



**HAL**  
open science

**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)**

Marine Quiers, Claire Chanteraud, Andréa Maris-Froelich, Emilie Chalmin, Stéphane Jaillet, Camille Noûs, Sébastien Pairis, Yves Perrette, Hélène Salomon, Julien Monney

► **To cite this version:**

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)

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# 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)

Marine Quiers <sup>a\*</sup>, Claire Chanteraud <sup>b,c</sup>, Andréa Maris-Froelich <sup>a</sup>, Émilie Chalmin-Aljanabi <sup>c</sup>, Stéphane Jaillot <sup>c</sup>, Camille Noûs <sup>e</sup>, Sébastien Pairis <sup>d</sup>, Yves Perrette <sup>c,b</sup>, Hélène Salomon <sup>c</sup>, Julien Monney <sup>c</sup>

<sup>a</sup>Laboratoire Commun SpecSolE, Envisol – CNRS - Univ. Savoie Mont Blanc, Chambéry, 73000, France

<sup>b</sup>Missouri University Research reactor - University of Missouri 65203 Columbia MO

<sup>c</sup>EDYTEM UMR5204, CNRS, Univ. Savoie Mont Blanc, Chambéry, 73000, France

<sup>d</sup>Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, Grenoble, 38000, France

<sup>e</sup>Laboratoire Cogitamus, 1 ¾ rue Descartes, Paris, 75005, France

\* Corresponding author: [m.quiers@envisol.fr](mailto:m.quiers@envisol.fr)

### 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  $\mu$ -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  $\mu$ -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,  $\mu$ -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**

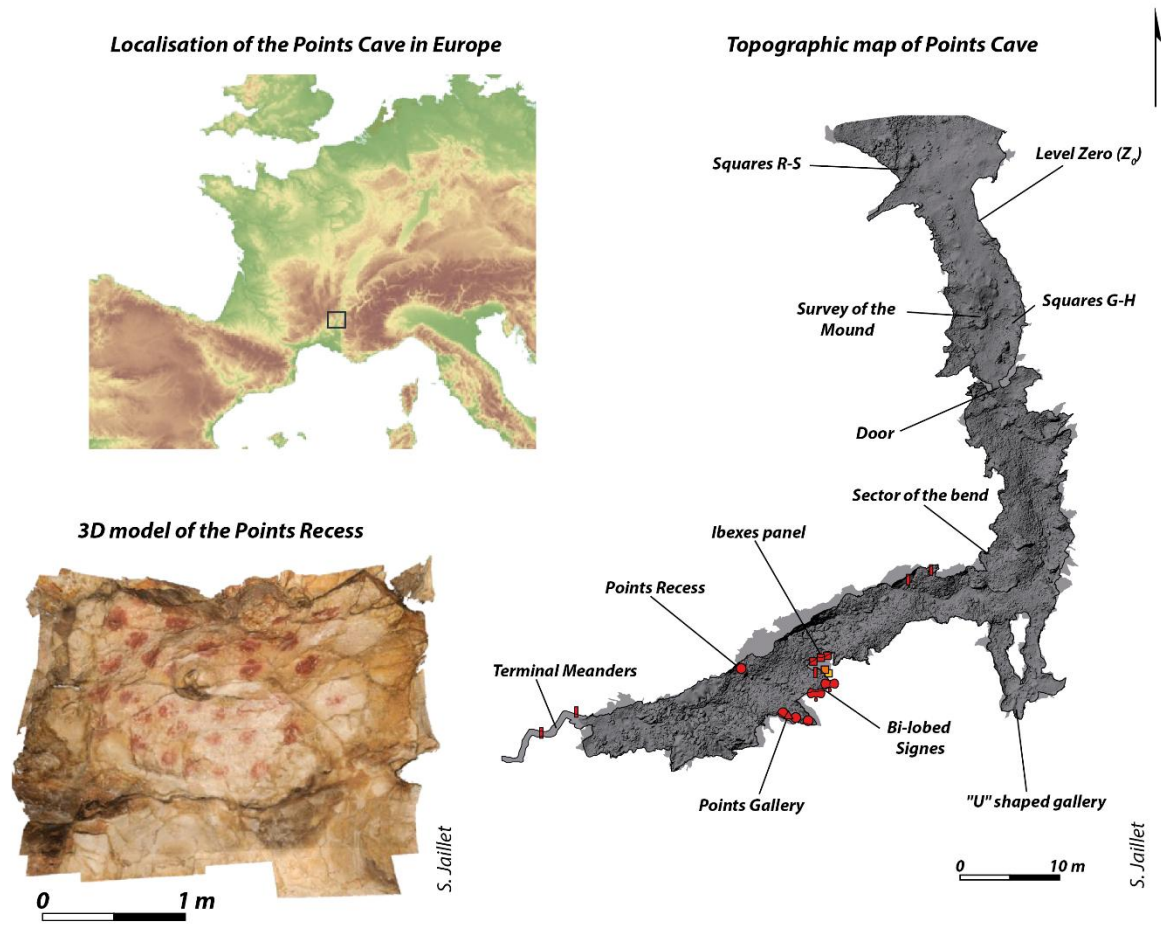
106

### 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.

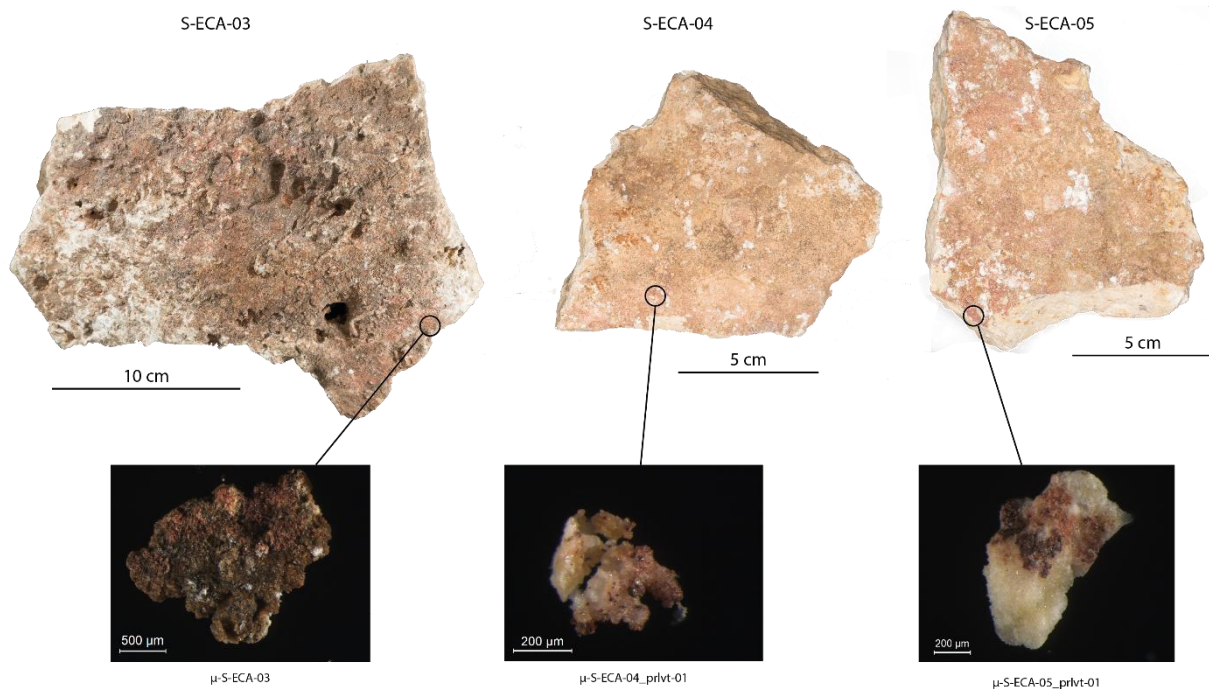
146

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).  $\mu$ -sampling of pictorial matter was performed on the coloured  
151 flakes:  $\mu$ -S-ECA-03,  $\mu$ -S-ECA-04,  $\mu$ -S-ECA-05. These last two have been fragmented during  
152 sampling giving:  $\mu$ -S-ECA-04\_prlvt\_01,  $\mu$ -S-ECA-04\_prlvt\_02 and  $\mu$ -S-ECA-04\_prlvt\_03, and  $\mu$ -S-  
153 ECA-05\_prlvt\_01 and  $\mu$ -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  $\mu$ -sampling.

