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Near infrared signature of opaline silica at Mars-relevant pressure and temperature

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Abstract

Opal is a mineral of great interest for tracing the aqueous Mars' history. Detection of opal on Mars is based on the near infrared (NIR) absorption bands related to the presence of water and hydroxyl. Because pressure and temperature can affect the amount and configuration of water in hydrated minerals, the associated absorption bands can be sensitive and vary according to the environmental conditions at the surface of Mars. In this study, the effects of Mars' relevant surface pressure and temperature on opal's NIR signature was investigated. By exposing opal samples to pressures varying between 1 and 8 mbar, and temperatures between -51.1 and -96.5°C, significant changes in opal samples' NIR features were observed. It was demonstrated that opal releases molecular water at low pressure, inducing changes on all NIR bands, as also observed in previous studies. However, such dehydration was not systematic, as it was noticed for only six out thirteen opal samples. When exposed to low temperature, water molecules in opal froze, inducing significant variation in shape and position of the bands at 5200 cm⁻¹ and 7000 cm⁻¹ (1.9 μm and 1.4 μm respectively). Low temperature experiments demonstrate that opal, and particularly opal-CT, can exhibit a water ice-like spectral signature. Such experimental data were compared with silica signature detected on Mars by CRISM and it was evident that martian opaline silica has a spectral signature specific of water ice, notably a shoulder near 5100 cm⁻¹ (1.96 μm) and a wider 7000 cm⁻¹ (1.4 μm) feature. We

show that opal can retain water under martian conditions, and that ancient water can be trapped following its precipitation.

Keywords: Opal, water, CRISM, low pressure, low temperature, ice

1 **1. Introduction**

2 Tracing the presence of liquid water, and its association with potential habitable environments
3 during Mars' history, is an outstanding science goal and a major driver for Mars exploration.
4 There is now clear evidence of the past presence of liquid water at the surface of Mars, based
5 on geomorphological (e.g. Fassett and Head, 2008; Hauber et al., 2013) and mineralogical
6 (e.g. Bibring et al., 2005; Carter et al., 2013a; Mustard et al., 2008) studies. The interaction of
7 rocks with liquid water triggers the hydrolysis of anhydrous minerals, releasing silica in the
8 altering fluids, and subsequently the precipitation of a variety of secondary hydrated minerals.
9 Among all hydrated phases identified so far, hydrated silica has been detected through both
10 orbit- and rover-based instruments (Milliken et al., 2008; Squyres et al., 2008) at many places
11 across the planet (e.g. Carter et al., 2013a; Pan et al., 2021; Pineau et al., 2020; Sun and
12 Milliken, 2018). This phase represents a promising target for astrobiological purposes, as
13 opaline silica hosts the most ancient biological signatures on Earth (Djokic et al., 2017). In
14 this respect, if well-preserved hydrothermal deposits were identified on Mars, they would be
15 high priority targets for investigating evidence of past life (Des Marais and Walter, 2019;
16 Teece et al., 2020). Importantly, the recent finding of a nymphal fossil, along with well-
17 preserved organic material, in an opaline silica formed through recent continental weathering,
18 has revealed that silica formed in weathering context may constitute a new source of ancient
19 life fossils (Chauviré et al., 2020; Pan et al., 2021; Pineau et al., 2020).

20 The exact formation pathway of these opaline silica occurrences remains interpretative;
21 however, it appears in a wide range of geological contexts, from sedimentary environments to
22 hydrothermal systems. For instance, rovers surveying Mars surface have detected the presence
23 of opaline silica; at Gusev crater, the rover Spirit (Mars Exploration Rover-A) reported silica-
24 rich soils, interpreted as an evidence of hydrothermal activity, either formed by acid leaching
25 or by direct precipitation (Ruff et al., 2020, 2011; Ruff and Farmer, 2016; Squyres et al.,

26 2008). Moreover, the *Curiosity* rover (Mars Science Laboratory, MSL) found silica-rich
27 materials, identified as tridymite in a laminated mudstone (Morris et al., 2016), as well as
28 diagenetic amorphous to crystalline silica in the Gale crater's stratigraphic sequence
29 (Czarnecki et al., 2020; Frydenvang et al., 2017; Rampe et al., 2017; Rapin et al., 2018).
30 Hydrated silica is also present on the landing site chosen for both the NASA rover
31 *Perseverance* (Mars 2020 in Jezero crater; Pan et al., 2021; Tarnas et al., 2019) and the ESA
32 rover *Rosalind Franklin* (ExoMars2022 in Oxia Planum ; Carter et al., 2012; Pan et al., 2021,
33 2019).

34 The ongoing or future rovers could provide sufficient information to distinguish the exact
35 silica phases. Importantly, among opaline silica, which refers to a large family of silica
36 phases, opal ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) represents the natural hydrated non-crystalline to poorly crystalline
37 silica phases. Two main types of opal are usually differentiated: (1) opal-A, consisting of
38 amorphous silica; and (2) opal-CT composed by tridymite nano-domains with variable
39 proportion of non-crystalline domains. Opal-CT can be interpreted as a solid solution
40 depending on the proportion of various domains (Elzea and Rice, 1996; Fröhlich, 2020; Jones
41 and Segnit, 1971; Wilson, 2014). Opal types can easily be determined by either XRD or
42 Raman spectroscopy (Curtis et al., 2019; Fritsch et al., 2012; Ostrooumov et al., 1999).

43 All opal varieties may contain water species (molecular water and OH groups; up to 15 %
44 weight), entailing strong absorptions bands in the near infrared (NIR) region (Boboň et al.,
45 2011; Chauviré et al., 2017; Langer and Flörke, 1974; Rice et al., 2013). In the 4500 cm^{-1} (2.2
46 μm) region, the combination of OH stretching and siloxane bending indicates the presence of
47 silanols groups. By contrast, the combination of OH and H_2O modes in molecular water
48 absorbs in the 5200 cm^{-1} ($1.9 \mu\text{m}$) region. Both bands are characterized by two main
49 overlapping absorptions [at 4500 cm^{-1} ($2.21 \mu\text{m}$) and 4420 cm^{-1} ($2.26 \mu\text{m}$); 5250 cm^{-1} (1.91
50 μm) and 5100 cm^{-1} ($1.96 \mu\text{m}$)], with the higher energy component attributed to less H-bonded
51 silanols or molecular water (Langer and Flörke, 1974). Similarly, the 7000 cm^{-1} ($1.4 \mu\text{m}$)

52 region exhibits two main components, due to a combination of OH stretching and bending in
53 water molecules near 6850 cm^{-1} ($1.46\text{ }\mu\text{m}$) and OH stretching overtones near 7100 cm^{-1} (1.41
54 μm). In commercial silica gel, Christy (2010) identified the presence of isolated silanols by
55 the band at 4579 cm^{-1} and 7316 cm^{-1} ($2.18\text{ }\mu\text{m}$ and $1.37\text{ }\mu\text{m}$), never seen in natural opal except
56 after heating or low-pressure exposure (Boboň et al., 2011; Milliken et al., 2008; Rice et al.,
57 2013).

58 Infrared signatures are the main criteria used to identify opaline silica by orbital instruments
59 (e.g. Compact Reconnaissance Imaging Spectrometer for Mars – CRISM ; Milliken et al.,
60 2008; Pineau et al., 2020; Sun and Milliken, 2018; Weitz et al., 2010). Previous studies had
61 shown that these features may vary depending on the analytical conditions, specifically in
62 terms of atmospheric pressure and temperature (Milliken et al., 2008; Sun, 2017; Sun and
63 Milliken, 2018; Swayze et al., 2007; Thomas et al., 2020). Consequently, the use of laboratory
64 opal spectra acquired in ambient terrestrial conditions for detection on Mars' surface should
65 be made cautiously.

