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Marine Quiers, Claire Chanteraud, Andréa Maris-Froelich, Emilie Chalmin, Stéphane Jaillet, et al.. Light in the Cave: Opal coating detection by UV-light illumination and fluorescence in a rock art context. Methodological development and application in Points Cave (Gard, France). 2022. hal-03383193v4

HAL Id: hal-03383193

<https://hal.science/hal-03383193v4>

Preprint submitted on 13 May 2022 (v4), last revised 14 Jun 2022 (v5)

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Light in the Cave: Opal coating detection by UV-light illumination and fluorescence in a rock art context

Methodological development and application in Points Cave (Gard, France)

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Abstract

Silica coatings development on rock art walls in Points Cave questions the analytical access to pictorial matter specificities (geochemistry and petrography) and the rock art conservation state in the context of pigment studies. However, classical *in situ* spectroscopic techniques appear unsuccessful to identify these coatings, which also prevent pigment characterization. In this study, we propose using a UV fluorescence method for opal coating detection based on the fluorescence specificities of uranyl-silica complexes composing these deposits. A coupling of spectral identification using UV laser-induced fluorescence spectroscopy with UV illumination was performed on samples and μ -samples from the Points Cave rock art site. The well-defined peaks observed in fluorescence emission spectra due to uranyl ions validate opal detection and its correspondence with green fluorescence observed under UV light at micro- and macroscopic scales. *In situ* optical measurements under UV illumination reveal the presence of opal coating, especially on rock art walls in Points Cave. Opal occurrence and repartition observations provide the first insights into Points Cave wall evolution and chronological constraints linked to opal coating development. Regarding the strong interactions with pigment

35 suggested by multiscale observations of samples and μ -samples, the impact of the presence of opal
36 coating on Points Cave rock art conservation quality is questioned. Thus, by developing a specific and
37 non-destructive characterization method for opal coatings, this study opens up a new approach for the
38 study of decorated wall taphonomy and proposes utilizing mineralization both as markers of the
39 natural history of caves and as an indication for their uses by ancient human groups.

40

41 **Keywords:** Silica coating, uranyl, UV fluorescence, *in situ* detection, rock art, Quaternary,
42 archaeology, Ardèche, France, optical methods

43

44

45 **1. Introduction**

46 Natural activity in caves, mostly water weathering (Delvigne, 1998; Chalmin *et al.*, 2019; Salomon *et*
47 *al.*, 2021), transforms the surface of the walls by physical, chemical, biological and mechanical action.
48 Thus, the traces of all these transformations (environmental input) can be a source of information
49 regarding natural and anthropological events on the wall surface, such as drawing and painting
50 realizations, cave environment evolution, and human presence in the cave (Sadier, 2013; Pons-
51 Branchu *et al.*, 2014; Quilès *et al.*, 2015; Shao *et al.*, 2017; Valladas *et al.*, 2017; Monney & Jaillet,
52 2019).

53

54 Among the taphonomic processes impacting rock art pictorial matter, mineral-coating formation as
55 weathering products is well described in rock art research (Vignaud *et al.*, 2006; Huntley, 2012;
56 Bassel, 2017; Chalmin *et al.*, 2018; Mauran *et al.*, 2019). Silica rich amorphous deposits, also called
57 silica skins, have been observed at different cave and open-air rock art sites (Watchman, 1990; Aubert
58 *et al.*, 2004; Aubert *et al.*, 2012; Huntley, 2012). Those studies have suggested both a positive and
59 negative impact on rock art conservation due to opal coating development. Indeed, the strong
60 interaction suspected with hematite pigments has been suggested as an element of conservation

61 enhancement, notably compared with other pigments (Watchman, 1990). However, some authors have
62 also observed exfoliation processes of silica skins, which could play a role in rock art weathering
63 (Aubert *et al.*, 2004; Green *et al.*, 2017). To our knowledge, there is still no clear answer on the role of
64 silica coatings as conservation factors of pictorial matter. In addition to this conservation issue, silica
65 skins have been proposed as tools for indirect dating of rock art, especially in the case of inorganic
66 pictorial matter (Aubert *et al.*, 2004; Aubert *et al.*, 2012). Indeed, this mineral phase is known to be
67 enriched in uranyl ions, but the U-Th dating application remains hypothetical due to silica skin
68 thickness and absence of stratigraphy, which complicate both sampling and measurement reliability
69 (Green *et al.*, 2017).

70

71 Thus, silica skin characterization represents a key issue in the context of rock art studies. However, it
72 remains difficult to identify and characterize, especially with non-invasive techniques. Currently, the
73 use of *in situ* spectroscopic techniques in rock art studies is increasing, as these methods can provide
74 information on both pictorial matter and pigment environments (substrate, deposits, concretions, etc.).
75 The portability and decreasing cost of instruments coupled with the rapidity and the non-destructive
76 character of analyses have led to a quasi-systematic use of these techniques in recent rock art studies
77 (Huntley, 2012, Mauran *et al.*, 2019; Trosseau *et al.*, 2021; Chanteraud *et al.*, 2021). However,
78 amorphous silica characterization, even in rock art context, is generally based on laboratory
79 observations such as SEM or XRD analyses (Watchman, 1990; Gaillou *et al.*, 2008; Garcia-Guinea *et*
80 *al.*, 2013; Huntley *et al.*, 2015; Green *et al.*, 2017). In addition, the signal of pictorial matter acquired
81 with portable spectroscopic techniques could be impacted by the presence of silica skins, as observed
82 by Huntley (2012) in the case of pXRF measurements.

83

84 In this paper, we propose a new method for *in situ* detection and characterization of amorphous silica
85 in a rock art context based on UV laser-induced fluorescence (LIF). Indeed, uranyl fluorescence
86 characteristics under UV light are well known and have been observed in silica mineralization,
87 especially in opal (deNeufville *et al.*, 1981; Gorobets *et al.*, 1977; Fritsch *et al.*, 2001; Gaillou *et al.*,

88 2008). UV spectroscopy presents the same advantages as other portable spectroscopic techniques, but
89 the bright green fluorescence and the specific spectral features displayed by uranyl ions enable the
90 targeted identification of opal coatings. To our knowledge, only one study has reported opal detection
91 in caves using optical methods based on UV techniques (Garcia-Guinea *et al.*, 2013), and no study has
92 applied UV spectroscopic methods in a rock art context for opal identification. Here, we propose a
93 methodological development based on laboratory and field experiments to validate the use of *in situ*
94 UV techniques for opal detection in a rock art context by coupling *in situ* optical and spectroscopic
95 analyses to obtain multiscale information.

96

97 This study was performed in Points Cave (Aiguèze, Gard, France), which contains an important spread
98 of opal coating on the cave walls. In this approach, Points Cave perfectly illustrates the importance of
99 environmental input characterization in the study of rock art (Chanteraud *et al.*, 2021). In Points Cave,
100 some pieces of the rock wall bearing colouring matter were discovered during archaeological
101 excavations in front of some rock art panels which allowed transport, μ -sampling and analysis in the
102 laboratory. Analysis of these coloured flakes allows us to identify and measure the environmental
103 input, which modifies and obscures the identification of pictorial matter characteristics.

104

105 **2. Material**

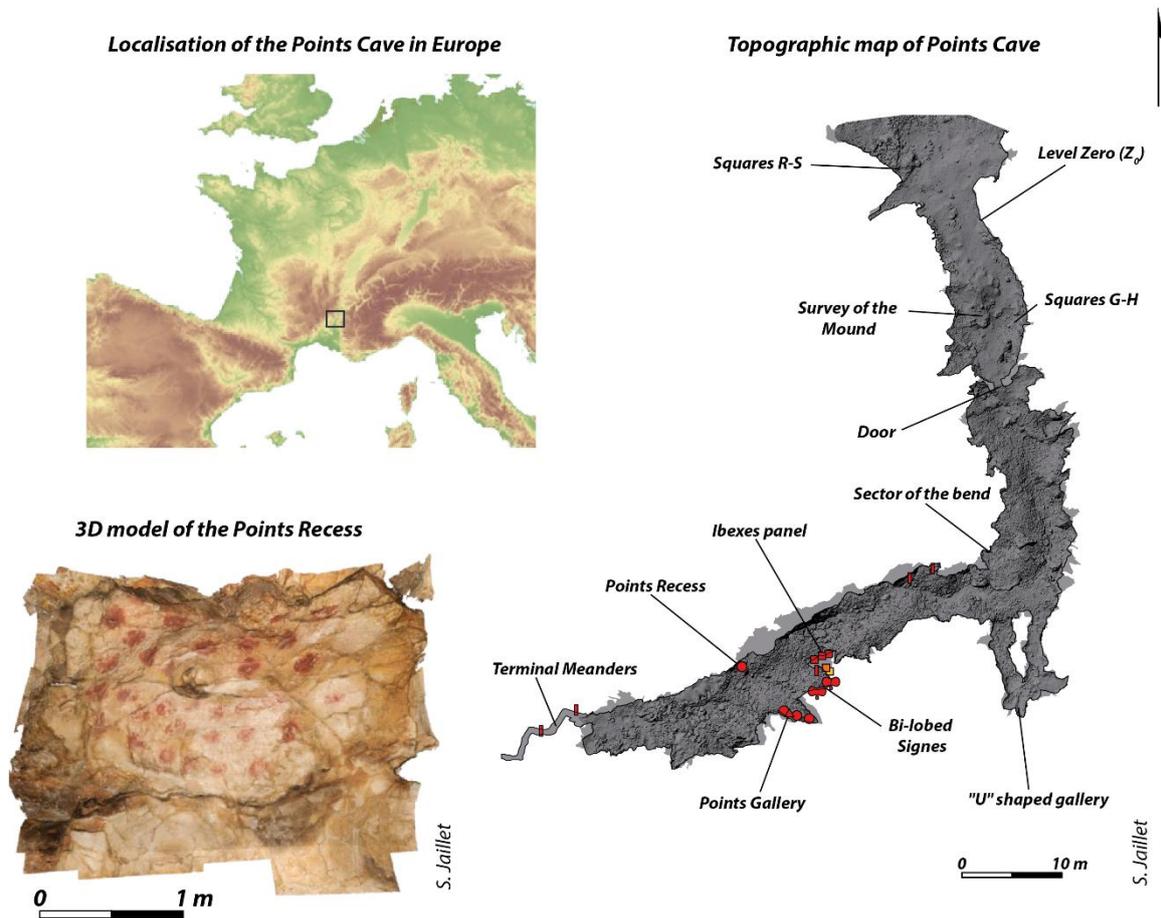
106

107 **2.1 Study site: Points Cave**

108

109 Located in the Ardèche River Canyon, less than 10 km downstream of Chauvet Cave, Points Cave is a
110 Palaeolithic rock art site identified in 1993 (Figure 1) (Deschamps *et al.*, 2018). Archaeological studies
111 have been performed since 2011 as part of the “Datation Grottes Ornées” project (“Cave Art Dating”
112 project, Monney, 2011; 2018). The entrance opens on a hundred-metre long cave in Urgonian
113 limestone. The rock art which is exclusively composed of red drawings and paintings, is located in the
114 middle part of the cave preserved from sunlight (Figure 1). Excavations conducted at the entrance

115 indicated human and animal occupation since the late Pleistocene to the present day (Monney &
 116 Jaillet, 2019).
 117



118

Figure 1: Points Cave location in southeastern France, topographic map of the cave with location of the excavations and the rock art panels (J. Monney); 3D model of the “Points Recess” panel (J. Monney)

119

120 Points Cave is currently disconnected from hydrogeological flows (Jaillet & Monney, 2018). Only a
 121 few infiltrations can be observed after strong precipitation events. The low level of leaching on the
 122 wall and the low relative presence of a calcite veil are due to this weak hydrogeological activity.
 123 Millimetric to centimetric concretions and efflorescence’s (coralloid type of crystallization) have also

124 developed on the wall surface in the rock art sector (Mauran, 2019 in Monney et al., 2019; Barbaran &
125 Nouet, 2020).

