Decision for round #1 : ***Revision needed***

Decision round #1

Dear authors,

Thank you for your submission to PCI Archaeology. As you can see, up to four reviewers have accepted my request to review your manuscript. Despite all of them are very positive, some highlighted a few details and shortcomings that deserve your attention. Thus, the reviewers recommend reconsideration of your manuscript following revision and modification. I kindly invite you to resubmit your manuscript after addressing the comments. Please, pay special attention to the remaks made by Laure Dayet and Alain Queffelec, as they highlighted a number of specific issues that should be adressed.

PCI Archaeology values your contribution and I really look forward to receiving your revised preprint.

Kind regards,

Aitor Ruiz-Redondo

*by **Aitor Ruiz-Redondo**, 10 Dec 2021 09:14*
Manuscript: **https://hal.archives-ouvertes.fr/hal-03383193**

Review by anonymous reviewer, 11 Nov 2021 16:13

The work specifically addresses the problem related to the formation of certain types of concretions formed on rock art, given their eventual impact on dating carried out using the U / Th method. The work presents very concretely a novel in situ, non-invasive methodological approach to identify these silica-rich concretions. The work is very systematic and clear. It is very well-structured and easy to understand. The literature cited and consulted is adequate and very well supports the study issue and methodological proposal presented, which is also very rigorous and of high quality. For all these aspects, in addition to the disciplinary contribution and relevance in terms of the results obtained, its publication is suggested.

Review by Juan Francisco Ruiz López, 24 Nov 2021 09:05

- ⇨ *We thank Dr. Juan Francisco Ruiz Lopez for his precise review of our paper, and the good understanding he has of our work.*
  We want to ensure the readers that the issue of the UV lighting on organic life at the surface of the wall was taken into account during the development of the methodology. To preserve bacteria and other microorganisms that may be present on the walls we choose DEL with very low energy, a small range of lightning (few centimeters), and we take care of lightning the walls as less as possible. The acquisition time of the LIF spectroscopy, a hundred of millisecond for one point, combined with the small size of the laser spot (around 30 µm in diameter) is also one of this main advantage allowing rapid recording of surface fluorescence and minimizing the impact of radiation on the wall.

This paper is a remarkable piece of research about a number of topics which are crucial for Prehistoric art studies. It offers an interesting proposal for the identification of silica skins, or opal coatings, by means of a new methodology that allows a quick characterization. Additionally, this research combines different analytical strategies and studies about the origin of these accretionary crusts and its taphonomy. The result is a well-balanced proposal that could be considered an example for researching the extremely challenging rock art systems at a global scale.

This research program was developed for the specific case of Points Cave, a limestone cave in central France with remarkable hand imprints and some other Palaeolithic style pictographs. Many of these paintings based in iron oxides are obscured by the silica skins, which has been preventing a precise characterization of the pictorial substances. This issue motivated the development of an in situ methodology to identify positively the distribution of silica skins in the rock walls.

Silica skins were considered some years ago as a possibility to constrain the age of rock art stratigraphically connected to these accretionary crusts. This research considers this possibility as well, but it goes beyond that focusing on issues ranging from direct in situ characterization, preservation of rock art, weathering or taphonomy. One of the main strengths of this paper is the exploration of the possibilities of in situ identification of these coatings by the emission of

fluorescence under specific wavelengths of UV lighting. This is based in fluorescence properties of the uranium content of silica skins, which offer a green fluorescence under UV light (280 nm LED), with emission peaks at 501, 521, 545 and 572 nm. The absence of UV fluorescence of iron oxides is well-known, helping to an easy discrimination of the distribution of these pigments on the walls, in contrast to silica skins. This is the first time that this methodology is used in a rock art cave.

The spectroscopic analyses in laboratory of five flakes naturally detached from the walls of Points Cave confirmed these results. Moreover, the laboratory analyses revealed the taphonomic effects of these opal coatings on the rock art. The crusts are scatteredly distributed in the samples, and in the walls as well. Opal coatings develop as a continuous layer that embed the iron oxide of pigments, making the morphology of haematite no longer observable on the surface. This point is crucial, because it is the reason of the absence of signals of the pigments during in situ analyses with spectroscopic techniques like pXRF and Raman, that have a limited penetration. This way, a map of the distribution of these crusts on the decorated walls could offer a crucial information to select the points of analyses in the walls.