66 The effect of Mars-relevant pressure and temperature on opaline silica has been investigated
67 by few studies (Poitras et al., 2018; Rice et al., 2013; Sun 2017; Sun and Milliken, 2018). At
68 Mars' relevant temperatures, the silica phase containing water molecules should exhibit
69 infrared features typical of ice, as observed in low temperature experiments (Poitras et al.,
70 2018; Rice et al., 2013; Sun and Milliken, 2018; Thomas et al., 2020). In natural opal, the
71 water freezing point is depressed (from -5°C to -47°C) due to the surficial interaction
72 (Chauviré and Thomas, 2020; Thomas et al., 2020, 2013); this is a phase transition that occurs
73 within the range of temperatures prevailing on Mars (Smith et al., 2017). The effect of Mars-
74 like pressure was demonstrated to cause significant change in the opal's NIR strongest
75 absorption bands, thus showing that molecular water is pumped out from the pores; on the
76 other hand, effects of low temperature remain scarcely investigated.

77 In this study, we investigate the effect of typical martian pressures and temperatures on the
78 NIR signature of a series of natural opal samples, and provide spectral proxies to facilitate
79 their detection through infrared remote sensing. Transmission infrared spectra were collected
80 on opaline silica chips, providing insights into compositional changes in bulk samples. We
81 report on the water speciation and its evolution according to pressure and temperature
82 conditions, and the associated spectral evolution in the near-infrared spectral range. The
83 effects of different conditions are estimated in term of positions (apparent maximum, thus the
84 local maximum independently of the position of the constitutive component) and ratio
85 between components, i.e., parameters that can be easily compared with reflectance spectra.
86 The application of these new spectral tracers to Mars NIR observations suggest that water is
87 mostly present as water ice in opaline silica.

88 **2. Materials and Methods**

89 *2.1. Opal Samples*

90 For this study, we selected 17 samples among the 38 samples studied in Chauviré et al.
91 (2017), based on the remaining materials from previous studies (Table A 1 in Appendix).
92 Samples were sliced in thin sections, 150 to 350 μm thick, and polished on both sides for
93 transmission acquisition. Among the 17 samples, 4 were opal-A and 13 were opal-CT. The
94 type of opal (opal-CT and opal-A) was deduced from Raman spectroscopy, since it has been
95 previously used to reliably classify opal and extensively used for this purpose. Raman
96 spectroscopy is a non-destructive (no grinding required), a significant advantage in our study
97 that focus on bulk samples (opal chips). Opal-A has a low-frequency T-O-T region-
98 vibrational modes associated to bridging tetrahedron-oxygen-tetrahedron Si-O-Si- with a
99 maximum near 430 cm^{-1} , whereas opal-CT has a maximum between $330\text{-}370\text{ cm}^{-1}$ (e.g.
100 Ostrooumov et al., 1999). Homogeneity of each pieces used has been checked by measuring
101 Raman spectra on a minimum of five points ($300\text{ }\mu\text{m}$ radius), and pieces that show variations

102 in their structure have been discarded. Some opals are yellow to red (Table A 1), showing
103 that they contain iron oxides and hydroxides as inclusions (Fritsch et al., 2002), however
104 Raman and infrared spectra did not show any features characteristic of these components in
105 our samples. Eight samples were analysed both at low pressure and low temperature (but
106 independently), while other five samples were only exposed to low pressure, and four were
107 exclusively used for low temperature experiments. To prevent potential irreversible changes,
108 each piece has been used only for one type of experiment. Table 2 presents each sample and
109 the respective exposure conditions.

110 2.2. *Infrared spectra acquisition*

111 Most of the near-infrared spectra were acquired using a Bruker Vertex 70 spectrometer
112 coupled with a Bruker Hyperion 3000 microscope using a halogen lamp as source, an InGaAs
113 detector and a CaF₂ beam splitter. Samples were placed in a cell (designed at the Institut de
114 Planétologie et d'Astrophysique de Grenoble) with sapphire windows enabling transmission
115 spectra, where the temperature and the pressure were lowered using, respectively, an internal
116 circuit for liquid nitrogen and an air pump (HiCube, Pfeiffer). The sample was placed on a
117 sapphire window enclosed in a core metallic piece acting as thermal exchanger either for
118 cooling (by circulating liquid nitrogen) or heating (by two heating resistances). Schema of the
119 experimental apparatus is available in Figure A 1 .

120 During low-pressure experiments, pressure was stabilized to between 7.2 to 10 millibars. The
121 low pressure was maintained for a minimum period of one hour (for samples with no reaction
122 visible in the spectra) or until a variation lower than 1% per minute between the acquired
123 spectra and the previous one is observed in the OH and H₂O related absorptions (up to 21
124 hours).

125 Low-pressure experiments for samples 785, 1039, 1085, 1543d, 1552a, WT86 were
126 performed using a Bruker Vertex 70V, which enables to have a vacuum in the sample

127 chamber of about 1 mbar, and to keep all the optical paths under the same condition. A
128 detector InGaAs, with a CaF₂ beam splitter, and a tungsten halogen source equip this
129 spectrometer.

130 Low-temperature experiments were all performed at ambient pressure; the gas in the cell was
131 replaced by dry nitrogen, flushed during few minutes before maintaining ambient pressure.
132 The sample was isolated from the external metal which was heated to 45 °C (318K) to avoid
133 condensation, which was checked periodically by acquiring a “blank” spectrum (i.e. without
134 the sample). The temperature was measured by a thermocouple PT100 inserted in the core
135 metallic piece, close to the sapphire windows holding the sample (Figure A 1). The
136 temperature was lowered to a range between -88°C to -95°C (185K to 178K; temperature
137 given by the cell sensor). The exact temperature of the sample was estimated using the ice
138 NIR features and its dependency with temperature, considering the effect of porosity
139 depressing the water freezing point (more details are available in Appendix 1). Table 2
140 presents the temperature measured for the presented spectra, as well as temperature of the
141 sample estimated through the aforementioned approach.

142 Each spectrum was an accumulation of 100 scans with a spectral resolution of 4 cm⁻¹ and a
143 beam size of 300x300 μm. Infrared spectra were acquired from 4000 to 10 000 cm⁻¹, but the
144 focus was on the 4000 to 8000 cm⁻¹ (2.5 μm to 1.25 μm) near-infrared spectral range, due to
145 an important spectral artefact around 8300 cm⁻¹.

146 2.3. *Laboratory Data Processing*

147 The spectra's baselines were corrected using five anchor points located at the minimum
148 absorptions near the 4200, 4700, 5400, 5700 and 7400 cm⁻¹ wavelengths. For each anchor
149 point, a Virtual Basic for Applications (VBA) program was developed to find the position of
150 the local minimum in a 100 cm⁻¹ region surrounding the anchor points defined above. Once

151 the minimum was found, a linear function was calculated between each anchor point. The
152 functions were calculated and subtracted from the spectrum as shown in Appendix (
153 Figure A 3). Both corrected and raw data are available in the open access SSHADE database
154 (<https://www.sshade.eu/> :
155 https://doi.org/10.26302/SSHADE/EXPERIMENT_LB_20200201_001).

156 2.4. *Processing of CRISM hyperspectral images*

157 The Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) on-board Mars
158 Reconnaissance Orbiter (MRO) is a hyperspectral imaging spectrometer. It operates in the
159 visible to NIR range from 0.36 μm to 3.92 μm through 544 channels with an average spectral
160 resolution of about 6.55 nm (Murchie et al., 2007). CRISM data were derived from the TRR3
161 calibration (Seelos et al., 2011), and converted into surface reflectance signal by processing
162 photometric and atmospheric gas absorptions using the empirical volcano-scan method
163 (McGuire et al., 2009), as commonly used in previous work (e.g. Sun and Milliken, 2018).
164 Opaline silica was detected on Mars by adapting spectral parameters related to its specific
165 absorption features (e.g. the 2.2 μm absorption - Viviano-Beck et al., 2014). Extraction of the
166 spectra was then completed by using the methodology of Carter et al. (2013). Hydrated
167 signatures were highlighted by subtracting a mean neutral spectral contribution (i.e. without
168 the signature of hydrated phases) to hydrous mineral exposures over each observation. This
169 method of extraction produces flat reflectance spectra close to a value of zero for spectrally
170 neutral mineralogy. Arbitrary ratios of spectra of interest by spectra of selected neutral
171 mineralogy were therefore not included, thus avoiding a process generally completed by the
172 user. Spatial detection and localization of hydrated silica exposures were based on the spectral
173 parameter BD2.25 introduced by Carter et al. (20013), which provides evidence of specific
174 presence of hydrated silica within a CRISM scene. In a simplified way, this spectral
175 parameter consists of the averaged band depth of the absorption band 2.25 μm , using moving

176 anchor points in the ranges 2.05-2.15 and 2.35-2.40 μm . Averaged spectra of opaline silica in
177 the CRISM images were calculated by encompassing as many pixels as possible (up to
178 several tens) to increase the signal-to-noise ratio.

