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1 **Significance of H<sub>2</sub> and CO release during thermal treatment of natural**  
2 **phyllosilicate-rich rocks**

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5

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13

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15

16 **Keywords:** natural hydrogen, hydrogen isotope, dehydrogenation, chlorite, talc

17

18 **Highlights**

- 19
- 20 • H<sub>2</sub> is produced by dehydrogenation of Fe-poor phyllosilicates
  - 21 • H<sub>2</sub> produced by dehydrogenation has very low δD values
  - 22 • Large mineral-H<sub>2</sub> hydrogen isotope fractionations are induced by dehydrogenation
  - 23 • Dehydrogenation is a potential H<sub>2</sub> source term in the hydrogen geochemical cycle
- 24

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26

27

28 **Abstract**

29 Phyllosilicates may trap hydrogen (H<sub>2</sub>) in the crust, but they may also produce it  
30 through various processes, including oxidative dehydrogenation. The dehydrogenation  
31 temperature depends on the type and composition of the phyllosilicates considered, but it may  
32 be as low as 300 °C. Here, we document the release of H<sub>2</sub> and CO during thermal treatment of  
33 chloritite (300 °C) and talc (500 °C) from the Trimouns deposits (Eastern Pyrenees, France).  
34 Thermal release of gases coupled to stable isotope analysis has been used to recover and  
35 characterize H<sub>2</sub> and CO, the two detected gases. Hydrogen content may be as high as 7 ppm  
36 with δD<sub>H<sub>2</sub></sub> values ranging from -258 ‰ to -224 ‰ for sub-pure chloritite and -140 ‰ for pure  
talc. CO content ranges between 3 ppm and 35.3 ppm with very homogeneous δ<sup>13</sup>C<sub>CO</sub> values  
between -27.6 ‰ and -25.7 ‰. This study supports the idea that H<sub>2</sub> was produced during

37 experiments by dehydrogenation. The origin of CO remains enigmatic, but its carbon isotope  
38 composition suggests a link to the few amounts of graphite documented in chloritite and talc  
39 from the deposit. This work also reports extensive hydrogen isotope fractionation between H<sub>2</sub>  
40 produced by dehydrogenation and both talc and chloritite. Dehydrogenation of phyllosilicates  
41 is a potential source term of H<sub>2</sub> in numerous magmatic-hydrothermal settings and must thus be  
42 accounted for in the budget of the H<sub>2</sub> geochemical cycle.

43

44

## 45 **1. Introduction**

46

47 Recent investigations have demonstrated that phyllosilicates are excellent traps for  
48 gaseous species migrating in the Earth's crust. Entrapment of CH<sub>4</sub> or CO<sub>2</sub> by phyllosilicates is  
49 already well documented in the context of shale gas exploration, CO<sub>2</sub> sequestration, and nuclear  
50 waste storage (Busch et al., 2016; Klewiah et al., 2020; Sanz et al., 1983; Ziemiański et al.,  
51 2020). High H<sub>2</sub> contents (up to 500 ppm) have been recently reported in clay-rich rock  
52 surrounding the Cigar Lake U-ore deposit in Canada (Truche et al., 2018). In this latter case,  
53 H<sub>2</sub> was released sequentially within minutes after thermal heating of the samples within the 80  
54 – 300 °C temperature window.

55 For this study, the first intention was to study the paleo-gas(es) entrapped or adsorbed in  
56 talc and chloritite from the Trimouns deposit (France). In this area, hydrothermal fluids could  
57 have been enriched in H<sub>2</sub>, CH<sub>4</sub>, and CO as lherzolites are serpentinized in the talc deposit  
58 surroundings. This work proposes quantifying and measuring the stable isotope composition of  
59 gases released during the heating of natural chloritite and talc samples from the Trimouns  
60 deposit (Pyrenees, France) and discussing their origin and geological significance.

61

62

63

## 64 **2. Material and Methods**

### 65 **2.1 Material**

66

67 Chloritites and talc from the Trimouns deposit (Fig. 1) result from the hydrothermal  
68 alteration of host rocks (pegmatites, micaschists and dolostone) by primary brines circulation  
69 (Boiron et al., 2005; Boiron et al., 2007; Boulvais et al., 2006; Moine et al., 1989; Parseval (de)  
70 et al., 2004; Quesnel et al., 2019). In this study, three types of samples from the Trimouns  
71 deposit and La Porteille area - the north extension of the main deposit - have been studied (Fig.  
72 1). Alteration of pegmatite yield to Chloritite-P, micaschist to Chloritite-M, and talc (Fig. 2)  
73 formed at the expense of the three lithologies (Moine et al., 1989; Parseval (de), 1992).

74

## 75 **2.2 Sample characterization methods**

### 76 2.2.1 Bulk rock characterization

77

78 Major and trace element concentrations were determined according to the analytical  
79 procedure developed by Carignan et al. (2001). Total CO<sub>2</sub> and sulfur have been measured using  
80 a HORIBA EMIA 320V2 analyzer. Organic carbon content has been measured using a  
81 HORIBA EMIA 320V2 analyzer on decarbonated samples after hydrochloric acid digestion of  
82 carbonates. For FeO, whole-rock samples have been digested by a sulpho-nitric solution, and  
83 Fe<sup>2+</sup> content has been determined by volumetric titration. The latter consists of using a titrated  
84 potassium dichromate solution with potentiometric marking (platinum electrode and reference  
85 electrode Hg/Hg<sub>2</sub>Cl<sub>2</sub>, saturated KCl) of the equivalent point using an automatic Titroline Schott  
86 Titrimeter. Unfortunately, the digestion of most of the samples was incomplete, and Fe<sub>2</sub>O<sub>3</sub>  
87 analyses corresponding to the total iron content of whole-rock samples will be used for  
88 diagrams and discussions. In contrast, FeO analyses will be presented for indicative purposes  
89 only. These whole rock analyses have been performed at Service d'Analyses des Roches et des  
90 Minéraux (SARM) at Centre de Recherche Pétrographiques et Géochimiques (CRPG), Nancy,  
91 France.

92

93 Qualitative and quantitative minerals composition of bulk samples were performed  
94 using X-ray powder diffraction (XRD) analysis on a Thermo X'TRA diffractometer working in  
95 Bragg-Brentano geometry. Powder diffraction analytical conditions involved an X-ray tube  
96 with a copper anode (CuK $\alpha$  – 1.54178 Å, voltage 45.2 kV, current 35 mA), the 0.9 mm  
97 divergence slit, and 1.6 mm anti-scatter slit were used on the primary side while on the  
98 secondary side, 1.6 mm anti-scatter slit and 0.3 mm receiving slit were used; soller slits 2.3° on  
99 both sides and a scintillation X-ray detector. Samples were scanned from 4 to 80°2 $\theta$  with step  
100 size 0.02°2 $\theta$ . Before the measurements, all samples were ground in a McCrone micronizing  
101 mill for 3 minutes. Mineral quantification was performed by the Rietveld refinement method  
102 using the BGMN program ([www.bgm.de](http://www.bgm.de)), based on the XRD patterns collected on randomly  
103 oriented specimens for #CH4, #CH5, #CH6, #CH8, and #PORT7 samples, and on oriented  
104 specimens for #CH3 and #TLC1.