159

160 Moreover, 12  $\mu$ -samples of pictorial matter on limestone and 8  $\mu$ -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  $\mu$ -samples of pictorial matter were observed and analysed without any  
163 preparation.

164

165

166



167  
 168  
 169  
 170  
 171  
 172  
 173  
 174

**Table 1:** Inventory of  $\mu$ -samples with colouring matter coming from the rock art panels

<i>Sample N°</i>	<i>Rock Art</i>	<i>Type</i>
<b>– Ibexes Panel –</b>		
<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>
<b>– Horse Panel –</b>		
<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>
<b>– Bi-lobed Signs Panel –</b>		
<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>
<b>– Dots Galerie –</b>		
<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>
<b>– Dots Gallery (cluster 11) –</b>		
<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>
<b>– Points Recess –</b>		
<i>Prm-19-18</i>	<i>In the center of the panel</i>	<i>Wall Blank</i>
<b>– Between Ibexes panel and Horse panel –</b>		
<i>Prm-19-19</i>	<i>On the limestone</i>	<i>Wall Blank</i>
<b>– Points Recess –</b>		

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>
<b>Laboratory</b>	White light		F/7.1	1/320	1600
	UV light		F/7.1	10	1600
<b>Field</b>	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  $\mu$ -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  $\mu$ -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 ( $\sim 30$   
213  $\mu\text{m}$ ) 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  $\mu$ -samples:  $\mu$ -S-ECA-03,  $\mu$ -S-ECA-04  
222 and  $\mu$ -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  $100\times 100$   $\mu\text{m}$  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  $\mu$ -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  $\mu$ -samples both of  
246 the rock art and the flakes under stereomicroscope, pXRF analyses (1 cm<sup>3</sup> 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.

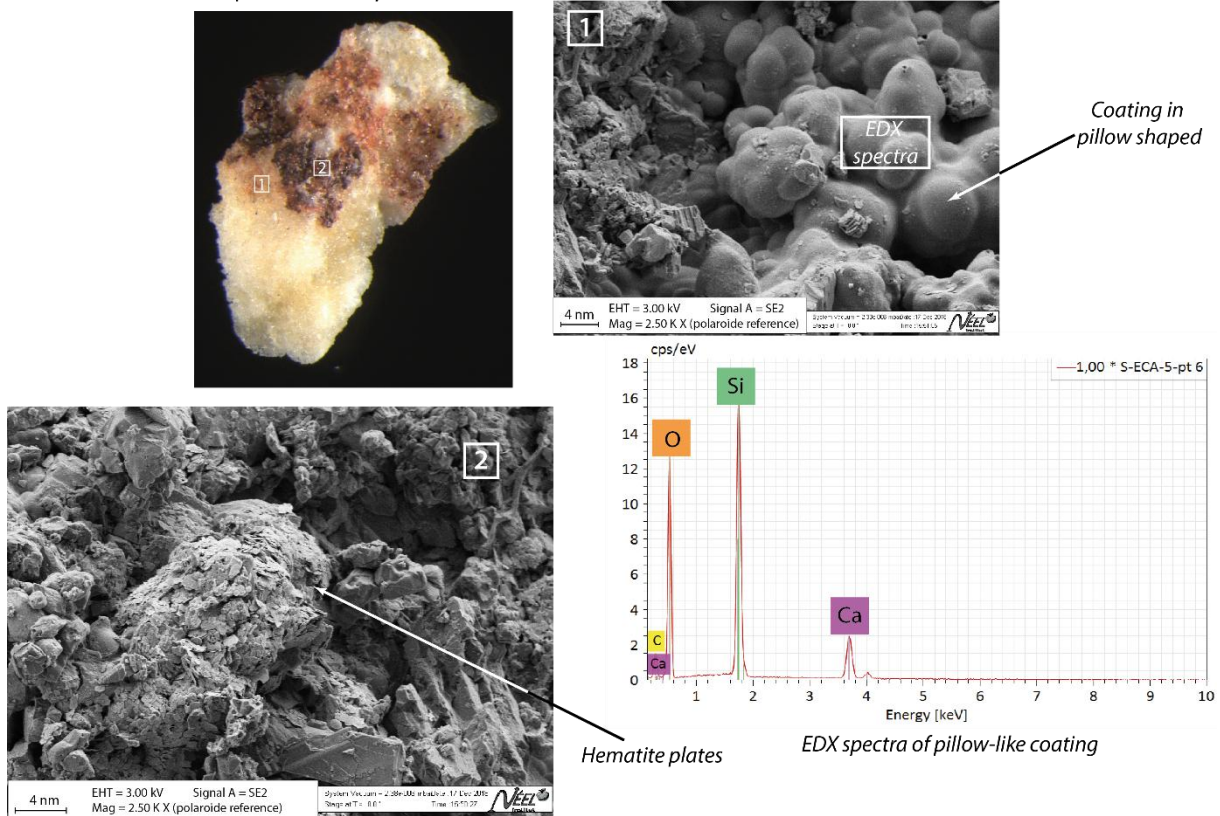
250

#### 251 *4.2 Microscopic scale observations*

252

253 At the microscopic scale, a 1  $\mu$ m-thin mineral film consisting of nonordered spheres was identified as  
254 silica mineralization on  $\mu$ -S-ECA-03,  $\mu$ -S-ECA-04-prlvt-02,  $\mu$ -S-ECA-05-prlvt-01 (Figure 3; S.I.2).  
255 However,  $\mu$ -S-ECA-03 shows less opal coating than the two other  $\mu$ -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.

$\mu$ -S-ECA-05-prlvt-01



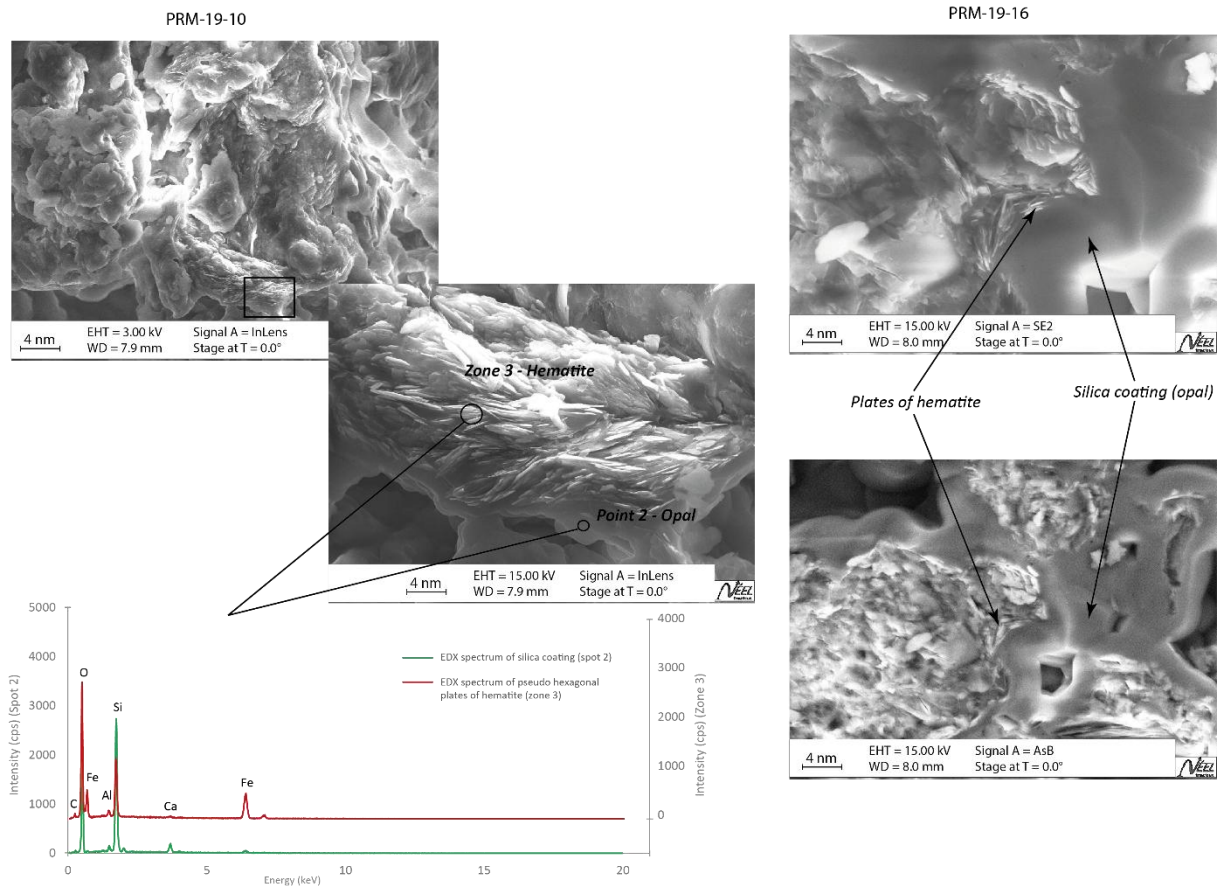
262

**Figure 3:** SEM observations of  $\mu$ -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  $\mu$ -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  $\mu$ -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  $\mu$ -samples ( $\mu$ S-ECA-03,  $\mu$ S-ECA-04 and  $\mu$ 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  $\mu$ 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):

