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1 **Significance of H₂ and CO release during thermal treatment of natural**
2 **phyllosilicate-rich rocks**

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15

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

17

18 **Highlights**

- 19
- 20 • H₂ is produced by dehydrogenation of Fe-poor phyllosilicates
 - 21 • H₂ produced by dehydrogenation has very low δD values
 - 22 • Large mineral-H₂ hydrogen isotope fractionations are induced by dehydrogenation
 - 23 • Dehydrogenation is a potential H₂ source term in the hydrogen geochemical cycle
- 24

25

26

27

28 **Abstract**

29 Phyllosilicates may trap hydrogen (H₂) 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 H₂ 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 H₂ and CO, the two detected gases. Hydrogen content may be as high as 7 ppm
36 with δD_{H₂} 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 δ¹³C_{CO} values
between -27.6 ‰ and -25.7 ‰. This study supports the idea that H₂ 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 H₂
40 produced by dehydrogenation and both talc and chloritite. Dehydrogenation of phyllosilicates
41 is a potential source term of H₂ in numerous magmatic-hydrothermal settings and must thus be
42 accounted for in the budget of the H₂ 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 CH₄ or CO₂ by phyllosilicates is
49 already well documented in the context of shale gas exploration, CO₂ sequestration, and nuclear
50 waste storage (Busch et al., 2016; Klewiah et al., 2020; Sanz et al., 1983; Ziemiański et al.,
51 2020). High H₂ 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 H₂ 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 H₂, CH₄, 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 CO₂ 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 Fe²⁺ 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/Hg₂Cl₂, saturated KCl) of the equivalent point using an automatic Titroline Schott
86 Titrimeter. Unfortunately, the digestion of most of the samples was incomplete, and Fe₂O₃
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 α – 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 θ with step
100 size 0.02°2 θ . 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), 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, N₂ 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 H₂.
118 Produced gas was separated on a chromatographic column maintained at 60 °C, and H₂ 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 ‰), (iii) fine-grained marine sediment from the Bay of Bengal (SO188: $\delta D = -83 \text{ ‰}$).
123 Produced H₂ was corrected from the H³⁺ contribution using in-house H₂ 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 δD .

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 μg , and a thermal drift
130 between 200 and 1000°C of <4 μg . 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 cm³
132 min⁻¹. 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⁻¹ 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 H₂O 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 H₂O and CO₂) 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 H₂ and CO were not released at lower temperatures. The progressively released non-
152 condensable gases (H₂, 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 Cu₂O grains to be oxidized into H₂O and CO₂ for isotopic
156 measurements (see section 2.4). Before being used, the CuO and Cu₂O grains were heated few
157 minutes under vacuum at 350°C and pumped overnight at room temperature to remove
158 adsorbed gases such as H₂O and CO₂. Finally, the condensable gases still trapped in the line
159 were separated cryogenically. CO₂ was evacuated, and H₂O 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 H₂ and CO and quantification**

164 After extraction, CO and H₂ are oxidized into CO₂ and H₂O with CuO and Cu₂O,
165 respectively, at 450 °C for 1 hour. The produced CO₂ and H₂O are then separated cryogenically
166 under vacuum. Water is then reduced into H₂ at 800 °C in a uranium furnace. H₂ and CO₂ 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 H₂O

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 δ¹⁸O and
181 δD, respectively.

182

183 2.5.2 H₂ and CO

184 Hydrogen isotopic compositions of released H₂ 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 δ notation relative to the V-SMOW-SLAP scale.
187 Two internal standards were analyzed, and each weekly batch of H₂ 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 CO₂ 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 δ 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-clinocllore (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 SiO₂, depleted in MgO, and depleted in Al₂O₃ for the latter (Table 1). One can remark that
203 #CH5 is also slightly enriched in SiO₂ and slightly depleted in Al₂O₃. 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 Fe₂O₃) 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 (Fe_2O_3), which is consistent with both the FeO (indicative
222 purpose only) and the total iron content (Fe_2O_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 (H_2O (+), 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 H₂ 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 H₂ and CO

