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# 1 **Hydrogen generation during hydrothermal alteration of peralkaline granite**

2

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12

## 13 **Abstract**

14 It is well known that oxidation of ferrous to ferric iron by water can generate molecular  
15 hydrogen (H<sub>2</sub>), with the most widely recognized natural manifestation being serpentinization  
16 of olivine and pyroxene in ultramafic rocks. A less known yet extremely important source of  
17 natural H<sub>2</sub> are peralkaline igneous intrusions, where spectacular enrichments of H<sub>2</sub> are  
18 documented from fluid inclusions and as free gas migrating through fractured rocks and soils.  
19 Of these occurrences, the best studied are those at Strange Lake in Canada, Lovozero and  
20 Khibiny in Russia, and Ilímaussaq in Greenland. Based on petrographic observations and  
21 fluid inclusions analysis, it has been proposed that the hydrothermal alteration of arfvedsonite,  
22 an Fe<sup>II</sup>-bearing amphibole, is the source of H<sub>2</sub> in this context, although it is yet to be  
23 unequivocally demonstrated. To investigate the generation of H<sub>2</sub> during alteration of

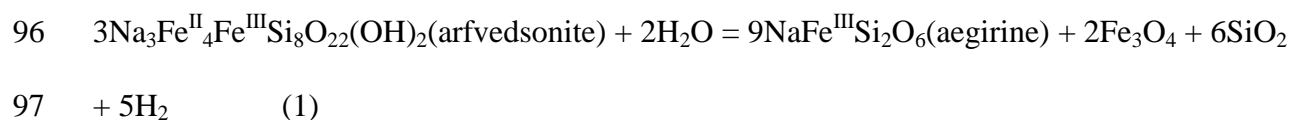
24 peralkaline granites, we performed hydrothermal experiments on pure arfvedsonite grains and  
25 arfvedsonite-bearing granite (10 wt% arfvedsonite) from the Strange Lake pluton (Canada).  
26 These materials, in the presence of aqueous solutions, were sealed inside gold capsules or  
27 placed within titanium autoclaves, which allowed monitoring H<sub>2</sub> generation in function of  
28 temperature (280–400 °C), chlorinity (0 and 3 m NaCl), pH, and starting mineral assemblage.  
29 Blank experiments were conducted to quantify the background amounts of H<sub>2</sub> generated from  
30 Au/Ti oxidation, diffusing through the reaction cells, release from fluid inclusions or  
31 otherwise occluded in minerals. Solids were characterized by XRD, SEM, TEM on FIB foils,  
32 and STXM-XANES. Outcomes of this study demonstrate the production of H<sub>2</sub> in agpaitic  
33 peralkaline rocks by the hydrothermal alteration of arfvedsonite. The rate of H<sub>2</sub> production,  
34 normalized to the specific surface area of arfvedsonite, increases with temperature from 1100  
35 to 2200 pmol cm<sup>-2</sup> day<sup>-1</sup> between 280 and 400 °C, respectively. Chlorinity tends to have a  
36 negative impact on the reaction rate, while circumneutral to alkaline conditions clearly  
37 promote H<sub>2</sub> generation. Altering whole granite samples instead of arfvedsonite grains only  
38 also enhances H<sub>2</sub> production rate. The presence of aluminum, released from microcline and  
39 albite dissolution, may increase both the solubility and the dissolution rate of arfvedsonite by  
40 promoting precipitation of phyllosilicates. At least two different types of phyllosilicates were  
41 observed, chlorite and montmorillonite. Magnetite and secondary zircon were also identified  
42 at the surface of reacted arfvedsonite (Zr content = 1200 ppm). The H<sub>2</sub> production rates  
43 reported here at 280–400 °C are comparable, and even faster than those documented for  
44 serpentinization of olivine and harzburgite. A major feature of arfvedsonite alteration in  
45 peralkaline plutons is the formation of aegirine as a replacing mineral. However, aegirine was  
46 never observed in the reacted solids from our experiments, under the condition tested (up to  
47 400 °C and 400 bar). This may be an effect of pressure, oxygen fugacity, or reaction progress,  
48 parameters that remain to be investigated to better constrain the reaction mechanism of

49 arfvedsonite alteration. Agpaitic peralkaline igneous intrusions thus represent a fertile  
50 geological setting for deep microbial subsurface ecosystems, abiotic synthesis of organic  
51 molecules, and natural H<sub>2</sub> exploration for an alternative source of energy.

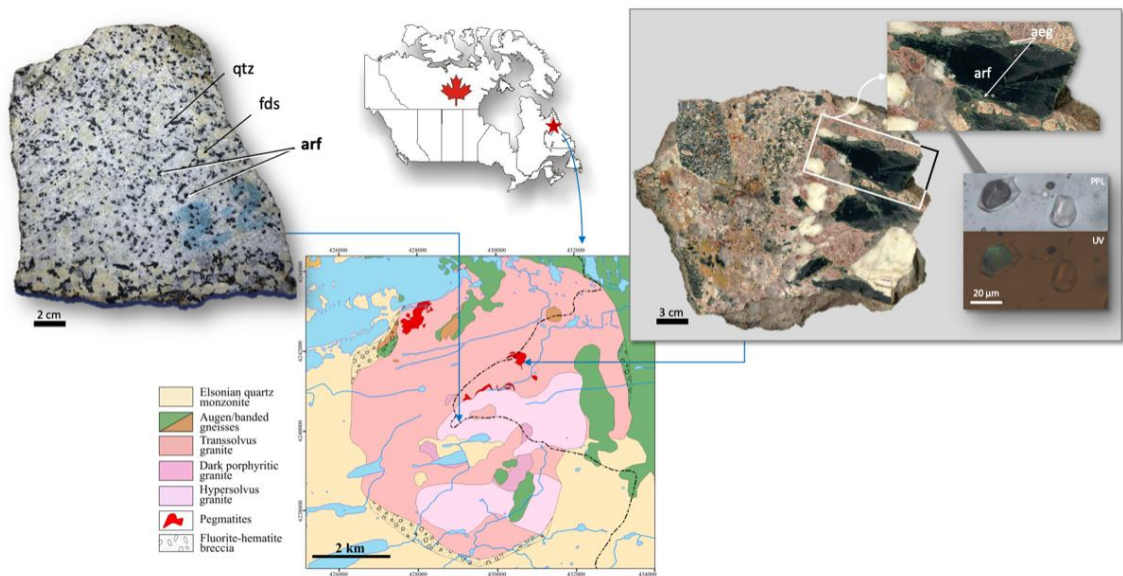
## 52 1. Introduction

53 Production of molecular hydrogen (hereafter hydrogen or H<sub>2</sub>) is a phenomenon that  
54 can occur naturally during water-rock interaction (Klein et al., 2020). Recently, this process  
55 has drawn increasing scientific attention owing to the central role that this molecule plays in  
56 supporting deep microbial subsurface ecosystems and in promoting abiotic synthesis of  
57 organic molecules (Ménez et al., 2020; Sleep et al., 2004; Truche et al., 2020). Furthermore,  
58 in the last couple of years, growing pressure on our society to develop carbon-free technology  
59 has sparked an unprecedented interest in naturally occurring H<sub>2</sub>, as it could represent a  
60 potential alternative resource to fossil fuels (Donzé et al., 2020; Gaucher, 2020; Murray et al.,  
61 2020; Prinzhofer et al., 2018; Truche and Bazarkina, 2019, Smith et al., 2005). Spontaneous  
62 production of H<sub>2</sub> in nature involves nonbiological processes in the Earth's crust, driven by  
63 reactions such as (1) reduction of water during the oxidation of iron in minerals (Klein et al.,  
64 2013, McCollom et al., 2016; McCollom et al., 2020a; Milesi et al., 2015), (2) radiolysis of  
65 water due to radioactive decay of U, Th, and K (Lin et al., 2005; Truche et al., 2018), (3)  
66 reaction of water with surface radicals during mechanical fracturing of silicate-bearing rocks  
67 (Hirose et al., 2011), and (4) reaction of FeS with water to generate FeS<sub>2</sub> plus H<sub>2</sub> (Drobner et  
68 al., 1990). Among these reactions, the most thoroughly investigated has been undoubtedly  
69 those taking place during hydrothermal alteration of ultramafic rocks (i.e. serpentinization),  
70 where hydration of Fe<sup>II</sup>-bearing olivine and pyroxene leads to the concomitant reduction of  
71 water into H<sub>2</sub> (Cannat et al., 2010; Klein et al., 2020; Worman et al., 2016, 2020). The  
72 numerous occurrences of H<sub>2</sub>-bearing fluids documented in ultramafic geological  
73 environments such as mid-oceanic ridges (Charlou et al., 2002; Seewald et al., 2003),  
74 ophiolites (Chavagnac et al., 2013; Coveney et al., 1987; Neal and Stranger, 1983; Vacquand  
75 et al.; 2018), Precambrian terrains or greenstone belts (Boreham et al., 2021; Sherwood Lollar  
76 et al., 2014) have of course motivated these researches.

77 Less known than the above-mentioned geological contexts, high H<sub>2</sub> contents are also  
78 reported in olivine free, agpaitic peralkaline igneous intrusions among which those of Strange  
79 Lake (Canada), Ilímaussaq (Greenland), Lovozero and Khibiny (Kola Peninsula, Russia) are  
80 world-class occurrences (Krumrei et al., 2007; Marks and Markl, 2017; Nivin, 2019; Potter et  
81 al., 2013; Salvi and Williams-Jones, 1992, 2006). In the latter two cases, H<sub>2</sub>, together with  
82 CH<sub>4</sub> and higher hydrocarbons, in addition of being observed in fluid inclusions entrapped in  
83 minerals (up to 40 mol%), also occurs as a free gas phase in fracture networks in the rocks, as  
84 well as in underground mine galleries where it poses serious safety issues (Ikorskiy, 1986;  
85 Nivin, 2016, 2019, 2020; Nivin et al., 1995; 2001). Such unique occurrences of H<sub>2</sub> occluded  
86 in minerals, diffusely dispersed and freely migrating in rock fractures and soils, raise  
87 important questions about the source of this gas. The two main processes that have been  
88 proposed to account for H<sub>2</sub> production in these rocks rely either on early magmatic degassing  
89 (Beeskow et al., 2006; Konnerup-Madsen, 2001; Vasyukova et al., 2016; Vasyukova and  
90 Williams-Jones, 2019) or on late subsolidus hydrothermal alteration of ferrous minerals (Salvi  
91 and Williams-Jones, 1992, 1997; Potter and Konnerup-Madsen, 2003; Potter et al., 2013;  
92 Vasyukova et al., 2016; Vasyukova and Williams-Jones, 2019). The latter hypothesis is  
93 supported by fluid-inclusion evidence and by the petrographic observation of pseudomorphic  
94 replacement of the Fe<sup>II</sup>-bearing amphibole arfvedsonite by aegirine, a Fe<sup>III</sup>-bearing pyroxene,  
95 as shown in **Figure 1**. Such a reaction may lead to H<sub>2</sub> production according to:



98 At Strange Lake, this reaction is interpreted to have been caused by relatively saline  
99 orthomagmatic brines released during crystallization of the transsolvus granite at T ≥ 350 °C  
100 (e.g. Salvi and Williams-Jones, 1992; 1996, 1997).



102  
 103 **Figure 1.** Geological map of the Strange Lake pluton (courtesy of O. Vasyukova) locating the  
 104 sample of hypersolvus granite used for the experiments (left-hand side). On the right-hand  
 105 side is shown a sample of altered pegmatite where incipient replacement of arfvedsonite  
 106 (large dark green crystals) by aegirine (light green) is clearly visible. The fluid inclusions  
 107 displayed in the inset represent an example of coexisting L- and V-rich individuals, where the  
 108 latter contain hydrogen as well as higher-order hydrocarbons, showing fluorescence under UV  
 109 illumination. qtz = quartz, fds = feldspars, arf = arfvedsonite, aeg = aegirine.

110

111           Recently, Vasyukova et al. (2016), and Vasyukova and Williams-Jones (2019)  
 112 documented in more details the fluid evolution of the hydrothermal systems at Strange Lake,  
 113 on the basis of a meticulous fluid and melt inclusion study. According to these authors, fluid  
 114 evolution commenced with the exsolution of a brine (~25 wt% NaCl eq.) coexisting with an  
 115 immiscible CH<sub>4</sub>-dominant vapor from a pegmatitic melt, at temperatures of ~450–500 °C and  
 116 a pressure of ~1100 bar. During isobaric cooling path, the vapor phase gradually evolved  
 117 from CH<sub>4</sub>-dominant to a CH<sub>4</sub>-bearing mixture with a significant proportion of H<sub>2</sub> and higher-  
 118 order hydrocarbons. Formation of C<sub>2</sub> to C<sub>6</sub> hydrocarbons, and at least part of the hydrogen,  
 119 was synchronous to the alteration of arfvedsonite to aegirine and occurred at ~325–360 °C.  
 120 The last stage of fluid evolution – after cessation of arfvedsonite alteration – is characterized  
 121 by a CO<sub>2</sub>-dominant fluid at ~300 °C. Along this temperature-pressure paths, the apparent

122 salinity of the aqueous fluid decreased from ~25 to ~4.5 wt% NaCl eq. due to fluid-rock  
123 interaction.

124         Based on this knowledge, we constructed an experimental study that, for the first time,  
125 reproduces the production of H<sub>2</sub> by altering arfvedsonite from peralkaline granite. As starting  
126 material, we used separate arfvedsonite grains and whole granite samples from the Strange  
127 Lake pluton and, by controlling temperature, pH and salinity of the fluid we obtained the  
128 amounts, rate and mechanisms of H<sub>2</sub> generation between 280 and 400 °C at various pressures.  
129 These results are compared to available experimental data on H<sub>2</sub> generation during  
130 serpentinization of olivine and ultramafic rocks. Our findings provide new, important insights  
131 into H<sub>2</sub> generation during the interaction of aqueous fluids with peralkaline rocks.