179 2.5. *Selection of Mars sites*

180 To compare our results with Martian signature, three sites were selected based on (i) the
181 quality of the available CRISM spectral cubes (*i.e.*, low dust content, satisfying atmospheric
182 corrections, good signal-to-noise ratio) and (ii) the occurrence of spectrally “pure” opaline
183 silica (*i.e.*, which spectra do not show any additional spectral absorption, indicating the
184 presence of other hydrated phases). These sites were: (1) The Antoniadi crater region, (2) the
185 Iani Chaos region, and (3) the Camichel crater.

186 In the Antoniadi crater region, opaline silica-rich materials formed aeolian accumulation (*i.e.*
187 dunes) of crystalline silica phase around the central peaks of the impact craters, where zeolites
188 and Fe/Mg-smectites or chlorites were detected (Ehlmann et al., 2009). It is suggested that the
189 Antoniadi crater silica represents the erosional product of silica-rich materials altered by
190 either hydrothermal activity of the crust under alkaline conditions or diagenetic processes in
191 the subsurface (Ehlmann et al., 2009; Smith and Bandfield, 2012; Pineau et al., 2020).

192 The geomorphological context of Iani Chaos hydrated silica is reminiscent of the observations
193 made for Antoniadi crater: *i.e.*, in aeolian dunes around the central peak of an impact crater.
194 Fe/Mg-smectites (or chlorites) and hydrated sulfates are also detected on the crater rims and
195 walls (Thomas et al., 2017). Iani Chaos silica-rich materials have been suggested to have been
196 formed through similar geological processes as those of the Antoniadi crater (Pineau et al.,
197 2020).

198 In the Camichel crater, hydrated silica was detected within light-toned materials in the distal
199 part of an intra-crater fan delta. These silica-rich deposits are less crystalline than the deposits
200 detected at Antoniadi crater or Iani Chaos and are interpreted as being formed in-situ during

201 delta formation or as product of continental weathering of deltaic silicic materials (Carter et
202 al., 2012; Hauber et al., 2013; Pan et al., 2021; Pineau et al., 2020).

203 **3. Results**

204 *3.1. Low pressure effects*

205 Among the thirteen opals exposed to low pressure (all spectra available in Figure 1, and the evolution of the
206 parameters of the bands are displayed in
207 Figure 2), six opals reacted. In Figure 1, a lower Signal-to-Noise Ratio (SNR) is observed near 5400 cm⁻¹ and
208 7300 cm⁻¹, due to the variations in the uniformity of the purge during pumping. An example of the evolution of
209 bands with time is shown in

210 Figure 3. Only one opal-A (86.2) slightly dehydrated, and five opal-CT reacted significantly
211 (from very strong for WT86 to weak for 1085). For reacting opals, the band area near 5200
212 cm⁻¹ decreased strongly. Among the six reacting opals, two (i.e. 86.2 and 1085) displayed a
213 weak reaction, with a decrease of the 5200 cm⁻¹ absorption bands of less than 10% of the
214 initial band area. The other four strongly reacting opals showed a decrease in this band
215 between 50% and 70% of the initial band area. In addition, it was noticed that the low-
216 frequency wing reduced more than the high-frequency component, inducing an increase of the
217 ratio between the two components (5250 cm⁻¹ /5100 cm⁻¹) from 2.4-2.9 to 3.3-4.0.

218 A strong reaction to the low pressure was associated to an increase of the band near 4500 cm⁻¹
219 (from 35% to 67%), transforming the nearly flat band into a sharper asymmetrical band with a
220 apparent maximum shifted toward 4570 cm⁻¹. However, the sample 86.2 showed a reduction
221 of the 4500 cm⁻¹ band, with no change in shape or apparent maximum. For sample 1085, this
222 band was too weak to monitor its evolution. Similarly to the band at 5200 cm⁻¹, the 7000 cm⁻¹
223 band waned, but with slighter changes in the proportion of its two components. Only the 86.2
224 sample showed a slight increase in such proportion, but this could be attributed to an
225 increased noise in the spectra.

226 Interestingly, a band at 7315 cm⁻¹, present as a small shoulder in the spectra at ambient
227 pressure, significantly increased the NIR spectra of samples VTB, YM12, WT86 and FT1111.

228 For VTB, the strengthening of such band was not sufficient to become the maximum.
229 Evolution of silica's NIR features at low pressure observed herein were consistent with
230 previous studies (Poitras et al., 2018; Rice et al., 2013; Sun, 2017; Sun and Milliken, 2018).

231 3.2. *Low temperature effects*

232 Spectra of all the 13 opals measured before and after exposure to low temperature are presented in
233 Figure 4, and the evolution of the band parameters are displayed in
234 Figure 5. All opals reacted strongly, with significant changes in the 5200 cm^{-1} and 7000 cm^{-1} bands. The 4500
235 cm^{-1} band showed no significant variations, except for those induced by the change in the 3300 cm^{-1} absorption
236 band. The 4500 cm^{-1} band is actually located on the higher wavenumber edge of the main hydration band (3300
237 cm^{-1} ; 3 μm) which shifts to lower wavenumbers with lower temperature (Cloutis et al., 2008). Opal-A and opal-
238 CT exposed to low temperature in this study had different reactions. The 5200 cm^{-1} band in the opal-A samples
239 showed no shift of the apparent maximum position, but displayed a rise of the low-frequency component,
240 leading to a decrease of the ratio of the two components (5250/5100 cm^{-1} - 1.91/1.96 μm). Simultaneously, the
241 low frequency component in the 7000 cm^{-1} regions rose, causing a shift of the apparent maximum toward lower
242 frequencies. This shift of the low frequency component increased the gap between the two components. This
243 region thus exhibits two defined bands: one band near 6650 cm^{-1} , and a second band near 7100 cm^{-1} (

244 Figure 4), with a ratio 7100/6650 cm^{-1} (1.41/1.50 μm) greater than at ambient temperature.

245 Except for sample 521, which showed a behaviour similar to opal-A, the studied opal-CT show a different
246 evolution. The 5200 cm^{-1} band substantially shifted toward lower frequency (approximately 200 cm^{-1}), with a
247 small shoulder persisting for the high-frequency component (i.e. near 5250 cm^{-1} ,

248 Figure 4). Additionally, the band became symmetrical. A similar reaction was observed in the
249 7000 cm^{-1} regions: an increase of the low-frequency component, an in turn of the ratio
250 7100/6850 cm^{-1} , and a shift of the position of the apparent maximum, with a small remaining
251 shoulder near 7100 cm^{-1} (sometimes not visible).

252 4. Discussion

253 4.1. *Low pressure effects*

254 Six samples (among thirteen) reacted at Mars simulated pressure. By contrast, previous
255 studies showed that most opals dehydrate at low pressure (Poitras et al., 2018; Rice et al.,
256 2013; Sun, 2017; Sun and Milliken, 2018). One of the explanations could be the difference in

257 the acquisition method (reflectance for previous studies, compared to transmission in this
258 study); however, the band shape and position used here to characterize the effect of pressure,
259 is not affected by the mode of acquisition (Pineau et al., 2020). Samples preparation also
260 differed from previous studies; opals are prepared as thin sections here, whereas opals were
261 grinded in other studies. The grinding increases the surface available and opens the water-
262 filled porosity, facilitating the release of water; an effect demonstrated by thermal methods
263 (Smallwood et al., 2008). It has been proposed to explain the difference of water content
264 measured between the instrument SAM (after grinding) and ChemCam (directly on
265 unprepared sample), aboard MSL rover (Rapin et al., 2018).

