145	146.9	0.074	0.07	543	22.9	15	0.6	0.027	0.00	480	16.7	287	158.0	0.598	0.33
Gd	3211	108.7	97	76.0	0.030	0.02	786	32.3	7	0.3	0.009	0.00	1054	37.8	148	75.2	0.140	0.07
Tb	3383	116.6	89	63.2	0.026	0.02	826	33.0	5	0.2	0.006	0.00	1093	40.6	113	57.5	0.103	0.05
Dy	3687	124.5	92	60.8	0.025	0.02	923	34.7	4	0.2	0.004	0.00	1190	42.6	79	41.9	0.067	0.04
Ho	4057	137.2	86	47.6	0.021	0.01	1005	37.7	3	0.1	0.003	0.00	1282	46.1	48	24.7	0.037	0.02
Er	4023	137.0	68	34.5	0.017	0.01	1005	39.4	2	0.1	0.002	0.00	1283	46.5	26	13.2	0.020	0.01
Tm	4226	145.4	48	26.9	0.011	0.01	1050	38.8	1	0.1	0.001	0.00	1335	49.4	15	7.5	0.011	0.01
Yb	3947	141.1	136	59.3	0.035	0.02	996	37.4	3	0.1	0.003	0.00	1222	48.0	51	25.9	0.042	0.02