265 The quantities of H₂ and CO released during heating and the hydrogen stable isotopic
266 compositions of H₂ are correlated to the mineralogy of rock samples (Fig. 6a and 7a; Table 2).
267 The highest quantity of H₂ 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 H₂ and CO are released from
270 the pure talc sample (> 98 % of talc): 0.7 ppm and 3.8 ppm, respectively. The amounts of H₂
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 H₂, 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 H₂ from chloritite-M are intermediate with
276 -183 ‰ and -160 ‰. For CO, δ¹³C 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 H₂, 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 H₂ released during experiments are not correlated between them (Fig. 7d).

281

282 4. The origin(s) of H₂ release during thermal treatment of samples

283 As presented in Figure 8, several processes can lead to the release of H₂ upon heating
284 of phyllosilicates. The question is whether the released H₂ was initially entrapped in our
285 samples or produced during the experiments.

286

287 4.1 H₂ entrapped in minerals

288 Recent studies demonstrated that physisorption of H₂ 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 H₂ pressure), making them difficult to
292 extrapolate to the natural system. Truche et al. (2018) showed that H₂ is entrapped in clay-rich
293 rocks naturally exposed to radiogenic H₂. In the alteration halo of the Cigar Lake U-deposit, H₂
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 H₂ initially entrapped in the natural rock samples is
297 unlikely. The main argument is related to the lack of H₂ 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, H₂ was not released abruptly but
300 progressively. Compared to the release of H₂ documented by Truche et al. (2018) between 80
301 °C and 300 °C with a maximum flux of H₂ at ~200 °C, it is difficult to argue that H₂ released
302 during our experiments was initially entrapped in the studied samples. The amount of H₂
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 H₂.

307

308 **4.2 Reduction of H₂O by Fe(II) oxidation**

309 One can envision that H₂ production resulted from the reduction of adsorbed/interstitial
310 H₂O, initially contained in the rock samples, associated with Fe(II) oxidation contained in
311 chlorite. Alternatively, the production of H₂ could have been formed by the same process, but
312 from H₂O 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 H₂O 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 H₂O occurring at T < 300 °C and the subsequent H₂ 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 H₂O upon heating (Fig. 3).
323 The low-temperature release, combined with the quick transfer and trapping of H₂O, makes
324 very unlikely the possibility to reduce water by oxidizing structural Fe(II). In comparison, H₂
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 H₂ 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 H₂ release would be related to the reduction of
329 H₂O, their isotopic compositions should be in isotopic equilibrium. For δD_{H₂O} values between
330 -100 ‰ and -60 ‰ (Table 2, Fig. 5), the hydrogen isotopic composition of H₂ 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 H₂O 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_r is the residual oxygen in the structure.

343 The newly formed H₂O could oxidize structural Fe(II) and form H₂ by reducing H₂O following
344 the equation (1) as proposed by Villiéras et al. (1992) to explain the release of H₂ 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 H₂ 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 H₂ 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 H₂
352 was formed by reduction of H₂O, 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 H₂ at a temperature above 450 °C and 750
355 °C (Fig. 8) for chloritite and talc, respectively. Thus, the question of the origin of H₂ 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 H₂ by reducing H₂O formed during dehydroxylation on structural Fe(II).

360

361 **4.3 H₂ produced by dehydrogenation and significance of δD_{H₂} values**

362 Dehydroxylation and dehydrogenation are competitive processes that can co-occur in
363 a similar range of temperatures and produce H₂O and H₂ 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 H₂ (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 H₂ 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 H₂ 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 H₂ release
394 was attributed only to oxidative dehydrogenation. Lempart et al. (2020) also challenged these

395 conclusions by showing the absence of H₂ 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, H₂ 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 clinochlore (Lempart and Derkowski, 2019;
400 Lempart et al., 2018; Lempart et al., 2020). The samples used in this work are relatively iron-
401 poor clinochlore, but the few ppm of H₂ 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 H₂ released and the total iron content is observed (Fig. 6c). Thus, these results
404 suggest that the dehydrogenation probably produced H₂ during our experiments.