266 In the study of hydration state of minerals, the relative humidity (RH), referring to the ratio of
267 real water content in an atmosphere compared to the water content at saturation of the same
268 atmosphere, is a key parameter. Rice et al. (2013) and Sun (2017) have demonstrated that, at
269 high RH, opal rehydrates, and Sun (2017) demonstrated that at low RH, opal dehydrates. In
270 our experiments, we estimate the RH assuming a RH of the air-conditioned air (40%) at the
271 pressure of the experiments. In the first setup (using a Bruker Vertex 70V under a pressure of
272 approximately 1 mbar), we calculate a $RH \approx 0.04\%$, and a $RH \approx 0.32 \%$ (at 8 mbar) for the
273 second setup. According to the previous studies, the low RH in our experiments should
274 involve a dehydration. However, seven samples did not lose water.

275 The maximum duration of our experiments was 21 hours, compared to previous studies that
276 exposed samples for days or months. Our samples reacted in the first hours, but our results
277 should be considered as a lower limit for duration. It appears that our observations are
278 consistent with previous studies (Poitras et al., 2018; Rice et al., 2013; Sun, 2017; Sun and
279 Milliken, 2018), demonstrating that one day of exposure could be sufficient to observe
280 spectral variations at Mars-relevant pressure if water loss is possible through opal's porosity.

281 In the literature, opaline silica exposed to low pressure showed a shift of the 7000 cm^{-1} band
282 ($1.4 \mu\text{m}$) toward greater frequencies, a decrease of the 5200 cm^{-1} ($1.9 \mu\text{m}$) band, and an

283 increase with a shift of the band at $4500\text{ cm}^{-1}/2.2\mu\text{m}$ (Poitras et al., 2018; Rice et al., 2013;
284 Sun, 2017; Sun and Milliken, 2018). The band shapes changed through narrowing of the high-
285 frequency component, and in combination with the decrease of the low frequency component
286 on all bands, this leads to a change in the ratio between the two components (Poitras et al.,
287 2018; Rice et al., 2013; Sun and Milliken, 2018). All position shifts mainly resulted from the
288 change in the proportion of each component of the band, the weakening of a component,
289 and/or the strengthening of the other component, implying a shift of the apparent maximum.
290 Our results are consistent with previous studies. Quantitatively, the shift of the position of the
291 apparent maximum of the 7000 cm^{-1} -band in reacting opal-CT is greater than observed by Sun
292 & Milliken (2018), but consistent with Poitras et al. (2018). Our study shows that
293 distinguishing both types of opals using the band near 7000 cm^{-1} ($1.4\ \mu\text{m}$) is more challenging
294 than previously thought.

295 In Chauviré et al. (2017), it was proposed that opal-A could be distinguished from other
296 varieties using the position of the apparent maximum of the 5200 cm^{-1} (limit between 5240
297 and 5245 cm^{-1}). After exposure, the strongly reacting opal-CT has an apparent maximum
298 overlapping with the opal-A's position; hence the limit is more blurred than previously
299 defined, consistent with Pineau et al. (2020).

300 Three of our sensitive opal-CT samples (WT86, FT1111 and YM12) showed an apparent
301 maximum near 7300 cm^{-1} after dehydration, caused by the growth of the band at 7316 cm^{-1} ,
302 attributed to isolated silanols OH stretching, similar to silica gel after heating or low-pressure
303 treatment (Boboň et al., 2011; Christy, 2011, 2010; Milliken et al., 2008; Rice et al., 2013).
304 The emergence of the band near 7300 cm^{-1} is consistent with the change of shape of the band
305 at 4500 cm^{-1} , attributed to a combination of siloxane and silanol groups. The four strongly
306 reacting opals (VTB, WT86, FT1111 and YM12) showed a decreasing $4425/4510\text{ cm}^{-1}$
307 ($2.26/2.21\ \mu\text{m}$) ratio and an apparent maximum close to isolated silanols bands at 4579 cm^{-1}

308 (Christy, 2011, 2010); this is in agreement with previous studies (Poitras et al., 2018; Sun and
309 Milliken, 2018).

310 All these changes demonstrate that water was extracted from pores for almost half of the
311 analysed samples. No correlation between colour, and thus presence of iron, and reaction at
312 low pressure was observed. Similarly, both types of opal reacted, which is consistent with
313 previous observations. The discrepancies between reacting and none-reacting samples could
314 arise from their microstructure. Opal displays a variety of microstructures (Fritsch et al., 2006,
315 2002; Gaillou et al., 2008) that changes according to the formation environments and/or aging
316 (e.g. Herdianita et al., 2000). Liquid-like water in opal is trapped inside nanometres to
317 micrometres size pores (Chauviré and Thomas, 2020; Thomas et al., 2013). The proportion
318 between open and closed porosity (i.e., respectively, connected to atmosphere and isolated
319 from it) could explain the varying behaviour observed. The role of the microstructure on the
320 opal dehydration by low pressure should be a major consideration when collecting sample
321 containing water as a possible return martian sample target. In any case, the presence of free
322 H₂O-molecules clusters in silica phases samples could be identifiable based on the 1.4 and 1.9
323 µm bands, which can be monitored by Supercam/IRS or Micromega (Bibring et al., 2017;
324 Maurice et al., 2021).

325 The loss of water induces changes in the silanol configuration, by increasing the number of
326 isolated silanols as proposed in earlier studies (Poitras et al., 2018; Sun, 2017; Sun and
327 Milliken, 2018). The emergence of the 7320 cm⁻¹ and the rise of the band component near
328 4520 cm⁻¹ demonstrate the increasing amount of isolated silanols. Water molecules, initially
329 adsorbed into surficial silanols, are lost during low-pressure exposure and transform bonded
330 silanols into isolated ones, inducing a rising of the 4520 cm⁻¹ and 7320 cm⁻¹ bands. The
331 increase of the area of the 4500 cm⁻¹ band could be associated to either the creation of silanol
332 on opal surface or to a difference in the molar absorptivity between isolated and bonded
333 silanols. Considering the condition of the experiments, i.e. at ambient temperature and

334 without any chemical treatments, silanol genesis is deemed unlikely (Christy, 2011; Kondo et
335 al., 1992). Therefore, water releases at low pressure affects all bands of NIR spectra of opal
336 (A or CT) directly (by loss of water molecules) or indirectly (by reconfiguring silanols).

337 4.2. *Low temperature effects*

338 Our results show a significant shift of the apparent maximum for the bands at 7000 cm^{-1} and
339 5200 cm^{-1} , a decrease of the ratio $5250/5100\text{ cm}^{-1}$ ($1.91/1.96\text{ }\mu\text{m}$) and an increase of the ratio
340 between components constitutive of the 7000 cm^{-1} ($1.4\text{ }\mu\text{m}$). The shift of the 5200 cm^{-1} is
341 greater for opal-CT ($> 100\text{ cm}^{-1}$, except for sample 521) than opal-A, which can be explained
342 by the difference in water molecules enclosed. Opal-CT has more liquid-like water molecules,
343 as demonstrated by NIR and thermal analysis (Chauviré and Thomas, 2020; Langer and
344 Flörke, 1974), whereas opal-A mostly contains water molecules in a single layer that do not
345 freeze due to surficial interaction (Ishikiriya et al., 1995; Landry, 2005). Consequently,
346 more water molecules freeze in opal-CT than in opal-A, involving greater changes in the 5200
347 cm^{-1} bands. The reaction of opal-CT 521, similar to opal-A, could be explained by a lower
348 amount of water molecules as multilayers compared to the opal-CT samples. Sample 521 can
349 be differentiated from other opal-A samples by the local minimum between 5100 cm^{-1} and
350 5250 cm^{-1} (deeper in opal-A).