Lu	4381	155.1	18	13.7	0.004	0.00	1186	43.3	1	0.0	0.000	0.00	1417	54.7	5	2.5	0.003	0.00

Na = Number of analyses

**Table 6:** D/D\* ratios calculated for oldhamite/melt partitioning experiments.

Run	1244	1263	1250	1240	1305	1304	1246	1208
<b>La</b>	0.87	0.82	0.80	0.86	0.85	0.84	0.88	0.85
<b>Ce</b>	0.90	0.91	0.90	0.87	0.90	0.90	0.93	0.89
<b>Pr</b>	0.90	0.90	0.92	0.9	0.90	0.88	0.91	0.91
<b>Nd</b>	1.06	1.06	1.06	1.06	1.04	1.03	1.03	1.05
<b>Sm</b>	1.08	1.07	1.12	1.06	1.09	1.07	1.08	1.11
<b>Eu</b>	2.98	3.09	3.67	2.20	2.31	1.90	2.48	2.60
<b>Gd</b>	1.00	0.98	0.98	1.00	1.00	1.00	1.01	1.01
<b>Tb</b>	0.99	1.00	0.99	0.98	1.00	1.00	1.00	1.00
<b>Dy</b>	1.00	1.01	1.00	1.01	0.99	1.00	1.00	0.97
<b>Ho</b>	1.02	1.02	1.03	1.01	1.02	1.01	1.01	1.01
<b>Er</b>	1.03	1.03	1.03	1.03	1.03	1.01	1.02	1.02
<b>Tm</b>	1.04	1.02	1.03	1.01	1.01	1.01	1.01	1.02
<b>Yb</b>	2.14	2.11	2.65	2.03	1.92	1.77	2.13	2.57
<b>Lu</b>	1.09	1.09	1.09	1.11	1.11	1.08	1.09	1.12