405 From an isotopic point of view, δD_{H₂} 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 H₂ by dehydrogenation. The correlation between the quantity of H₂ released during
409 the experiments and the δD_{H₂} 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 H₂ 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 H₂.

419

420 5. The origin of CO

421

422 As for H₂, 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 H₂ (active pumping before heating and lack of CO during
425 progressive heating). Carbon monoxide formed by reducing adsorbed/interstitial CO₂ on
426 structural Fe(II) following the equation (5) is also unlikely.

427



429

430 As for H₂O, the low-temperature release of CO₂ and its quick transfer and trapping in a
431 liquid nitrogen trap make very unlikely the possibility to reduce CO₂ by oxidizing structural
432 Fe(II) (see section 4.2). An alternative hypothesis could consist in reducing CO₂ 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 H₂ 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 H₂ 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 δD 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 H₂ 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 H₂ and CO. Finally,
456 dehydrogenation may occur in various magmatic-metamorphic-hydrothermal environments
457 and should be accounted for as a potential H₂ source term in the hydrogen geochemical cycle.
458 The isotopic signature of H₂ produced by dehydrogenation has to be better constrained to
459 evaluate the geological significance of this process.

460

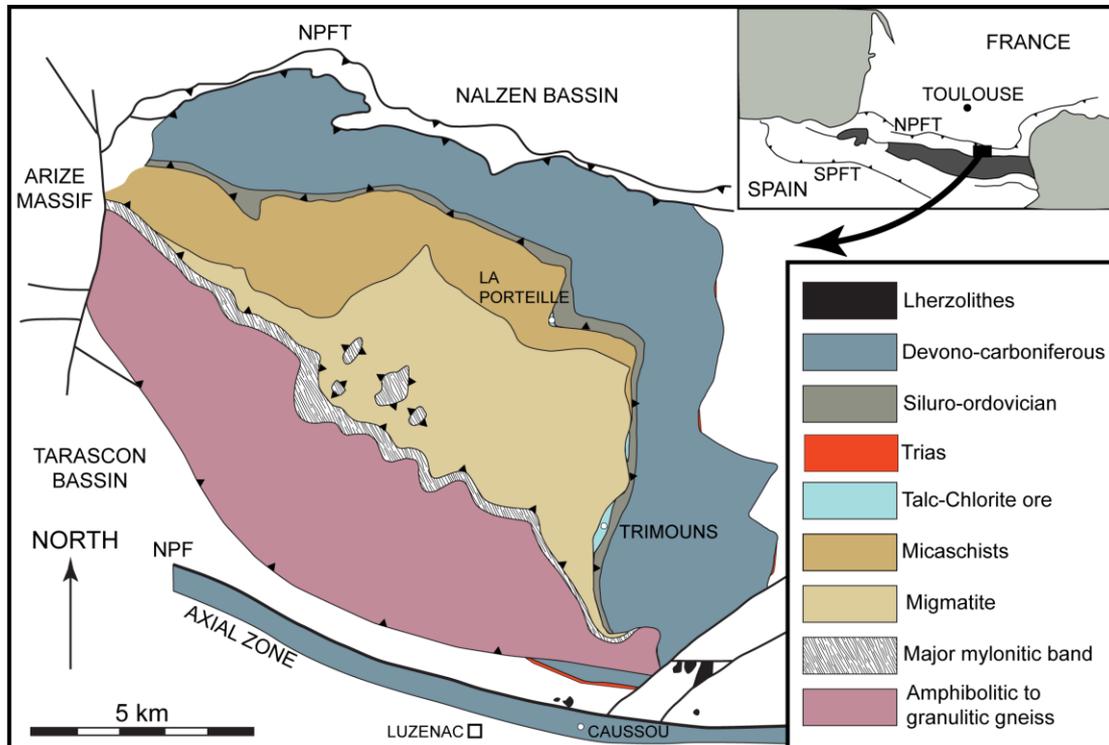
461

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 468 support from the Institut Universitaire de France