105

### 106 2.2.2 Whole Rock hydrogen isotope analysis

107 Hydrogen isotopic measurements of the different samples were performed online using  
108 the EA Eurovector – GV Isoprime IRMS System at CRPG laboratory (Nancy, France)  
109 according to the procedure developed by Lupker et al. (2012). First, the samples were weighed  
110 in tin capsules (1–5 mg). To remove atmospheric water potentially adsorbed by the samples,

111 these capsules were then loaded in a sample carousel and degassed at 120 °C under vacuum for  
112 48h in a degassing canister (Lupker et al., 2012). After dehydration, the degassing canister was  
113 open into a dry, N<sub>2</sub> flushed glove box, and the sample carousel was transferred into a sealed  
114 auto-sampler initially pre-flushed with He. The auto-sampler was then connected to the EA and  
115 pumped out for 20 min before opening it to the reduction column. Then, samples were  
116 combusted at 1450 °C on an EA glassy carbon reaction tube, filled with glassy carbon chips,  
117 and placed itself into a ceramic liner to reduce hydroxyls (OH) release by the samples into H<sub>2</sub>.  
118 Produced gas was separated on a chromatographic column maintained at 60 °C, and H<sub>2</sub> was  
119 introduced into the mass spectrometer and analyzed for D/H isotopic composition. Isotopic  
120 compositions were determined by comparison with three internal standards routinely included  
121 during the analysis: (i) phlogopite (Mica-Mg:  $\delta D = -77 \text{ ‰}$ ), (ii) muscovite (MuscD65:  $\delta D = -$   
122  $85 \text{ ‰}$ ), (iii) fine-grained marine sediment from the Bay of Bengal (SO188:  $\delta D = -83 \text{ ‰}$ ).  
123 Produced H<sub>2</sub> was corrected from the H<sup>3+</sup> contribution using in-house H<sub>2</sub> standard injections.  
124 The hydrogen isotopic composition is expressed as  $\delta D \text{ (‰)}$  relative to Standard Mean Ocean  
125 Water (SMOW). The reproducibility of the method is better than 2‰ for  $\delta D$ .

126

### 127 2.2.3 Thermogravimetric (TG) analysis

128 Thermogravimetric (TG) analysis was performed using a TA Discovery instrument (TA  
129 Instruments, USA), which had a weight measurement accuracy of <0.1  $\mu\text{g}$ , and a thermal drift  
130 between 200 and 1000°C of <4  $\mu\text{g}$ . A 20 mg air-dried powder sample placed in a Pt crucible  
131 was heated in a dry nitrogen gas atmosphere (>99.999 % purity) with a flow rate of 100 cm<sup>3</sup>  
132 min<sup>-1</sup>. Before the TG experiment, each sample was dried in situ in the TG furnace isothermally  
133 for 15 min at 200 °C to remove the adsorbed water. A ramp heating to 1000 °C at a rate of 10  
134 °C min<sup>-1</sup> was used for each measurement. The total mass loss was calculated as the difference  
135 between mass loss recorded at 205 °C and 1000 °C (endpoint of heating). The thermal events  
136 temperature was analyzed using the first derivative of the TG curve (DTG).

137 The use of thermal analysis allows observing the thermal decomposition reactions,  
138 involving mostly dihydroxylation (in the range 400 °C – 800 °C). Dehydroxylation occurs  
139 during the heating of all phyllosilicates leading to the formation and migration of H<sub>2</sub>O formed  
140 by neighbouring OH groups in the octahedral sheet (Heller-Kallai and Rozenon 1980; Drits et  
141 al. 1995).

142

## 143 2.3 Thermal treatment

144 Between 55 g to 80 g of the 0.5-5 mm grain size fraction of the rock samples were  
145 loaded in a pyrex tube, connected to the vacuum separation line (Fig.3), and pumped less than  
146 1 minute at ambient temperature to reach good vacuo condition ( $\sim 10^{-3}$  mbar). During

147 progressive heating to reach stationary temperatures, most of the condensable gases were  
148 released below 300°C (mainly adsorbed H<sub>2</sub>O and CO<sub>2</sub>) and were immediately trapped in liquid  
149 nitrogen. Fixed temperatures of 300 °C and 500 °C have been chosen for chloritite and talc  
150 samples, respectively, because preliminary tests revealed that non-condensable gases such as  
151 H<sub>2</sub> and CO were not released at lower temperatures. The progressively released non-  
152 condensable gases (H<sub>2</sub>, CO) were regularly transferred in a calibrated volume using a Toepler  
153 pump (Fig. 3). All the samples were heated for about 20 hours, although most gases were  
154 released in the first hours. After 20 hours, the non-condensable gases were transferred in a  
155 sealed pyrex tube containing CuO and Cu<sub>2</sub>O grains to be oxidized into H<sub>2</sub>O and CO<sub>2</sub> for isotopic  
156 measurements (see section 2.4). Before being used, the CuO and Cu<sub>2</sub>O grains were heated few  
157 minutes under vacuum at 350°C and pumped overnight at room temperature to remove  
158 adsorbed gases such as H<sub>2</sub>O and CO<sub>2</sub>. Finally, the condensable gases still trapped in the line  
159 were separated cryogenically. CO<sub>2</sub> was evacuated, and H<sub>2</sub>O was collected using a clean syringe  
160 and transferred in a 2mL vial for isotopic analysis by CRDS (Cavity Ring Down Spectroscopy  
161 – see section 2.5.1).

162

## 163 **2.4 Separation of H<sub>2</sub> and CO and quantification**

164 After extraction, CO and H<sub>2</sub> are oxidized into CO<sub>2</sub> and H<sub>2</sub>O with CuO and Cu<sub>2</sub>O,  
165 respectively, at 450 °C for 1 hour. The produced CO<sub>2</sub> and H<sub>2</sub>O are then separated cryogenically  
166 under vacuum. Water is then reduced into H<sub>2</sub> at 800 °C in a uranium furnace. H<sub>2</sub> and CO<sub>2</sub> are  
167 separately quantified using calibrated volume and transferred in a pyrex vessel for isotope  
168 analysis.

169

## 170 **2.5 Hydrogen stable isotope analysis**

### 171 2.5.1 H<sub>2</sub>O

172 All water samples were analyzed at the CRPG UMR 7358 CNRS-UL (Nancy, France)  
173 using a CRDS L2140-i Picarro water isotope analyzer coupled to a A0211 vaporization module.  
174 Water released during thermal treatment of the rock samples was transferred into 2 mL Pyrex  
175 vials with a 0.1 mL conic insert and sealed by an ultraclean 9 mm septum. For each sample, 10  
176 injections of 1.8 µL of water were performed. Only the 6 last injections were used for  
177 measurements to avoid any memory effect.

178 Isotopic compositions are reported in δ notation relative to the V-SMOW-SLAP scale. All  
179 samples were adjusted to three internal references calibrated on the international standards  
180 SLAP, GISP, and SMOW. Instrument precision was better than 0.1 ‰ and 1 ‰ for δ<sup>18</sup>O and  
181 δD, respectively.

182

## 183 2.5.2 H<sub>2</sub> and CO

184 Hydrogen isotopic compositions of released H<sub>2</sub> were analyzed at the CRPG UMR 7358  
185 CNRS-UL (Nancy, France) using a Dual-Inlet VG Isoprime Isotope Ratio Mass Spectrometer  
186 (IRMS). Isotopic compositions are reported in  $\delta$  notation relative to the V-SMOW-SLAP scale.  
187 Two internal standards were analyzed, and each weekly batch of H<sub>2</sub> samples was obtained  
188 following the same procedure of reducing uranium at 800 °C. Reproducibility for standards was  
189 estimated to be lower than 2 ‰.

190 Carbon isotopic compositions of CO<sub>2</sub> formed by oxidation of CO (see section 2.4) were  
191 analyzed at the CRPG UMR 7358 CNRS-UL (Nancy, France) using a Dual-Inlet VG Isoprime  
192 Isotope Ratio Mass Spectrometer (IRMS). Isotopic compositions are reported in  $\delta$  notation  
193 relative to the V-PDB scale. Reproducibility is estimated to be lower than 0.2 ‰.

194  
195

## 196 3. Results

### 197 3.1 Chemical and mineral composition

198 Three types of samples (chloritite-P, chloritite-M, and talc) have been sampled (Fig.  
199 2). First, major elements composition shows that chlorites are magnesian-clinochlore (Table.  
200 1) which is consistent with the nature of chlorite documented at Trimouns (Boutin, 2016;  
201 Parseval (de), 1992). Compared to other chloritite samples, #CH3 and #CH8 are enriched in  
202 SiO<sub>2</sub>, depleted in MgO, and depleted in Al<sub>2</sub>O<sub>3</sub> for the latter (Table 1). One can remark that  
203 #CH5 is also slightly enriched in SiO<sub>2</sub> and slightly depleted in Al<sub>2</sub>O<sub>3</sub>. Based on XRD results  
204 (Table 2), we can explain the major element concentrations in sample #CH3 by mixing with  
205 quartz and muscovite and in sample #CH8 by a talc-chlorite mixture (chlorite ~11 % and talc  
206 ~ 85 %). Regarding sample #CH5, the XRD results attest for a half-half mixing between  
207 chlorite and talc.