351 Molecular water enclosed in the nanometric pores of opal freezes if temperature is low enough, i.e. usually $< -$
352 30°C ($< 243\text{K}$) for most opals, but up to -47°C (226K) in some cases (Chauviré and Thomas, 2020; Thomas et
353 al., 2020, 2013). The change in shape and position of the apparent maxima of bands at 5200 cm^{-1} and 7000 cm^{-1}
354 is similar to frozen water (

355 Figure 6). At 4500 cm^{-1} , no change that can be attributed to silanol reconfiguration was
356 observed. A slight change was visible, but it is likely due to the proximity of the $3\text{-}\mu\text{m}$ water
357 band, evolving with the crystallization of water. At the same time, we did not observe the
358 isolated silanols band near 7320 cm^{-1} , but a shallow band remained near 7100 cm^{-1} . Therefore,
359 during low temperature experiments, no isolated silanols, as seen for low-pressure
360 experiments, were created. This can be explained by the non-freezable layer of water

361 molecules on silica surface, due to surface interaction (Ishikiriya et al., 1995; Landry,
362 2005). It is thus consistent with the absence of silanol reconfiguration. The remaining
363 shoulder near 5250 cm^{-1} ($1.91\text{ }\mu\text{m}$) and the shallow band near 7100 cm^{-1} , attributed to
364 molecular water bonded to silanols (Christy, 2011, 2010), are evidence of such non-freezable
365 layer.

366 Rice et al. (2013) exposed 11 opals to -13°C (260K), and they observed results consistent
367 with our study; water phase changed in most of their samples, with low-temperature spectra
368 dominated by water ice. Freezing point of water enclosed in nanometres-sized porous
369 materials, including opals, shifts toward lower temperatures according to the size of water-
370 filled pores (Chauviré and Thomas, 2020; Ishikiriya et al., 1995; Landry, 2005; Thomas et
371 al., 2020, 2013). The presence of ice at -13°C demonstrates that their samples contained larger
372 pores, but the temperature may not be sufficient to freeze water-clusters in smaller pores
373 (Chauviré and Thomas, 2020; Thomas et al., 2020, 2013). In parallel, grinding the samples
374 exposes them to water from the terrestrial atmosphere, which will inevitably adsorb at the
375 surface of the grains, which is limited in our study by using silica chips. Also since samples
376 were analysed through transmission, we are probing deeper in the sample compared to
377 reflectance spectroscopy, which tends to analyse more surficial parts of the samples. Poitras et
378 al. (2018) have subjected opal to low temperature in Winnipeg's Mars Environment chamber
379 (Craig et al., 2001), but the specific temperature was not mentioned in their study.
380 Nevertheless, Poitras et al. (2018) did not observe a crystallization of water. This can be
381 explained by either the operating temperature being higher than the water phase changes (the
382 operating temperature of ME is -25°C ; Craig et al., 2001), or by the low pressure causing the
383 removal of all molecular water that may freeze (phenomenon enhanced by the grinding
384 effect). The final spectra after exposure (Poitras et al (2018)) had a 3000 cm^{-1} band ($3\text{ }\mu\text{m}$),
385 characteristic of H_2O vibrations, and a low frequency wing of 5200 cm^{-1} band ($1.9\text{ }\mu\text{m}$),
386 demonstrating that molecular water remained in the silica.

387 Our observations are consistent with the freezing of “liquid” water in opals, as observed by
388 Rice et al. (2013) and Sun (2017). Additionally, Sun (2017) also observed a rehydration of
389 opal at RH > 90%. In our experiment, the low-temperature (circa -90°C) required a small
390 amount of water to reach saturation, and even with the water impurity in nitrogen gas cylinder
391 (maximum at 5 ppm), the RH was expected to be near 100%. High-RH prevented dehydration
392 of our sample that could occur at lower RH, and it could explain why all samples contained
393 ice, and at the same time the lack of rehydration. The main difference between Sun (2017)
394 and the present study could be the result of the grinding effect. It should also be noted that
395 thermalization of samples is a key issue in reflectance studies under low temperature, in
396 particular for powders which can be subjected to strong temperature gradients.

397 4.3. *Implications for opal on Mars*

398 We present in
399 Figure 7 a comparison between two representative spectra of opaline silica from our
400 experiments and spectra acquired with CRISM at three locations on Mars: Antoniadi crater,
401 Iani Chaos and Camichel crater.

402 The temperature of the surface during the acquisition has been estimated from the location
403 and local time using the last version of the Martian Climate Database developed from the
404 General Circulation Model (Forget et al., 1999). Details on location, local time and the
405 deduced atmospheric conditions are displayed in Appendix (Table A 2). These conditions,
406 i.e. between -28 and -43°C, are favourable for the crystallization of water in opals (Chauviré
407 and Thomas, 2020; Thomas et al., 2013).

408 All martian spectra exhibit an asymmetrical band at 4500 cm⁻¹ (2.2 μm), with a greater
409 contribution of the high frequency component. This may suggest, according to the spectra
410 acquired at low pressure (here and by Poitras et al., 2018 and Sun & Milliken, 2018), that
411 opaline silica was dehydrated. In the Camichel crater, the significant band near 7250 cm⁻¹ is

412 an additional evidence of strong dehydration, and its absence in other spectra suggests that
413 other deposits have experienced a dehydration to a lesser extent.

414 All spectra exhibited a band near 5200 cm^{-1} ($1.9\text{ }\mu\text{m}$) with an apparent maximum between
415 5100 and 5250 cm^{-1} . In our spectra, the crystallization of ice inside opal induced either a shift
416 of the maximum (for opal-CT except 521) or the increase of the low-frequency shoulder (for
417 opal-A and 521). No significant shift is visible in the martian spectra, suggesting that not
418 enough water crystallizes to become the main contributor, which is consistent with the
419 dehydration features observed in the 4500 cm^{-1} and 7000 cm^{-1} regions.

420 On the other hand, spectra from Antoniadi crater and Iani Chaos showed absorptions between 6500 and 6750
421 cm^{-1} , which is characteristic of the presence of OH in water molecules (Table 1). According to the atmospheric
422 conditions (between 5.9 and 7.5 mbar and -28 and $-43\text{ }^\circ\text{C}$), and from the thermal data on opal (Chauviré and
423 Thomas, 2020; Thomas et al., 2013), water is likely in ice form, explaining the shoulder centred near 5100 cm^{-1}
424 ($1.96\text{ }\mu\text{m}$,

425 Figure 4) in Antoniadi crater and Iani Chaos spectra . The proximity of atmospheric carbon
426 dioxide near $2\text{ }\mu\text{m}$ prevents the use of this shoulder only (Gerakines et al., 2005; Khayat et al.,
427 2019). Nevertheless, the large band near 6650 cm^{-1} associated with the shoulder near 5100
428 cm^{-1} suggest the presence of a small amount of water-ice.

429 As commonly discussed for mineral detections on Mars, a mixture of mineral phases is likely
430 detected. Other hydrated phases, like sulphates and zeolites, possess absorption bands in the
431 same regions. Sulphates, like gypsum or alunite, have a clear absorption at 5715 cm^{-1} ($1,75$
432 μm ; Carter et al., 2013a; Ehlmann et al., 2016), not observed in our spectra. In addition,
433 zeolites have a very shallow absorption near 4500 cm^{-1} ($2,2\text{ }\mu\text{m}$), as opposed to opaline silica.
434 In addition, Mg-sulfates such as hexahydrate, epsomite or kieserite, have complex 1.4 and 1.9
435 μm absorption features that overlap water ice absorptions (e.g., Dalton et al., 2005). Thus, the
436 presence of small amounts of Mg-sulfates with opaline silica can be responsible for the
437 spectral signatures that we observe. However, obvious spectral evidence for the presence of
438 Mg-sulfates were not observed; this strengthens the hypothesis of opaline silica with water ice

439 formation inside its structure. In any case, clear absorptions other than silica and water species
440 were not identified in this study.

441 Water-ice particle (that would be intimately mixed with silica) are not expected to be the
442 source of the absorption feature observed. In the spectra presented here for the Antoniadi
443 crater and Iani Chaos, ice is unlikely, considering their geographical position in the martian
444 tropical zone (respectively at 21.3°N and 2.06°S), on flat surface inside craters during either
445 spring or summer martian seasons. Detection of water frost is more common at low- and mid-
446 latitudes, but only on polar-faced slopes during fall or winter (Carrozzo et al., 2009;
447 Vincendon et al., 2010). Moreover, except for hydrated silica detections, none of the
448 surroundings exhibit absorptions typical of ice. A contribution of water ice clouds could
449 interfere with the detection (Vincendon et al., 2011), but during the selection of the CRISM
450 images, we prevented this interference by highlighting the presence of water ice through the
451 application of the BD1500_2 from Viviano-Beck et al. (2014): only images that did not
452 present any feature of ice, potentially originating from water-ice clouds or surface frost, were
453 used here.