126

127

128 **2.2 Points Cave rock art and pictorial matter**

129

130 Rock art, composed exclusively of red drawings and paintings, is currently observed in the middle part
131 of the cave. It comprises five animal figures (3 ibexes, 1 horse, 1 bison), five indeterminate tracings,
132 two bi-lobed signs, one open-angle sign and four clusters containing a total of 59 palm-printed dots,
133 commonly referred to as "palm dots" (Monney, 2018). On-site spectroradiometric analysis showed
134 that Points Cave rock art is homogenous in colour (Lafon & al., 2022). Moreover, pieces of colouring
135 matter were found during the archaeological excavations in the sedimentary sequence at the entrance
136 of the cave (Chanteraud *et al.*, 2019; Chanteraud, 2020).

137

138 Investigations carried out at the foot of the rock art panel known as the "Bi-lobed Signs" revealed the
139 presence of five coloured wall flakes on the ground in the chaos of rocks: S-ECA-01 to S-ECA-05.
140 These 3 to 20 cm flakes are composed of limestone fragments detached from the wall by mechanical
141 action and covered on one side with colouring matter (Monney, 2011). They more than likely come
142 from the large bilobed sign (PTS-10) or from other unknown rock art that may have crumbled entirely
143 from the walls nearby (Monney, 2018). These flakes are a major asset of Points Cave because they
144 allow to investigate the cave walls surface with accurate instruments by bringing them in the
145 laboratory.

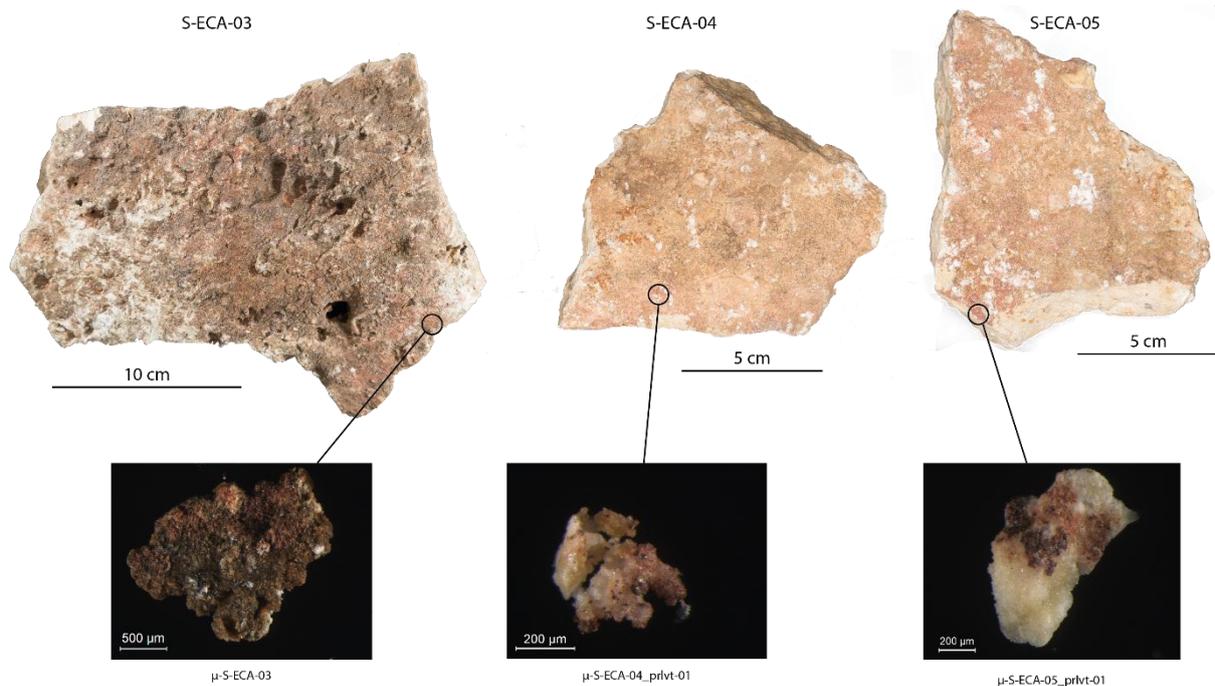
146

147 To identify both the iron-oxide morphologies and the natural mineralization that can form on the
148 surface of the decorated walls, our study was focused on three of the five wall flakes (S-ECA-03, S-
149 ECA-04, S-ECA-05) discovered in the rock art sector of Points Cave, because of the presence of opal

150 coating on their surface (Figure 2). μ -sampling of pictorial matter was performed on the coloured
151 flakes: μ -S-ECA-03, μ -S-ECA-04, μ -S-ECA-05. These last two have been fragmented during
152 sampling giving: μ -S-ECA-04_prlvt_01, μ -S-ECA-04_prlvt_02 and μ -S-ECA-04_prlvt_03, and μ -S-
153 ECA-05_prlvt_01 and μ -S-ECA-05_prlvt_02 (S.I.1).

154

155



156

157 **Figure 2:** Limestone flakes found in the archaeological excavations at the foot of the Bi-lobed Signs
158 panel and location of μ -sampling.

159

160 Moreover, 12 μ -samples of pictorial matter on limestone and 8 μ -samples of the undecorated cave
161 walls (limestone) were directly sampled on and/or around the rock art panels of the cave and added to
162 the study (Table 1, S.I.2). All μ -samples of pictorial matter were observed and analysed without any
163 preparation.

164

165

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 174

Table 1: Inventory of μ -samples with colouring matter coming from the rock art panels

| <i>Sample N°</i> | <i>Rock Art</i> | <i>Type</i> |
|---|-------------------------------------|-------------------------|
| – Ibexes Panel – | | |
| <i>Prm-19-01</i> | <i>Near to the Ibex n°5</i> | <i>Wall Blank</i> |
| <i>Prm-19-02</i> | <i>Ibex n°5</i> | <i>Pictorial matter</i> |
| – Horse Panel – | | |
| <i>Prm-19-03</i> | <i>Near to the Horse</i> | <i>Wall Blank</i> |
| <i>Prm-19-04</i> | <i>Horse n°7</i> | <i>Pictorial matter</i> |
| <i>Prm-19-05</i> | <i>Bison n°8</i> | <i>Pictorial matter</i> |
| – Bi-lobed Signs Panel – | | |
| <i>Prm-19-06</i> | <i>Near to the Sign n°9</i> | <i>Wall Blank</i> |
| <i>Prm-19-07</i> | <i>Small Bi-lobed Sign n°9</i> | <i>Pictorial matter</i> |
| <i>Prm-19-08</i> | <i>Large Bi-lobed Sign n°10</i> | <i>Pictorial matter</i> |
| <i>Prm-19-09</i> | <i>Palm-dot n°14-02</i> | <i>Pictorial matter</i> |
| <i>Prm-19-10</i> | <i>Open-angle Sign n°13</i> | <i>Pictorial matter</i> |
| – Dots Galerie – | | |
| <i>Prm-19-11</i> | <i>Near to the Palm-dot n°11-02</i> | <i>Wall Blank</i> |
| <i>Prm-19-12</i> | <i>Palm-dot n°11-02</i> | <i>Pictorial matter</i> |
| <i>Prm-19-13</i> | <i>Palm-dot n°11-03</i> | <i>Pictorial matter</i> |
| – Dots Gallery (cluster 11) – | | |
| <i>Prm-19-14</i> | <i>Near to the Palm-dot n°11-01</i> | <i>Wall Blank</i> |
| <i>Prm-19-15</i> | <i>Palm-dot n°11-01</i> | <i>Pictorial matter</i> |
| <i>Prm-19-16</i> | <i>Palm-dot n°15-21</i> | <i>Pictorial matter</i> |
| <i>Prm-19-17</i> | <i>Palm-dot n°15-01</i> | <i>Pictorial matter</i> |
| – Points Recess – | | |
| <i>Prm-19-18</i> | <i>In the center of the panel</i> | <i>Wall Blank</i> |
| – Between Ibexes panel and Horse panel – | | |
| <i>Prm-19-19</i> | <i>On the limestone</i> | <i>Wall Blank</i> |
| – Points Recess – | | |

175

176

177 **3. Methods**

178

179 **3.1 Macroscopic and microscopic observations**

180

181 *3.1.1 Laboratory and in situ observations at macroscopic scale*

182

183 Image capture for macroscopic observations was performed in two steps: 1) a photograph was taken
 184 under white light, and 2) another photograph was taken under UV light illumination. Observations at
 185 macroscopic scale in the laboratory and in the cave were realized with a Canon EOS 5D Mark III
 186 camera and a Canon EOS 7D camera fixed on a tripod. A detached flash was used for image capture
 187 under white light. For UV light illumination, 4 UV LEDs (280 nm, 2.26 W, NewEnergy) were fixed
 188 on orientable macroflash bars on each side (2 LEDs per side) of the camera, allowing both
 189 macrophotography and general views of cave walls. Camera parameters are available in Table 2.

190

Table 2: *Camera parameters used for both white and UV light illumination during field and laboratory macroscopic observations.*

| | | | <i>Aperture</i> | <i>Obturation speed (sec)</i> | <i>Iso</i> |
|-------------------|-------------|------------------|-----------------|-------------------------------|------------|
| Laboratory | White light | | F/7.1 | 1/320 | 1600 |
| | UV light | | F/7.1 | 10 | 1600 |
| Field | White light | <i>Macro</i> | F/11 | ½ | 320 |
| | | <i>Wall view</i> | F/11 | 1/60 | 100 |
| | UV light | <i>Macro</i> | F/4.5 | ½ | 320 |

191

192 Laboratory observations were also performed using a stereomicroscope (LEICA M165 C) under white
193 and UV light. The same 4 LEDs were used for UV illumination.

194

195 3.1.2 Laboratory observations at microscopic scale

196

197 At microscopic scale, observations of μ -samples of flakes on carbon tape were realized with a field-
198 emission scanning electronic microscope (SEM) ZEISS Ultra+ associated with an EDX (energy
199 dispersive X-ray) probe (SDD, Bruker) working in high-vacuum mode with a 15 keV voltage. Images
200 were taken with secondary electrons using in-lens or Everhart-Thornley detectors (SE2) and with
201 backscatter electrons (BSE-AsB detector) (Néel Institut, Grenoble).