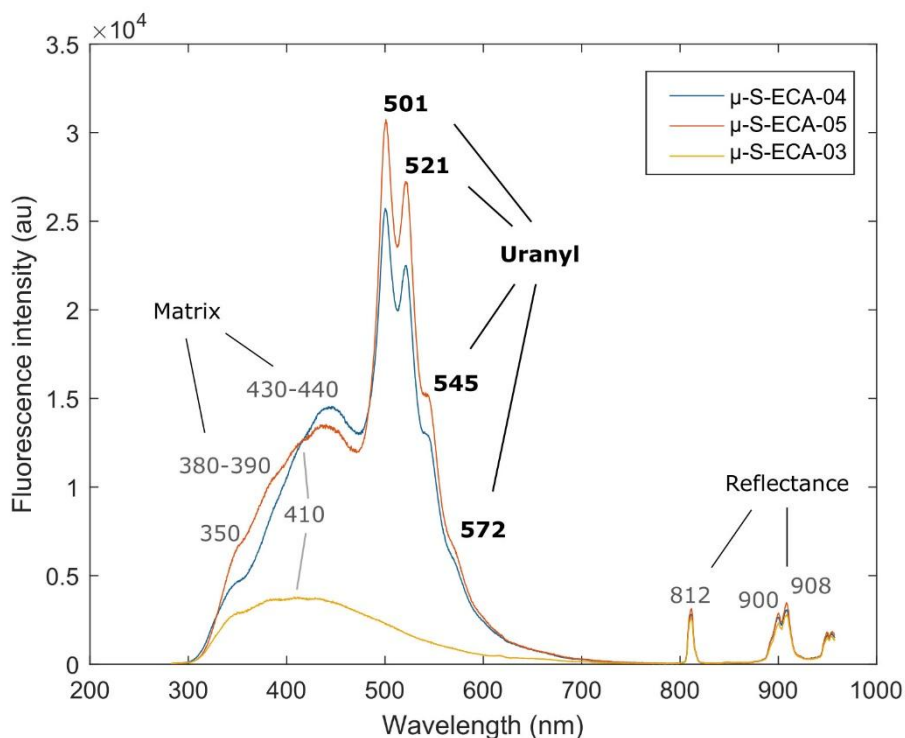
283

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  $\mu$ S-  
 292 ECA-04 and  $\mu$ -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  $\mu$ -samples  $\mu$ S-ECA-04 and  $\mu$ -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  $\mu$ -  
 296 S-ECA-03 spectra.



297

298 **Figure 5:** Mean fluorescence emission spectra (excitation: 266 nm) of samples  $\mu$ -S-ECA-04,  $\mu$ -S-  
 299 ECA-05 and  $\mu$ -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 ( $\geq 1$  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  $\mu$ -samples have not been  
321 measured due to the particularly thin opal layer and the impossibility of destroying  $\mu$ -samples.

322

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

---

---

**Fluorescence emission peaks (nm)**

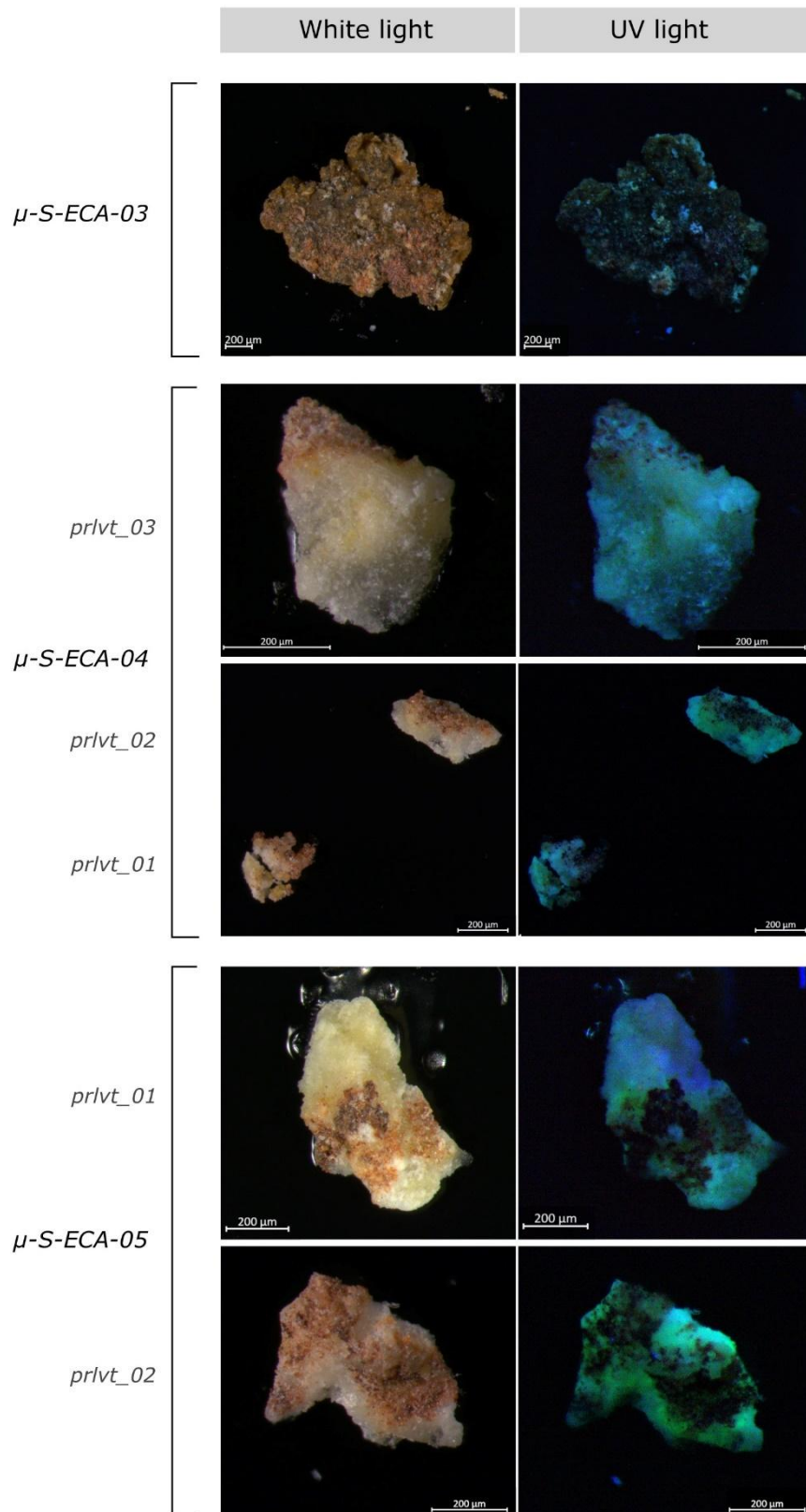
	504	524	546	570	-
Othmane <i>et al.</i> 2016	504	523	545	573	-
Fritsch <i>et al.</i> 2015	504	524	546	572	604
Brennan & White 2013	502	520	-	-	-
Garcia-Guinea <i>et al.</i> 2013	505	524	543	569	-
<b><i>This study</i></b>	<b>501</b>	<b>521</b>	<b>545</b>	<b>572</b>	-

325

326 *4.4 Opal visual detection under UV light*

327

328 As explained previously, minerals containing uranyl ions ( $\text{UO}_2^{2+}$ ) 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  $\mu$ -  
333 samples were exposed to UV light (see 3.1.1). The results show that  $\mu$ -samples  $\mu$ -S-ECA-04 and  $\mu$ -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  $\mu$ -sample  $\mu$ -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  $\mu$ -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  $\mu$ -samples taken on flakes under white and UV light.

