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Jean-Christophe Viennet, Benjamin Bultel, Stephanie C Werner. Experimental reproduction of the martian weathering profiles argues for a dense Noachian CO2 atmosphere. Chemical Geology, 2019, 10.1016/j.chemgeo.2019.07.009. hal-03127691

# HAL Id: hal-03127691 https://hal.science/hal-03127691

Submitted on 1 Feb 2021

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1	Experimental reproduction of the martian weathering profiles argues
2 3	for a dense fydacinan CO <sub>2</sub> atmosphere
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#### Abstract

15 On Mars, mineral sequences have been detected and they are composed of a top layer of Al-rich clay 16 minerals, then (Al, Fe)-rich clay minerals and a bottom layer composed of (Mg, Fe)-rich clay minerals. By 17 analogy with Earth, such sequences are interpreted as weathering profiles formed by the interaction of acidic 18 solutions in equilibrium with the atmosphere and the parent rock. Thus, understanding of the aqueous 19 solution composition leading to the above mineral description allows deciphering the atmosphere 20 composition. We designed an experimental column system with three levels containing powdered basaltic 21 rock to test the influence of different acidic fluids on the mineralogical formation. Five solutions were used: 22  $H_2SO_4$  and HCl at pH 3 in equilibrium with N<sub>2</sub> atmosphere, pure water in equilibrium with 0.1 and 1 23 atmospheric pressure  $CO_2$  leading to pH values of 3.9 and 4.4, respectively and a  $H_2SO_4$  solution at pH 3 in 24 equilibrium with 0.1 atmospheric pressure  $CO_2$  leading to a pH value of 2.98. The results obtained show 25 that the content of Al-rich clay minerals and the evolution from Al, (Al, Fe) to (Fe, Mg)-rich clay minerals formed are better reproduced with an originally high pCO<sub>2</sub>. Hence, we suggest that acidic alteration driven 26 27 by a dense  $CO_2$  atmosphere reproduced better the observed martian weathering profiles. The experiments 28 involving  $CO_2$  led to the formation of carbonates. Their identification by near infrared (NIR) detection 29 methods is challenged, because even the laboratory NIR spectra acquired on the experimental products show 30 that: (i) the absorption bands related to carbonates are very weak, and (ii) the strongest feature at 3.95 µm 31 is beyond the CRISM NIR range. Such carbonate formation is consistent with the recent carbonate detection 32 at a planetary scale in weathering profiles, which goes toward that the weathering profiles could have been 33 formed under a dense CO<sub>2</sub>-rich atmosphere as suggested also by climatic models.

35	
36	Key words
37	Mars, Clay Minerals, Carbonates, Column Experiments, Weathering Profiles, Atmosphere.
38	
39	Highlights
40	
41	• Martian weathering profiles (MWP) are simulated in open system column experiments.
42	• CO <sub>2</sub> rich fluid better reproduces the clay mineralogy observed in MWP.
43	• Carbonates should be present in MWP but their detection are challenging with NIR.
44	• Experimental investigation of early Mars suggests a dense CO <sub>2</sub> -rich atmosphere.
45	

#### 1. Introduction

47 Widespread weathering profiles have been observed on the martian surface older than ~3.7 Gyrs 48 (Carter et al., 2015). From top to bottom, they are composed of an evolutionary sequence from Al-rich clay minerals (kaolins and smectites), then (Al,Fe)<sup>3+</sup>-rich clay minerals (mainly smectitic), to finally Fe,Mg-rich 49 50 clay minerals (mainly smectitic) (Carter et al., 2015; McKeown et al., 2009). These alteration sequences 51 were formed by weathering and they are remarkably consistent with clay mineralogy observed in soil 52 profiles developed from basaltic rocks on Earth (Gaudin et al., 2011). Recently, carbonates have been 53 detected in the middle section of weathering profiles (Bultel et al., 2019). High resolution images across 54 these sequences suggest the absence of unconformities (Carter et al., 2015; Michalski et al., 2013), which 55 exclude a two-steps process where first Fe/Mg-rich clay minerals were formed and then a Al-rich clay 56 minerals were deposited. Finally, the sequences are widespread over the equatorial to mid-latitudinal regions 57 of Mars, which argues for a regional to planetary scale climatically controlled formation process (Carter et 58 al., 2015).

59 The formation of weathering profiles implies the presence of surface liquid water. Several 60 modelling studies have evaluated the possibilities to sustain liquid water by evoking a sufficient greenhouse 61 effect on Early Mars (Forget et al., 2013; Halevy and Iii, 2014; Kerber et al., 2015; Ramirez, 2017; 62 Wordsworth, 2016; Wordsworth et al., 2017). CO<sub>2</sub> and H<sub>2</sub>O gasses appear to be the main gasses causing a 63 rise of the mean surface temperature, but their sole contribution appears to be insufficient (Wordsworth, 64 2016). Other possibilities have been explored to episodically warm up the martian surface requiring the 65 presence of SO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> with CO<sub>2</sub> gas. Finally, even if at the present time there is no clear and definitive solution to explain the presence of liquid water on Mars, the different climatic simulations tend toward a 66 67  $CO_2$ -rich and dense atmosphere of up to 0.5-2 bars with potentially other greenhouse gasses to a lesser extent (from ppm to few percent). 68

Weathering as an acidic chemical process appears to be the most reasonable pathway for the
formation of the clay mineral sequence (Zolotov and Mironenko., 2007; Farrand et al;, 2008; Gaudin et al.,

71 2011; Michalski et al., 2013; Dehouck et al., 2014a; Farrand et al., 204; Zolotov and Mironenko, 2016; 72 Gaudin et al., 2018, Peretyazkho et al., 2018; Bultel et al., 2019). The acidic solutions leading to the 73 formation of the weathering profiles are a key to better understand Early Mars. They represent the link 74 between the weathering profiles and the martian atmosphere during this epoch. Various chemical 75 compositions have been put forward leading to the formation of the mineralogical sequences as S-bearing 76 solution or CO<sub>2</sub>-rich fluids.

77 S-bearing solutions have been proposed in experimental hydrothermal studies (Peretyazkho et al., 78 2018) and geochemical simulations (Zolotov and Mironenko, 2016). In their study, Zolotov and Mironenko 79 (2016) used geochemical simulations with different acidic solutions composed of CO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>-HCl acids 80 to reproduce the mineral sequence of the martian weathering profiles. Because so far no carbonate has been 81 detected in these martian sequences, Zolotov and Mironenko (2016) concluded that: "Weathering by low -82 pH H<sub>2</sub>SO<sub>4</sub> - bearing solutions is more consistent with observations than alteration by S-free fluids". The pH 83 dependencies on clay mineral formation from basaltic glass hydrothermal experiments in closed system at 84  $200^{\circ}$ C show that H<sub>2</sub>SO<sub>4</sub> acid at pH ~ 3 leads to the formation of dioctahedral smectite and sulfate, while at 85 higher pHs, trioctahedral smectite and sulfate are formed (Peretyazhko et al., 2018). Peretyazhko et al., 86 (2018) also argue for a SO<sub>2</sub>-rich atmosphere on Early Mars, which should inhibit carbonate formation as 87 proposed by previous studies (Halevy et al., 2007; Bullock and Moore, 2007; Fernández-Remolar et al., 88 2011). The patchy occurrences of sulfates at Marwth Vallis (one of the martian weathering profiles) can be 89 explained by the weathering with H<sub>2</sub>SO<sub>4</sub> fluids (Bishop et al., 2013; Michalski et al., 2013; Farrand et al., 90 2014; Zolotov and Mironenko, 2016). Nevertheless, the patchy presence of sulfates can also be due to 91 localized alteration postdating the formation of the weathering profiles (Altheide et al., 2010). In addition, 92 S-bearing gasses would also lead to the end of warm conditions necessary to sustain liquid water at the 93 surface (Kerber et al., 2015).

94 The hypothesis of  $CO_2$  weathering fluids has also been investigated by chemical modelling and 95 experimental studies. Zolotov and Mironenko (2016) show that the clay minerals evolution can be

96 reproduced but even with the presence of  $H_2SO_4$  acid in solution, carbonates should form in the weathering 97 profiles at depth where the pH is neutral due the dissolution of the basaltic rock. Dehouck et al., (2014a) 98 and Gaudin et al., (2018) have performed experiments of weathering of olivine at different water rock ratio 99 (evaporitic and 10) and duration (from 45 to 470 days) at 45°C under 1 bar of  $CO_2$  or air atmosphere. For 100 both studies, Fe,Mg smectite can form under such conditions. Also, for the longest experiments with a water 101 rock ratio of 10, they observed the formation of Al-rich clay minerals. They conclude that the Al-rich upper 102 horizons of the weathering profiles can form under a  $CO_2$  dense atmosphere even if the parent material is 103 poor in aluminum. In such condition, carbonates have formed. Such hypothesis appeared counterintuitive 104 as carbonates have not been observed in the martian weathering profiles at that time. Yet, such atmosphere 105 is more favorable to sustain liquid water on the surface of Mars (Wordsworth, 2016).