202

203 3.2 UV fluorescence analyses

204

205 Stationary fluorescence signal of flake and flake μ -samples was measured in the laboratory with a
206 solid-phase spectrofluorimeter designed in the EDYTEM laboratory for non-destructive solid-phase
207 measurements (Perrette *et al.*, 2000).

208

209 This instrument is divided into excitation and detection compartments associated with a translation
210 stage system for sample surface measurement. For this experiment, the excitation system was
211 composed of a Nd:YAG laser (Crylas, FQSS266-Q1) with a 266 nm excitation wavelength. The
212 fluorescence emission response was collected after sample excitation by focusing the laser beam (~ 30
213 μm) on its surface. The detection system was composed of a low-pass filter monochromator (Jobin
214 Yvon, MicroHr) for light diffraction, fitted with a 300-g/mm diffraction-grating centred at 620 nm,
215 associated with a thermoelectric-cooled, back-illuminated CCD (Jobin Yvon, Sincerity) for high-
216 efficiency signal detection in the UV-visible light domain. As no manipulation, modification or

217 destruction of the sample surface occurred during analysis, this technique is suitable for archaeological
218 sample measurements.

219

220 Two types of fluorescence measurements were realized:

221 - Single point measurements were performed on flake μ -samples: μ -S-ECA-03, μ -S-ECA-04
222 and μ -S-ECA-05-02 (S.I.3). One spectrum was independently acquired on the sample.
223 Measurement location was determined manually. An acquisition time of 1 s and a
224 monochromator entrance slit of 0.25 mm (\sim 1 nm spectral resolution) were used for spot
225 spectrum acquisition.

226 - Surface measurement was performed on flake S-ECA-05 (S.I.4). The motorized translation
227 stage system allowed movements in two directions for surface measurements. The image was
228 obtained by stacking lines along the Y-axis. For this study, fluorescence surface imaging was
229 performed with a 100×100 μ m resolution using a 0.1 s acquisition time and a 0.05 mm
230 entrance slit.

231

232 Data pre-processing was performed with MATLAB software (S.I.5). Spectra were corrected from
233 baseline and instrument responses and then filtered with the Savitsky-Golay method (Savitzky &
234 Golay, 1964).

235

236 **4. Results**

237

238 *4.1 Macroscopic scale observations*

239

240 At macroscopic scale (by visual inspection), beside the centimetric coralloid crystallization there is no
241 other mineralization visible than the limestone on the walls, flakes or μ -sample surfaces. In fact, at this
242 observation scale, surfaces seemed to be well preserved with strong colouration from the pictorial
243 matter and clear access to the calcareous substrate (Figure 2).

244

245 Despite the results of the visual inspection of the walls and the observation of the μ -samples both of
246 the rock art and the flakes under stereomicroscope, pXRF analyses (1 cm³ spot) showed that decorated
247 panels of the cave display mineralization, such as calcium sulphate (Chanteraud *et al.*, 2020; S.I.6).
248 This contradiction between observation and geochemical analysis reveals the need for microscopic
249 inspection using SEM device.

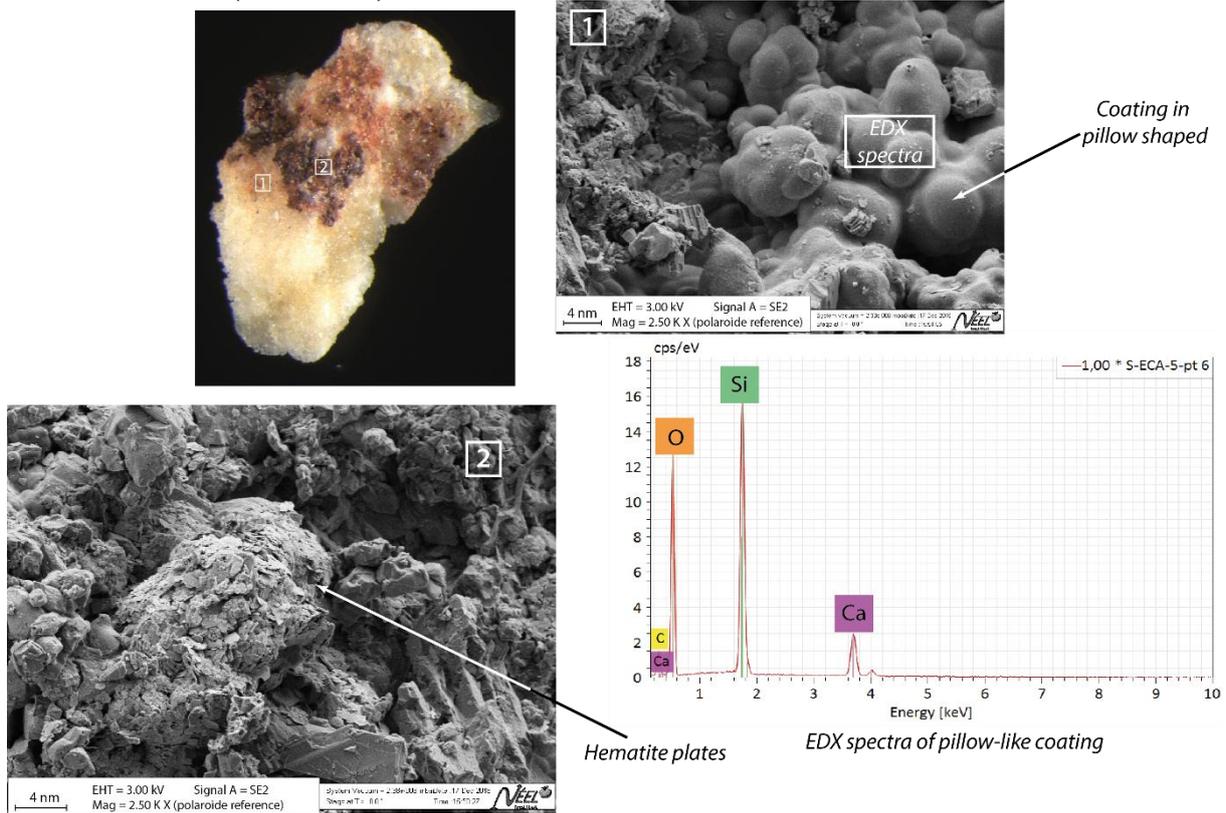
250

251 *4.2 Microscopic scale observations*

252

253 At the microscopic scale, a 1 μ m-thin mineral film consisting of nonordered spheres was identified as
254 silica mineralization on μ -S-ECA-03, μ -S-ECA-04-prlvt-02, μ -S-ECA-05-prlvt-01 (Figure 3; S.I.2).
255 However, μ -S-ECA-03 shows less opal coating than the two other μ -samples. The geochemistry and
256 hummocky morphology of the opal could be related to a type A-g amorphous opal with a $\text{SiO}_2n\text{H}_2\text{O}$
257 formula (Flörke *et al.*, 1991). The mineral structure present on coloured flakes suggests its formation
258 from a water film containing a high concentration of silica (Monger & Kelly, 2002; Curtis *et al.*,
259 2019). With this mode of formation, it is difficult to assume if the opal came before the hematite
260 deposit. In fact, it is possible that the opal coating grows at the interface between the limestone
261 substrate and the colouring matter.

μ -S-ECA-05-prlvt-01



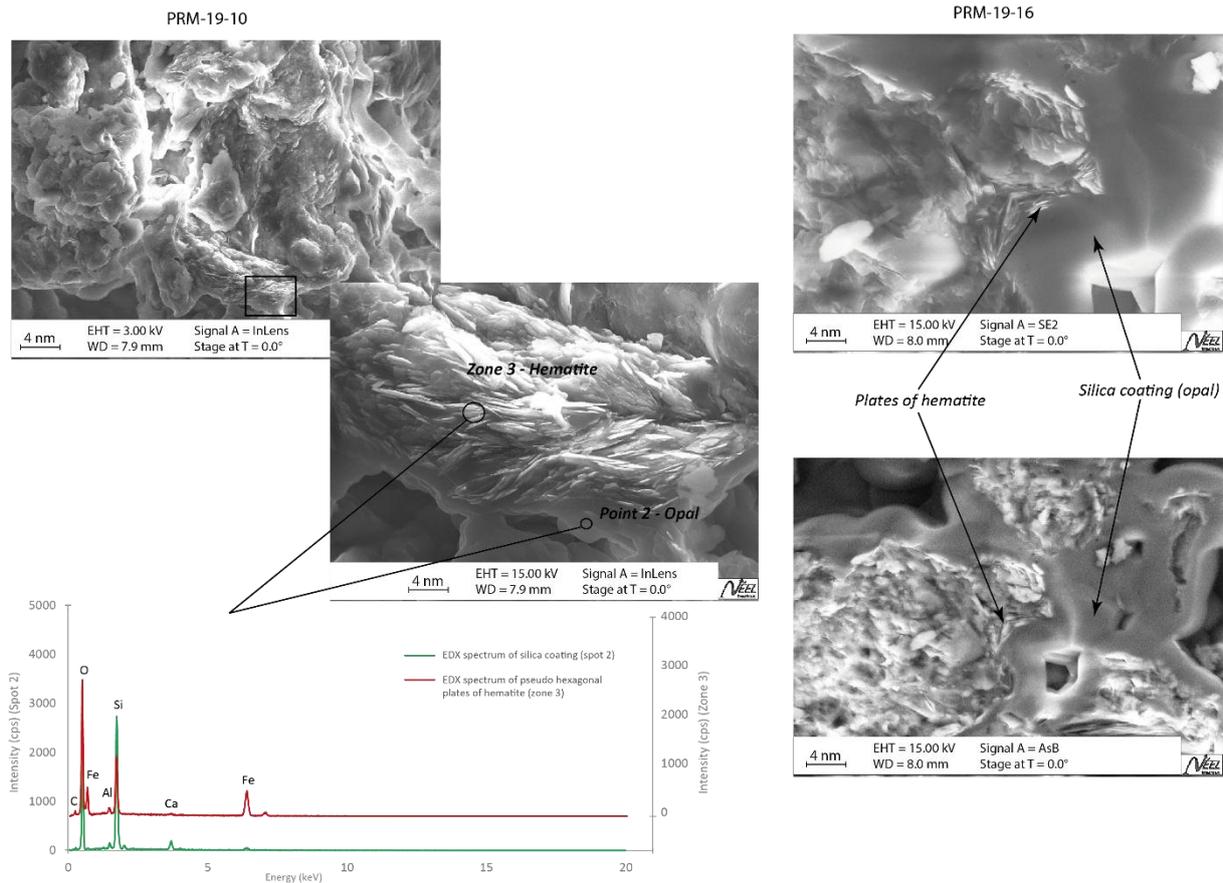
262

Figure 3: SEM observations of μ -S-ECA-05_prlvt_02. 1/ Hematite plate observation in Secondary Electron mode (SE); 2/ Pillow-like silica coating on surface in SE mode; White rectangle = Area of EDX spectra on the pillow-like silica coating.

