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# 1 **Combination of ERDA, FTIR spectroscopy and NanoSIMS for the characterization of** 2 **hydrogen incorporation in natural diamonds**

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12 **Keywords:** ERDA, FTIR, NanoSIMS, Natural diamonds, Hydrogen

## 13 **Highlights.**

- 14 \* Hydrogen is the second major impurity in natural diamonds
- 15 \* ERDA measurements show that natural diamonds contain up to 25 wt. ppm of  
16 hydrogen
- 17 \* Hydrogen content in natural diamonds is not correlated with nitrogen content
- 18 \* Hydrogen content in natural diamonds depends on growth habit
- 19 \* No chemical equilibration of diamonds' hydrogen by diffusion through geological times

## 20 **Abstract.**

21 Hydrogen is a volatile element involved in several geological processes ranging from rock  
22 weakening to the initiation of tectonic plates. Because it is present in diamond, the  
23 investigation of hydrogen content in natural diamonds could provide valuable information.  
24 Such studies are scarce despite hydrogen being among the main impurities in their structure.  
25 Using Elastic Recoil Detection Analysis, Fourier Transform Infrared spectroscopy and  
26 Nanoscale Secondary Ions Mass Spectrometry, we analyzed the incorporation of hydrogen in  
27 three diamonds growth habits: octahedral, cuboid and fibrous. Up to 25 wt. ppm of hydrogen  
28 was measured in some samples, placing hydrogen as the second most abundant impurity in  
29 natural diamonds after nitrogen and before boron. Comparison between the three methods  
30 indicates a difference in the main mode of hydrogen incorporation depending on the growth  
31 habit. Hydrogen is more readily incorporated in the fibrous and cuboid habits compared to the  
32 octahedral one. We also show that the incorporation of hydrogen is not correlated with the  
33 incorporation of nitrogen. Results suggest no chemical equilibration of hydrogen by diffusion  
34 through geological times and also confirm that not all hydrogen may be infrared active.

## 35 **1. Introduction.**

36 Natural diamonds are the deepest geological samples which formation occurs at depth from  
37 150 to more than 800 km [1]. They contain a large wealth of information about the Earth  
38 mantle, either through their crystalline structure [2] or the fluid and mineral inclusions  
39 encapsulated inside [1], making them unique witnesses of the deep Earth interior and of its  
40 history. Hydrogen (H) is among the most abundant impurities in natural diamonds along with  
41 nitrogen [3,4] and boron [5]. The presence of H plays an important role in several geological  
42 processes that take place in its interior: from weakening the structure of rocks and minerals  
43 [6,7] to the possible initiation of tectonic plates [8–10]. Studies on the incorporation of H in

44 minerals have proposed the existence of a cycle within the Earth interior and that a significant  
45 amount of H is stored in the deep Earth [11,12]. Characterizing the incorporation of H in natural  
46 diamonds and their inclusions constitutes an indirect way to study its cycle in the deep Earth  
47 (from the lithosphere to the core-mantle boundary) and thus helps at understanding the  
48 geological processes that led to the evolution of our planet. How H is incorporated and  
49 distributed in natural or synthetic diamonds is also crucial in gemology since it changes the  
50 color of the gem[13] but also in material sciences since H is a poison in high-tech diamonds  
51 applications [14].

52 Aside from a few pioneer studies [15–19], the total H content of natural diamonds has not  
53 been studied much. The quantity of incorporated H, although suggested to go from a few up  
54 to 4000 at. ppm (338 wt. ppm) [18,20], is still not precisely known. For the past two decades  
55 or so, H content in natural diamonds has mainly been studied using Fourier Transform Infrared  
56 (FTIR) spectroscopy. The presence of H leads to a series of infrared active defects as  
57 indicated by the numerous absorption bands [21,22]. The height (or area) of the band at 3107  
58  $\text{cm}^{-1}$ , considered as the major absorption band and related to a C–H bond in the  $\text{N}_3\text{VH}$  defect  
59 [23,24], is used to estimate if a diamond is “H rich” [25]. Real quantification, however, is not  
60 possible due to the lack of knowledge of the absorption coefficient of each H related absorption  
61 band. FTIR is also limited because of its dependence on the structure of the H related defects.  
62 It was also conjectured that not all H is infrared active [18], making any quantification using  
63 FTIR highly questionable.

64 Elastic Recoil Detection Analysis (ERDA), an ion beam analysis technique already applied to  
65 a wide range of materials, can be used to quantify the H content in natural diamonds. Contrarily  
66 to FTIR, ERDA is a speciation and calibration independent technique, allowing the absolute  
67 quantification of H [26]. The technique has been greatly improved in term for spatial resolution  
68 [26,27], allowing its application on geological samples such as nominally anhydrous minerals  
69 (NAMs) [28,29], silicates glasses [30,31] and metallic phases [30,32]. ERDA is also routinely  
70 employed to calculate the absorption coefficient of water related infrared absorption bands in  
71 NAMs [31,33] or to obtain the standards needed for the quantification in Secondary Ions Mass  
72 Spectrometry (SIMS) [34–36]. We present here the combined use of ERDA, FTIR and  
73 NanoSIMS for the characterization of H in natural monocrystalline diamonds of octahedral,  
74 fibrous and cuboid growths. The absolute H content was measured in various areas of the  
75 samples using ERDA and compared to H-related absorption bands to evaluate its infrared  
76 active proportion. NanoSIMS was used to check the homogeneity of H distribution at the  
77 microscale. Finally, we compared results of each method to determine if the amount of H and  
78 its mode of incorporation changes among the three growth habits.