106 Based on this, no consistent conclusion can be drawn. In order to provide additional constraints on 107 the acidic solutions, the present study aims at investigating the scenarios proposed, which could lead to the 108 martian weathering profiles. The acidic scenarios (i.e. acidic event driven by  $H_2SO_4$ , HCl and/or CO<sub>2</sub>) have 109 been evaluated using a setup dedicated to mimicking the martian weathering profiles. We designed an open 110 column system consisting of three stacked shelves where the solution passes through from bottom to top. In 111 order to decrease the experiment duration, the experiments were performed at 150°C and the water is kept 112 liquid in the system via a backpressure regulator set at 5 bars. The consequences of such higher temperature 113 on the mineral formation are discussed in section 4.2.1. Five acidic solutions were used: pure water in 114 equilibrium with 1 and 0.1 pCO<sub>2</sub> leading to pH values of 3.9 and 4.4 respectively, H<sub>2</sub>SO<sub>4</sub> and HCl acidic 115 solution at pH 3 in equilibrium with 1 pN<sub>2</sub> and finally  $H_2SO_4$  solution at pH 3 in equilibrium with 0.1 pCO<sub>2</sub> 116 leading to pH value of 2.98. The mineral formation pathways are investigated through the cationic 117 composition and the pH measurements of the output solutions. In addition, solid analyses by using X-Ray 118 Diffraction (XRD) and near-infrared (NIR) measurements were performed to characterize the alteration 119 products. The obtained results show that acidic fluids rich in CO<sub>2</sub> better reproduce the general trend of the 120 weathering profile sequence. Finally, we suggest that the mineralogical weathering profile observations

121	could have been formed through acidic weathering in a dense CO <sub>2</sub> -rich atmosphere in accordance with the
122	recent carbonate detection in these weathering profiles (Bultel et al., 2019).

### 2. Materials and Methods

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#### 2.1. Sample selection and preparation

125 The basaltic powder used for the experiments was prepared from a volcanic basaltic glass of 126 tholeiitic composition from Iceland (Stapafell, Reykjanes Peninsula, Iceland). Particle sizes of less than 127 10 µm were crushed by micronizing (for more details see Viennet et al. (2017)) and used to conduct the 128 experiments. The chemical composition of the final powder has been obtained by fusion and XRF analysis 129 (Actlabs, Canada, Table 1). The chemical composition of the basaltic glass is in the range of the chemical 130 composition range of the martian surfaces (Bell, 2008) and from the in-situ measurements of basaltic rock 131 at Gusev Crater (McSween et al., 2006). Basaltic glass was chosen because it has the highest rate of 132 dissolution compared to the crystalline basaltic minerals (Gislason and Hans, 1987; Gislason and Arnórsson, 133 1993; Gislason et al., 1996; Stefánsson et al., 2001) leading to a decrease of experiments duration. Also, 134 volcanic glass has been measured as one of the main component of the rocks analysed with the Curiosity 135 rover on Mars (Bish et al., 2013; Meslin et al., 2013; Dehouck et al., 2014b; Smith et al., 2018).

136

# 2.2. Experimental set up and procedure

137 The experiments were performed in a newly-developed open system column with three stacked 138 shelves for the rock powders to mimic the natural weathering process. The technical sketch of the 139 experimental setup is presented in Figure 1. One liter of input aqueous solution was flushed with the desired 140 gas for 10 min. Then, the input aqueous solution was put in equilibrium with the same desired gas 141 composition at atmospheric pressure and that throughout the experiment. Five different experiments were 142 performed, which correspond to five input aqueous solutions in equilibrium with the considered gas at 20°C 143 and 1 bar (Table 2). Two of them were performed with pure water equilibrated with either a gas composed 144 of 100 % of CO<sub>2</sub> leading to an initial calculated pH value of 3.9 (referred as water - 1 pCO<sub>2</sub>) or with a gas

145 composed of 10% CO<sub>2</sub> ( $\pm < 1\%$ ) and 90% N<sub>2</sub> leading to an initial calculated pH value of 4.4 (referred as 146 water - 0.1 pCO<sub>2</sub>). Two solutions correspond to H<sub>2</sub>SO<sub>4</sub> and HCl acidic water calculated and measured at pH 147 3 ( $\pm 0.05$ ) equilibrated with a gas composed of 100% N<sub>2</sub> (referred as H<sub>2</sub>SO<sub>4</sub> - 0 pCO<sub>2</sub> and HCl - 0 pCO<sub>2</sub>, respectively). The acidic solutions were prepared from standard 1 mol.L<sup>-1</sup> HCl or H<sub>2</sub>SO<sub>4</sub> solutions diluted 148 149 with pure water. The last experiment corresponds to an input solution composed of  $H_2SO_4$  acid at pH 3 150 ( $\pm 0.05$ ) in equilibrium with a 10% CO<sub>2</sub> / 90% N<sub>2</sub> gas leading to an initial calculated pH value of 2.98 151 (referred as  $H_2SO_4 - 0.1 pCO_2$ ). The initial pH values evolve before the alteration due the temperature 152 dependency of pH (see below, the recalculated pH at 150°C). The aqueous solutions were injected in the 153 column from the bottom via a high pressure liquid chromatography pump at a flow rate of 0.05 mL.min<sup>-1</sup> ( $\pm$ 154 5%). The column consists of a titanium cylinder and stainless steel tubing able to resist the acidic conditions. 155 In order to decrease the time of reaction, the aqueous solution is heated to 150°C with a furnace around the 156 column and kept liquid applying a 5 bars constant pressure in the system via a backpressure regulator. This 157 pressure corresponds to the above water vapor limits pressure at such temperature. The initial pH value at 158 150°C and 5 bars were calculated using the EQ3/6 software (Wolery, 1992). Hence, the initial pH at 150°C 159 and 5 bars of the water - 1 pCO<sub>2</sub> experiment is 4.1, for the water - 0.1 pCO<sub>2</sub> experiment is 4.6, for the  $H_2SO_4$ 160 or HCl - 0 pCO<sub>2</sub> experiments are 3.2 and for the  $H_2SO_4$  - 0.1 pCO<sub>2</sub> experiment is 3.17 (Table 2). The input 161 aqueous solutions were injected through the three rock powder holders, labelled level #1, #2 and #3 from 162 bottom to top. Each holder contains 0.5 grams of basaltic glass powder at the start of the experiments. Each 163 experiment was conducted for a period of 20 days and the output solution was collected every ~48 hours. 164 After the 20 days of experiments, the furnace was turned off and the system cooled down to  $\sim$ 50°C within 165 4 hours. Then, the three holders with the altered materials are collected from the column. The three samples 166 from each level were dried in an oven at 80°C (for around 10 h) prior to their characterization.

167

#### 168 **2.3. Aqueous solution analysis**

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#### 2.3.1. Analytical measurements

170 Directly after the output solution sampling, the pH of the solution is measured at 20°C with an 171 AgCl–KCl combination electrode calibrated at ~20°C with pH buffer solutions. The uncertainty for each 172 measurement was  $\pm 0.05$  pH units. Prior to the analytical measurements, the output solutions were filtered 173 through 0.2 µm sterile cellulose nitrate filter. The Si concentrations were measured by cation 174 chromatography instrument (Dionex ICS-2000) by a calorimetric method based on the reduction of silico-175 molybdate in acidic solution to "molybdenum blue" by ascorbic acid (Skougstad et al., 1978). The lower 176 detection limit was 0.02 ppm and the maximum uncertainty was estimated at 5% based on reproducibility 177 test. The Mg<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> concentrations were measured by cation chromatography with the Dionex 178 ICS-1000 Ion Chromatography System. The detection limits for all elements were lower than 0.1 ppm and 179 the maximum uncertainty was estimated at 5% based on reproducibility test. The Al and Fe concentrations 180 of the input and output solutions were measured with an inductively coupled plasma mass spectrometry 181 (aurora Elite Bruker) equipped with a Cetac ASX-250 autosampler and an ESI oneFAST sample 182 introduction system. The detections limits were lower than 5 ppb and the uncertainty was estimated at 5%. 183 The pH values at 150°C were calculated from the pH measurements at 25°C to take into account the ion 184 concentrations and the chemical composition of the output aqueous solution by using the EQ3/6 software 185 (Wolery, 1992).

186 **2.4. Solids analysis** 

187 *2.4.1 XRD analysis* 

188 XRD analyses were performed on the unreacted and the weathered samples for each experiment. 189 Bulk analyses were performed on powder preparation. The DIFFRAC.EVA software with the PDF4 190 database has been used for the mineral identification. To determine the clay mineral nature on oriented 191 preparation, each clay mineral sample was Ca- and K-saturated by using four saturation cycles of 0.5 mol.L<sup>-</sup> 192 <sup>1</sup> of CaCl<sub>2</sub> and 1 mol.L<sup>-1</sup> of KCl (W/R = 200). Then, the samples were washed in distilled water and dried 193 at 50°C. For each saturated sample, oriented preparations were performed by pipetting slurries of the

194 particles dispersed in distilled water on glass slides and dried at room temperature (preparation referred as 195 air dried -AD). The Ca-preparations were solvated by exposing the glass slides to ethylene-glycol vapor at 196 50°C overnight (Ca-EG). Concerning the K-saturated samples, each K-AD preparations were successively 197 heated at, 110, 330 and 550°C in an oven for 4 hours. XRD acquisitions were obtained after each temperature 198 step. The treatments are referred as K-110, K-330 and K-550. The XRD patterns were recorded on a D8 199 Advance Bruker (CuK $\alpha_{1+2}$  radiations) from 2 to 55°2 $\theta$  using a step interval of 0.25°2 $\theta$  and a counting time 200 per step of 2.5 s. The size of the divergence slit, the two soller slits and the antiscatter slit were  $0.25^{\circ}$ ,  $2.5^{\circ}$ , 201  $2.5^{\circ}$  and  $0.5^{\circ}$ , respectively.

202

#### 2.4.2. Near infrared analysis

203 The near-infrared reflectance spectra were obtained with a PerkinElmer Fourier-transform infrared 204 spectroscopy (FTIR) spectrometer from 1 to 4  $\mu$ m wavelengths with a spectral resolution of 4 cm<sup>-1</sup> at IAS-205 Orsay, France. The light source is a broadband source and the detector is a deuterated-triglycine sulfate 206 detector. The spectrometer was calibrated by using Spectralon 99% (0.9 to 1.2 µm) and Infragold (1.2 to 4 207 µm) samples. The different spectra were acquired under ambient temperature and pressure conditions on 208 the same powder preparations as for the bulk XRD analysis.