The authors are proposing to improve these positive results by the application of a new method based on a portable UV laser-induced fluorescence (LIF), specifically developed for this research, that will be used in situ, trying to replicate the results achieved up to now in laboratory with this well-known technique very often used in Biology for the identification of bacteria and viruses.

In my opinion, the most positive contributions of this paper fall in the methodological development of a new approach to the analyses of silica skins. It has been of special interest for me the taphonomic studies, the discussion about the origin of these accretionary crusts, and the possibilities to consider them a proxy for environmental change over time that could help to the chronological interpretation of rock art.

The authors pose UV LIF as a future in situ methodology. While this contribution will be for sure remarkable in the future, in my opinion it has not had such a significant impact in the results offered in the paper as to be highlighted in the abstract, across the main text and in the

conclusions. The possibilities opened by UV LIF would need and independent paper in the future when this equipment is ready to be used on site.

I am worried as well by the effect of UV light on the microscopic biome living on cave and rock art walls. UV light in wavelengths under 300 nm is well known for its germicidal effects. I think an independent research would be worthwhile in order to have a clear idea on the long-term effects of UV lights on the biome of the rock art systems.

Review by Laure Dayet, 09 Dec 2021 15:03

- ⇨ *We would like to thank Dr. Laure Dayet for taking the time to review our work and for her comments that improved our paper. It is certain that the study must be continued in order to refine the links between the chemical elements and the amorphous siliceous phase(s), posed here as a hypothesis. The methods we have used (SEM-EDX, UV-LIF, UV photography, Raman) do not allow us at this stage to specify the chemical links between opal and uranyl, neither from a structural point of view nor on the uranium enrichment mechanism of this siliceous phase.*
  In this sense, we agree with Dr. Dayet that further analyses should be carried out to clarify the link between opal and uranyl groups. In this regard, but also to understand the interaction between opal and pictorial material (iron oxide), a request for analysis time on a synchrotron is being written.

Review of Quiers et al. “Light in the Cave: Opal coating detection by UV-light illumination and fluorescence in a rock art context”

The paper “Light in the Cave: Opal coating detection by UV-light illumination and fluorescence in a rock art context” presents in-depth observation and measurements of UV radiation of siliceous materials. I have been impressed by the quality of the data presented. The paper is well structured and the results are consistent enough for publication. The methodology used is reliable and the text is quite clear and straight forward. My only concern is the high number of sentences that present green light UV-fluorescence as a clear pattern for the detection of opal occurrences. In the paper the demonstration that uranyl groups do characterize the green light UV-fluorescence at the microscopic scale is fully achieved. However, two other working hypotheses elaborated in the paper are not fully demonstrated yet: the fact that uranyl groups

solely belong to opal and the fact that the green light UV fluorescence on the photographs of the panels solely belongs to opal or siliceous materials. We would like to see the fluorescence signal of a part of the wall where chemical and mineralogical analyses depict a total absence of opal and siliceous materials. In absence of such witness sample, the theoretical data about the UV-fluorescence colours of the compounds composing the cave wall should at least be given. This being said, the interest of this works makes no doubt as it proposes consistent leads of research for opal detection in rock art and for a better understanding of the formation of opal microfilms in the vicinity of the pictorial layers of rock paintings.