## 79 **2. Materials and Methods.**

### 80 **2.1. Analyzed samples.**

81 For this study, we choose samples among the most common types of diamonds found in  
82 nature [37].

83 These four natural type Ia diamonds exhibit three different growths: octahedral, fibrous and  
84 cuboid (Figure S1). They are (1) two monocrystalline octahedral diamonds (PCS6, VEN03),  
85 which are typical of natural diamonds from lithospheric cratons (2) one coated diamond  
86 (CART11), having an octahedral core surrounded by a fibrous diamond rim, fibrous diamonds  
87 consisting of microscopic parallel fibers; (3) and one asteriated diamond (ASTER) presenting  
88 the association of octahedral sectors together with cuboid sectors which are well known to  
89 contain detectable and possibly significant amounts of hydrogen [38].

90 PSC6 is a commercial diamond window from Almax EasyLab, while ASTER is a mirror  
91 polished asteriated diamond from Marange alluvial deposits in Zimbabwe. Asteriated  
92 diamonds are characterized by the simultaneous growth of the octahedral and cuboid sectors  
93 [38], which appear transparent and grey respectively (Figure S1). CART11 is a coated diamond  
94 from Democratic Republic of Congo. VEN03 is a monocrystalline octahedral rough diamond  
95 from the alluvial deposit in Santa Elena de Uairén in Venezuela which we polished using an  
96 Ion Beam Milling System at -120°C following the protocol described previously [39] to expose  
97 one of its olivine inclusions. All samples were carbon coated for the ERDA and CART11 was  
98 also gold coated for the NanoSIMS analysis.

## 99 2.2. Elastic Recoil Detection Analysis.

100 The total H contents of each diamond were determined by ERDA using the nuclear microprobe  
101 at the Laboratoire d'Etude des Elements Légers (LEEL) in CEA Saclay, France [40]. A detailed  
102 description of the followed analytical procedure can be found in the literature [26,27]. In brief,  
103 a 2.8 MeV, 500 pA  $^4\text{He}^+$  ion beam was focused to  $2 \times 2 \mu\text{m}^2$  and raster scanned to  $200 \times 200$   
104  $\mu\text{m}^2$  on samples' surface. An 11  $\mu\text{m}$  thick aluminum foil is placed in front of the ERDA detector  
105 to stop the transmission of forward scattered  $^4\text{He}^+$  particles. The resulting investigated depth  
106 is of 215 nm. The experimental setup permits to conduct simultaneously Rutherford  
107 Backscattering (RBS), used to monitor the elemental composition and the total deposited  
108 charge. Solid angles for both RBS and ERDA detectors were measured using a set of  
109 standards ( $\text{Al}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{FeS}_2$ ,  $\text{SiO}_2$  and Zr for RBS; Kapton ( $\text{C}_{22}\text{H}_{10}\text{O}_5\text{N}_2$ ), plus two glass  
110 standards: 2πD45 [41] and STR10 [26] for ERDA). ERDA and RBS spectra were acquired  
111 during 3600 or 7200 s and measurements were conducted on various areas of each sample.  
112 We evaluated the detection limit using the residual ERDA signal from a nominally anhydrous  
113 San Carlos olivine (0.16 wt. ppm H [42], Figures S2). Transposed to a diamond matrix, this  
114 detection limit is 6 wt. ppm. H content. Uncertainties take into account the Poisson statistical  
115 counting contribution and those originating from spectrum energy calibration, measured RBS  
116 and ERDA solid angles and tilt angle of the sample holder [27]. RBS and ERDA spectra were  
117 processed using the modeling software SIMNRA [43].

## 118 2.3. Fourier Transform Infrared spectroscopy.

119 Infrared analyses were made using a Nicolet 6700 (ThermoFisher) IR spectrometer equipped  
120 with an IR-Plan microscope at the spectroscopic platform of the Institut de Minéralogie, de  
121 Physique des Matériaux et de Cosmochimie (IMPMC) at Sorbonne Université, France. A  
122 spectrum was recorded at each ERDA mark between 400 and 7000  $\text{cm}^{-1}$  in transmission mode  
123 with an aperture of  $100 \times 100 \mu\text{m}^2$ . 128 scans were collected for each spectrum with a spectral  
124 resolution of 4  $\text{cm}^{-1}$ . We used the DiaMap and DiaMapFluid Excel spreadsheets [44] to  
125 calculate the height of selected H related absorption bands and determine the total nitrogen  
126 content of each sample.