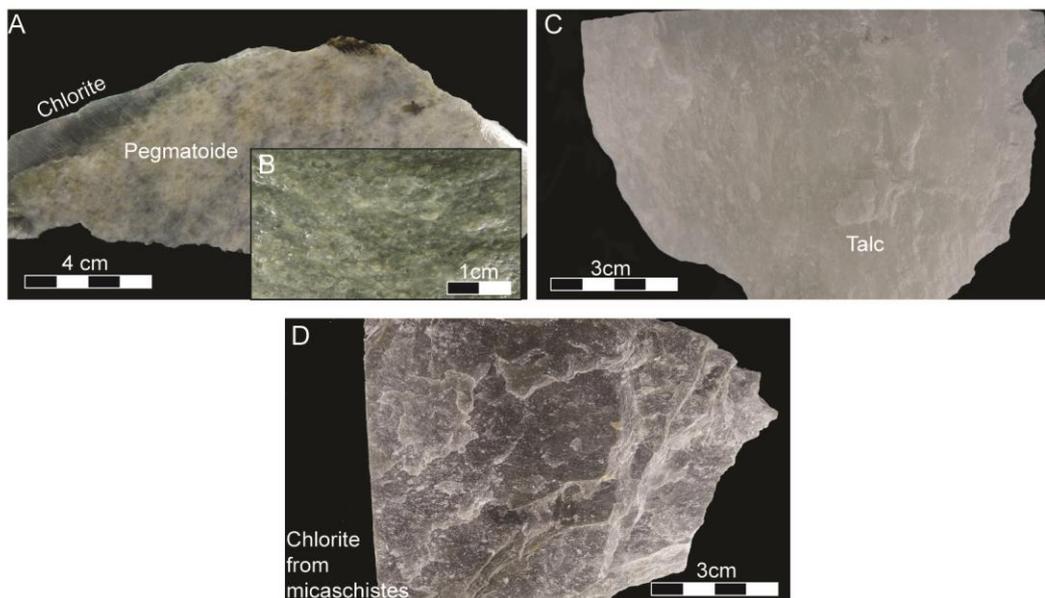
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472 **Figure 1** Simplified geological map of the Saint Barthelemy Massif modified after Boutin et
 473 al. (2016) and Saint Blanquat (de) (1989)

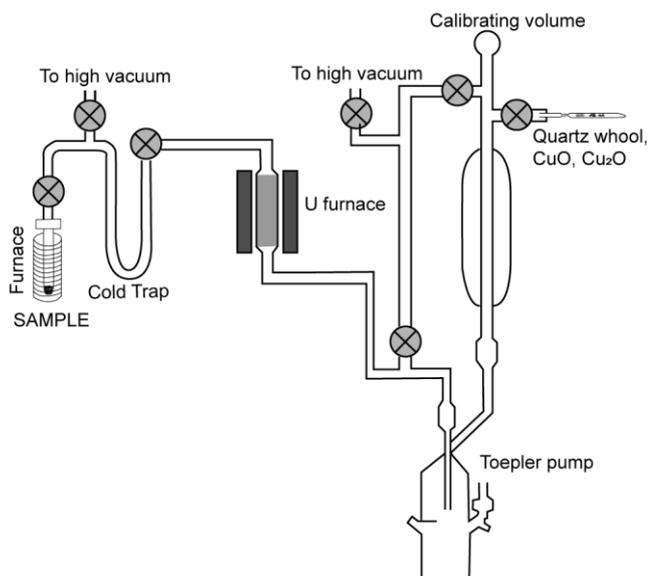
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475