209

#### 2.4.3. SEM-EDS analysis

210 All backscattered electrons pictures were obtained using a TESCAN VEGA II LSU scanning 211 electron microscope at the Museum National d'Histoire Naturelle, Paris (Plateau Technique de Microscopie 212 Electronique, PTME). The SEM observations were performed on carbon-coated samples with an 213 accelerating voltage of 15kV. A silicon drift detector with a 133 eV resolution allowed us to perform energy 214 dispersive X-rays spectroscopy in order to get qualitative information about the chemistry of the materials.

215 **3. Results** 

#### 216 3.1. Chemical elements release in the output solution

218 The final pH values measured are higher than the initial pH values at 25°C (Figures 2.a - e). After 219 300 hours, the final pH values (20°C) are nearly constant through time and they increase with the decrease 220 of pCO<sub>2</sub>. The pH final values are circumneutral to alkaline (Figures 2.a, and Table 3). With the increase of pCO<sub>2</sub>, the pH values (at 20°C) evolve from 6.35, 8.10, 8.32 to  $\sim$ 8.5 for the water - 1 pCO<sub>2</sub>, water - 0.1 pCO<sub>2</sub>, 221 222 H<sub>2</sub>SO<sub>4</sub>, - 0.1 pCO<sub>2</sub> and 0 pCO<sub>2</sub> experiments, respectively (Table 3). Hence, the solutions containing CO<sub>2</sub> 223 have not been completely neutralized and buffered by the rocks. The H<sup>+</sup> consumptions have been calculated 224 by the difference between the initial and final pH values. The H<sup>+</sup> consumptions decrease with the pCO<sub>2</sub> 225 increase (Figures 2.a - e). The same  $H^+$  consumption can be noticed for the experiments with HCl and  $H_2SO_4$ 226 - 0 pCO<sub>2</sub>. Consistently, the H<sup>+</sup> consumption of the H<sub>2</sub>SO<sub>4</sub> – 0.1 pCO<sub>2</sub> experiment corresponds to the sum of 227 the H<sup>+</sup> consumption for water - 0.1 pCO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> - 0 pCO<sub>2</sub> experiments. The pH values have been 228 simulated for the experimental temperature 150°C and are presented in Figures 2.f - j and table 3. The values 229 are nearly constant through times. They decrease with the pCO<sub>2</sub> increase but in a lesser extent than at  $25^{\circ}$ C 230 due to the pH temperature dependence. The final pH values at 150°C are 6.07, 7.01, 6.88, 7.04, 7.02 for the 231 water - 1 pCO<sub>2</sub>, water - 0.1 pCO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> - 0.1 pCO<sub>2</sub> and 0 pCO<sub>2</sub> experiments, respectively (Table 3).

232

#### 3.1.2. Composition of the output solution

233 The Figures 3.a - e present the total quantities in mol of the main chemical elements released in the 234 output solutions from the original basaltic glass dissolution. The quantities of Si released increase with the increase of pCO<sub>2</sub>. The values of Si released (comprised between 3.1 and 9.6 . 10<sup>-3</sup> mol at the end of the 235 experiments) are the highest compared to the other chemicals elements.  $Mg^{2+}$  is released for the sole water 236 - 1 pCO<sub>2</sub> experiment (9.6,  $10^{-4}$  mol at the end of the experiment, Fig. 3.b). The highest Ca<sup>2+</sup> quantities 237 released is for the water - 1 pCO<sub>2</sub> experiment (2.0. 10<sup>-3</sup> mol at the end of the experiment, Fig. 3.c). The Ca<sup>2+</sup> 238 values of the experiments involving H<sub>2</sub>SO<sub>4</sub> acid are similar (1.1 and 1.3 10<sup>-3</sup> mol, for the 0 pCO<sub>2</sub> and 0.1 239 pCO<sub>2</sub> respectively, at the end of the experiments) and the Ca<sup>2+</sup> values for the water - 0.1 pCO<sub>2</sub> and HCl - 0 240

pCO<sub>2</sub> experiments are alike and the lowest (respectively,  $7.7 \cdot 10^{-4}$  and  $9.4 \cdot 10^{-4}$  mol at the end of the experiments, Fig. 3.c). The quantities of Na<sup>+</sup> and K<sup>+</sup> released (comprise between 1 and 7  $\cdot 10^{-4}$  mol at the end of the experiments) are lower than for Ca<sup>2+</sup> and Si and the values are similar among the experimental conditions (Fig. 3). The Al and Fe values are not shown, because they are two orders of magnitudes lower than the Si values, despite that they are of about the same order of magnitude in the structure of the original basaltic glass (see table 1).

247 The Figures 3.f, g, h and i show the Mg/Si, Ca/Si, Na/Si and K/Si ratios of the elements released in 248 the output solutions and of the unreacted material. For all experiments after 300 hours, the chemical ratios 249 of the output solutions are constant. The Mg/Si ratios are null except for the water - 1 pCO<sub>2</sub> experiment 250 (value of 0.1), for which the Mg/Si ratio is lower than for the unreacted material (ratio of 0.29, Fig. 3.f). The 251 Ca/Si ratios for the HCl and H<sub>2</sub>SO<sub>4</sub> - 0 pCO<sub>2</sub> experiments are slightly above the Ca/Si ratio of the unreacted 252 material (Fig. 3.g), while the Ca/Si ratios of the experiments involving  $CO_2$  (the ratios are at the end of the 253 experiments: 0.21, 0.14 and 0.19 for the water - 1 pCO<sub>2</sub>, water - 0.1 pCO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> - 0.1 pCO<sub>2</sub> 254 experiments, respectively, Fig. 3.g) are lower than the unreacted material ratio (value of 0.26, Fig. 3.g). For 255 the Na/Si and K/Si ratios for all experimental conditions, the ratios are those of the pristine material ratio 256 (respectively values of 0.07 and 0.01, Fig. 3.h and i). These low output solution ratio variations are due to 257 the formation of the corresponding secondary minerals as functions of the initial conditions. Finally, the 258 chemical ratios and the pH of the output solutions are constant after 250 hours (Fig. 2 and 3), which indicates 259 that the reactions achieved solid-solution equilibration.

260

#### **3.2.** Characterization of the solid samples

261 *3.2.1. Characterization of the unreacted sample* 

Figure 4 presents the XRD pattern and NIR spectrum obtained on the pristine material. The XRD pattern exhibits a large and high bump between 5 - 2.33 Å and centered at 3.23 Å corresponding to basaltic glass. Minor minerals (<10 %, SEM measurements see figure S2 and Gysi and Stefánsson (2012a)) can also 265 be identified by XRD peaks (Figure 4) such as quartz (triangles), olivine (diamonds) and pyroxene (squares). 266 The NIR spectrum (Figure 4) highlights the presence of olivine (diamonds) (Cloutis et al, 1986) and 267 pyroxenes (squares) at 1 µm (Adams, 1974; Cloutis et al, 1986) as the basaltic glass and quartz are not 268 visible in such NIR range. The absorption bands at  $\sim 2.82 \,\mu m$  correspond to water molecules probably 269 adsorbed on the basaltic particles. The SEM measurements have shown that the olivine is close to the 270 chemical composition of forsterite (Figure S2.c). The pyroxene is close to the chemical composition of 271 augite (Figure S2.c). Small patch of chromite also have been detected in inclusions of the glass and forsterite 272 (Figure S2.a and c). The main phase carrying Fe is the basaltic glass, since the proportion of augite and 273 chromite is low in the bulk material. In such basaltic glass, Fe is present in the oxidation degree II (Christie 274 et al., 1986; Gysi and Stefánsson, 2012a). Quartz cannot be found in such basaltic rocks and its presence is 275 interpreted as a contamination during the filed collection.

276

### 3.2.2. Characterization of the reacted samples

277 The XRD patterns of the reacted samples are presented in Figure 5. Compared to the pristine 278 material, the intensities of the XRD peaks corresponding to the basaltic glass decrease and new XRD peaks 279 and absorption bands appear. These indicate that the basaltic glass was dissolved and new minerals formed 280 (Figure 5). Quartz, forsterite and augite are not dissolved during the experiment because their XRD 281 intensities are similar to the pristine material. In such conditions, the percentage of dissolution of the basaltic 282 glass can be obtained by using the full pattern fitting method (Chipera & Bish, 2013; Viennet et al., 2017). 283 This method consists of determining the difference in area between the XRD peaks corresponding to both 284 the original glass and the altered sample. Preliminary tests have been performed on laboratory mixtures for 285 various proportions of basaltic glass and zinc. The results show that the content of glass can be determined 286 with an accuracy of  $\pm 2.5\%$ . The results obtained on experimental residues are presented in the Table 3. For 287 a given experimental condition, the percentage of dissolution decreases with the increase of level #. Also, 288 the percentage of dissolution increases with the increase of pCO<sub>2</sub>.

Concerning the non-clay mineral formation, the XRD peaks at 3.00, 2.84, 2.5, 2.01, 1.99 and 1.98 Å 289 290 (Figure 5) and the absorption bands at 3.85 and 3.95 µm (Figure 6) exhibit the presence of calcite (Hunt and Salisbury, 1971; Cloutis et al., 2003) at the three levels of the water - 0.1 pCO<sub>2</sub> experiment. Ca-Mg-291 Fe carbonates are noticed by the 3.0 and 2.1 Å peaks and the absorption band at 3.85 and 3.95 µm for the 292 293 level #2 and #3 of the  $H_2SO_4 - 0.1 pCO_2$ . The water - 1 pCO<sub>2</sub> experiment exhibit XRD peaks at 3.0 Å and 294 2.01 Å and absorption bands at 3.85 and 3.95 µm only present for the samples of level #3 indicating Ca-Mg-Fe carbonate. Interestingly, boehmite (AlO(OH)) can be observed with the XRD peaks at 6.1 Å only 295 296 for the sample of level #1 of the  $H_2SO_4 - 0.1 pCO_2$  experiment (Figure 5).