344  
345  
346  
347  
348  
349  
350  
351  
352  
353  
354  
355  
356  
357  
358  
359  
360  
361  
362  
363  
364  
365  
366  
367  
368  
369  
370

#### 4.4 From the lab to the cave

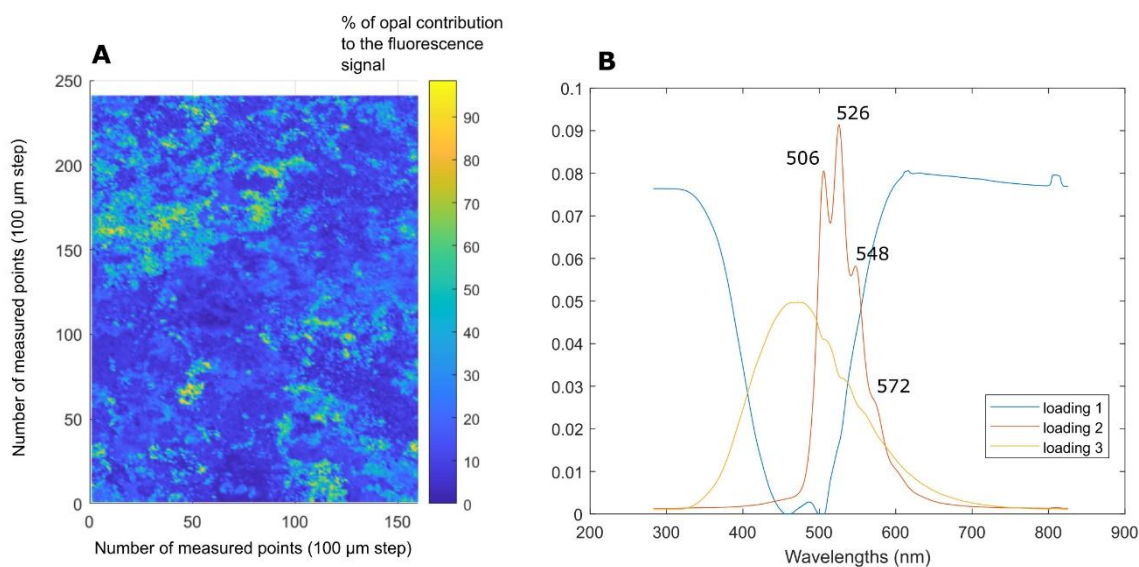
##### 4.4.1 Comparison between UV methods

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

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

A singular value decomposition (SVD) method was first applied on the entire raw dataset in the MCR calculation to define the number of initial loadings (S.I.5). Based on the eigen values obtained with the SVD method, three components were graphically determined as mainly contributors to the fluorescence signal and represent 76.8% of the explained variance. These three initial loadings were then calculated in the MCR-ALS method using the PURE algorithm, a commonly used method to find 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  $\mu$ -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).