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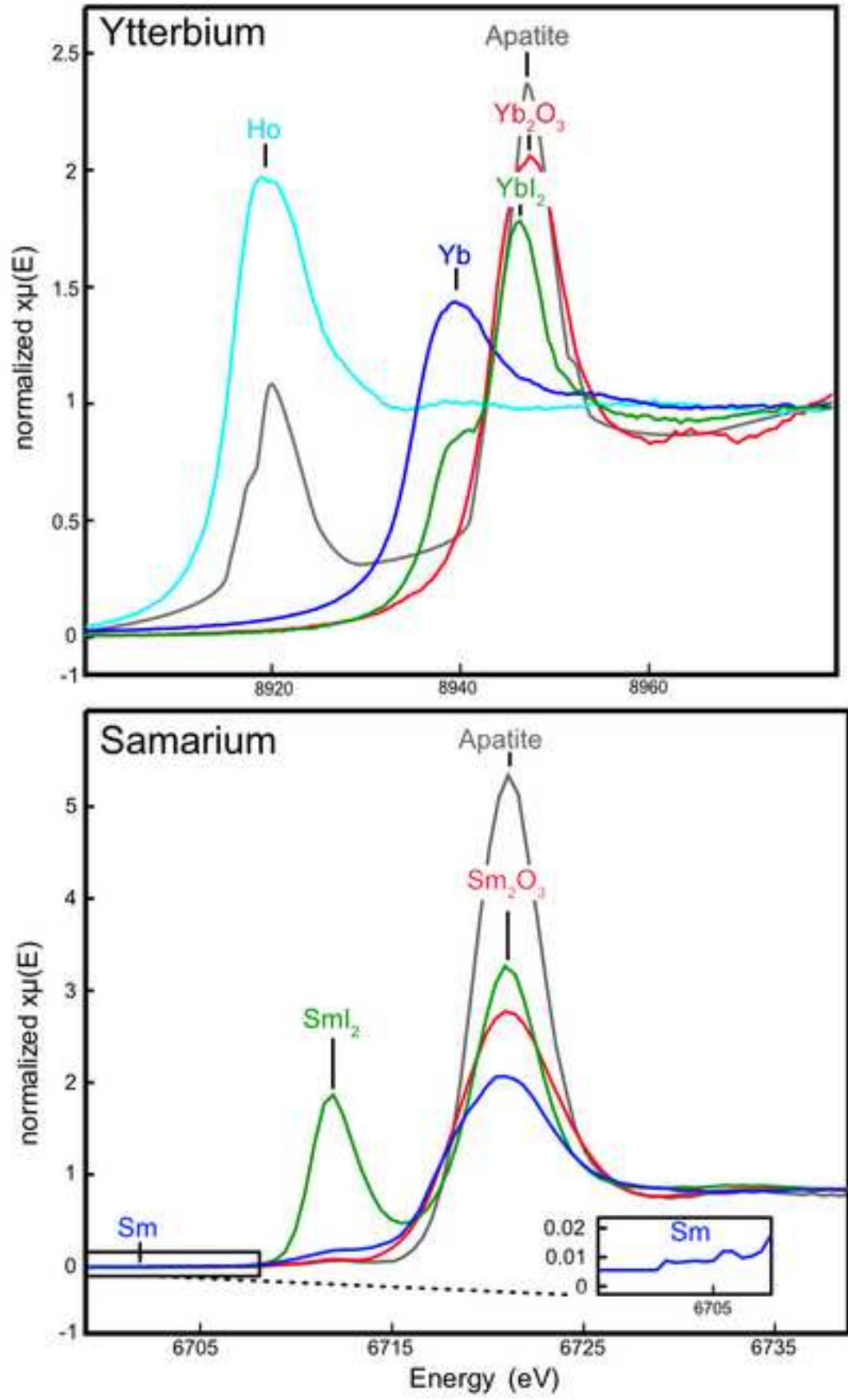
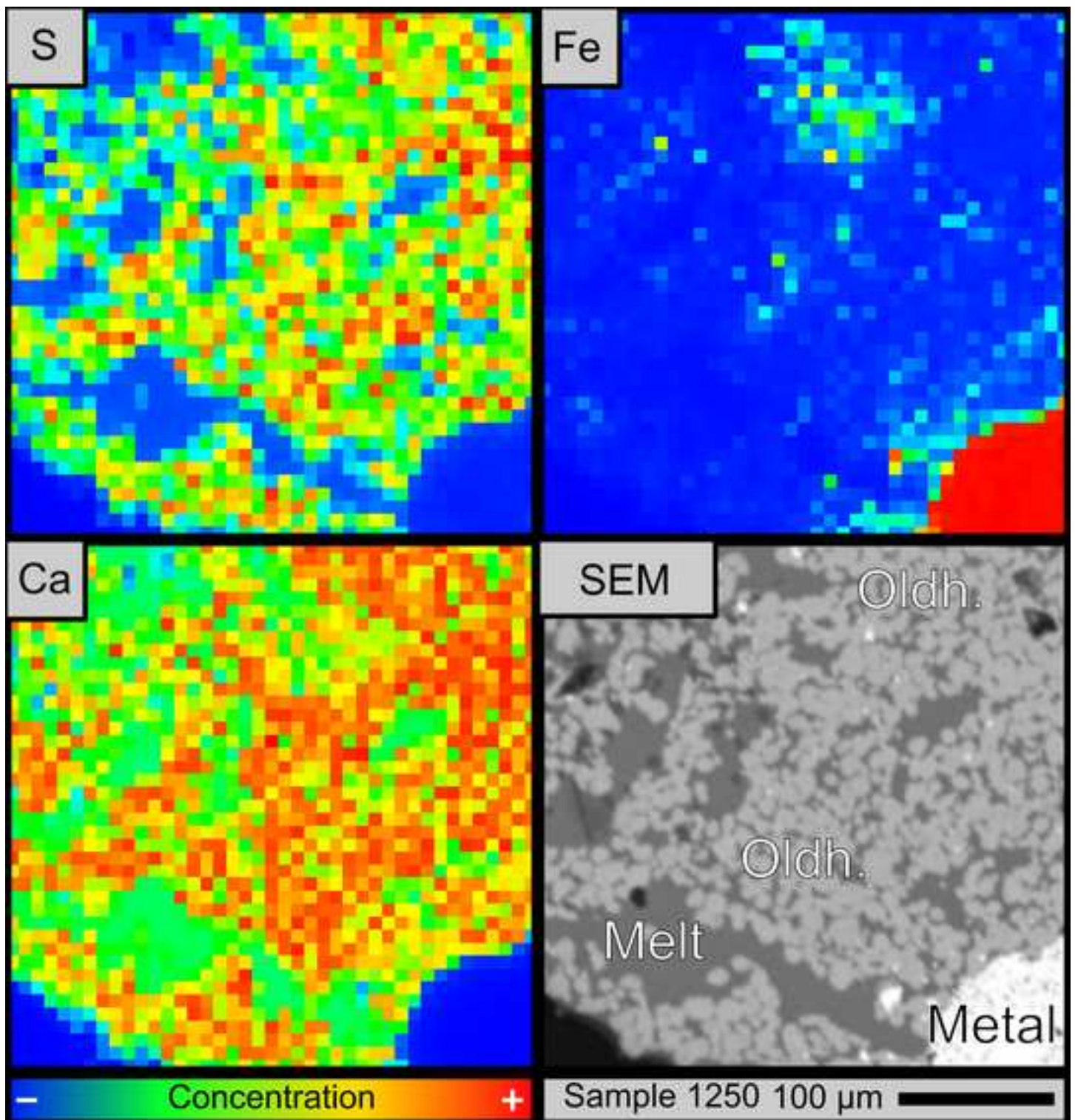


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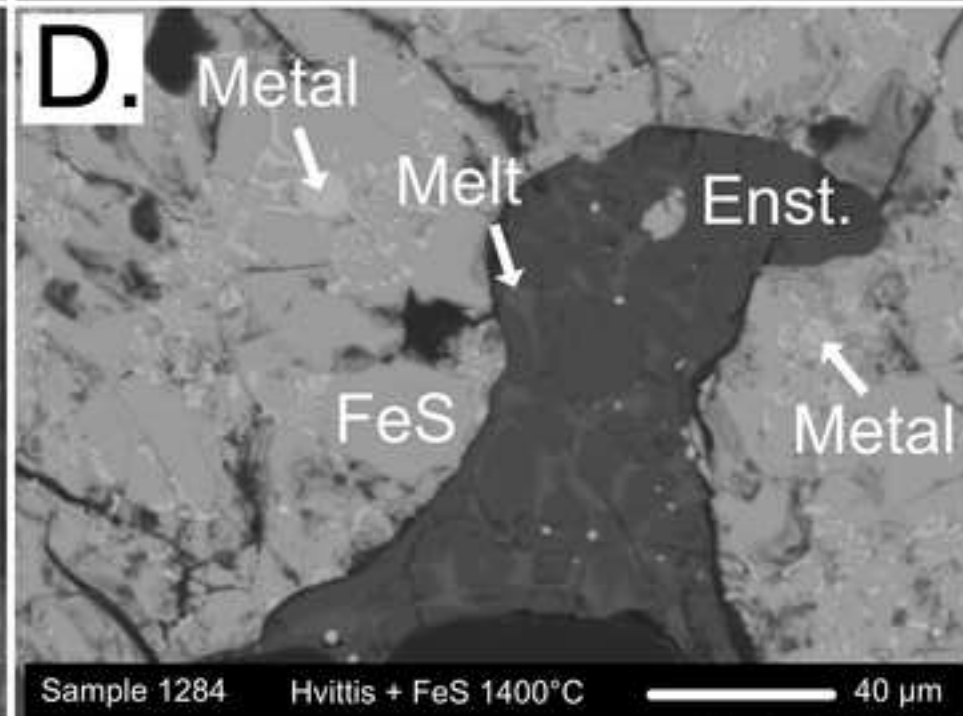
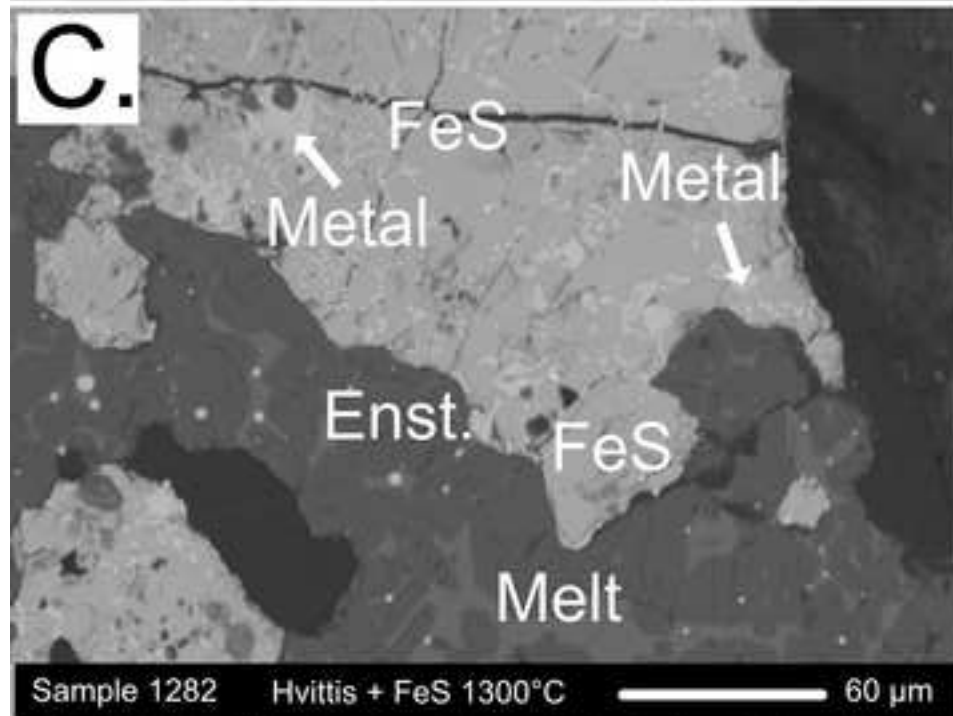
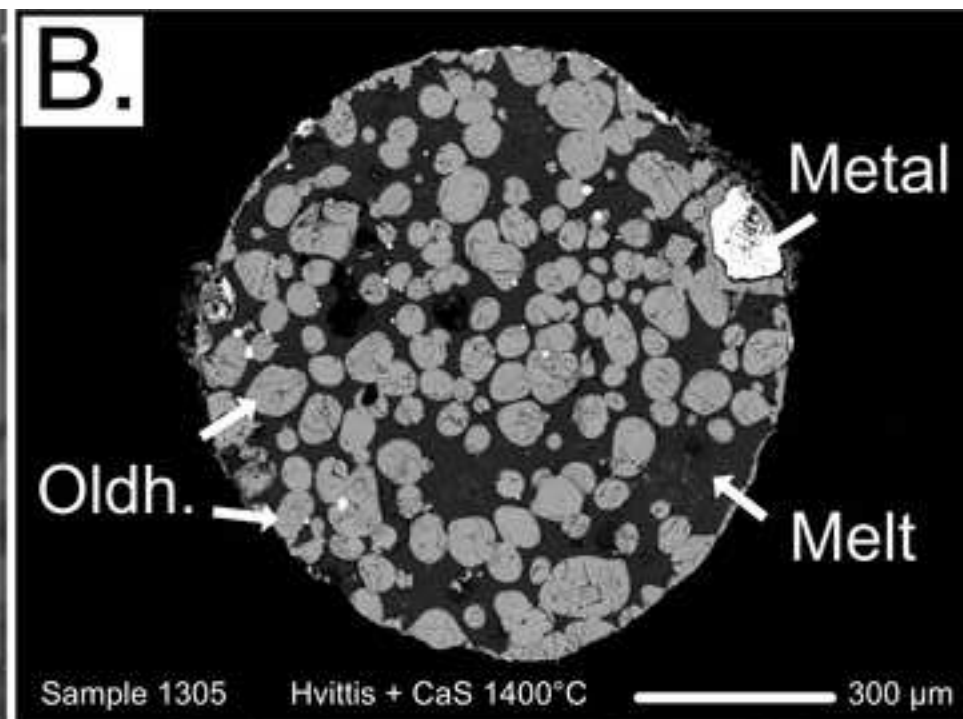
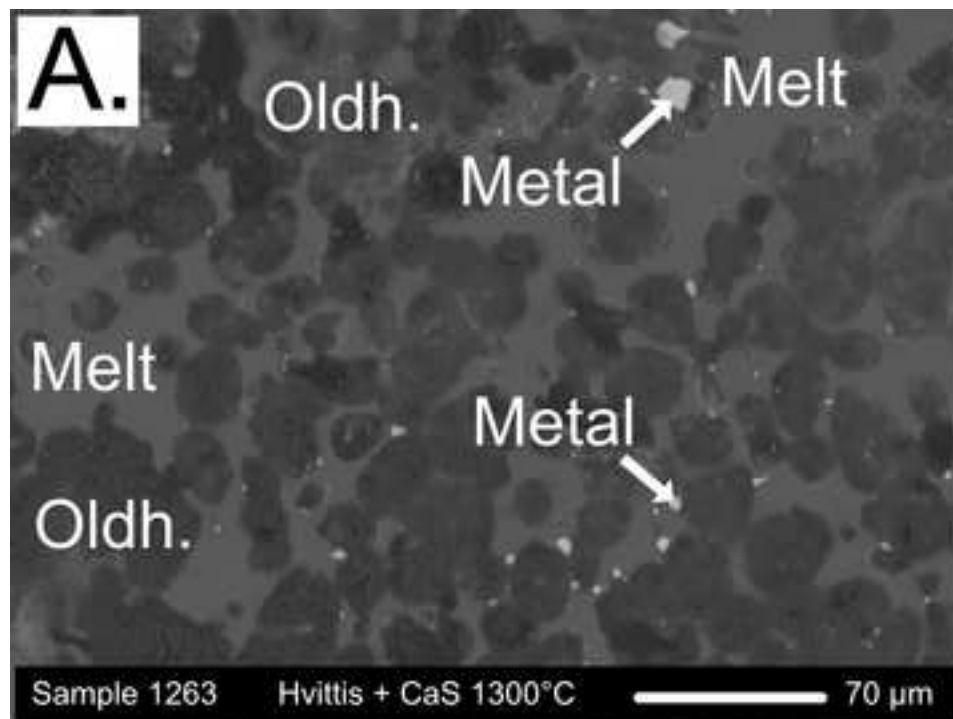