## 127 2.4. Nanoscale Secondary Ions Mass Spectrometry.

128 H contents were determined by NanoSIMS. Measurements were conducted on the Cameca  
129 NanoSIMS 50 installed at Muséum National d'Histoire Naturelle (MNHN) in Paris, France to  
130 check the homogeneity of H distribution at the microscale. Secondary ions of  $^{12}\text{C}^-$ ,  $\text{H}^{12}\text{C}^-$ ,  
131  $^{12}\text{C}^{12}\text{C}^-$  and  $^{13}\text{C}^{12}\text{C}^-$  were collected by electron multipliers in multicollection mode to obtain H  
132 contents. The calibration needed for quantification was made of a set of diamond standards  
133 whose H content was determined by ERDA: a type Ia natural diamond (15 wt. ppm) and a  
134 synthetic type IIa diamond (13 wt. ppm) [45], and an implanted type Ia natural diamond (70  
135 wt. ppm). The primary  $\text{Cs}^+$  beam was set to 1 pA and was scanned over a surface area of  $5 \times$   
136  $5 \mu\text{m}^2$ . To avoid surface contamination, only ions from the inner  $2 \times 2 \mu\text{m}^2$  region were

137 collected with the “beam blanking mode”. Each analysis consisted in a stack of 100 cycles,  
 138 with each stack lasting 4.096 s. Mass resolving power was set at minimum 9000, enough to  
 139 resolve interferences on measured secondary ions. Before each analysis, a  $7 \times 7 \mu\text{m}^2$  surface  
 140 area was initially pre-sputtered for 300 s with a 250 pA primary  $\text{Cs}^+$  rastering beam, in order  
 141 to remove the gold coating and reach a sputtering steady-state [46]. AFM measurements show  
 142 that the depth investigated is of about 120 nm. An electron flooding gun was used for charge  
 143 compensation at the surface of the sample to improve the secondary ions emission.

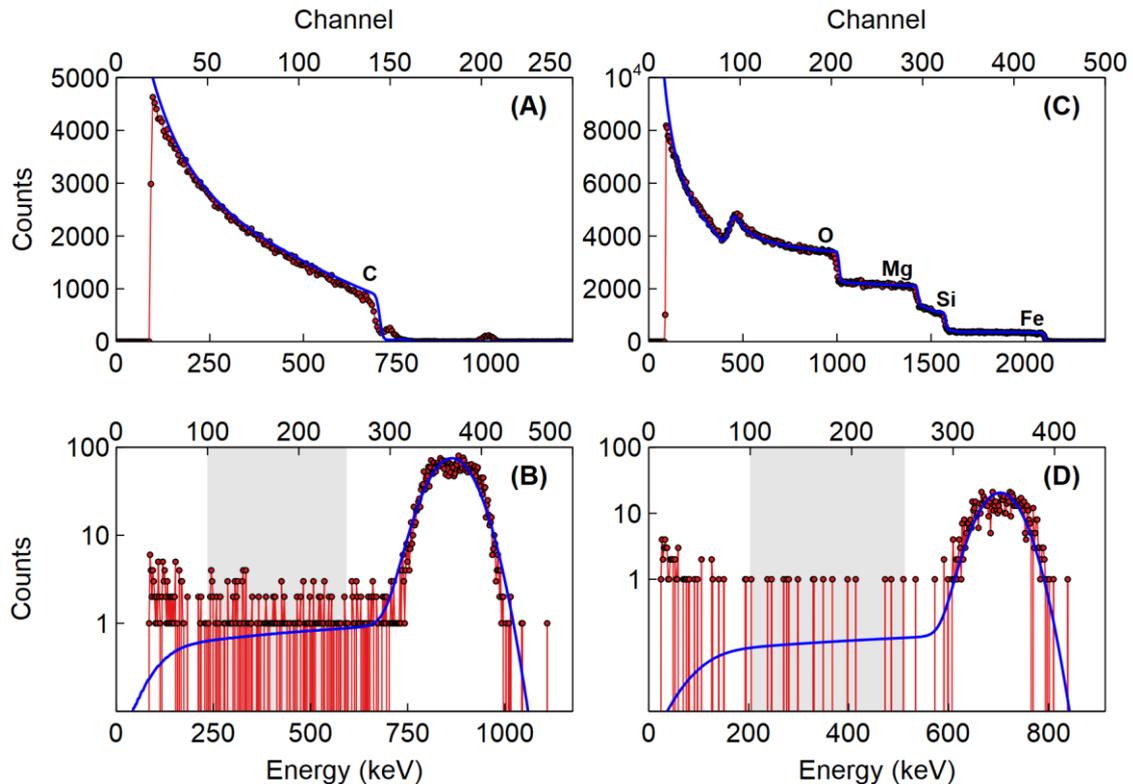
### 144 3. Results.

#### 145 3.1. ERDA and NanoSIMS results.

146 ERDA results are exemplified in Figure 1, which displays the RBS (1A, 1C) and ERDA (1B,  
 147 1D) spectra of one analyzed region of ASTER and the olivine inclusion of VEN03. Two  
 148 contributions can be seen on the ERDA spectra (Figures 1B, 1D): (1) the large peak at high  
 149 energy due to the H surface contamination; (2) the counts at lower energies coming from the  
 150 H situated deeper in the sample. The grey region on the ERDA spectra indicates the region of  
 151 interest used to evaluate the H content in each analyzed region.

152 **Table 1.** Results of ERDA, NanoSIMS and FTIR analyses.