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

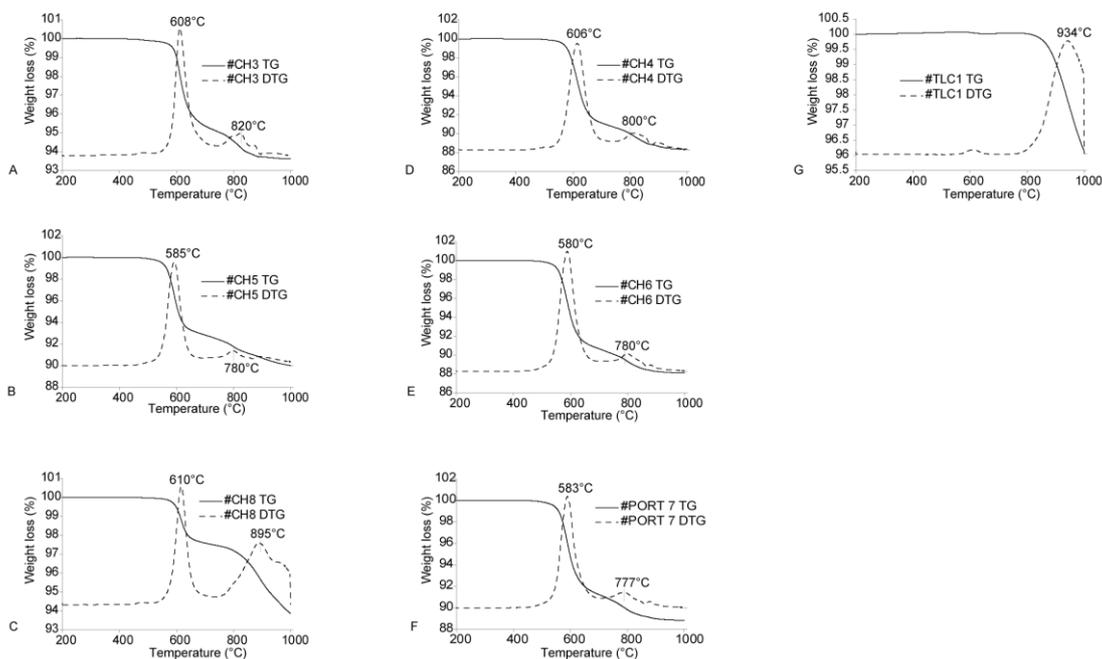


480

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 N₂ gas.