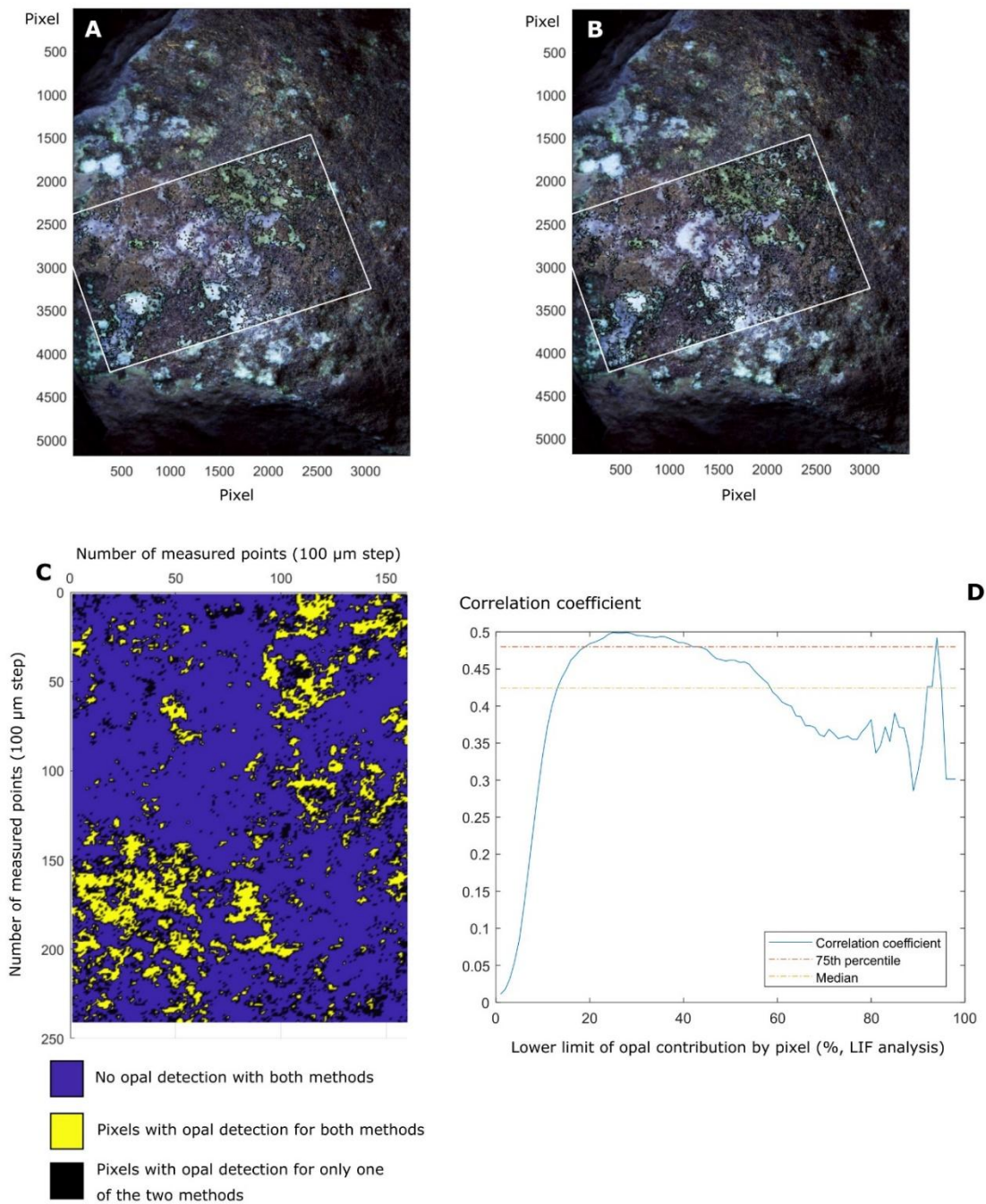
400

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

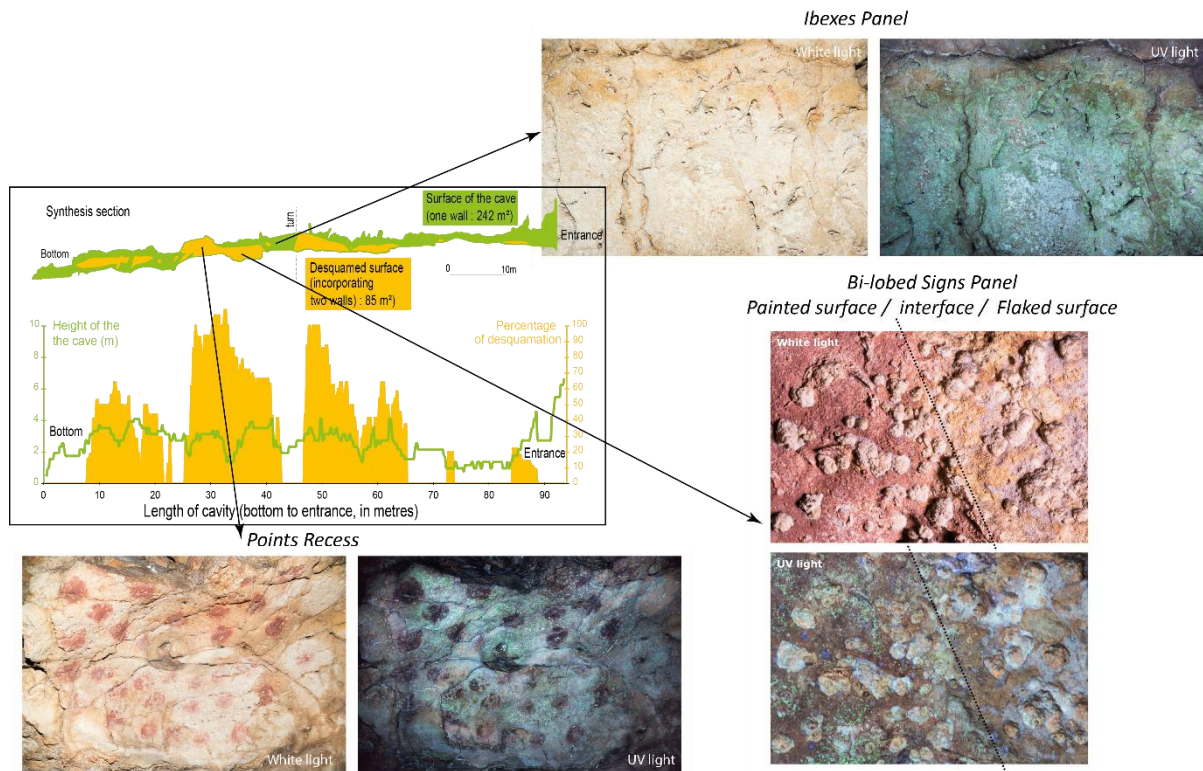
428 An *in situ* photographic protocol that alternated white light and UV illumination was applied to the  
429 Points Cave walls. As shown in Figure 1, three rock art panels and one wall devoid of any rock art  
430 were investigated. Pictures were taken at both the wall and macroscopic scales.

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  $\mu$ -  
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

## 5.1 Contribution of UV fluorescence techniques

457  
458  
459  
460  
461  
462  
463  
464  
465  
466  
467  
468  
469  
470  
471  
472  
473  
474  
475  
476  
477  
478  
479  
480  
481  
482  
483

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

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

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  $\mu$ -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  $\mu$ -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  $\mu$ -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 SiO<sub>2</sub>, 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  $23.9 \pm 8.1$  ka and  $31.1 \pm 3.9$  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  $\text{U}/\text{Pb}$  (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  $\text{U}/\text{Pb}$  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  $\mu\text{m}$  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  $\mu$ -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  $\mu$ -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  $\mu$ -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  $\mu$ -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  $\mu$ -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>

805

## 806 **Bibliography**

807 Ahtelik M., Floss H., Nagel M., Monney, J., 2019. Analyse chirosopique des points-paumes de la  
808 grotte aux Points (Aiguèze, Gard). *Karstologia* 73, pp 33-40.

809

810 Amelin, Y., Back, M., 2006. Opal as a U–Pb geochronometer: search for a standard. *Chemical*  
811 *Geology* 232, 67–86. <https://doi.org/10.1016/j.chemgeo.2006.02.018>

812

813 Araya, J.A., Carneiro, R.L., Arévalo, C., Freer, J., Castillo, R. del P., 2017. Single pixel quantification  
814 strategies using middle infrared hyperspectral imaging of lignocellulosic fibers and MCR-ALS  
815 analysis. *Microchemical Journal* 134, 164–172. <https://doi.org/10.1016/j.microc.2017.05.019>

816

817 Aubert, M., 2012. A review of rock art dating in the Kimberley, Western Australia. *Journal of*  
818 *Archaeological Science* 39, 573–577. <https://doi.org/10.1016/j.jas.2011.11.009>

819

820 Aubert, M., Watchman, A., Arsenault, D., Gagnon, L., 2004. L'archéologie rupestre du Bouclier  
821 canadien : Potentiel archéométrique. *Canadian Journal of Archaeology/Journal Canadien*  
822 *d'Archéologie* 51–74. <http://www.jstor.org/stable/41103470>

823

824 Aubert, M., O'Connor, S., McCulloch, M., Mortimer, G., Watchman, A., Richer-LaFlèche, M., 2007.  
825 Uranium-series dating rock art in East Timor. *Journal of Archaeological Science* 34, 991–996.  
826 <https://doi.org/10.1016/j.jas.2006.09.017>

827

828 Aubert, M., Brumm, A., Taçon, P.S., 2017. The timing and nature of human colonization of Southeast



829 Asia in the late Pleistocene: A rock art perspective. *Current Anthropology* 58, S553–S566.  
830 <https://doi.org/10.1086/694414>  
831

832 Backes, C. J., 2004. More Than Meets the Eye: Fluorescence Photography for Enhanced Analysis of  
833 Pictographs. *Journal of California and Great Basin Anthropology*, 24(2), 193–206.  
834 <http://www.jstor.org/stable/27825774>  
835

836 Barbarand, J., Nouet, J., 2020. Pétrographie et minéralogie des coralloïdes de la grotte au Points, in:  
837 Monney J. (Dir.). *Projet Datation Grottes Ornées : Rapport d’activité 2020. Grotte Aux Points*  
838 (Aiguèze). Rapport Non Publié., Ministère de La Culture, SRA Occitanie, Montpellier.  
839

840 Bassel, L., 2017. Genèse de faciès calcitiques : mondmilch et coralloïdes. Étude multiphysique des  
841 concrétions de la grotte laboratoire de Leye (Dordogne) (Thèse). Université Bordeaux Montaigne.  
842 <https://tel.archives-ouvertes.fr/tel-01729035>  
843

844 Bednarik, R.G., 1994. A taphonomy of palaeoart. *Antiquity* 68, 68–74.  
845 <https://doi.org/10.1017/S0003598X00046202>  
846

847 Boyko, V., Dovbeshko, G., Fesenko, O., Gorelik, V., Moiseyenko, V., Romanyuk, V., others, 2011.  
848 New optical properties of synthetic opals infiltrated by DNA. *Molecular Crystals and Liquid Crystals*  
849 535 (1), 30-41. <https://doi.org/10.1080/15421406.2011.537888>  
850

851 Brennan, E. S., White, W. B., 2013. Luminescence of speleothems: a comparison of sources and  
852 environments. *Journal of Cave & Karst Studies*, 75(3).  
853

854 Castro, R.C., Ribeiro, D.S., Santos, J.L., Páscoa, R.N., 2021. Near infrared spectroscopy coupled to  
855 MCR-ALS for the identification and quantification of saffron adulterants: Application to complex

856 mixtures. Food Control 123, 107776. <https://doi.org/10.1016/j.foodcont.2020.107776>

857

858 Chalmin, E., Hoerlé, S.H., Reiche, I., 2018. Taphonomy on the Surface of the Rock Wall: Rock-Paint-  
859 Atmosphere Interactions. Bruno David; Ian J. McNiven. The Oxford Handbook of the Archaeology  
860 and Anthropology of Rock Art, Oxford Handbook. <https://hal.archives-ouvertes.fr/hal-01801656/>

861

862 Chalmin, E., Salomon, H., Chassin de Kergommeaux, A., Chanteraud, C., 2019. Construction d'une  
863 Pigmentoθήque : un outil pour comprendre l'approvisionnement en matériaux colorants durant la  
864 Préhistoire : Rapport d'activité 2019. [Rapport de recherche] DRAC/SRA; Auvergne Rhône Alpes.  
865 2019. [hal-02429867](https://hal-02429867)

866

867 Chanteraud, C., 2020. Matières colorantes et grottes ornées des gorges de l'Ardèche. Méthodes  
868 d'analyse des ressources et liens culturels au Paléolithique supérieur : application à la grotte aux Points  
869 (Aiguèze, Gard, France) (Thèse). Université Savoie Mont Blanc. [https://tel.archives-ouvertes.fr/tel-](https://tel.archives-ouvertes.fr/tel-03184877)  
870 [03184877](https://tel.archives-ouvertes.fr/tel-03184877)