Sample	Probed region	H content (ERDA, wt. ppm)	H content (NanoSIMS, wt. ppm)	H peaks height (FTIR, $\text{cm}^{-1}$ )	Fluid inclusions H content (FTIR, wt. ppm)	N content (FTIR, wt. ppm)
PSC6	Octahedral	5 – 9	-	0.01 – 0.07	-	1370 – 1470
VEN03	Octahedral	5 – 9	-	0.10 – 0.20	-	1020 – 1120
	Olivine incl.	8	-	-	-	-
ASTER	Cuboid	16 – 21	-	40.0 – 50.0	-	1990 – 2320
	Octahedral	5 – 12	-	4.0 – 8.0	-	3080 – 3280
CART11	Fibrous	12 – 23	10 – 14	1.5 – 2.0	5 – 15	1250 – 1390
	Octahedral	5 – 9	8 – 11	0.10 – 1.5	-	1120 – 1440



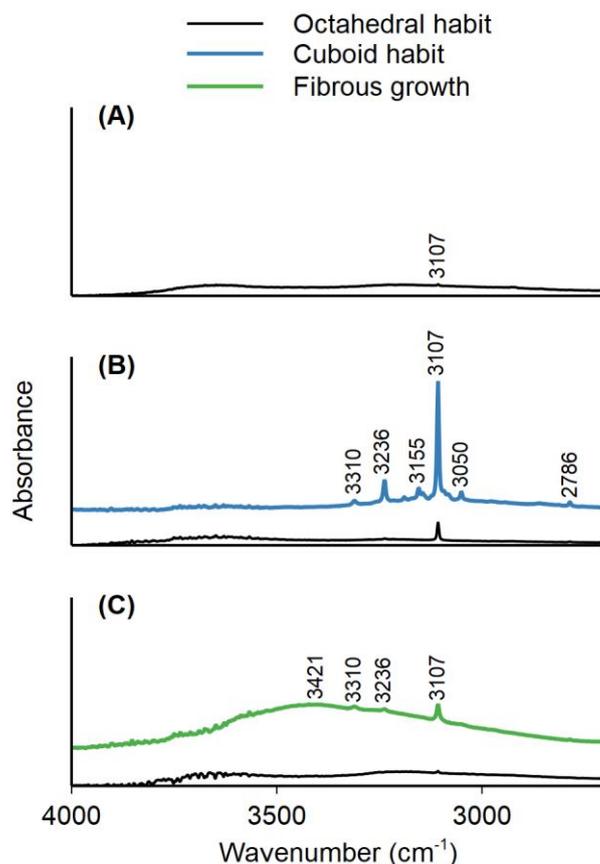
154 **Figure 1.** (A) RBS and (B) ERDA spectra of the cuboid sector of ASTER. (C) RBS and (D) ERDA  
 155 spectra of the olivine inclusion of VEN03. The counts are given in logarithmic scale. The simulated  
 156 spectra (blue) represent the fit of the experimental spectra (red).

157 With ERDA, the highest H contents were measured in the cuboid growth of ASTER and the  
 158 fibrous growth of CARTI1 with values ranging from 12 to 23 wt. ppm (Table 1). The H contents  
 159 of the octahedral growth of each diamond was significantly lower: CARTI1, PSC6 and VEN03  
 160 contained between 5 to 9 wt. ppm of total H while the values for ASTER were slightly higher,  
 161 going up to 12 wt. ppm (Table 1). We also determined the H content of the olivine inclusion of  
 162 VEN03 (Figure 1), which contained 8 wt. ppm. The H contents measured by NanoSIMS for  
 163 CARTI1 ranged from 8 to 11 wt. ppm for the octahedral habits and from 11 to 14 wt. ppm for  
 164 the fibrous habit (Table 1). The relative error was of 10–20% for ERDA and of 3–5% for  
 165 NanoSIMS (Tables S2 and S8).

### 166 3.2. FTIR results.

167 We identified four kinds of FTIR spectra: two for the octahedral growth habits, one for the  
 168 cuboid sector of ASTER and another for the fibrous sector of CARTI1 (Figure 2). In the case  
 169 of the octahedral growth, the absorption of the hydrogen related features was so weak that  
 170 either none could be detected or only the line at 3107  $\text{cm}^{-1}$  could be seen. Contrarily, the FTIR  
 171 spectrum of the cuboid sector of ASTER is characterized by several absorption bands related  
 172 to the presence of H. Among them are the bands related to the  $\text{N}_3\text{VH}$  defect [24] at 1405, 2786  
 173 and 3107  $\text{cm}^{-1}$ . Other bands identified in the literature [21,22] are also present at 3050, 3124,  
 174 3145, 3155, 3236, 3190 and 3310  $\text{cm}^{-1}$ . Lastly, the FTIR spectrum of the fibrous sector of  
 175 CARTI1 is characterized by the presence of three thin and relatively low in intensity bands at  
 176 3107, 3236 and 3310  $\text{cm}^{-1}$  but also by two much broader bands at 1642 and 3421  $\text{cm}^{-1}$  (Figure  
 177 2C, Figure S10). The last two bands are respectively associated to the H–O–H bending and  
 178 the O–H stretching which indicates the presence of water in the fibrous sector of CARTI1 [47].  
 179 We calculated up to 15 wt. ppm of hydrogen in the water detected in the fibrous sector of

180 CARTI1 using the absorption coefficient leading to the highest value in DiaMapFluid (87  
181 AU.L.mol<sup>-1</sup>.cm<sup>-1</sup>) [48].



