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## Determination of the initial hydrogen isotopic composition of the solar system

J. Aléon, D. Lévy, A. Aléon-Toppani, H. Bureau, H. Khodja, F. Brisset

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1 **Initial hydrogen isotopic composition of the solar system**

2

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4 J. Aléon<sup>1,\*</sup>, D. Lévy<sup>1,2,3</sup>, A. Aléon-Toppani<sup>2</sup>, H. Bureau<sup>1</sup>, H. Khodja<sup>4</sup>, F. Brisset<sup>5</sup>

5

6 1 Institut de Minéralogie de Physique des Matériaux, de Minéralogie et de Cosmochimie,  
7 Museum National d'Histoire, Naturelle, Sorbonne Université, UMR CNRS 7590, 61 rue  
8 Buffon, 75005 Paris, France

9 2 Institut d'Astrophysique Spatiale, UMR 8617, CNRS, Univ. Paris-Saclay, Bât 120-121,  
10 91405 Orsay cedex, France

11 3 Laboratoire des Fluides Complexes et leurs Réservoirs (LFCR), E2S UPPA - Université  
12 de Pau et des Pays de l'Adour, CNRS, Total, France

13 4 Université Paris-Saclay, CEA, CNRS, NIMBE, LEEL, 91191 Gif sur Yvette Cedex, France

14 5 Université Paris-Saclay, CNRS, Institut de Chimie Moléculaire et des Matériaux d'Orsay,  
15 91405 Orsay cedex, France

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19 \*Corresponding author: [jerome.aleon@mnhn.fr](mailto:jerome.aleon@mnhn.fr)

20 ORCID: 0000-0001-5729-0166

21

22

23 **In spite of numerous studies, the initial isotopic composition of water in the solar**  
24 **system remains unknown. Here we use the isotopic composition of hydrogen in**  
25 **calcium, aluminum-rich inclusions (CAIs) from primitive meteorites, the oldest**  
26 **solar system rocks, to establish the hydrogen isotopic composition of water at the**  
27 **onset of solar system formation. We report the hydrogen isotopic composition of**  
28 **nominally anhydrous minerals from CAI fragments trapped in a once-melted host**  
29 **CAI. Primary minerals have extremely low D/H ratios, with  $\delta D$  values down to -**  
30 **850‰, recording the trapping of nebular hydrogen. FeO-rich minerals formed**  
31 **before capture of the fragments record the existence of a nebular gas reservoir**  
32 **with an oxygen fugacity significantly above solar and a D/H ratio within 20% of**  
33 **that of the Earth oceans. H isotopes further correlate with oxygen and nitrogen**  
34 **isotopes indicating that planetary reservoirs of volatile elements formed within**  
35 **the first  $2 \times 10^5$  years of the solar system, during the main CAI formation epoch.**  
36 **We propose that the isotopic composition of inner solar system water was**  
37 **established during collapse of the protosolar cloud core owing to a massive**  
38 **admixture of interstellar water.**

39  
40 As water is a major ingredient in the recipe of planet formation and origin of life, its  
41 origin and chemistry and notably its H and O isotopic compositions have extensively  
42 been studied and modeled in solar system objects<sup>1-5</sup>. H isotopes indicate injection of D-  
43 rich molecules from the cold interstellar medium / outer protoplanetary disk into the  
44 inner regions where terrestrial planets formed and have widely been used as a tracer of  
45 water origin. However, the initial isotopic composition of water in the protoplanetary  
46 disk has always been lacking so that models often rely on astronomical observation of  
47 remote forming stellar systems. In addition, most models consider static T-Tauri disks<sup>2-4</sup>  
48 and neglect the fact that the D/H ratio of water probably evolved during the disk-  
49 building phase. However, a few models have shown the influence of this early phase, not  
50 only on the distribution of D/H ratios<sup>5</sup>, but also on other isotopic and chemical  
51 properties of early planetary materials<sup>6</sup>. A correct understanding of D/H systematics in  
52 the solar system and origin of water in planetary bodies thus require to know the  
53 isotopic composition of H as recorded in the most ancient solar system materials formed  
54 during the disk-building phase, while the presolar cloud core was still collapsing.