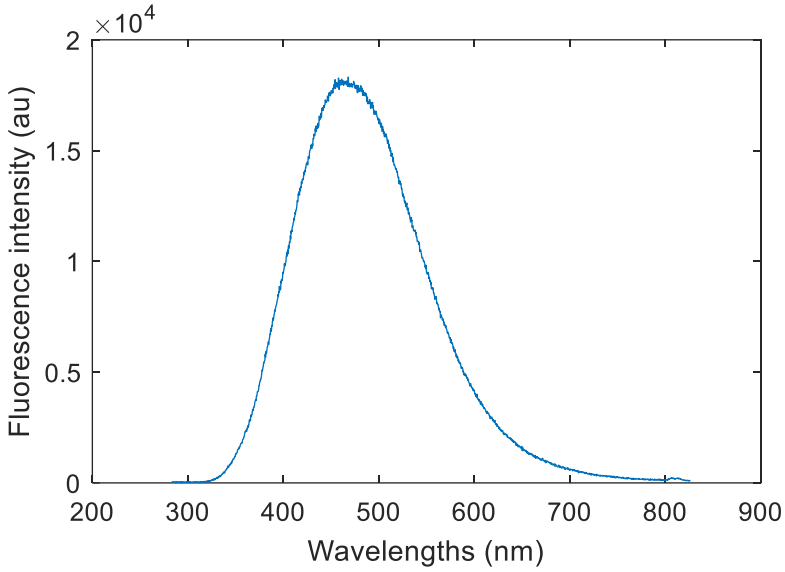
Detailed comments:

Line 278-284: The authors jump a bit too fast to the conclusions. Further argumentation would be needed here. It has not been demonstrated that the uranyl groups come from opal and not from another silica structure. It must be demonstrated that in the micro-samples where uranyl peaks are observed, opal is the sole type of silica observed. Line 365-385: That's a great job, I am impressed by the quality of this work, the demonstration that green light fluorescence under UV light correlates with the uranyl peaks is complete. There is just one small step that remains to be demonstrated: the fact that uranyl groups do belong to opal and not to other silica structures.

> Observation of samples under SEM shows that silica structures present here were identified as opal. As no other particular silica structure has been observed in the µ-samples, we assume that the uranyl fluorescence signal we detected is linked to opal. However, we agree with the reviewer that uranyl can be entrapped in another silica structure and display similar spectral features. On a different site, it is not excluded that uranyl can be detected in a silica coating which would not be identified as opal crystalline structure, that's why we insist on the necessity of laboratory observation and analyses of sample when it's possible.

Line 355-356: The fact that green-light UV fluorescence is a feature of opal contents is a logical conclusion but the demonstration that this UV fluorescence light does belong to opal is not completely achieved. Here we would like to see a witness sample, a sample of the cave wall that do not contain opal at all or a sample of painting with a similar hematite pigment that do not contain opal at all.

> Fluorescence cartography realized on sample S-ECA-05 presents spectra which do not contain uranyl spectral features in zones where no green fluorescence was observed (figure 9). The figure above shows an example of fluorescence spectrum obtained in a zone where no opal (and green emission) was detected. You can see the absence of uranyl spectral features.



However, in the absence of precise information on the distribution of opal on the surface and in the limestone of the Points cave, it is difficult to propose a control sample absolutely without opal to test the negative response.

Line 398-399: What is the colour of UV fluorescence of the other minerals present at the surface of the cave wall? Why a green colour indicates the presence of opal instead of any other mineral? I would not be as affirmative as the author about the clear detection of opal from the photographs.

> Uranyl ions are the most common fluorescence activators in minerals under short UV which produce bright green fluorescence. Entrapment of uranyl ions are common in silica structures and especially opal. Based on the analyses performed on µ-samples from flakes and walls, we did not observe 1/ any other silica structure than opal, 2/ any particular minerals known for green fluorescence emission or 3/ any spectra presenting a green emission with a spectral shape different from uranyl. Calcite can present varying fluorescence colour but often fluoresces in violet-blue region (similar to the spectrum above; probably the mineral phase observed in Great Signs panels for example). As µ-samples are from the same

walls analysed with UV light, and no particular other green signature was observed, we are quite confident this green signal is linked to uranyl in opal.

However, reasonable doubt exists for greenish fluorescence which can be also observe on other cave walls. We agree with the reviewer that UV photographs needs in situ spectral validation as mentioned in the next paragraph. We hope to realize these measurements when we'll have access to the cave again.

Line 632: Are you sure of this concentration limit? A concentration in U lower than 1 ppm must not be very common.