263

264 Concerning the μ -samples directly collected on the decorated walls, the same observations were noted,
265 including pseudo-hexagonal platy hematite and strong indications of opal (S.I.1). Importantly, these
266 samples showed significant opal development, with a complete coating of the pictorial matter to the
267 extent that the morphology of the hematite was no longer observable on the surface (Figure 3).
268 Weathered hematite plates seem to have been "ingested" by the silicate coating and could only be
269 observed when a section was accessible on the surface of the sample (Figure 4 + S.I.2). However,
270 preliminary studies on the walls of Points Cave using portable spectroscopic techniques (pXRF and
271 Raman) could not identify the presence of opal coating *in situ* (Chanteraud *et al.*, 2020).

272



273

Figure 4: Hematite plates embedded in the silica coating on PRM-19-10 and PRM-19-16 μ -samples (SEM observation in SE and BSE mode).

274

275

276

4.3 Opal identification by UV-fluorescence

277

278 Fluorescence analyses were first performed on 3 flake μ -samples (μ S-ECA-03, μ S-ECA-04 and μ S-

279 ECA-05) that were previously characterized by different geochemical analyses and on which opal was

280 detected. Due to the small size of the samples (approximately 200 μ m), only a few localized spectra

281 were recorded. The spectra obtained could be divided into different emission regions depending on the

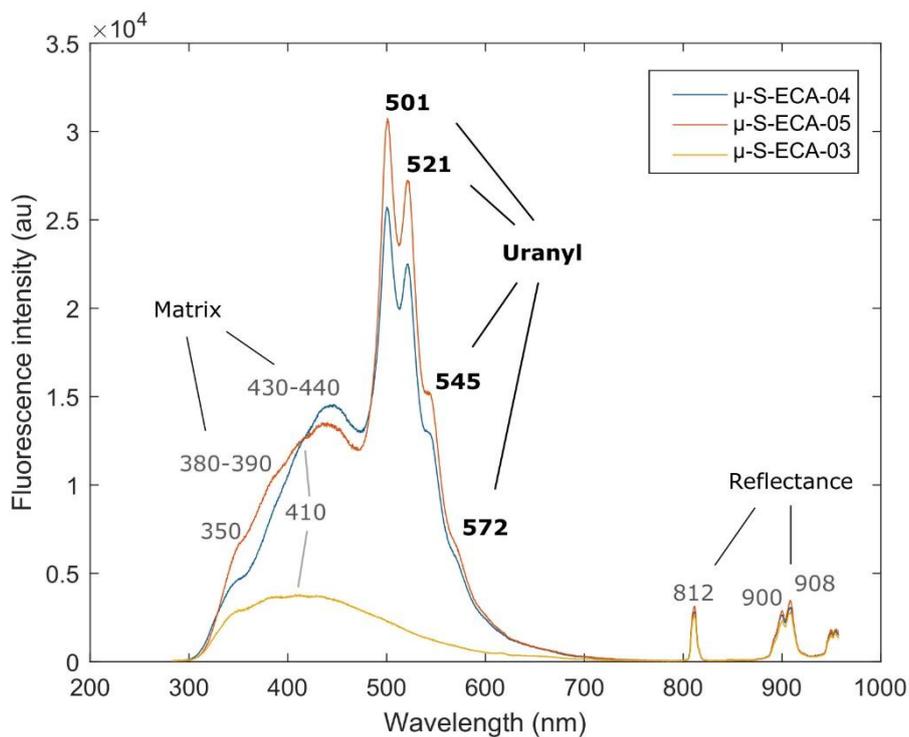
282 main signal sources (Figure 5, S.I.3):

283

284 - From 300 to 470 nm, this region corresponds to the fluorescence emission of the sample matrix.

285 Peaks and shoulders were detected at approximately 350 nm, 380-390 nm, 410 nm and 430-440
 286 nm. According to the literature, they could be associated with organic matter entrapped in the
 287 crystalline matrix (McGarry & Baker, 2000; Perrette *et al.*, 2000; Van Beynen *et al.*, 2001;
 288 Perrette *et al.*, 2005; Quiers *et al.*, 2015) or with the silica material fluorescence response to
 289 UV-light excitation (Boyko *et al.*, 2011; Garcia-Guinea *et al.*, 2013).

290
 291 - From 470 to 750 nm, special features were identified in this part of the spectra for samples μ S-
 292 ECA-04 and μ -S-ECA-05. They were characterized by a sequence of 3 defined peaks at 501,
 293 521, and 545 nm and a shoulder at approximately 572 nm. These peaks were identical in all
 294 spectra measured on μ -samples μ S-ECA-04 and μ -S-ECA-05 and coincided with the uranyl ion
 295 spectrum in silica matrices based on a review in the literature (Table 3), but were absent from μ -
 296 S-ECA-03 spectra.



297
 298 **Figure 5:** Mean fluorescence emission spectra (excitation: 266 nm) of samples μ -S-ECA-04, μ -S-
 299 ECA-05 and μ -S-ECA-03. Spectra are divided into three different regions as a function of the main

300 *fluorescence signal sources: sample matrix, uranyl ions and laser emission reflectance.*

301

302 Entrapment of uranyl ions in siliceous matrices, especially opal phases, is well documented in the
303 literature (Zielinski, 1980; Kasdan *et al.*, 1981; Kinnunen & Ikonen, 1991; Neymark *et al.*, 2000;
304 Fritsch *et al.*, 2001; Gaillou *et al.*, 2008; Devès *et al.*, 2012; Fritsch *et al.*, 2015; Othmane *et al.*, 2016).

305 The strong affinity of uranyl groups for amorphous silica leads to a strong U-opal association, which is
306 stable at the scale of geological time (Othmane *et al.*, 2016). As opal was the only silica phase
307 identified on these samples, uranyl-specific spectra could be associated, in this case, with the presence
308 of opal on samples, and UV fluorescence analysis represents an efficient tool for its identification.

309

310 As opal detection was subject to uranyl fluorescence properties, detection using UV fluorescence was
311 dependent on uranium entrapment in silica crystalline structures. In their study of opal gems from
312 different geographic and geological contexts, Gaillou *et al.* (2008) showed that not all opals are
313 fluorescent. Opal fluorescence can be divided into two classes: blue fluorescence caused by intrinsic
314 oxygen-related defects typical of amorphous silica structures and green fluorescence attributed to
315 uranyl groups (Fritsch *et al.*, 2001, 2003), which is believed to be typical of common opals. A low
316 content of U (≥ 1 ppm) automatically induces a green fluorescence response to UV light excitation.
317 This content can reach more than 100 ppm in some deposits (Gaillou *et al.*, 2008). Garcia-Guinea *et*
318 *al.* (2013) measured a uranium amount of 193 ppm in stalactites in Castañar Cave. Thus, detection of
319 opal via UV fluorescence is not systematic but common, as a low content of uranium allows
320 fluorescence emission. However, uranium concentration in Points Cave μ -samples have not been
321 measured due to the particularly thin opal layer and the impossibility of destroying μ -samples.

322

323 **Table 3:** *Fluorescence emission peaks for different opal or amorphous silica deposits reviewed in the*
324 *literature.*

Fluorescence emission peaks (nm)

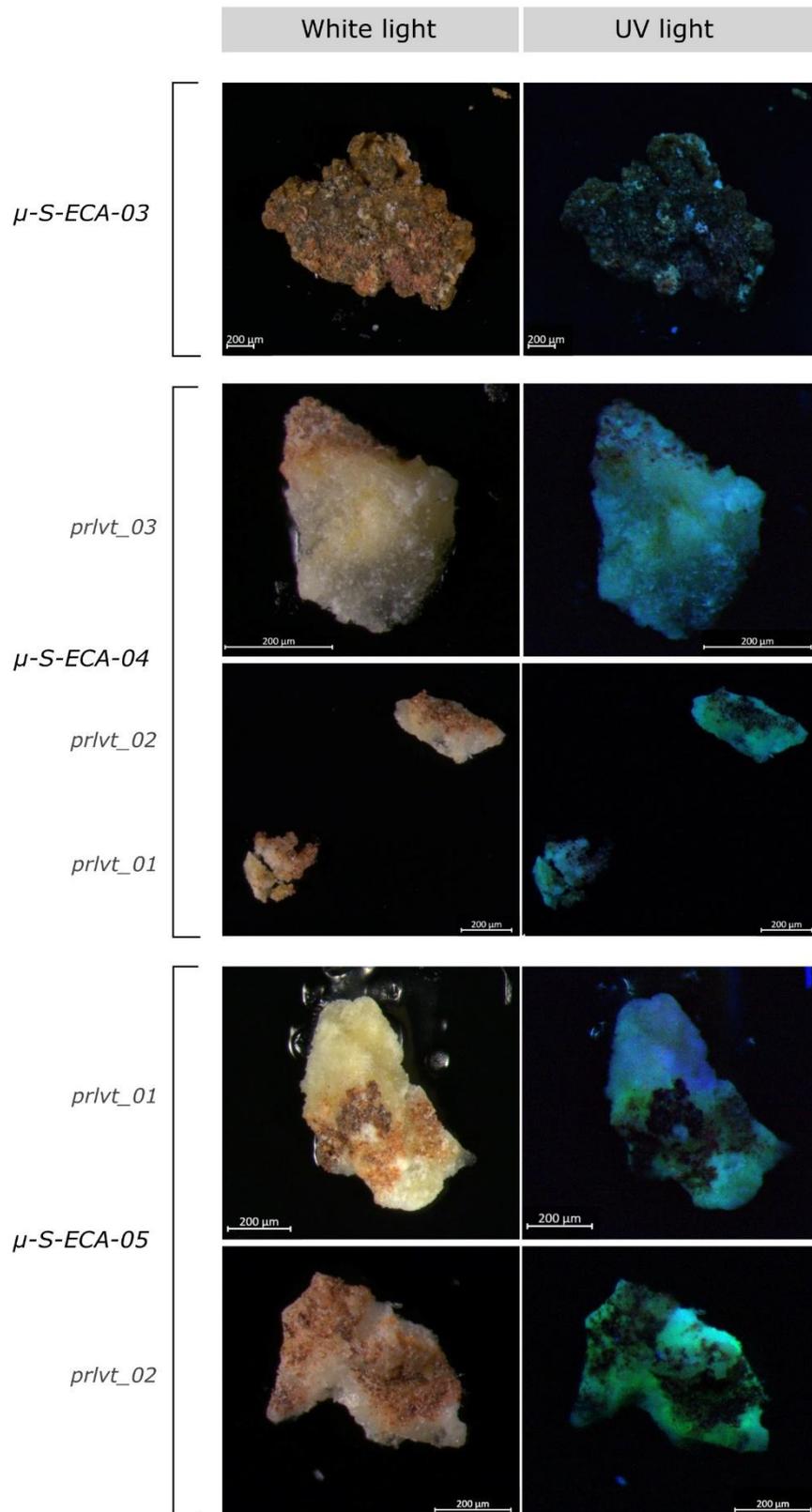
| | | | | | |
|----------------------------------|------------|------------|------------|------------|-----|
| | 504 | 524 | 546 | 570 | - |
| Othmane <i>et al.</i> 2016 | 504 | 523 | 545 | 573 | - |
| Fritsch <i>et al.</i> 2015 | 504 | 524 | 546 | 572 | 604 |
| Brennan & White 2013 | 502 | 520 | - | - | - |
| Garcia-Guinea <i>et al.</i> 2013 | 505 | 524 | 543 | 569 | - |
| <i>This study</i> | 501 | 521 | 545 | 572 | - |

