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## **In situ and laboratory analysis of colouring agent from multiple contexts in the Palaeolithic rock art cave Grotte aux Points (Gard, France)**

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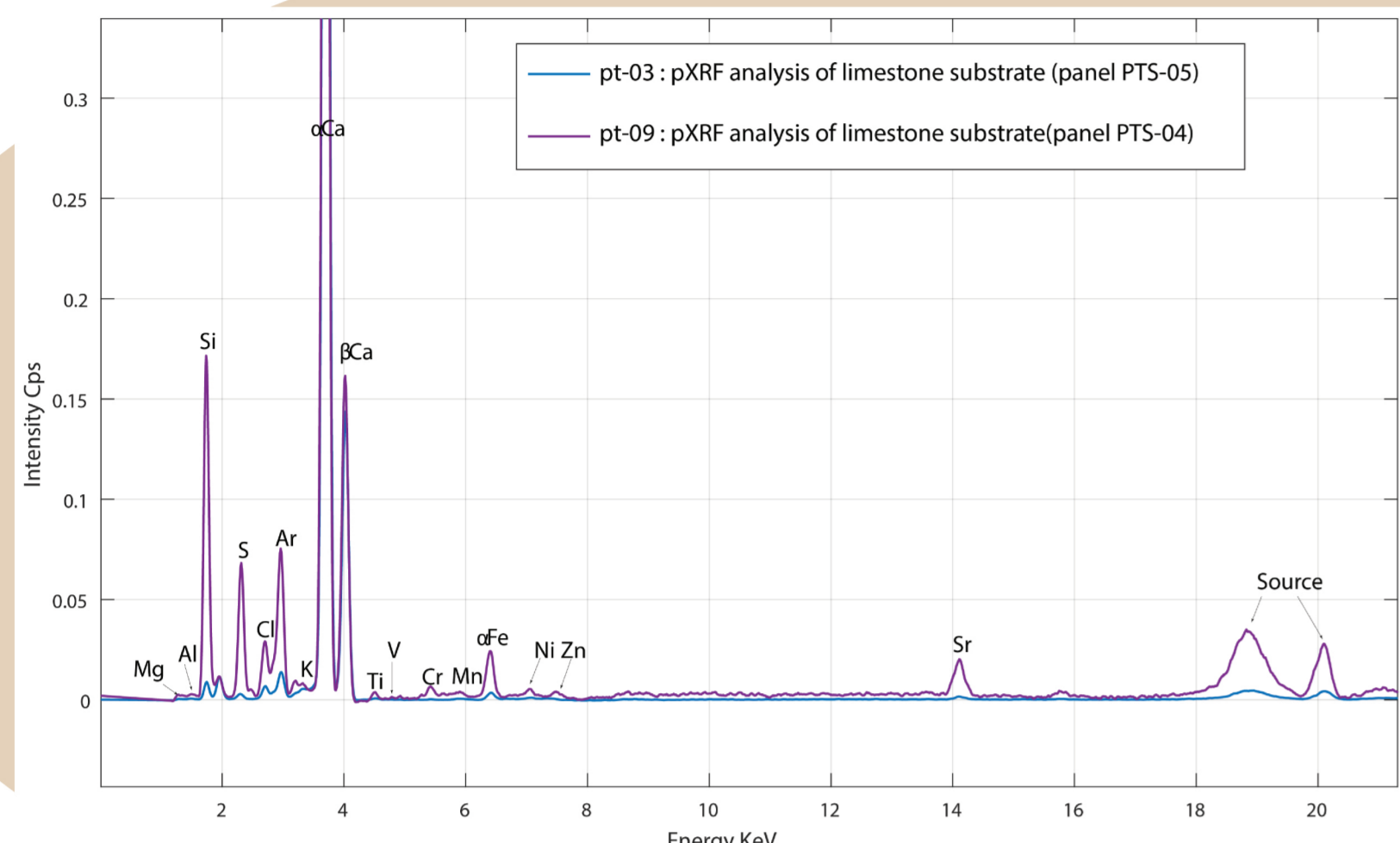
<sup>2</sup>Histoire Naturelle de l'Homme Préhistorique (MNHP), CNRS, Muséum National d'Histoire Naturelle

The Grotte aux Points is a rock art cave in the Ardèche canyon. Archaeological excavations reveal a collection of red colouring agents in the archaeological sequence excavated at the entrance of the cave. In order to appreciate the **evolution of supply and uses** of coloring agents over time at the Grotte aux Points, we realized sets of analysis.

