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In-situ XRF study of black colouring matter of the Palaeolithic figures in the Font-de-Gaume cave

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Abstract

The study aims at characterizing prehistoric cave art by a non-invasive approach using portable X-ray fluorescence spectroscopy. Technical difficulties such as restricted access and heterogeneous material are discussed and a reliable, informative protocol was implemented for characterizing the chemical constituents of black painted figures. Two different data evaluation protocols were compared in the laboratory on mock-ups samples with respect to their applicability, limits and deviations, one relying on elemental ratios and the other one on an internal standard. The mock-ups were made of a calcareous substrate and natural Manganese oxide minerals likely to be found in the prehistoric cave art. The best-suited data evaluation protocol was applied to 19 analyzed figures in-situ in the prehistoric cave of Font-de-Gaume, Dordogne, France. Different chemical groups could be defined among the Manganese oxide-based paints and discussed within the cave context. Confirmation of the defined groups could be provided by complementary Raman investigations and they are consistent with chemical groups found in comparable cave art, namely in the Rouffignac cave, Dordogne, France.

Introduction

In-situ and non-invasive physicochemical analyses of the graphical entities in prehistoric decorated caves are currently used to study this fragile exceptional heritage. Techniques like portable X-ray fluorescence spectrometry (pXRF), portable X-ray diffraction (pXRD) or portable Raman spectrometry have already produced interesting results on rock art, allowing the user to distinguish different colouring matters¹⁻⁷, to assess the paintings preservation^{1-3,5}, to identify the chemical phases constituting the colouring matters^{2,3,5-7} or to discuss the paintings organization¹⁻⁵. However, their application and especially the interpretation of the data is more complex than it seems⁸. Particularly, elemental analyses are used to answer questions such as the differentiation of parietal representations or the determination of the sequence of production^{9,10}. A successful example was the study of the black drawings of the Rouffignac cave^{11,12}.

Nevertheless, there is still progress to be made because the full potential of portable analyses is still to be exploited. New results can be expected using a semi-quantitative approach and when more sensitive analyses methods are used in a combined approach. Additionally, every cave site with rock art represents a special case^{7,13}. Portable XRF is traditionally used to identify and quantify the chemical elements (between $Z = 13$ and $Z = 56$) in homogeneous matrices¹⁴. Generally, it is limited to semi-quantification in heritage science, and particularly in the case of cave art, due to the non-ideality of the studied systems¹⁵. Indeed, the studied prehistoric drawings and paintings were created directly on the cave wall, which is porous and chemically heterogeneous. Because of the relatively long depth penetration of the X-rays, this substrate will be probed along with the colouring matter and will add variable components to the resulting spectra. In addition, the colouring matters employed are micro- and nanocrystalline in powdered form and applied irregularly. At the scale of the analysed volume, the

system can therefore be considered as inhomogeneous and often even not as layered (Figure 1). Last but not least, the configuration of the system can change from one analysis point to another as the cave walls are not flat and the analysis with pXRF is thus geometrically heterogeneous. All these factors explain why the usual methods used for data evaluation based on fundamental parameters or calibration curves cannot be applied. Instead of attempting to quantify the elements in the colouring matter, several previous studies focused on the variation of the fitted intensity of the elemental characteristic lines in the spectra^{1,5,6,9,13}.

Different types of Mn oxides can be observed in archaeological contexts of painted Palaeolithic figures and several of them contain barium (Ba) in different proportions¹⁹. This is the case of romanechite ($\text{Ba}_2\text{Mn}_5\text{O}_{10}, x\text{H}_2\text{O}$) and hollandite ($\text{Ba}_{1-2}\text{Mn}_8\text{O}_{16}, x\text{H}_2\text{O}$). Others do not contain any, such as pyrolusite (MnO_2), todorokite ($(\text{Ca}, \text{Na}, \text{K})(\text{Mn}, \text{Mg}^{2+})_6\text{O}_{12}, x\text{H}_2\text{O}$), manganite (MnOOH), bixbyite (Mn_2O_3 or $(\text{Fe}, \text{Mn})_2\text{O}_3$), haussmannite (Mn_3O_4) and cryptomelane ($(\text{K})_{1-2}\text{Mn}_8\text{O}_{16}, x\text{H}_2\text{O}$). Potassium (K) is also encountered in natural Mn oxides. Therefore, the Ba/Mn, K/Mn and Fe/Mn ratios can in principle be used as potential differentiation markers between Mn oxides. To further complicate the differentiation, colouring matter based on micro- or nanocrystalline Mn oxides cannot be identified based on these ratios as natural Mn oxides are often associations of different Mn and Fe phases together with other minerals. Elemental ratios thus only represent distinction criteria of Mn-based black colouring matter.