55

56 CAIs are the oldest solar system rocks<sup>7</sup> and their mineralogy, chemistry and isotopic  
57 composition are commonly used as benchmarks to establish the physico-chemical  
58 conditions at the onset of planetary formation. They formed primarily by condensation  
59 at high temperature of refractory solids from a gas of solar composition in the innermost  
60 solar system, grew by coagulation and subsequently experienced various degrees of  
61 reheating up to the point of partial melting and eventually late modifications on their  
62 asteroidal parent-bodies<sup>8</sup>. Measuring the hydrogen isotopic composition of nominally  
63 anhydrous minerals formed below 100 Pa and at 1200-1500°C is challenging, especially  
64 given that most meteorites experienced fluid circulations after accretion, which could  
65 have masked a primary composition inherited from the protoplanetary disk. Compound  
66 CAIs (i.e. composed of several lithological units that were once individual CAIs) from the  
67 least altered and least metamorphosed chondrites are choice targets to identify  
68 preserved pre-accretionary nebular isotopic signatures. Efremovka 101.1 (E101.1, Fig.  
69 1) is a compound CAI from the reduced CV3 chondrite Efremovka, a petrologic type 3.1-  
70 3.4 chondrite<sup>9</sup>, i.e. having suffered only modest amounts of metamorphic modifications  
71 and little fluid circulations. It contains fragments of a first CAI rich in Al-diopside  
72 trapped in a once-melted melilite-rich host CAI that underwent only little alteration<sup>10,11</sup>.  
73 O, Mg and Si isotopes demonstrate that the Al-diopside-rich fragments (hereafter  
74 xenoliths) were initially foreign to the host CAI and were captured while the host was  
75 still partially molten<sup>11</sup>. The xenoliths contain an unusual assemblage of secondary  
76 minerals replacing primary minerals and having formed in oxidizing conditions before  
77 capture of the xenolith by the host (ref 12 and supplementary material). Using  
78 NanoSIMS imaging<sup>13</sup>, we estimated the H content and measured the H isotopic  
79 composition of individual  $\mu\text{m}$ -sized minerals from E101.1 xenoliths, with the aim to  
80 identify pristine nebular H components predating the capture of the xenoliths by the  
81 host. Targeted minerals include (i) primary Al-diopside, (ii) anorthite whose primary or  
82 secondary nature is often debated in CAIs, (iii) secondary kirschsteinite occurring both  
83 as coarse  $\mu\text{m}$ -sized Fe-rich crystals and as fine-grained aggregates of 100 nm-sized Mg-  
84 enriched crystals sometimes associated with nanoscale diopside and minute Fe metal,  
85 (iv) Fe-rich åkermanite, a type of secondary melilite unusual in CAIs and (v) secondary  
86 wollastonite. For comparison, we measured the glass in melt pockets resulting from  
87 impact melting of the host-xenoliths interface, as well as melilite and secondary phases  
88 from the host CAI (a Na-rich phase and alteration in a fracture).

89

90 The distribution of D/H as a function of H<sup>-</sup> secondary ion intensity, a proxy for the H  
91 content (methods), which can be expressed as equivalent water content, shows a  
92 trimodal distribution in E101.1 with two hydrogen poor-components having large D-  
93 excesses with  $\delta D$  values up to +1000‰ and deficits down to  $\delta D$  values of -850‰ (Fig.  
94 2), with  $\delta D$  being the deviation relative to the Earth oceans given in ‰. The third  
95 component is a hydrogen-rich component ( $H_2O \geq \sim 3.5$  wt%) with a  $\delta D$  value of  $\sim 0$ ‰,  
96 restricted to secondary minerals outside the xenoliths. When only xenoliths analyses are  
97 considered, the range of H content and D/H composition is well accounted for by a  
98 three-component mixing between the D-rich, D-poor components and a component with  
99 intermediate H content ( $\sim 0.5$  wt%  $H_2O$ ) and a  $\delta D$  value of  $\sim 0$ ‰ (Fig. 2b and  
100 Supplementary Fig.1). This mixing is partially of analytical origin due to the relatively  
101 large size of the ion beam used for the analyses ( $\sim 1.5$   $\mu m$ ) relative to the mineral grain  
102 size (100 nm to a few  $\mu m$ ) but reflects also the intermediate composition of  
103 homogeneous phases, such as that of the impact glass. None of these components can be  
104 ascribed to analytical contamination (methods). Furthermore, residual contamination  
105 would only contribute to a decrease of the most extreme values, which must be  
106 considered as indicating minimal D-depletion and D-enrichment, respectively. We  
107 therefore consider the measured values as conservative estimates. Textures and  
108 mineralogy further rule out the contribution of terrestrial weathering before collection  
109 of the Efremovka meteorite (supplementary material).