In order to discuss potential **connections between archaeological levels and wall's paintings**, a pXRF system (Elio XGlab) is used **in laboratory** for the collection of solid colouring remains and **in situ** for the paintings.

**Can we compare pXRF result of raw coloring agents from archaeological sequence with pXRF result of in situ analysis of pictorial matter on the walls?**

## In situ analysis of rock surface



pXRF spectra of limestone surface: elemental composition variability

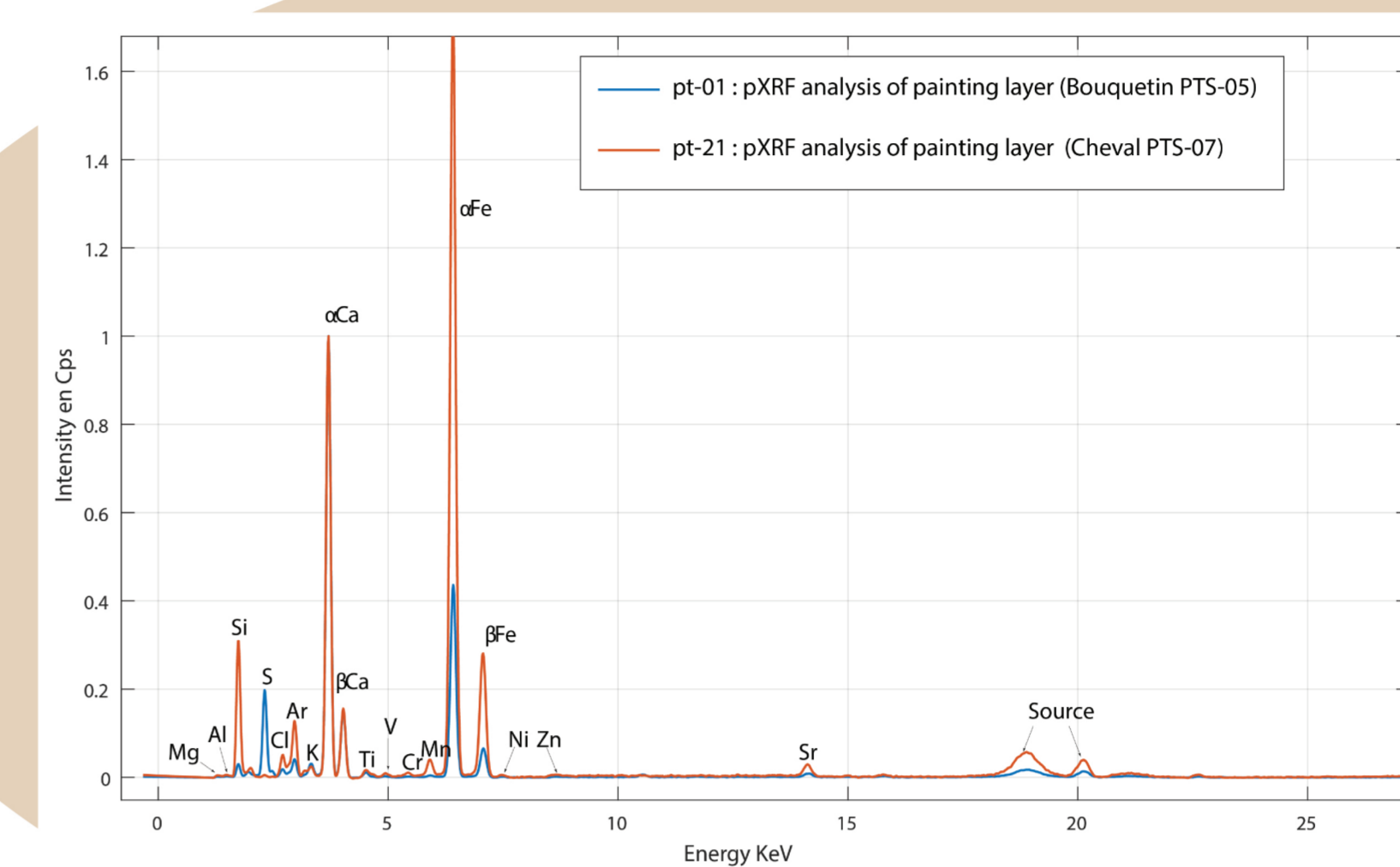


Morphology of rock surface with black pollution

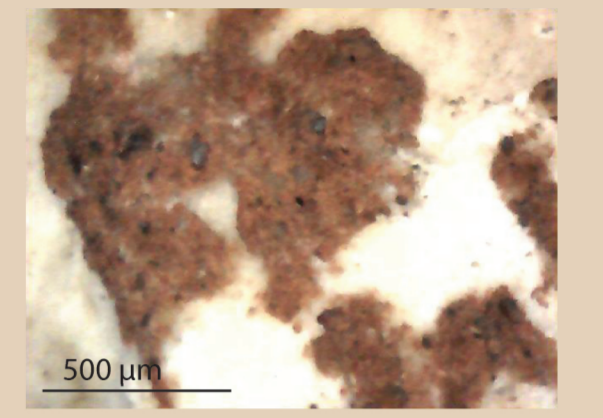


Morphology of non-altered rock surface

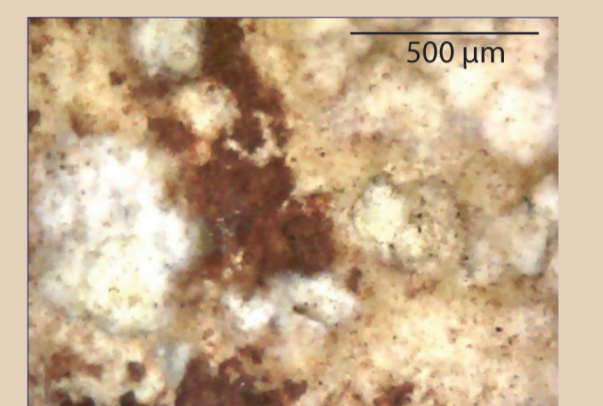
## In situ analysis on red painting layer