132

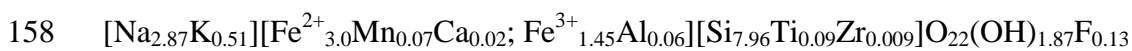
## 133 2. Experimental Methods

### 134 2.1. Materials

135 A sample of unaltered peralkaline granite from Strange Lake (Canada), hereafter noted SL-  
136 granite, was used as a starting material for all experiments (**Fig. 1**). This granite, of  
137 hypersolvus composition, represents the earliest and least evolved intrusive facies of the  
138 pluton (Siegel et al., 2018). The sample was collected from an outcrop in the southern parts of  
139 the pluton, a unit known to be unattained by hydrothermal alteration (e.g. Salvi & Williams-  
140 Jones 1990; Siegel et al., 2018). Attention was also paid to eliminate all parts that were  
141 exposed to weathering. The unaltered nature of the sample was verified by petrographic  
142 observations. The modal mineralogical composition of SL-granite, deduced by X-Ray  
143 diffraction (XRD) analysis, is as follows: 33 ±2 wt% albite, 28 ±2 wt% microcline, 28 ±2  
144 wt% quartz, 10 ±2 wt% arfvedsonite, 0.6 ±0.2 wt% fluorite, and minor rutile. Aegirine was  
145 neither detected by XRD analysis nor by any other technique used in this study.



146 The SL-granite sample was ground with an agate mortar, sieved (53–212  $\mu\text{m}$ ), sonicated in  
147 Milli-Q water (resistivity of 18.2  $\text{M}\Omega\cdot\text{cm}$  at 25  $^{\circ}\text{C}$ ) to remove adhering fine particles, and  
148 dried in a glove box under inert argon atmosphere ( $[\text{O}_2] < 1 \text{ ppm}$ ) at room temperature.  
149 Arfvedsonite and quartz were recovered separately using a hand magnet and hand-picked  
150 under a binocular microscope, respectively. Quartz was used in some blank experiments to  
151 evaluate possible sources of  $\text{H}_2$ . Once separated, the solids were washed with 1 M HCl, rinsed  
152 several times with Milli-Q water and stored under anoxic conditions (using Ar gas) in a glove  
153 box ( $[\text{O}_2] < 1 \text{ ppm}$ ). The chemical composition of arfvedsonite was obtained by electron  
154 microprobe analysis (**Supplementary Table S1**) and its  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio was measured by  
155 Scanning Transmission X-Ray microscopy (STXM - see analytical methods below). Based on  
156 these data and using the methods proposed by Li et al. (2020), we obtained the following  
157 arfvedsonite formula:



159 The BET surface areas of SL-granite and arfvedsonite measured using Kr as the  
160 adsorbate gas are similar:  $0.30 \pm 0.03 \text{ m}^2 \text{ g}^{-1}$ .

161

## 162 2.2. Experiments

### 163 2.2.1. Experimental Strategy

164 Initially, we performed a number of blank experiments to ensure that all hydrogen measured  
165 was produced from the experimental charges, and, conversely, that no hydrogen escaped the  
166 experimental systems. More details on blank runs are provided in subsequent sections. To test  
167 the potential effect of minerals other than arfvedsonite, in addition of using arfvedsonite-only  
168 powders we also ran experiments using whole SL-granite. Experiments were carried out at  
169 280 to 400  $^{\circ}\text{C}$ , in order to cover the expected temperature range at which arfvedsonite is

170 interpreted to be replaced by aegirine in nature (Salvi and Williams-Jones, 1992; 1996, 1997,  
171 2006; Potter et al. 2013). For similar reasons, the pressure during the experiments ranged  
172 from 70 to 500 bar. A parametric investigation of the effect of pH and salinity was performed  
173 at 350 °C and 500 bar. A salinity of 3 m NaCl (i.e. 17.4 wt% NaCl) was chosen to reproduce  
174 those measured in fluid inclusions (Vasyukova et al., 2016). Finally, as the pH of the fluids  
175 responsible for the alteration of the Strange Lake granite was quite variable (i.e., ranged from  
176 3 to 10; Vasyukova and Williams-Jones, 2019), we investigated very contrasted pH  
177 conditions using 0.1 m HCl (pH = 1) or 0.1 m NaOH (pH = 13) starting solutions. The pH  
178 value was free to evolve over the course of the experiments but, regardless, such acidic or  
179 alkaline solutions impose drastically different pH conditions.

180 Two experiments were designed to measure the rate of H<sub>2</sub> production during SL-granite  
181 alteration. One experiment was carried out at 280 °C and 70 bar, in the presence of SL-granite  
182 and pure water. Another experiment, performed at 350 to 400 °C, was designed to study the  
183 effect of salinity and fluid density on H<sub>2</sub> production rate. This experiment aimed at  
184 reproducing the vapor-liquid immiscibility that occurs when adiabatically decompressing a  
185 supercritical brine from 400 °C/400 bar to 400 °C/260 bar. The sections below detail the  
186 experimental setups and conditions.

187

### 188 *2.2.2. Experiments performed at 350°C/500 bar in gold capsules*

189 A set of 17 experiments were carried out in gold capsules loaded in cold-seal pressure  
190 vessels and reacted at 350 °C and 500 bar for 15 days (360 hours) (runs #1 to #15 in **Table 1**).  
191 The experimental charges consisted of ~50 mg of solids (SL-granite, arfvedsonite, or quartz)  
192 and ~50 mg of solution (milli-Q water, or 3 m NaCl brines ± 0.1 m HCl ± 0.1 m NaOH).  
193 Blank experiments without solid (fluid only) or without fluid (solid only) were performed to  
194 quantify possible background H<sub>2</sub> generation due to Au capsule oxidation, or released from

195 minerals. The Au capsules (volume of ~0.2 mL) were filled under anoxic condition inside a  
196 glove box under Ar atmosphere ( $[O_2] < 1$  ppm), and their extremities were pinched shut  
197 before extracting them out of the glove box. The capsules were then immediately welded and  
198 placed inside an oven at 90 °C overnight to ensure absence of leakage (the mass of the  
199 capsules was weighted before and after heating). For the experiment, the capsules were  
200 loaded into a cold-seal pressure vessel filled with water as the pressure medium, pressurized  
201 at 500 bar and heated to 350 °C for 15 days. After reaction, the autoclaves were quenched  
202 with a flux of compressed air for up to 15 minutes and opened. The Au capsules were  
203 weighted again to verify leakage had not occurred. A syringe equipped with an indenter and a  
204 three-way valve was used to pierce the Au capsules and to release the produced gas. The  
205 syringe was previously flushed with Ar to remove air. The gas mixture (Ar + released gases)  
206 was sampled through a septum placed on one of the valve's taps and analyzed by gas  
207 chromatography for H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>. All details of gold capsule piercing, gas recovery and  
208 analysis are described by Malvoisin et al. (2013). The pH and chemical composition of the  
209 reacted fluids were not measured in these experiments because of the difficulty in retrieving  
210 sufficient amount of fluid after capsule piercing and gas analysis. The solids were recovered  
211 and immediately transferred into the anoxic glove box where they were rinsed with milli-Q  
212 water, dried at ambient temperature under Ar atmosphere and stored until the time of analysis.  
213

214 **Table 1:** List of experiments and conditions.

#run	Initial fluid composition	Starting material	Experimental setup	T (°C)	P (bar)	W/R mass ratio
1	- (dry)	SL-granite	gold capsule	350	500	no solution
2	- (dry)	arfvedsonite	gold capsule	350	500	no solution
3 and 3'	H <sub>2</sub> O	SL-granite*	gold capsule	350	500	1
4 and 4'	H <sub>2</sub> O	arfvedsonite*	gold capsule	350	500	1
5	H <sub>2</sub> O	no solid	gold capsule	350	500	no solid
6	3 m NaCl	SL-granite	gold capsule	350	500	1
7	3 m NaCl	arfvedsonite	gold capsule	350	500	1
8	3 m NaCl	quartz	gold capsule	350	500	1
9	3 m NaCl	no solid	gold capsule	350	500	no solid
10	3 m NaCl + 0.1 m HCl	SL-granite	gold capsule	350	500	1
11	3 m NaCl + 0.1 m HCl	arfvedsonite	gold capsule	350	500	1
12	3 m NaCl + 0.1 m HCl	no solid	gold capsule	350	500	no solid
13	3 m NaCl + 0.1 m NaOH	SL-granite	gold capsule	350	500	1
14	3 m NaCl + 0.1 m NaOH	arfvedsonite	gold capsule	350	500	1
15	3 m NaCl + 0.1 m NaOH	no solid	gold capsule	350	500	no solid
QTZ280	H <sub>2</sub> O	Quartz	Ti autoclave	280	70	20
SL1	H <sub>2</sub> O	SL-granite	Ti autoclave	280	70	20
SL9	H <sub>2</sub> O	SL-granite	flexible-cell autoclave	350 → 400	400 → 260	10

215 *“\*” indicates that the experiment was replicated, “m” stands for molality in mol kg<sub>w</sub><sup>-1</sup>*

216

217 *2.2.3. Experiments performed at 280 °C in a batch autoclave*

218 Two experiments were conducted in a 450-mL Parr® stirred batch hydrothermal

219 reactor made of pure titanium (Ti grade 4). The reactor was equipped with several

220 connections that enable periodic on-line sampling of reaction liquid (Ti sampling line fitted

221 with a 1 μm Ti porous filter) and gas, to monitor reaction progress. The autoclave was heated

222 in air at 400 °C for 48 hours to make sure all surfaces were oxidized prior to the experiment to  
223 form a quasi-inert TiO<sub>2</sub> passivated layer. The investigated system was composed of 300 g of  
224 Milli-Q water and 15 g of powdered (53–212 μm) SL-granite (#SL1) or pure quartz  
225 (#QTZ280), for an initial water-to-rock mass ratio (W/R) of 20 (**Table 1**). The experiment  
226 conducted with pure quartz was used as a blank to monitor background H<sub>2</sub> production from  
227 eventual autoclave corrosion or fluid inclusion decrepitation. The reaction vessel was bubbled  
228 and flushed with Ar to ensure anoxic condition prior to heating. The reactor was then rapidly  
229 heated to 280 ±1 °C within 15 min. The experiments were conducted at 70 bar total pressure  
230 and 280 °C, during 4 weeks. This pressure resulted from the vapor pressure (64 bar at 280 °C)  
231 plus the background Ar pressure that ensured anoxic condition and leakage detection during  
232 the run. The calculated partial pressures of H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> produced during the experiment  
233 remained < 0.2 bar during the entire run.

234         Liquid and gas were sampled regularly throughout the experiments. During each  
235 sampling, three separate liquid aliquots were collected for a total volume of ~6 mL. The first  
236 aliquot allowed purging of the sampling line. The second aliquot was used for pH  
237 measurements. Total dissolved cations (Ca, Na, K, Mg, Al, Si, Fe, Mn) were determined from  
238 the third aliquot, after filtration at 0.2 μm and HNO<sub>3</sub> dilution. Gas was sampled directly into a  
239 gas-tight, Ar-purged glass syringe and analyzed by gas chromatography for the abundance of  
240 H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>. Each successive sampling induced a slight pressure decrease – from 70 to  
241 66 bar over the entire duration of the experiments. Necessary corrections were made to  
242 calculate the total amount of H<sub>2</sub> produced by considering the volume of liquid and gas  
243 sampled, the remaining volume of liquid or gas in the reactor at each step, and the pressure  
244 change. The amount of H<sub>2</sub> dissolved in the aqueous phase was calculated using the Henry's  
245 law constant at water saturation pressure reported by Fernández-Prini et al. (2003):  
246  $\text{Log}_{10}(k_H/\text{MPa}) = 1.88$  at 280 °C and  $P_{\text{sat}}$ . After reaction, the autoclave was quenched in cold

247 water and opened. Solids were immediately transferred into a glove box, rinsed with Milli-Q  
248 water and then dried at room temperature.

249

250 *2.2.4. Experiments performed at temperatures ranging from 350 to 400 °C in a flexible-cell*  
251 *hydrothermal autoclave*

252 One experiment (#SL9) was carried out in a flexible-cell hydrothermal apparatus  
253 (CoreTest®) using a 155 mL flexible titanium reaction cell fitted with a titanium sampling  
254 line (1 µm Ti porous filter, Ti tube and valve). All titanium components were heated in air for  
255 at least 48 hours at 400 °C prior to the experiment in order to form a relatively inert TiO<sub>2</sub>  
256 surface layer. The reaction cell was contained within a stainless-steel pressure housing, with  
257 water used as an external pressurizing fluid. The external pressurizing water was spiked with  
258 1 mmol L<sup>-1</sup> SrCl<sub>2</sub>, and the concentration of Sr inside the flexible Ti cell was monitored over  
259 the course of the experiment to test for leakage. The reaction cell was initially loaded with 7.3  
260 g of SL-granite of uniform grain size (53–212 µm) and 73 g of Milli-Q water - W/R = 10  
261 (**Table 1**). Fluids were sampled during the experiments in order to monitor reaction progress  
262 over time. At each instance, two separate aliquots were sampled for a total mass of fluid of 3  
263 to 7 g. The first one corresponded to the sampling of the purge line and the second one was  
264 used for gas and total dissolved cation analysis. These samples were collected in two separate  
265 titanium cells previously evacuated (primary vacuum). The pressure was returned to the  
266 targeted value after each sampling point. This experiment consisted of 3 consecutive stages:  
267 1) 350 °C and 400 bar, for 336 hours; 2) 400 °C and 400 bar, for 216 hours; and finally 3) 400  
268 °C and 260 bar, after NaCl-bearing solution injection, for 210 hours. During the first two  
269 stages of the experiment (up to 400 °C and 400 bar), the reaction occurred in a single-phase  
270 fluid. The flexibility of the Ti reaction cell allowed fluids to be sampled without loss of  
271 pressure and eliminated the presence of a vapor headspace so that reactions remained

272 confined to the aqueous phase. The density of the fluid decreased slightly, from 0.67 to 0.62 g  
273  $\text{cm}^{-1}$ , from stage 1 to stage 2 (single-phase fluid). In contrast, the last stage was conducted in  
274 the presence of two fluid phases: brine and vapor. Ten milliliters of a 5 molar NaCl brine  
275 were injected inside the Ti flexible cell at 400 °C and 400 bar by means of a high-pressure  
276 hand (capstan) pump. After brine injection, the pressure decreased to 260 bar, inducing phase  
277 separation. The respective density, volume and salinity of the brine and vapor phases were as  
278 follow: 0.70  $\text{g cm}^{-1}$  / 16 mL / 2.7 m NaCl, and 0.19  $\text{g cm}^{-1}$  / 89 mL / 0.028 m NaCl. During  
279 this last stage, only the vapor phase was sampled to avoid damaging the flexible cell and  
280 strong fluctuations of the W/R ratio. After reaction, the autoclave was quenched with a flux of  
281 compressed air for up to 20 minutes and opened. Solids were immediately transferred into the  
282 glove box, rinsed with Milli-Q water and then dried at room temperature.

