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1 **Mapping the redox state of the young Solar System using ytterbium valence state**

2

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20 **Abstract**

21 We have determined the valence state of Ytterbium (Yb) in a collection of meteorites covering
22 4 to 5 orders of magnitude in oxygen fugacity (f_{O_2}) by X-ray absorption near-edge structure
23 (XANES) spectroscopy at the Yb L2 edge. In the studied meteorite minerals, Yb abundance
24 was between 1 and 30 ppm. The data were obtained from merrillite grains (theoretical formula
25 $Ca_{18}Na_2Mg_2(PO_4)_{14}$) from two equilibrated ordinary chondrites (one H6 and one LL6), on
26 oldhamite grains (theoretical formula CaS) from three EH enstatite chondrites (from EH3 to
27 EH5) and four EL enstatite chondrites (from EL3 to EL6), on one merrillite grain and one
28 stanfieldite grain (theoretical formula $Ca_4(Mg,Fe,Mn)_5(PO_4)_6$) from a pallasite, on merrillite
29 grains from a eucrite, and in a phosphorous-bearing phase from an ungrouped primitive
30 achondrite (NWA 11119). The obtained Yb XANES spectra were compared to those measured
31 in terrestrial apatites (containing 17 to 79 ppm Yb) and in synthetic materials (metallic Yb, YbS,
32 Yb_2S_3 , Yb_2O_3). In terrestrial apatites, as well as in ordinary chondrites, in the eucrite, in the
33 pallasite, and in the ungrouped achondrite NWA 11119, Yb is present as Yb^{3+} only. In enstatite
34 chondrites, about half of the Yb in CaS is in the Yb^{2+} form and the fraction of Yb^{2+} may be
35 slightly higher in EH compared to EL. It appears that Yb redox state can be used to build a
36 redox scale for the most reduced objects of the Solar System as shown by this slight difference
37 between EH and EL. However, the absence of a strong difference in Yb redox state between
38 EH and EL chondrites suggests that the observed difference in Yb abundance anomalies in
39 oldhamites found between EH and EL is not due to oxygen fugacity prevailing during parent-
40 body equilibration but rather to fractionation related to volatility.

41

42 **Keywords:** redox state, rare-earth elements, ytterbium, enstatite chondrites, Solar System,
43 synchrotron radiation.

44 **1. Introduction**

45 Rare-earth elements (REE, restricted here to the lanthanides) are commonly used for
46 geochemical modeling purposes because, as trace elements, their equilibrium partitioning
47 between phases does not depend on their concentrations (Henry's law).

48 At ground state, lanthanides occur as $[\text{Xe}] 4f^n 6s^2$ (or $[\text{Xe}] 4f^{n-1} 5d^1 6s^2$ in the case of La,
49 Ce, and Gd), and all elements of the group have the same outer electron shell configuration.
50 They only differ by their 4f (or 5d) filling. Therefore, chemical bonding of the REE with ligands
51 is similar along the series from La to Lu. In Earth's processes, REE usually occurs as 3+
52 cations, whose radii decrease smoothly from La to Lu (the lanthanide contraction). As a
53 consequence, REE abundance patterns in minerals vary smoothly because REE incorporation
54 is controlled only by size mismatch between cation radii and crystallographic sites, as modelled
55 by Wood and Blundy (1997) for the pyroxene-basalt case. Sometimes, however, Eu is
56 observed to stick out from the rest of the REE. This is commonly interpreted as attesting for
57 the reduction to Eu^{2+} , which has a larger radius and better fits in plagioclase Na-Ca site.
58 Therefore, for terrestrial rocks, the so-called Eu anomaly is explained by valence change and
59 reduction to Eu^{2+} . This conclusion may be extended to extraterrestrial material, such as lunar
60 rocks (Papike et al., 1996), eucrites (Pun and Papike, 1996), and other achondrites (Frossard
61 et al., 2019). In terrestrial materials, anomalies in Ce can also be found, which are explained
62 by Ce oxidation to Ce^{4+} (Elderfield, 1988). A recent discussion about the significance of REE
63 abundance anomalies can be found in Barrat et al. (2023). The potential of Eu and Ce to be
64 used as redox sensors in silicate melts has been the subject of several experimental
65 calibrations (e.g., Burnham et al., 2015; Smythe and Brenan, 2015).