454 Therefore, in the Antoniadi regions and Iani Chaos, the detection of hydrated silica showed a
455 slight but visible contribution of ice, suggesting that ice is present in opal structure at the time
456 of the detection. This implies that for these regions, in contrast to the Camichel crater, opaline
457 silica more efficiently retains molecular water in its structure. Opaline silica showing the
458 presence of water in the porosity could be an interesting target for exploring the aqueous
459 history of Mars. In addition to this, opaline silica could be used as a potential sample return
460 target and in turn an efficient way to collect martian water (possibly ancient, preserved since
461 the precipitation of silica).

462 **5. Conclusion**

463 By comparing data from available opal samples and from water ice at the same temperature (from Grundy &
464 Schmitt, 1997, 1998), this study demonstrated that opal-CT and water/ice spectra are very close for bands near
465 5200 cm⁻¹ and 7000 cm⁻¹ (1.9 and 1.4 μm) (

466 Figure 6). The main band which allows to differentiate opal from water is the 4500 cm^{-1} (2.2
467 μm) band, and the contributions at 7100 cm^{-1} and 5250 cm^{-1} (1.405 and 1.905 μm).

468 For the detection of opal on Mars, the variety of band shapes according to the type of silica
469 needs to be considered (as showed in Chauviré et al., 2017). Most of the studies aiming to
470 improve silica detection focus on the most amorphous silica phases (i.e. opal-A or volcanic
471 glasses), whereas opal-CT could be the most challenging to decipher. Ice features do not
472 interfere with a potential identification of the opal-type, as opal-A appears to have an apparent
473 maximum at higher frequency (shorter wavelength) than opal-CT, with two distinct bands
474 whereas opal-CT exhibits only one broad band.

475 It was observed that in the Antoniadi crater and Iani Chaos martian opaline silica have a
476 spectrum consistent with the presence of ice in their structure. Our results show that some
477 opals may preserve molecular water in their structure, even when exposed to Mars
478 atmosphere conditions, and that opaline silica could be a prime target for future sample return
479 missions.

480 **6. Author contributions**

481 Boris Chauviré: Conceptualization, Methodology, Data curation, Investigation, Writing –
482 Original draft, Visualization. Maxime Pineau: Data curation, Resources, Writing – Review
483 and editing, Visualization. Eric Quirico: Validation, Resources, Writing – Review and
484 Editing. Pierre Beck: Validation, Resources, Writing – Review and Editing

485 **7. Competing interests**

486 The authors declare that they have no known competing financial interests or personal
487 relationships that could have appeared to influence the work reported in this paper.

488

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9. Figures captions

Figure 1 (single column): Near infrared spectra of samples used in this study before (black) and after (green) exposure to low pressure. Spectra has been offset for clarity.

Figure 2 (1.5 column): Evolution of the parameters for each band (a: 4500cm^{-1} , b: 5200 cm^{-1} , c: 7000 cm^{-1}) between ambient conditions (black filled) and after low-pressure exposition (empty green symbols). Each plot represents the evolution of the ratio of the two components of the band versus the apparent maximum. Reacting samples are shown with an arrow between the initial state and after exposition. Circles represent opal-A sample and triangles opal-CT. For the band at 4500 cm^{-1} , only reacting samples with a variation greater than 10% in area (implying a variation on other parameters) have been represented to improve readability.

Figure 3 (single column): evolution of bands with time during exposure to low pressure for opal-CT WT86. Shown spectra were acquired at room temperature every 30 minutes, demonstrating a strong evolution during the first hours. The last spectrum was acquired 16h45 after the beginning of the experiment.

Figure 4 (single column): Spectra before (grey) and after (blue) exposure to low temperature (applied temperatures are noted in Table 2). Spectra has been offset for clarity.

Figure 5 (1.5 column): Evolution of parameter of the band at 5200 cm^{-1} (a) and 7000 cm^{-1} (b); with the ratio of the two components versus the position of the apparent maximum. In black, parameters at room temperature and in blue at low temperature (temperature given in Table 2). Circles represent opal-A samples, and triangles opal-CT.

Figure 6 (single column): Absorption spectra of water (solid line) and an opal-CT (1543b; dotted line) at both room temperature (black line; 293.5 K) and low temperature (blue line; 180K measured and 220K from calibrated temperature for opal, 230 K for water). Data for water was extracted from Grundy & Schmitt (1997). Y-axis was normalized and offset for clarity.

Figure 7 (single column): Continuum removed CRISM spectra from three locations where opaline silica was identified (Antoniadi crater, Iani Chaos region and Camichel crater) compared to the laboratory spectra acquired at similar temperature. To improve the comparison, the reflectance spectra of terrestrial opal has been simulated from transmission spectra according to Hapke model (Hapke, 1993). Blue areas indicate water ice regions and vertical dotted line indicates absorptions bands specific to hydrated silica. The penultimate spectrum is a CRISM spectrum of water ice at the northern cap of Mars to make comparison with the 1551 opal-CT sample. The last one is a montmorillonite spectrum from the USGS dataset showing a 4500 cm^{-1} absorption band narrower than opaline silica.

| Band positions cm ⁻¹ (μm) | Band attributions | Vibration mode |
|---|---|--|
| 4420 (2.26) | Combination of OH stretching (hydrogen bonded to water molecules) and siloxane (Si-O-Si) bending | δ _{SiOH} + ν _{OH} |
| 4500 (2.21) | Combination of free OH stretching (not hydrogen bonded to water molecules) and siloxane (Si-O-Si) bending | δ _{SiOH} + ν _{OH} |
| 5100 (1.96) | Combination of OH stretching and bending in water molecules (hydrogen bonded) | ν ₂ + ν ₃ |
| 5250 (1.91) | Combination of OH stretching and bending in water molecules (free) | ν ₂ + ν ₃ |
| 6850 (1.46) | Combination of OH stretching and bending in water molecules (hydrogen bonded) | 2ν ₂ + ν ₃ * 2ν ₃ * ν ₁ + ν ₃ * |
| 7090 (1.41) | OH stretching in silanols | 2ν _{OH} |

10. Tables

Table 1 : NIR absorptions (between 4000 and 8000 cm⁻¹) of molecular water (H₂O_{mol}), silanol groups (SiOH) and OH in amorphous silica (after Anderson & Wickersheim 1964; Flörke et al., 1982; Kronenberg, 1994). Vibration mode: δ_{SiOH} = SiOH bending in plane; ν_{OH} = OH-stretching; ν₂ = symmetric bending; ν₃ = antisymmetric stretching. *The attribution of the band at 6580 cm⁻¹ (1.46 μm) is debated.

| Sample | Variety | Mars simulated | | | |
|--------|---------|-----------------|--------------|------------------|--------|
| | | Pressure | | Temperature (°C) | |
| | | Measured (mbar) | Time (h:min) | Measured | Sample |
| 86.2 | Opal-A | 7.21 | 4:10 | -90.4 | -88.9 |
| 785 | | 1 | 17:10 | -89.8 | -89 |
| 1039 | | 1 | 2:40 | | |
| 1040 | | 7.2 | 1:00 | -91 | -81.1 |
| 521 | Opal-CT | | | -91.6 | -51.1 |
| 1085 | | 1 | 5:35 | -90.8 | -62.9* |
| 1543a | | | | -89.2 | -64.2* |
| 1543b | | 7.36 | 3:40 | -94 | -87.8* |
| 1543d | | 1 | 2:00 | -88.1 | -57.7 |
| 1548 | | | | -89.2 | -68.9* |
| 1551 | | 7.25 | 14:20 | -91.6 | -57.2 |
| 1552a | | 1 | 2:50 | -94 | -96.5* |
| 1552b | | | | -92.5 | -78.1* |
| WT86 | | 1 | 16:45 | | |
| FT1111 | | 7.85 | 21:00 | | |
| VTB | | 7.24 | 20:00 | | |
| YM12 | | 10 | 1:50 | | |

Table 2 : Samples used for the experiments at Mars-relevant pressure and temperature. The column “Measured” is the temperature measured by the sensor in the cell, the column “Sample” is the temperature calculated from the calibration based on the NIR ice bands. *indicates the sample used to recalculate the calibration from Fink & Larson (1975) to take account of the onset temperature. The other sample’s temperature has been calculated using the recalculated calibration by taking account of the onset temperature from the DSC measurements available (Chauviré and Thomas, 2020).