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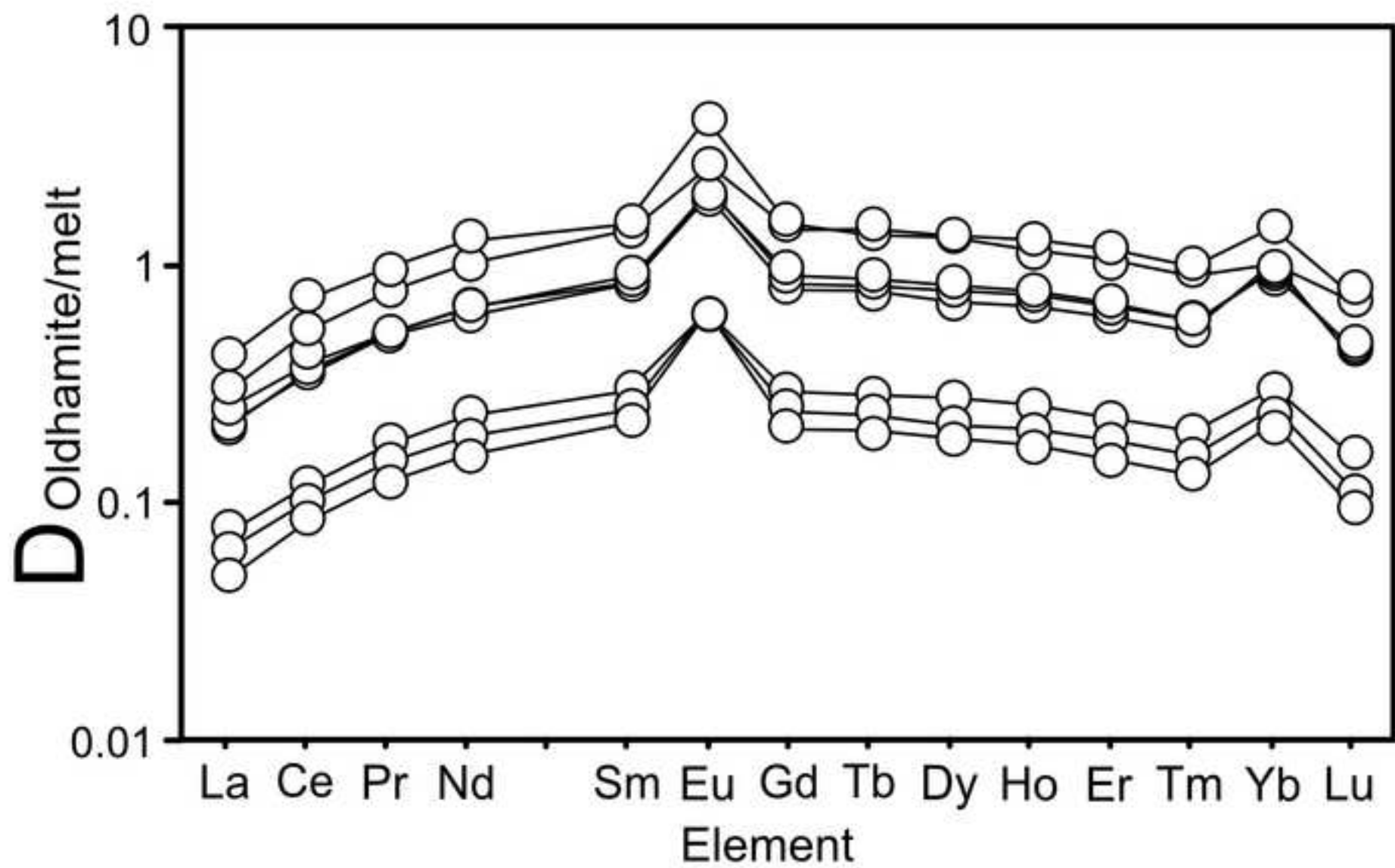
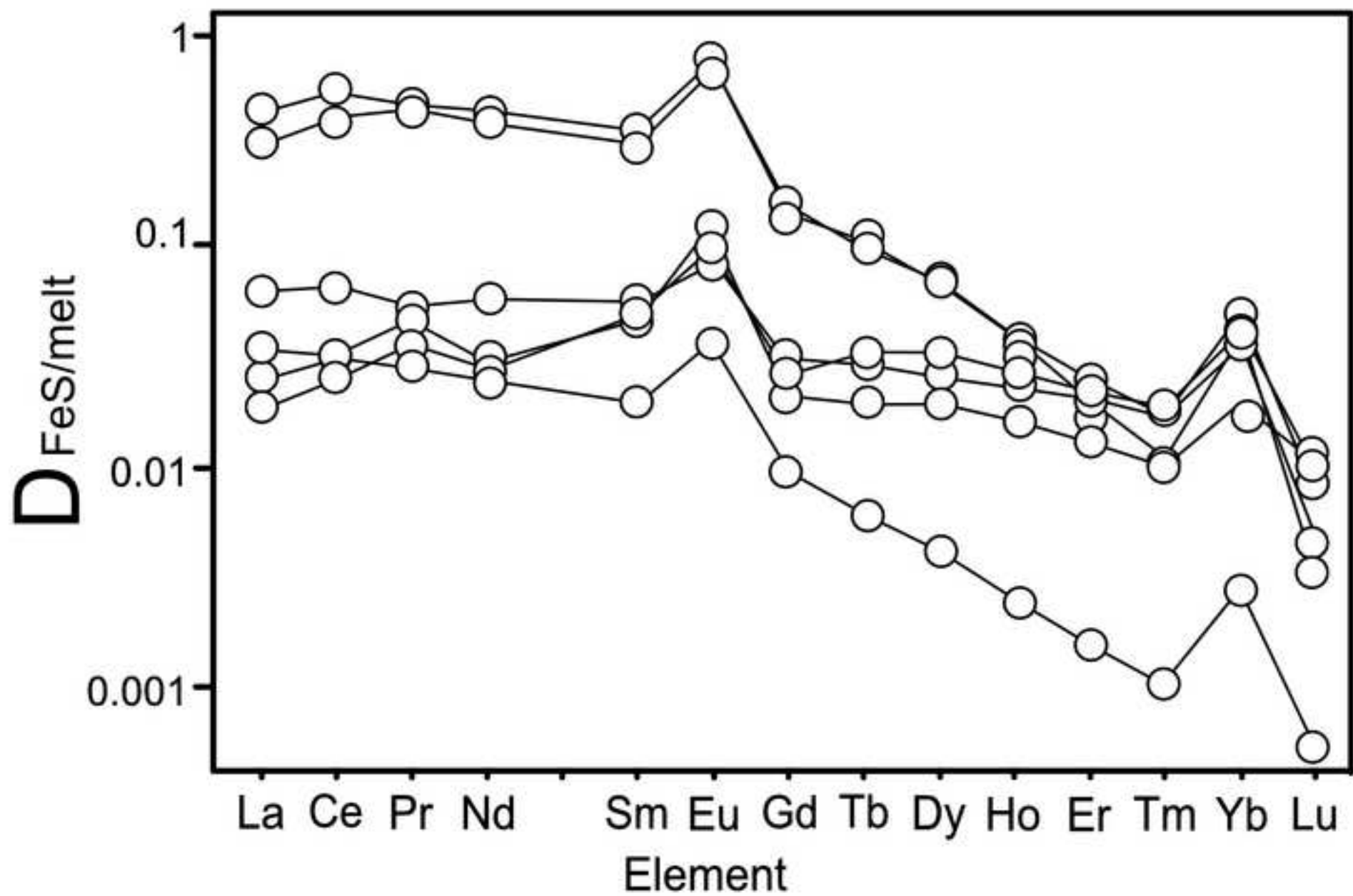
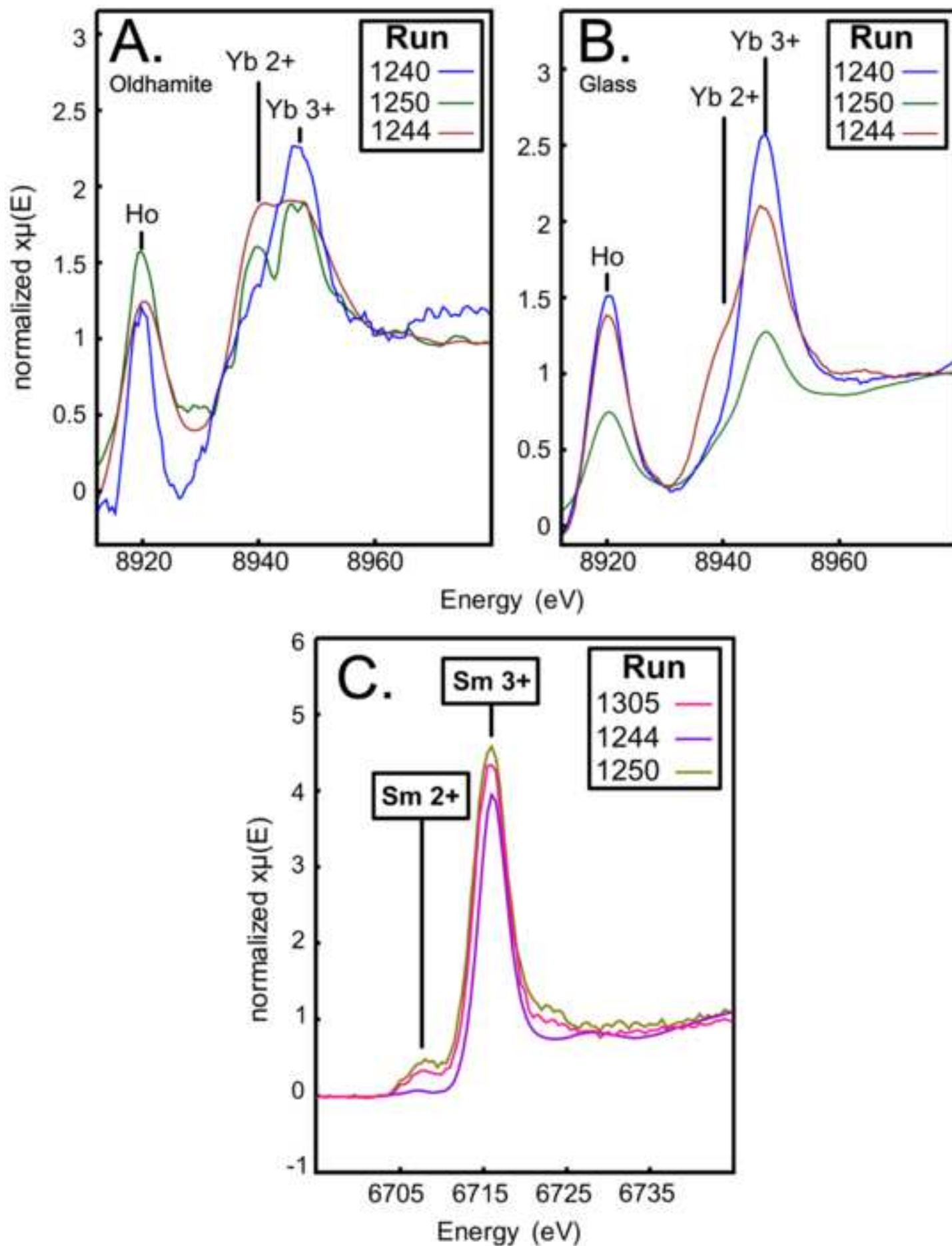


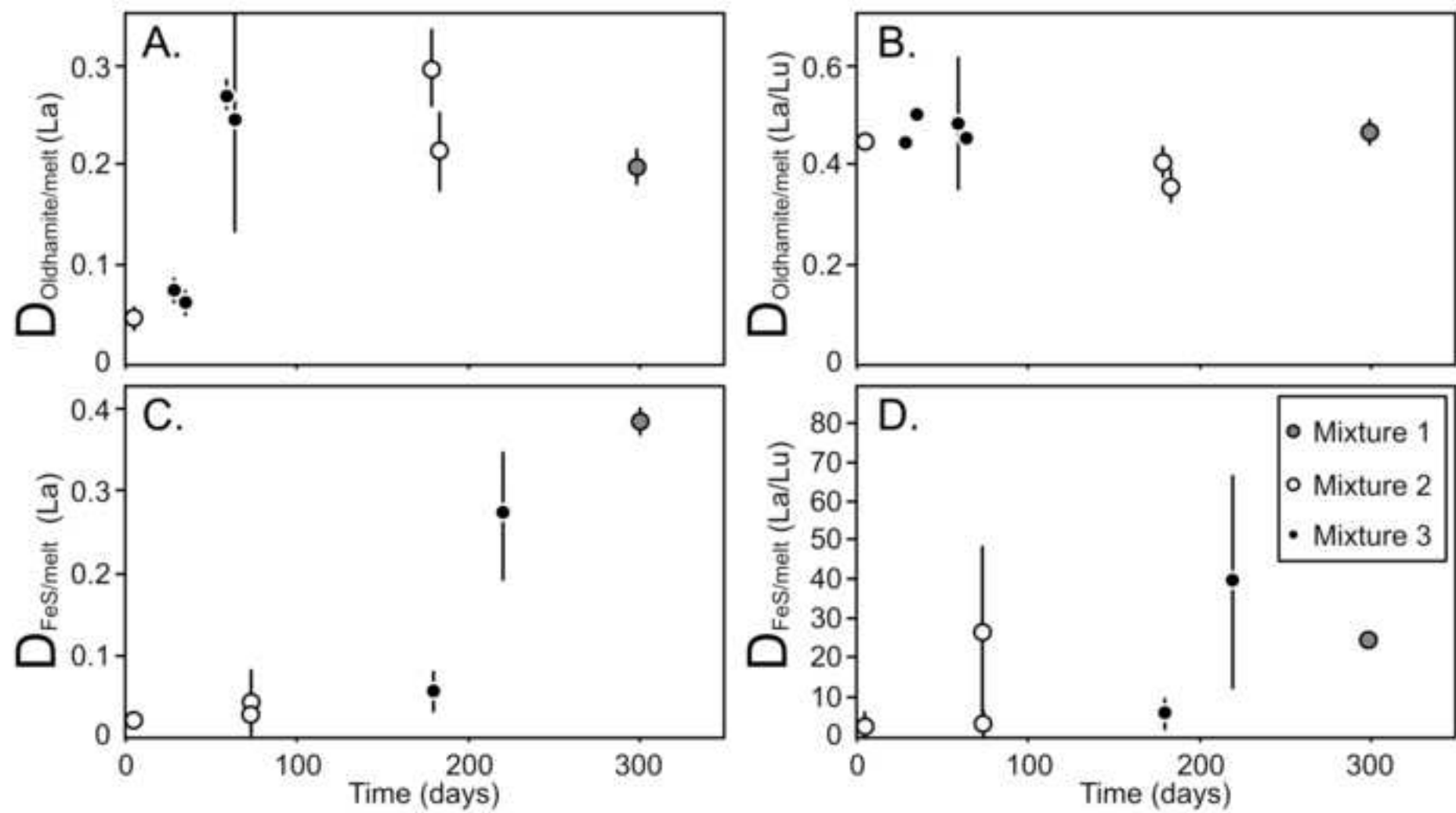
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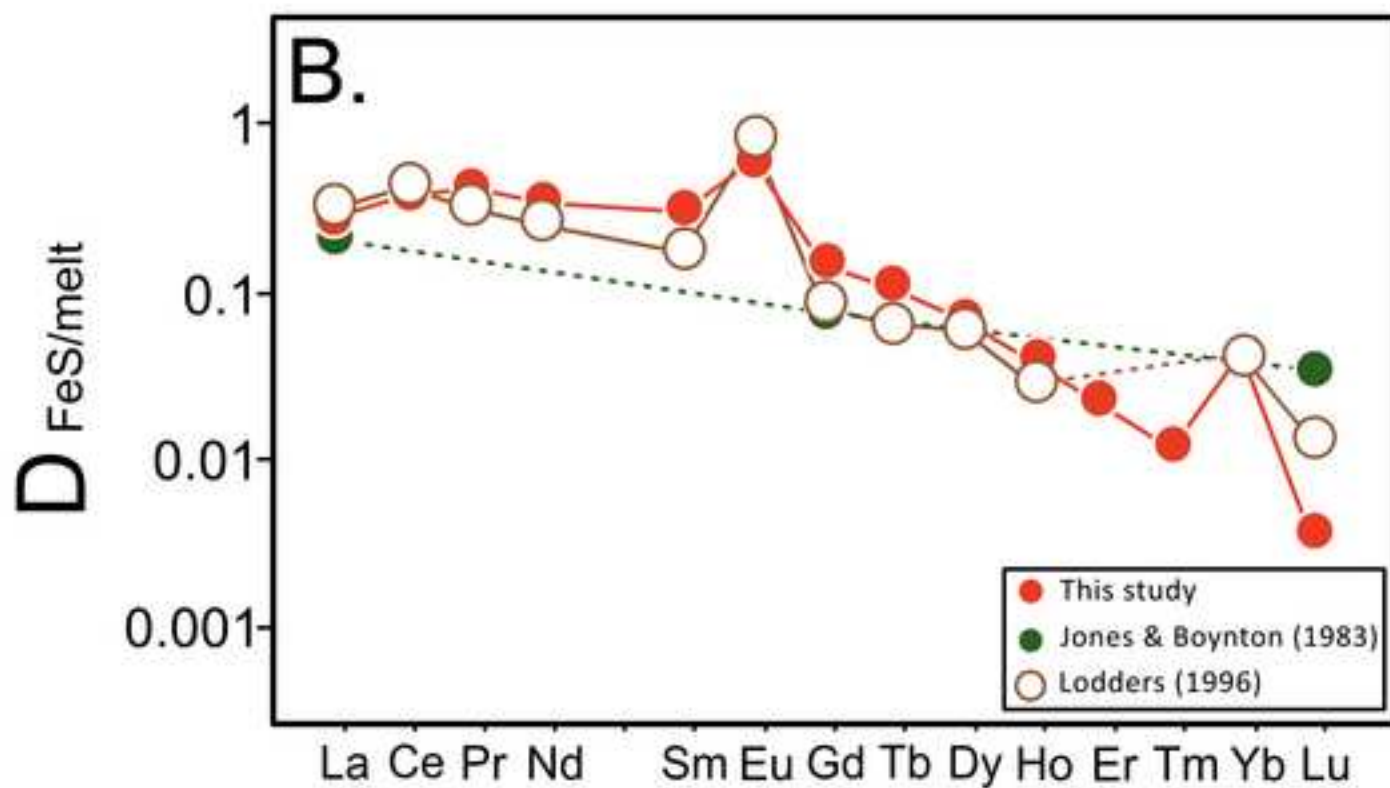