66 In the case of Yb, no concentration anomalies have been reported so far in terrestrial
67 rocks, although the presence of Yb^{2+} has been suggested in some mantle rocks (Albalat et al.,
68 2012). In enstatite chondrite, however, positive Yb anomalies have been reported in calcium
69 sulfide (oldhamite, CaS) of the unequilibrated EH group (Crozas and Lundberg, 1995;
70 Gannoun et al., 2011; Hammouda et al., 2022). These anomalies occur together with Eu
71 anomalies and, in some cases with Sm anomalies (to a lesser extent, as observed in
72 oldhamites of unequilibrated EH chondrites (Gannoun et al., 2011; Hammouda et al., 2022).
73 By comparison with experimental data Ingrao et al. (2019) interpreted the Yb anomalies as
74 being caused by the presence of reduced Yb^{2+} . However, because Eu and Yb are the two most
75 volatile REE in nebular processes (Lodders and Fegley, 1993), Hammouda et al. (2022)
76 proposed that the observed positive anomalies in unequilibrated EH chondrites are due to a
77 complex interplay between volatility and valence state, in which the oldhamite grains record
78 the condensation of a residual gas after earlier condensation of material having negative Eu
79 and Yb anomalies.

80 The purpose of the present work is to provide the first documentation of the valence state
81 of Yb in natural objects and, in particular, to sample the Yb redox state in rocks coming from
82 different regions of the Solar System. The most reduced objects studied are enstatite
83 chondrites (EC). Their equilibrium redox conditions have been estimated by Brett and Sato
84 (1984) using electrochemical methods and by Larimer and Buseck (1974), using the Si content
85 of the metallic phase. The former found values of the order of IW-3 (that is, 3 log units below
86 IW, where IW represents the Iron-Wustite equilibrium), whereas the latter calculated values
87 below IW-10. When discussing their results, Brett and Sato recognized that their
88 measurements on EC may have been contaminated by ambient atmosphere during sample
89 preparation. The highly reduced character of enstatite chondrites is further attested by the
90 study of Cr valence state in one EL3 of McKeown et al. (2014) who found that almost all Cr of
91 olivine was present as Cr^{2+} , suggesting equilibration at about IW-6. Cartier et al. (2014)
92 compiled some literature values and gave values around IW-6 for EH and IW-3 for EL
93 chondrites. Therefore, we conclude that EC were equilibrated at conditions below IW-3,
94 although a precise value may not be available at present. Brett and Sato (1984) also

95 determined the oxygen fugacity of a pallasite (ca. IW-3), and of ordinary chondrites (ca. IW-1),
96 two meteorite groups that are part of the present database. Although we did not study the
97 same specimen as Brett and Sato did, we consider that their estimated values give a range of
98 equilibrium conditions that are applicable to our case. Finally, we also studied a eucrite (NWA
99 15965) and the ungrouped achondrite NWA 11119, which formation conditions may be around
100 IW-4 (Srinivasan et al., 2018). The dataset is completed by terrestrial apatites, which is an
101 important repository for the REE for terrestrial samples.

102

103 2. Methods

104 X-ray absorption near-edge structure spectroscopy

105 The ytterbium valence state was determined by X-Ray Absorption Near Edge Structure
106 (XANES) spectroscopy at the Yb L2 edge on 13-ID-E station of sector 13 (GSECARS) at the
107 Advanced Photon Source. Both the L3 and the L2 edges were tested on an oldhamite crystal
108 from enstatite chondrite. Previous work had shown that the L3 edge was fitted to study Yb
109 valence state in experimental material, in which REE were doped to concentrations of the order
110 of 100 ppm (Ingrao et al., 2019). In the case of the natural oldhamite, the spectra obtained at
111 the L3 edge did not display a clear signal, which may be due to overlap with peaks from other
112 REE or from transition metals that are present in the crystal. This point was not investigated
113 further as the spectra at the L2 edge appeared suitable for studying Yb valence state.

114 Ytterbium L2-edge absorption spectra of a collection of samples of terrestrial and
115 extraterrestrial origins were collected in fluorescence mode using a four-element, silicon-drift-
116 diode detector array (Vortex-ME4, Hitachi High-Technologies Science America, Inc.) with
117 pulse-processing provided by an Xspress 3 digital X-ray processor system (Quantum
118 Detectors). All the fluorescence-mode XAFS data collected were corrected for detector dead
119 time. Measurements of the samples were performed on optically-polished resin mounts, using
120 a microbeam (ca. 2 x 3 micrometers) with an incident angle of 45 degrees. Given the low Yb
121 concentrations involved (<80 ppm in the natural samples), self-absorption was considered
122 negligible. Positioning on the sample surface was achieved using a dual optical microscope
123 setup (Offline Sample Coordinate And Registration system), in which x – y coordinates were
124 recorded outside the experimental station on a first microscope equipped with a motorized
125 stage. The recorded coordinates were then transferred to a second microscope located inside
126 the station, allowing for quick positioning. Both microscope optical axes were oriented normal
127 to the surface sample, yielding excellent observation conditions for position checking and for
128 focusing.