297 As far as clay minerals are concerned, 00l and 020 reflections of clay minerals can be noticed. A 298 detailed characterization of the XRD patterns dedicated to clay mineralogy can be found in supplementary 299 information (text and Figures S2, S3, S4, S5, S6 and S7). Briefly, the irrational 00l reflections at 14.4 and 300 2.6 Å correspond to a random (R0) smectite/chlorite mixed-layer mineral (MLM). The irrational 00l 301 reflections at 7.2, 3.5, 2.4 and 1.99 Å correspond to a R0 Fe-rich chlorite/smectite MLM. With the increase 302 of pCO<sub>2</sub> or with the decrease of level #, the content of the R0 Fe-rich chlorite-smectite MLM increase 303 relatively compared to the R0 smectite/chlorite MLM. The clay minerals formed and their evolution with 304 the pCO<sub>2</sub> are in line with previous experiments performed in closed systems on the same basaltic rocks (Viennet et al., 2017). In addition, the 020 reflections of the clay minerals shift from 4.49 to 4.59 Å with the 305 306  $pCO_2$  decrease and the increase of level #. Similarly, a slight shift can also be noticed on the 060 XRD 307 patterns (Figure S1). Such behavior could be assigned to an evolution from dioctahedral to trioctahedral 308 structure. In order to better identify these evolution, NIR spectrum with continuum removed between 2.1 309 and  $2.5 \,\mu m$  are presented in Figure 7. Note that, the characterization of the octahedral evolution on the 310 martian weathering profiles is also made in this spectral range.

311

3.2.3. Octahedral characterization of the clay minerals formed

The XRD identification has shown that the minerals present in the samples are a mixture of R0 Ferich/smectite MLM and R0 smectite/chlorite MLM. The NIR spectra confirm the presence of smectite and chlorite by their characteristic adsorption bands at 1.41 and 1.91 µm corresponding to the bending and stretching overtone of bond water and between 2.19-2.5 µm corresponding to cation-OH bond (Figures 6 and 7) (Bishop et al., 1994; Clark et al., 1990; Hunt and Salisbury, 1970).

317 The XRD identification (see supplementary file and section 3.2.2) shown that with the  $pCO_2$ 318 increase and the level #, the content of the R0 Fe-rich/smectite MLM increase relatively to the R0 319 smectite/chlorite MLM. The NIR measurements show a similar tendency as the adsorption bands at 2.31-320 2.35 decrease relatively compare to the adsorption bands at 2.19 and 2.25  $\mu$ m. Indeed, regarding the level 321 #1 of the water - 1 pCO<sub>2</sub> experiment, the XRD identification shows that the residue is manly made of a R0 322 Fe-rich chlorite/smectite MLM. The adsorption bands at 2.19 and 2.25 µm of the NIR spectrum are the 323 highest for this sample (Figures 6 and 7). This bands are related to  $Al_2$ -OH and  $(Al_Fe)_2$ -OH bonds of 324 dioctahedral smectite and or chlorite (Clark et al., 1990). Hence, the combined XRD and NIR measurements 325 confirm that this mineral is a dioctahedral R0 Fe-rich chlorite-smectite MLM. Also, the NIR measurements 326 show adsorptions bands at 2.31 and 2.35  $\mu$ m. These bands are mainly present in the CO<sub>2</sub> free experiments. 327 The XRD interpretations have shown that the main clay mineral is a R0 smectite/chlorite MLM. The NIR 328 bands at 2.31 can be related to (Fe,Mg)<sub>3</sub>-OH stretching and bending bands of trioctahedral smectite. Also, 329 the absorption band at 2.35 µm could correspond to (Fe,Mg)<sub>3</sub>-OH in Fe-rich trioctahedral chlorite (Figure 330 7.c and d) (Bishop et al., 2008; King & Clark, 1989, Clark et al., 1990). Hence, this mineral is a trioctahedral 331 R0 smectite-chlorite MLM.

For all experiments, the absorption bands depths decrease with the increase of the level # (Figure 7). This indicates that the amount of clay minerals formed decreases. As noticed by the XRD and NIR mineral identification, the octahedral (i.e. di- to trioctahedral) composition of the R0 MLM changes as function of the experiments. This can be followed by the respective absorption band depth ratio between  $Al_2-OH + (Al,Fe)_2-OH$  bands and  $(Fe,Mg)_3-OH$  bands (Figure 8.a). With the increase of level #, the 337 dioctahedral bonds decrease in favor of the trioctahedral bonds in clay minerals as noticed by the di/tri ratios 338 decrease (Figure 8.a). Finally, more (Fe,Mg)<sub>3</sub>-OH bonds are present in the clay minerals formed in the upper 339 levels (Figure 8.a). In addition, more dioctahedral clay minerals are formed with the  $pCO_2$  increase as the 340 increase of the di/tri ratios values for a same level # shows (Figure 8.a). Finally, the evolution from Al<sub>2</sub>-OH 341 to (Al,Fe)<sub>2</sub>-OH bonds in the octahedral sheet of clay minerals can be experimentally investigated by 342 following the respective absorption band depth ratios between the  $Al_2$ -OH and  $Al_2$ -OH + (Al,Fe)<sub>2</sub>-OH bands 343 (Figure 8.b). The highest  $Al_2/(Al_2+[Al,Fe]_2)$  ratio is measured in the 1 pCO<sub>2</sub> experiment. In addition, the 344 ratios decrease gradually from level #1 to #3 but never reach null value. In all other experiments, the ratios 345 exhibit null values along the column and a non-regular decrease of the ratios as a function of the level #. 346 This evolution is due to the predominance of  $Al_2$ -OH bands for the 1 pCO<sub>2</sub> experiments compared to the 347 other experiments where such absorption band is fairly weak. Table 3 gives an overview of the mineral 348 identification and evolution highlighted by the XRD and NIR measurements.

349

#### 4. Discussion

# **4.1. Effect of the acid used on the evolution of geochemical conditions and**

#### 351 minerals formation

352 For all of the experimental conditions, the decrease of dioctahedral bonds in favor of trioctahedral 353 ones with the increase of level # (Figure 8.a, table 3) can be related to the pH increase due to dissolution 354 along the column system (Table 3). Indeed, the octahedral composition evolves with the pH of alteration. 355 The pH dependency was evaluated by experiments and geochemical modelling in closed systems with 356 basaltic glass of similar composition (Peretyazhko et al., 2018; Viennet et al., 2017) and by numerical 357 models on basaltic rock of similar composition (Zolotov and Mironenko, 2016). These studies show an 358 increase of dioctahedral clay mineral formation with the decrease of pH. The rock powder present in the 359 level #1 is reacting at the initial acidic pHs, which are the lowest in the column experiments. Hence, the minerals formed are enriched in Al<sub>2</sub>-OH and (Al,Fe)-OH. In the levels above (second and third), more Mg<sup>2+</sup> 360

is incorporated in the octahedral sheet of the clay mineral structure due to the increase of pH by the bufferingof the basaltic glass dissolution (Table 3 and Figure 8.a).

363 With the increase of  $pCO_2$ , the dissolution of the basaltic glass increases as shown by the increase 364 of percentage of dissolution by XRD (Table 3) and hence highest Si quantities are released (Figure 3). This 365 evolution argues for lower acidity during the alteration with the increase of  $pCO_2$  (Table 3). This is in 366 accordance with the fact that basaltic glass dissolution increases with the pH decrease (Oelkers and Gislason, 367 2001; Gislason and Oelkers, 2003; Strachan, 2017 and references therein). Nevertheless, the initial pH 368 values are higher for the water - 1 and 0.1 pCO<sub>2</sub> experiments compared to the HCl/H<sub>2</sub>SO<sub>4</sub> - 0 pCO<sub>2</sub> 369 experiments. Gysi and Stefánsson (2011) noticed, by performing numerical simulation for closed systems, 370 that with increasing pCO<sub>2</sub>, the system is shifted towards the  $CO_2$  - basalts buffered alteration system and it 371 requires more time and dissolved basaltic glass to reach pH values >8, as for the zero pCO<sub>2</sub> experiments. 372 This evolution was also noticed by Viennet et al. (2017) performing closed systems experiments on basaltic 373 glass dissolution for the same duration of reaction. The continuous renewal of the input solution the pH of 374 the solution is too low for the formation of carbonates in the two first layers of the water - 1  $pCO_2$ 375 experiment. The lack of carbonates means that CO<sub>2</sub> fluids are not buffered by the basaltic glass in the first 376 layers, so low-pH solutions penetrate more efficiently to the next less altered solids. In the experiments free 377 of CO<sub>2</sub>, the pH is not controlled by CO<sub>2</sub> buffering but by the buffering of the basaltic glass itself. As the 378 reactivity of basaltic glass is high upon dissolution (Gislason and Hans, 1987; Gislason and Arnórsson, 379 1993; Gislason et al., 1996; Stefánsson et al., 2001), the increase of pH is important. Hence, the final pH values are lower for the CO<sub>2</sub> experiments than for the CO<sub>2</sub>-free experiments even though the initial pH 380 381 values of the experiments involving CO<sub>2</sub> are higher.

In acidic conditions, alkaline cations such as Mg, Ca, Na and K are more mobile than Al, Fe and Si (Martini and Chesworth, 2013; Mason and Moore, 1982; Pedro and Delmas, 1970). Such evolution driven by the initial experimental conditions is supported by the investigation of the chemicals elements released in the output solution. Of note, no SiO<sub>2</sub> formation and dissolution were measured during the experiments. 386 Despite the fact that Ca is a mobile cation in acidic conditions, the Ca/Si ratios in the output solutions are 387 highest for the CO<sub>2</sub>-free experiments, while the final pH values are the highest. Ca was trapped in Ca-388 carbonate formation lowering the Ca released into the output solutions.