11. Appendix

11.1. Temperature of sample

As the sample is placed on a sapphire window (to acquire transmission spectra), and the temperature sensor is located on the surrounding freezing circuit, a difference between the temperature of the sample and the sensor exists. As water in opal could freeze at low temperature, we used the temperature dependency of the 5500-7000 cm^{-1} (1.82-1.43 μm) region of water ice (Fink and Larson, 1975; Grundy and Schmitt, 1998) to estimate the exact temperature of the sample (consequently, this method is only applicable when ice is present in the sample). The area of the shoulder near 6050 cm^{-1} divided by all the area between 5500 cm^{-1} and 7000 cm^{-1} is dependent of the temperature of the ice (Appendix

Figure A 2): the larger the ratio is, the lower the temperature is (Fink and Larson, 1975). Given that our spectra were acquired above 100K, it avoids the unreliability of this calibration at lower temperatures (Grundy and Schmitt, 1998). In addition, the crystallization of water in opals demonstrates that this amount of water did not interact with the silica surface, or silanols linked to it (Ishikiriya et al., 1995; Landry, 2005). Fink & Larson (1975) established the following linear equation:

$$T = -2862 * \frac{R_{6050}}{6600} - 2.15$$

Where T is the temperature in $^{\circ}\text{C}$, and $\frac{R_{6050}}{6600}$ is the ratio between the area of the 6050 cm^{-1} band and the area of the 5500-7000 cm^{-1} region.

As the water trapped inside nanometric pores freezes at lower temperature due to surficial interaction, the temperature deducted from ice-related NIR bands needs to be corrected from the freezing point depression. In Chauviré and Thomas (2020), the six samples used to recalculate the calibration (1085, 1543a, 1543b, 1548, 1552a, 1552b) have been analyzed by low-temperature Differential Scanning Calorimetry (DSC), and the onset temperature (corresponding to the start of water freezing) has been added to the calibrated temperature. Based on the measured temperature, the temperature from the calibration and the onset temperature, we established a calibration equation as below:

$$T_m = 5.518 * (T_c + \Delta T_{on}) + 429.14$$

Where T_m is the measured temperature, T_c is the temperature from the Fink and Larson (1975) calibration and ΔT_{on} is the onset temperature, with a $R^2 = 0.81$.

11.2. Figures captions

Figure A 1 : Schematics of the cell used to analyse at Mars-relevant conditions.

Figure A 2: Area of bands used for the temperature calibration. NIR spectrum of pure ice from Gundry & Schmidt (1998) at 180 K (-93 °C).

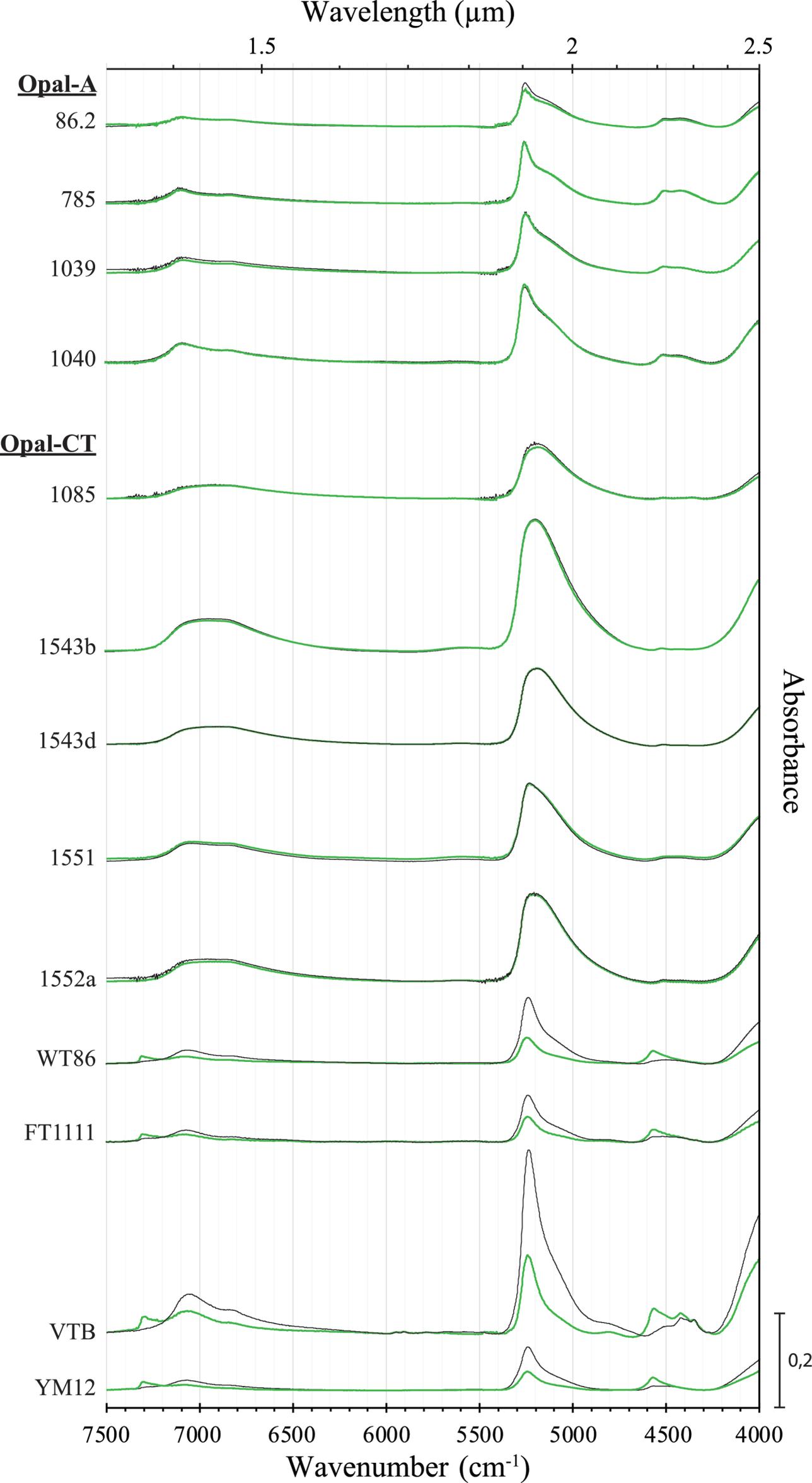
Figure A 3 : Process used to remove the baseline from the spectra (here shown for opal 86.2)