129 The energy was scanned between 9878 and 10214 eV using the Si(111) crystal setup.
130 The monochromator was calibrated using a Cu foil, which gave an E_0 (1st derivative of the
131 edge) of 8980.44 eV for the K edge. Scan steps were 2.5 eV in the pre-edge region, 0.25 eV
132 in the edge region. The post-edge region was scanned with a k-space step of 0.06 Å.
133 Calibration of Yb absorption energy was achieved using commercial Yb metal foil
134 (Goodfellow), YbS (NEYCO) for the divalent state and Yb₂S₃ (NEYCO) and Yb₂O₃ (Sigma
135 Aldrich) for the trivalent state. Studying both sesquisulfide and sesquioxide allowed us to check
136 whether the nature of the ligand would shift the position of the Yb³⁺ white line. All Yb
137 compounds (oxide and sulfides) were studied as powder layers enclosed in tape, with no
138 dilution. For YbS, the incident flux was decreased for analysis to reduce beam-induced
139 speciation changes, which was observed in the specific case of this compound after repeated
140 analysis on the same spot. Reference material data were acquired in transmission mode. Their
141 edge-absorption energies were defined by the first maximum of the derivative in the spectra.

142 Raw data were processed using the Athena suite software (Ravel and Newville, 2005).
143 The treatment included inspection of the individual spectra, correction, normalization, and
144 merging. We also examined the variations of the derivative of the absorption relative to energy,
145 which permits a more accurate estimation of the absorption edge, defined by the first maximum
146 of the derivative. Finally, the software permits to decompose the absorption spectra in order to
147 determine the contributions of the various ion valence states and coordinations to the total
148 spectra.

149 For each studied sample, several grains of Yb-host phases were studied, when possible,
150 that is depending on occurrence. In some cases, several analyses were performed in the same
151 grain, to check for zoning.

152

153

154 **Studied materials**

155 We have selected materials that cover a range of Solar System objects (Earth, chondrites,
156 achondrites) that were equilibrated under various redox conditions, from the most oxidized
157 (Earth) to the most reduced (enstatite chondrites). For comparison with previous work, we also
158 reinvestigated synthetic material that was previously analyzed at ESRF beamline BM23
159 (Ingrao et al., 2019). Although our collection does not reach the most oxidized objects of the
160 Solar System (Cartier et al., 2014) its range is adapted to document Yb reduction. The selected
161 materials are described in the following and their main features are summarized in Table 1.
162 For most samples, information on REE concentrations were available. In some rare case, we
163 did not have this information. This is not a problem, however, because here, we focus on Yb
164 redox state and the shape of the XANES spectra does not depend on trace element
165 concentration. (Self-absorption is negligible.)

166 For Earth's reference material, we used 3 different apatites. Apatite was chosen because
167 this mineral can contain significant amounts of REE, thus facilitating spectra acquisition. In
168 addition, because in most of the extraterrestrial material studied, the REE were also hosted in
169 phosphates, it seemed fitted to have a terrestrial phosphate for comparison. The only
170 exception is the group of enstatite chondrites, in which calcium sulfide represents a major REE
171 reservoir. In phosphate minerals, REE incorporation in the crystal lattice is controlled by
172 various potential charge-balanced substitution mechanisms, in which the REE substitute for
173 Ca, such as $\text{Si}^{4+} + \text{REE}^{3+} = \text{Ca}^{2+} + \text{P}^{5+}$, $2 \text{REE}^{3+} + \text{vacancy} = 3 \text{Ca}^{2+}$, $\text{REE}^{3+} + \text{O}^{2-} = \text{Ca}^{2+} + (\text{OH},$
174 $\text{F}, \text{Cl})^-$, and $\text{Na}^+ + \text{REE}^{3+} = 2 \text{Ca}^{2+}$ (Fleet and Pan, 1995). In calcium sulfide, experimentally-
175 obtained CaS/melt partition coefficient values display a relation with ionic radii of the REE
176 (Ingrao et al., 2019). This also suggests crystal chemical control with the REE substituting for
177 Ca, although the details of the substitution mechanism have not been explored.

178 The hydrothermal Durango apatite is a reference mineral for geochronology (Yang et al.,
179 2014, Doucelance et al., 2020). Our specimen was provided by the National Museum of
180 Natural History, Smithsonian Institution (sample #144954-4). Yang et al. (2014) compared
181 different fragments analyzed by different groups and it appears that Durango apatite is slightly
182 variable in composition. Its Yb content ranges between 27 and 59 ppm. Our fragment contains
183 29 ppm Yb (laser-ablation ICP-MS, E. Bruand, personal communication). The apatite from the
184 carbonatitic complex of In Ouzal (Ahaggar, Algeria) is similar to type III green apatite
185 described in Ouzegane et al. (1988). It has high levels of sulfur, SiO_2 and Sr and its LREE
186 reach the oxide weight percent level. Its Yb concentration was determined by laser-ablation
187 ICP-MS (Hammouda et al., 2010) and is 79 ppm. The Xuxa apatite from Brazil (Borborema,
188 state of Paraíba) is found in skarns. It contains about 16 ppm Yb (Santos Schuch, 2018 by
189 laser-ablation ICP-MS). It is currently being assessed as a reference material for
190 geochronology (Santos Schuch, 2018, Antoine et al., 2020). Apatite having a hexagonal
191 symmetry, it is possible that crystal orientation may affect the Yb absorption spectra. No such
192 effect, however, was observed in the present investigation.