325

326 *4.4 Opal visual detection under UV light*

327

328 As explained previously, minerals containing uranyl ions (UO_2^{2+}) have been known to exhibit strong
329 fluorescence marked by specific spectral features and temporal characteristics since at least early 1900
330 (deNeufville *et al.*, 1981). The bright green fluorescence of uraniferous opal is a well-known
331 characteristic of this mineral phase and has been related to the presence of uranium (Gorobets *et al.*,
332 1977; Fritsch *et al.*, 2001). To evaluate whether this specificity can be used for opal detection, flake μ -
333 samples were exposed to UV light (see 3.1.1). The results show that μ -samples μ -S-ECA-04 and μ -S-
334 ECA-05 exhibited a bright green-light response (Figure 6). These two sample spectra contained
335 specific features corresponding to the fluorescence emission of uranyl ions. Green illumination was
336 thus associated with the presence of U-opal on these samples. The case of μ -sample μ -S-ECA-03 was
337 more complex. In this case, the absence of uranyl characteristic peaks in fluorescence spectra can be
338 attributed to the low opal occurrence on the μ -sample surface as observed with SEM. However,
339 localized greenish fluorescence could be distinguished on the sample under UV light illumination.
340 This could be explained by a less precise measurement due to a more difficult targeting of opal
341 because of the higher sample size or more scattered opal distribution. Second, the sample surface was
342 more coloured and had more pictorial matter (cf. §4.1), suggesting decreased ability for detection.



343

Figure 6: Photographs of μ -samples taken on flakes under white and UV light.

344

345

4.4 From the lab to the cave

346

347

4.4.1 Comparison between UV methods

348

349 Considering that uranyl green illumination is representative of the presence of opal, detection
350 concordance between spectral and visual techniques was tested at a larger scale by comparing UV-
351 illuminated photographs with UV fluorescence cartography of flake S-ECA-05.

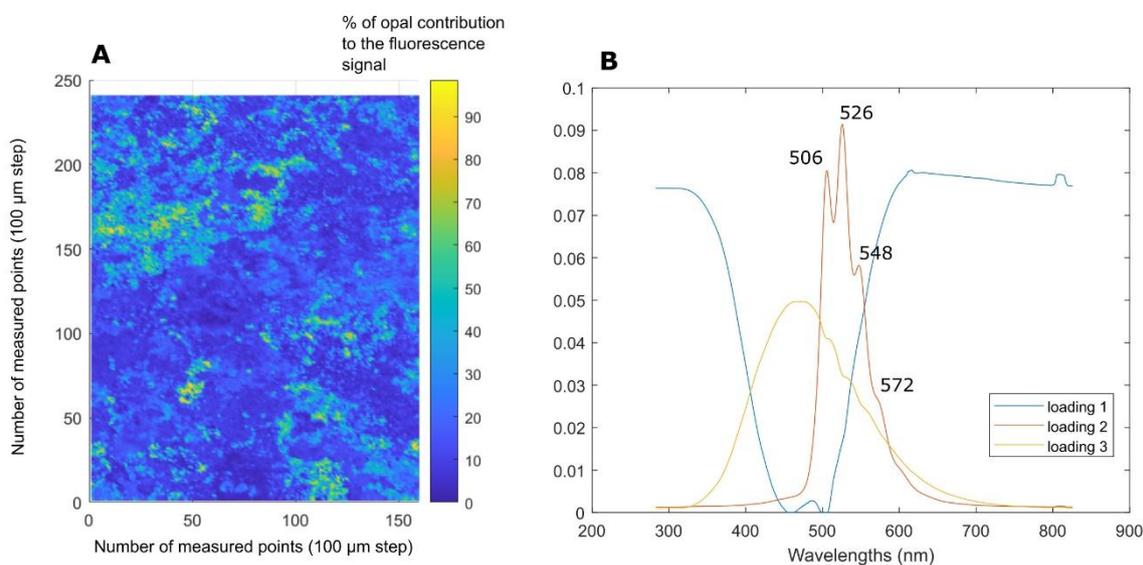
352

353 First, to evaluate UV LIF method accuracy at a larger scale, a second experiment was performed
354 directly on flake S-ECA-05. UV fluorescence cartography (100 x 100 μm resolution, S.I.4) showed a
355 range of spectra presenting uranyl spectral characteristics. Indeed, uranyl peaks present different
356 intensities or ratios compared to the fluorescence signal of the matrix, or cannot be detected.
357 Assuming that the fluorescence signal can be interpreted as a mixing of a uranyl signal with a global
358 matrix signal, opal information was extracted from fluorescence cartography using a mixing
359 algorithm, MCR-ALS, with the MCR-ALS toolbox in MATLAB software (Jaumot *et al.*, 2015).
360 MCR-ALS has become a popular chemometric method in solving mixture analytical models. It is
361 based on an additive bilinear model of pure contributions that depends on the concentration and the
362 specific spectral sensitivity of each component. This algorithm can also be applied to obtain
363 quantitative information (Jaumot *et al.*, 2005; de Juan *et al.*, 2014; Zhang & Tauler, 2013).

364

365 A singular value decomposition (SVD) method was first applied on the entire raw dataset in the MCR
366 calculation to define the number of initial loadings (S.I.5). Based on the eigen values obtained with the
367 SVD method, three components were graphically determined as mainly contributors to the
368 fluorescence signal and represent 76.8% of the explained variance. These three initial loadings were
369 then calculated in the MCR-ALS method using the PURE algorithm, a commonly used method to find
370 the purest variable. MCR-ALS was then performed based on these 3 initial loadings on the same entire

371 dataset. Non-negativity constraint was applied for model optimization. For each spectrum, model
372 results ($r^2=99.8$) provided a proportion of each recalculated loading (Figure 7). The second loading
373 represents the uranyl spectrum from which is calculated a proportion of uranyl contribution to the total
374 fluorescence signal. This contribution can be associated with a proportion of opal at the sample surface
375 for each pixel as presented in Figure 7. The other loadings correspond to the contribution of different
376 fluorescence parts in the spectra related to the matrix fluorescence (loading 3) and to some specific
377 highly intense signals at the sample surface (loading 1), probably due to particular minerals.
378



379

Figure 7: MCR-ALS results: A/ Representation of the proportion of opal in the total fluorescence signal calculated from loading 2 on the S-ECA-05 surface, B/ Loadings obtained after model optimization.

380

381 Evaluation of opal proportions on the sample using this method is, however, subject to certain biases.
382 Similar to the majority of spectroscopic techniques, this detection method can only detect surface
383 deposits. Thus, opal mineralization located under other mineral or organic deposits cannot be detected.
384 Moreover, for quantitative measurement, the measurement sensitivity to changes in sample surface

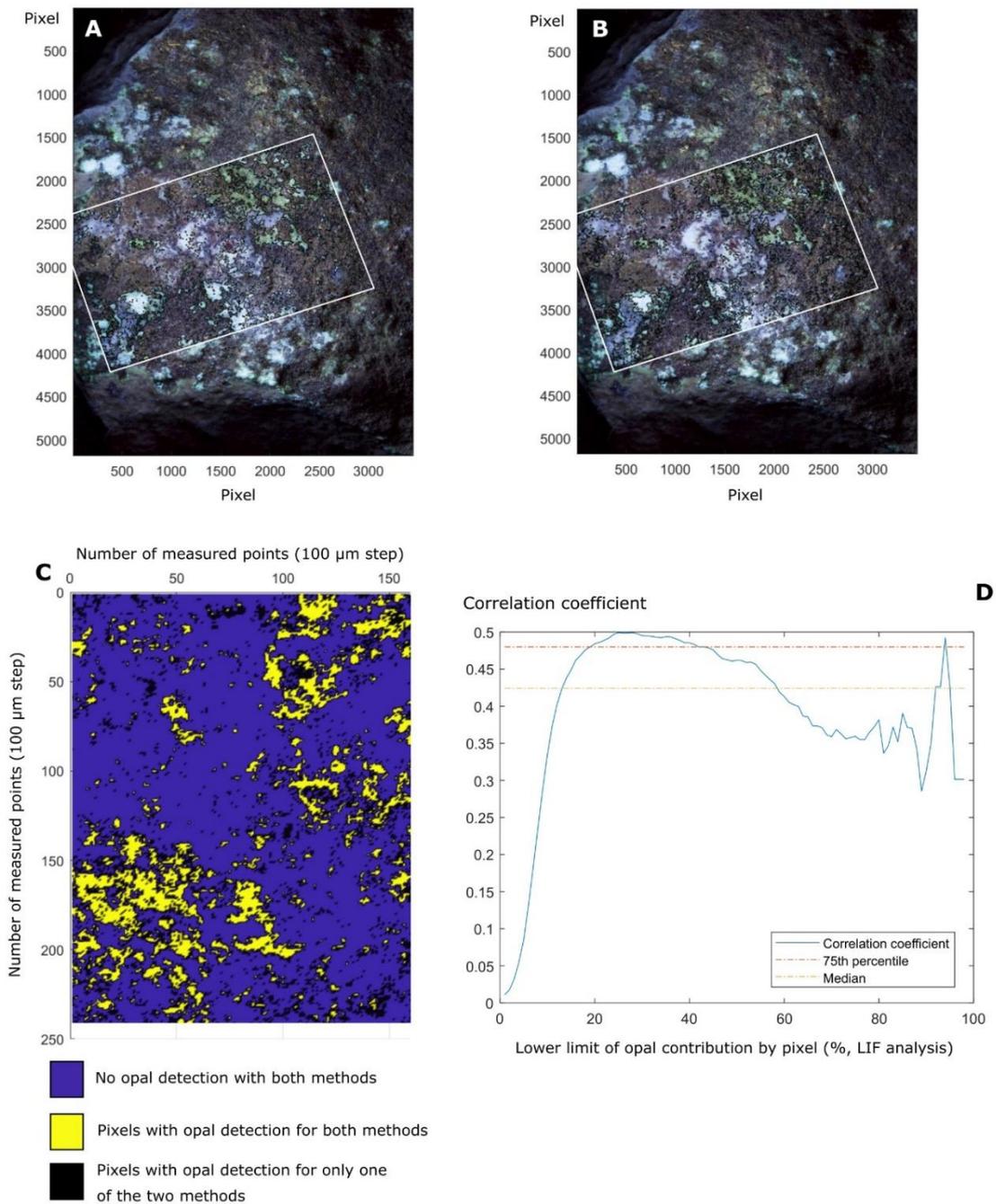
385 microtopography must be taken into account. As the laser beam is focused on the surface, variations in
386 fluorescence intensities measured on the sample, and thus opal estimations, can be biased by
387 millimetric changes in surface relief.