208 Based on the work of Parseval (de) (1992) we used Cr, Ni, and V contents of chloritite  
209 samples to determine their origins (i.e. derived from the alteration of pegmatoid or micaschist).  
210 Cr, Ni, and V contents presented in Table 1 show that samples #CH4, #CH6, #CH10 and  
211 #PORT-7 are pegmatoid-derived, whereas samples #CH3, #CH5, and #CH8 are micaschist-  
212 derived. One could notice that the nickel content of samples #CH5 and #CH8 is slightly lower  
213 than expected (~20 ppm whereas 25-60 ppm were expected) – a fact that could be explained by  
214 mixing with significant quantities of talc, which is depleted in Ni (Table 1).

215 Finally, the total iron contents (expressed as Fe<sub>2</sub>O<sub>3</sub>) of chloritites and talc are low and  
216 comparable to those documented in the literature (Parseval (de), 1992; Parseval (de) et al.,  
217 1991) with values ranging from 1.43 wt% to 7.41 wt% for chloritites and of 0.42 wt% for talc.  
218 As shown in Parseval (de) et al. (1991), Fe(III) in chlorite is located in tetrahedral sites only,

219 whereas Fe(II) is located in the three sites of the two octahedral sheets with most of the Fe(II)  
220 residing in the interlayer hydroxide sheet. Parseval (de) et al. (1991) showed that Fe(III)  
221 represents 20 to 30% of the total iron ( $\text{Fe}_2\text{O}_3$ ), which is consistent with both the FeO (indicative  
222 purpose only) and the total iron content ( $\text{Fe}_2\text{O}_3$ ) documented for chloritite samples in the present  
223 study (Table 1). Villiéras et al. (1992) showed that very few Fe(II) was hosted by talc, the  
224 substitution of Mg by Fe(II) in the talc lattice being estimated at 1 %.

225

### 226 **3.2 Whole-rock hydrogen isotope composition**

227 Whole-rock hydrogen isotope compositions (Table 2) of studied samples are very  
228 homogeneous with values ranging between -48 ‰ and -43 ‰ with no specific variation related  
229 to the mineralogy of the samples.

230

### 231 **3.3 Thermal evolution by thermogravimetry**

232 The thermal behavior of all samples (except for #CH10) was tested using  
233 thermogravimetric (TG) analysis (Fig. 4). Under dynamic heating conditions, no significant  
234 mass change occurs below 500 °C, indicating no intense thermal decomposition reactions in  
235 this temperature range, which is consistent with TG results known for clinochlore (Lempart et  
236 al., 2018), talc (Čavajda et al., 2015), and muscovite (Mazzucato et al., 1999). The two-step  
237 (for chloritites) and one-step (for talc) rapid mass loss between 500 and 1000 °C is due to the  
238 dehydroxylation. The recorded total mass losses differed among all tested samples, resulting  
239 from different proportions of chlorite, talc, and muscovite (minerals that contributed to the  
240 weight loss on TG curves) and quartz. For the samples mainly containing chlorite: #CH4,  
241 #CH6, and #PORT7, the total mass losses range between 11.2 and 11.9 %, which are values  
242 close to the theoretical mass loss due to dehydroxylation of clinochlore ( $\text{H}_2\text{O}$  (+), 12-13 wt%;  
243 Lempart et al., 2018). The total mass losses are much lower for the other samples, and thermal  
244 events do not seem to be completed at 1000°C. The dehydroxylation of talc-dominated samples,  
245 #CH8 and #TLC1, is represented by one DTG peak that is not completed up to 1000 °C, which  
246 is a common feature of talc (Čavajda et al., 2015). The complete dehydroxylation of talc  
247 requires a higher temperature, up to 1350 °C (Zhang et al. 2006). Chlorite-dominated samples  
248 (Fig. 4a, b, d, e, f) display two DTG peaks of mass loss with the maxima at ~600 °C and ~800  
249 °C, which correspond to the dehydroxylation of the two octahedral sheets. The first peak is  
250 related to an interlayer (brucite) sheet, and the second to the octahedral sheet of the 2:1 layer  
251 (Lempart et al., 2020). Talc contributes to the latter thermal event due to its structural and  
252 chemical similarity and the 2:1 layer of clinochlore.

253

### 254 **3.4 Thermal treatment**



### 255 3.4.1 Stable isotope composition of interstitial/adsorbed water

256 As described in section 2.3, interstitial/adsorbed water is mainly released at a  
257 temperature lower than 300 °C. It is immediately condensed in a liquid nitrogen trap to avoid  
258 any exchange with H<sub>2</sub> released at a higher temperature. The released water was analyzed for its  
259 hydrogen and oxygen stable isotopic composition. Data reported in Table 2 fall on, or very  
260 close to, the Meteoric Global Water Line (Fig. 5). Only one water sample (#CH10) displays a  
261 slightly lower isotopic composition in oxygen and hydrogen, suggesting that this sample  
262 preserved meteoric water from another area (e.g. sampling area vs storage area).

263

### 264 3.4.2 Quantification and stable isotopic composition of released H<sub>2</sub> and CO

265 The quantities of H<sub>2</sub> and CO released during heating and the hydrogen stable isotopic  
266 compositions of H<sub>2</sub> are correlated to the mineralogy of rock samples (Fig. 6a and 7a; Table 2).  
267 The highest quantity of H<sub>2</sub> and CO are released from chloritite-P samples (4.7 to 7.4 ppm and  
268 11.1 to 35.3 ppm, respectively), which are dominated by chlorite (> 85 %) with little talc (< 11  
269 %) and few amounts of quartz (< 7 %). The lowest quantities of H<sub>2</sub> and CO are released from  
270 the pure talc sample (> 98 % of talc): 0.7 ppm and 3.8 ppm, respectively. The amounts of H<sub>2</sub>  
271 and CO released from chloritite-M samples, constituted by ~10 to 50 % of chlorite, are  
272 intermediate (0.5 to 1.7 ppm and 3 to 7 ppm, respectively). For H<sub>2</sub>, a correlation between the  
273 quantity of gas released, the nature of the sample, and the hydrogen isotopic composition is  
274 observed (Fig. 6b). The lowest δD values (-258 ‰ to -224 ‰) are documented for chloritite-P  
275 and the highest for talc (-140 ‰). The δD values of H<sub>2</sub> from chloritite-M are intermediate with  
276 -183 ‰ and -160 ‰. For CO, δ<sup>13</sup>C values are very homogeneous, ranging between -27.4 ‰  
277 and -25.7 ‰ with no apparent correlation to the quantity of gas released (Fig. 7b). For CO and  
278 H<sub>2</sub>, no correlation is identified between the amount of gas released and the total iron content of  
279 samples (Fig. 6c and 7c). However, a linear correlation is identified for chloritite-P (Fig. 6c).  
280 Amounts of CO and H<sub>2</sub> released during experiments are not correlated between them (Fig. 7d).

281

## 282 4. The origin(s) of H<sub>2</sub> release during thermal treatment of samples

283 As presented in Figure 8, several processes can lead to the release of H<sub>2</sub> upon heating  
284 of phyllosilicates. The question is whether the released H<sub>2</sub> was initially entrapped in our  
285 samples or produced during the experiments.

286

### 287 4.1 H<sub>2</sub> entrapped in minerals

288 Recent studies demonstrated that physisorption of H<sub>2</sub> on phyllosilicates is possible  
289 (Didier et al., 2012; Edge et al., 2014; Gil et al., 2009; Mondelli et al., 2015). However, all  
290 these studies were performed under particular conditions (including low to cryogenic

291 temperatures, dry condition, pre-exposure to high H<sub>2</sub> pressure), making them difficult to  
292 extrapolate to the natural system. Truche et al. (2018) showed that H<sub>2</sub> is entrapped in clay-rich  
293 rocks naturally exposed to radiogenic H<sub>2</sub>. In the alteration halo of the Cigar Lake U-deposit, H<sub>2</sub>  
294 produced by water radiolysis when in contact with U-minerals was trapped on clay minerals.  
295 The mechanism may be comparable to methane adsorption on shale.