193 For the extraterrestrial material, we studied phosphates (merrillites, theoretical formula
194 $\text{Ca}_{18}\text{Na}_2\text{Mg}_2(\text{PO}_4)_{14}$) from two ordinary chondrites (OC), Kernouvé (H6, Heck et al., 2020) and
195 Saint-Séverin (LL6, this study). Phosphates in ordinary chondrites are usually considered of
196 secondary, metamorphic origin (Zanda et al., 1991) with formation ages younger than that of
197 the Solar System by a several My (e.g., ~4555 Myr for Saint-Séverin phosphates; Bouvier et
198 al., 2007). Both chondrites contain apatite and merrillite. Apatites in both, however, have low
199 Yb concentrations (between 1 and 3.5 ppm). Therefore, we focused on merrillites, which have
200 Yb concentrations of 33 and 30 ppm in Kernouvé and Saint-Séverin, respectively.

201 Seven EC were studied, 3 EH (Sahara 97158 (EH3), Abee (EH4-IMB), Oudiyat Sbaa
202 (EH5)) and 4 EL (MS 189 (EL3), MS 196 (EL4/5), Adrar Bous (EL5), Hvittis(EL6)). In EC, REE
203 are mainly hosted by calcium sulfide (CaS, oldhamite). Rare-earth element concentrations in

204 the CaS of these 7 EC have been determined by Hammouda et al. (2022) using laser-ablation
205 ICP-MS, and Yb concentrations in CaS range between 7 and 16 ppm. Because oldhamite has
206 a cubic symmetry, no effect of crystallographic orientation on the Yb absorption spectra is
207 expected. Typical oldhamite textures in EC have been presented in Hammouda et al. (2022).
208 Additional scanning electron images are provided in Supplementary Material, with indication
209 of XANES spots positions.

210 Three achondrites were studied. Seymchan is a pallasite. Our section contains two
211 grains of phosphates: one merrillite and one stanfieldite (theoretical formula
212 $\text{Ca}_4(\text{Mg,Fe,Mn})_5(\text{PO}_4)_6$). Phosphates in pallasite are not primary phases. They have been
213 interpreted as resulting from a reaction between melt and phosphoran olivine or by subsolidus
214 reaction between metal and olivine (Davis and Olsen, 1991; Bosenberg et al., 2012). For the
215 present study, we did not analyze our section for trace elements. By comparison with literature
216 data (Hsu, 2003; Chernonozhkin et al., 2021), we infer Yb concentrations of the order of 6 to
217 9 ppm in merrillite, and of 1 to 3 ppm in stanfieldite. One eucrite (NWA 15965) contains
218 merrillite and apatite grains and one ungrouped achondrite (NWA 11119) contains an unknown
219 phosphorus-bearing phase. For the latter two samples, we do not have information on REE
220 concentrations in the analyzed mineral phases.

221

222 3. Results

223 The recorded spectra are presented in Figs. 1 to 9. In the figure display, the energy range was
224 restricted to between 9930 and 10080 eV. Table 1 provides information of the number of
225 spectra merged for the figure display. Table 1 also summarizes the observed valence states
226 of Yb. Additional data, including individual spectra used for the merges and some enstatite
227 chondrite samples listed in Table 1 but not presented in the figures are provided in the
228 Supplementary Material.

229

230 Reference compounds

231 XANES spectra for metallic Yb, YbS, Yb_2S_3 , and Yb_2O_3 are displayed on Figure 1. Metallic Yb
232 exhibits an absorption peak at 9970 eV. YbS, in which Yb is theoretically divalent, displays a
233 first peak at 9972 eV, followed by a second peak at 9979 eV. Finally, both Yb_2S_3 , and Yb_2O_3
234 have a single absorption peak at 9979 eV, indicating that the nature of the ligand (whether it
235 is sulfur or oxygen) does not affect the Yb absorption energy. Post-peak spectra of the two
236 compounds differ, however. Although both have an oscillation at 10020 eV, the oxide has an
237 additional oscillation at 10000 eV. Contrary to V (Wong et al., 1984) Nb and Ta (Cartier et al.,
238 2015), there is no linear relation between Yb valence state and the energy of the absorption
239 edge. In addition, the absorption edge of metallic Yb is very close to that of Yb^{2+} in YbS.
240 Previous works on metallic Yb (Fuse et al., 2004; Dallera et al., 2006) have shown that the X-
241 ray absorption edge of metallic Yb corresponds to a 2+ valence state at ambient conditions
242 with a transition to the 3+ state at high pressure. A structural transformation, which was also
243 attributed to the Yb^{2+} to Yb^{3+} transition, has been observed in Yb metal crystals by Hall et al.
244 (1963) at 4 GPa with a change from face-centered cubic to body-centered cubic. Although
245 these observations show that the notion of valence state as understood by material scientists
246 may differ from that of mineralogists, further discussion on this topic is beyond the scope of
247 the present paper.