Figure 1: Macrophotography of a pigmented area of the ensemble 5 of the principal gallery of the Font-de-Gaume cave. The colouring matters can be seen as superimposed and powdered materials unequally distributed on the rough calcareous substrate. © C2RMF, Anne Maigret.

The cave of Font-de-Gaume is a prehistoric site hosting an impressive collection of parietal art^{16,17}. It contains more than 200 animal and abstract figures combining diverse execution methods and several themes. The polychromy and the Magdalenian attribution makes this painted cave comparable to Lascaux in France and Altamira in Spain. Despite its rich potential, the studies of Font-de-Gaume by physicochemical methods has just resumed in 2013¹⁸.

At Font-de-Gaume, the colouring matter can be mixed, superimposed or applied directly on the cave wall without a preparation of the substrate (scarping). However, the use of engraving alongside the painting is frequent. This is especially the case of the black colouring matter, which is often used to underline the shape of the represented animals, either in paintings using other colours (red or brown, which is a mixture of red and black materials) or in drawing made of black only. A striking example of the complex graphical panel is the panel of the bison 4 on the left-hand side of the principal gallery. A panel can be composed of different graphical entities, that are totally or partially superimposed on each other. In the panel 4 a bison figure is superimposed on at least one probably engraved mammoth, a reindeer and likely another small animal. In addition, the tusks of the mammoth 5 also touch the rear part of the superimposed bison/reindeer. It seems that the contours of the rear part of the reindeer were followed while drawing the contours of the rear part of the bison. In this case it is difficult to determine, which animal was executed first (Figure 2). A detailed description of the graphical representations of the analysed figures is given in the supplementary information (SI: Figures 4-15).

The complexity of the panel composition explains the need of further investigations in order to understand its composition and sequence as well as highlights the analytical challenge that the prehistoric graphical entities represent at the Font-de-Gaume cave.

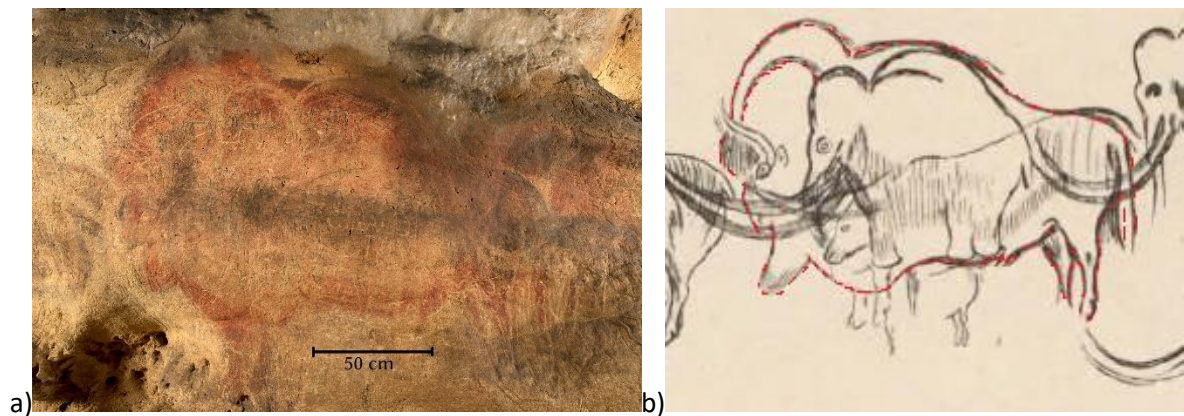


Figure 2: a) Photographic image of the panel 4 representing a superimposition of four animals (a painted and engraved bison, horse, reindeer and an engraved mammoth) at the Font-de-Gaume cave. © C2RMF, Anne Maigret. The figures are superimposed and altered (more details see SI Figure 6) ¹⁶. b) a drawing of the featured animals by the H. Breuil highlighting the bison, modification: © A Trosseau, C2RMF.