pXRF spectra of painted wall zones: elemental composition variability

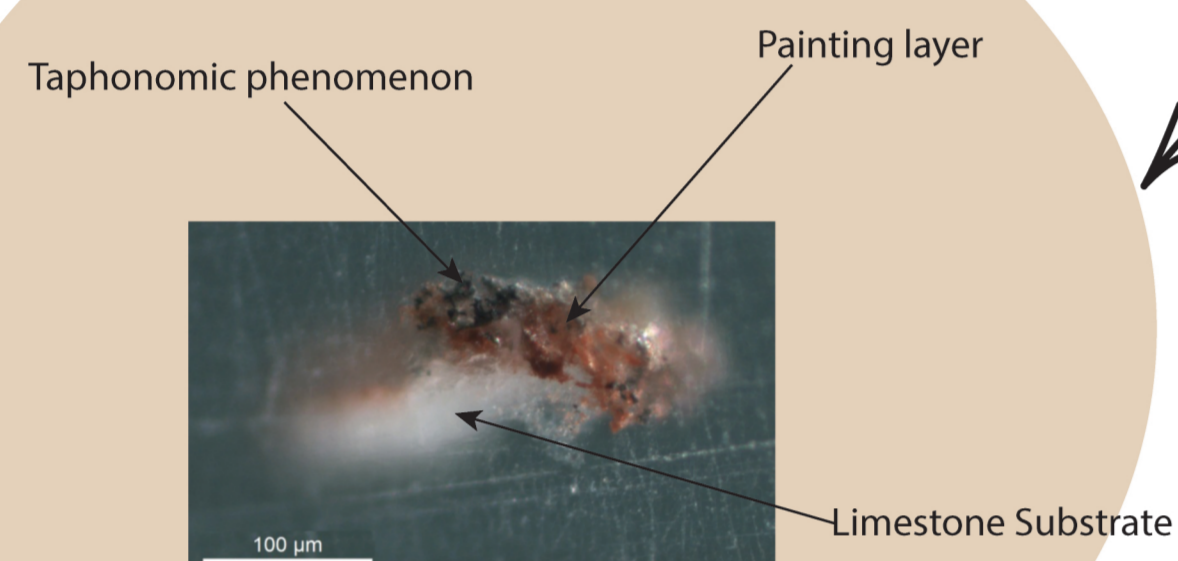


Morphology of red/black crystals < 100µm



Morphology of painting layer with white/yellow accretion

## Example of painting matter sampling



Sample of painting layer carried out at the Grotte aux Points in 2013 (Photo: S. Hoerlé)

## Disjunction between painted walls and archaeological layers



Colouring agents in archaeological layer

Upper Palaeolithic archaeological layer

Accretion of calcite and/or gypsum

Ornated wall

Archaeological layer

Similarity: relative datation?

## Methods

### 1) In laboratory analysis of solid colouring agent:

- Identification of Fe phases, with a cortège of minor and trace elements: Al, Si, P, S, Cl, Ca, Ti, V, Cr, Mn, Ni, Cu, Zn, As, Rb, Sr, Zr (cf. pXRF spectra). Two groups of remains are identified: (i) with strong environmental input, (ii) without environmental input (cf. PCA)

### 2) In situ analysis of paintings:

- Analysis of painting layer: identification of two phases (i) limestone and (ii) calcium sulfate  $CaSO_4$

- Analysis of pictorial layer: the pXRF results show a strong similarity between all the ornated panels. The trace element variability is low and doesn't permit to discuss the link between the panels.

### 3) Mathematical treatment:

- Normalisation of spectra by Fe or Ca allows to observe minor and trace elements linked with those elements. However the environmental input is too important to use this method.