> This concentration only refers to an upper limit from which sampling quantity of the sample needed for the analysis can be reduced, according to the papers cited in the text. Uranium concentration can vary a lot depending on the sample, and to our knowledge, concentration lower than 1 ppm could be common on some type of samples such as stalagmite.

Review by Alain Queffelec, 07 Dec 2021 15:31

- ⇨ *Many thanks to Alain Queffelec for is very careful review. By tracking all the typos in the text, the form of the figures and their legends, as well as the content developed in our article, it allows a clear improvement of the paper both in form and content.*
  We made sure to make the necessary corrections in the text, and we hope to have left no typos, and the same goes for the figures.
  A number of additional data were missing for the understanding of the study of opal at the Points cave, so we added these data to the Figshare directory and these are accessible via the citation in the manuscript in the "additional information" section.
  We made specific responses to some of the remarks in the proofreading report below.

The manuscript entitled « 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)" submitted by Marine Quiers et al. proposes a new method for detection and study of opal coatings in caves by means of UV fluorescence spectroscopy. Based on

identification performed on samples and micro-samples, the authors confirm the possibility of in situ identification and therefore spatial distribution of such coatings directly on the cave walls. They summarize the importance of such studies and identifications of mineral phases for several problematics around rock art in caves.

This manuscript is very interesting and, in my opinion, could be improved with the following suggestions. These are mostly details, but the main recommendation would be to balance more effectively the information and hypothesis about opal coatings between the introduction and the discussion. Some information indeed arrive too late for the reader who reads the manuscript without having an idea of the reasons why such a nice methodology is developed.

Authors made a really nice effort in the open data and open code perspective. Integrating in a better way this data by calling the SEM images in the text, and describing a bit more the fluorescence files would benefit to the reader and would strengthen the manuscript.

Introduction:

- Line 61: “Hematite”, rather than “haematite, is the name of this mineral in the International Mineralogical Association (IMA) list of mineral, which is kind of the international standard for mineral names. It is also “hematite” in scientific papers related to it like “Blake R L , Hessevick R E , Zoltai T , Finger L W , American Mineralogist , 51 (1966) p.123-129, Refinement of the hematite structure”, on all main mineralogical websites (Webmineral, Mindat), and so on. Could you change “haematite” to “hematite” throughout the manuscript or explain why you do not follow the IMA? A research on Google Scholar shows that “hematite” is used more than 10 times over “haematite”, and so is if compared in Google Books

> we agree on this point and we made the correction in the manuscript

2- Material

There are minor comments for the Material text, but the main question arises from the Results part that uses samples not described in this part (Line 235 + PRM in Fig. 4)

- Line 137: is it possible to know which face was directed upwards and downwards at the time of excavation?

> Regarding the coloured flakes of limestone, it is important to understand that they were found in the chaos of blocks at the bottom of the rock art panels. That implies to things: 1/ they were not in direct contact with the sedimentary ground and 2/ they have been moved by the chaos of blocks disturbances several times during the historical period, probably for the exploitation of the sediments. The archaeologist Julien Monney have found them during a visual survey of this chaos and probably notice them because of their colour, so I would say that they were find with the colour face upward.

- Line 150: We can see a second µ-Sample in the Supplementary Information folder MEB-FEG-datas_S_ECA_05. Could you mention it in the text please?

> You are right, the samples splitted themselves during the sampling which results in multiple parts of the same sample. Corrections were made in the manuscript and you could find photos in the supplementary information files.

- Figure 2: the "covered on one side by colouring matter" in the text (line 137) is not that clear on this figure. Would it be possible to add D-stretch treated images?

> We agree that the image is not very good to see the pictorial matters at the surface of the flake. Unfortunately, D-stretch treatment does not give results significant enough to be presented.

3- Methods

The current Methods part is clearly written but would benefit from integrating other methodological paragraphs that are presented in the Results section. It would also be important that the authors make reference to the Supplementary Information files that they provide, and how to use them. Especially, the fluorescence data are not detailed and, by opening the folders, I do not know at all how to use them, in which software, what are the qeccd.txt files etc. A readme file in the .zip files on figshare would be helpful, and/or an explanation here in the Methods section.