First qualitative analyses of the black cave pigment of the Font-de-Gaume cave have shown that their Ba content is variable¹⁸. Therefore, the elemental ratio of Ba/Mn can be used as a characteristic marker. Another possible way to establish links between the prehistoric black paintings with the elemental intensities is to consider the one of K. Just like Ba, K is a minor element of several Mn oxides, namely todorokite and cryptomelane ¹⁹. Thus, it would be theoretically possible to define a distinction criterion based on the K / Mn ratio. In the case of Font-de-Gaume, the walls bear K in their mineral composition due to the presence of micas and feldspaths scattered among the calcite matrix of the Coniacian limestone. Consequently, the intensity of the K line is comparable in both the wall and the coloured areas. In addition, a pure phase of K-bearing Mn oxide would show a K line of the same order of magnitude that those of several substrate points. This is why, the K intensity is not reliable and cannot be used as a discrimination marker at the Font-de-Gaume cave.

This article focuses on the semi-quantitative analysis of black prehistoric graphical entities of the Font-de-Gaume cave (France). The objective of this work is to set up a characterization procedure both

reliable and the most informative possible of pXRF data on the colouring matter used for the creation of prehistoric figures. Portable XRF was complemented by photographic imaging and portable Raman spectroscopy. Especially, we compare and discuss in this paper two procedures of data treatment that can be applied to pXRF spectra, the first being a re-evaluation of an already existing protocol and the second being a new one. These protocols concern the black colouring matters that are made of manganese (Mn) oxides. There are also red and yellow colouring matters in the prehistoric figures on the karstic walls in the caves, which contain iron (Fe) oxides. Other dedicated evaluation procedures need to be developed to semi-quantify these colouring matters⁷, which is too far-reaching and out of the scope of this paper. The chosen protocols are developed and evaluated on pXRF data obtained on mock-up samples and then applied on in-situ pXRF data of prehistoric figures of the decorated walls in the Font-de-Gaume cave.

Materials and methods

Preparation and analysis of mock-ups

A first step was to perform tests in the laboratory with experimental conditions similar to those in the cave to assess the feasibility and efficiency of these protocols. The analyses were conducted on natural (thus, not pure) Mn oxides minerals already studied by E. Chalmin²⁰ (Table 1), and on mock-up samples made of a calcareous substrate and the same natural Mn oxide minerals. The substrate chosen is a Coniacian limestone sampled near the cave, which is of the same type as the one of the cave walls. It contains a majority of calcite with inclusions of quartz that ranges from 10 to 25 % (v/v), as well as K-bearing minerals (approximately 0.5 wt.%) such as micas and in a lesser extent feldspaths and finally Fe oxides (less than 0.1 wt.%).

Cubic samples of a few cm³ with at least 1 cm thickness were cut out of the limestone and roughly polished with SiC paper 1200. The colouring matters were ground in an agate mortar and analysed by means of pXRF in powdered form. Then, they have been applied on the substrate with a wet (water-based) brush. Some areas of deposited colouring matter were removed with a dry brush to obtain different thicknesses of paints on the substrate. Portable XRF analyses were then conducted with the same portable device used for *in-situ* measurements with the same conditions.

Table 1: Prepared mock-ups with mineral Mn oxide phases. Psilomelane is a denomination for a natural unknown mixture of manganese oxides.