296 For our study, the release of H<sub>2</sub> initially entrapped in the natural rock samples is  
297 unlikely. The main argument is related to the lack of H<sub>2</sub> release during progressive heating of  
298 the samples before reaching the stationary temperature of 300 °C for chloritite and 500 °C for  
299 talc (section 2.3). When reaching these temperatures, H<sub>2</sub> was not released abruptly but  
300 progressively. Compared to the release of H<sub>2</sub> documented by Truche et al. (2018) between 80  
301 °C and 300 °C with a maximum flux of H<sub>2</sub> at ~200 °C, it is difficult to argue that H<sub>2</sub> released  
302 during our experiments was initially entrapped in the studied samples. The amount of H<sub>2</sub>  
303 released is also very different between the Truche et al. (2018) study and the present one: up to  
304 500 ppm and 8 ppm, respectively. Moreover, our samples have been exposed to active pumping  
305 before heating for less than 1 min to reach vacuum condition in the extraction line (section 2.3),  
306 which could have extracted the hypothetical entrapped/adsorbed H<sub>2</sub>.

307

#### 308 **4.2 Reduction of H<sub>2</sub>O by Fe(II) oxidation**

309 One can envision that H<sub>2</sub> production resulted from the reduction of adsorbed/interstitial  
310 H<sub>2</sub>O, initially contained in the rock samples, associated with Fe(II) oxidation contained in  
311 chlorite. Alternatively, the production of H<sub>2</sub> could have been formed by the same process, but  
312 from H<sub>2</sub>O formed at higher temperatures during the dehydroxylation stage of the rock (Villieras  
313 et al., 1992). The generalized reaction can be represented according to:

314



316

317 The first hypothesis, involving the reduction of H<sub>2</sub>O initially entrapped in the rock  
318 samples, is very unlikely for the following reasons. A time/temperature gap exists between the  
319 release of adsorbed/interstitial H<sub>2</sub>O occurring at T < 300 °C and the subsequent H<sub>2</sub> release  
320 occurring at 300 °C (for chloritite) and 500 °C (for talc). Moreover, the experiments were  
321 performed under vacuum conditions, and a liquid nitrogen trap was emplaced since the  
322 beginning of the experiments to remove the adsorbed/interstitial H<sub>2</sub>O upon heating (Fig. 3).  
323 The low-temperature release, combined with the quick transfer and trapping of H<sub>2</sub>O, makes  
324 very unlikely the possibility to reduce water by oxidizing structural Fe(II). In comparison, H<sub>2</sub>  
325 production related to experimental serpentinization of olivine grains is kinetically hindered at  
326 T < 300 °C. Several hundreds of hours are required to produce detectable amount of H<sub>2</sub> at T >  
327 200 °C (McCollom et al., 2016). Finally, the stable isotopic compositions (O and H) of retrieved

328 waterfall lie perfectly on the GMWL (Fig. 5). If H<sub>2</sub> release would be related to the reduction of  
329 H<sub>2</sub>O, their isotopic compositions should be in isotopic equilibrium. For δD<sub>H<sub>2</sub>O</sub> values between  
330 -100 ‰ and -60 ‰ (Table 2, Fig. 5), the hydrogen isotopic composition of H<sub>2</sub> should be  
331 between ~ -615 ‰ and -575 ‰ at 300 °C and between -420 ‰ and -380 ‰ at 500 °C (Bottinga,  
332 1969).

333 The second hypothesis considers the reduction of H<sub>2</sub>O formed during dehydroxylation  
334 of the rock by oxidizing Fe(II) contained in chlorite. Dehydroxylation is a high-temperature  
335 process occurring in a broad range of temperatures for trioctahedral phyllosilicates (Fig. 8),  
336 from 400 to 850 °C for chlorites (Lempart et al., 2018) and from 750 to 1100 °C for talc (Zhang  
337 et al., 2006). This process consists of a reaction between hydroxyl groups (OH) forming water  
338 molecules (Drits et al., 1995; Drits et al., 2012a; Drits et al., 2012b; Guggenheim et al., 1987;  
339 Vedder and Wilkins, 1969):

340



341

342 where O<sub>r</sub> is the residual oxygen in the structure.

343 The newly formed H<sub>2</sub>O could oxidize structural Fe(II) and form H<sub>2</sub> by reducing H<sub>2</sub>O following  
344 the equation (1) as proposed by Villiéras et al. (1992) to explain the release of H<sub>2</sub> during heating  
345 of talc and chloritite from Trimouns. In this latter study, the authors also followed the method  
346 of Zimmermann et al. (1988) to recover and separate the different gases released at various  
347 temperature steps (talc: from 200 to 1100 °C; chloritite from pegmatite: from 280 to 1100 °C;  
348 chloritite from micaschist: from 300 to 1080 °C). The authors documented H<sub>2</sub> release, between  
349 0.01 and 0.8 ppm, at low temperature (between 200 and 300 °C) for chloritite and talc. The  
350 release of H<sub>2</sub> reached a maximum at 600 °C and 850 °C for chloritite and talc, respectively,  
351 with values of several tens of ppm. The main conclusion of Villiéras et al. (1992) was that H<sub>2</sub>  
352 was formed by reduction of H<sub>2</sub>O, released during dehydroxylation, and concomitant oxidation  
353 of Fe(II) to Fe(III) contained in the minerals following the equations (1). However, this  
354 conclusion only explains the significant release of H<sub>2</sub> at a temperature above 450 °C and 750  
355 °C (Fig. 8) for chloritite and talc, respectively. Thus, the question of the origin of H<sub>2</sub> released  
356 at a temperature lower than 450 °C remains open.

357 Here, the experiments have been performed at temperatures significantly lower than  
358 those expected to initiate dehydroxylation (see section 3.2). Consequently, it is improbable to  
359 explain the release of H<sub>2</sub> by reducing H<sub>2</sub>O formed during dehydroxylation on structural Fe(II).

360

361 **4.3 H<sub>2</sub> produced by dehydrogenation and significance of δD<sub>H<sub>2</sub></sub> values**

362 Dehydroxylation and dehydrogenation are competitive processes that can co-occur in  
363 a similar range of temperatures and produce H<sub>2</sub>O and H<sub>2</sub> gas independently (Lempart et al.,  
364 2018; Lempart et al., 2020).

365 Dehydrogenation is a thermally induced reaction overlapping with dehydroxylation.  
366 One proposed reaction mechanism proceeds by a release of one hydroxyl hydrogen atom per  
367 one oxidized Fe(II) atom octahedrally coordinated with OH groups, leading to the generation  
368 of H<sub>2</sub> (Brindley and Youell 1952; MacKenzie and Berezowski 1984):

369



370 The dehydrogenation process was observed for all Fe(II)-containing phyllosilicates and  
371 was thoroughly described for biotites, amphibolites (Vedder and Wilkins 1969; Rouxhet et al.  
372 1972; Sanz et al. 1983), and/or chlorites (Borggaard et al. 1982; Steudel et al. 2016; Lempart  
373 et al. 2018). The dehydrogenation occurs under an inert and oxidizing gas atmosphere or  
374 vacuum conditions and prefers long-term heating over fast ramp heating conditions (Lempart  
375 et al., 2018; Rouxhet et al., 1972; Sanz et al., 1983; Vedder and Wilkins, 1969). For chamosite,  
376 dehydrogenation was observed at a temperature as low as 350°C during isothermal heating,  
377 whereas for Fe(II)-poor clinocllore temperature of dehydrogenation was between 400-450 °C  
378 (Lempart et al., 2018; Lempart et al., 2020) (Fig. 8). However, such results were tested by using  
379 an inert carrier gas during thermogravimetry analysis that only allows tracking relatively high  
380 mass loss, mostly related to dehydroxylation. Hence, traces of hydrogen released at lower  
381 temperatures are not detectable by that method.