182

183 **Figure 2.** FTIR spectra of the H-related absorption region for the different growths of (A) VEN03, (B)  
184 ASTER and (C) CARTI1. Black line: Octahedral habit. Blue line: Cuboid habit. Green line: fibrous habit.  
185 The full FTIR spectra can be found in the supporting information (Figure S10).

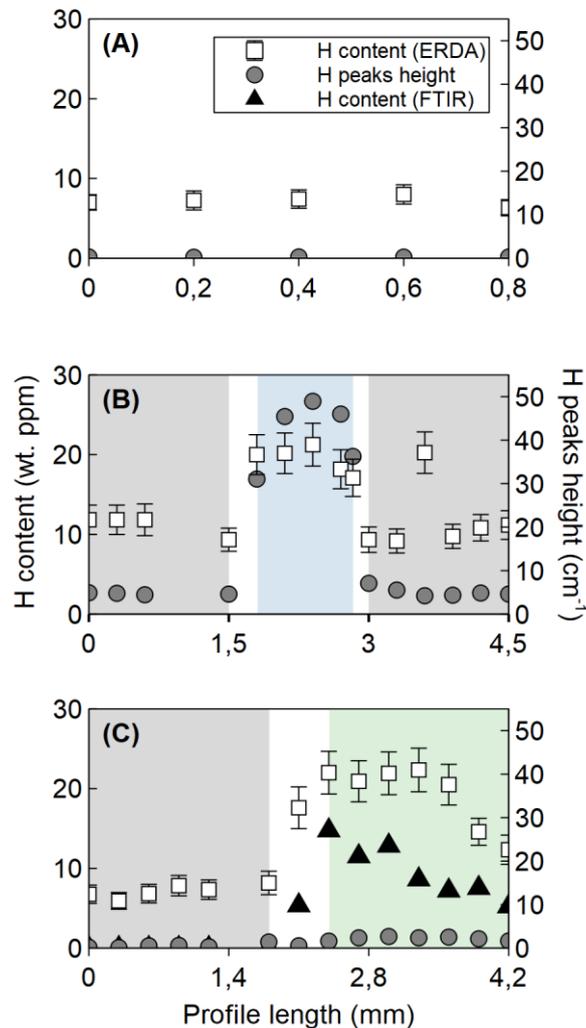
186 The highest values were measured in ASTER with values ranging from 40 to 50 cm<sup>-1</sup> for the  
187 cuboid growth and values ranging from 4 to 8 cm<sup>-1</sup> for the octahedral one (Table 1). The lowest  
188 values came from the octahedral habits of CARTI1, PSC6 and VEN03 and ranged from nearly  
189 zero to 1.5 cm<sup>-1</sup> (Table 1).

190 Each octahedral growth had a different N content. The highest values were measured in the  
191 octahedral and cuboid sectors of ASTER with values ranging from 3080 to 3280 wt. ppm and  
192 1990 to 2320 wt. ppm, respectively. We measured between 1020 and 1120 wt. ppm for  
193 VEN03, between 1370 and 1470 wt. ppm for PSC6. Finally, we measured between 1120 and  
194 1440 wt. ppm of nitrogen for the octahedral core of CARTI1 and between 1250 and 1390 wt.  
195 ppm for its fibrous coat.

196 3.3. Comparison between ERDA and FTIR results.

197 Despite the lack of any H-related IR absorption band for PSC6 (Figure S10A), its H content  
198 (from ERDA) is almost identical to the values for the octahedral sector of CARTI1 and VEN03  
199 which both display the 3107 cm<sup>-1</sup> absorption band. The octahedral sector of ASTER shows a  
200 much higher absorption band at 3107 cm<sup>-1</sup> than the other octahedral growths and is also  
201 associated to a higher H content. Both the cuboid growth of ASTER and the fibrous growth of

202 CARTI1 show the highest H content of all growths but the H peaks height of ASTER is almost  
 203 twenty times higher than in CARTI1.



204

205 **Figure 3.** Profile of the total H content (ERDA, white squares), H peaks height (FTIR, grey circles) and  
 206 H content of water (FTIR, black triangles) in (A) VEN03, (B) ASTER and (C) CARTI1. Grey region:  
 207 Octahedral habit. Blue region: Cuboid growth (ASTER). Green region: Fibrous growth (CARTI1). The  
 208 high H content value in the octahedral sector of ASTER is due to the presence of a fracture on the  
 209 analyzed area. Additional profiles made in ASTER can be found in the supporting information (Figure  
 210 S11).

211 For ASTER, the H content and the H FTIR peaks height of its octahedral sector are much  
 212 higher than in the octahedral growth of any other diamond. When passing to the cuboid sector,  
 213 these values increase with the H content almost doubling (from 10 to 20 wt. ppm, Figure 3)  
 214 while the H peaks height is multiplied by ten (from 5 to 50 cm<sup>-1</sup>, Figure 3B).