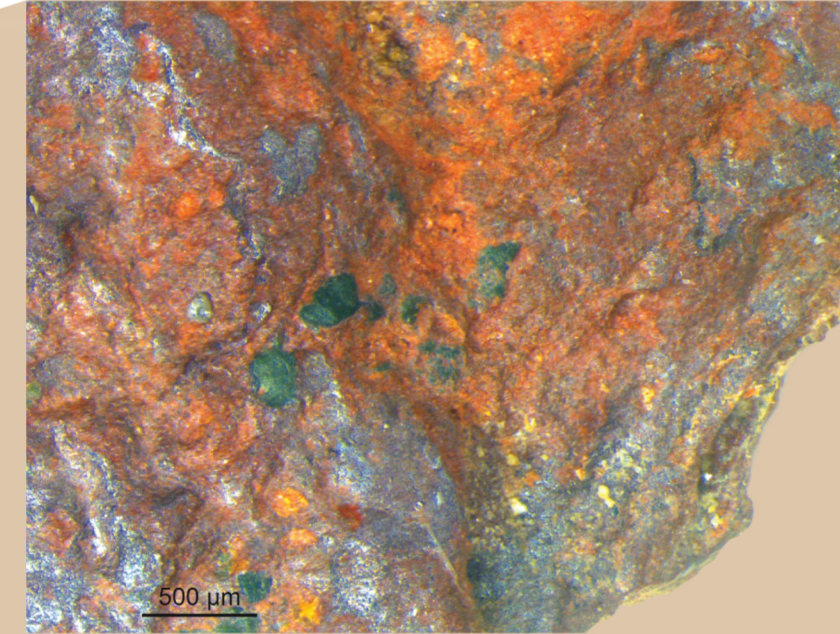
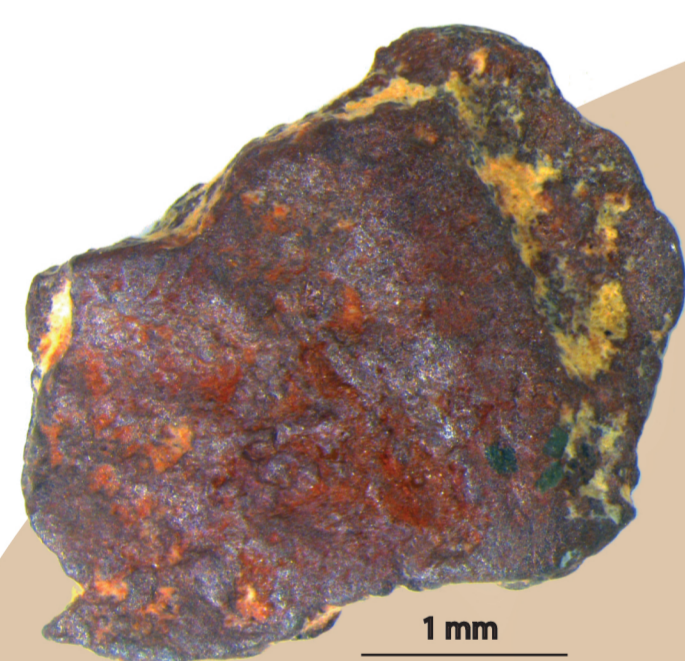
- Subtracting pXRF signal of substrate and environmental input in the analysis of pictorial matter and colouring agents need strong mathematical treatments that didn't work all the time (Gay et al., 2015).