382 Although the formation of H<sub>2</sub> upon heating of Fe(II)-rich phyllosilicates is indisputable,  
383 it is also documented in some studies concerning iron-poor minerals. Several studies showed  
384 that the release of hydrogen upon heating in vacuo of kaolinite occurs only in the course of, or  
385 after, dehydroxylation (Heide and Földvari, 2006; Heller-Kallai, 1997). Detailed mechanisms  
386 remain, however, obscure. Some authors suggested that H<sub>2</sub> production depends on structural  
387 properties, such as the specific arrangement of OH-ions and formation of lattice vacancies,  
388 making possible the reaction between residual OH- groups as follow (Heide and Földvari, 2006;  
389 Heller-Kallai, 1997):

390



391

392 However, the conclusions proposed by Heide and Földvari (2006) and Heller-Kallai  
393 (1997) were also partially questioned by the study of Lempart et al. (2020) where H<sub>2</sub> release  
394 was attributed only to oxidative dehydrogenation. Lempart et al. (2020) also challenged these

395 conclusions by showing the absence of H<sub>2</sub> generation during the heating of the same kaolinite  
396 as tested by Heide and Földvari (2006) and Heller-Kallai (1997) in an inert gas atmosphere.

397 In the present study, H<sub>2</sub> release is documented at a temperature significantly lower than  
398 those required to reach dihydroxylation, but dehydrogenation has also been reported at lower  
399 temperatures, between 350 °C and 450 °C, even for clinocllore (Lempart and Derkowski, 2019;  
400 Lempart et al., 2018; Lempart et al., 2020). The samples used in this work are relatively iron-  
401 poor clinocllore, but the few ppm of H<sub>2</sub> released may be consistent with structural Fe(II)  
402 oxidation. Indeed, precisely for chloritite-P, the purest chloritite samples, a correlation between  
403 the quantities of H<sub>2</sub> released and the total iron content is observed (Fig. 6c). Thus, these results  
404 suggest that the dehydrogenation probably produced H<sub>2</sub> during our experiments.

405 From an isotopic point of view, δD<sub>H<sub>2</sub></sub> values are significantly lower than the very  
406 homogeneous δD values around -45 ‰ for chloritite and talc whole-rock samples (Table 2).  
407 These values could suggest that large hydrogen isotope fractionations occur during the  
408 formation of H<sub>2</sub> by dehydrogenation. The correlation between the quantity of H<sub>2</sub> released during  
409 the experiments and the δD<sub>H<sub>2</sub></sub> values could suggest that this fractionation evolves with the  
410 intensity of dehydrogenation and the mineralogy of the starting material (Fig. 6b).

411 This hydrogen isotope fractionation associated with dehydrogenation has also been  
412 documented by Feeley and Sharp (1996) who have shown that biotite having experienced  
413 dehydrogenation have high δD values compared to the initial material. The released H<sub>2</sub> is  
414 consequently supposed to have low δD values compared to the starting material. These  
415 conclusions are consistent with our observations and should deserve additional investigation to  
416 determine the effect of the nature of the mineral, the temperature, and the rates of  
417 dehydrogenation on the hydrogen isotope fractionation between OH-rich minerals and released  
418 H<sub>2</sub>.

419

## 420 5. The origin of CO

421

422 As for H<sub>2</sub>, CO could have been initially entrapped in the natural rock or produced  
423 during experiments. However, it is unlikely that CO could have been initially entrapped in our  
424 samples for the same reasons as H<sub>2</sub> (active pumping before heating and lack of CO during  
425 progressive heating). Carbon monoxide formed by reducing adsorbed/interstitial CO<sub>2</sub> on  
426 structural Fe(II) following the equation (5) is also unlikely.

427



429

430 As for H<sub>2</sub>O, the low-temperature release of CO<sub>2</sub> and its quick transfer and trapping in a  
431 liquid nitrogen trap make very unlikely the possibility to reduce CO<sub>2</sub> by oxidizing structural  
432 Fe(II) (see section 4.2). An alternative hypothesis could consist in reducing CO<sub>2</sub> formed by  
433 decarbonation of samples as proposed by Villiéras et al. (1992) for similar talc and chloritite  
434 samples from the Trimouns deposit. However, decarbonation is a high-temperature process that  
435 consists of the thermal decomposition of carbonate at a temperature above 600°C (Sharp et al.,  
436 2003), significantly higher than the temperature of our experiments.

437 Even if the origin of CO released at 300 °C remains enigmatic, we suggest that CO could  
438 be derived from a process involving the graphite contained in few amounts in talc and chlorite  
439 samples from the deposit (Table.1, Parseval (de), 1992). Indeed, the carbon isotope  
440 compositions of CO released in this study are exceptionally homogeneous between -27.4 ‰ to  
441 -25.7 ‰ (Table 2) and very close to the  $\delta^{13}\text{C}_{\text{Graphite}}$  value of -24.4 ‰ documented from whole  
442 rock analysis of Chlorite-P (Parseval (de), 1992).

443

## 444 **6. Conclusion and perspectives**

445 In this study, we document H<sub>2</sub> and CO release during heating of talc and chloritite from the  
446 Trimouns deposit at 300 and 500°C, respectively. If the origin of CO remains enigmatic but  
447 could be linked to reaction with graphite, we propose that H<sub>2</sub> has been produced during the  
448 experiments by dehydrogenation of the starting material. Very low  $\delta\text{D}_{\text{H}_2}$  values compared to  
449 the initial  $\delta\text{D}$  values of sampled material are documented and question the isotopic  
450 fractionations that dehydrogenation could induce. This extensive hydrogen isotopic  
451 fractionation between OH-rich minerals and produced H<sub>2</sub> during dehydrogenation would  
452 deserve further investigations to fully understand the effects of mineral composition,  
453 temperature, and the rates of dehydrogenation. An important recommendation from this work  
454 is that thermal degassing of rocks must be performed at a temperature lower than 300 °C to  
455 ensure the absence of dehydrogenation of clays and in situ generations of H<sub>2</sub> and CO. Finally,  
456 dehydrogenation may occur in various magmatic-metamorphic-hydrothermal environments  
457 and should be accounted for as a potential H<sub>2</sub> source term in the hydrogen geochemical cycle.  
458 The isotopic signature of H<sub>2</sub> produced by dehydrogenation has to be better constrained to  
459 evaluate the geological significance of this process.

460

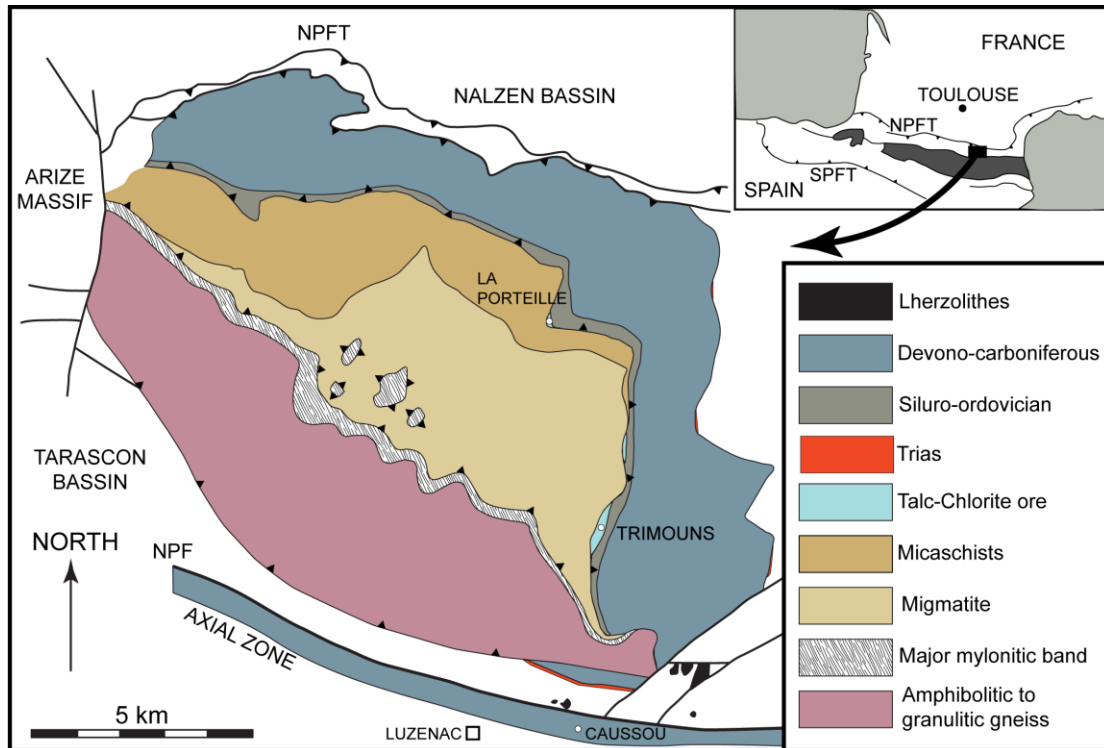
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## 462 **ACKNOWLEDGEMENTS**