215 In the case of CARTI1, the FTIR profile of the octahedral sector is similar to VEN03's with a  
 216 low (if not almost absent) H peaks height associated to a H content of 5–8 wt. ppm (Figure  
 217 3A, 3C). Within the fibrous sector, the ERDA and FTIR results branch out. The H content  
 218 reaches values up to 23 wt. ppm while the H peaks height goes up to 2 cm<sup>-1</sup>, which remains  
 219 lower than the octahedral sector of ASTER. Because of the presence of water on the FTIR  
 220 spectrum of the fibrous growth of CARTI1, we also plotted a profile comparing the distribution  
 221 of the H content measured by ERDA and the one measured from FTIR for fluid inclusions

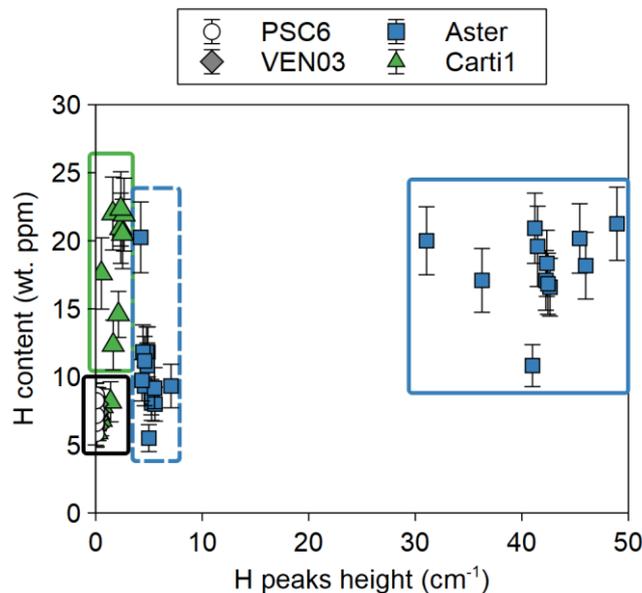
222 (Figure 3). The profiles in the fibrous habit are similar, the one from FTIR exhibiting lower  
223 values.

## 224 4. Discussion

225

226 4.1. Relationship between H content and H peaks height.

227 The absence of correlation between the values obtained by both methods, as highlighted by  
228 Figure 4, confirms what was hypothesized by the only other study[49] comparing ERDA and  
229 FTIR results. Not all H measured by ERDA comes from infrared active defects. Consequently,  
230 we classified each growth in four categories: A “low H” group (octahedral growth of CARTI1,  
231 PSC6 and VEN03); A “high H” group (cuboid sector of ASTER); An “intermediate H” group  
232 (octahedral sector of ASTER); A “high water” content group (fibrous sector of CARTI1).



233

234 **Figure 4.** Comparison of the H peaks height measured by FTIR and the total hydrogen content  
235 measured by ERDA. The lack of correlation highlights that not all H in diamonds is IR active. Each  
236 growth habit can be classified in distinct categories based on H distribution (see text). For the asteriated  
237 diamond, the bold blue line is corresponding to the cuboid sector when the dashed blue lines is  
238 corresponding to the octahedral one. For the coated diamond, the dark bold line octahedral is  
239 corresponding to the octahedral core when the green bold line is corresponding to the fibrous rim.

240 4.2. H incorporation in monocrystalline octahedral and cuboid growths.

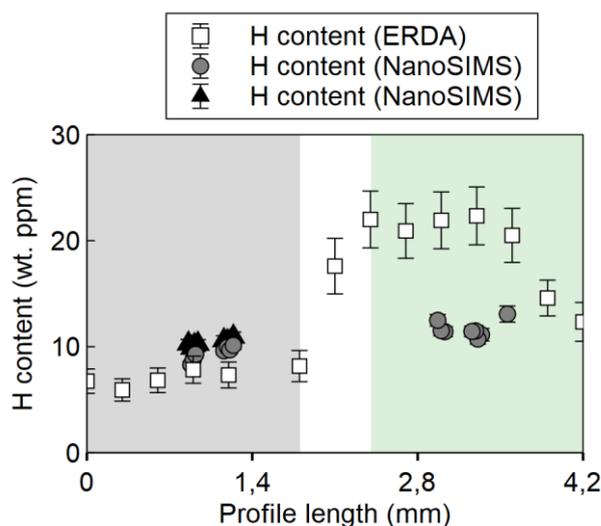
241 Since PSC6 is a commercial diamond window, we do not have any information on its  
242 preparation conditions. We do suspect that the original diamond was laser cut which could  
243 have removed some of, if not all, the H in the sample during the preparation. However, PSC6  
244 shows the same range of H content values as VEN03 who was cryo-polished to preserve the  
245 H in the diamond and in the inclusion. This could mean that the sample preparation, whether  
246 it is laser cutting or ion beam milling, does not affect the H within the sample.

