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Determination of the initial hydrogen isotopic composition of the solar system

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

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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 δD 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 2×10^5 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 objects¹⁻⁵. 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 disks²⁻⁴
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 ratios⁵, but also on other isotopic and chemical
51 properties of early planetary materials⁶. 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 rocks⁷ 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-bodies⁸. 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 chondrite⁹, 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^{10,11}.
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 molten¹¹. 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 imaging¹³, we estimated the H content and measured the H isotopic
79 composition of individual μm -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 μm -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⁻ 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 δD values up to +1000‰ and deficits down to δD values of -850‰ (Fig.
94 2), with δD 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 δD value of ~ 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 (~ 0.5 wt% H_2O) and a δD value of ~ 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 (~ 1.5 μm) relative to the mineral grain
102 size (100 nm to a few μm) 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 δD 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 diopside¹¹ 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 ~ 500 ppm equivalent water (~ 55 ppm H_2), which
120 is surprisingly high, a common observation in meteoritic NAMs^{14,15}. 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 H₂ increases with f_{H_2} (ref 16), which may favor the
123 solubilization of H₂ in clinopyroxene (diopside) and anorthite, as H₂ 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 δD 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 grossular¹⁷, 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 (~ 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 H₂O content up to ~ 3.5 wt% and igneous melilite with H₂O content ≤ 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}O -rich composition,
159 whereas FeO-rich minerals and igneous melilite have a planetary-like ^{16}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^{18,19}. 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‰ ²⁰, while an igneous CAI has a
168 planetary-like composition at $\delta^{15}\text{N} \sim 0\text{‰}$ ²¹. 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 collapsing²². The relationship between N isotopes and
172 heavy metal nucleosynthetic anomalies in iron meteorites²³ 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 system²⁴, rather than being
180 produced in a more evolved protoplanetary disk^{2,3}. 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 plasma²⁵ could be an alternative hypothesis
190 (supplementary discussion) provided it is associated with mass independent
191 fractionation of oxygen²⁶ 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 patterns¹⁰. 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 state¹¹. 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 report¹² 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 (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 nepheline¹¹. 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 μm -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 kirschsteinite-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 wollastonite¹².
218 Veins filled with a Ca-poor amorphous phase crosscut all mineral assemblages from the
219 xenoliths and extend into the host¹² (Supplementary Fig.2). Finally melt pockets up to
220 100 μm 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 μm 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 μm) of 2 μm 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 μm x 8 μm image acquired using a $\sim 1.5 \mu\text{m}$ Cs⁺ beam of 100 pA and 8
237 kV. A 250 pA Cs⁺ beam was rastered over 20 x 20 μm 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 μs /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 standards¹³ (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 correction²⁷.

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 minerals²⁸. 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 ratio²⁹. But in NAMs such as kirschsteinite, there is no such octahedral site, as H is

287 included mostly as point defects in the crystalline network¹⁷. 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% H₂O,
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 H₂O by weight. To obtain precise H or water
304 content, the H⁻/O⁻ or H⁻/Si⁻ 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⁻ 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 H₂O as established previously¹³, 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 value³⁰, plots outside the H signal vs H₂O 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 3σ 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 3σ 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 H₂ mobility (evaporation of H as H₂) 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 H₂O 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 H₂ 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 H₂ 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 δD values as a
396 function of H⁻ secondary ion intensity and equivalent H₂O 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 isotopes¹¹. hib/gros CAIs = hibonite-rich and/or grossite-rich
405 CAIs.

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