110

111 The  $\delta D$  value of the first xenolith component observed in anorthite and diopside at -  
112 850‰ is equal to that of nebular  $H_2$ . Within error, it cannot be distinguished from pure  
113 solar protons ( $\delta D = -1000$ ‰). Negatively fractionated Mg, Si isotopes and near solar O  
114 isotopes in diopside<sup>11</sup> with  $\Delta^{17}O = -20$ ‰ and petrological context (ref 12 and  
115 supplementary material) support formation of diopside by condensation from a solar  
116 gas. Hence, this isotopic composition can be ascribed to trapping of solar H or  $H_2$  in the  
117 crystal structure during condensation. Most likely, H is present in diopside and anorthite  
118 as protonated point defects or molecular  $H_2$  dissolved in the crystal lattice. The  
119 measured H signal is consistent with  $\sim 500$  ppm equivalent water ( $\sim 55$  ppm  $H_2$ ), which  
120 is surprisingly high, a common observation in meteoritic NAMs<sup>14,15</sup>. Whereas low  
121 pressures in the nebula are not in favor of storage of a significant amount of H in the

122 structure of NAMs, the solubility of H<sub>2</sub> increases with  $f_{\text{H}_2}$  (ref 16), which may favor the  
123 solubilization of H<sub>2</sub> in clinopyroxene (diopside) and anorthite, as H<sub>2</sub> is by far the  
124 dominant gas species. Alternatively, significant H abundance may result from the  
125 trapping of protons in a solar plasma. Note that anorthite has the lowest  $\delta\text{D}$  value found  
126 in meteorites, which rules out a secondary and a parent-body origin of anorthite.

127

128 Ca, O, Si and Fe are the main targets for the production of D by spallation. As they are  
129 major elements in all xenolith minerals, whereas the D-excesses are restricted to fine-  
130 grained kirschsteinite aggregates, the latter cannot be ascribed to spallation. The  
131 association of D-excesses with low H contents also rules out alteration in a D-rich fluid,  
132 which would result in high D/H ratios associated with high H content. By contrast, the D-  
133 excesses are well accounted for by kinetic fractionation during intra-crystalline diffusion  
134 of H atoms (Fig. 2b) driven by H loss, independently of the speciation of the lost  
135 molecule. Such a kinetic fractionation has been demonstrated in grossular<sup>17</sup>, another Ca-  
136 rich nesosilicate, where fractionation was attributed to the migration of protonated  
137 point defects driven by water loss. Mineralogy shows that fine-grained kirschsteinite  
138 formed during capture of the xenoliths by reduction of coarse-grained kirschsteinite (ref  
139 12 and supplementary material). The latter has a large range of H content and its highest  
140 H content ( $\sim 5000$  ppm) and Earth-like isotopic composition (within 20%) are  
141 consistent with those of the precursor expected from the diffusive loss calculations (Fig.  
142 2b). Therefore deuteration occurred during reduction of coarse-grained kirschsteinite,  
143 and capture of the xenoliths by the partially molten host. This implies that coarse-  
144 grained kirschsteinite formed before accretion of the CV chondrite parent-body in an  
145 oxidizing nebular gas reservoir having an Earth-like D/H ratio within 20%. All minerals  
146 from the host CAI also have Earth-like isotopic composition, including Na-rich minerals  
147 with H<sub>2</sub>O content up to  $\sim 3.5$  wt% and igneous melilite with H<sub>2</sub>O content  $\leq 5000$  ppm.