247 The octahedral sector of ASTER is different from the other octahedral growths since its H  
248 content and its summed H peaks height are higher. The same observation can be applied to  
249 its cuboid sector which shows a combination of the highest H content and summed H peaks  
250 height measured in any diamond of this study. The difference of H incorporation between the  
251 octahedral and cuboid sectors has already been observed in previous studies on asteriated  
252 diamonds [38,51,52]. Since most analyses were conducted using optical techniques such as

253 UV-Vis or FTIR spectroscopies, there was no information on whether this observation could  
254 also be applied to the total H content. Our results confirm that the cuboid sectors incorporate  
255 more H than the octahedral ones. More specifically, H seems to be far more incorporated as  
256 infrared active defects in the cuboid growth than the octahedral one. It has been hypothesized  
257 that kinetics could be the main driving force behind the different growth habits of diamonds,  
258 with the cuboid sector growing much faster than the octahedral one [53]. The reason behind  
259 the simultaneous growth of these two habits in asteriated diamonds is still unknown, although  
260 H might be playing an important role based on the difference of incorporation between the  
261 cuboid and octahedral habits.

#### 262 4.3. H incorporation in fibrous growths.

263 The low H peaks height combined with the presence of water related absorption bands on the  
264 FTIR spectrum of the fibrous habit of CARTI1 hinted an additional contribution from the fluid  
265 inclusions to the H content (Figure 3). Fibrous diamonds are known to contain a high density  
266 of inclusions between their fibers. These inclusions, either fluid or solid, are usually composed  
267 of a mix of a hydrous saline, a silicic and a carbonatitic endmembers [54]. The fibrous habit is  
268 also believed to grow much faster than the monocrystalline cuboid habit, which often leads to  
269 the encapsulation of their growth medium (fluids or melts) as inclusions [55]. Studies on the  
270 micro-fluid inclusions in natural diamonds associate the simultaneous presence of the bands  
271 around  $1600\text{ cm}^{-1}$  (H–O–H bending) and  $3400\text{ cm}^{-1}$  (O–H stretching) to the presence of water  
272 molecules, indicating that the fibrous inclusions in the fibrous coat of CARTI1 are mostly water.



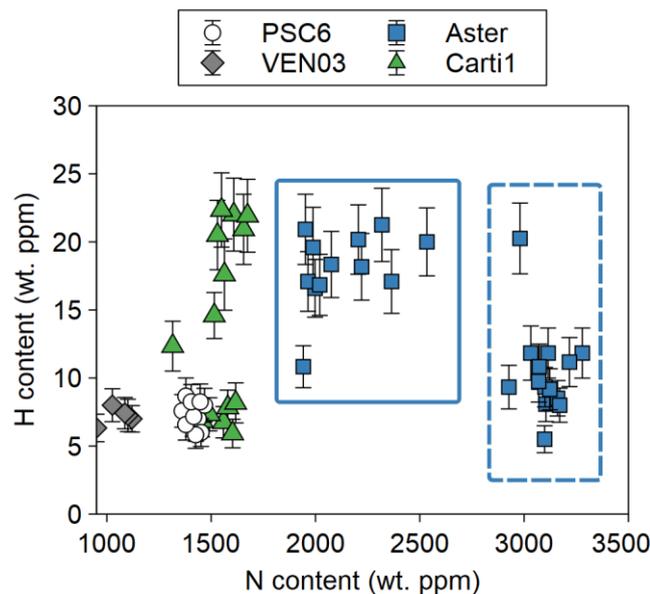
273  
274 **Figure 5.** Profile of the total H content measured by ERDA (white squares) and NanoSIMS (grey circle,  
275 black triangles) in the octahedral (grey region) and the fibrous sectors (green region) of CARTI1. Grey  
276 circles represent analyses made on top of ERDA spots while black triangles represent analyses made  
277 next to ERDA spots.

278 In Figure 3C, we observed that H contents measured by ERDA is higher than measured by  
279 FTIR (related to fluid inclusions). This suggests that fibrous diamond matrix also contains H.  
280 This is confirmed when comparing the H contents measured by ERDA and NanoSIMS (Figure  
281 5). Whereas the H contents in the octahedral sector are similar for both methods, those  
282 measured in the fibrous coat are smaller in NanoSIMS than in ERDA (Figure 5, Table 1). Since  
283 NanoSIMS probes about 120 nm, most of the fluid inclusions are eroded during the pre-  
284 sputtering step preceding the analysis. Hence, a major part of H from the fluid inclusions is  
285 lost before acquisition and the detected H can be attributed to the fibrous matrix itself. For this  
286 diamond, the H content of the fibrous sector seems to be a little higher than in the octahedral  
287 one.

288 Comparison between ERDA, FTIR and NanoSIMS suggests that the distribution of H within  
289 one sector is homogeneous at the micrometer scale.

#### 290 4.4. Relationship between H and N.

291 Nitrogen, which defines type I diamonds, has already been thoroughly studied in the past [50].  
292 From DFT calculation studies, it is proposed that H is mainly located in the N<sub>3</sub>VH defect [24].  
293 This would suggest a strong relationship between N and H incorporation in diamond. However,  
294 no correlation is observed between H and N contents of the series of diamonds analyzed in  
295 the present study (Fig. 6). Even for octahedral diamonds PSC6, VEN03 and the core of the  
296 coated diamond CARTI, where the H contents are similar, the N contents significantly differ.  
297 We observed less nitrogen in the cuboid sector of ASTER than in the octahedral one.