283

## 284 2.3. Analytical techniques

### 285 2.3.1 Gas and liquid analysis

286 The gas samples were analyzed using a Perkin Elmer® CLARUS 500 gas  
287 chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a 2-m long  
288 column (RESTEK® Shin Carbon ST 80/100) traversed by Ar as carrier gas. The GC was  
289 calibrated using several Ar+H<sub>2</sub>+CH<sub>4</sub>+CO<sub>2</sub>+CO gas mixtures of different concentrations  
290 injected with a gas syringe of calibrated volume. The estimated analytical error is  $\pm 5\%$ . In  
291 most cases the reported H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> concentration are averages of 3-4 gas injection into  
292 the GC. For comparative purposes, the measured H<sub>2</sub> concentrations were normalized to the  
293 total number of moles of H<sub>2</sub> generated per gram of SL-granite or arfvedsonite to account for  
294 variations in the amount of solid reactants used in different experiments and for the changing  
295 mass of fluid present in the reaction vessel as aliquots are removed during sampling.

296 Liquid aliquots from experiments carried out in Ti autoclaves (both Parr and Coretest)  
297 were filtered (0.2  $\mu\text{m}$ ), diluted and acidified (2 vol. %  $\text{HNO}_3$ ), and analyzed for major cations  
298 with matrix-matched standards using inductively coupled plasma-atomic emission  
299 spectroscopy (ICP-AES; Varian® 720ES) with a precision of 3 % at the 95 % confidence  
300 level. Fluid chemistries as analyzed and corrected for acid dilution are reported in  
301 **Supplementary Tables S2.**

302

### 303 2.3.2. *Electron microscopy*

304 Scanning Electron Microscopy (SEM) was used for examination of the morphology  
305 and texture and for chemical investigation of the powdered samples before and after reaction.  
306 SEM images were obtained using a Tescan® Vega3 electron microscope operating at 15 kV,  
307 equipped with an Energy Dispersive X-ray Spectrometer (EDXS). Photomicrographs were  
308 recorded both in secondary (SE) and backscattered (BSE) electron modes.

309 Additional compositional data were obtained by Electron Microprobe Analysis  
310 (EMPA) using a JEOL® JXA 8230 electron microprobe equipped with five wavelength-  
311 dispersive spectrometers. Arfvedsonite was analyzed with an accelerating voltage of 15 kV, a  
312 beam current of 12 nA and a defocused beam diameter of 5  $\mu\text{m}$ . The standardization was  
313 made using natural minerals and synthetic oxides standard set (P&H Developments Ltd.). The  
314 Smithsonian hornblende USNM143965 (Jarosewich et al., 1980) was measured as an  
315 unknown together with our samples to verify analytical accuracy and precision.

316 Transmission Electron Microscopy (TEM) micrographs and Energy-dispersive X-ray  
317 (EDX) analysis were obtained on thin section cut with a Focused Ion Beam (FIB). The areas  
318 of interest were milled with a FIB in order to obtain ultrathin samples – with conservation of  
319 the texture of the mineral phases – transparent to the TEM electrons. This was done on a cut  
320 oriented vertically and perpendicular to the sample surface, using the FEI strata DualBeam



321 235 of Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN, Lille),  
322 and cut out to a size of approximately 15  $\mu\text{m}$  by 5  $\mu\text{m}$  and a thickness around 80 nm. Such  
323 preparation allows a cross sectional view of the altered material. To check the preservation of  
324 the mineral crystalline structure after FIB milling, lattice-fringe imaging was systematically  
325 carried out with the TEM, following the protocol of Bourdelle et al. (2012). The FEI Tecnai®  
326 G2-20 model TEM used (Plateforme de Microscopie Electronique de Lille (PMEL) – Institut  
327 Chevreul of Lille, France) operates at 200 kV, and is equipped with a Charged-Coupled  
328 Device (CCD) camera and an EDX spectrometer allowing to acquire chemical analysis (on 50  
329 nm diameter surface area) with a counting time of 30 s for a dead time of less than 10 %.

330

### 331 2.3.3. X-ray diffraction

332 Powder X-ray diffraction (XRD) patterns were acquired from both random and  
333 oriented mounting of the samples. The diffractometer was a Bruker® D8 equipped with a  
334 SolX Si(Li) solid state detector from Baltic Scientific Instruments using  $\text{CuK}\alpha$  radiation ( $\lambda =$   
335  $1.5406 \text{ \AA}$ ) generated at 40 kV and 40 mA. On the primary side, a divergence slit ( $0.298^\circ$ ) and  
336 a soller slit ( $2.5^\circ$ ) were used, while on the secondary side an antiscattering slit ( $0.298^\circ$ ), a  
337 soller slit ( $2.5^\circ$ ) and a receive slit ( $0.06^\circ$ ) were used. Intensities were recorded at  $0.026^\circ 2\theta$   
338 step intervals from  $5$  to  $90^\circ$  (5 s counting time per step) and from  $2$  to  $50^\circ$  (4 s counting time  
339 per step) for bulk and clay mineralogy determination, respectively. The bulk mineralogy was  
340 determined on the  $<2 \text{ mm}$  fraction (obtained after grinding the samples using a McCrone®  
341 micronizing mill). The clay mineralogy was determined on the  $<2 \mu\text{m}$  fraction. Following  
342 sonication of the samples, this fraction was extracted by centrifugation. Oriented mounts were  
343 prepared by drying the resulting suspension onto glass slides. Ethylene-glycol (EG) solvation  
344 of the slides was achieved by exposing them to EG vapor at  $50^\circ\text{C}$  for a minimum of 12 h.  
345 Estimates of modal abundance of minerals were performed using the Rietveld refinement

346 method using the BGMN computer program ([www.bgm.de](http://www.bgm.de)), based on the XRD patterns  
347 collected on randomly oriented samples.

348

#### 349 2.3.4. STXM-XANES

350 X-ray adsorption near-edge structure spectroscopy (XANES) data were acquired using  
351 the Scanning Transmission X-ray microscope (STXM) of the PolLux beamline (for details  
352 about the beamline, see Raabe et al., 2008) at the Swiss Light Source (Paul Scherrer Institute  
353 – SLS, Switzerland) and the HERMES beamline (Belkhou et al., 2013) at the SOLEIL  
354 synchrotron (France). During data collection, the SLS and SOLEIL synchrotron storage rings  
355 operated at 2.4 GeV / 400 mA current and 2.75 GeV / 450 mA current, respectively. STXM  
356 allows to collect XANES data on crystallites with a thickness < 100 nm to allow X-ray  
357 transmission. The thin crystallites of arfvedsonite were recovered in each reaction product,  
358 and dispersed in ethanol; a drop of which is placed (then evaporated) on a carbon holey  
359 support film placed on a TEM 200 mesh copper grid. Stacks of images were obtained by  
360 scanning – with a spatial resolution of 30 nm – the area of interest in the x–y direction over  
361 the 700–730 eV energy range (Fe L<sub>2,3</sub>-edge). Each image of a stack was recorded at one  
362 energy, so that the compilation of the same pixel on each image gives one spectrum. Spectra  
363 were extracted from stacks using the aXis2000 software (Hitchcock, 2012) and processed  
364 following the protocol of Bourdelle et al. (2013). Data were recorded using a circularly  
365 polarized light and a dwell time per pixel and energy point of 10 ms.

366 Spectra acquired through the Fe L<sub>2,3</sub>-edge energy range were used to estimate the  
367 Fe<sup>3+</sup>/ΣFe ratio with an uncertainty around 5 %. This estimate of Fe<sup>3+</sup>/ΣFe ratio is extracted  
368 from the ratio of the two (L<sub>3</sub>-b and L<sub>3</sub>-a) major peak intensities, following the calibration of  
369 Bourdelle et al. (2013). This calibration was established on standard samples, all silicates: five  
370 iron-silicate glasses (containing various Fe<sup>3+</sup> contents), eight phyllosilicates (several chlorites,

371 micas and smectite with various Fe<sup>3+</sup> contents) and a fayalite. This calibration is not  
372 dependent on the silicate structure. To evaluate the result reproducibility, 2 or 3 crystallites of  
373 each sample were analyzed, and for each of them 2 to 3 spectra were extracted (i.e. 4 to 6  
374 spectra per sample).

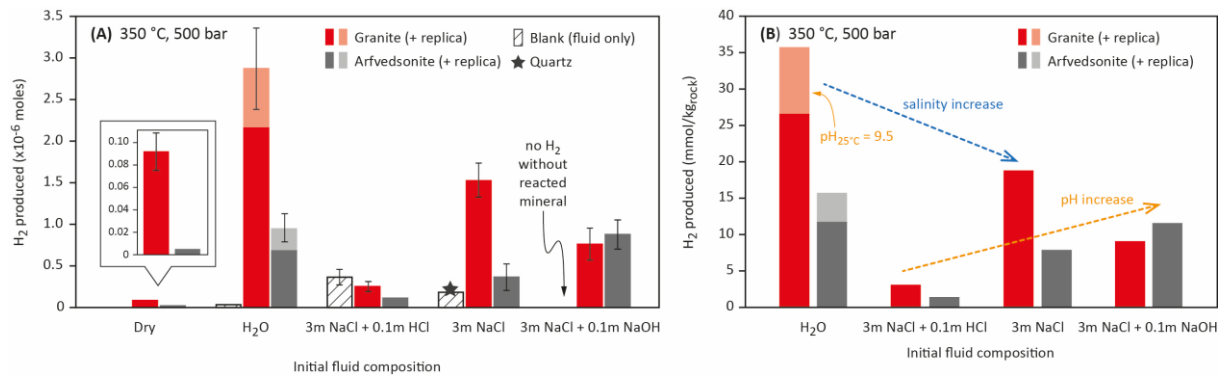
375

### 376 3. Results

#### 377 3.1 H<sub>2</sub> generation from alteration of peralkaline granite and of pure arfvedsonite at 350 °C, 378 500 bar

379 A total of 15 experiments were carried out in gold capsules at 350 °C and 500 bar  
380 during 15 days (360 hours) in order to evaluate the effect of both pH and salinity on H<sub>2</sub>  
381 generation from peralkaline granite and pure arfvedsonite hydrothermal alteration. Some of  
382 these experiments were replicated twice to ensure good reproducibility of the measurements  
383 (**Table 1, Fig. 2**). As for potential H<sub>2</sub> loss, the very low H<sub>2</sub> permeability of gold below 350 °C  
384 has been previously demonstrated (Chou, 1986; Malvoisin et al., 2013). Particular attention  
385 was paid at evaluating blank conditions of our experiments, *i.e.*, test whether H<sub>2</sub> could be  
386 produced from oxidative dissolution of the gold capsules, fluid inclusion decrepitation, or by  
387 releasing of gases occluded in the minerals. We therefore designed a series of runs to  
388 determine possible background blank values. The total amounts of H<sub>2</sub> produced during blank  
389 experiments are shown in **Figure 2a**.

390



391

392 **Figure 2.** Production of H<sub>2</sub> after 360 hours elapsed time in the gold capsule experiments  
 393 carried out at 350 °C and 500 bar. Different initial fluid compositions were tested to evaluate  
 394 the effect of pH and salinity. (a) Experiments carried out in the presence of SL-granite (red)  
 395 or arfvedsonite (black) are compared to the blanks: fluid only (dashed lines) or quartz + 3 m  
 396 NaCl (grey star). The notation “dry” indicates that the gold capsule was loaded with solid  
 397 material only (no fluid). The 2 replicates performed in the presence of water + SL-granite or  
 398 arfvedsonite are shown in light red and light grey, respectively. (b) Production of H<sub>2</sub>  
 399 normalized to the mass of solids (SL-granite or arfvedsonite) as a function of fluid  
 400 composition. Error bars reflect the cumulative uncertainty associated with measuring the  
 401 volume of gas released after piercing the gold capsules and with the analytical uncertainty.  
 402

403 Hydrogen production from gold capsule oxidative dissolution (Equation 2) was  
 404 measured as a function of pH in a 3 m NaCl brine (no solid loaded in the capsule).