388
389 This method remains effective in extracting information on opal mineralization even on heterogeneous
390 matrices, such as the Points Cave μ -samples. Due to its specific spectral shape, uranyl signal can be
391 easily extracted from mixed fluorescence signals. Mixing algorithms could provide quantitative
392 information if combined with calibration methods. Indeed, the MCR-ALS algorithm has been used for
393 the quantification of different target molecules based on various spectroscopic data (Mas *et al.*, 2010;
394 Araya *et al.*, 2017; Kumar *et al.*, 2018; Castro *et al.*, 2021). Regarding sample complexity, calibration
395 protocols based on standard references and prepared or artificial mixtures are difficult to apply (Araya
396 *et al.*, 2017). Quantification strategies need to be developed for archaeological materials, reaching a
397 balance between sample destruction and model result robustness, such as those developed for
398 hyperspectral data. Then, the estimated concentration accuracy will depend on the legitimacy of the
399 assumption made in the quantification strategy (Araya *et al.*, 2017).

400
401 For field purpose, opal information provided by UV illumination and UV LIF methods were
402 compared. The green component of the RGB image was extracted from UV-light photos. The
403 grayscale image was subtracted to avoid the luminosity effect, and a threshold was applied to the
404 image obtained to select only pixels containing green colour (S.I.5). To help compare the opal
405 information provided by both techniques, images were aligned using point control selection and
406 geometric transformation functions in MATLAB.

407
408 The results show a high correspondence between spectral and visual detection methods (Figure 8). To
409 evaluate the efficiency of the optical method, opal cartographies with different detection limits were
410 simulated by modifying lower boundaries to select pixel associated with opal presence. These
411 boundaries are based on % of opal contribution to the fluorescence signal for spectroscopic

412 measurements. The best correlation coefficient ($R^2=0.50$) is obtained for an opal contribution
413 threshold of 25% of the total fluorescence signal. Graph D on figure 8 shows that optical method was
414 the most efficient when opal fluorescence emission contributed at least from 20% to 43% of the total
415 fluorescence signal of the sample. If the opal proportion limit for pixel selection is settled too low, the
416 number of pixels selected is too important to provide a good correlation and conversely. For example,
417 80% of pixels in the image were selected with a limit settled from 8% of opal contribution, providing a
418 correlation coefficient of only 0.24. The rather low correlation coefficient between both images could
419 mainly be explained by the point control selection and geometric transformation applied to readjust
420 them together. Angle disposition of the sample and detector combined with image resolution could
421 have led to difficulties in adjusting the images. Further research in the computational image domain
422 could improve the methodology and enhance the correlation between the two techniques.
423



424

Figure 8: Comparison of detection of opal mineralization on flake S-ECA-05 with UV illumination and UV LIF. A and B/ Photo under UV light and contour plot (black line) of opal presence calculated from the green component of the image (at least 8% of green) and from the MCR results (contribution of at least 25% of the total fluorescence) respectively for A and B, after geometric transformation (white square). C/ Cartography of pixels associated with the presence of opal comparing A and B (no

geometric transformation). D/ Correlation coefficient between opal presence images obtained with the two methods (% of opal contribution correspond to lower boundaries applied for pixels selection).

425

426 *4.4.2 Visual detection under UV light: field experiments*

427

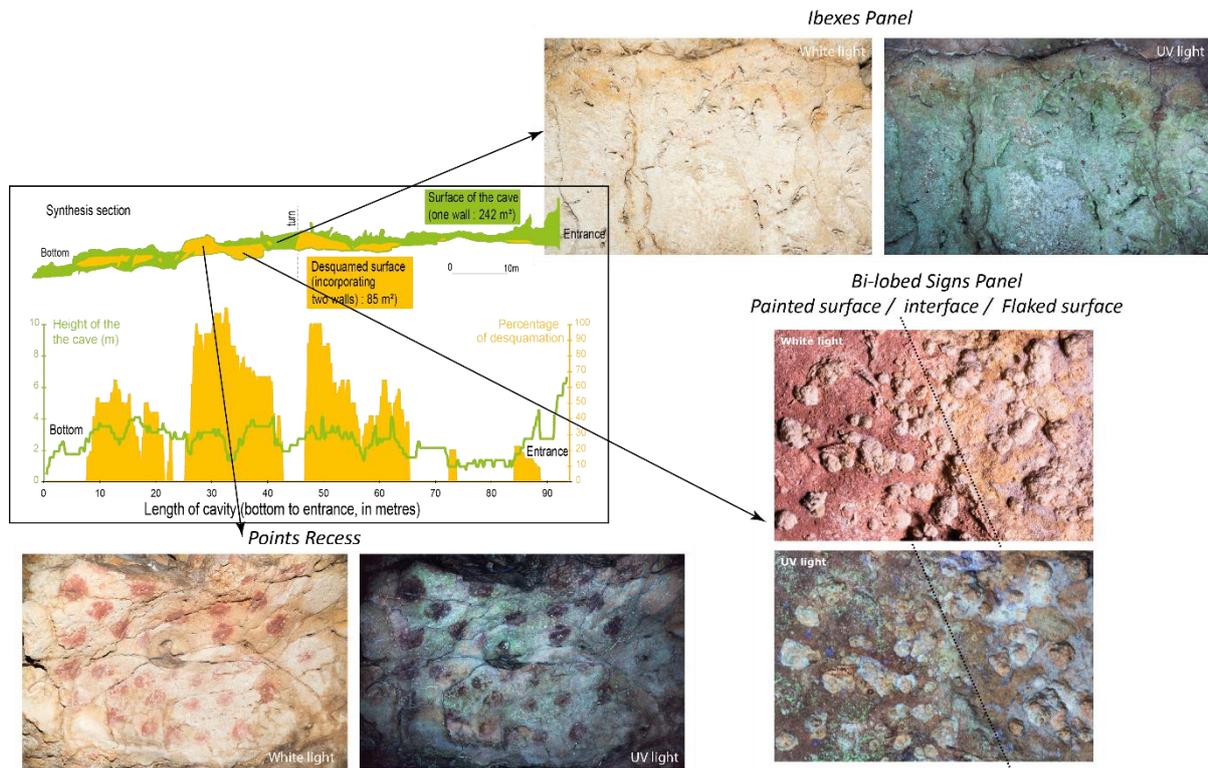
428 An *in situ* photographic protocol that alternated white light and UV illumination was applied to the
429 Points Cave walls. As shown in Figure 1, three rock art panels and one wall devoid of any rock art
430 were investigated. Pictures were taken at both the wall and macroscopic scales.

431

432 At the wall scale, the rock art panels investigated (Points Recess, Bi-lobed Signs and Ibexes) displayed
433 large green fluorescent zones when illuminated by UV LEDs (Figure 9). This green fluorescence
434 response was consistent with preliminary results obtained in the laboratory on cave wall flakes and μ -
435 samples from these zones. Thus, UV illumination successfully enabled the detection of opal coatings
436 on these walls, according to the green response observed in photographs.

437

438 In contrast, no opal signal appeared clearly distinguishable in photographs of the wall situated a few
439 metres before the art panel (S.I.7). These photographs displayed greenish fluorescence mixed with
440 other signals, making it difficult to identify and extract green colour with accuracy. Spectroscopic
441 measurements need to be performed to precisely identify the presence of opal.



442

443 *Figure 9: Topographic section of Points Cave with estimated flaking rate of the cave walls according*
 444 *to the distance to the entrance and location of white and UV light photographs according to Jaillet &*
 445 *Monney, 2018.*

446

447 Macroscopic-scale observations under UV light allowed the targeting of specific deposits or zones on
 448 cave walls. In the particular case of the Bi-lobed Signs panel, macroscopic investigation targeting
 449 flaked zones revealed a contrast between the well-preserved rock art panels and the afterwards flaked
 450 areas. Indeed, the painted surface of the UV photograph (left part of photograph, Figure 9) displayed
 451 numerous green fluorescent spots, whereas they were absent from the right part of the photograph.
 452 Efflorescence concretions on cave walls, which are widely spread in Points Cave, were also
 453 investigated, but the presence of opal has not yet been validated.

454

455 **5. Discussion: Implications of opal detection for rock art studies at Points Cave**

456

457 5.1 Contribution of UV fluorescence techniques

458

459 According to the first results obtained using the *in situ* UV illumination method and the preliminary
460 results obtained in the laboratory on cave wall flakes and μ -samples from rock art panels, *in situ*
461 measurements successfully detected the presence of opal in Points cave. Indeed, the green
462 fluorescence observed on Points Recess, Bi-lobed Signs and Ibexes panels suggests that opal
463 development covers a large area of cave walls, especially in rock art sector. Macroscopic observations
464 also help to provide initial insights into rock art-opal interactions, as UV light allows for the targeting
465 of specific deposits or zones on cave walls. It provides complementary information on opal
466 distribution and interaction with archaeological material. For example, investigation of the flaking
467 zone suggests a current absence of extended opal film or opal mineralization, probably due to
468 desquamation occurring on this wall.

469

470 However, the opal signal is not always clearly distinguishable, as observed on the wall outside of the
471 rock art sector or on coralloid concretions. Yet, these speleothems are known to contain a silica layer
472 enriched with uranium (Barbarand & Nouet, 2020). Alternating layers of silica and calcite or the
473 presence of calcite cover could explain the ambiguous signal. First, this highlights the need for *in situ*
474 fluorescence spectroscopic measurements to validate the photographic identification of the opal
475 mineral phase in cases where the green response is not clearly detectable. Second, colour perception
476 varies greatly from one image to another, even within the same site, making it difficult to evaluate the
477 mineral phase distribution. Even if camera and image treatment parameters influencing colour display
478 (white balance, exposure time, filters, etc.) can be easily standardized, lighting variations (LED
479 orientation, position, distance from wall, etc.) are difficult to homogenize. As this paper presents
480 preliminary results attempting to validate the detection method, no protocol for colour calibration was
481 applied on UV photographs. Further research on the Points Cave site will be subject to the
482 development of a colour calibration procedure.

483

484 Finally, UV illumination also highlights various types of deposits, sometimes not clearly detected
485 under white light. After fluorescence analyses in the laboratory or directly *in situ*, this technique could
486 help to detect other mineral or organic phases. Moreover, it is interesting to note that UV illumination
487 emphasizes the presence of pigments due to their iron composition. Indeed, iron ions are known to
488 have a quenching effect on the fluorescence signal, including that of uranyl ions (Backes, 2004;
489 Gaillou *et al.*, 2008; Chen *et al.*, 2011). Thus, pigments appear clearly as no fluorescence zones on UV
490 photographs, which can be an interesting tool for rock art analysis, such as determination of sampling
491 protocol or dermatoglyph analysis.