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 468 support from the Institut Universitaire de France

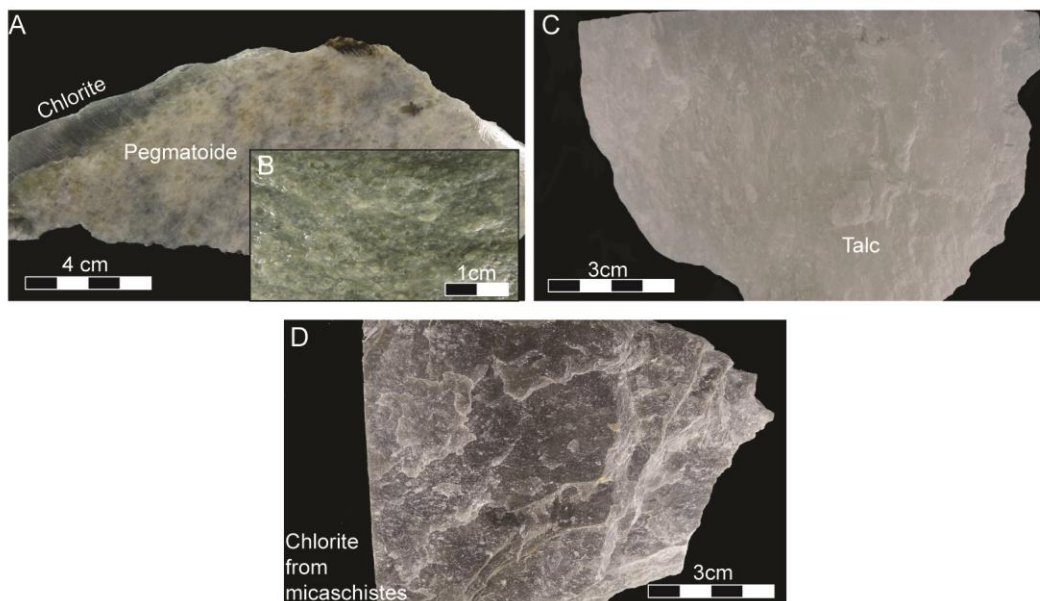
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472 **Figure 1** Simplified geological map of the Saint Barthelemy Massif modified after Boutin et  
 473 al. (2016) and Saint Blanquat (de) (1989)

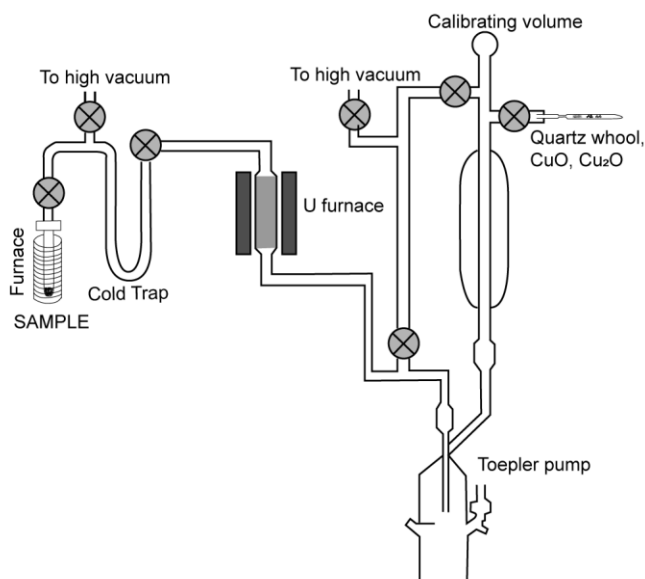
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476 **Figure 2** Photos of the three types of samples studied in this work. A, B: samples #CH10 and  
 477 #CH4, chloritite-P with their typical light green color; C: sample #TLC1, talc with its  
 478 characteristic white color; D: sample #CH5, chloritite-M with its dark green-black color

479

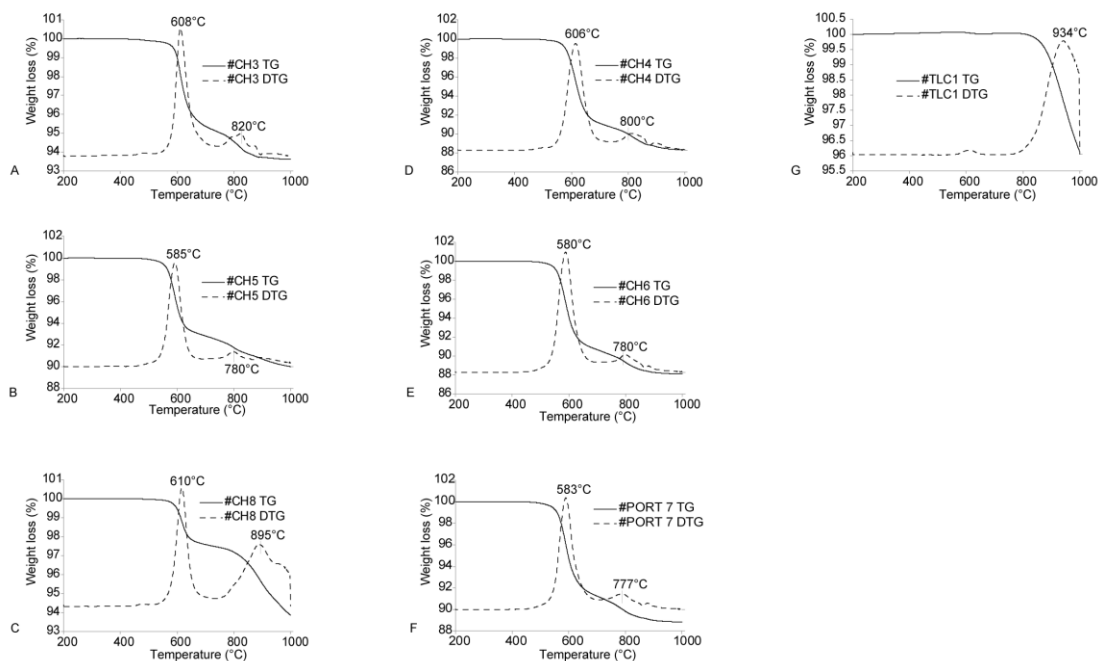


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481 **Figure 3** Schematic diagram of the extraction and separation line inspired from Zimmermann  
 482 et al. (1988)

483

484



485

486 **Figure 4** Thermogravimetric (TG) pattern of studied samples ramp heated with a 10 °C/min  
 487 rate to 1000 °C under N<sub>2</sub> gas.