389 The increase of dioctahedral clay minerals with the  $pCO_2$  increase (Figure 8.a) follows the trend of the final pH values leading to the highest  $Mg^{2+}$  released for the 1 pCO<sub>2</sub> experiment. Indeed,  $Mg^{2+}$  is a mobile 390 391 cations in acidic conditions (Martini and Chesworth, 2013; Mason and Moore, 1982; Pedro and Delmas, 392 1970), which has also already been seen in natural conditions and is an important step for the mineralogical 393 formation in weathering profiles similar to the martian one (Gaudin et al., 2011; Martini and Chesworth, 394 2013; Velde and Meunier, 2008). In addition, due to the higher formation of Al and Fe-rich clay minerals compared to the Fe,Mg-rich clay minerals during the water - 1  $pCO_2$  experiment, Mg<sup>2+</sup> is less involved in 395 the framework building of clay minerals, which let more  $Mg^{2+}$  in the solution (Gysi and Stefánsson, 2011). 396 397 On the same initial material, Viennet et al. (2017) already showed the increase of dioctahedral bonds with 398 the pCO<sub>2</sub> related to the pH decrease. The extents of dioctahedral layers were less important and carbonate 399 formed because the experiments were performed in closed system setting. In closed system experiments, 400 the continuous depletion of the alteration solution by the dissolution of the basaltic glass allows carbonate 401 formation and lead to lesser dioctahedral clay minerals formation compared to the open system. Similar 402 results have been obtained by Zolotov and Mironenko (2016) in their geochemical simulation devoted to 403 the martian weathering profiles. Indeed in the simulation of 1  $pCO_2$  (Zolotov and Mironenko, 2016), the 404 upper part of the soil is composed of Al-rich clay minerals and deeper, with the pH increase due to dissolution of the parent rock, (Al,Fe)<sup>3+</sup>-rich clay minerals and carbonates are formed. 405

Except for the  $H_2SO_4 - 0.1 pCO_2$  experiment, no oxides have been formed, thus the clay mineral formation explains the low release of Al and Fe into the output solution. Compared to Si, both Na and K have a high release, probably because they are not involved in the building of the framework minerals. Finally, the behavior of the chemical elements released controls the nature of the clay minerals formed.

#### 410 4.2. Martian weathering profiles could have been formed under a dense CO<sub>2</sub>

#### 411 atmosphere

#### 412 4.2.1. Experimental applicability

413 The experiments were performed at 150°C in order to decrease the reaction time. Indeed, with the 414 increase of temperature, the dissolution rate of basaltic glass increases (Gislason and Oelkers, 2003; 415 Gudbrandsson et al., 2011) leading to the reduction of the experiment duration. On Mars though, the 416 weathering profiles were probably formed at much lower temperature. The temperature effect on the clay 417 mineral evolution has already been described in geological systems. Observations for hydrothermal or 418 diagenetic systems have shown that smectites, kaolinite or berthierine can be transformed into chlorites with 419 increasing temperature (Beaufort et al. (2015) and references therein). The results obtained during the 420 experiments show a non-negligible content of chlorites, which is probably higher than those of the martian 421 weathering profiles (Noe Dobrea et al., 2010). Chlorites were over-formed, because of the 422 hydrothermal/diagenetic chloritization process of smectite, kaolinite or berthierine (Beaufort et al., 2015; 423 Meunier, 2005). In the review of Beaufort et al. (2015), three series of chloritization processes have been 424 considered and described as Mg-series, Fe-series and Al, Mg-series. The Mg-series is identified by their 425  $Fe/(Fe+Mg)_{octahedral} < 0.5$  while the Fe-series has ratios > 0.5. The Mg-series consists of the conversion of 426 saponite to chlorite via corrensite. The Fe-series consists of the conversion of berthierine to chlorite to Fe-427 chlorite. And, the Al,Mg-series consists of the conversion of kaolinite to sudoite via tosudite. During the 428 experiments presented here, the clay minerals formed are mainly composed of tri- and dioctahedral R0 429 smectite/chlorite and Fe-rich chlorite/smectite MLMs. The present experiments conducted at room 430 temperature would probably have led to less chlorite formation in favor of smectite and kaolinite and to 431 berthierine layers for the Fe-rich chlorite layers (Beaufort et al., 2015). Berthierine has not been identified 432 in the weathering profiles but its presence cannot be excluding as its identification is close to Fe-rich 433 smectite/chlorite MLM by NIR remote sensing (Calvin and King, 1997). Hence, the potential clay minerals 434 formed at lower temperature are in line with the previous mineralogical description of the martian weathering profiles (Carter et al., 2015). The temperature effect modifies the relative proportion of chlorite, smectite, kaolinite or berthierine layers via mixed layering (Beaufort et al., 2015) but the octahedral compositions are partly influenced by the temperature (Beaufort et al., 2015; Cathelineau, 1988; Eberl et al., 1978; Inoue, 1983). Thus, the martian clay mineralogy, which is based on the octahedral composition investigated by NIR, can be compared to the NIR spectra of the experiment products by following the octahedral clay mineral composition evolution as presented in Figure 8.

441 The formation of the mineralogical assemblages is also dependent on the temperature. By 442 performing experimental and modelling studies on basaltic glass of similar composition than the present 443 study, Gysi and Stefánsson (2011, 2012a, 2012b) have shown that with the decrease of temperature the 444 formation of carbonates is enhanced. Indeed, the formation of clay minerals is less important at lower temperature which let more  $Fe^{2+}$ ,  $Mg^{2+}$  and  $Ca^{2+}$  be available for the carbonates formation. In a martian 445 446 context, similar trend has been observed by geochemical modelling (Griffith and Shock, 1995) as with the 447 temperature decrease, the formation of carbonates is promoted. Based on these studies, the content of 448 carbonates formed can be enhanced up to ~15% between 150°C to 50°C. When applied to martian 449 weathering profiles, our study minimized the content of carbonates formed. Also, the temperature effect 450 (between 65 - 200°C) on the formation of sulfates in a martian context has been evaluated by Marcucci and 451 Hynek, (2014). The type of sulfates formed is similar among the temperature tested but the amount of 452 sulfates decreases with the temperature. Since no sulfate is formed during our experiments (Figures 3 and 453 Table 3), no sulfate is expected to form at lower temperatures in the present experimental conditions either.

Summarizing the findings, the observed mineral assemblages produced at  $150^{\circ}$ C would evolve at lower temperature. Regarding the experiments involving CO<sub>2</sub>, the carbonate content would increase (up to ~15%) with the temperature decrease and the content of clay minerals would decrease. No sulfate formed during the experiments involving H<sub>2</sub>SO<sub>4</sub> fluids, and in colder conditions it is even less likely. Concerning the clay minerals, the temperature effect affects the relative proportions of the different species and mixed layering (Beaufort et al., 2015), as well as the octahedral compositions (Beaufort et al., 2015; Cathelineau, 460 1988; Eberl et al., 1978; Inoue, 1983). For the detailed comparison of the martian clay mineralogy the NIR
461 spectra of the experiment products showing the octahedral clay mineral composition evolution as presented
462 in Figure 8, can be used.

463

#### 4.2.2. Martian clay mineral sequences better experimentally reproduced with CO<sub>2</sub>-rich fluids

464 The widespread weathering profiles detected on the martian surface are composed of a sequence of 465 dioctahedral clay minerals overlying di-trioctahedral clay minerals (Figure 9.a). The dioctahedral sequence 466 is split in two from top with Al-rich clay minerals to bottom with an enrichment of Fe<sup>3+</sup>-rich clay minerals 467 (Carter et al., 2015; McKeown et al., 2009). The Figures 8 and 9.b show the experimental evolution of the 468 octahedral composition of the clay minerals with the level # as a function of the pCO<sub>2</sub>. As the experiments 469 are performed from bottom to top, the level #1 corresponds to the top part of the stratigraphy while the 470 levels #2 and #3 represent deeper soil horizons. In the present study,  $H_2SO_4$  and HCl bearing solutions do 471 not lead to significant dioctahedral clay mineral content (Figure 8.a and 9.b) nor to the evolution of Al to 472 (Al,Fe)<sup>3+</sup>-rich clay minerals (Figure 8.b) as observed on the martian weathering profiles (Figure 9). In 473 addition, lower initial pH values lead to the formation of sulfates and inhibit smectite formation 474 (Peretyazhko et al., 2018). Hence, the top layer of the martian weathering profiles is not experimentally 475 reproduced by pure  $H_2SO_4$  and HCl bearing solutions (Figure 9). The experiment able to form a top layer 476 rich in dioctahedral clay minerals is the water - 1  $pCO_2$  (Figures 8.a and 9). In addition, this experiment is the only one suggesting horizons of Al-rich clay minerals above (Al, Fe)<sup>3+</sup>-rich clay minerals (Figure 8.b). 477 478 A  $CO_2$ -rich atmosphere is also in line with the alteration of olivine at low temperature under a dense  $CO_2$ 479 atmosphere (Gaudin et al., 2018). Indeed, a dense CO<sub>2</sub> atmosphere enables Al-rich clay mineral formation 480 despite of an Al-poor parent rock. Drawing on the point of view of the clay mineralogy trend seen in the 481 martian weathering profiles, we suggest that acidic alteration prompted by a dense CO<sub>2</sub>-rich atmosphere 482 better reproduce the martian weathering profiles (Figure 9). However, under a dense CO<sub>2</sub> atmosphere, 483 carbonates are formed. The presence of carbonates in the weathering profiles is consistent with the thermal 484 infrared spectra modelling predictions at Mawrth Vallis, which suggests up to 8% of carbonate (Bishop and Rampe, 2016). Nevertheless, the mineral identification in the weathering profiles based on NIR measurements have not detected carbonates. Hence, Zolotov and Mironenko (2016) concluded that the weathering profiles were formed by low-pH  $H_2SO_4$ -bearing solutions rather than by S-free fluids (such as CO<sub>2</sub>) and excluded the possibility of CO<sub>2</sub>-rich fluids. Several previous studies argued that carbonate formation could have been inhibited despite of a dense CO<sub>2</sub> atmosphere by the addition of acidic solutions rich in sulfur. In the following, we discuss the geochemical consistency of proposed carbonate formation and of the carbonate detection limitation in light of our experimental results.