871

872 Chanteraud, C., Chalmin, E., Hoerlé, S., Salomon, H., Monney, J., 2019. Relation entre les matières  
873 colorantes issues des fouilles et des parois ornées. Méthodologie et première perspective comparative  
874 à la Grotte aux Points (Aiguèze, Gard, France). *Karstologia* 73, pp 1-12. [https://hal.archives-](https://hal.archives-ouvertes.fr/hal-01756858/)  
875 [ouvertes.fr/hal-01756858/](https://hal.archives-ouvertes.fr/hal-01756858/)

876

877 Chanteraud, C., Chalmin, É., Lebon, M., Salomon, H., Jacq, K., Noûs, C., Delannoy, J.-J., Monney, J.  
878 2021. Contribution and limits of portable X-ray fluorescence for studying Palaeolithic rock art: a case  
879 study at the Points cave (Aiguèze, Gard, France). *Journal of Archaeological Science: Reports* 37:  
880 102898. <https://doi.org/10.1016/j.jasrep.2021.102898>

881

882 Chauviré, B., Rondeau, B., Mangold, N., 2017. Near infrared signature of opal and chalcedony as a

883 proxy for their structure and formation conditions. *European Journal of Mineralogy* 29, 409–421.  
884 <https://doi.org/10.1127/ejm/2017/0029-2614>  
885

886 Chen, C.-C., Pestov, D., Nelson, J.D., Anderson J.E. and G. Tepper, 2011. Uranyl Soil Extraction and  
887 Fluorescence Enhancement by Nanoporous Silica Gel: pH effects. *J Fluoresc* 21, 119–124.  
888 <https://doi.org/10.1007/s10895-010-0695-0>  
889

890 Curtis, N.J., Gascooke, J.R., Johnston, M.R., Pring, A., 2019. A review of the classification of opal  
891 with reference to recent new localities. *Minerals* 9, 299. <https://doi.org/10.3390/min9050299>  
892

893 De Juan, A., Jaumot, J., Tauler, R., 2014. Multivariate Curve Resolution (MCR). Solving the mixture  
894 analysis problem. *Analytical Methods* 6, 4964–4976. <https://doi.org/10.1039/C4AY00571F>  
895

896 Defrasne, C., Chalmin, E., Bellot-Gurlet, L., Thirault, E., and G. André, 2019. From archeological  
897 layers to schematic rock art? Integrated study of the Neolithic pigments and pigmented rocks at the  
898 Rocher du Château (Western Alps, Savoie, France). *Archaeol Anthropol Sci* 11, 6065–6091.  
899 <https://doi.org/10.1007/s12520-019-00882-9>  
900

901 Delvigne, Jean E. 1998. *Atlas of Micromorphology of Mineral Alteration and Weathering*. The  
902 Canadian Mineralogist 3. Ottawa: Paris: Mineralogical Association of Canada; ORSTOM.  
903

904 DeNeufville, J., Kasdan, A., Chimenti, R., 1981. Selective detection of uranium by laser-induced  
905 fluorescence: a potential remote-sensing technique. 1: Optical characteristics of uranyl geologic  
906 targets. *Applied Optics* 20, 1279–1296. <https://doi.org/10.1364/AO.20.001279>  
907

908 Deschamps, E.B., Chauvet, J.M., Hillaire, C., 2018. La grotte aux Points d'Aiguèze : récits de  
909 découverte d'une ornementation pariétale. *Karstologia* 72, 13–14.

910

911 Devès, G., Perroux, A.-S., Bacquart, T., Plaisir, C., Rose, J., Jaillet, S., Ghaleb, B., Ortega, R., Maire,  
912 R., 2012. Chemical element imaging for speleothem geochemistry: Application to a uranium-bearing  
913 corallite with aragonite diagenesis to opal (Eastern Siberia, Russia). *Chemical Geology* 294, 190–202.  
914 <https://doi.org/10.1016/j.chemgeo.2011.12.003>

915

916 Flörke, O., Graetsch, H., Röller, K., Martin, B., Wirth, R., 1991. Nomenclature of micro-and non-  
917 crystalline silica minerals. *Neues Jahrbuch für Mineralogie, Abhandlungen* 163, 19–42.

918

919 Fritsch, E., Mihut, L., Baibarac, M., Baltog, I., Ostrooumov, M., Lefrant, S., Wery, J., 2001.  
920 Luminescence of oxidized porous silicon: Surface-induced emissions from disordered silica micro-to  
921 nanotextures. *Journal of Applied Physics* 90, 4777–4782. <https://doi.org/10.1063/1.1410887>

922

923 Fritsch, E., Wéry, J., Jonusauskas, G., Faulques, E., 2003. Transient photoluminescence from highly  
924 disordered silica-rich natural phases with and without nanostructures. *Physics and chemistry of*  
925 *minerals* 30, 393–400. <https://doi.org/10.1007/s00269-003-0329-z>

926

927 Fritsch, E., Megaw, P.K., Spano, T.L., Chauviré, B., Rondeau, B., Gray, M., Hainschwang, T., Renfro,  
928 N., 2015. Green-luminescing hyalite opal from Zacatecas, Mexico. *J. Gemmol* 34, 490–508.

929

930 Gaillou, E., Delaunay, A., Rondeau, B., Bouhnik-le-Coz, M., Fritsch, E., Cornen, G., Monnier, C.,  
931 2008. The geochemistry of gem opals as evidence of their origin. *Ore Geology Reviews* 34, 113–126.  
932 <https://doi.org/10.1016/j.oregeorev.2007.07.004>

933

934 Garcia-Guinea, J., Fernandez-Cortes, A., Alvarez-Gallego, M., García-Antón, E., Casas-Ruiz, M.,

935 Blázquez-Pérez, D., Teijón, O., Cuezva, S., Correcher, V., Sanchez-Moral, S., 2013. Leaching of  
936 uranyl–silica complexes from the host metapelite rock favoring high radon activity of subsoil air: case  
937 of Castañar cave (Spain). *Journal of Radioanalytical and Nuclear Chemistry* 298, 1567–1585.  
938 <https://doi.org/10.1007/s10967-013-2587-7>  
939  
940 Genuite, K., Delannoy, JJ., Bahain, JJ., Gresse M., Jaillet S., Philippe A., Pons-Branchu E., Revil A.,  
941 and P. Voinchet, 2021. Dating the landscape evolution around the Chauvet-Pont d’Arc cave. *Sci*  
942 *Rep* 11, 8944. <https://doi.org/10.1038/s41598-021-88240-5>  
943  
944 Gorobets, B., Engoyan, S., Sidorenko, G., 1977. Investigation of uranium and uranium-containing  
945 minerals by their luminescence spectra. *Soviet Atomic Energy* 42, 196–202.  
946 <https://doi.org/10.1007/BF01121388>  
947  
948 Green, H., Gleadow, A., Finch, D., Hergt, J., Ouzman, S., 2017. Mineral deposition systems at rock art  
949 sites, Kimberley, Northern Australia—Field observations. *Journal of Archaeological Science: Reports*  
950 14, 340–352. <https://doi.org/10.1016/j.jasrep.2017.06.009>  
951  
952 Huntley, J., 2012. Taphonomy or paint recipe: In situ portable x-ray fluorescence analysis of two  
953 anthropomorphic motifs from the Woronora Plateau, New South Wales. *Australian Archaeology* 75,  
954 78–94. <https://doi.org/10.1080/03122417.2012.11681952>  
955  
956 Huntley, J., Aubert, M., Ross, J., Brand, H. E., Morwood, M. J., 2015. One colour, (at least) two  
957 minerals: a study of mulberry rock art pigment and a mulberry pigment ‘quarry’ from the Kimberley,  
958 northern Australia. *Archaeometry* 57 (1), 77-99. <https://doi.org/10.1111/arcm.12073>

959

960 Jaillet, S., Monney, J., 2018. Analyse 3D des volumes et remplissages souterrains de la grotte aux  
961 Points au temps des fréquentations paléolithiques (Aiguèze, Gard). *Karstologia* 72, 27–36.