406 The amount of H<sub>2</sub> produced by gold dissolution increased when pH decreased. The  
 407 concentration of dissolved hydrogen was below the detection limit under alkaline condition  
 408 (0.1 m NaOH + 3 m NaCl), but reached  $8.6 \pm 0.2 \times 10^{-4}$  m at 350 °C and 500 bar in 0.1 m HCl  
 409 + 3 m NaCl solution. Such a concentration is in very good agreement with thermodynamic  
 410 predictions using the HCh software (Shvarov, 2008), based on the stability constant reported  
 411 by Stefansson and Seward (2003) for the chloridogold(I) complex ( $m_{\text{H}_2(\text{aq})} = 6.3 \times 10^{-4}$  m at  
 412 350 °C and 500 bar in equilibrium with native Au in a 0.1 m HCl + 3 m NaCl solution).

413 Under acidic condition, H<sub>2</sub> production recorded during SL-granite and pure  
 414 arfvedsonite hydrothermal alteration experiments was so low that it can be simply explained  
 415 by the oxidative dissolution of the gold capsule alone (**Fig. 2a**). However, under

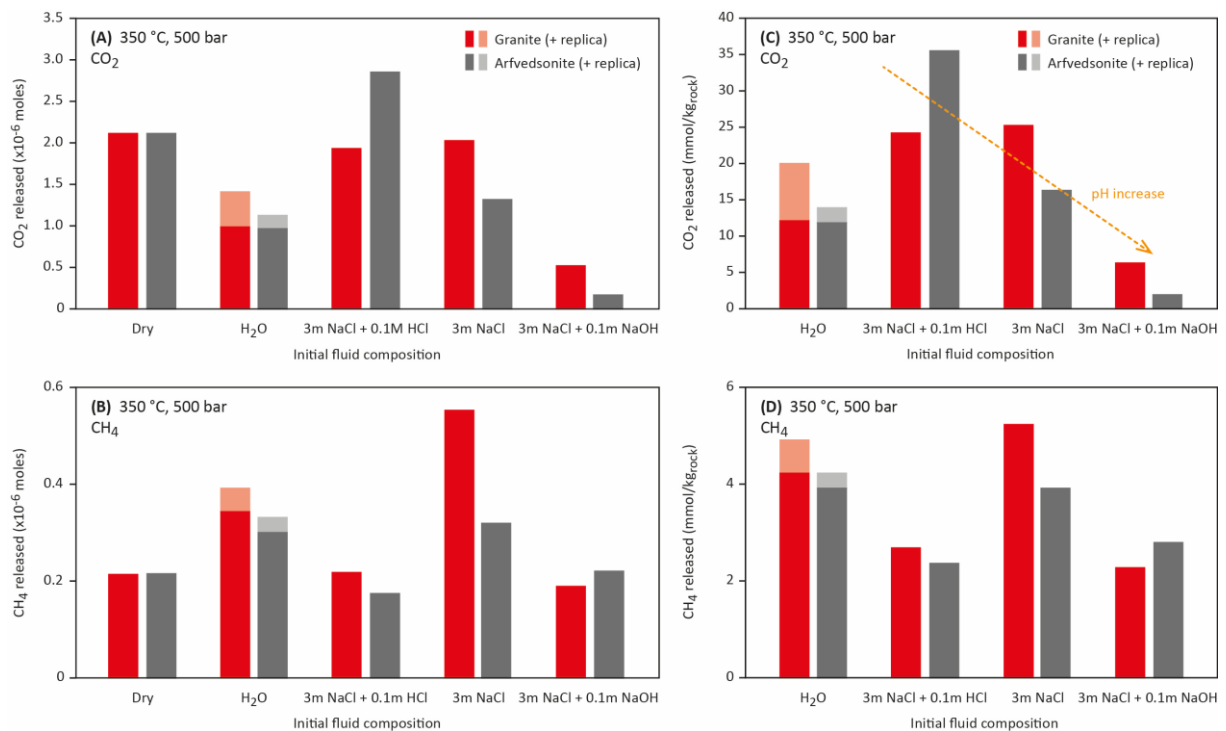
416 circumneutral to alkaline conditions, H<sub>2</sub> produced by gold dissolution represents only a  
417 negligible fraction of the total amount of H<sub>2</sub> generated during hydrothermal alteration of SL-  
418 granite and pure arfvedsonite (**Fig. 2a**).

419 Blank experiments performed under dry condition (powdered SL-granite or  
420 arfvedsonite loaded without water in the gold capsules), or only with quartz from SL-granite  
421 reacted with 3 m NaCl brine, revealed that the release of pre-existing H<sub>2</sub> from gases occluded  
422 in the minerals or entrapped in fluid inclusions is also negligible. Indeed, less than 5 % of the  
423 total amount of H<sub>2</sub> produced in the experiments where SL-granite or pure arfvedsonite were  
424 hydrothermally reacted can be attributed to pre-existing H<sub>2</sub>.

425 To better compare the effect of pH, salinity and mineralogical assemblage, the total  
426 amounts of H<sub>2</sub> produced during both SL-granite and arfvedsonite-bearing experiments were  
427 normalized to the mass of solid initially introduced inside the gold capsules (**Fig. 2b**). Clearly,  
428 H<sub>2</sub> production was promoted by circumneutral to alkaline conditions. The maximum amount  
429 of H<sub>2</sub> produced was recorded after reaction of SL-granite with water: from 27 to 36 mmol  
430 kg<sub>rock</sub><sup>-1</sup> of H<sub>2</sub> were produced within 15 days (**Fig. 2b**). Note that hydrothermal alteration of  
431 SL-granite naturally imposes alkaline conditions (pH<sub>25°C</sub> = 9.5 and 8.2 were measured after  
432 runs #SL1 and #SL9 carried out at 280 °C and 400 °C, respectively - see below). Altogether,  
433 these experiments demonstrated that H<sub>2</sub> production from the hydrothermal alteration of SL-  
434 granite and of pure arfvedsonite strongly depends on pH. The comparison of experiments  
435 conducted with and without dissolved NaCl reveals that salinity decreases the production of  
436 H<sub>2</sub>, by 10 to 40 %. Comparatively, SL-granite alteration produced more H<sub>2</sub> than arfvedsonite  
437 alone.

438 Carbon dioxide and CH<sub>4</sub> were also quantified in the gold capsules after 15 days of  
439 reaction (**Fig. 3**). As expected, neither of these species were detected in the experiments  
440 conducted with fluid only (no solid charge). Remarkably, in runs where SL-granite or

441 arfvedsonite were reacted, the presence of fluid did not seem to have an impact on CO<sub>2</sub> and  
442 CH<sub>4</sub> production, as both molecules were detected in similar amounts under dry condition  
443 (**Fig. 3a, b**). This observation contrasts with the near absence of H<sub>2</sub> released under dry  
444 condition (**Fig. 2**). The mineralogical assemblage, i.e., SL-granite or arfvedsonite, also has  
445 only a weak impact on CO<sub>2</sub> and CH<sub>4</sub> production (**Fig. 3c, d**). Also expected, a clear effect of  
446 pH was observed on gaseous CO<sub>2</sub> production under hydrothermal conditions – from 25 to 35  
447 mmol kg<sub>rock</sub><sup>-1</sup> under acidic condition (0.1 m HCl + 3 m NaCl) to less than 6 mmol kg<sub>rock</sub><sup>-1</sup>  
448 under alkaline condition (0.1 m NaOH + 3 m NaCl) – but this result can be easily explained  
449 by carbonate speciation and CO<sub>2</sub> solubility as a function of pH. Methane on the other hand,  
450 was released in a much lower amount: from 2 to 5 mmol kg<sub>rock</sub><sup>-1</sup>, with no clear fluid,  
451 mineralogical or pH effect. This notwithstanding, a discussion on the sources of CO<sub>2</sub> and CH<sub>4</sub>  
452 is beyond the scope of this study, and these results are provided for information purposes  
453 only. We do point out, however, that minerals such as nahcolite and REE (Rare-Earth  
454 Elements)-Sr-carbonates have been reported in the hypersolvus granite at Strange Lake and  
455 that both CH<sub>4</sub> and CO<sub>2</sub> may be occluded or trapped in melt/fluid inclusions in these minerals  
456 (Vasyukova et al., 2016; Vasyukova and Williams-Jones, 2019; Gysi et al., 2013, 2016).



457

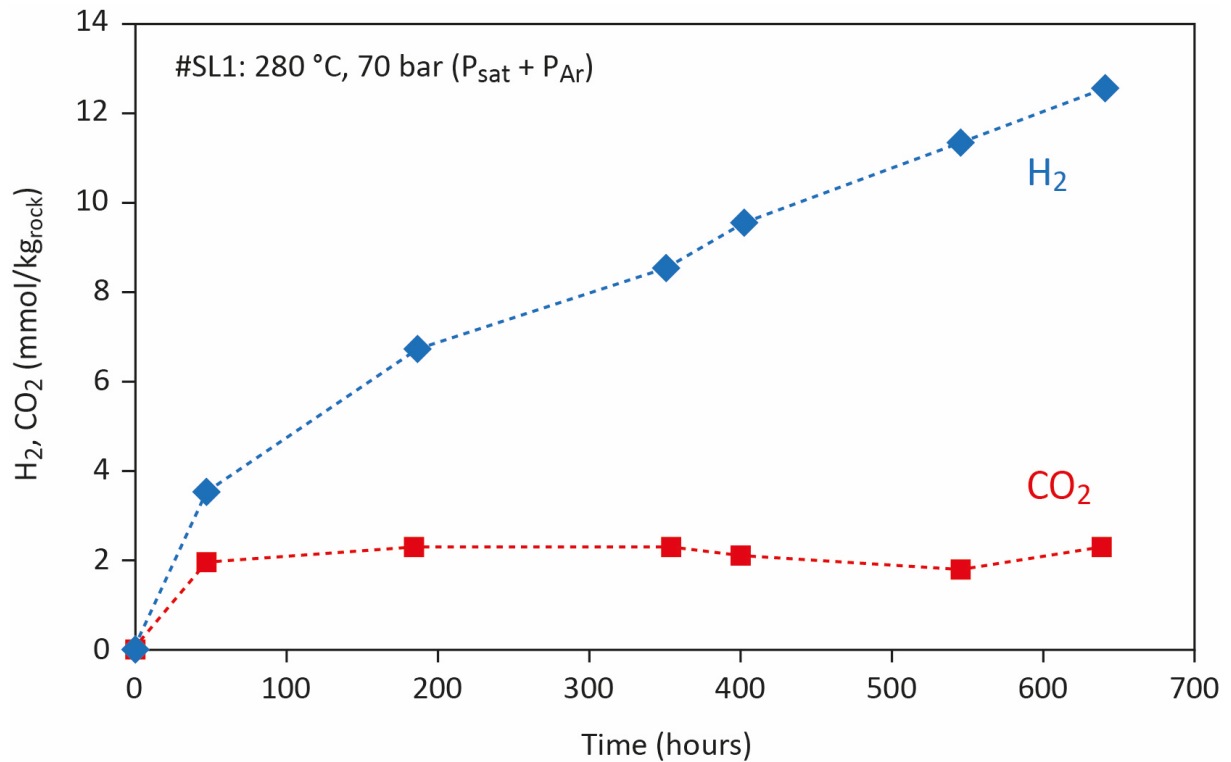
458 **Figure 3.** Production of CH<sub>4</sub> and CO<sub>2</sub> after 360 hours elapsed time in gold capsule  
 459 experiments carried out at 350 °C and 500 bar. (a) and (b) moles of CO<sub>2</sub> and CH<sub>4</sub> produced in  
 460 the gold capsules as a function of fluid composition, respectively. The annotation “dry”  
 461 indicates that the gold capsule was loaded with solid material only (no fluid). (c) and (d) show  
 462 production of CO<sub>2</sub> and CH<sub>4</sub> normalized to the mass of solids (SL-granite or arfvedsonite) as a  
 463 function of fluid composition, respectively. The orange dashed line depicts a trend of  
 464 decreasing CO<sub>2</sub> concomitant with increasing pH of the fluid.  
 465

### 466 3.2 H<sub>2</sub> generation from peralkaline granite alteration at 280 °C and vapor saturation pressure

467 At 280 °C and vapor saturation pressure, H<sub>2</sub> was produced continually over 650 hours  
 468 when reacting SL-granite with pure water (**Fig. 4**). After 650 hours had elapsed, H<sub>2</sub>  
 469 concentration reached 13 mmol kg<sub>rock</sub><sup>-1</sup>. The concentration of CO<sub>2</sub> remained nearly constant at  
 470 2 mmol kg<sub>rock</sub><sup>-1</sup> throughout the run, and traces of CH<sub>4</sub> were detected (below the quantification  
 471 limit of 10 ppm) at the end of the experiment. Note that the total carbonate concentration is  
 472 unknown as most of the CO<sub>2</sub> is dissolved in the aqueous phase, given the alkaline pH value  
 473 recorded on the liquid samples throughout the experiment. The concentrations of major  
 474 dissolved elements (Si, Al, Na, K, Ca, Mg, Mn, Fe) measured throughout the experiment are  
 475 provided in the **Supplementary Table S2** and the **Figure S1**. No H<sub>2</sub>, CH<sub>4</sub> or CO<sub>2</sub> were

476 detected when reacting the purified quartz fraction from SL-granite under the same condition  
477 (#QTZ280, **Supplementary Table S2**).

478



479

480 **Figure 4.** Production of H<sub>2</sub> (blue diamonds) and CO<sub>2</sub> (red squares) as a function of time  
481 during experiment #SL1 carried out at 280 °C, 70 bar (P<sub>sat</sub> + Ar) in the presence of water and  
482 SL-granite. Error bars are smaller than the size of the symbols.