Sample N°	Main Mn oxide on Coniacian limestone	Corresponding sample no. (thesis of E. Chalmin) ²⁰
MP_1	psilomelane	46
MP_2	romanechite	33971
MP_3	psilomelane (romanechite + pyrolusite)	11
MP_4	pyrolusite	24
MP_5	arbitrary mixture of psilomelane 46 + psilomelane 11	

Studied prehistoric figures

The analysis campaigns took place from 2017 to 2021, through four field trips. The research team analysed 163 points among which 45 were made of red colouring matter, 55 on black colouring matter, 16 on polychrome areas of the prehistoric figures and 47 on the wall substrate. It covers 19 of the 222 known figures in Font-de-Gaume: 11 bisons (labelled Bx, with x a number), 2 reindeer (labelled Rx), 2 deers (labelled Cx), 2 mammoths (labelled Mx) and 1 bull (labelled Tx). The detailed description of the

studied figures can be found in the Figures 4-15 of the SI. This article focuses on the presentation and discussion of 78 analytical points recorded with pXRF on black figures with an exploitable Mn signal or the substrate.

Photographic imaging

Photographic imaging allows observing colouring matters at the scale of the panels and figures in the cave. The points for chemical analyses by pXRF and for mineralogical analyses by portable micro-Raman spectroscopy can be judiciously chosen. This also limits the number of analyses required per figure and allows extrapolating the results of the physico-chemical analyses to the whole figure or at least the remaining visible part of it. The results of the analysis can therefore be read and discussed in the prehistoric context at the scale of a figure, a panel or even an area in the cave.

Photography under visible light or direct light (LD) was performed with the use of two 500 W halogen lamps on stands with umbrella that allows to obtain images in high definition (Nikon, 24 MPixel) with well-lit figures for identification of the areas to be analysed and the detailed study of the figures without traveling on site.

Experimental conditions of pXRF

Portable XRF analyses were conducted on the prepared mock-up samples with the same portable device used for *in-situ* measurements in the cave using the same conditions. The spectrometer was an ELIO of the brand XG-Lab/Bruker®. This standardized device holds a 50 kV X-ray tube with a Rh anode that can deliver a power of 4 W. The detector is a 17 mm² SDD with an energy resolution of 140 eV at the Mn K α line. It is also equipped with a collimator able to focus the beam into a 1mm spot, two lasers, a positioning system and a tripod. The spectrometer is equipped with a camera. The experimental conditions were 600s of analysis with 40kV and 40 μ A delivered by the tube.

Data treatment procedures

Linear regression based on elemental ratios

This protocol aims at bringing a first description of the black colouring matter based on Mn oxides by discriminating several groups corresponding to different phases or mixtures from pXRF spot measurements directly on the prehistoric paintings. It has been previously used by other scholars^{4,11,12} but it has to be checked and possibly improved for the current case study of the decor of the Font-de-Gaume cave.

The pXRF spectra obtained during these measurements are processed with the PyMca software²¹. This software allows to fit the elemental peaks and to obtain an intensity in number of counts. As stated above, we use the intensity of Ba and Mn in this protocol. The signal of Mn is several orders of magnitude stronger in the colouring matter than in the substrate, while Ba is only found in the colouring matter. Thus, it is possible to use the signal ratios of these elements as distinction markers of the different types of colouring matters used. Depending on the Ba/Mn intensity ratio, several raw materials are then differentiated. In practice, the intensities of Ba are plotted versus those of Mn in a graph, and a linear regression is performed, allowing to assess the uncertainty. By doing so, an offset appears in the linear regression, so the meaningful quantity to study is actually the slope of these curves. Last but not least, this protocol allows studying colouring matters that are not pure, because only two characteristic elements are used in the process.

“Internal Standard” procedure

The goal of this second protocol is to estimate the intensities of several elements of the colouring matter without the signal of the substrate. It is based on the hypothesis that only one colouring matter is used at the scale of a graphical entity, so that we can extract a chemical signature from the set of measurements of elemental intensities of each figure, allowing us to compare these signatures to each other. It is important to notice that the obtained signatures are not compositions but only values representative of X-ray intensities. Moreover, physical effects such as secondary X-ray fluorescence and higher order matrix effects occurs and vary for each analysis point and are not totally corrected during the process, due to the varying two-layer nature of the analysed systems. It is not possible to quantify accurately the chemical signature to determine a real chemical composition.