#### 492

#### 4.2.3. Are carbonates present in the martian weathering profiles?

493 Mineral detections challenged the geochemical interpretation of the weathering profile formation 494 on Mars due to the lack of carbonate. Two main possibilities were proposed to explain the "missing" 495 carbonates: i) a second acidic event, which led to carbonate dissolution (Bibring et al., 2006) or ii) a mixture 496 of CO<sub>2</sub>-rich and dense atmosphere with another gas leading to acidic solutions inhibiting the carbonate 497 formation (Bullock and Moore, 2007; Fairén et al., 2004; Fernández-Remolar et al., 2011; Halevy et al., 498 2007). The first possibility suggests a second acidic event, driven by an acidic sulfuric fluid in equilibrium 499 with a dense  $CO_2$  atmosphere, dissolved any carbonates previously formed. However, such a secondary 500 acidic event will dissolve carbonates, but carbonation would occur deeper in the profiles sequences as in-501 situ CO<sub>2</sub>-storage experimentation have shown (Matter et al., 2016). In addition, the dissolution of carbonates 502 could also lead to the release of  $CO_2$  back into the atmosphere, cancelling the carbon sequestration, and thus 503 not solving the "missing" carbonate paradox (Edwards and Ehlmann, 2015). The second possibility (Bullock 504 and Moore, 2007; Fernández-Remolar et al., 2011; Halevy et al., 2007) aims to directly inhibit the carbonate 505 formations during the alteration event. Acidic solutions rich in  $CO_2$  mixed with other acids such as sulfuric 506 acids were proposed to decrease the pH solutions lower than the pH range stability of carbonates. To test 507 this possibility, the  $H_2SO_4 - 0.1 \text{ pCO}_2$  experiment was carried out. The results indicate that carbonates 508 formed in the levels #2 and #3 and not in the level #1 (Figure 4). In contrast during the water - 0.1  $pCO_2$ 509 experiment, carbonates were formed in all three levels. These results are supported by geochemical

510 simulations. Xu et al. (2007) have shown that the quantities of carbonates formed are the same, 511 independently of any presence of  $SO_2$ , but the carbonate precipitation is found deeper in the profiles with 512 the addition of sulfur fluid alteration. The numerically simulated martian weathering profiles (Zolotov and 513 Mironenko, 2016) show that H<sub>2</sub>SO<sub>4</sub>-solution with a low-pCO<sub>2</sub> dissolved led to carbonates in the middle part 514 of weathering profiles when the pH solution rises up neutral values. Lastly, even if a sulfuric-rich solution 515 mixed with CO<sub>2</sub> has ever existed on early Mars, the acidic consumption due to the parent rock dissolution 516 along the hundreds of meters depth of the weathering profiles (i.e. such as Mawrth Vallis, Carter et al. 517 (2015)) would have led to carbonation. Hence, the detections of carbonates in the middle section of the 518 weathering profiles (Bultel et al., 2019) are in agreement with the above results.

519 A confident identification of carbonates is difficult when they are mixed with clay minerals and/or 520 present in small amounts (this study, Sutter et al., 2007). Figure 10 displays examples of NIR spectra of 521 hydrothermal carbonates detected on the Martian surface (Viviano et al. 2014), in the martian weathering 522 profiles (Bultel et al., 2019) and our spectrum of experimentally produced carbonate mixed with clay 523 minerals obtained during in the level #1 of the water -  $0.1 \text{ pCO}_2$  experiment (Figure 10.c). The qualitative 524 carbonate identification on Mars with the Compact Reconnaissance Imaging Spectrometer for Mars 525 (CRISM) in the NIR range is based on the combination band near 2.30, 2.50, 3.50 and 3.85 µm (Figure 10) (i.e. Bultel et al., (2019)). No 2.3 and 2.5 µm adsorption band of carbonate are present in our experimental 526 527 spectra nor in the spectra of the observed weathering profiles on Mars. In the CRISM NIR range, without 528 the 3.95 µm band and the carbonate XRD peaks for the experiments, it would be impossible to attribute the 529 weak 3.85 µm bands to carbonates. Hence, the detection of carbonates in the martian weathering profiles is 530 challenging. Nevertheless, as discussed in the section 4.2.1, the content of carbonate should increase by 531 15% if the experiments would have been carried out at lower temperature (i.e.  $<50^{\circ}$ C). In such conditions, 532 the detections of carbonates from orbit could perhaps be possible as shown by Bultel et al., (2019). Indeed, 533 on Mars, the only place where carbonates have been detecting by both orbital instrument and in-situ analysis 534 is at Gusev crater (Morris et al., 2010; Carter and Poulet, 2012). The origin of carbonates is hydrothermal, and the carbonate content measured *in-situ* was between 16-34 weight % (Morris et al., 2010). Such content of carbonate allows their detection from the orbit. As shown here, more carbonates could be detected on the martian surface but it would be challenging due to the potential low carbonate proportions, the mixture of carbonates with clay minerals, the low spatial resolution of the orbital instruments, and the low signal to noise ratio at  $> 3.5 \mu m$  wavelengths (Murchie et al, 2007).

540 Our study is a first attempt to reproduce the entire stratigraphy by experimental work. The present 541 results cannot explain all observations made in the weathering profiles. Several more parameters can be 542 tested to better decipher the martian environment when the weathering profiles formed. The temperature 543 effect on the mineral formation has to be more documented experimentally. Also, the present study does not 544 explain the local presence of sulfates at Marwth Vallis, which would require additional information of 545 whether they formed simultaneously or subsequently. Testing more various mixtures between  $H_2SO_4$  acid 546 and  $CO_2$  gas will adds constraints to the formation competition between sulfates, carbonates and clay 547 minerals. This would help to determine if it is possible to form sulfates during the weathering profile 548 formation or rather subsequently during the Hesperian when Mars has become a sulfuric rich environment. 549 Finally, such investigations would provide more information on the chemical composition of acidic fluids 550 and hence would better determine the atmospheric composition during the weathering profile formation.

551

#### 5. Conclusion and remarks

552 In the present study, an open column experimental system is used to mimic martian weathering of 553 the Noachian. We tested different input solution in equilibrium with various pCO<sub>2</sub> (water - 1 pCO<sub>2</sub>, water -554 0.1 pCO<sub>2</sub>, HCl - 0 pCO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> - 0 pCO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> - 0.1 pCO<sub>2</sub>) to investigate the composition of early 555 martian atmosphere. The results obtained show that the output pH values decrease with the increase of  $pCO_2$ 556 leading to an enhanced dioctahedral clay mineral formation when CO<sub>2</sub> is present. In addition, the Al-rich to 557  $(Al,Fe)^{3+}$ -rich clay mineral zone observed in the martian weathering profiles are better reproduce during the 558 water - 1 pCO<sub>2</sub> experiment. Comparing the experimentally produced and remotely observed clay mineral 559 sequences, the top part of the weathering profiles is better reproduced by acidic solution under a dense  $CO_2$  560 atmosphere. With such CO<sub>2</sub>-rich fluids, carbonates form. Despite previous studies explaining the absence 561 of carbonates by the role of acidic fluids, we suggest that carbonates should be present in the weathering 562 sequences even if additional acidic solutions were present. It could explain the recent detections of 563 carbonates in the middle part of the weathering profiles. We propose that the identification of carbonates 564 using the NIR CRISM instrument is challenged by their low abundance, the presence of clay minerals and 565 the orbital instruments limitations, such as the wavelength range and the spatial/spectral resolutions. Finally, 566 we suggest that the predominance of dioctahedral-rich clay minerals and their evolution in the top horizons, 567 are in better agreement with an acidic weathering under a dense CO<sub>2</sub> atmosphere. In such conditions, 568 carbonates are formed in the middle part of the weathering profiles as observed by Bultel et al., (2019). Such 569 atmosphere is in line with the climatic studies (Wordsworth, 2016) investigating the liquid water stability 570 on the martian surface. Nevertheless, further experimental work and observation of the surface mineral 571 composition of Mars (in situ or remote sensing) are needed to better constrain the early martian environment 572 and atmosphere. The contribution of various  $pCO_2$  and  $H_2SO_4$  (or other acids, gasses) concentrations in 573 future experiments will allow for additional constraints on the boehmite, sulfate and carbonate precipitations 574 and their positions with respect to the clay mineralogy of the weathering sequence. The influence of 575 temperature has to be evaluated to highlight the evolution of the mineralogical assemblages. Finally, 576 mineralogical association and formation competition (Viennet et al., 2017 and this study) are a promising 577 proxy to decipher the early martian fluid compositions and consequently the early atmospheric compositions 578 and conditions as well.

# Figure captions

Figure 1: Schema of the open-column system used for performing the experiments. The input fluid is in equilibrium with the gas reservoir. Then this solution is injected into the titanium cylinder using a high pressure liquid chromatography (HPLC) pump. The fluid passes through the three shelves containing basaltic powder. Finally the output solution passes through a backpressure regulator (BPR) and is collected in a container. The pressure inside the system is controlled by the BPR and measured a pressure gauge. To decrease the time of reaction, the temperature was set at 150°C and the fluid was kept liquid by setting the pressure to 5 bars.