148

149 The H isotope systematics of E101.1 thus points toward the co-existence of two gaseous  
150 reservoirs during the earliest phase of solar system formation. Although the speciation  
151 of H in minerals, notably in NAMs, is different from that in the gas, the relationship  
152 between H isotopes and redox state indicates that condensate diopside and anorthite  
153 recorded the composition of the solar nebular hydrogen gas, while FeO-rich secondary  
154 minerals and possibly igneous melilite recorded the composition of a water-enriched

155 nebular gas with Earth-like H isotopic composition. Given that a warm environment is  
156 required for kirschsteinite formation, water and hydrogen were most likely in isotopic  
157 equilibrium. The O isotopes we measured previously in E101.1 (ref. 11) show a similar  
158 systematics with condensate diopside having a typical near solar  $^{16}\text{O}$ -rich composition,  
159 whereas FeO-rich minerals and igneous melilite have a planetary-like  $^{16}\text{O}$ -poor isotopic  
160 composition. This O isotope systematics is common in igneous CAIs and attributed to  
161 interactions between a precursor of solar composition with a nebular gas reservoir of  
162 planetary composition<sup>18,19</sup>. Hence H and O isotopes in CAIs show a co-existence of H and  
163 O isotopes with light near-solar composition ( $\delta\text{D} \sim -850\text{‰}$  and  $\Delta^{17}\text{O} \sim -25\text{‰}$ ) in  
164 condensate minerals and planetary isotopic composition ( $\delta\text{D} \sim \Delta^{17}\text{O} \sim 0\text{‰}$ ) in minerals  
165 processed in the solar nebula. This relationship suggests that the planetary composition  
166 is carried by water vapor. N isotopes show a similar systematics, with TiN in a  
167 condensate CAI having a near solar  $\delta^{15}\text{N}$  value at  $-364\text{‰}$ <sup>20</sup>, while an igneous CAI has a  
168 planetary-like composition at  $\delta^{15}\text{N} \sim 0\text{‰}$ <sup>21</sup>. This indicates that H, O and N isotopes co-  
169 evolved from a near solar composition to a planetary composition (Fig. 3) during the  
170 formation of igneous CAIs, in the first 200,000 years of the solar system, while the  
171 presolar cloud envelope was still collapsing<sup>22</sup>. The relationship between N isotopes and  
172 heavy metal nucleosynthetic anomalies in iron meteorites<sup>23</sup> further testifies that the  
173 planetary N reservoir built up during early infall of interstellar material.

174

175 Hence, the ubiquitous H isotopic composition ( $\text{D}/\text{H} \sim 1\text{-}2 \times 10^{-4}$ ) observed in large early-  
176 formed telluric planetesimals such as the howardites-eucrites-diogenites (HED) parent-  
177 body (Vesta) or the angrite parent-body and in the mantle of the Earth and Mars was  
178 reached in the first few  $10^5$  years of the solar system owing to a massive influx of  
179 interstellar matter infalling directly in the inner solar system<sup>24</sup>, rather than being  
180 produced in a more evolved protoplanetary disk<sup>2,3</sup>. Accretion of primitive materials at  
181 different stages of infall allows for some isotopic heterogeneity between planetesimals  
182 (supplementary discussion). The relationship observed for H, O, N isotopes between the  
183 Sun, condensate CAIs and planetary gas (Fig. 3) suggests that igneous CAIs formed from  
184 solar matter at the inner edge of the protoplanetary disk, and were processed to some  
185 extent in the planetary gas. Raising the bulk D/H ratio of the disk to the planetary value  
186 by addition of interstellar water having a typical D/H ratio between  $10^{-3}$  and  $10^{-2}$  would  
187 require an enhancement of the ice/gas ratio of a factor 10 to 100, which in turn would

188 increase the  $fO_2$  of the gas by 2 to 4 orders of magnitude. In-situ production of D-  
189 excesses by chemical reactions in a plasma<sup>25</sup> could be an alternative hypothesis  
190 (supplementary discussion) provided it is associated with mass independent  
191 fractionation of oxygen<sup>26</sup> and a change in redox conditions.