962 <https://hal.archives-ouvertes.fr/hal-01878453/>

963

964 Jaumot, J., Gargallo, R., de Juan, A., Tauler, R., 2005. A graphical user-friendly interface for MCR-  
965 ALS: a new tool for multivariate curve resolution in MATLAB. *Chemometrics and intelligent  
966 laboratory systems* 76, 101–110. <https://doi.org/10.1016/j.chemolab.2004.12.007>

967

968 Jaumot, J., de Juan, A., Tauler, R., 2015. MCR-ALS GUI 2.0: New features and applications.  
969 *Chemometrics and Intelligent Laboratory Systems* 140, 1–12.

970 <https://doi.org/10.1016/j.chemolab.2014.10.003>

971

972 Karkanas, P., Kyparissi-Apostolika, N., Bar-Yosef, O., Weiner, S., 1999. Mineral assemblages in  
973 Theopetra, Greece: a framework for understanding diagenesis in a prehistoric cave. *Journal of  
974 Archaeological Science* 26, 1171–1180. <https://doi.org/10.1006/jasc.1998.0354>

975

976 Kasdan, A., Chimenti, R.J.L., deNeufville, J.P., 1981. Selective detection of uranium by laser-induced  
977 fluorescence: a potential remote-sensing technique. 2: Experimental assessment of the remote sensing  
978 of uranyl geologic targets. *Appl. Opt.* 20, 1297–1307. <https://doi.org/10.1364/AO.20.001297>

979

980 Kinnunen, K.A., Ikonen, L., 1991. Opal, a new hydromorphic precipitate type from gravel deposits in  
981 southern Finland. *Bulletin of the Geological Society of Finland* 63, 95–104.

982

983 Kumar, K., 2018. Application of Genetic Algorithm (GA) Assisted Partial Least Square (PLS)  
984 Analysis on Trilinear and Non-trilinear Fluorescence Data Sets to Quantify the Fluorophores in  
985 Multifluorophoric Mixtures: Improving Quantification Accuracy of Fluorimetric Estimations of Dilute  
986 Aqueous Mixtures. *Journal of fluorescence* 28, 589–596. <https://doi.org/10.1007/s10895-018-2221-8>  
987  
988 Lafon D., Konik S., Monney J. 2022. On-site spectroradiometric analysis of palaeolithic cave art:  
989 Investigating colour variability of red rock art at Points cave (Aiguèze, Gard, France). *Journal of*  
990 *Archaeological Science – report* 42, 103384. <https://doi.org/10.1016/j.jasrep.2022.103384>  
991  
992 Lundberg, J., Brewer-Carias, C., and D., McFarlane, 2010. Preliminary results from U-Th dating of  
993 glacial-interglacial deposition cycles in a silica speleothem from Venezuela. *Quaternary Research*, 74  
994 (1), 113-120. <https://doi.org/10.1016/j.yqres.2010.03.005>  
995  
996 Mas, S., de Juan, A., Tauler, R., Olivieri, A.C., Escandar, G.M., 2010. Application of chemometric  
997 methods to environmental analysis of organic pollutants: a review. *Talanta* 80, 1052–1067.  
998 <https://doi.org/10.1016/j.talanta.2009.09.044>  
999  
1000 Mauran, G., Lebon, M., Détroit, F., Caron, B., Nankela, A., Pleurdeau, D., Bahain, J.-J. 2019. First in  
1001 Situ PXRF Analyses of Rock Paintings in Erongo, Namibia: Results, Current Limits, and Prospects.  
1002 *Archaeological and Anthropological Sciences* 11 (8): 4123–45. [https://doi.org/10.1007/s12520-019-](https://doi.org/10.1007/s12520-019-00787-7)  
1003 [00787-7](https://doi.org/10.1007/s12520-019-00787-7)  
1004  
1005 McGarry, S. F., Baker, A., 2000. Organic acid fluorescence: applications to speleothem  
1006 palaeoenvironmental reconstruction. *Quaternary Science Reviews* 19(11), 1087-1101.  
1007 [https://doi.org/10.1016/S0277-3791\(99\)00087-6](https://doi.org/10.1016/S0277-3791(99)00087-6)  
1008  
1009 Mocochain L., Audra, P., Clauzon, G., Bellier, O., Bigot, J.-Y., Parize, O., and P. Monteil, 2021. The

1010 effect of river dynamics induced by the Messinian Salinity Crisis on karst landscape and caves:  
1011 Example of the Lower Ardèche river (mid Rhône valley), *Geomorphology*, 106 (1–2), 46–61.  
1012 <https://doi.org/10.1016/j.geomorph.2008.09.021>.  
1013  
1014 Monger, H.C., Kelly, E.F., 2002. Silica minerals. *Soil mineralogy with environmental applications* 7,  
1015 611–636.  
1016  
1017 Monney, J., 2011. *Projet Datation Grottes Ornées : Rapport d'activité 2011*. Grotte aux Points  
1018 (Aiguèze). Rapport non publié, Ministère de la Culture, SRA Occitanie, Montpellier.  
1019  
1020 Monney, J., 2018. L'art pariétal paléolithique de la grotte aux Points d'Aiguèze: définition d'un  
1021 dispositif pariétal singulier et discussion de ses implications. *Karstologia* 72, 45–60.  
1022  
1023 Monney, J. 2019. *Projet Datation Grottes Ornées : Rapport 2019 (12ème volet) : 12.1. Grotte aux*  
1024 *Points (Aiguèze). [Rapport de recherche] Ministère de la Culture, SRA Occitanie, Montpellier. 2019.*  
1025 [hal-01972949](https://hal.archives-ouvertes.fr/hal-01972949)  
1026  
1027 Monney, J., Jaillet, S., 2019. Phases de fréquentations humaines, ornementation pariétale et processus  
1028 naturels : Mise en place d'un cadre chronologique pour la grotte aux Points d'Aiguèze. *Karstologia* 72,  
1029 49–62. <https://hal.archives-ouvertes.fr/hal-01957634/>  
1030  
1031 Morwood, M.J., Walsh, G.L., Watchman, A.L., 2010. AMS radiocarbon ages for beeswax and  
1032 charcoal pigments in north Kimberley rock art. *Rock Art Research: The Journal of the Australian*  
1033 *Rock Art Research Association (AURA)* 27 (1), 3–8.  
1034 <https://search.informit.org/doi/10.3316/informit.153070840500133>  
1035  
1036 Neymark, L., Paces, J.B., 2013. Ion-probe U–Pb dating of authigenic and detrital opal from Neogene-



1037 Quaternary alluvium. *Earth and Planetary Science Letters* 361, 98–109.  
1038 <https://doi.org/10.1016/j.epsl.2012.11.037>  
1039  
1040 Neymark, L.A., Amelin, Y.V., Paces, J.B., 2000. 206Pb–230Th–234U–238U and 207Pb–235U  
1041 geochronology of Quaternary opal, Yucca Mountain, Nevada. *Geochimica et Cosmochimica Acta* 64,  
1042 2913–2928. [https://doi.org/10.1016/S0016-7037\(00\)00408-7](https://doi.org/10.1016/S0016-7037(00)00408-7)  
1043  
1044 Nomade, S., Genty, D., Sasco, R., Scao, V., Féruglio, V., Baffier, D., Guillou, H., Bourdier, C.,  
1045 Valladas, H., Reigner, E., others, 2016. A 36,000-year-old volcanic eruption depicted in the Chauvet-  
1046 Pont d' Arc Cave (Ardèche, France)? *PloS one* 11(1), e0146621.  
1047 <https://doi.org/10.1371/journal.pone.0146621>  
1048  
1049 Northup, K.H., Diana, Lavoie, 2001. Geomicrobiology of caves: a review. *Geomicrobiology journal*  
1050 18, 199–222.  
1051  
1052 Oster, J.L., Kitajima, K., Valley, J.W., Rogers, B., Maher, K., 2017. An evaluation of paired  $\delta^{18}\text{O}$  and  
1053  $(^{234}\text{U}/^{238}\text{U})_0$  in opal as a tool for paleoclimate reconstruction in semi-arid environments. *Chemical*  
1054 *Geology* 449, 236–252. <https://doi.org/10.1016/j.chemgeo.2016.12.009>  
1055  
1056 Othmane, G., Allard, T., Vercouter, T., Morin, G., Fayek, M., Calas, G., 2016. Luminescence of  
1057 uranium-bearing opals: Origin and use as a pH record. *Chemical Geology* 423, 1–6.  
1058 <https://doi.org/10.1016/j.chemgeo.2015.12.010>  
1059  
1060 Perrette, Y., Delannoy, J.-J., Bolvin, H., Cordonnier, M., Destombes, J.-L., Zhilinskaya, E.A.,