Figure 2: (a-e) the solid lines with symbols correspond to the measured pH at 25°C of the output solution as a function of time. The solid lines correspond to the initial pH at 25°C. The symbols correspond to the consumption of H<sup>+</sup> in mol.L<sup>-1</sup> as a function of time:  $[H^+]_{consumption} = [H^+]_{initial} - [H^+]_{final}$ . (f-j) The solid lines correspond to the initial pH calculated at 150°C. The pH values at 150°C are calculated from the chemical concentrations of the major chemical elements and the pH measurements of the output solution (filled symbols on the right).

**Figure 3:** (a-e) total quantities of elements released in mol in the output solutions as a function of time. The quantities of Al and Fe are considered negligible because their concentrations are two orders of magnitude lower than Si and are not shown. (f) Mg/Si, (g) Ca/Si, (h) Na/Si and (i) K/Si ratios of the elements measured in the output solutions as a function of time. The black solid line corresponds to the ratios of the unreacted samples (Table 1).

599 **Figure 4:** Bulk XRD patterns and NIR spectra of the unreacted basalt. The XRD measurement 600 shows that the main content is a basaltic glass with olivine, pyroxene (forsterite and augite, respectively, 601 see EDS measurements Figure S1) and quartz. The NIR measurement highlights the presence of forsterite 602 and augite. Figure 5: Comparison of the bulk XRD patterns of the reacted basaltic glass as a function of the
level # and the experimental conditions.

Figure 6: Comparison of the NIR spectra of the reacted basaltic glass as a function of the level #
and the experimental conditions.

**Figure 7:** Comparison of the NIR spectra with continuum removed for the range between 2.1 and 2.5  $\mu$ m as a function of the level # and experimental conditions. The adsorption bands related to the Al<sub>2</sub>and (Al,Fe)<sub>2</sub>-OH bonds (at 2.19 and 2.25  $\mu$ m) decrease with the pCO<sub>2</sub> and the increase of level # in favor of the (Fe,Mg)<sub>3</sub>-OH bonds (at 2.31 and 2.35  $\mu$ m).

611 Figure 8: Evolution of the octahedral composition of the clay minerals formed as a function of the 612  $pCO_2$  and level #. **a.** Evolution of the di-/trioctahedral character of the clay minerals formed as a function 613 of pCO<sub>2</sub> and acid used.  $(Al_2 + (Al,Fe)_2/(Fe,Mg)_2)$  absorption band depths correspond to the ratio of the 614 absorption band related to dioctahedral clay minerals (sum of the 2.20 and 2.25 µm absorption bands depths) 615 and trioctahedral clay minerals (sum of the 2.31 and 2.35 µm bands depths). The results show that with the 616 increase of pCO<sub>2</sub>, the clay minerals formed are more dioctahedral. **b.** Evolution of the Al<sub>2</sub> and (Al,Fe)<sub>2</sub> 617 character of the clay minerals formed as a function of pCO<sub>2</sub> and acid used. The Al<sub>2</sub> /(Al<sub>2</sub> + (Al,Fe)<sub>2</sub>) 618 corresponds to the absorption band depth of the Al<sub>2</sub>-OH band at 2.20 µm. (Al,Fe)<sub>3</sub> corresponds to the 619 absorption band depth of the (Al,Fe)<sub>2</sub>-OH band at 2.31 µm. A transition from Al<sub>2</sub> rich to Al,Fe rich clay 620 minerals is only produced during the water -  $1 \text{ pCO}_2$  experiment. The grey bar, representing the noise level, 621 corresponds to the level at which a low adsorption due to metal-OH bonds and noise cannot be differentiate. 622 In such case, the adsorption is considered null.

Figure 9: Sketch of the mineral detection for the martian weathering profiles (a.) compared to the experimental results for each level# placed in the stratigraphy based on the di-trioctahedral ratio (see Figure 8.a). Based on this comparison, the weathering profiles are better reproduced by using a pCO<sub>2</sub> of 1. Figure 10: NIR spectra comparing carbonates detections on Mars from the orbit of hydrothermal carbonates (Viviano-Beck et al., 2014), carbonates in weathering profiles (Bultel et al., 2019) and one experimental residue (level #1 of the water  $-0.1 \text{ pCO}_2$  experiment) where the presence of carbonate have been confirmed by XRD measurements. The comparison shows the difficulty to detect carbonate in the martian weathering profiles.

Tables

#### Table 1: Total chemistry in oxides of the original basalt used in the present study.

%         48.2         14.2         10.8         9.4         1.9         0.3         11.7         1.6         1.9

Table 2: Initial experimental conditions showing the fluid and gas composition and their related

#### initial pH.

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Exporimont	Gas composition	Fluid	pH initial
Experiment	at 1 bar and 20°C	composition	(20°C)/(150°C)
water $-1 \text{ pCO}_2$	100 % CO <sub>2</sub>	Pure water	3.90 / 4.10
water $-0.1 \text{ pCO}_2$	90 % CO <sub>2</sub> / 10 % N <sub>2</sub>	Pure water	4.40 / 4.60
$H_2SO_4 - 0 pCO_2$	100 % N <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub> at pH3	3.00 / 3.20
$HCl - 0 pCO_2$	100 % N <sub>2</sub>	HCl at pH3	3.00 / 3.50
$H_2SO_4 - 0.1 pCO_2$	90 % CO <sub>2</sub> / 10 % N <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub> at pH3	2.98 / 3.17

Table 3: Overview of the minerals formed as a function of the experiments conditions and level #. The symbols -, +, ++, +++ represents the relative abundance of minerals estimated from XRD and NIR measurements. \*boehmite is not reported in the table because it has been formed only for the H<sub>2</sub>SO<sub>4</sub> - 0.1  $pCO_2$  experiments in the level # 1. 

		Dissolution			Dioctahedral		Trioctahedral		Car	hon	otoc		
			%		chlor	rite/sm	ectite	sme	ectite/o	chlorite	Cal	DOII	ales
Experimente	pH final		Level			Level			Lev	el	]	Leve	el
Experiments	(20°C/150°C)	#1	#2	#3	#1	#2	#3	#1	#2	#3	#1	#2	#3
water – 1 pCO <sub>2</sub>	6.35 / 6.07	75	60	45	+++	+++	++	+	+	++	-	-	+
water $-0.1 \text{ pCO}_2$	8.08 / 7.01	60	55	40	++	++	+	+	++	++	+	$^{++}$	$^{++}$
$H_2SO_4 - 0 pCO_2$	8.59 / 7.04	55	40	30	+	-	-	++	+++	+++	-	-	-
$HCl - 0 pCO_2$	8.53 / 7.02	55	40	30	+	-	-	++	+++	+++	-	-	-
$H_2SO_4 - 0.1 \ pCO_2^*$	8.32 / 6.88	60	50	40	++	-	-	++	+++	+++	-	+	+

#### Acknowledgments

646 This work was partly supported by the Research Council of Norway through its Centre of Excellence 647 funding scheme, project 223272. This project has received funding from the European Union's Horizon 648 2020 (H2020-COMPET-2015) Research and Innovation Program under grant agreement 687302 (PTAL). 649 This study is supported by the Research Council of Norway (235058/F20 CRATER CLOCK). The authors 650 would like to thank B. Foroughinejad (Chemistry, University of Oslo) for technical support setting up the 651 experiments, F Poulet and L. Riu (IAS-University Paris-Sud) for access and help during the NIR 652 measurements, and H. Hellevang and H. Dypvik (Geosciences, University of Oslo) for providing the sample. 653 We would like to greatly thank the Plateau Technique de Microscopie Electronique (Museum National 654 d'Histoire Naturelle, Paris) for the SEM pictures and the EDS analyses. A special thanks goes to S. Pont for 655 performing the SEM and EDS analysis. The authors wish to acknowledge the editor in chief Dr. Michael E. 656 Böttcher and the three anonymous reviewers for their constructive comments that greatly improved the 657 quality of this work.

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# 880 **Experimental reproduction of the martian weathering profiles argues** 881 for a dense Noachian CO<sub>2</sub> atmosphere 882 883 884 Jean-Christophe Viennet<sup>a</sup>\*, Benjamin Bultel<sup>a</sup>, Stephanie C. Werner<sup>a</sup> 885 <sup>a</sup> Centre for Earth Evolution and Dynamics, Department for Geosciences, University of Oslo, 886 Postboks 1028 Blindern, 0316 Oslo, Norway 887 \* Now at Muséum National d'Histoire Naturelle, Institut de Minéralogie, Physique des Matériaux 888 et Cosmochimie, CNRS UMR 7590, Sorbonne Université, CNRS, F-75005 Paris, France.\* Author to whom 889 correspondence should be addressed: 890 Jean-Christophe Viennet 891 Email address: jean.christophe.viennet25@gmail.com

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**Table S1:** Total quantities of elements released in mol in the output solutions as a function of time and of

the experiments.