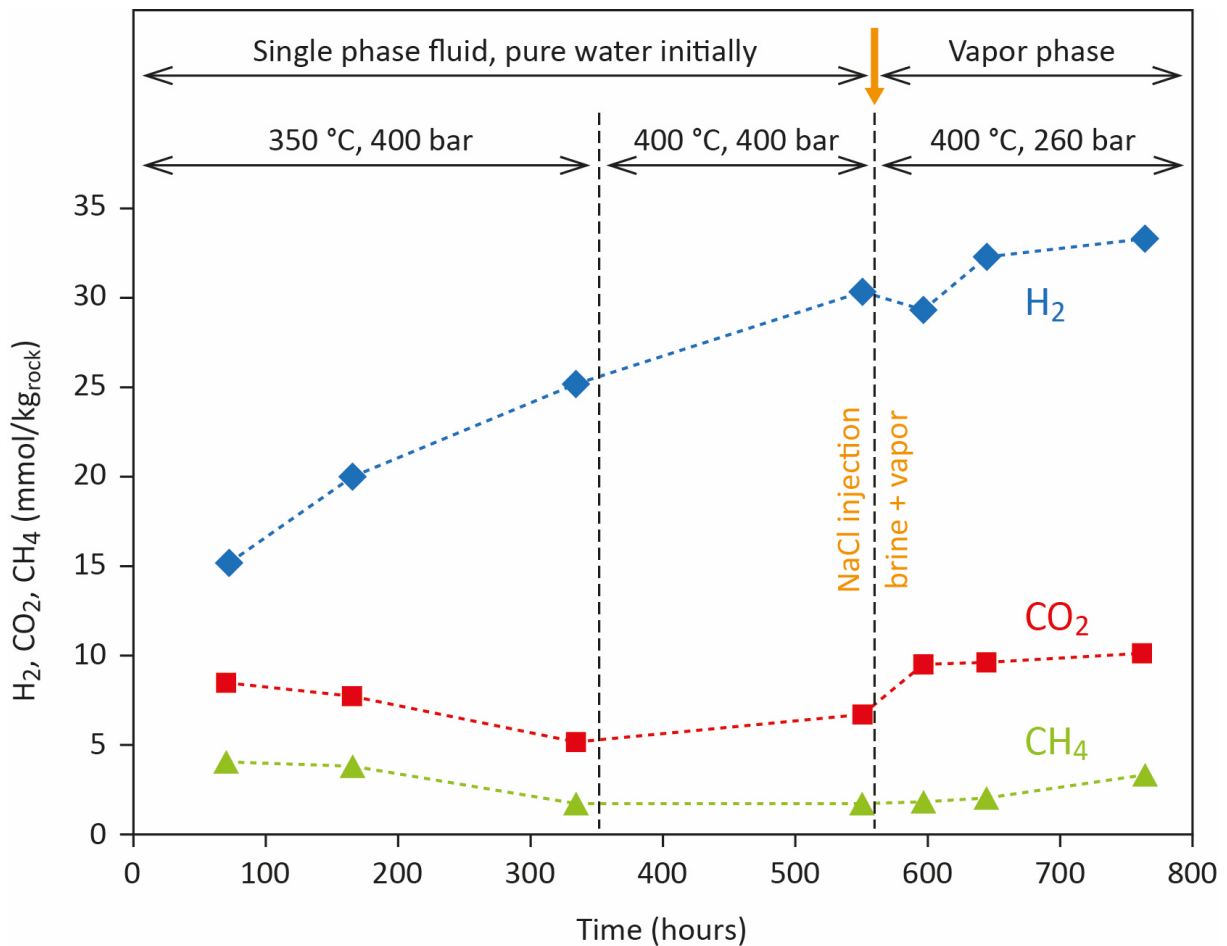
483

### 484 3.3 H<sub>2</sub> generation from peralkaline granite alteration up to 400 °C: effect of vapor-brine 485 immiscibility

486 At 350 °C and 400 bar in a single-phase fluid, H<sub>2</sub> concentration increased rapidly  
487 within the first 72 hours of reaction and then followed a relatively constant increase at a  
488 slower rate (**Fig. 5**). No significant change in the production rate was observed when  
489 temperature was increased from 350 to 400 °C at constant pressure (400 bar). After 552 hours  
490 of reaction, NaCl was injected and pressure dropped to 260 bar. Either of these actions alone  
491 would have induced phase separation, however, the hydrogen production rate was only



492 slightly impacted, for a few hours following state change. Despite the fact that a substantial  
 493 amount of H<sub>2</sub> was generated during the first stage of the experiment, at 350°C and 400 bar, its  
 494 concentration in the aqueous phase remained well below its solubility threshold, which is ~1.7  
 495 m in pure water (Seward and Franck, 1981). Conversely, after phase separation induced by  
 496 NaCl injection and pressure decrease most of the H<sub>2</sub> was certainly in the vapor phase.  
 497 Although to this day there is no thermodynamic data to predict the solubility of H<sub>2</sub> in brine  
 498 nor the vapor/liquid partitioning of H<sub>2</sub> under such condition, it is reasonable to expect the  
 499 vapor phase to be enriched in H<sub>2</sub> with respect to the liquid phase, due to salting out effect  
 500 (Bazarkina et al., 2020).



501  
 502 **Figure 5.** Production of H<sub>2</sub> (blue diamonds), CO<sub>2</sub> (red squares) and CH<sub>4</sub> (green  
 503 triangles) as a function of time during experiment #SL9 carried out in the presence of water  
 504 and SL-granite. Temperature, pressure and fluid composition evolve according to 3  
 505 consecutive steps as indicated on the figure: 1) 350 °C, 400 bar, pure water initially, then 2) a  
 506 temperature increase to 400 °C at constant pressure 400 bar, and finally 3) NaCl injection and

507 pressure decrease to 260 bar at 400 °C. This last step induced phase separation to produce  
508 coexisting brine (density = 0.70 g cm<sup>-1</sup>, 2.7 m NaCl) and vapor (density = 0.19 g cm<sup>-1</sup>, 0.028  
509 m NaCl). During this stage, sampling was performed from the vapor phase. Error bars are  
510 smaller than the size of the symbols.

511

512 The concentrations of CO<sub>2</sub> and CH<sub>4</sub> remained relatively constant throughout the  
513 experiments, at ~7 and 3 mmol kg<sub>rock</sub><sup>-1</sup>, respectively. Sodium concentrations measured in the  
514 vapor phase (~27 mmol kg<sup>-1</sup>) are in agreement with our thermodynamic predictions (28 mmol  
515 kg<sup>-1</sup>) using the HCh software (Shvarov, 2008). Concentrations of major dissolved elements  
516 (Si, Al, Na, K, Ca, Mg, Mn, Fe) measured during the experimental runs are provided in the  
517 **Supplementary Table S2** and the **Figure S2**.

518

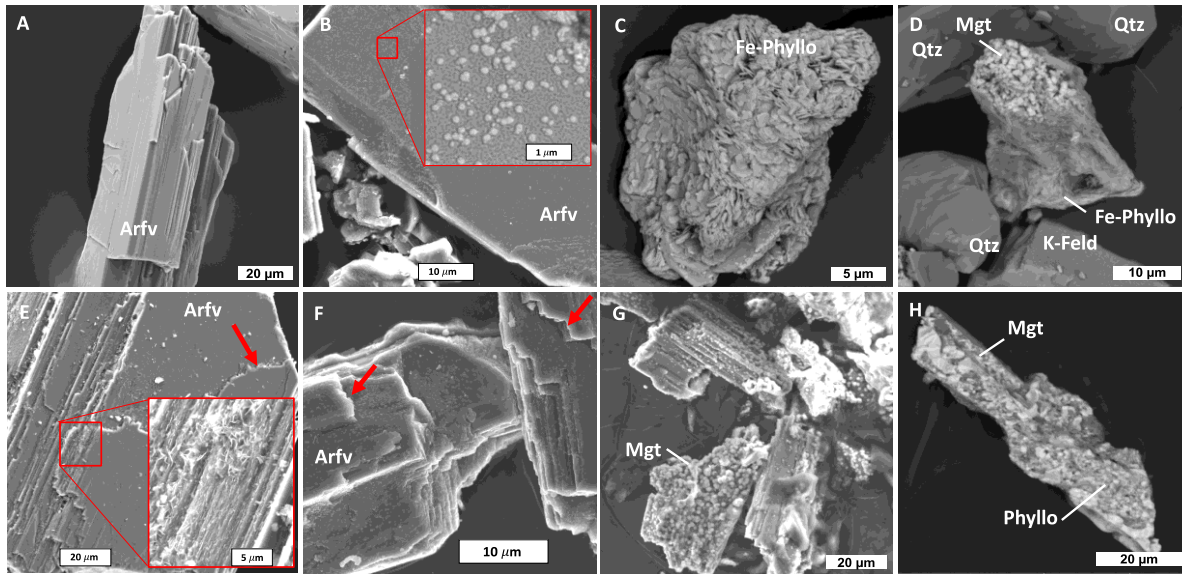
### 519 3.4 Investigation of solid reaction products

520 X-Ray diffraction patterns performed on the bulk SL-granite powders, before and after  
521 reaction at 280 °C (#SL1) and 400 °C (#SL9) do not provide any clear evidence for the  
522 precipitation of secondary minerals (**Supplementary Figure S3a**). After reaction at 280 °C in  
523 #SL1 experiment, the most striking feature we observed is extensive dissolution of quartz  
524 (**Supplementary Figure S3a**). This observation is consistent with the fact that the reacted  
525 solid were cemented in the vessel after this experiment by amorphous silica precipitation.  
526 Traces of chlorite (1.8 %), magnetite (0.9 %) and zircon (0.8 %) improved the quantitative  
527 analysis (Rietveld refinement) of the XRD pattern collected on solids reacted at 280 °C  
528 (#SL1). At 400 °C, magnetite was the only secondary mineral that could be detected by XRD  
529 quantitative analysis (0.6 %). However, at such low volumes, identification and quantification  
530 of secondary minerals by XRD analysis is challenging. Similarly, no significant mineral  
531 neoformation was detected by XRD analysis after reaction of pure arfvedsonite at 350°C, 500  
532 bar in the presence of 3 m NaCl + 0.1 m NaOH (**Supplementary Figure S3b**). However, the  
533 X-Ray diffraction patterns collected on the <2 μm fraction recovered after #SL1 and #SL9

534 experiments confirm the formation of minor chlorite and reveal the presence of other minerals  
535 displaying peaks at 11.87, 10.55 and 9.43 °2θ (**Supplementary Figure S3c**), which could be  
536 assigned to palygorskite and sepiolite. The presence of a hydrous zirconosilicate tentatively  
537 identified as catapleiite was also noticed. Experiments carried out at 350 °C in the presence of  
538 SL-granite and 0.1 m NaOH (run #13, Table 1), led to the formation of montmorillonite  
539 (**Supplementary Figure S3d**). Aegirine was not detected in the reacted SL-granite samples  
540 (bulk and clay fraction).

541         Regardless, extensive SEM analysis performed on all reacted SL granite powders  
542 reveals the presence of clear dissolution features at the surface of arfvedsonite at all  
543 temperatures investigated (280, 350, 400 °C) under circumneutral to hyperalkaline condition  
544 (**Fig. 6**). The dissolution textures are clearly visible along the edges, corners and cleavages of  
545 arfvedsonite crystallites. For runs at 280 °C and 350 °C, the surface of recovered arfvedsonite  
546 is partially covered by sub-micrometric (< 200 nm) isolated mounds or lumps of a high-  
547 density mineral (bright color under BSE mode). Magnetite, another high-density secondary  
548 mineral, was also present in the reaction products from all experiments carried out in the  
549 presence of SL-granite + H<sub>2</sub>O ± NaOH. Magnetite primarily occurs as small (<1 to ~5 µm)  
550 euhedral crystals dispersed throughout the reacted solids or coating on the arfvedsonite  
551 surface, in particular after reaction at 400 °C (run #SL9). In addition, tiny precipitates of a  
552 fibrous mineral are commonly observed on the edge and cleavages of arfvedsonite, for all  
553 temperatures investigated. Phyllosilicates displaying two different textures, fibrous and flaky,  
554 are observed either at the surface of arfvedsonite or as isolated aggregates, respectively. Most  
555 secondary minerals precipitated at the surface of arfvedsonite during the runs are too small for  
556 representative EDX analysis, however, in the case of the platy phyllosilicates aggregates, Fe,  
557 Mg, K, Na and Al were clearly detected. The presence of chlorite would reconcile this texture  
558 with the chemical analyses and the interpretation of the XRD patterns.

559 When arfvedsonite was reacted alone (350 °C and 500 bar) in pure water or under  
 560 hyperalkaline conditions, the dissolution features were far less pronounced and no secondary  
 561 phases were detected at its surface, by SEM observation. Also, no signs of alteration were  
 562 observed on arfvedsonite in runs done under acidic condition, independently of whether it was  
 563 alone or embedded within SL-granite.