248

249 Synthetic, experimental samples

250 X-ray absorption spectra of Yb in selected experiments published by Ingrao et al. (2019)
251 are shown on Figure 2. Here, we used the L2-edge, whereas Ingrao et al. (2019) studied the
252 L3-edge on BM23 beamline of ESRF. The present data confirm the presence of both Yb²⁺ and
253 Yb³⁺ with a preference of Yb²⁺ for the crystalline CaS relative to the melt. These results will not
254 be further discussed in the following.

255

256 **Natural terrestrial apatites**

257 X-ray absorption spectra of Yb in terrestrial apatites are displayed in Figure 3. All three
258 apatites display a sharp absorption peak at 9979 eV, attesting for the presence of Yb³⁺ only.
259 The chemical differences between the three apatite samples appear to have no effect on the
260 post-peak region.

261

262 **Ordinary chondrite phosphates**

263 X-ray absorption spectra of Yb in merrillites from Kernouvé and from Saint-Séverin are
264 shown in Figure 4. All merrillite grains display a single peak at 9979 eV, corresponding to Yb³⁺.
265 Compared to terrestrial apatite, the position of the absorption edge is identical. Moreover, the
266 post-edge oscillations of ordinary chondrite spectra are identical to those of terrestrial apatites,
267 attesting for a similar crystallographic environment (nature of neighbors, coordination number
268 and bond length), which is not much surprising given that the REE substitute for Ca in both
269 phosphates, despite the difference in crystal structure between apatite and merrillite.

270

271 **Enstatite chondrites oldhamites**

272 X-ray absorption spectra of Yb in the studied oldhamites are shown in Figure 5 for the
273 EH chondrites and Figure 6 for the EL chondrites. All spectra have a first edge at 9972 eV,
274 followed by a second peak at 9979 eV. This attests for the presence of both Yb²⁺ and Yb³⁺ in
275 all enstatite chondrites. Given the low Yb concentration, it is difficult to assess whether
276 differences exist between the various enstatite chondrites. At first view, they seem identical,
277 suggesting that all enstatite chondrites have the same Yb²⁺/Yb³⁺ ratio. This point will be further
278 addressed later.

279

280 **Achondrites**

281 X-ray absorption spectra of Yb in merrillite and stanfieldite from the pallasite Seymchan
282 are shown in Figure 7. In both cases, only Yb³⁺ is present. Because of the very low Yb
283 concentration (about 1 to 3 ppm as discussed above) the spectra obtained in the stanfieldite
284 grain are noisy but their interpretation is straightforward.

285 X-ray absorption spectra of Yb in merrillites from eucrite NWA 15965 are shown in Figure
286 8. Apatites were not studied, due to the anticipated low concentration of Yb by comparison
287 with ordinary chondrites where merrillite and apatite are present together (see Table 1). In the
288 studied eucrite, Yb is present in the form of Yb³⁺ in the merrillite grains and the post-peak
289 oscillations are similar to those of the terrestrial apatites.

290 X-ray absorption spectra of Yb in the phosphorus-bearing phase of the ungrouped
291 achondrite NWA 11119 are shown in Figure 9. Here too, Yb appears to be mainly in the Yb³⁺

292 form. The post-peak oscillations are more difficult to discuss, which we attribute to a lower Yb
293 concentration in the analyzed grains. If true, the main oscillation is compatible with a phosphate
294 phase as the host for Yb.

295

296 **4. Discussion**

297 The redox state of the Solar System objects is important because, as an intensive
298 parameter, it controls equilibrium phase relation, element behavior and distribution between
299 coexisting phases during the accretion of planetary materials and planet growth. The material
300 of choice in such endeavor is the direct study of meteorites, among which chondrites, primitive
301 achondrites, and iron meteorites represent fossils of the early stages of the Solar System
302 evolution.

303 Various methods have been used to decipher the equilibrium redox conditions of
304 meteorites. Phase equilibria between the metallic and the silicate phases have been used by
305 Williams (1971), Larimer and Buseck (1974), among others. Metal – phosphate equilibria have
306 also been considered (Olsen and Fuchs, 1967). Brett and Sato (1984) determined the intrinsic
307 oxygen fugacity of a collection of meteorites (carbonaceous, ordinary, and enstatite chondrites
308 and one pallasite) using an electrochemical cell. Another approach consists of studying the
309 fractionation of elements with variable valence states, such as the transition elements (Cr, Fe,
310 Ti, V) whose partitioning is sensitive to ambient redox conditions (Papike et al., 2004 and 2005;
311 Cartier et al., 2014, among others). Summaries of present knowledge of the oxidation state of
312 various objects of the Solar System can be found in Wadhwa (2008) and Cartier et al. (2014).