192

### 193 **Methods**

194

195 *Sample description.* Efremovka 101.1 is a complex compound CAI consisting of multiple  
196 lithological units, all characterized by ultra-refractory Rare Earth Elements (REE)  
197 patterns<sup>10</sup>. O, Mg and Si isotopes have demonstrated that sinuous fragments dominated  
198 by Al-diopside have an extraneous origin and were captured by the host inclusion in a  
199 partially molten state<sup>11</sup>. An unusual FeO-rich mineral assemblage is associated with and  
200 restricted to these xenoliths. The detailed mineralogical study of the xenolith and their  
201 mineral assemblage is beyond the scope of the present study, but major observations  
202 obtained by scanning electron microscopy, electron probe microanalysis and  
203 transmission electron microscopy from a preliminary report<sup>12</sup> are recalled here and as  
204 supplementary materials to support the H isotope study.

205 The host E101.1 CAI is a compact type A CAI consisting mainly of Al-rich melilite ( $\text{Åk}_{20-}$   
206  $_{30}$ , refs 10-11), which contains Al-Mg spinel aggregates and metal grains associated with  
207 perovksite and Sc-Zr-rich clinopyroxene and locally with anorthite intergrown with a  
208 Na-rich mineral postulated to be nepheline<sup>11</sup>. By contrast, E101.1 xenoliths consist  
209 predominantly of Al-bearing diopside, associated with anorthite and containing pockets  
210 of FeO-rich minerals characterized as (1) a  $\mu\text{m}$ -sized Ca-Fe-rich olivine (hereafter  
211 coarse-grained (CG) kirschsteinite, kir), (2) a fine-grained (FG) aggregate of 100 nm  
212 crystals of kirschsteinite enriched in Mg relative to CG-kir plus minute Fe metal grains  
213 and in some cases fine-grained Fe-rich diopside (Supplementary Fig.2), (3) an unusual  
214 Mg-Fe-rich melilite (hereafter Fe-åkermanite) (Supplementary Fig.3). CG-kir has a  
215 composition on the join kirschteinite-monticellite with 61-79 mol% kir, while kir in the  
216 FG-assemblage is enriched in Mg with a wide range of composition ranging from 68  
217 mol% kir to 17 mol% kir. These FeO-rich minerals are associated with wollastonite<sup>12</sup>.  
218 Veins filled with a Ca-poor amorphous phase crosscut all mineral assemblages from the  
219 xenoliths and extend into the host<sup>12</sup> (Supplementary Fig.2). Finally melt pockets up to  
220 100  $\mu\text{m}$  in size and containing melilite dendrites and fractured Al-diopside crystals are



221 observed at the xenolith-host interface (Supplementary Fig 4). The distribution of Fe, Na  
222 and Ni throughout the compound CAI (Supplementary Fig.5) shows (i) high abundance  
223 of Na and Fe associated with the xenoliths and with metal-anorthite-nepheline  
224 inclusions, (ii) Fe enrichment in spinel limited to the outermost 30  $\mu\text{m}$  of the CAI  
225 periphery and (iii) Fe and Na associated with sub-parallel impact induced compaction  
226 fractures either connected to the outer rim or to FeNi metal beads.

227

228 *NanoSIMS imaging of FIB sections.* D/H ratios were measured by NanoSIMS at Institut de  
229 Minéralogie de Physique des Matériaux et de Cosmochimie, Paris, France, using optimal  
230 analytical conditions determined in ref 13. 5 Focused Ion Beam (FIB) sections ( $\sim 10 \times 5$   
231  $\mu\text{m}$ ) of 2  $\mu\text{m}$  thickness prepared at Institut d'Electronique, Microélectronique et  
232 Nanotechnologie, Lille, France, were extracted from the E101.1 CAI with the aim to  
233 sample all minerals and mineral associations encountered in the xenoliths and were  
234 deposited on a polished Al disk and coated with Au. All reference minerals including  
235 standard amphiboles and terrestrial NAMs were prepared similarly. Each analysis  
236 consisted of an 8  $\mu\text{m}$  x 8  $\mu\text{m}$  image acquired using a  $\sim 1.5 \mu\text{m}$  Cs<sup>+</sup> beam of 100 pA and 8  
237 kV. A 250 pA Cs<sup>+</sup> beam was rastered over 20 x 20  $\mu\text{m}$  during 8 min before analysis to  
238 remove Au, sputter clean the sample and achieve sputtering equilibrium. Electron  
239 flooding was used for charge compensation. H and D were collected simultaneously on  
240 two electron multipliers using a 1000  $\mu\text{s}$ /pixel dwell time. 256 x 256 pixels images  
241 consist of 20 planes acquired sequentially during 20 minutes. Secondary and  
242 backscattered electron images of the sections were acquired by Field Emission Gun-  
243 Scanning Electron Microscopy (FEG-SEM) at Institut de Chimie Moléculaire et des  
244 Matériaux d'Orsay, Orsay, France, after NanoSIMS analysis to identify minerals  
245 remaining in the sections at the end of the analyses.