At the beginning several spectra were collected on the colouring matter of a mock-up in the laboratory and in-situ on the figure, but also on nearby uncoated areas of substrate. All spectra of the substrate are added together into a sum spectrum. The same operation is applied to those of the colouring matter of the figure or the mock-up. The sum spectra of the colouring matter and of the substrate are fitted to obtain their elemental intensities. In the sum spectra, the variations of elemental intensities due to the variation of composition at the analysed points are averaged. Furthermore, in the sum spectrum of the colouring matter, a part of the signal corresponds to the underlying substrate, but is also averaged. Thus, the intensities of calcium (Ca), the proposed “internal standard”, are used to calculate a coefficient S representing the part of the signal due to the substrate:

$$S = \frac{Ca_{Sum}}{Ca_{Wall}}$$

With Ca_{Sum} the intensity of Ca in the sum spectrum of the colouring matter and Ca_{Wall} the intensity of Ca in the sum spectrum of the substrate.

The final sum spectrum is obtained by subtracting the sum spectrum of the colouring matter by that of the substrate multiplied by the factor S. Thus, only the counts produced by the colouring matter elements alone are supposed to remain in the spectrum. However, a major source of uncertainty produces a lack of accuracy. The sum spectra are corresponding to averaged intensities representing heterogeneous materials, so depending on the number of measured raw spectra the sum spectrum can be different. With a large number of raw spectra the statistical deviation due to the variation of composition can be reduced. This is not the case of the physical effects that modify the counts for each element in the raw spectrum. These effects depend on factors specific to each spectrum (composition, geometry, thickness of colouring matter) and unless these parameters are known, the physical effects cannot be corrected before the averaging procedure, leading to an error. Finally, the chemical signatures are normalized by their amount of Mn to be comparable between different figures.

Experimental conditions of portable micro-Raman spectroscopy

The mobile Raman measuring device used was developed by Jobin-Yvon HORIBA and consists of components that can be easily moved during a measurement campaign. The device is equipped with a "Superhead SH 532" measuring head with an Olympus "Long working distance" objective. In-situ Raman measurements require an arrangement with high flexibility and high stability at the same time. The head is mounted on a stable tripod with one axial translation (forward and backwards) and three rotation axes. Such long working distances guarantee the safety of the paint. The measuring head is connected to an air-cooled Nd: YAG laser (Coherent DPSS 532; $\lambda = 532$ nm; laser power on the sample lower than 5 mW) and to the spectrometer via a 5 m long, flexible fiber optic cable. The Raman device is mounted with the HE 532 spectrometers from Jobin-Yvon HORIBA. A Peltier-cooled CCD detector

(only for $\lambda = 532$ nm laser excitation; focal length 3 mm; fixed grating 920 lines / mm; fixed wavenumber from 100 cm^{-1} to 3215 cm^{-1} ; spectral resolution of about 3 cm^{-1}) was used for quick identification of the coloring matter. The integration time during the measurements was ranging between one second and 6 second with 10 to 30 accumulations. Analogous conditions were employed than those used at Rouffignac². The spectra are evaluated with the LabSpec software in order to obtain the characteristic Raman shift and to correct the artifact of the Edges filter and baseline correction.

Results and discussion

Protocols tested on the mock-ups

Linear regression based on elemental ratios

The analysis of the colouring matter alone (measured spectra are shown in the Figures 2 of the SI) allowed us to verify the proportion that should be obtained with the linear regression protocol. It also allowed to check the expected ratios of Ba/Mn intensities (Table 2). For the sake of representability, the used colouring matters do not correspond to pure synthetic materials but are natural geological minerals presenting inhomogeneities.

The mock ups MP_1-5 have been analysed. The slope of the intensity of Ba versus Mn has been calculated for each colouring matter by linear regression (figure 3). Moreover, a linear correlation coefficient r has also been calculated to confirm that a set of points is part of the group, thus the analysed colouring matter is of the same type. Compared to those of bulk Mn oxides, the intensity ratios are relatively accurate and correspond well to the ratios that can be expected (Table 2). The uncertainty of the slope is calculated by comparing the regression with a line between the points at the extremes. Depending on the colouring matter applied, different slope coefficients allow the efficient recognition of different mixtures or types of Mn oxides on the mock-ups.