313

314 **Relation between host phase and Yb redox state**

315 The Yb host phases studied here in extraterrestrial rocks can be divided into two
316 categories: phosphates and sulfides. Phosphates host Yb (as well as other REE) in ordinary
317 chondrites, in eucrites, in pallasite, as well as in other achondrites (except for aubrites, the
318 enstatite achondrites, not studied here). In these meteorites, phosphates do not only host
319 phosphorus, but they also carry halogens (F, Cl), in addition to hydrogen (in the form of (OH)
320 groups). Therefore, they are important accessory minerals, as in terrestrial rocks.

321 Here, we found that the Yb XANES spectra of all investigated merrillites and stanfieldite
322 grains are similar to those of terrestrial apatites, including the extended spectra. This is
323 expected given that REE substitute for Ca in phosphates and that Ca crystallographic sites are
324 similar in all the investigated phosphate phases. In all investigated merrillites and stanfieldite
325 grains, Yb appears to exist only in the trivalent state, Yb^{3+} .

326 In enstatite chondrite, a major host phase for the REE is oldhamite. In the specific case
327 of Sahara 97158, which is a primitive EH chondrite, Hammouda et al. (2022) found that more
328 than 80% of the Yb budget was controlled by oldhamite. Because all enstatite chondrites have
329 about the same amount of oldhamite (ca. 1%) and all oldhamites have about the same Yb
330 concentrations (Hammouda et al., 2022), it can be safely assumed that the $\text{Yb}^{2+}/\text{Yb}^{3+}$ of
331 oldhamite is a good proxy for that of the whole rock. In addition, because Yb (as the other
332 REE) substitutes for Ca and because there is only one crystallographic site involved in the
333 substitution, it can be safely assumed that the oldhamite $\text{Yb}^{2+}/\text{Yb}^{3+}$ is solely controlled by the
334 ambient oxygen fugacity, contrary to the case of Ti in hibonite, for which site preference has
335 been shown to occur for Ti^{3+} and Ti^{4+} (Berry et al., 2017). Using the Athena software routine,
336 we found that about 50% of Yb^{2+} is present in this mineral. Yb^{2+} fraction was estimated by
337 decomposing the Yb L2 edge absorption spectra using YbS and Yb_2S_3 as components and

338 using the fraction of YbS contribution as a proxy for Yb²⁺. The results are displayed in Figure
339 10. The presence of oldhamite in enstatite chondrite is evidence for the highly reducing
340 environment prevailing during their formation. In such conditions, refractory lithophiles
341 elements, such as Ca, the lanthanides, the actinides become chalcophile (Lodders and
342 Fegley, 1993; Gannoun et al., 2011). Here, we see that the change in REE chemical affinity is
343 accompanied by reduction of the valence state of Yb.

344

345 **Distribution of redox conditions in the early Solar System**

346 Our results on Yb valence state on ordinary chondrites, and all the studied achondrites,
347 with only Yb³⁺ present confirms that these meteorites are less reduced than enstatite
348 chondrites. Brett and Sato (1984) report values of between IW-0.5 and IW-1.5 for ordinary
349 chondrites and of about IW-3 for pallasites.

350 In the case of the pallasite Seymchan, phosphate grains are the host phase for the REE.
351 The presence of phosphates (such as apatite, merrillite, stanfieldite, as reported in the present
352 study, or other phases not studied here) in equilibrium with phosphides (schreibersite,
353 (Fe,Ni)₃P or (Ni,Fe)₈(Si,P)₃, among others) or Fe alloys containing phosphorus in solution has
354 been used by Olsen and Fuchs (1967) to compute the oxygen fugacity of iron meteorites. The
355 obtained values range between IW-2 and IW-3, in agreement with Brett and Sato (1984)
356 results. This moderately reduced value fits well with the absence of Yb²⁺ in Seymchan.

357 In the case of the eucrite we have no evidence of a highly reduced parent body. On the
358 basis of Si isotope measurements, Pringle et al. (2013) suggested that core segregation took
359 place at redox condition of IW-4 on 4-Vesta, the proposed parent body of howardite-eucrite-
360 diogenite (HED) meteorites. Righter and Drake (1997) and more recently Sikdar and Rai
361 (2020) proposed that the HED parent body formed in the same region as that of ordinary and
362 carbonaceous chondrites, at moderately reducing conditions around IW-2. Our results on Yb
363 valence state cannot help in discriminating between the two oxygen fugacity values (see below
364 for NWA 11119) but for later discussion, we will keep the IW-2 value, which appears to be
365 more reasonable for the HED parent body.