488

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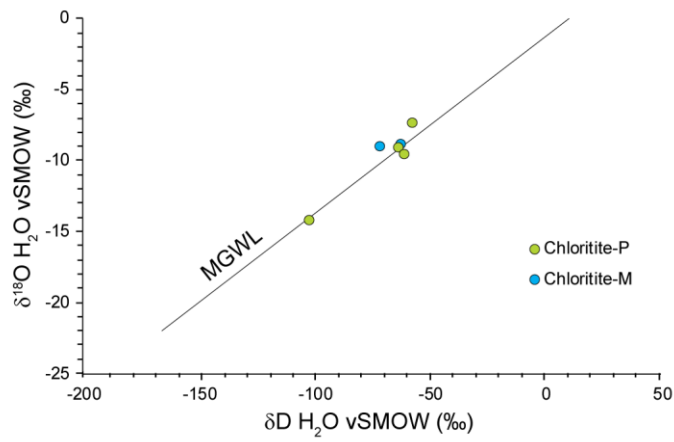
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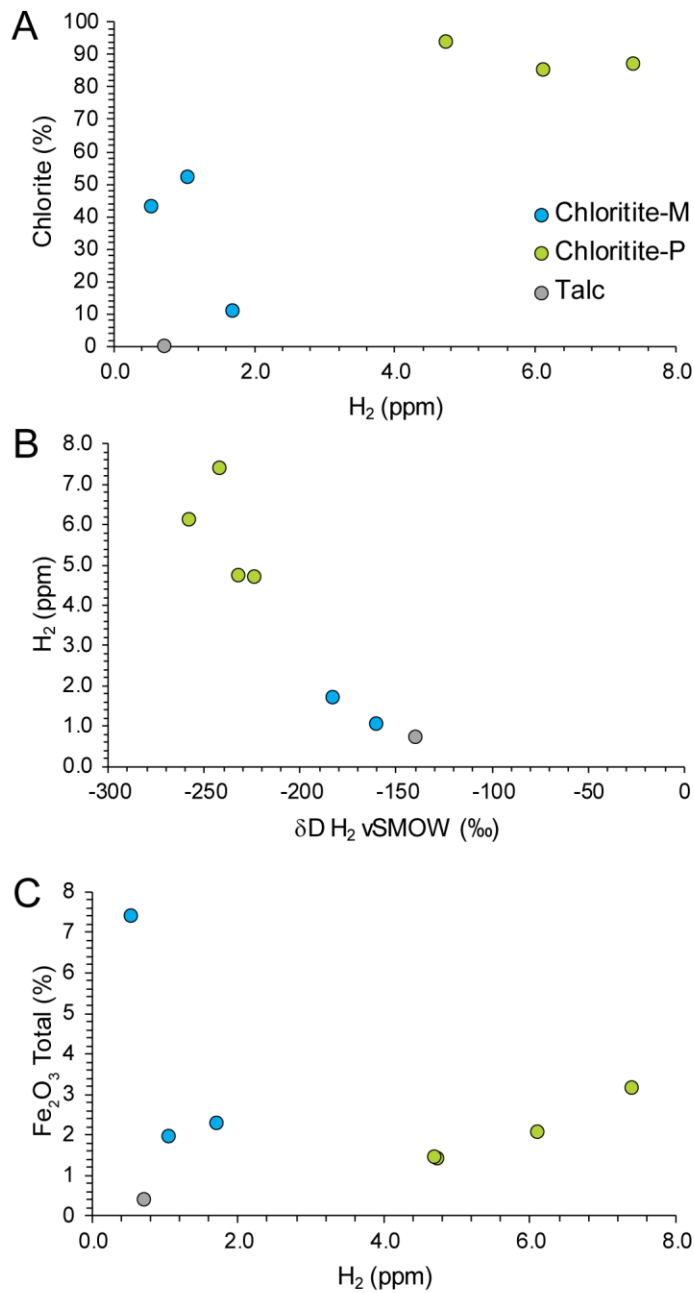
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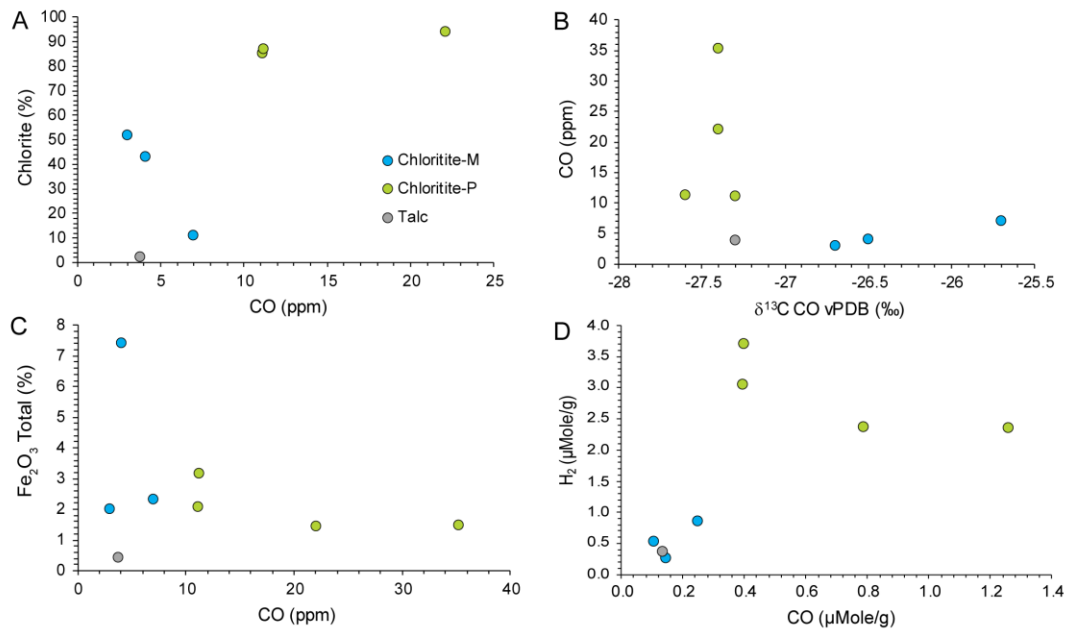
495 **Figure 5** Oxygen and hydrogen isotope compositions of adsorbed/entrapped water released  
496 from chloritite-P and chloritite-M samples during the first heating steps. Meteoric Global Water  
497 Line (MGWL) has been drawn using the following equation:  $\delta\text{D} = 8 \times \delta^{18}\text{O} + 10$

498



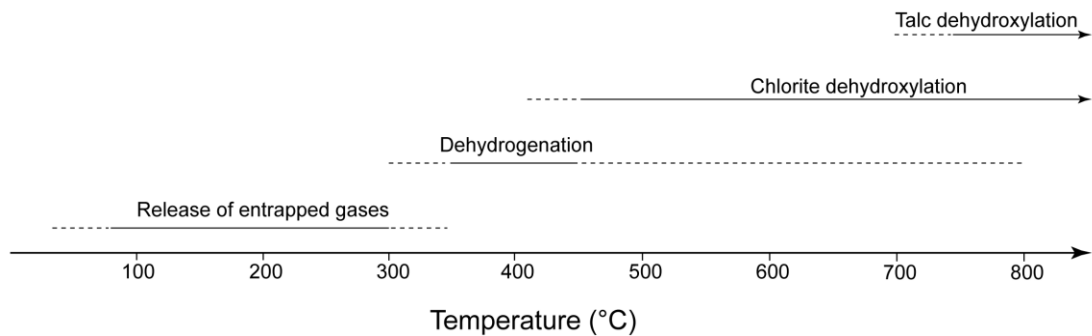
499 **Figure 6** A: Quantity of H<sub>2</sub> released during experiments as a function of the mineralogy of  
 500 the sample. The chlorite amount is given in Table 2, based on XRD analyses of rock samples.  
 501 B: Hydrogen isotopic composition of H<sub>2</sub> as a function of the quantity of H<sub>2</sub> released during  
 502 experiments. C: Quantity of H<sub>2</sub> released during experiments as a function of the total iron  
 503 content of the sample.  
 504

505



506  
 507 **Figure 7** A: Quantity of CO released during experiments as a function of the mineralogy of the  
 508 sample. The chlorite proportions are given in Table 2 based on XRD analyses of rock samples.  
 509 B: Carbon isotopic composition of CO as a function of the quantity of CO released during  
 510 experiments. C: Quantity of CO as a function of the total iron content of the sample. D: Quantity  
 511 of CO as a function of the quantity of  $\text{H}_2$  released during experiments.

512  
 513



514  
 515 **Figure 8** Sketch summarizing the range of temperatures in which various gas producer  
 516 processes are likely to occur. See text for details.