> References to the Supplementary Information were added in the text as advised. However, all information on data are already available in the data file description on Figshare (by scrolling down after clicking on the data file name) and comment in the data treatment script.

We still added some precision to the data description and hope it make it clearer. Software used for data treatment is Matlab, as mentioned in the Methods part and in the script file description.

- Line 174-177: You do not mention any carbon or metal coating of the samples. But you mention analysis in high-vacuum mode. Since the samples are not highly conductive, can you confirm that there is no mistake here, just to be sure.

> yes, the samples were put without any preparation in the SEM chamber in high vacuum mode. We consider that the iron composition of the pictorial matters is enough conductor to evacuate the charges and we work in a low energy mode around 1.5 kV. I also want to mention here the great experience of Sebastien Pairis who led the SEM-EDS observation and analysis and achieve to get us these beautiful images.

4- Results

4.1 Macroscopic scale observations

- Line 220-222: Would it be possible to hypothesize that these calcium sulphates deposited on the wall after the falling of the flakes? Or it could have been removed from the flakes since they were on the ground?

> Everything is possible here. The mineralization on the walls are an issue to investigate to understand the sequence of natural/mineral events.

4.2 Microscopic scale observations

This section of the manuscript shows strong evidence of the presence of the opal coating, surely, but the text and the description of samples needs a reworking so that it becomes much easier to follow for the reader.

- Could you explain why there no SEM images from µ-S-ECA-01 in the Supplementary Information folders? So that we do not think there is a mistake in the SI links. Or maybe there is a folder but the link is missing?

> There is no mistake in the deposited files on Figshare or the link in the Supplementary information. S-ECA-1 doesn't have an associate µ-sample as at the time of the study, S-ECA-1 was in another lab for methodological development on reflectance spectroscopy. We

apologize for this missing sample that probably doesn't change the substance of the article. Further study will integrate this flake that was put aside.

- SI Images from other µ-Samples that µ-S-ECA-05 show clearly that hematite plates are covering opal coatings. Could you show that in the Figure 3 also and mention it in the text? I think it could be important for relative chronology discussion. Even for µ-S-ECA-02 the hematite plates are spread on the wall flake in the same manner as the hematite plates on the opal spheres in µ-S-ECA-04 for example. So it really looks like hematite is posterior to opal formation.

> We agree that the SEM images seem to show that the hematite is laid down on the opal film. However, in the absence of information on the mode of development of the opal, it is difficult to discuss the relative chronology. Indeed it is not impossible for the opal to form at the interface between the substrate (limestone) and the pictorial material (hematite) and thus to present a micro-stratigraphy where the oldest phase is found at the top. This hypothesis is based on the pictures of the µ-sample PRM-19-16 where the siliceous film seems to embed the hematite plates.
This again illustrates the need for further study, particularly with regard to the mode of formation of the opal and its interaction with the pictorial material.

- Line 235: Which samples from the decorated walls? You only mentioned samples from the flakes so far. Are there other samples that should be described in the Material section?

> Corrections were made in the manuscript and data are available on Figshare, link to these files are in S.I.2

4.3 Opal identification by UV-fluorescence

- Table 2: it could be interesting to explain what are the 604 nm and 650 nm bands from Fritsch et al. and Garcia-Guinea et al. since it seems to be quite different in wavelength, and not seen by all studies. Is this very light shoulders that you couldn't see in your analysis? Is this specific to their own study? Is 604 and 650 the same thing?

> There is indeed a mistake in the table 2 (table 3 in the new version), as the 650 nm peak described by Garcia-Guinea et al. (2013) is not related to uranyl signal in their paper. This peak was removed from our table. 604 nm shoulder described by Fritsch et al. is however

related to uranyl fluorescence signal (see for example Drobot et al., 2015 DOI: 10.1039/C4SC02022G) but is not always detected in studies on natural samples.

- Line 311-313: could you explain how you decided to take 3 loadings and not 2 or 4? Is there an arbitrary threshold somewhere in the method? If so can you give the reader the value of this threshold? All this part should be in the Method section rather than in the Results section. There should be a sub-section of chemometrics/cartography in the Methods.