366 For the ungrouped achondrite NWA 11119 we also find no evidence of Yb²⁺. Srinivasan
367 et al. (2018) proposed that NWA 11119 was formed by melting of a precursor body of chondritic
368 composition at conditions of the order of IW-4. The present data suggest that, even at IW-4,
369 Yb remains in the trivalent state. Thus, because all enstatite chondrites appear to be more
370 reduced than NWA 11119 on the basis of their Yb²⁺/Yb³⁺ ratio, the value of IW-4 must represent
371 an upper bound for fO₂ equilibrium conditions of enstatite chondrites.

372 Our Yb data confirm the highly reduced conditions of the enstatite chondrites. Earlier
373 oxygen fugacity of EC estimation by Brett and Sato (1984) is about IW-3, a value the authors
374 considered as being an upper limit, due to potential contamination by the laboratory
375 atmosphere. Larimer and Buseck (1974) have obtained values of EC oxygen fugacity using
376 the Si content of the metal. They give values below IW-11, which is highly reducing. When
377 plotted on a ΔIW vs reciprocal temperature diagram, Larimer and Buseck (1974) results may
378 suggest that EH could be more reduced than EL because the two data subsets are offset by
379 about 0.5 log unit (Figure 11). Our results on Yb²⁺/Yb³⁺ ratios shown in Figure 10 may confirm
380 this difference but both our data and those of Larimer and Buseck (1974) have significant
381 uncertainties. As shown in Figure 11, EH and EL data points can be collapsed to a single line
382 if a 25 K value is added or removed to either data subset. This 25 K values is largely within the
383 uncertainty of thermodynamic modeling. Similarly, our data on Yb valence state have
384 significant error bars and it is not so clear as to whether the observed difference between EH
385 and EL is real. Cartier et al. (2014) compiled literature data and have suggested values of the

386 order of IW-6 for EH and IW-3 for EL. In light of the present results on Yb valence state, the
387 EL value should be lowered in order to match that of EH. Lastly, it is remarkable that all
388 analyzed CaS have similar Yb XANES spectrum, although their REE abundance patterns vary
389 widely among enstatite chondrites as recently documented, with EH3 having concave upward
390 Cl-normalized REE patterns with positive Eu and Yb anomalies, EH5 having flat patterns, and
391 EL having convex upward Cl-normalized REE patterns with a Eu negative anomaly and no Yb
392 anomaly (Hammouda et al., 2022). Therefore, whatever the complex processes that yielded
393 such a variety of patterns, they must have yielded only a slight, if any, change in oxygen
394 fugacity between EH and EL. This conclusion is further substantiated by the absence of any
395 clear relation between Yb^{2+} abundance and Yb concentration anomalies in enstatite
396 chondrites, as illustrated in Figure 12.

397 The relation of Yb^{2+} fraction vs. intrinsic meteorite oxygen fugacity is summarized in
398 Figure 13. This diagram attempts to document Yb valence change in Solar System objects, as
399 a function of oxygen fugacity. In this diagram, the position of the enstatite chondrites is
400 somehow arbitrary given the difficulty to obtain a reliable value for their $f\text{O}_2$. The present Yb
401 valence-state data suggest that enstatite chondrite redox state should be below IW-4.

402

403

404 5. Conclusion

405 Although Yb²⁺ appears to be restricted to the most reduced objects of the Solar System, the
406 ytterbium valence state could be used to discriminate meteorite parent body redox state on
407 the low end of the oxygen fugacity range. Synchrotron-based X-ray absorption near-edge
408 spectroscopy is a powerful tool to investigate the redox state of seldom-considered elements,
409 given their high dilution in minerals (ppm level). It is remarkable that highly reduced states can
410 be preserved in the meteorite record, not only for observed falls but also for finds, such as the
411 Sahara samples. Our approach may open new ways of studying the redox state of the Solar
412 System materials.

413 Recently, Hammouda et al. (2022) proposed a complex, multistage scenario involving
414 fractional condensation, high-temperature events including partial vaporization and melting at
415 a very early stage of the Solar System to explain the diversity of REE patterns of oldhamites
416 in enstatite chondrites. A complex history involving partial evaporation followed by
417 recondensation was also proposed for refractory calcium-, aluminum-rich inclusions (CAI) of
418 Allende CV chondrite by Hu et al. (2021) using REE stable isotope fractionations. In the case
419 of enstatite chondrites, whatever the details of the thermal history, the present Yb redox state
420 data suggest that CaS evolution has taken place under rather constant redox conditions,
421 despite the loss of a fraction of iron and sulfur from the EL parent body relative to that of EH.
422 Whether this oxygen-fugacity buffering was internally or externally imposed on the parent body
423 (closed vs. open system) is yet to be discussed when modeling small planetesimal-collision
424 processes.

425

426

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443

444 Appendix A. Supplementary Material

445 A supplementary file is attached to this article. This file is divided in 3 sections. S1 presents
446 scanning electron images of oldhamite grains from a selection of enstatite chondrites, in which
447 the positions of the areas analyzed by XANES are indicated. S2 presents the individual Yb L2-
448 edge absorption edge spectra of the analyzed meteorites, whose averages are displayed in

449 the figures of the main text. S3 presents fits of the reference materials (YbS and Yb₂S₃) to the
450 oldhamite spectra recorded in enstatite chondrites.