Water - 1 pCO2											
Т (Н)	Si (mol)	Al (mol)	Fe (mol)	Na (mol)	K (mol)	Mg (mol)	Ca (mol)				
69	1.59E-03	2.58E-06	0.00E+00	1.50E-04	3.00E-05	1.94E-04	2.00E-04				
122	2.70E-03	5.96E-06	0.00E+00	2.43E-04	4.23E-05	3.34E-04	3.77E-04				
166	3.53E-03	9.99E-06	0.00E+00	3.18E-04	5.00E-05	4.08E-04	6.12E-04				
214	4.50E-03	1.51E-05	0.00E+00	3.95E-04	6.80E-05	4.87E-04	8.71E-04				
262	5.53E-03	2.01E-05	0.00E+00	4.74E-04	7.81E-05	5.66E-04	1.13E-03				
310	6.59E-03	2.52E-05	0.00E+00	5.43E-04	9.52E-05	6.61E-04	1.40E-03				
358	7.81E-03	2.98E-05	0.00E+00	6.09E-04	1.06E-04	7.78E-04	1.60E-03				
431	9.59E-03	3.46E-05	5.38E-08	7.02E-04	1.36E-04	9.57E-04	2.03E-03				

	Water - 0.1 pCO2											
T (H)	Si (mol)	Al (mol)	Fe (mol)	Na (mol)	K (mol)	Mg (mol)	Ca (mol)					
42	4.95E-04	2.57E-06	0.00E+00	8.48E-05	2.54E-05	0.00E+00	6.35E-05					
90	1.17E-03	7.04E-06	0.00E+00	1.57E-04	5.30E-05	0.00E+00	1.48E-04					
137	1.79E-03	1.20E-05	0.00E+00	2.17E-04	7.32E-05	0.00E+00	2.32E-04					
210	2.73E-03	2.05E-05	0.00E+00	3.09E-04	9.57E-05	0.00E+00	3.67E-04					
260	3.34E-03	2.66E-05	0.00E+00	3.66E-04	1.06E-04	0.00E+00	4.59E-04					
431	5.51E-03	4.20E-05	0.00E+00	5.74E-04	2.15E-04	0.00E+00	7.67E-04					

H2SO4 - 0 pCO2										
Т (Н)	Si (mol)	Al (mol)	Fe (mol)	Na (mol)	K (mol)	Mg (mol)	Ca (mol)			
53	6.10E-04	3.31E-07	0.00E+00	7.03E-05	1.35E-04	0.00E+00	1.61E-04			
118	1.30E-03	7.55E-06	1.79E-08	1.47E-04	2.19E-04	0.00E+00	3.62E-04			
189	2.00E-03	1.55E-05	1.79E-08	2.25E-04	2.40E-04	0.00E+00	5.71E-04			
238	2.46E-03	1.78E-05	1.79E-08	2.75E-04	2.57E-04	0.00E+00	7.13E-04			
286	2.92E-03	2.34E-05	2.53E-08	3.24E-04	2.71E-04	0.00E+00	8.57E-04			
315	3.20E-03	2.62E-05	5.77E-08	3.52E-04	2.81E-04	0.00E+00	9.41E-04			
360	3.60E-03	3.14E-05	6.29E-08	3.93E-04	3.01E-04	0.00E+00	1.07E-03			
406	4.01E-03	3.68E-05	6.29E-08	4.38E-04	3.15E-04	0.00E+00	1.20E-03			
431	4.14E-03	3.93E-05	6.29E-08	4.53E-04	3.68E-04	0.00E+00	1.26E-03			

HCl - 0 pCO2											
Т (Н)	Si (mol)	Al (mol)	Fe (mol)	Na (mol)	K (mol)	Mg (mol)	Ca (mol)				
46	3.71E-04	8.00E-07	2.19E-08	6.62E-05	5.90E-05	0.00E+00	1.10E-04				
90	7.08E-04	1.58E-06	4.54E-08	1.08E-04	8.17E-05	0.00E+00	2.10E-04				
162	1.26E-03	2.45E-06	6.32E-08	1.74E-04	1.53E-04	0.00E+00	3.77E-04				
210	1.57E-03	3.00E-06	7.44E-08	2.08E-04	2.24E-04	0.00E+00	4.65E-04				
258	1.91E-03	3.61E-06	9.44E-08	2.47E-04	2.61E-04	0.00E+00	5.59E-04				
286	2.10E-03	4.97E-06	9.44E-08	2.69E-04	2.78E-04	0.00E+00	6.17E-04				
334	2.45E-03	5.56E-06	9.44E-08	3.07E-04	2.99E-04	0.00E+00	7.21E-04				
379	2.79E-03	6.21E-06	9.44E-08	3.39E-04	3.24E-04	0.00E+00	8.42E-04				
430	3.11E-03	6.85E-06	2.96E-07	3.76E-04	3.64E-04	0.00E+00	9.36E-04				

H2SO4 - 0.1 pCO2												
T (H)	Si (mol)	Al (mol)	Fe (mol)	Na (mol)	K (mol)	Mg (mol)	Ca (mol)					
27	4.23E-04	3.32E-06	3.47E-09	5.69E-05	3.23E-05	0.00E+00	7.78E-05					
121	1.69E-03	1.47E-05	3.47E-09	1.92E-04	7.65E-05	0.00E+00	3.17E-04					
200	2.86E-03	2.49E-05	3.47E-09	2.84E-04	1.66E-04	0.00E+00	5.26E-04					
300	4.30E-03	4.02E-05	3.47E-09	3.99E-04	1.93E-04	0.00E+00	7.92E-04					
350	5.02E-03	4.43E-05	1.47E-08	4.48E-04	2.09E-04	0.00E+00	9.28E-04					
431	6.25E-03	4.66E-05	3.23E-08	5.26E-04	2.36E-04	0.00E+00	1.14E-03					

- **Figure S1:** SEM and EDS analysis of the original basalt. a. SEM image illustrating the basaltic glass,
- 915 forsterite and inclusion of chromite. b. SEM image showing augite. c. qualitative EDS spectra of the
- 916 minerals illustrated in a. and b.





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- 931 **Figure S2:** XRD patterns devoted to the 060 peak position of the unreacted and the reacted samples: a.
- 932 pristine material, b. H2SO4 0.1 pCO2, c. H2SO4 0 pCO2, d. HCl 0 pCO2, e. water -0.1 pCO2 and
- 933 f. water -1-pCO2. The peak positions are labelled in Å.





#### Supplementary results: clay minerals identification

# The Figures S3, S4, S5, S6 and S7 present the XRD patterns obtained on oriented preparation devoted to the clay mineral analysis. As noticed in the bulk analysis, with the pCO<sub>2</sub> increase and the level # 940 decrease, the contribution of the mixed-layer-mineral (MLM) at 7.22 Å in the Ca-AD state increases in 941 disfavor of the MLM content at around 14-15 Å in the Ca-AD state. Similar XRD behavior as a function of 942 the treatment can be observed with the different experiments or level #. Hence for simplification, the clay 943 mineral identification will be described in detail by using the experiment where the contribution of the 944 corresponding XRD peak is the most intense.

The identification of the MLM corresponding to the XRD peak at 7.22 Å in the Ca-AD state is 945 performed for the water – 1 pCO<sub>2</sub> experiment (Figure S3). The XRD peak at 7.22 Å in the Ca-AD state shift 946 slightly to 7.4 Å in the Ca-EG state, which is an indication of the presence of smectite layers. A slight shift 947 948 towards higher angles between Ca-AD and K-AD state confirm their presence. Between K-AD, K-110, K-949 330 treatments, no differences can be observed. This is an indication that no Al-hydroxy interlayer layers 950 are present even during the acidic conditions (Viennet et al., 2015). This XRD peak disappears after K-550 951 treatment. This XRD behavior could be the indication of kaolinite layers or of the 002 reflection of Fe-rich 952 chlorite layers (Viennet et al., 2017). The NIR spectra figures 5 and 6 of the main manuscript do not show 953 the presence of kaolinite layers with their characteristic bands at 2.16 and 2.2 µm. Hence, this MLM is a R0 954 MLM Fe-rich chlorite/smectite with a low amount of smectite layers. Between the Ca-AD and Ca-EG 955 treatments, the XRD peaks shift between the experiments and the level #, which indicate that the smectite 956 layer content is similar in the R0 Fe-rich chlorite/smectite MLM.

The nature of the MLM corresponding to the XRD peaks at around 14-15 Å in the Ca-AD state is identified for the  $HCI - 0 pCO_2$  experiment (Figure S5). The XRD peak at 14.20 Å shift to 16.30 Å between the Ca-AD and Ca-EG treatments and the apparition of the 002 reflections at 7.52 Å show the presence of smectite layers. Between the Ca-AD, K-AD to K-550 treatments, the XRD peaks shift towards 10.62 Å. This behavior is attributed to the dehydration of water molecules in the interlayer space of the smectite

layers with the temperature increase. The position and broad XRD peak after K-550 indicate that not only 962 963 smectite layers compose such MLM but also chlorite layers to account for both the higher position than a pure smectite at ~10 Å and for mixed layering between ~10 Å and 14.2 Å layers, which broaden the XRD 964 peak. Hence this MLM is a smectite-rich R0 MLM smectite/chlorite. Similar XRD behavior tendencies are 965 966 noticeable for this MLM as a function of the experiments and the level # (Figures S2, S3, S4, S5 and S6). Nevertheless, noticeable differences can be observed on the peak intensities, width and shift between Ca-967 968 AD and Ca-EG treatments depending of the experiments considering. These differences can be related to 969 the decrease of proportion and the lower coherent scattering domain size of such MLM with the  $pCO_2$ 970 increase and the level # decrease. Hence, in the water  $-1 \text{ pCO}_2$  experiments, the shift between the XRD 971 patterns at ~14.40 Å of the Ca-ED and Ca-EG states and between the Ca-AD and K-AD states indicates the 972 presence of the R0 MLM smectite/chlorite; The low intensities and the large XRD peak show that this mineral low coherent scattering domain size. The XRD peaks at 7.22 Å in the Ca-AD state and 7.52 Å in 973 974 the Ca-Eg state of the 0 pCO<sub>2</sub> experiments, show the presence of the R0 MLM Fe-rich chlorite/smectite.

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**Figure S3:** XRD patterns recorded on oriented preparations devoted to the clay minerals identification as 978 a function of the level # for the water  $-1 \text{ pCO}_2$  experiment.



**Figure S4:** XRD patterns recorded on oriented preparations devoted to the clay minerals identification as 981 a function of the level # for the water  $-0.1 - pCO_2$  experiment.







**Figure S6:** XRD patterns recorded on oriented preparations devoted to the clay minerals identification as 987 a function of the level # for the H<sub>2</sub>SO<sub>4</sub> – 0 pCO<sub>2</sub> experiment.



**Figure S7:** XRD patterns recorded on oriented preparations devoted to the clay minerals identification as 990 a function of the level # for the  $H_2SO_4 - 0.1$  pCO<sub>2</sub> experiment.



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