## Discussion

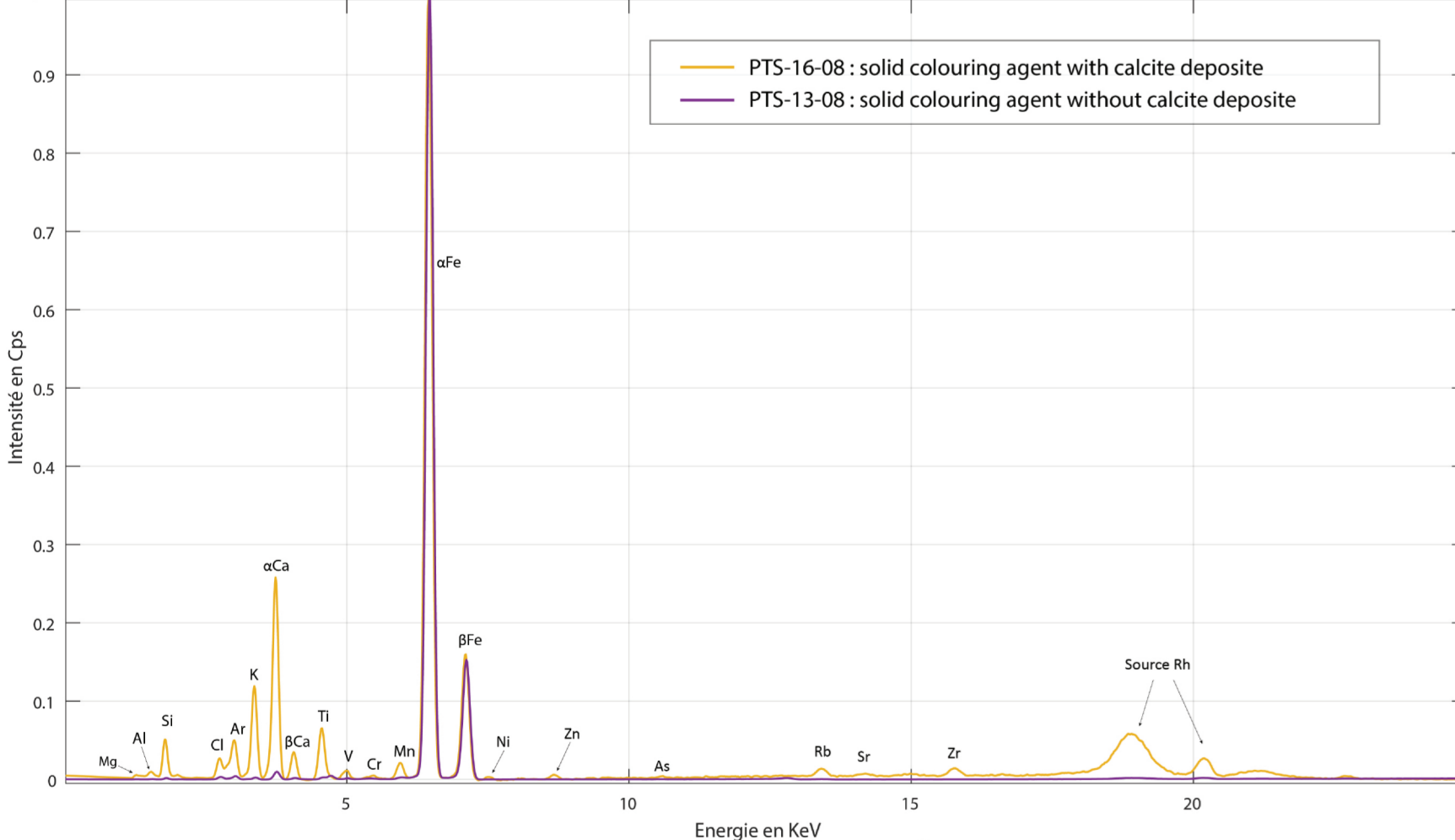
1/ The taphonomic phenomenon with the environmental input needs to be precisely characterized. The information obtained by those methods can be interesting but it is not enough.