> Number of loading was determined using SVD method from the MCR-ALS editor in Matlab. This number was determined graphically according to the % of explained variance of the different loadings (76.8% for the first 3 loadings). These precisions were added in the text.

- Line 313-315: from what I understand, the loading 1 is, probably, the one with the highest load. The shape of the Initial loading 1 as seen in Figure 6 is quite strange since it is totally absent from Figure 5. Could you explain this?

> The loading 1 is associated with specific spectra recorded on the sample surface (only few points) probably due to particular minerals. As data used for the model is not normalized in intensity, this probably explained why this is the first loading. Figure 5 only represent few measurement points on the µ samples, and not an exhaustive measurement which explain why this spectral shape is not observed.

- Line 329: is the laser beam focused once for all the cartography, or is there an auto focus for each pixel? If the former, how did you choose the focus? In the middle of the sample?

> Concerning the single measurements, focus was made before each measure. However, this is not possible for the cartography measurement, as the focus is made manually on our instrument. This is a bias we are aware of and focus made prior the measurement is realized in order to limit at maximum this bias. For instance, is the surface of the sample presents variations of its elevation, focus is made on the mean elevation to limit the biases when the measure is made on high or low elevations. We are currently developing an instrumental solution for field experiments which would allow focus at each measurement points to avoid this issue.

4.4 Visual detection under UV light: laboratory experiments

I would have guessed lines 348-361 and Figure 8 would have bene placed in the manuscript before the more advanced techniques like spectral analysis, chemometrics, cartography. Just looking at the samples with a binocular under UV light should be placed before UV spectral measurements? Moreover, this section includes general bibliography on uranyl fluorescence and so on, so it should be placed before. Line 345-355 also should be before the 4.3 part. And Lines 358-359 clearly would benefit also to be integrated before: in this section you would write that µ-S-ECA-03 shows localized greenish fluorescence, and then, in the section with the current Fig. 5, you would explain that the fluorescence spectra of this sample does not show the uranyl signal, because of bad targeting or other. And lines 365-389 and figure 9, the comparison between visible and spectral, would remain here, after both methods are used and explained.

> We understand that the construction of this paper can be discussed, as it was the subject of numerous discussions between the co-authors. The present organization was for us the clearest way to explain both the results and the methodology after we tried different possibilities. Notably, green emission of fluorescence obtained with UV illumination is presented after LIF methodology because it's the presence of uranyl in fluorescence spectra which led us to propose to use UV illumination as field methodology, and because the green illumination cannot be linked properly with opal and uranyl signal without analysis of the fluorescence spectra. We choose to integrate data treatment and chemometric methods in the results as this study is mainly on methodology development. However, we made some rearrangements in the organization which, we hope, take into account this remark and help the understanding of our work.

- Lines 365-372: I think the protocol here should be placed in the Methods section and should be more precise since I don't think any reader of the manuscript could redo your work on his own photos. I can see in the Matlab code the way you compare, but the way the RGB file is treated to extract the green part is not that clear to me. Moreover, please do not hesitate to refer to your Supplementary information files (especially here the matlab code) whenever it is necessary for the reader to understand that what you write is in the matlab file. (same as for SEM images, do not hesitate to call them when necessary in the text)

> UV image file is an RGB image which is composed of 3 colour layers: red, green and blue. We used only the green layer to access the green component in the image but we also

subtracted grayscale to avoid luminosity effects. We added some comments in the script file and hope it's easier to understand.

4.5 Visual detection under UV light: field experiments

- Lines 402-405: If I read it well, there is no figure showing that. It would interesting to see the difference so that the green fluorescence response reported in lines 396-400 would be even more obvious, by comparison with the other part of the gallery. I confess I am not familiar with UV light images in caves, and that I am lightly color blind, and it seems that non colour blind sees it easily, but a comparison with another part of the cave would be welcomed.

> We added some photos from field experiment, including walls from non decorated panels, in supplementary files in order to allow comparison between the walls.