492

493 UV methodology appears to be an efficient non-invasive tool for the *in situ* identification of U-silica
494 mineralization, and of U-opal mineralization in this case. Due to the green fluorescence resulting from
495 UV excitation, it allows rapid *in situ* detection of the opal mineral phase with direct results and very
496 simple and low-cost equipment. As this method has already been applied with success in some caves,
497 rarely calcareous, for the detection of U-silica complex deposits or concretions, as in Castañar Cave
498 (Garcia-Guinea *et al.*, 2013), this study differs in two ways. First, to our knowledge, this method has
499 never been applied to opal detection in a rock art context. Second, we propose *in situ* opal
500 identification based on spectral features for result validation using a portable UV LIF instrument. This
501 instrument is currently in development and could not yet be taken into the cave, but preliminary tests
502 applied to flakes in the laboratory confirm its ability to detect opal. Finally, opal mineral
503 characterization can also be achieved with high-spatial resolution at the microscopic scale with a
504 laboratory UV LIF instrument. Spatially high-resolution fluorescence maps can also provide more
505 information on mineral phase repartition, development and interaction with other organic and mineral
506 phases present on the sample. Thus, the combination of these two methodologies provides a complete
507 solution for the identification and detection of opal mineralization in both sampling and analytical
508 strategies and *in situ* characterization.

509

510 5.2 What we know about Points Cave opal

511

512 The results obtained with the analyses presented in this paper and with UV methods applied to
513 samples and *in situ* have provided the first information on opal coatings in Points Cave. Indeed, based
514 on SEM analyses of flakes and μ -samples, Points Cave opal can be identified as the amorphous opal
515 type (type A). XRD is usually performed for precise opal type determination (Curtis *et al.*, 2019).
516 However, in the case of Points Cave opal, this analysis is difficult to perform due to the thinness of the
517 opal layer and to the presence iron-rich pigments. Analyses at macro- and microscopic scales suggest
518 thin film deposition as a mineralization type, such as silica skins observed at various rock art sites
519 (Watchman, 1990; Green *et al.*, 2017). This film appears to be deposited under or at the interface with
520 pigment and other crusts. SEM analyses show that the opal structure encapsulates hematite plates on
521 several samples, suggesting strong interactions with pictorial matter (Figure 4). Further studies must
522 be conducted to understand how these two phases interact, but a preliminary hypothesis regarding
523 dissolution and corrosion of hematite plates by opal can be proposed.

524

525 The presence of uranyl ions entrapped in the opal structure was verified by UV spectroscopic analyses.
526 High fluorescence intensities of opal at Points Cave suggest significant content of uranium trapped in
527 the crystalline structure. Similar enrichment in uranium has been found in numerous common opals
528 (Amelin & Back, 2006). However, at Points Cave, no quantification of uranium content has yet been
529 realized. Although uranium isotopic measurements were realized on speleothems from Points Cave
530 (stalagmites and coralloids), because of their destructive character, none was applied on flakes, or
531 flake and wall μ -samples. According to the literature, as no minerals containing U^{4+} are known to
532 fluoresce, uraniferous silica precipitation involves oxidizing conditions sufficient to mobilize U^{6+}
533 (Zielinski, 1982). For example, Garcia-Guinea *et al.* (2013) explained uranium-bearing opal
534 deposition in Castañar Cave by oxidation of host rocks with meteoritic waters. Zielinski (1982)
535 explained that the initial precipitation of silica was as an amorphous silica gel, with which dissolved
536 uranium coprecipitated before the silica gel dehydrated to form opal. The formation of uranyl-silica
537 complexes is favoured by the natural affinity between aqueous uranyl ions and the silica gel surface,

538 which is very sensitive to pH (optimum range = pH 5-5.5) (Garcia-Guinea *et al.*, 2013).

539

540 The *in situ* approach shows an important spread of this coating on Points Cave walls, especially on
541 rock art panels. Concerning the undecorated walls a few metres away from the rock art sector, the
542 presence of opal needs to be confirmed by spectroscopic measurement and laboratory analyses. Points
543 Cave chronology is constrained by different periods marked by cave wall evolution under climatic and
544 anthropogenic factors (Monney & Jaillet, 2019). The presence of opal mineralization throughout its
545 formation and developmental processes could provide insights into cave chronology. A flaking period
546 was identified subsequent to the rock art phase, resulting from mechanical expansion or desquamation,
547 affecting the deepest zones of the cave, and possibly concurrent with gelifraction at the end of MIS2
548 (Marine Isotope Stage) and/or beginning of MIS1 (Monney & Jaillet, 2019). As described previously,
549 UV photographs indicated the absence of a well-developed opal film in the flaking zone, suggesting
550 that opal formation occurred principally before this flaking period. This could also explain why
551 photographs taken on walls between the cave angle and the rock art sectors displayed less marked
552 fluorescence, as this zone presents high flaking rates (Jaillet & Monney, 2018) (Figure 9).

553

554 The chronology of opal deposits over rock paintings and drawings cannot be confirmed at this stage.
555 SEM observations show that opal mineralization colonizes empty spaces above, below, and inside
556 pictorial matter. These observations suggest an opal deposition subsequent to painting realization,
557 although prior mineralization cannot be ruled out.

558

559 Thus, ongoing studies are crucial in completing opal coating characterization in Points Cave. This is a
560 tool in understanding cave wall and pigment interactions throughout the factors and processes of opal
561 formation and other mineralization.

562

563 *5.3 Opal factors and formation*

564

565 Mineralization origin and formation mechanisms and factors are clues for understanding past climate
566 and cave wall evolution. As this paper presents preliminary results, only hypotheses for opal origin
567 and formation are presented.

568

569 Opal, as a hydrated mineral, is associated with fluid circulation. Thus, water is generally involved in
570 precipitation, and silica has to be in solution before precipitation (Chauviré *et al.*, 2017). In Points
571 Cave, the presence of silica coating with high uranium content in the limestone context supports the
572 hypothesis of mineralization originating from groundwater. Wall humidification and water
573 physicochemical properties directly influence the coating formation rate. In very wet sites, the silica
574 skin growth rate can reach 0.25 mm per millennia, whereas occasionally wet sites present a
575 mineralization rate on the order of 0.02 mm per millennia (Aubert *et al.*, 2004). Silica coatings can
576 only be formed and preserved if low infiltration volumes occur, as higher volumes favour dissolution
577 of soluble compounds and decrease silica precipitation (Aubert *et al.*, 2004).

578

579 Chauviré *et al.* (2017) explained that even though opal is found in various geological contexts, three
580 main types of formation can be identified: 1) hydrothermal activity, 2) biological precipitation and 3)
581 continental weathering. As no hydrothermal activity was identified at Points Cave, only the latter two
582 types can be involved in opal formation at this site.

583

584 Biological formation of opal in caves is less documented than hydrothermal alteration and continental
585 weathering. Various microbial forms and algae have been observed to be associated with opal in
586 caves, such as siliceous algal diatoms (Northup *et al.*, 2001), and are often linked to coralloid
587 concretions. In the case of Points Cave, a few microscopic and cave wall μ -sample observations show
588 undetermined structures containing high carbon content, which could be associated with biological
589 activity. Nevertheless, the hypothesis of biological formation of opal cannot be ruled out or confirmed
590 at this stage.

591

592 Continental weathering is defined by rock transformation by meteoric water and a precipitation
593 temperature below 50°C, in contrast to hydrothermal alteration (Chauviré *et al.*, 2017). Silica anions
594 released by this process precipitate because of fluid supersaturation due to various changes in
595 conditions, such as pH or temperature (Devès *et al.*, 2012; Chauviré *et al.*, 2017). Thus,
596 supersaturation of silica solutions may be initiated by a drop in temperature or pH, or an increase in
597 salinity. When a solution is supersaturated in SiO₂, silicic acid could polymerize to form a colloidal
598 suspension from which amorphous silica can precipitate. Polymerization is controlled by temperature
599 (decreasing T° increases the polymerization rate), degree of supersaturation, salinity and mainly pH
600 (maximum polymerization rate around pH 7.5; minimum polymerization rate under pH 3 and above 9)
601 (Devès *et al.*, 2012). One of the most efficient pH-driven mechanisms for silica precipitation involves
602 acidification of highly alkaline solutions (Zielinski, 1982). Such alkaline conditions are not common,
603 but in the case of calcite-dominant material in sediment, pH could reach this threshold (Karkanis *et*
604 *al.*, 1999). Freezing temperature has also been shown to help supersaturation, polymerization and
605 rapid precipitation of opal, whereas low or moderate temperatures induce slow polymerization
606 (months or years) (Devès *et al.*, 2012). Cryo-segregation is another reported genesis, caused by
607 moisture freezing on cave walls, which concentrates dissolved salts. They precipitate out in the case of
608 supersaturation of the solution (Devès *et al.*, 2012). As opal formation probably occurred during the
609 Late Pleistocene possibly up until the Tardiglacial era and because freezing temperatures have been
610 shown to have modified Points Cave wall topography, a temperature decrease represents a realistic
611 factor for opal formation. However, there is currently a lack of evidence to confirm this hypothesis.

612

613 To help understand opal formation, the source of silica and uranium forming this mineralisation can
614 also be questioned. Silica can originate from 1) superficial cover, 2) host rock, or 3) volcanic ash in a
615 continental weathering context (Devès *et al.*, 2012). Volcanic ash is an interesting hypothesis, as it is
616 assumed to provide both high contents of silica and uranium, and because the Ardèche region had
617 recent volcanic episodes during the Upper Palaeolithic. Indeed, volcanic eruptions in the Bas-Vivarais
618 region were dated between 23.9 ± 8.1 ka and 31.1 ± 3.9 ka (Nomade *et al.*, 2016; Sasco *et al.*, 2017).

619 The current alluvial plain and the lowest former alluvial level (+8 m) deposits contain much basaltic
620 material partly derived from Bas-Vivarais lava, which were subjected to intense erosion and
621 weathering in the alluvium terraces (Genuite *et al.*, 2021). Thus, the location and chronology of the
622 volcanic activity (approximately 45 km away from Points Cave) represent an interesting origin
623 hypothesis for both silica and uranium contents in opal. However, determining the origin of uranyl-
624 enriched silica solutions is difficult with our current information. Another hypothesis for silica
625 solution origin can be supported by the presence of a marl layer within the Urgonian limestone, which
626 constitutes the cave environment (Sadier, 2013); or by pebbles originating from former fluvial deposits
627 originated from the Ardèche River and providing silica by infiltration from the overlaying alluvium
628 terrace or by river deposition (Mocochain *et al.*, 2009; Tassy *et al.*, 2013; Genuite *et al.*, 2021).

629
630 Thus, understanding the origin and mineralization factors that influence opal formation could provide
631 information on chemical and physical processes occurring on the cave wall surface. According to
632 Green *et al.* (2017), this knowledge is “crucial for targeted sample collection and the application of a
633 range of dating techniques as well as for the development of conservation strategies”.

634

635 *5.4 Chronology and dating*

636

637 Red pigments used in rock art are difficult to date precisely (Aubert *et al.*, 2007). Thus, several studies
638 have proposed indirect dating methods using associated mineral deposits interlaying pictorial matter to
639 date or to provide chronological constraints on rock paintings (Watchman, 1990; Aubert *et al.*, 2007;
640 Aubert *et al.*, 2017), such as opal coatings.

641

642 Indeed, in the first place, opal coating could help to precise relative chronology thanks to knowledge
643 regarding climatic and environmental factors controlling its mineralization, and to its distribution on
644 walls in comparison to other deposits and archaeological material.