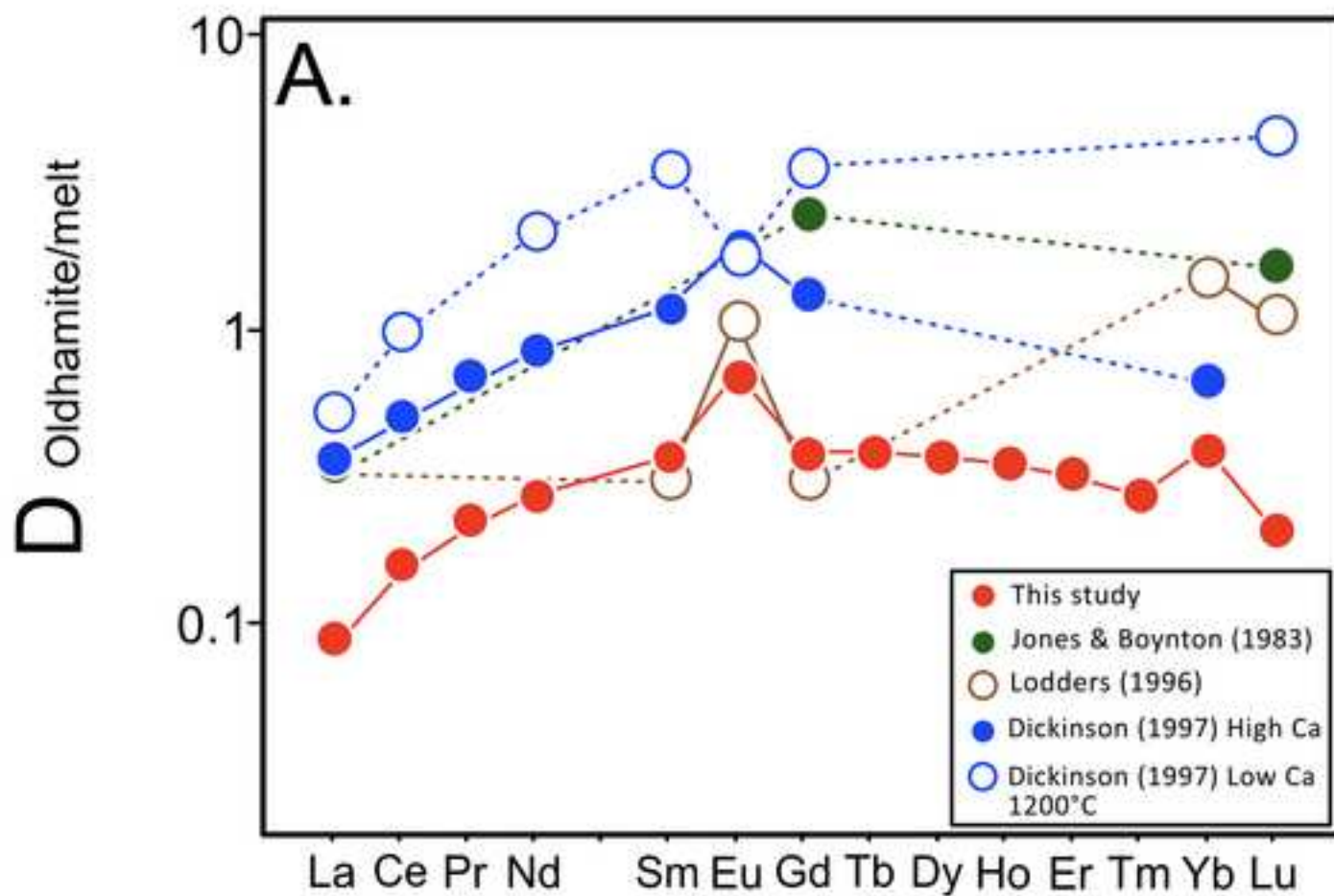


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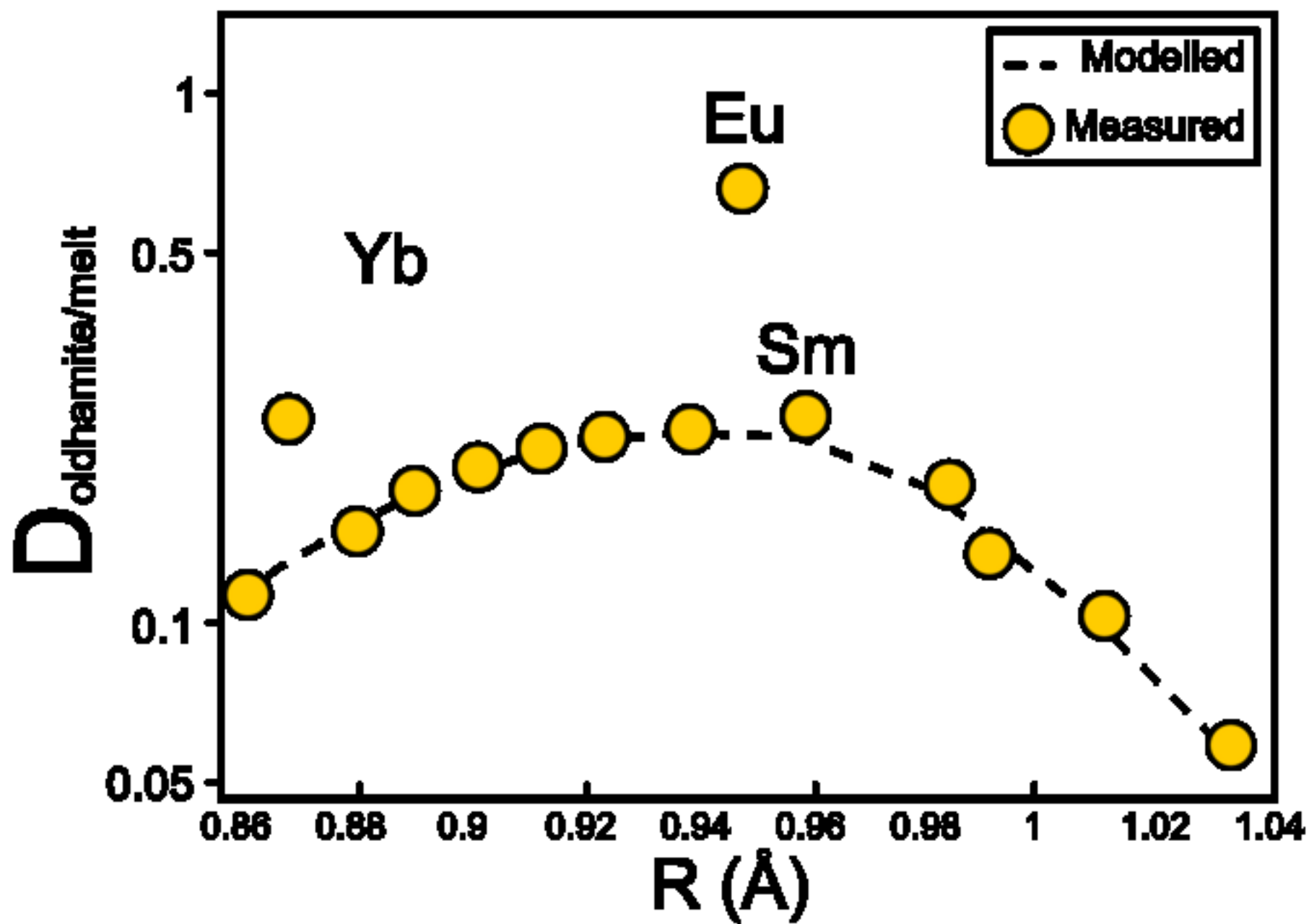


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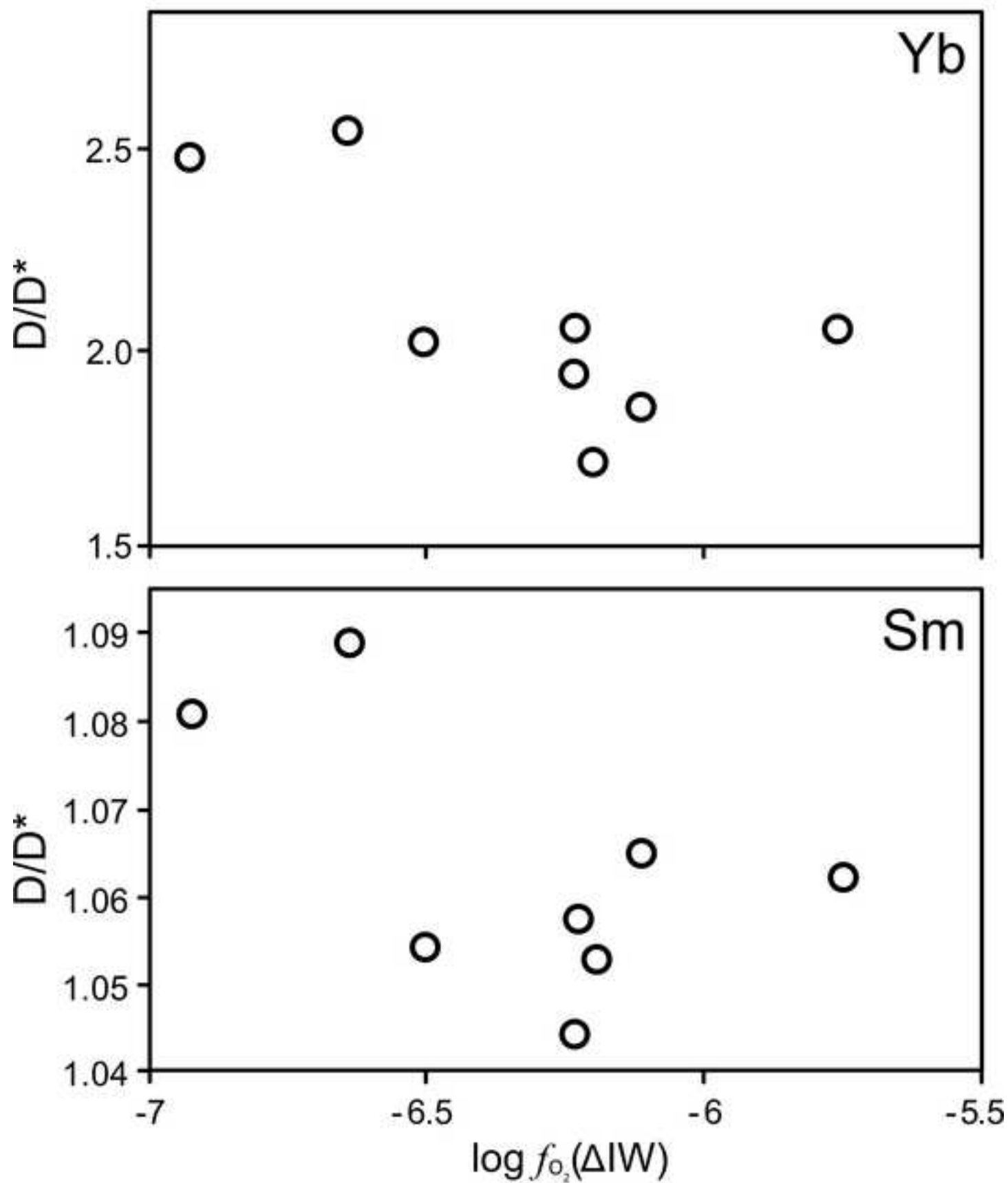
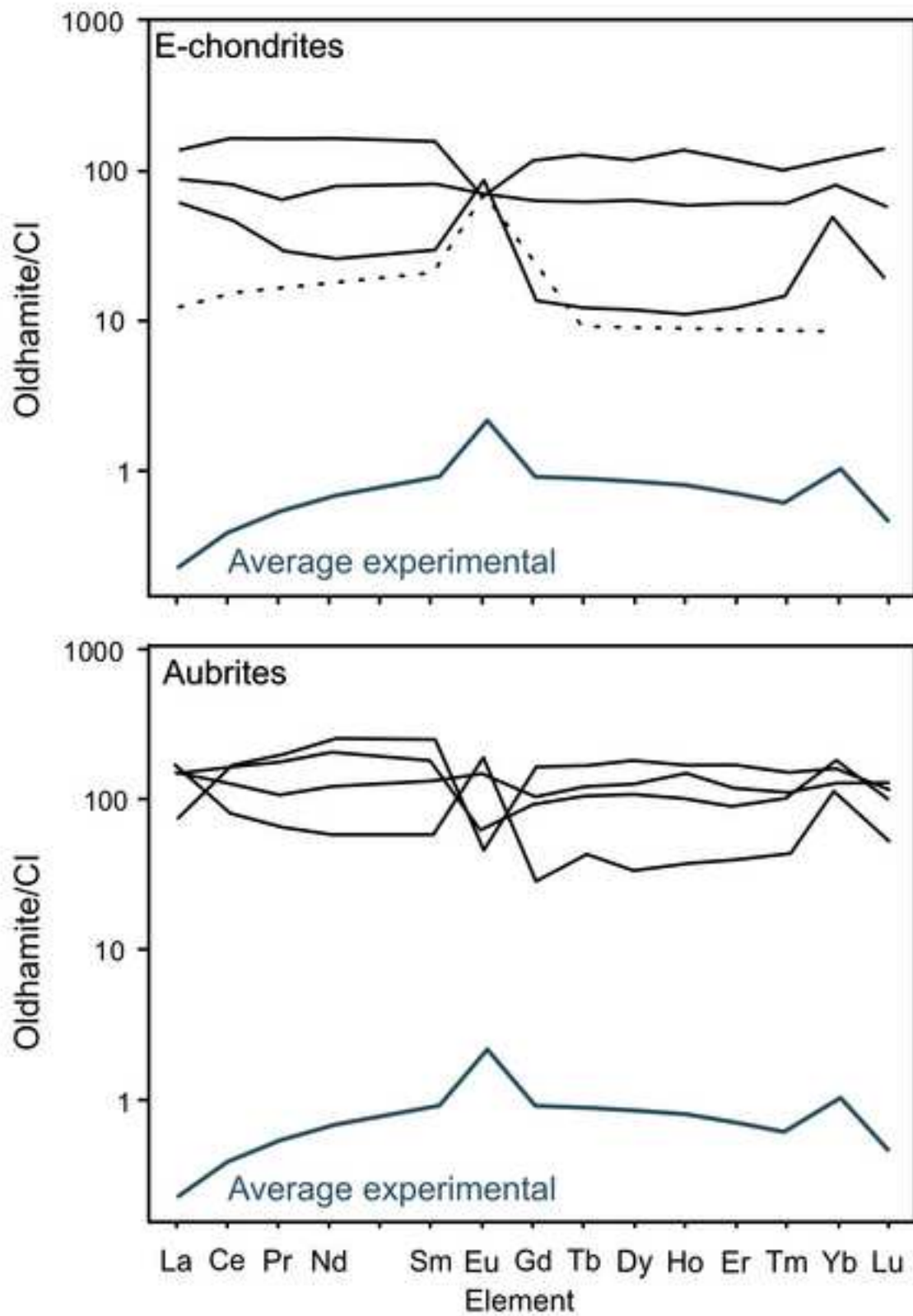




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