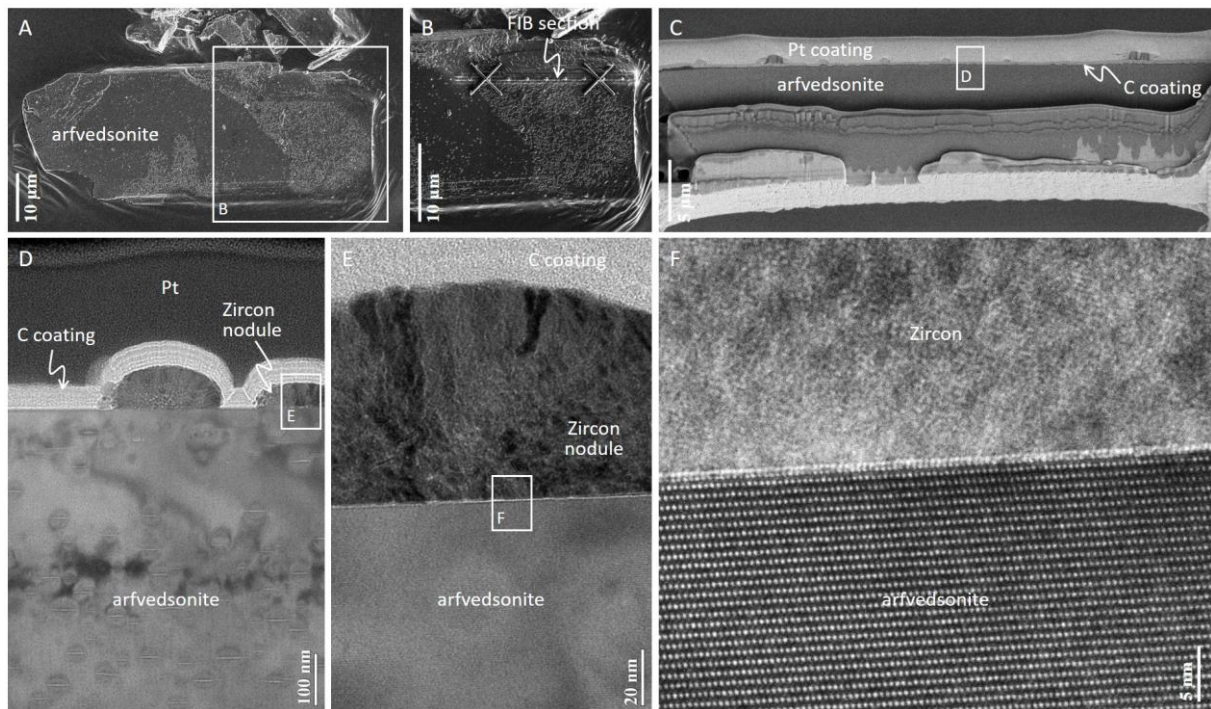
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565 **Figure 6.** Backscattered electron (BSE) and secondary electron (SE) images of  
 566 unreacted arfvedsonite and representative reaction products after hydrothermal alteration of  
 567 SL-granite at 280, 350 and 400 °C. (a) BSE image of unreacted arfvedsonite (Arfv). (b) BSE  
 568 image of arfvedsonite after reaction at 280 °C (run #SL1) with tiny isolated zircon lumps  
 569 (<200 nm) on its surface (inset). (c) BSE image of Fe-rich phyllosilicate (Fe-Phyllo) observed  
 570 in the bulk solids after hydrothermal alteration of SL-granite at 280 °C (run #SL1). (d) BSE  
 571 images of magnetite (Mgt) crystals imbedded in mats of platy Fe-phyllosilicate after reaction  
 572 at 280 °C (run #SL1). Quartz (Qtz) and K-feldspar (K-Feld) crystals from SL-granite are also  
 573 visible. (e) and (f) SE images of arfvedsonite after hydrothermal alteration of SL-granite at  
 574 350 °C in the presence of water. The surface of arfvedsonite displays clear dissolution  
 575 features on the edges, corners and cleavage surfaces (red arrows). The inset in (e) shows the  
 576 presence of tiny fibrous precipitates along the arfvedsonite cleavages. The surface of  
 577 arfvedsonite in (f) is also covered with tiny zircon lumps. (g) BSE image of arfvedsonite  
 578 crystals nearly fully coated by interbedded octahedral magnetite (Mgt) crystals after reaction  
 579 at 400 °C (run #SL9). (h) BSE image of arfvedsonite crystals fully coated by magnetite and  
 580 phyllosilicates after reaction at 400 °C (run #SL9).

581

582 TEM-EDX observations and analysis performed on FIB ultrathin sections milled  
 583 perpendicularly to the arfvedsonite surface reacted at 280 °C (#SL1) and 350 °C, initially in  
 584 the presence of granite and pure water, reveal without any ambiguity that the sub-micrometric

585 isolated lumps detected by SEM imaging are  $ZrSiO_4$  nodules precipitated at its surface (**Fig.**  
 586 **7**). These nodules consist of polycrystalline zircons, with radial growth, constituting half-  
 587 spheres whose radius does not exceed 200 nm (**Fig. 7d**). They sit on the surface of the  
 588 arfvedsonite crystallites without crystal connection to them, indicated by the extremely clean  
 589 and sharp interface between zircon and arfvedsonite (**Fig. 7e, f**). In the same way, zircon  
 590 nodules seem to precipitate preferentially on large flat and clean arfvedsonite surfaces, rather  
 591 than in dissolution pits. TEM observations on FIB sections also reveal that monocrystalline  
 592 arfvedsonite, apart from dissolution areas (edges, corners and cleavages), is not altered, even  
 593 at the nanoscale, where zircon precipitated (**Fig. 7f**).



594

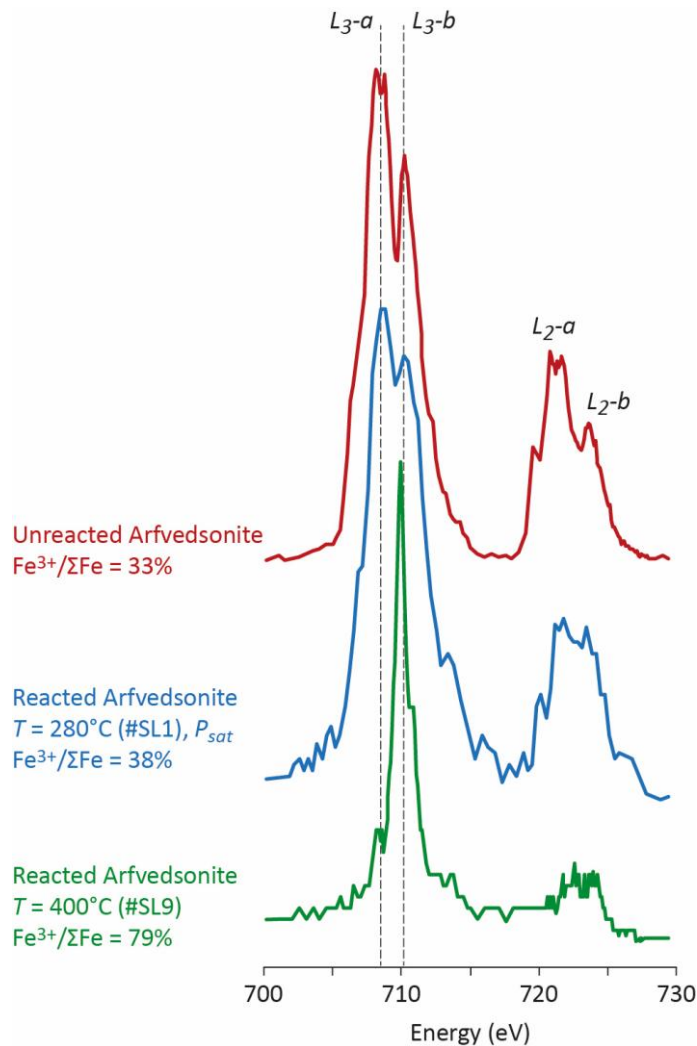
595 **Figure 7.** SEM and TEM images of arfvedsonite-zircon nodule interface. (a) SEM image of  
 596 carbon-coated arfvedsonite crystal covered with nanometric nodules. (b) SEM image of the  
 597 crystal area targeted for FIB foil cutting. The emplacement of the FIB foil is identified by a  
 598 platinum deposit (in the shape of a cross and dots). (c) FIB foil extracted from the section  
 599 defined in (b), with a continuous platinum strap on top of it. The FIB foil presents different  
 600 cutting thicknesses, the arfvedsonite-zircon nodule interface being the thinnest area. Carbon  
 601 coating is also visible. (d) Bright-field TEM image of the FIB foil from (c) showing radial-  
 602 growth of zircon nodules placed on the clean surface of the arfvedsonite crystal. Platinum  
 603 strap (Pt) and carbon coating are indicated. (e) Expanded view from image (d) presenting a  
 604 polycrystalline zircon nodule in contact with arfvedsonite. (f) High-resolution TEM image of  
 605 the interface, showing the crystalline structure of the two phases, with no inter-crystalline  
 606 connection.

607

608           The iron redox state of three arfvedsonite samples – unreacted arfvedsonite and  
609 reacted arfvedsonite at 280 °C and at 400 °C (respectively runs #SL1 and #SL9) – was  
610 studied by STXM-XANES. The **Figure 8** compares rescaled representative spectra from each  
611 sample, corrected for background. Fe L<sub>2,3</sub>-edge spectra display four major peaks, two for the  
612 L<sub>3</sub>-edge are noted L<sub>3</sub>-a (~708.7 eV) and L<sub>3</sub>-b (~710.2 eV), two for the L<sub>2</sub>-edge are noted L<sub>2</sub>-a  
613 (~720 eV) and L<sub>2</sub>-b (~723.5 eV). L<sub>3</sub>-a and L<sub>2</sub>-a peaks are mainly affected by the Fe<sup>2+</sup> content,  
614 while the L<sub>3</sub>-b and L<sub>2</sub>-b peaks are affected by the Fe<sup>3+</sup> content. Here, unreacted arfvedsonite  
615 and #SL1 spectra have a similar shape, i.e. a high L<sub>3</sub>-a peak and a small L<sub>3</sub>-b peak indicating  
616 ferrous phases, while #SL9 spectrum shows an inverted intensity ratio, typical of ferric phases  
617 (**Fig. 8**). The estimation of Fe<sup>3+</sup>/Fe<sub>total</sub> ratio is based on the L<sub>3</sub>-b/L<sub>3</sub>-a peak intensity ratio as  
618 proposed by Bourdelle et al. (2013), and indicates 33 %, 38 % and 79 % of ferric iron in  
619 unreacted, reacted #SL1 and reacted #SL9 arfvedsonite, respectively. These estimates are  
620 based on 4 to 6 spectra per samples, showing intrasample homogeneity.

621





622

623 **Figure 8.** Representative XANES spectra at the Fe  $L_{2,3}$ -edges for unreacted (in red) and  
 624 reacted (#SL1 in blue, #SL9 in green) arfvedsonites. Spectra have been normalized to the  
 625 integral Fe  $L_3$ -edge intensity, and shifted vertically for clarity (normalised intensity with  
 626 arbitrary unit). The vertical dashed lines represent the energies fixed to determine the  
 627  $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$  ratio from the intensities of  $L_3$ -peaks, according to the procedure of Bourdelle et al.  
 628 (2013).

629

## 630 4. Discussion

### 631 4.1 Source of $\text{H}_2$

632 From the experimental results detailed in the preceding sections, we learned that  
 633 hydrogen generation in the presence of SL-granite or arfvedsonite occurs under near-neutral  
 634 to alkaline hydrothermal condition, at  $T \geq 280^\circ\text{C}$ . A range of blank experiments assessed that  
 635 no  $\text{H}_2$  was produced from the experimental apparatus and that the release of the  $\text{H}_2$  occluded

636 in minerals or entrapped in quartz-hosted fluid inclusions from SL-granite was negligible (< 5  
637 %). Thus, we can be confident that H<sub>2</sub> in our experiments was indeed produced during water-  
638 rock interaction.

639 Production of H<sub>2</sub> occurred when arfvedsonite was the only mineral introduced in the  
640 hydrothermal system. Even higher amounts of H<sub>2</sub> were generated when SL-granite  
641 (containing 10 wt% arfv) was reacted (**Fig. 2**). The role of granite could either imply that H<sub>2</sub>  
642 is supplied by more than one source, or that arfvedsonite alteration is enhanced in the  
643 presence of other minerals. The presence of Fe is reported in alkali feldspar from the  
644 hypersolvus granite, however, it consists of small amounts of ferric iron (0.23 wt% Fe<sub>2</sub>O<sub>3</sub>, or  
645 about 0.01 apfu Fe<sup>3+</sup> - Siegel et al., 2018), which cannot oxidize to produce H<sub>2</sub>. On the other  
646 hand, the second hypothesis is more plausible, given that hydrothermal alteration of granite  
647 naturally leads to alkaline conditions that, as seen above, favor the H<sub>2</sub>-producing reaction. In  
648 addition, altering a rock instead of only a mineral will release a range of elements into  
649 solution that are likely to enhance precipitation of additional secondary minerals, in particular  
650 phyllosilicates. This is consistent with the presence of higher amounts of secondary minerals  
651 such as magnetite and phyllosilicates when the granite, instead of arfvedsonite alone, was  
652 included in the experimental runs.

653 Experimental replicates performed at 350 °C in gold capsules, using pure water as  
654 starting solution, showed a 10 to 30 % difference in the amount of H<sub>2</sub> produced, when  
655 comparing two runs carried out under the same conditions. Nevertheless, despite these  
656 significant uncertainties on the amount of H<sub>2</sub> produced, a constant result was that alkaline  
657 conditions promoted H<sub>2</sub> generation and that salinity of the reacting fluid had a slightly  
658 negative impact on H<sub>2</sub> production (**Fig. 2b**). Similar conclusions were drawn recently from  
659 laboratory experiments of olivine serpentinization at 200–280 °C (Lamadrid et al., 2017;  
660 McCollom et al., 2020b).