298 **Figure 6.** Comparison of the total N content measured by FTIR and the total H content measured by  
299 ERDA. The lack of correlation highlights/hints that there is not any relation between H and N. Two  
300 domains are observed in the asteriated diamond corresponding to octahedral (bold blue line) and cuboid  
301 (dashed blue line) sectors.

#### 302 4.5. H incorporation in natural diamonds and implication for its cycle in the deep Earth.

303 Other than H, natural diamonds incorporate nitrogen and boron as major elemental impurities.  
304 With a content that can reach up to a few thousand wt. ppm, nitrogen is considered as the  
305 main impurity in natural diamonds. Boron on the other hand, which defines type IIb diamonds  
306 is shown to reach up to 10 wt. ppm [5]. With a range of measured values between 5 and 25  
307 wt. ppm, H places itself as the second most abundant impurity in natural diamonds. These  
308 values are much lower than the observed few hundreds wt. ppm estimated by Nuclear  
309 Reaction Analysis [20]. Taking into account these values would mean that the amount of H  
310 incorporated into natural diamonds might vary in a larger range, but still below the range  
311 observed for N.

312 Another notable feature is the H content of asteriated diamonds, highest in the cuboid sector  
313 than the octahedral one, as also observed for N [38] which would imply that the incorporation  
314 of N and H is not dependent of the common parent fluid composition for the two simultaneously  
315 grown sectors.

316 H being the smallest element of the periodic table is assumed to diffuse fast in every material  
317 it is incorporated into, natural diamonds included. If H did diffuse as fast as claimed [56], then

318 ASTER would not have kept this notable difference between its two growth sectors during a  
319 long time of residence deep in the mantle. Instead, H would have been re-equilibrated in the  
320 diamond. The significant difference between the growth sectors of ASTER indicates the  
321 opposite. This lack of re-equilibration could be explained by H being inserted in energetically  
322 favorable centers, like a covalent C–H bond. We propose that the H distribution in natural  
323 diamonds has been preserved since their formation.

324 Studying the H content of diamond inclusions is crucial since, compared to mantle xenoliths  
325 whose H content was modified during their ascent to the surface [28], they are preserved by  
326 their host. These inclusions can be analyzed by FTIR [57,58]. With ERDA, it is possible to  
327 simultaneously determine the H content of the inclusion and the diamond which allows, in the  
328 case of syngenetic inclusions, the determination of a partition coefficient. Hydrogen  
329 incorporation in natural diamonds may be dependent on several factors during the growth  
330 (composition of the parent fluids or melts, growth rate, depth and environment of growth such  
331 as redox conditions). Diamonds form in fluids or melts which can be water-rich as seen in the  
332 fibrous habit of CART11 [47] and as also shown in many experimental studies [59], and thus  
333 can be considered as a reliable way to study the cycle of H in the deep Earth. All these factors  
334 should be considered to better understand how hydrogen incorporates itself in natural  
335 diamond and, thus, in the mantle.

## 336 **5. Conclusion.**

337 Through the combination of ERDA, FTIR and NanoSIMS, we acquired a better understanding  
338 of how H incorporates into diamonds. While ERDA is sufficient on its own and gives us the  
339 total H content in diamonds, FTIR cannot be used for quantification since not all H is infrared  
340 active. Each method has however its advantages: with ERDA, it is possible to quantify H in  
341 the diamond and its inclusions (fluid or mineral) at the same time. NanoSIMS measurements  
342 gives access to the H content at the microscale of the fibrous diamonds with little to no  
343 contamination from the fluid inclusions, which nature and content can be determined with  
344 FTIR, and witnesses for the homogeneous repartition of H within a same sector.

345 The current range of measured H content in natural diamonds varies from 5 to 25 wt. ppm,  
346 making it the second most abundant impurity incorporated in their structure after nitrogen and  
347 before boron. There seem to be no relationships between the incorporation of H and N in the  
348 diamond lattice. The quantity of H and its main mode of incorporation change with the diamond  
349 growth habit. Within the analyzed samples, the cuboid growth contained the highest amount  
350 of H, followed by the fibrous and the octahedral growths. H is mostly incorporated as infrared  
351 inactive defects in octahedral habits while it is mostly found in active defects in the cuboid  
352 ones. In case of the fibrous habit, a part of the H was incorporated in H containing defects  
353 while the other came from aqueous fluids inclusions embedded between the diamond fibers.  
354 Since there is not much known about the proportion of the infrared inactive defects, FTIR  
355 cannot be used for H absolute quantification.

356 Natural diamonds can be used to probe the cycle of H in the deep Earth. Our results suggest  
357 that H does not re-equilibrate in the lattice during its time of residence in the mantle, as seen  
358 by the significant difference of distribution between the two growth sectors of the asteriated  
359 diamond. Fluid inclusions in fibrous diamonds give a direct insight on the composition of their  
360 growth medium, which can be rich in water. Since natural diamonds are the only preserved  
361 geological samples that come from the deepest parts of the planet interior, measuring their  
362 total H content (diamond and inclusions) will help us better constrain its distribution in the deep  
363 Earth.

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