451

452 **Data Availability**

453 XANES data files are available through <https://doi.org/10.25519/JFCN-B685>

Journal Pre-proofs

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620 redistribution of silicon, chromium, and phosphorus in the metal of chondrites, Science 265:
621 1846-1849.
- 622 Table 1: Information on the materials studied for x-ray absorption at the Yb L2 edge.
- 623

Class/type ^a	Host phase	Redox conditions ^b	Yb concentration (ppm) ^c	Nb of spectra ^d	Yb valence observed
Synthetic standards					
Yb ⁰	metal			1	Yb ⁰

YbS		sulfide			1	Yb ²⁺
Yb ₂ S ₃		sulfide			1	Yb ³⁺
Yb ₂ O ₃		oxide			1	Yb ³⁺
Experiments (Ingrao et al., 2019)						
#1250 (1300 °C)		CaS	IW-6.6 [1]	217 [1]	2	Yb ²⁺ and Yb ³⁺
		glass	IW-6.6 [1]	145 [1]	2	Yb ²⁺ and Yb ³⁺
#1244 (1400 °C)		CaS	IW-5.8 [1]	98 [1]	2	Yb ²⁺ and Yb ³⁺
		glass	IW-5.8 [1]	407 [1]	2	Yb ²⁺ and Yb ³⁺
Terrestrial material						
Apatite Durango		apatite		29 [6]	1	Yb ³⁺
Apatite Hoggar		apatite		79 [7]	1	Yb ³⁺
Apatite Xuxa		apatite		17 [8]	1	Yb ³⁺
Ordinary chondrites						
Kernouvé	H6	apatite	ca. IW-1 [2]	1 [9]	n.a. ^e	Yb ³⁺
		merrillite	ca. IW-1 [2]	33 [9]	2	Yb ³⁺

Saint-Séverin	LL6	apatite	ca. IW-1 [2]	3.5 [10]	n.a. ^e	Yb ³⁺
		merrillite	ca. IW-1 [2]	30 [10]	2	Yb ³⁺
Enstatite chondrites						
Sahara 97158	EH3	oldhamite	< IW-3 [2,3]	7 [11]	5	Yb ²⁺ and Yb ³⁺
Abee	EH4-IMB	oldhamite	< IW-3 [2,3]	10 [11]	0 ^f	--
Oudiyat Sbaa	EH5	oldhamite	< IW-3 [2,3]	11 [11]	10	Yb ²⁺ and Yb ³⁺
Almahata Sitta, MS 189	EL3	oldhamite	< IW-3 [2,3]	13 [11]	9	Yb ²⁺ and Yb ³⁺
Almahata Sitta, MS 196	EL4/5	oldhamite	< IW-3 [2,3]	13 [11]	2	Yb ²⁺ and Yb ³⁺
Adrar Bous	EL5	oldhamite	< IW-3 [2,3]	16 [11]	1	Yb ²⁺ and Yb ³⁺
Hvittis	EL6	oldhamite	< IW-3 [2,3]	14 [11]	10	Yb ²⁺ and Yb ³⁺
Achondrites						
NWA 15965	eucrite	apatite	IW-1 [4]	n.d.	n.a. ^e	--
		merrillite	IW-1 [4]	n.d.	4	Yb ³⁺
NWA 11119	ungroupe d	phosphat e	IW-4 [5]	n.d.	3	Yb ³⁺

Seymchan	pallasite	merrillite	IW-3 [2]	6-9 [12]	4	Yb ³⁺
		stanfieldite	IW-3 [2]	1-3 [12]	4	Yb ³⁺

624 Notes:

625 ^a Refers to the meteorite class or the chondrite petrographic type.

626 ^b Sources for redox conditions: [1] Ingrao et al. (2019); [2] Brett and Sato (1984) data for
627 chondrites and pallasite; [3] Larimer and Buseck (1974) for enstatite chondrites; [4] Wadhwa
628 (2008); [5] Srinivasan et al. (2018).

629 ^c Sources for Yb concentrations: [1] Ingrao et al. (2019); [6] Émilie Bruand (pers. comm.); [7]
630 Hammouda et al. (2010); [8] Santos Schuch (2018); [9] Heck et al. (2020); [10] this study; [11]
631 Hammouda et al. (2022); [12] estimated from Chernonozhkin et al. (2021) data on Brahin and
632 CMS 04071 pallasites (see main text); n.d., not determined.

633 ^d Number of spectra used for obtaining the merged spectra displayed in Figs 1 to 9.

634 ^e Given the anticipated low Yb concentrations in apatites, these phases were not analyzed in
635 ordinary chondrites and in the eucrite.

636 ^f For Abee, Yb concentration in oldhamite was too low to obtain acceptable spectra.

637

638