661

## 662 4.2. Reaction mechanism

663 Another question that needs addressing concerns the reaction mechanism of H<sub>2</sub>  
664 production. On the basis of petrographic observations, it has been proposed that arfvedsonite  
665 is replaced by aegirine under hydrothermal condition at  $T \geq 350$  °C, and that this replacement  
666 releases H<sub>2</sub>, according to the **Equation 1** (Salvi and Williams-Jones, 1997; Potter et al.,  
667 2013). Replacement of arfvedsonite by aegirine is a common feature of peralkaline rocks  
668 (e.g., Marks and Markl, 2017; Bernard et al., 2020), and a beautiful example of arfvedsonite  
669 alteration into aegirine is shown in **Figure 1**. In the laboratory, aegirine has been synthesized  
670 at temperatures as low as 200 °C in aqueous solutions; below this temperature Na– Fe-  
671 phyllosilicates form instead (Decarreau et al., 2004). In our study, however, aegirine  
672 formation was not detected, at any of the conditions tested. Possible reasons may include the  
673 relatively low pressure ( $\leq 400$  bar) and short duration ( $< 30$  days) of our experiments.  
674 Nonetheless, two important lines of evidence demonstrate the occurrence of arfvedsonite  
675 oxidative dissolution. Firstly, when observed under an electron microscope, the arfvedsonite  
676 surface clearly displays typical features of dissolution, such as dissolved edges and corners as  
677 shown in **Figure 6f**. In addition, reacted arfvedsonite is covered by an unexpected multitude  
678 of tiny distinct zircon lumps, particularly visible in the experiment carried out at 280 °C and  
679 350 °C in the presence of SL-granite + H<sub>2</sub>O (**Fig. 6b, e and f**). In SL-granite, zirconium is  
680 present in the form of zircon crystals, but also occurs in the structure of arfvedsonite (EMPA  
681 analysis indicate ~1200 ppm). Contrarily to arfvedsonite, primary zircon grains do not show  
682 any sign of dissolution. This, together with the fact that the secondary zircon lumps occur  
683 only at the surface of arfvedsonite, suggests that Zr was supplied by dissolution of the latter.  
684 Because of its extremely low solubility, zircon precipitated at the surface of its source, rather  
685 rapidly as suggested by the apparent botryoidal habit of these lumps (**Fig. 7**). A second line of

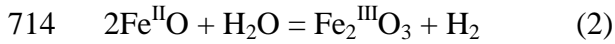
686 evidence for oxidative dissolution of arfvedsonite is the presence of several Fe<sup>III</sup>-bearing  
687 alteration minerals in the reacted experimental powders. Magnetite was identified on the  
688 surface of arfvedsonite and disseminated in the bulk powder, at all investigated temperatures  
689 and in the presence of SL-granite + H<sub>2</sub>O ± NaOH (**Fig. 6d, g and h**). Phyllosilicates were also  
690 detected, their presence confirmed by XRD and SEM analysis (**Fig. 6c, d, e and h**), and  
691 display either fibrous or flaky textures (**Fig. 6c and e**). Possibly, chlorite and Na-  
692 montmorillonite may also be present, according to some features of the XRD and EDX  
693 patterns recorded from SL-Granite reacted at 280 °C. Finally, STXM-XANES analysis  
694 revealed a clear increase of the Fe<sup>3+</sup>/Fe<sub>total</sub> ratio of the arfvedsonite after reaction at 280 °C  
695 and 400 °C (**Fig. 8**). Because the STXM-XANES probes particles through their thickness, only  
696 very thin fragments of arfvedsonite – transparent to X-ray (thickness < 100 nm) – were  
697 targeted, i.e. probably the most altered crystallites. Therefore, Fe<sup>3+</sup>/Fe<sub>total</sub> values (**Fig. 8**) could  
698 be considered either as resulting from structural oxidation of Fe<sup>II</sup> into Fe<sup>III</sup>, more detectable in  
699 very thin particles, or as an average between a preserved crystal core and an altered ultrathin  
700 external layer at the grain surface. The relationship between iron redox estimates and  
701 experiment conditions (increasing Fe<sup>3+</sup> proportions with increasing run temperature) can  
702 therefore testify of an ongoing process of arfvedsonite oxidation. This observation may also  
703 provide a hint for the absence of aegirine, whose precipitation would supposedly occur at a  
704 higher oxidative level, not yet attained during the experiments.

705

#### 706 4.3 Alteration progress

707 Assuming that H<sub>2</sub> is entirely produced by arfvedsonite dissolution through oxidation  
708 of structural Fe<sup>II</sup> into Fe<sup>III</sup>, one can calculate the extent of alteration progress. Given i) the  
709 molar mass of arfvedsonite (~960 g mol<sup>-1</sup>), ii) the Fe<sup>II</sup> stoichiometry in arfvedsonite (3.07  
710 mole Fe(II) per mole of arfvedsonite), and iii) the mass balanced H<sub>2</sub> production from Fe<sup>II</sup>

711 oxidation into Fe<sup>III</sup> (the generalized reaction can be represented according to the **Equation 2**),  
712 we estimate that 1 kg of arfvedsonite can produce a maximum of 1.54 moles of H<sub>2</sub> if all the  
713 Fe<sup>II</sup> is oxidized into Fe<sup>III</sup>.



715 Note that using the **Equation 1** to calculate the H<sub>2</sub> production from arfvedsonite  
716 oxidation leads to a similar result: 1.74 moles of H<sub>2</sub> produced per kg of arfvedsonite reacted.  
717 For comparison, McCollom et al. (2016) show that complete serpentinization of 1 kg San  
718 Carlos olivine produces up to 0.3 moles of H<sub>2</sub> at 265–300 °C. Thus, arfvedsonite alteration  
719 can produce ~5 times more H<sub>2</sub> than olivine serpentinization, per mass unit of mineral reacted.  
720 Similarly, the H<sub>2</sub> production from SL-Granite and peridotite can also be compared. The latter  
721 can produce about 0.37 moles of H<sub>2</sub> per kg of rock altered, assuming an FeO content of 8 wt%  
722 and that 66% of the iron gets oxidized during serpentinization (Klein et al., 2014). Because  
723 arfvedsonite represents only 10 wt% of SL-granite, the H<sub>2</sub> potential of this rock is 0.17 moles  
724 per kg, which is about two times less than that of peridotite.

725 Using these mass balance calculations, together with the known amounts of H<sub>2</sub>  
726 produced during the experiments, allows estimating the minimum amount of arfvedsonite  
727 reacted. It turns out that at least 23 wt% of arfvedsonite were dissolved in the experiment  
728 where SL-granite was reacted at 350–400 °C, in an initial pure water medium. Similarly, ~8  
729 wt% arfvedsonite was dissolved during run #SL1 where SL-granite was reacted at 280 °C in  
730 the presence of pure water. Given the proportions of arfvedsonite in SL-granite (10 wt%),  
731 these maximum estimates are in line with SEM and XRD observations made on the reacted  
732 solid reaction products. In the case of experiments conducted with pure arfvedsonite at 350 °C  
733 with either pure water, or water + 3 m NaCl + 0.1 m NaOH, our estimate implies that ~10  
734 wt% arfvedsonite would have reacted. This value contrasts with the rather weak  
735 dissolution/precipitation features observed at the surface of arfvedsonite after these two

736 experiments, and the non-detection of secondary by-products by XRD analysis. To account  
737 for the latter, one explanation may lie in the low water-to-rock mass ratio ( $W/R = 1$ ) in these  
738 experiments. Another possibility is that secondary phases were lost during the opening of the  
739 gold capsule, as its strong deformation and the low mass of reacted material render this  
740 operation quite complex. More experiments using longer reaction time and higher amounts of  
741 sample will help shedding more light on the mechanism of arfvedsonite alteration.

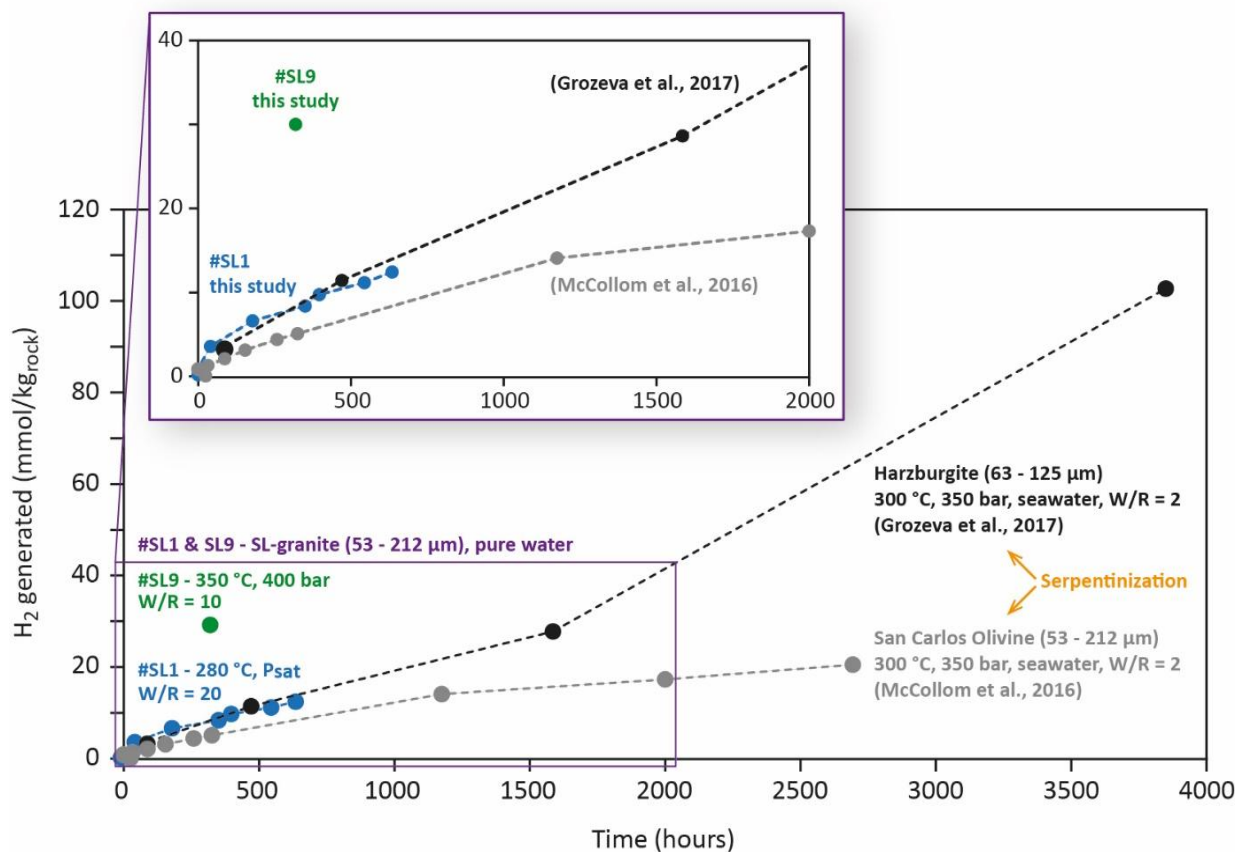
742

#### 743 4.4. Rate of $H_2$ generation and comparison with serpentinization

744 Hydrogen production recorded as a function of time during our hydrothermal  
745 experiment carried out at 280 °C (#SL1) and 350 °C in the presence of a sieved fraction of  
746 SL-granite (53 – 212  $\mu\text{m}$ ) can be compared with experiments carried out at 300 °C on  
747 harzburgite and San Carlos olivine powder of similar grain size by Grozeva et al. (2017) and  
748 McCollom et al. (2016), respectively (**Fig. 9**). The water/rock ratio is the main significant  
749 parameter that differs from these experiments. Hydrogen concentration data from Grozeva et  
750 al. (2017) have been recomputed to be plotted in the same unit as the other experiments (i.e  
751 mmol of  $H_2$  per kg of rock – see **Supplementary Table S3**). Hydrogen generation rates from  
752 SL-granite and harzburgite alteration are similar, at least during the early stage of reaction.  
753 After 500 hours of reaction time, the total amount of  $H_2$  generated during run #SL1 was 1.5  
754 times greater than that obtained with San Carlos olivine.

755 In our run, after 48 hours at 280 °C,  $H_2$  was generated at a relatively constant rate of  
756  $1.47 \times 10^{-5} \text{ mol kg}_{\text{rock}}^{-1} \text{ h}^{-1}$ . Assuming that all  $H_2$  is produced from arfvedsonite alteration (10  
757 wt% of granite), and given the specific surface area of this amphibole ( $0.30 \text{ m}^2 \text{ g}^{-1}$ ), we obtain  
758 a rate of  $H_2$  production of about  $1100 \text{ pmol cm}^{-2} \text{ day}^{-1}$ . This value lies within the range of  $H_2$   
759 production rate reported for olivine serpentinization by McCollom et al. (2016) at 300 °C: 100  
760 – 2000  $\text{pmol cm}^{-2} \text{ day}^{-1}$ . The rate of hydrogen production derived from the experiment carried

761 out at 350 – 400 °C and 400 bar (#SL9) is about 2 times higher than at 280 °C:  $3.0 \times 10^{-5}$  mol  
 762  $\text{kg}_{\text{rock}}^{-1} \text{h}^{-1}$  or  $2200 \text{ pmol} \cdot \text{cm}^{-2} \cdot \text{day}^{-1}$ . The absence of coating or passivation observed at the  
 763 surface of the arfvedsonite clearly plays in favor of a high rate of alteration, as no diffusion  
 764 process of the reactants through secondary phases is there to slow the reaction down. During  
 765 olivine serpentinization, hydrogen production rate peaks at about 300 °C and then decreases  
 766 abruptly as temperature increases. This is because olivine, being part of the equilibrium  
 767 mineral assemblage, limits the amount of Fe(II) available for  $\text{H}_2$  generation (McCollom et al.,  
 768 2016). Currently, the temperature dependence of  $\text{H}_2$  production rate during arfvedsonite  
 769 alteration is poorly constrained, but the trend observed for olivine serpentinization does not  
 770 seem to be valid for peralkaline granite.



771  
 772

773 **Figure 9.** Comparison of  $\text{H}_2$  generation during San Carlos olivine (grey dots), and harzburgite  
 774 (black dots) serpentinization at 300 °C, with SL granite hydrothermal alteration at 280 °C (red  
 775 dots) and 350 °C (green dot). The inset graph is a zoom on the first 2000 hours of reaction.