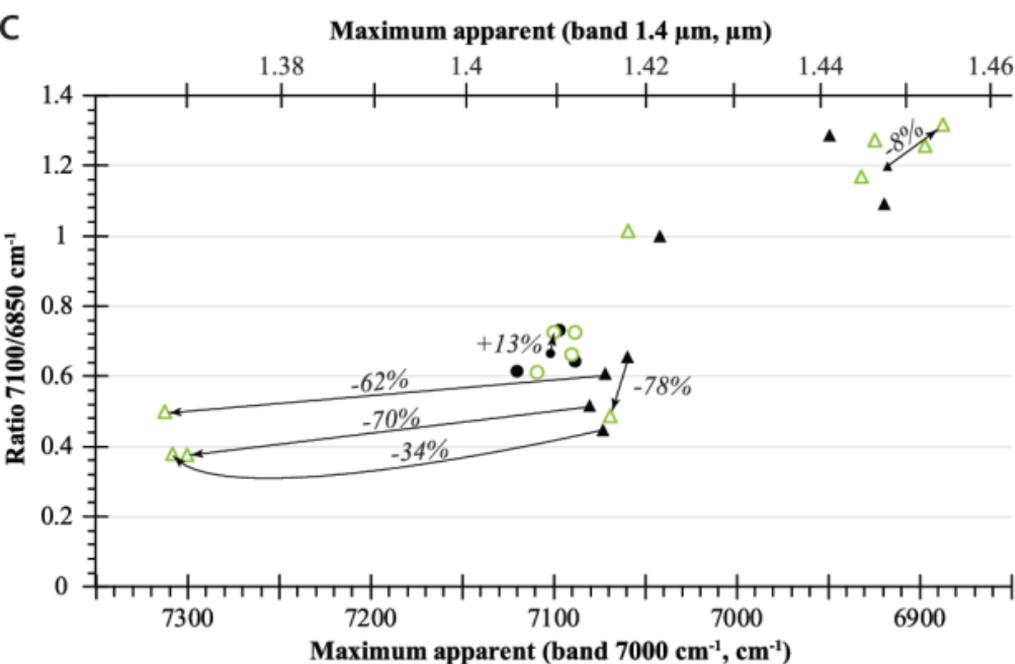
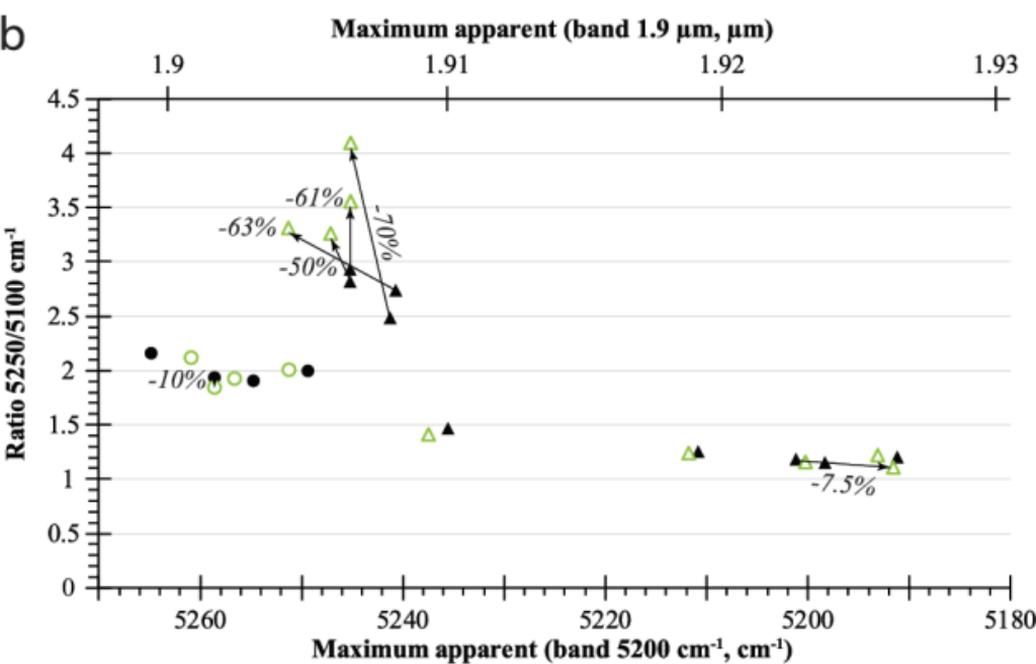
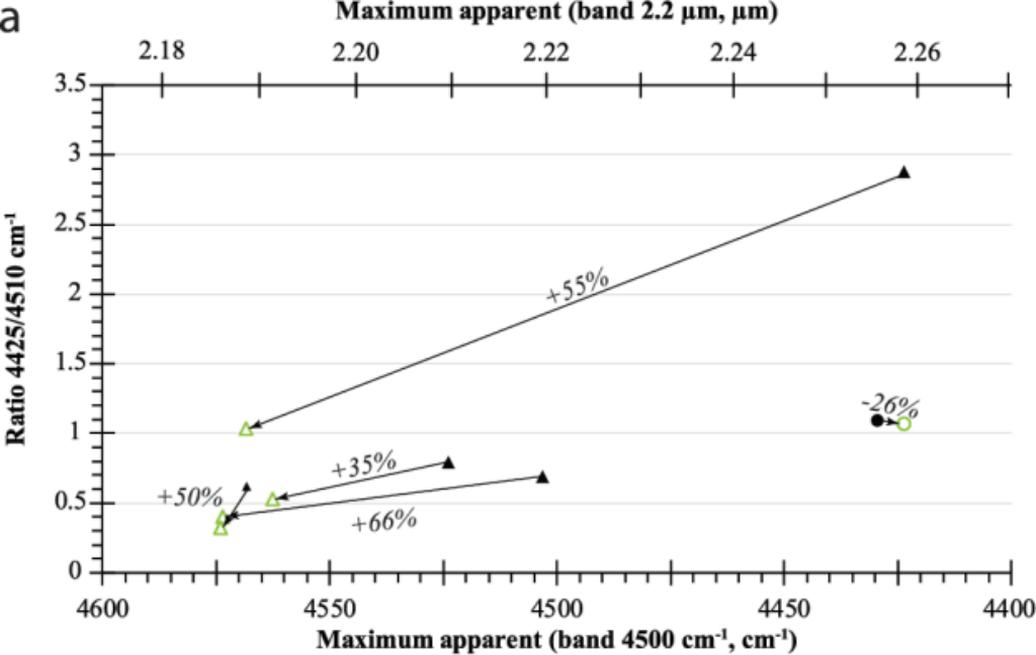
| Sample | Variety | Color | Origin | |
|--------|---------|-----------------|---|--------------|
| | | | Geographic | Geological |
| 86.2 | Opal-A | White | Kashau, Slovakia | Unknown |
| 785 | | White | Honduras | Unknown |
| 1039 | | Orange | Mintabie, South Australia, Australia | Weathering |
| 1040 | | Grayish-yellow | Cooper Pedy, South Australia, Australia | Weathering |
| 521 | Opal-CT | Dark brown | Mezezo, Ethiopia | Hydrothermal |
| 1085 | | Greenish yellow | “New Maternal”, Argentina | Unknown |
| 1543a | | Red | San Martin, Jalisco, Mexico | Hydrothermal |
| 1543b | | Brownish red | | |
| 1543d | | Orange | | |
| 1548 | | White | Fougères, Brittany, France | Unknown |
| 1551 | | Dark brown | Mezezo, Ethiopia | Hydrothermal |
| 1552a | | Red | Guadalupana, Nayarit, Mexico | Hydrothermal |
| 1552b | | Orange red | | |
| WT86 | | Light orange | Wegel Tena, Ethiopia | Weathering |
| FT1111 | | Whitish orange | | |
| VTB | | White | | |
| YM12 | | Orange | Mezezo, Ethiopia | Hydrothermal |

11.3. Tables

| Region | CRISM ID scene | Center Lat/Long | Terrestrial observation time | Solar longitude Ls | Martian observation time | Surface temperature | Surface pressure |
|-------------------------|----------------------------|------------------------|-------------------------------------|---------------------------|--|----------------------------|-------------------------|
| Antoniadi crater | FRT00009312_07_IF166L_TRR3 | 19.92°N. 65.86°E | 2008-01-04 @14:02 UT | 12.6° | MY29. MM01/12. sol 026/669 @08:56 LTST | 230.5 K (-42.7°C) | 5.9 mbar |
| | FRT00009BCE_07_IF166L_TRR3 | 18.52°N. 65.14°E | 2008-02-01 @07:51 UT | 25.7° | MY29. MM01/12. sol 053/669 @09:25 LTST | 244.9 K (-28.3°C) | 6.0 mbar |
| Iani Chaos | FRT000134D2_07_IF165L_TRR3 | -0.61°N. -18.03°E | 2009-06-19 @01:02 UT | 287.7° | MY29. MM10/12. sol 543/669 @17:24 LTST | 245.6 K (-27.5°C) | 7.5 mbar |
| Camichel crater | HRL0000985E_07_IF182L_TRR3 | 2.71°N. -51.66°E | 2008-01-19 @07:26 UT | 19.6° | MY29. MM01/12. sol 040/669 @09:20 LTST | 237.0 K (-36.2°C) | 6.9 mbar |

Table A 2 : Details of martian hydrated silica spectra and estimations of surface conditions from the GCM. UT = Universal Time.





- Opal-A at ambient pressure
- Opal-A at Mars-relevant pressure
- ▲ Opal-CT at ambient pressure
- △ Opal-CT at Mars-relevant pressure