517  
 518

Sample		#CH3	#CH5	#CH8	#CH4	#CH6	#CH10	#PORT-7	#TLC1
Lithology		Chloritite-M	Chloritite-M	Chloritite-M	Chloritite-P	Chloritite-P	Chloritite-P	Chloritite-P	Talc
SiO <sub>2</sub>	%	42.53	38.36	54.45	33.28	34.28	33.64	31.72	62.00
Al <sub>2</sub> O <sub>3</sub>	%	17.26	14.26	3.68	18.53	16.71	17.25	18.12	0.23
Fe <sub>2</sub> O <sub>3</sub>	%	7.41	1.99	2.31	2.08	1.43	1.46	3.17	0.42
MnO	%	0.05	B.D.L.	B.D.L.	0.02	B.D.L.	B.D.L.	0.02	B.D.L.
MgO	%	21.91	32.86	29.89	32.94	33.44	33.59	33.38	31.69
CaO	%	0.09	0.23	1.01	0.56	1.02	1.15	0.36	0.20
Na <sub>2</sub> O	%	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
K <sub>2</sub> O	%	0.17	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
TiO <sub>2</sub>	%	0.78	0.84	0.11	0.07	B.D.L.	B.D.L.	0.03	B.D.L.
P <sub>2</sub> O <sub>5</sub>	%	B.D.L.	0.16	0.79	0.43	0.77	0.87	0.26	B.D.L.
LOI	%	9.41	10.97	7.56	12.16	11.99	12.20	12.94	5.31
Total	%	99.60	99.67	99.80	100.07	99.64	100.16	100.00	99.85
CO <sub>2</sub> total	%	0.56	0.23	4.99	0.02	0.07	0.13	0.04	0.14
C <sub>org</sub>	%	0.13	0.06	1.37	<0.01	<0.01	<0.01	<0.01	0.01
FeO	%	6.16*	1.68*	1.72*	1.67*	1.18*	1.19	2.45	0.32
S total	%	<0.01	0.03	0.03	<0.01	<0.01	<0.01	<0.01	<0.01
As	ppm	0.84	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Ba	ppm	25.08	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Be	ppm	1.35	2.62	0.43	1.89	2.13	2.24	2.24	0.17
Bi	ppm	B.D.L.	0.07	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Cd	ppm	B.D.L.	0.03	B.D.L.	0.03	0.08	0.15	B.D.L.	B.D.L.
Ce	ppm	61.57	0.91	1.72	9.25	2.51	2.31	1.49	0.08
Co	ppm	11.52	1.94	2.96	1.57	0.80	1.90	3.61	0.70
Cr	ppm	87.08	68.60	30.04	0.73	B.D.L.	0.67	B.D.L.	B.D.L.
Cs	ppm	1.88	1.65	0.57	1.00	1.59	1.79	2.66	0.20
Cu	ppm	B.D.L.	B.D.L.	B.D.L.	B.D.L.	2.03	2.56	3.18	B.D.L.
Dy	ppm	2.64	0.37	0.57	1.41	7.66	5.49	0.85	0.02
Er	ppm	1.46	0.32	0.24	0.69	4.04	3.01	0.43	0.01
Eu	ppm	0.31	0.02	0.08	0.08	0.46	0.30	0.05	B.D.L.
Ga	ppm	22.37	20.37	5.60	22.18	21.30	21.70	25.18	0.34
Gd	ppm	3.30	0.27	0.62	1.17	4.12	2.78	0.56	0.01
Ge	ppm	1.30	0.87	2.01	1.04	0.87	0.82	0.77	1.54
Hf	ppm	4.08	6.54	0.51	1.75	1.59	1.24	1.96	B.D.L.
Ho	ppm	0.53	0.10	0.11	0.27	1.61	1.18	0.17	0.00
In	ppm	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
La	ppm	30.65	0.39	0.71	4.38	0.79	0.78	0.55	0.04
Lu	ppm	0.24	0.10	0.02	0.11	0.30	0.24	0.05	0.00
Mo	ppm	B.D.L.	B.D.L.	29.43	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Nb	ppm	12.83	14.00	2.88	15.01	69.44	40.83	16.16	0.09
Nd	ppm	25.61	0.59	1.61	4.49	3.25	2.36	1.23	0.05
Ni	ppm	43.88	20.19	19.33	6.13	5.63	6.09	7.88	6.47
Pb	ppm	0.49	B.D.L.	1.06	B.D.L.	1.68	1.94	1.24	B.D.L.
Pr	ppm	7.05	0.13	0.31	1.15	0.50	0.40	0.24	0.01
Rb	ppm	5.23	0.94	0.34	0.91	1.26	1.71	0.74	0.30
Sc	ppm	14.96	12.54	2.11	5.53	3.01	3.09	3.73	B.D.L.
Sb	ppm	B.D.L.	B.D.L.	0.08	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Sm	ppm	4.60	0.21	0.54	1.20	2.41	1.59	0.46	0.01
Sn	ppm	5.91	20.31	1.65	2.31	6.47	6.63	8.94	0.32
Sr	ppm	1.29	1.19	3.02	1.67	3.75	4.07	1.40	B.D.L.
Ta	ppm	1.30	1.25	0.94	4.49	106.27	45.70	7.16	0.12
Tb	ppm	0.45	0.05	0.10	0.23	1.05	0.74	0.12	0.00
Th	ppm	15.07	13.19	2.68	1.58	0.73	0.86	0.53	0.02
Tm	ppm	0.22	0.06	0.03	0.11	0.52	0.39	0.06	0.00
U	ppm	2.91	3.11	20.05	5.98	42.56	43.03	3.69	0.02
V	ppm	98.14	85.79	47.80	2.69	7.67	7.84	15.35	1.38
W	ppm	27.64	22.31	7.57	2.78	12.35	4.83	B.D.L.	B.D.L.
Y	ppm	13.60	2.61	2.86	6.70	25.82	19.22	2.94	0.11
Yb	ppm	1.51	0.50	0.17	0.77	2.76	2.18	0.37	0.01
Zn	ppm	51.10	B.D.L.	24.97	12.59	B.D.L.	B.D.L.	11.65	B.D.L.
Zr	ppm	148.19	252.95	20.13	39.27	18.23	14.69	32.62	B.D.L.

\* Incomplete dissolution, indicative value of FeO content

**Table 1** Major and trace element concentrations of studied samples

Sample	#CH3	#CH5	#CH8	#CH4	#CH6	#CH10	#PORT-7	#TLC1
Lithology	Chloritite-M	Chloritite-M	Chloritite-M	Chloritite-P	Chloritite-P	Chloritite-P	Chloritite-P	Talc
H <sub>2</sub> (ppm)	0.5	1.1	1.7	6.1	4.7	4.7	7.4	0.7
s		0.1	0.4	0.2	0.3	0.1	0.5	0.0
n	1	2	2	2	2	2	2	2
δD <sub>H<sub>2</sub></sub> vs. vSMOW (‰)	n/a	-160	-183	-258	-232	-224	-242	-140
s		11	13	3	3	5		
n		2	2	2	2	2	1	1
CO (ppm)	4.1	3	7	11.1	22.1	35.3	11.2	3.8
s		0.2	1.6	0	3.7	0.2	0.4	0.7
n	1	2	2	2	2	2	2	2
δ <sup>13</sup> C CO vs. vSMOW (‰)	-26.5	-26.7	-25.7	-27.3	-27.4	-27.4	-27.6	-27.3
s		0.6	0.9	0.2	0.1	0.1	0.2	0
n	1	2	2	2	2	2	2	2
δD <sub>H<sub>2</sub>O</sub> vs. vSMOW (‰)	n/a	-62	-71	-63	-57	-102	-61	n/a
s		0		4		4	5	
δ <sup>18</sup> O <sub>H<sub>2</sub>O</sub> vs. vSMOW (‰)	n/a	-8.9	-9.1	-9.1	-7.4	-14.3	-9.6	n/a
s		0.0		0.5		0.3	0.7	
n		2	1	2	1	2	2	
δD <sub>WR</sub> vs. vSMOW (‰)	-48	-45	-47	-48	-46	-44	-45	-43
Chlorite (%)	43	52	11	85	94	n/a	87	<2
Talc (%)	2	44	85	11	5	n/a	6	98
Quartz (%)	35	4	<2	4	<2	n/a	7	
Muscovite (%)	20							

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**Table 2** Amounts of H<sub>2</sub> and CO released during experiments, and stable isotope compositions of H<sub>2</sub> (δD<sub>H<sub>2</sub></sub>), interstitial/adsorbed H<sub>2</sub>O (δD<sub>H<sub>2</sub>O</sub>, δ<sup>18</sup>O<sub>H<sub>2</sub>O</sub>), CO (δ<sup>13</sup>C<sub>CO</sub>). Hydrogen isotope compositions of whole-rock chloritite and talc samples (δD<sub>WR</sub>). XRD quantitative estimation of mineral compositions of whole-rock samples. n: number of replicates; σ: Difference between the average and the replicates; n/a: not available.

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