776

777           However, it seems clear that the presence of the minerals forming the granite has a  
778 strong impact on the H<sub>2</sub> production rate, as mentioned previously. In particular, albite and  
779 microcline are an important source of aluminum, an element that plays a key role in the  
780 precipitation of phyllosilicates. As already observed for serpentinization (Andreani et al.,  
781 2013), presence of aluminum may increase both the solubility and dissolution rate of  
782 arfvedsonite, by enhancing the precipitation of phyllosilicates such as chlorite and  
783 montmorillonite.

784

#### 785 4.5 Implications for H<sub>2</sub> production and exploration in peralkaline rocks

786           If there is a consensus in the scientific community on the abiotic origin of hydrogen,  
787 methane, and associated higher-order hydrocarbons found in agpaitic peralkaline igneous  
788 intrusions, the source of these gases is still subject of debate in the literature (e.g., Marks and  
789 Markl, 2017). Some authors consider that CH<sub>4</sub> plus minor to moderate amounts of H<sub>2</sub> exsolve  
790 from the magma at 450–500 °C, together with an immiscible aqueous fluid of high salinity  
791 (25 wt% NaCl eq.) (Konnerup-Madsen et al., 1985; Beeskov et al., 2006; Krumrei et al.  
792 2007; Vasyukova et al., 2016, 2019). Other workers propose that the hydrocarbons formed by  
793 late to post-magmatic Fischer-Tropsch-like synthesis, with the H<sub>2</sub> needed to drive this  
794 reaction being produced from alteration of primary igneous minerals such as arfvedsonite  
795 (Salvi and Williams-Jones, 1997, Potter et al., 2004; 2013). Production of some H<sub>2</sub> by  
796 polymerization of primary hydrocarbons has also been proposed (Krumrei et al. 2007).

797           At Strange Lake, early CH<sub>4</sub>-rich inclusions may contain up to 97 mol% CH<sub>4</sub> and 3  
798 mol% H<sub>2</sub> (Salvi and Williams-Jones, 1992, 1997, 2006; Vasyukova et al., 2016). From the  
799 spatial distribution of fluid and melt inclusions, Vasyukova et al. (2016) inferred that the fluid  
800 carrying these reduced gases coexisted with a pegmatite melt at the time of entrapment and

801 concluded that it had exsolved from the melt. However, the fate of H<sub>2</sub> remains unclear, as this  
802 molecule was also measured in secondary fluid inclusions by the same authors. Also, most of  
803 the fluid inclusion data collected so far at Strange Lake rely on bulk gas analysis (Salvi and  
804 Williams-Jones, 1997; Vasyukova et al., 2016), and the few in-situ Raman measurements  
805 available (Vasyukova et al., 2016) were not designed to specifically target H<sub>2</sub> – as these  
806 authors point out, its strongest vibration at 4156 cm<sup>-1</sup> is beyond the wavenumbers range  
807 accessible with the spectrometer used. On the other hand, Potter et al. (2004) were able to  
808 measure up to 40 mol% H<sub>2</sub> at 400 bar in CH<sub>4</sub>-dominant fluid inclusions from the Lovozero  
809 pluton (Kola Peninsula, Russia), using a mass spectrometer coupled to an on-line GC-crusher  
810 system (see also Salvi and Williams-Jones, 2003). Based on detailed fluid inclusion  
811 petrography, in situ Raman spectroscopy and textural relationships, Potter and coworkers  
812 concluded that these inclusions were trapped during post-magmatic hydrothermal alteration of  
813 an early mineral assemblage. The rarity of H<sub>2</sub>O-dominant inclusions in the Lovozero samples  
814 and the coexistence of these inclusions in the same trails as the CH<sub>4</sub>-dominant inclusions  
815 implies coeval, immiscible trapping of the aqueous and the carbonic fluids, at or below the  
816 CH<sub>4</sub> - H<sub>2</sub>O solvus at ~350 °C, leaning towards a post-magmatic origin. This is also supported  
817 by the microthermometric data for the H<sub>2</sub>O-dominant inclusions, which homogenize to vapor  
818 between 290 and 350 °C.

819         The data presented here do not resolve this debate, but they clearly demonstrate that  
820 H<sub>2</sub> can be produced by water-rock interaction, i.e., during the post-magmatic stage, via the  
821 alteration of arfvedsonite to aegirine, a widespread process in peralkaline rocks, particularly  
822 the agpaitic variety (e.g., Bernard et al., 2020). Given the depth of these plutons (maximum of  
823 12.5 km for the Khibiny and Lovozero system; Arzamastsev et al., 2000, 2013), it is possible  
824 that, in some cases, temperatures of ca. 200 °C or above may sustain active hydrothermal  
825 activity that could produce alteration of these rocks at depth, thereby triggering H<sub>2</sub> generation,

826 nowadays. Agpaitic peralkaline igneous intrusion may thus represent fertile geological setting  
827 for H<sub>2</sub> exploration for energy production purposes.

828

## 829 5. Conclusion

830 The results of this study clearly show that H<sub>2</sub> can be produced via the hydrothermal  
831 alteration of arfvedsonite at  $T \geq 280$  °C in agpaitic peralkaline igneous intrusions. Oxidation  
832 of structural Fe<sup>II</sup> into Fe<sup>III</sup> with concomitant reduction of water explains well this observation.  
833 After experimental reaction, arfvedsonite exhibits obvious dissolution feature at its surface,  
834 and magnetite, phyllosilicates and secondary zircons become present. Circumneutral to  
835 alkaline conditions clearly promote H<sub>2</sub> generation as it is the case for serpentinization.  
836 Hydrogen generation is also enhanced when reacting granite instead of only arfvedsonite.  
837 Aluminum, from alkali feldspar dissolution, may increase the solubility of arfvedsonite  
838 through the precipitation of phyllosilicates. In terms of rate, H<sub>2</sub> generation from arfvedsonite  
839 alteration in the presence of granite is a more efficient process than serpentinization of olivine  
840 or harzburgite.

841 Aegirine, a very common product of arfvedsonite alteration in these granites, was not  
842 observed in this study. The effect of pressure, oxygen fugacity, and length of reaction time  
843 remains to be evaluated to better constrain the reaction kinetics. Vasyukova et al. (2016)  
844 propose that the cooling of Strange Lake pluton was isobaric and, based on the intersection of  
845 isochores for carbonic and aqueous fluid inclusions, took place at a pressure of ~1100 bar.  
846 They also note that late alteration of arfvedsonite may continue at temperature as low as 150  
847 °C, with hematite and Fe-celadonite as secondary alteration phases (Vasyukova and  
848 Williams-Jones, 2019). Thus, alteration of arfvedsonite and SL-granite at lower temperature  
849 would also deserve further investigations.



850

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864 (INSU, CNRS).

865

866 **Figure captions**

867

868 **Figure 1.** Geological map of the Strange Lake pluton (courtesy of O. Vasyukova) locating the  
869 sample of hypersolvus granite used for the experiments (left-hand side). On the right-hand  
870 side is shown a sample of altered pegmatite where the replacement of arfvedsonite (large dark  
871 green crystals) by aegirine (light green) is clearly visible. The fluid inclusions displayed in the  
872 inset represent an example of coexisting L- and V-rich populations, where the latter inclusions

873 contain hydrogen as well as higher-order hydrocarbons, showing fluorescence under UV  
874 illumination. qtz = quartz, fds = feldspars, arf = arfvedsonite, aeg = aegirine.

875

876 **Figure 2.** Production of H<sub>2</sub> after 360 hours elapsed time in the gold capsule experiments  
877 carried out at 350 °C and 500 bar. Different initial fluid compositions were tested to evaluate  
878 the effect of pH and salinity. (a) Experiments carried out in the presence of SL-granite (red)  
879 or arfvedsonite (black) are compared to the blanks: fluid only (dashed lines) or quartz + 3 m  
880 NaCl (grey star). The notation “dry” indicates that the gold capsule was loaded with solid  
881 material only (no fluid). The 2 replicates performed in the presence of water + SL-granite or  
882 arfvedsonite are shown in light red and light grey, respectively. (b) Production of H<sub>2</sub>  
883 normalized to the mass of solids (SL-granite or arfvedsonite) as a function of fluid  
884 composition. Error bars reflect the cumulative uncertainty associated with measuring the  
885 volume of gas released after piercing the gold capsules and with the analytical uncertainty.  
886

887 **Figure 3.** Production of CH<sub>4</sub> and CO<sub>2</sub> after 360 hours elapsed time in gold capsule  
888 experiments carried out at 350 °C and 500 bar. (a) and (b) moles of CO<sub>2</sub> and CH<sub>4</sub> produced in  
889 the gold capsules as a function of fluid composition, respectively. The annotation “dry”  
890 indicates that the gold capsule was loaded with solid material only (no fluid). (c) and (d) show  
891 production of CO<sub>2</sub> and CH<sub>4</sub> normalized to the mass of solids (SL-granite or arfvedsonite) as a  
892 function of fluid composition, respectively. The orange dashed line depicts a trend of  
893 decreasing CO<sub>2</sub> concomitant with increasing pH of the fluid.  
894

895 **Figure 4.** Production of H<sub>2</sub> (blue diamonds) and CO<sub>2</sub> (red squares) as a function of time  
896 during experiment #SL1 carried out at 280 °C, 70 bar (P<sub>sat</sub> + Ar) in the presence of water and  
897 SL-granite. Error bars are smaller than the size of the symbols.

898

899 **Figure 5.** Production of H<sub>2</sub> (blue diamonds), CO<sub>2</sub> (red squares) and CH<sub>4</sub> (green triangles) as a  
900 function of time during experiment #SL9 carried out in the presence of water and SL-granite.  
901 Temperature, pressure and fluid composition evolve according to 3 consecutive steps as  
902 indicated on the figure: 1) 350 °C, 400 bar, pure water initially, then 2) a temperature increase  
903 to 400 °C at constant pressure 400 bar, and finally 3) NaCl injection and pressure decrease to  
904 260 bar at 400 °C. This last step induced phase separation to produce coexisting brine  
905 (density = 0.70 g cm<sup>-1</sup>, 2.7 m NaCl) and vapor (density = 0.19 g cm<sup>-1</sup>, 0.028 m NaCl). During  
906 this stage, sampling was performed from the vapor phase. Error bars are smaller than the size  
907 of the symbols.

908

909 **Figure 6.** Back-scattered electron (BSE) and secondary electron (SE) images of unreacted  
910 arfvedsonite and representative reaction products after hydrothermal alteration of SL-granite  
911 at 280, 350 and 400 °C. (a) BSE image of unreacted arfvedsonite (Arfv). (b) BSE image of  
912 arfvedsonite after reaction at 280 °C (run #SL1) with tiny isolated zircon lumps (<200 nm) on  
913 its surface (inset). (c) BSE image of Fe-rich phyllosilicate (Fe-Phyllo) observed in the bulk  
914 solids after hydrothermal alteration of SL-granite at 280 °C (run #SL1). (d) BSE images of  
915 magnetite (Mgt) crystals imbedded in mats of platy Fe-phyllosilicate after reaction at 280 °C  
916 (run #SL1). Quartz (Qtz) and K-feldspar (K-Feld) crystals from SL-granite are also visible.  
917 (e) and (f) SE images of arfvedsonite after hydrothermal alteration of SL-granite at 350 °C in  
918 the presence of water. The surface of arfvedsonite displays clear dissolution features on the  
919 edges, corners and cleavage surfaces (red arrows). The inset in (e) shows the presence of tiny  
920 fibrous precipitates along the arfvedsonite cleavages. The surface of arfvedsonite in (f) is also  
921 covered with tiny isolated zircon lumps. (g) BSE image of arfvedsonite crystals nearly fully  
922 coated by octahedral interbedded magnetite (Mgt) crystals after reaction at 400 °C (run

923 #SL9). (h) BSE image of arfvedsonite crystals fully coated by magnetite and phyllosilicates  
924 after reaction at 400 °C (run #SL9).

925

926 **Figure 7.** SEM and TEM images of arfvedsonite-zircon nodule interface. (a) SEM image of  
927 carbon-coated arfvedsonite crystal covered with nanometric nodules. (b) SEM image of the  
928 crystal area targeted for FIB foil cutting. The emplacement of the FIB foil is identified by a  
929 platinum deposit (in the shape of a cross and dots). (c) FIB foil extracted from the section  
930 defined in (b), with a continuous platinum strap on top of it. The FIB foil presents different  
931 cutting thicknesses, the arfvedsonite-zircon nodule interface being the thinnest area. Carbon  
932 coating is also visible. (d) Bright-field TEM image of the FIB foil from (c) showing radial-  
933 growth of zircon nodules placed on the clean surface of the arfvedsonite crystal. Platinum  
934 strap (Pt) and carbon coating are indicated. (e) Expanded view from image (d) presenting a  
935 polycrystalline zircon nodule in contact with arfvedsonite. (f) High-resolution TEM image of  
936 the interface, showing the crystalline structure of the two phases, with no inter-crystalline  
937 connection.

938

939 **Figure 8.** Representative XANES spectra at the Fe L<sub>2,3</sub>-edges for unreacted (in red) and  
940 reacted (#SL1 in blue, #SL9 in green) arfvedsonites. Spectra have been normalized to the  
941 integral Fe L<sub>3</sub>-edge intensity, and shifted vertically for clarity (normalised intensity with  
942 arbitrary unit). The vertical dashed lines represent the energies fixed to determine the  
943 Fe<sup>3+</sup>/Fe<sub>total</sub> ratio from the intensities of L<sub>3</sub>-peaks, according to the procedure of Bourdelle et al.  
944 (2013).

945

946 **Figure 9.** Comparison of H<sub>2</sub> generation during San Carlos olivine (grey dots), and harzburgite  
947 (black dots) serpentinization at 300 °C, with SL granite hydrothermal alteration at 280 °C (red  
948 dots) and 350 °C (green dot). The inset graph is a zoom on the first 2000 hours of reaction.

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