645

646 Amorphous silica skins have been used for radiocarbon analyses based on organic remains trapped by
647 mineralization, such as diatoms or algal matter, on different Australian rock art sites (Watchman,
648 2000; Morwood *et al.*, 2010). However, as silica coatings may contain various organic materials, each
649 presenting a specific radiocarbon signature, dating could result in a mixture of different ages by
650 incorporation of younger or older material (Aubert *et al.*, 2017; Green *et al.*, 2017). In addition, the
651 formation processes of these coatings are not fully understood, requiring great caution when using
652 radiocarbon methods (Aubert *et al.*, 2017). Using compound-specific carbon analyses could
653 potentially avoid this problem (Aubert *et al.*, 2017) but are more difficult to apply to thin deposits,
654 especially in rock art contexts.

655

656 Moreover, opal often contains high uranium contents, which could be used for high-precision dating
657 with methods such as $^{230}\text{U}/\text{Th}$ or U/Pb (Zielinski, 1980; Oster *et al.*, 2017). Because of opal's ability to
658 concentrate uranium from water while rejecting Pb and Th, amorphous silica is an interesting
659 alternative to carbonate minerals (Amelin & Back, 2006). Indeed, $^{230}\text{Th}/\text{U}$ and U/Pb methods have
660 been applied to opal and have provided reliable ages (Neymark & Paces, 2013). They enable
661 chronological constraints or dating hydrogenic subsurface water flow, pedogenesis, and processes
662 such as ore formation deposits (Neymark & Paces, 2013). They also have been applied in the case of
663 paleoclimate reconstruction in silica speleothem studies (Lundberg *et al.*, 2010). Depending on the
664 formation processes, opal coating could thus be used for dating purposes.

665

666 In rock art research, dating of amorphous silica deposits could be used as an age constraint for rock
667 drawing events, depending on the pigments and mineral phase superimposition. In their study, Aubert
668 *et al.* (2007) performed U-series dating on a 2.5 mm thick calcite coating using the MC-ICPMS
669 technique, allowing high spatial and temporal resolution. Even though only micrograms of samples are
670 needed, authors (Aubert *et al.*, 2007; Aubert *et al.*, 2017) have suggested that for samples with U
671 concentrations > 1 ppm, sampling could be largely reduced, and LIBS techniques could also be
672 applied *in situ* with a 100-200 μm diameter ablation spot. As opal concentrates more U than calcite,

673 these techniques appear to be possible. However, for some authors, the application of uranium series
674 dating to silica skins appears difficult to achieve (Green *et al.*, 2017). Sampling that provides sufficient
675 intact fragments for LA-ICP-MS analysis without damaging rock paintings is one of the main issues
676 regarding this application. The difficulty of performing closed system conditions and replicability tests
677 for evaluating dating reliability has also been highlighted by authors.

678
679 Moreover, methods for opal detection could offer supplemental help before sampling for dating.
680 Indeed, precise targeting of uranium-bearing opal enables identification of pure silica phases in mixed
681 samples, detection of high uranium contents or impurity avoidance. In the case of thin layer deposits,
682 such as in coralloids, sampling could decrease dating accuracy when mixing different layers (Devès *et*
683 *al.*, 2012). Tracking the location of opal phases could avoid this issue by spatially constraining
684 sampling.

685 686 *5.5 Implication of opal mineral characterization for conservation of rock art material*

687
688 Taphonomy represents a range of transformations affecting archaeological material that distort
689 archaeological records. Thus, rock paintings have undergone a plurality of transformations impacting
690 pigment longevity, colour and identification (Bednarik, 1994; Huntley, 2012; Chalmin *et al.*, 2018;
691 Rousaki *et al.*, 2018; Defrasne *et al.*, 2019). At Points Cave, the extensive presence of dermatoglyphs
692 on 47 palm prints is exceptional (Achtelik *et al.*, 2019). In fact, to our knowledge, it has no equivalent
693 in European Palaeolithic cave art which raises the question of opal impact on pigment conservation.

694
695 If pigment weathering can be influenced by their own properties by inducing changes in surface area,
696 albedo, light transmissivity or moisture (Huntley, 2012), mineral deposits have been recognized to be
697 important factors in rock art taphonomy (Chalmin *et al.*, 2018). In addition to analytical impacts,
698 knowledge of mineral phases is essential because it informs us regarding the physical and chemical
699 impacts on pictorial matter and whether they favour conservation or degradation effects. Mineral

700 phase characterization is thus an important part of conservation strategies, and adapted identification
701 and analytical methods are needed.

702
703 The association of silica skins composed of opal and pigments has been frequently observed at rock art
704 sites, mainly in open-air sites on sandstone and quartzite substrates in Australia or Canada (Watchman,
705 1990; Aubert *et al.*, 2004; Aubert *et al.*, 2012; Huntley, 2012). Some studies have suggested that
706 pigment binding in silica coatings aids rock art visual preservation (Watchman, 1990), providing a
707 resistant layer to chemical weathering. SEM observations on Points Cave flake and wall μ -samples
708 indeed suggest a strong interaction between pigments and opal, as mineralization penetrates pigment
709 deposits. If the quality of Points Cave paintings tends to corroborate this hypothesis, exfoliation
710 impacting silica skins observed at some sites should also be mentioned, as it could cause removal of
711 associated pigments (Aubert *et al.*, 2004; Green *et al.*, 2017). Thus, exploiting the observed benefits of
712 silica film deposits for conservation strategies has not yet been proven (Green *et al.*, 2017).
713 Furthermore, it has also been observed at open-air sites that silica skins could reduce the colour tone of
714 paintings and drawings at some locations (Green *et al.*, 2017).

715

716 **6. Conclusion**

717

718 The methodological development proposed in this paper was motivated by the presence of opal in
719 cave art context at Points Cave. Its identification *in situ*, in the laboratory, on centimetric objects and
720 on μ -samples questions the possibility of accessing the specificities of the colouring matter applied on
721 the walls (petrography and geochemistry). Therefore, *in situ* identification of silica coating observed in
722 the laboratory was crucial for further studies on pigment characterization.

723

724 The results obtained on flakes and flake μ -samples from Points Cave show that UV LIF is an efficient
725 technique to detect and identify uranyl-silica complexes, even on heterogeneous and complex surfaces.

726 Although opal coating detection is limited by the outcropping nature of the deposit, UV LIF
727 spectroscopy offers a rapid and non-invasive tool that can easily be brought to the site and positioned
728 in front of the rock art panels. A photograph of green bright fluorescence emitted by opal was used
729 here as a method for *in situ* detection of this mineral coating. A comparison with the UV LIF method
730 shows a great correspondence between the two methods. The first tests of UV illumination in the cave
731 highlight the need to develop an accurate measurement protocol, especially to homogenize light and
732 colour, and the need to validate the identification using UV LIF spectroscopy. In addition to further
733 methodological development, UV optical technique shows great potential because it successfully
734 detects the presence of opal and its distribution on rock art panels.

735

736 The results obtained with our methodology provide insights into disturbances in the classical *in situ*
737 spectroscopic analyses (pXRF) observed at Points Cave (Chanteraud *et al.*, 2021). The identification
738 and characterization of opal coating is thus essential because its impact on *in situ* analysis could
739 disturb the detection of iron-oxide spectroscopic signal in case of Raman analysis for example. For
740 this reason, we propose early, on-site observations combined with sampling of surrounding material,
741 such as fallen flakes from cave walls, as an alternative strategy to i) characterize pigment-associated
742 mineral phases, ii) choose the best site-adapted combination of techniques and devices for *in situ*
743 analyses and iii) define laboratory analytical strategies depending on the pictorial matter environment.
744 Moreover, optical methods with *in situ* visual detection, such as the UV light illumination method
745 proposed in this paper, represent an interesting tool to add to sampling and analytical strategies.
746 Visualization at a larger scale of the presence and distribution of mineral deposits that could interfere
747 with pigment analyses is a great help in locating sampling or *in situ* measurements to avoid
748 interference.

749

750 In addition to analytical impacts, the detection and identification of mineral phases can provide
751 valuable information on the pigment environment and human practice chronology. If speleothems are
752 considered an accurate archive for past climate and environment, other mineral deposits could provide

753 informative records on the setting and evolution of archaeological evidence. Applying a specific
754 methodology for their characterization is thus an efficient tool in improving rock art knowledge.

755

756 Thanks to opal mineralization detection utilizing UV methodologies on cave walls, a discussion on its
757 formation and associated factors, such as climatic, hydrologic or geomorphologic conditions over time
758 can be started. Thus, the mineral form described as opal can provide elements on cave natural history.

759

760 **Acknowledgements**

761

762 We would like to thank Frédérique Charlot, microscopist at CMTC (INPE, Grenoble).
763 Funding was provided by ANR LabCom SpecSolE, DRAC Occitanie, DRAC AURA
764 (Pigmentoθήque project), French Ministry of Culture and University Savoie Mont Blanc.

765

766 **Conflict of interest disclosure**

767 The authors declare they have no conflict of interest relating to the content of this article.

768

769 **Data, script and code availability**

770 *S.I.1. Macroscopic pictures and SEM data of flakes μ -samples:*

771 <https://doi.org/10.6084/m9.figshare.16832593.v2>

772 <https://doi.org/10.6084/m9.figshare.16832557.v3>

773 <https://doi.org/10.6084/m9.figshare.16832452>

774 <https://doi.org/10.6084/m9.figshare.16832605>

775

776 *S.I.2. Macroscopic pictures and SEM data of rock art μ -samples:*

777 <https://doi.org/10.6084/m9.figshare.19142243.v1>

778 <https://doi.org/10.6084/m9.figshare.19142267.v1>

779 <https://doi.org/10.6084/m9.figshare.19142276.v1>

780 <https://doi.org/10.6084/m9.figshare.19142300.v1>

781 <https://doi.org/10.6084/m9.figshare.19142351.v1>

782 <https://doi.org/10.6084/m9.figshare.19142354.v1>

783 <https://doi.org/10.6084/m9.figshare.19142366.v1>

784 <https://doi.org/10.6084/m9.figshare.19142372.v1>

785 <https://doi.org/10.6084/m9.figshare.19142375.v1>

786 <https://doi.org/10.6084/m9.figshare.19142381.v1>

787 <https://doi.org/10.6084/m9.figshare.19142384.v1>

788 <https://doi.org/10.6084/m9.figshare.19142387.v1>

789

790 *S.I.3. Single UV fluorescence measurement (raw data):*

791 <https://doi.org/10.6084/m9.figshare.16837180.v1>

792

793 *S.I.4. UV fluorescence cartography measurement (raw data):*

794 <https://doi.org/10.6084/m9.figshare.16837324.v3>

795

796 *S.I.5. UV fluorescence data processing (Matlab script):*

797 <https://doi.org/10.6084/m9.figshare.16837405.v2>

798

799 *S.I.6. pXRF result of in situ analysis at the Points Cave:*

800 <https://doi.org/10.6084/m9.figshare.9791405.v1>

801 <https://doi.org/10.6084/m9.figshare.9791210.v1>

802

803 *S.I.7. In situ UV photographs*

804 <https://doi.org/10.6084/m9.figshare.19316588.v1>

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