488

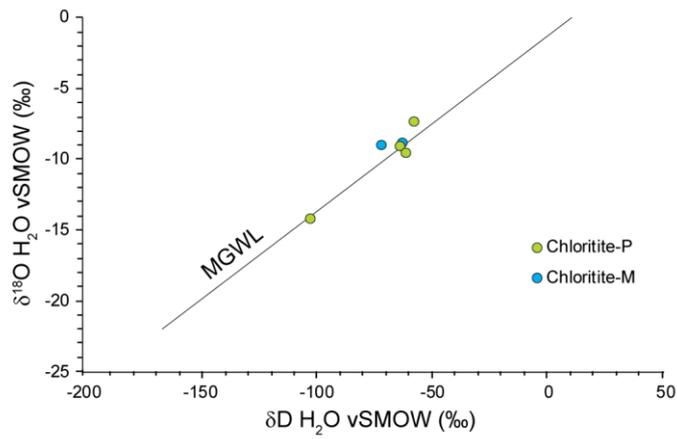
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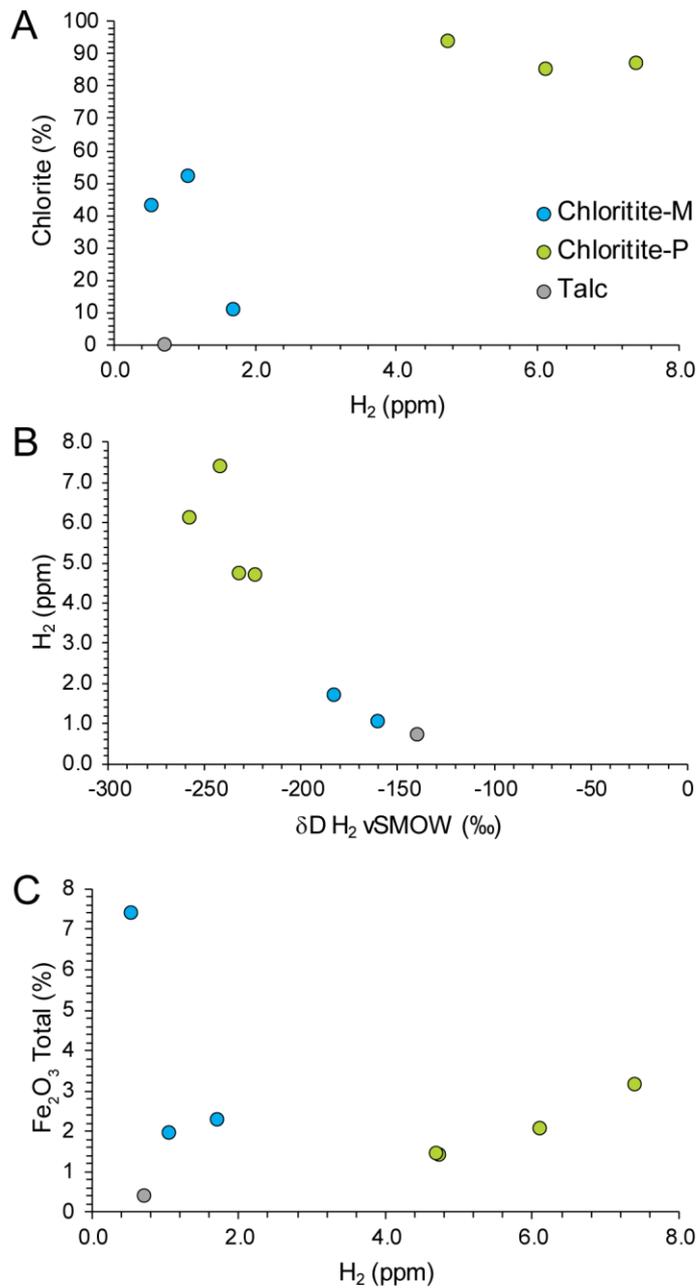
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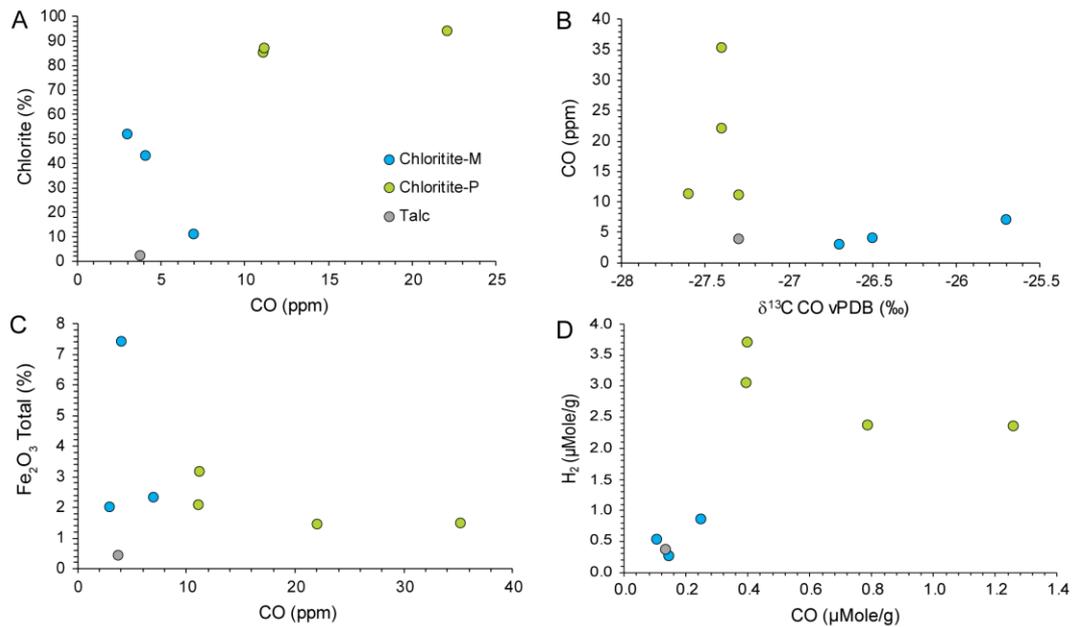
495 **Figure 5** Oxygen and hydrogen isotope compositions of adsorbed/entrapped water released
496 from chloritite-P and chloritite-M samples during the first heating steps. Meteoric Global Water
497 Line (MGWL) has been drawn using the following equation: $\delta D = 8 \times \delta^{18}\text{O} + 10$