246

247 *Image processing.* For all FIB sections, two different types of image processing were  
248 applied (Supplementary Fig.6). (1) All images were subdivided in squares having  $\sim$ the  
249 size of the primary beam, i.e. the lateral resolution of the analyses. These squares are  
250 referred to as xenolith ROIs and host ROIs depending on the FIB section. ROIs along the  
251 edges of the images were eliminated. For each ROI the D/H ratio was determined from  
252 the H and D ion counts extracted in the image using the LIMAGE software ((c) Larry  
253 Nittler, 1997), and uncertainties were determined using counting statistics following a

254 Poisson law. (2) Subsequently, additional ROIs corresponding to minerals identified  
255 with FEG-SEM images of the sections acquired after analysis were hand-drawn, taking  
256 care to define ROIs at least ~equal to the primary beam size in order to avoid under-  
257 sampling and statistical error. These are referred to as Mineral ROIs. D/H ratios were  
258 determined similarly. Counting statistics, reproducibility between acquisition cycles,  
259 reproducibility on the standards and uncertainty due to FIB section heterogeneities on  
260 standards<sup>13</sup> (all standard errors of the mean) were quadratically taken into account to  
261 determine the analytical errors. For both image processing, D/H ratios were determined  
262 using total ions counts over the course of an image acquisition rather than using the  
263 average of individual image planes, some of which may have 0 D counts, to avoid biases  
264 in the D/H ratios due to improper correction<sup>27</sup>.

265

266 *Correction of instrumental mass fractionation (IMF).* To correct for instrumental bias  
267 (referred to as IMF and denoted alpha), we used the Fe-rich arfvedsonite Illimaussaq  
268 and Mg-rich hastingsite Bamble amphiboles to encompass a large range of possible mass  
269 fractionation for H isotopes in minerals<sup>28</sup>. A basaltic glass with intermediate water  
270 content (SW-DR32-1-1) yielded a similar mass fractionation as Bamble (Supplementary  
271 Table 1).

272 We used Bamble to correct IMF for Fe-poor minerals and areas on FIB sections and SW-  
273 DR32-1-1 to correct IMF for glass in E101.1 CAI (of close to basaltic composition). For  
274 the Fe-rich minerals and Fe-rich areas we applied two corrections using either Bamble  
275 or Illimaussaq and compared the effects of the corrections. This is illustrated in Fig. S1  
276 where the most hydrogen-rich Fe-rich minerals and Fe-rich areas have similar  
277 composition to the water-rich Fe-poor samples if corrected similarly with Bamble. By  
278 contrast, correction with Illimaussaq yield a systematic offset equal in amplitude to the  
279 Bamble-Illimaussaq difference in alpha in these minerals suggesting that Fe-rich NAMs  
280 behave similarly to Fe-poor samples rather than to Fe-rich hydroxylated silicates.

281 Additionally, terrestrial NAMs yield uncorrected values comparable to Bamble/SW-  
282 DR32-1-1 within error, including the Fe-rich andradite, in line with this observation.

283 A possible explanation would be a different crystallographic control on the mass  
284 fractionation. Indeed the IMF in hydroxylated minerals is controlled by total  
285 electronegativity in the OH octahedral site, which can be approximated by the Fe/Fe+Mg  
286 ratio<sup>29</sup>. But in NAMs such as kirschsteinite, there is no such octahedral site, as H is

287 included mostly as point defects in the crystalline network<sup>17</sup>. We thus suspect that Fe-  
288 rich NAMs such as kirschsteinite are associated with a mass fractionation comparable to  
289 that of Fe-poor minerals. In the absence of a Fe-rich NAM sample with well-documented  
290 D/H ratios, it is not possible to conclude what would be the best correction to apply for  
291 the instrumental mass fractionation. However, either correction does not change our  
292 conclusions, so we use Bamble correction for the main text, as it is the most conservative  
293 in terms of D/H ratio amplitude, and provide results with the alternative correction in  
294 supplementary information (Supplementary Tables 2,3, Supplementary Fig.1).