2/ The analytical methodology needs to be improved

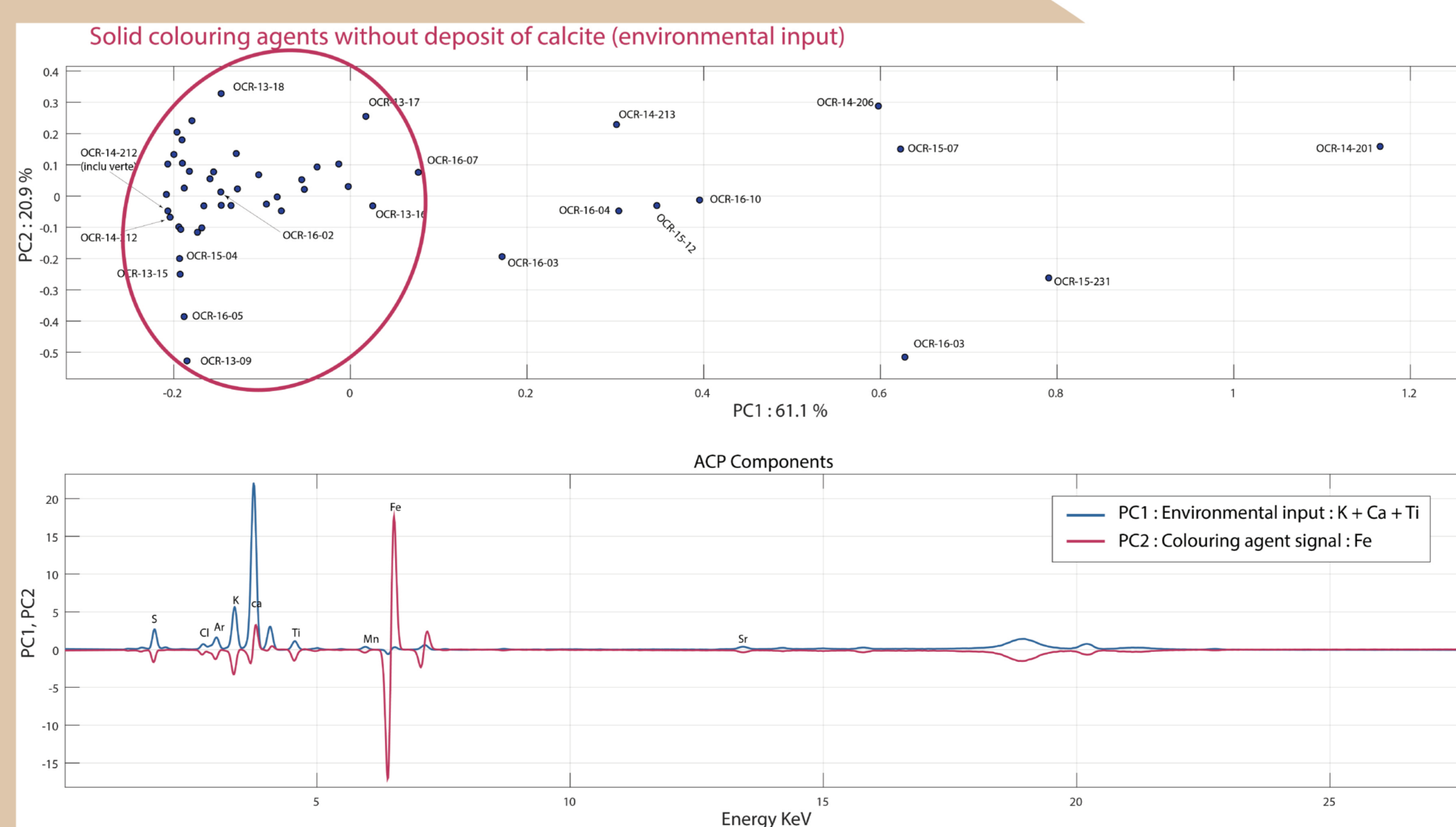
## Analysis of solid archaeological colouring agents in laboratory



Remain OCR-13-10: solid colouring agent representative of the collection with green inclusions (celadonite, characterization in progress) marker of raw material sourcing



Example of two characteristic spectra on colouring agents, normalized by Fe



Principal Component Analysis of pXRF result on the solid colouring agents.

## Scientific limitations

- Technical limitation of the pXRF device: good detection of element but starting from Si, influence of cave conditions on the analysis, quantification not reliable

- Geometry of caves wall: accessibility to the paintings, angle between detectors and walls

- Environmental input: less knowledge on taphonomic phenomenon

**At this step it's not possible to make comparison between solid colouring agents and painting layer**

## Bibliography

Gay, M. (2015). Développement de nouvelles procédures quantitatives pour une meilleure compréhension des pigments et des parois des grottes ornées préhistoriques. Ph. D. thesis, Université Pierre et Marie Curie-Paris VI.

PCR Pigmentotheque porté par E. Chalmin et H. Salomon, Service Régional d'Archéologie, Région Auvergne-Rhône Alpes, 2016-2019.

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## Methodological solution: Standard library - Pigmentotheque Project (Chalmin et al., 2016)

### Collection of rich iron geological standards:

- to improve the stability of the data acquisition and characterize the effect of iron in the matrix

- to test differences between the set of rich iron standards

- to make experimental archaeology and characterize the effect of environmental input on colouring agents signal

- to calibrate the device and develop reliable analytical methodology



Geological standard collected on the field: chose for its colouring and technical properties Bordezac (Gard, France) (photo: E. Chalmin)



Calibration of the device with geological standard



Archaeological experimentation of grounding with geological standard (photo: H. Salomon)