1061 Aboukais, A., 2000. Comparative study of a stalagmite sample by stratigraphy, laser induced  
1062 fluorescence spectroscopy, EPR spectrometry and reflectance imaging. *Chemical Geology* 162, 221–  
1063 243. [https://doi.org/10.1016/S0009-2541\(99\)00069-8](https://doi.org/10.1016/S0009-2541(99)00069-8)  
1064

1065 Perrette, Y., Delannoy, J. J., Desmet, M., Lignier, V., Destombes, J. L., 2005. Speleothem organic  
1066 matter content imaging. The use of a Fluorescence Index to characterise the maximum emission  
1067 wavelength. *Chemical Geology* 214 (3-4), 193-208. <https://doi.org/10.1016/j.chemgeo.2004.09.002>  
1068

1069 Pons-Branchu, E., Bourrillon, R., Conkey, M.W., Fontugne, M., Fritz, C., Gárate, D., Quiles, A.,  
1070 Rivero, O., Sauvet, G., Tosello, G., 2014. Uranium-series dating of carbonate formations overlying  
1071 Paleolithic art: interest and limitations. *Bulletin de la Société préhistorique française* 211–224.  
1072 <http://www.jstor.org/stable/24364541>  
1073

1074 Quiers, M., Perrette, Y., Chalmin, E., Fanget, B., Poulénard, J., 2015. Geochemical mapping of  
1075 organic carbon in stalagmites using liquid-phase and solid-phase fluorescence. *Chemical Geology* 411,  
1076 240-247. <https://doi.org/10.1016/j.chemgeo.2015.07.012>  
1077

1078 Quiles, A., Fritz, C., Alcaide, M.Á.M., Pons-Branchu, E., Torti, J.L.S., Tosello, G., Valladas, H.,  
1079 2015. Chronologies croisées (C-14 et U/Th) pour l'étude de l'art préhistorique dans la grotte de Nerja:  
1080 méthodologie. Presented at the *Sobre rocas y huesos: las sociedades prehistóricas y sus*  
1081 *manifestaciones plásticas*, UCO Press. Editorial de la Universidad de Córdoba, pp. 420–427.  
1082

1083 Rousaki, A., Vargas, E., Vázquez, C., Aldazábal, V., Bellelli, C., Calatayud, M. C., Hajduk A.,  
1084 Palacios O., Moens L., and P. Vandenabeele, 2018. On-field Raman spectroscopy of Patagonian  
1085 prehistoric rock art: Pigments, alteration products and substrata. *TrAC Trends in Analytical*  
1086 *Chemistry*, 105, 338-351. <https://doi.org/10.1016/j.trac.2018.05.011>  
1087

1088 Sadier, B., 2013. 3D et géomorphologie karstique : La grotte Chauvet et les cavités des Gorges de  
1089 l'Ardèche (Thèse). Université de Savoie, Le-Bourget-Du-Lac. <https://hal.univ-smb.fr/tel-01070711/>  
1090

1091 Salomon, Hélène, Claire Chanteraud, Aurélie Chassin de Kergommeaux, Julien Monney, Jean-Victor  
1092 Pradeau, Éric Goemaere, Yvan Coquinot, and Emilie Chalmin. 2021. 'A Geological Collection and  
1093 Methodology for Tracing the Provenance of Palaeolithic Colouring Materials'. *Journal of Lithic*  
1094 *Studies* 8 (1): 38-p. <https://doi.org/10.2218/jls.5540>  
1095

1096 Sasco, R., Guillou, H., Nomade, S., Scao, V., Maury, R. C., Kissel, C., & Wandres, C., 2017.  
1097 <sup>40</sup>Ar/<sup>39</sup>Ar and unspiked <sup>40</sup>K-<sup>40</sup>Ar dating of upper Pleistocene volcanic activity in the Bas-Vivarais  
1098 (Ardèche, France). *Journal of Volcanology and Geothermal Research*, 341, 301-314.  
1099 <https://doi.org/10.1016/j.jvolgeores.2017.06.003>  
1100

1101 Savitzky, A., Golay, M.J.E., 1964. Smoothing and Differentiation of Data by Simplified Least Squares  
1102 Procedures. *Analytical Chemistry*. 36, 1627–1639. <https://doi.org/10.1021/ac60214a047>  
1103

1104 Shao, Q.-F., Pons-Branchu, E., Zhu, Q.-P., Wang, W., Valladas, H., Fontugne, M., 2017. High  
1105 precision U/Th dating of the rock paintings at Mt. Huashan, Guangxi, southern China. *Quaternary*  
1106 *Research* 88, 1–13. <https://doi.org/10.1017/qua.2017.24>  
1107

1108 Tassy, A., Mocochain, L., Bellier, O., Braucher, R., Gattacceca, J., & Bourlès, D., 2013. Coupling  
1109 cosmogenic dating and magnetostratigraphy to constrain the chronological evolution of peri-  
1110 Mediterranean karsts during the Messinian and the Pliocene: Example of Ardèche Valley, Southern  
1111 France. *Geomorphology*, 189, 81-92. <https://doi.org/10.1016/j.geomorph.2013.01.019>  
1112

1113 Trosseau, Antoine, Anne Maigret, Yvan Coquinot, and Ina Reiche, 2021. In Situ XRF Study of Black  
1114 Colouring Matter of the Palaeolithic Figures in the Font-de-Gaume Cave. *Journal of Analytical Atomic*  
1115 *Spectrometry* 36 (11): 2449–59. <https://doi.org/10.1039/D1JA00202C>  
1116  
1117 Valladas, H., Pons-Branchu, E., Dumoulin, J.P., Quiles, A., Sanchidrián, J.L., Medina-Alcaide, M.Á.,  
1118 2017. U/Th and <sup>14</sup>C Crossdating of Parietal Calcite Deposits: Application to Nerja Cave (Andalusia,  
1119 Spain) and Future Perspectives. *Radiocarbon* 59, 1955–1967. <https://doi.org/10.1017/RDC.2017.120>  
1120  
1121 Van Beynen, P., Bourbonniere, R., Ford, D., Schwarcz, H., 2001. Causes of colour and fluorescence in  
1122 speleothems. *Chemical Geology* 175 (3-4), 319-341. [https://doi.org/10.1016/S0009-2541\(00\)00343-0](https://doi.org/10.1016/S0009-2541(00)00343-0)  
1123  
1124 Vignaud, C., Salomon, H., Chalmin, E., Geneste, J.-M., Menu, M. 2006. Le groupe des « bisons  
1125 adossés » de Lascaux. Étude de la technique de l'artiste par analyse des pigments. *L'Anthropologie*  
1126 110 (4): 482–99. <https://doi.org/10.1016/j.anthro.2006.07.008>.  
1127  
1128 Watchman, A., 1990. What are silica skins and how are they important in rock art conservation?  
1129 *Australian Aboriginal Studies* 1, 21–29.  
1130 <https://search.informit.org/doi/10.3316/ielapa.154935712026809>  
1131  
1132 Watchman, A., 2000. A review of the history of dating rock varnishes. *Earth-Science Reviews* 49,  
1133 261–277. [https://doi.org/10.1016/S0012-8252\(99\)00059-8](https://doi.org/10.1016/S0012-8252(99)00059-8)  
1134  
1135 Zhang, X., Tauler, R., 2013. Application of multivariate curve resolution alternating least squares  
1136 (MCR-ALS) to remote sensing hyperspectral imaging. *Analytica chimica acta* 762, 25–38.  
1137 <https://doi.org/10.1016/j.aca.2012.11.043>  
1138  
1139 Zielinski, R.A., 1980. Uranium in secondary silica; a possible exploration guide. *Economic Geology*

1140 75, 592–602. <https://doi.org/10.2113/gsecongeo.75.4.592>

1141

1142 Zielinski, R.A., 1982. Uraniferous opal, Virgin Valley, Nevada: Conditions of formation and

1143 implications for uranium exploration. *Journal of Geochemical Exploration* 16, 197–216.

1144 [https://doi.org/10.1016/0375-6742\(82\)90010-3](https://doi.org/10.1016/0375-6742(82)90010-3)

1145