498



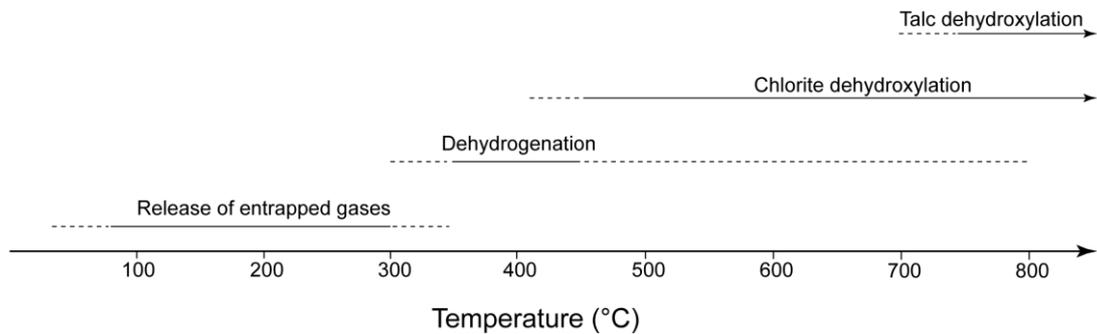
499 **Figure 6** A: Quantity of H₂ released during experiments as a function of the mineralogy of
 500 the sample. The chlorite amount is given in Table 2, based on XRD analyses of rock samples.
 501 B: Hydrogen isotopic composition of H₂ as a function of the quantity of H₂ released during
 502 experiments. C: Quantity of H₂ 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 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 ₂	%	42.53	38.36	54.45	33.28	34.28	33.64	31.72	62.00
Al ₂ O ₃	%	17.26	14.26	3.68	18.53	16.71	17.25	18.12	0.23
Fe ₂ O ₃	%	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 ₂ O	%	B.D.L.	B.D.L.						
K ₂ 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 ₂	%	0.78	0.84	0.11	0.07	B.D.L.	B.D.L.	0.03	B.D.L.
P ₂ O ₅	%	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 ₂ total	%	0.56	0.23	4.99	0.02	0.07	0.13	0.04	0.14
C _{org}	%	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.						
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 ₂ (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 _{H₂} 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 ¹³ 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 _{H₂O} vs. vSMOW (‰)	n/a	-62	-71	-63	-57	-102	-61	n/a
s		0		4		4	5	
δ ¹⁸ O _{H₂O} 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 _{WR} 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							

521

522

523 **Table 2** Amounts of H₂ and CO released during experiments, and stable isotope compositions524 of H₂ (δD_{H₂}), interstitial/adsorbed H₂O (δD_{H₂O}, δ¹⁸O_{H₂O}), CO (δ¹³C_{CO}). Hydrogen isotope525 compositions of whole-rock chloritite and talc samples (δD_{WR}). XRD quantitative estimation

526 of mineral compositions of whole-rock samples. n: number of replicates; σ: Difference

527 between the average and the replicates; n/a: not available.

528

529

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531

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