295

296 *Water content.* To measure water content we used 8 reference minerals with a large  
297 range of water content: Illimaussaq and Bamble amphiboles (1.6 and 2.0 wt% H<sub>2</sub>O,  
298 respectively), SW-DR32-1-1 glass and NAMs, whose H content was determined using  
299 ERDA at the nuclear microprobe at the Laboratoire d'Etude des Elements Légers, CEA,  
300 Saclay, France following analytical procedures described in ref 29. Those include  
301 andradite, grossular and nepheline, which are common CAI alteration minerals. Residual  
302 surface contamination in NanoSIMS was estimated using a San Carlos olivine, which H  
303 content is lower than 30 ppm equivalent H<sub>2</sub>O by weight. To obtain precise H or water  
304 content, the H<sup>-</sup>/O<sup>-</sup> or H<sup>-</sup>/Si<sup>-</sup> ratios are usually measured in SIMS in given minerals to  
305 overcome analytical effects known as matrix effects. Here, given the complexity of the  
306 mineral assemblages in E101.1 xenoliths, their ultra-fine grained and unusual nature, it  
307 has not been possible to overcome these matrix effects. Rather, we established that over  
308 a very large range of content and for silicate matrices reasonably close to those in  
309 E101.1, the H<sup>-</sup> secondary ion signal is proportional to the H content to a first  
310 approximation (Supplementary Fig.7). Assuming a typical background contamination of  
311 about 200 ppm equivalent H<sub>2</sub>O as established previously<sup>13</sup>, the average deviation of the  
312 standards data from the linear regression is ~21%, which indicates that well-known  
313 matrix effects can be ignored provided that the hydrogen content is approximated  
314 within 20% as equivalent water content by weight (Supplementary Fig.7). Note that the  
315 NSH9 pyroxene, which is the only NAM not measured by ERDA and for which we used a  
316 literature value<sup>30</sup>, plots outside the H signal vs H<sub>2</sub>O concentration correlation and was  
317 thus not included in the regression.

318

319 *Validity of the measured D/H ratios.* Given the low D signal of many ROIs, we ensured the  
320 validity of the determined D/H ratios first by comparing the measured D/H ratios with  
321 those of terrestrial reference materials measured in the same session with the same  
322 analytical conditions, including the standard amphiboles and basaltic glass but NAMs of  
323 unknown true D/H ratios as well. Supplementary Fig.8 shows that even at very low  
324 count rates terrestrial references exhibit D/H ratios within the terrestrial range,  
325 whereas the extreme values measured in the E101.1 xenoliths are well outside this  
326 range by several hundreds of per mil and more than  $3\sigma$  uncertainties, indicating with  
327 more than 99.7% confidence that the observed range cannot be an artifact of analytical  
328 origin.

329 Then, we calculated the theoretical uncertainty on a sample having a D/H ratio of  $1.55 \times$   
330  $10^{-4}$  equal to that of the Standard Mean Ocean Water as a function of H intensity. We  
331 included the Poisson counting statistics, the reproducibility on standards and the  
332 reproducibility within a FIB section in the calculation. As visible on Supplementary Fig.9,  
333 the extreme values measured in the E101.1 xenoliths plot well outside the  $3\sigma$  error  
334 envelope indicating again with more than 99.7% confidence that the measured range of  
335 D/H ratios range is not of statistical origin. As a result, we are confident that the  
336 observed variations are indeed indigenous to the samples and cannot be artifacts, in  
337 spite of large uncertainties due to the low D counting rates.

338 Finally, a common issue in the analysis of D/H ratio in meteorites, including by SIMS, is  
339 the contribution of H from organic matter associated with hydrated minerals. This is  
340 usually overcome by measuring simultaneously the D/H and C/H ratios and  
341 extrapolating D/H ratios to C/H=0 (e.g. ref 31). This approach is useful for fine-grained  
342 materials composed of mixtures of phyllosilicates and organics analyzed in bulk (or at  
343 the scale of SIMS analysis). By contrast, here we performed highly localized analysis of  
344 anhydrous minerals in regions devoid of matrix materials and organics, thus ensuring  
345 that the measured D/H ratios are free of organic contributions.

346

347 *Calculations of Rayleigh fractionation.* We compared the amplitude of D-excesses in the  
348 FG-kirschsteinite assemblage with the D-enrichments that could be achieved upon  
349 kinetic fractionation and Rayleigh distillation during H loss. The calculations were  
350 performed for three cases: using the kinetic fractionation factor for H mobility (case of  
351 intra-crystalline H diffusion), for H<sub>2</sub> mobility (evaporation of H as H<sub>2</sub>) and OH mobility

352 (evaporation of H as OH), where the kinetic fractionation factors are  $\alpha = \sqrt{\frac{M_{\text{Dspecies}}}{M_{\text{Hspecies}}}}$   
353 ( $M_{\text{Dspecies}}/M_{\text{Hspecies}}$ ), with M being the molecular mass, i.e.  $\alpha = \sqrt{2}$ ,  $\alpha = \sqrt{3/2}$  and  $\alpha = \sqrt{18/17}$ ,  
354 respectively. The H<sub>2</sub>O case was not evaluated as it is close to the OH case but of  
355 even lower amplitude. Different situations were investigated for each case: (1) differing  
356 initial water content, (2) differing initial D/H ratios and (3) data for Fe-rich  
357 minerals/areas corrected with either Illimaussaq or Bamble amphibole. Apart one  
358 simulation of H<sub>2</sub> loss with unrealistically high initial water content of at least 2.5 wt%,  
359 we found that only H mobility provides a good fit to the data, whereas H<sub>2</sub> loss falls short  
360 to produce the observed D-excesses (Supplementary Fig.10). Therefore the D-excesses  
361 observed in FG-kirschsteinite can be attributed to H mobility upon intra-crystalline  
362 diffusion driven by H loss, independently of the speciation of H in the lost molecule.

363

#### 364 ***Data availability statement***

365 All the data used in the manuscript are presented in the supplementary tables and any  
366 other request or correspondence should be addressed to Jérôme Aléon.

367

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375

#### 376 ***Authors contribution***

377 JA and AAT designed and supervised the study. DL characterized the sample, performed  
378 the NanoSIMS analyses and reduced the data. HB and HK characterized the standards by  
379 ERDA. FB performed SEM imaging of the FIB sections. JA, AAT and DL interpreted the  
380 data. JA and AAT wrote the manuscript with input from all others co-authors.

381

382 The authors declare no competing interests

383

384 Supplementary information is available for this paper.

385

### 386 **Figure Legends**

387 **Figure 1.** Petrographic description of CAI Efremovka 101.1. a. Backscattered electron  
388 image of the whole CAI. Arrows show the sinuous xenolithic fragments. Dashed box :  
389 contour of image in b. b. Detail of a xenolith, backscattered electron image, dashed box :  
390 contour of image in c. c. False color multi-element combined X-ray map showing the  
391 mineralogy of the xenolith. CG kir = coarse-grained kirschsteinite; FG = fine-grained  
392 assemblage; di = Al-diopside; an = anorthite; Fe-åk = Fe-rich åkermanite; wo =  
393 wollastonite; gl = glass.

394

395 **Figure 2.** Distribution of hydrogen isotopic composition shown as  $\delta D$  values as a  
396 function of H<sup>-</sup> secondary ion intensity and equivalent H<sub>2</sub>O content. a. All data. b. data  
397 from the xenoliths only and predictions of D enrichments upon H loss for several  
398 mechanisms. The maximal D-excesses are only matched by intra-crystalline diffusion of  
399 H atoms. Errors are 2 standard errors of the mean. Al, Ti cpx : Al,Ti-rich clinopyroxene.

400

401 **Figure 3.** Comparison between H isotopes and isotopes of other volatile elements in  
402 CAIs and planetary components. a. Comparison between H and O isotopes. b.  
403 Comparison between H and N isotopes. Error bars: 2 standard error of the mean on H  
404 isotopes (this work) and O isotopes<sup>11</sup>. hib/gros CAIs = hibonite-rich and/or grossite-rich  
405 CAIs.

406

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