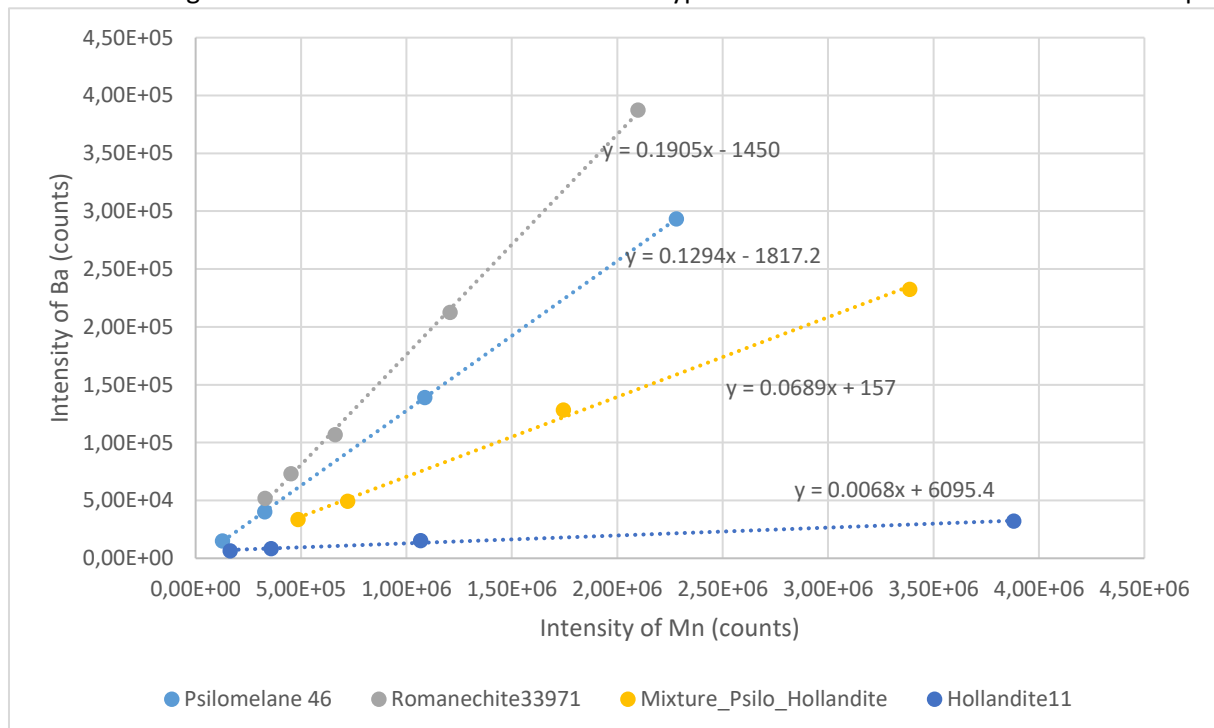


Figure 3: Ba intensity versus that of Mn of the mock-ups with the corresponding linear regression equation.

Table 2: Comparison of the experimental results between the pure material and the mock-ups.

Colouring matter	Romanechite33971 / MP_2	Psilomelane46 / MP_1	Psilomelane11 / MP_3	Mixture / MP_5
Experimental ratio of Ba/Mn intensities of the pure material	0.21 ±0.03	0.126 ± 0.03	0.006 ±0.001	0.074 ±0.007
Experimental slope of Ba/Mn intensities determined by linear regression on mock-up	0.1905 ±0.0006	0.1294 ±0.0003	0.0068 ±0.0003	0.069 ±0.00005
Correlation coefficient r	0.9997 (N=5)	1.0000 (N=4)	0.9947 (N=4)	0.9990 (N=4)
Difference between the Ba/Mn ratio/slope of the pure material and the corresponding mock-up	11%	2%	14%	7%

The differences between the determined Ba/Mn slopes for the mock-ups and the measured Ba/Mn ratios of the pure material can firstly be explained by the fact that the geological references used are not pure Mn oxides phases and can be naturally heterogeneous. Indeed, if a part of the material is constituted of a small amount of another Mn oxide, then the ratio Ba/Mn will be affected, which leads to an offset of the function $Ba=f(Mn)$. It corresponds to an excess or lack of Ba in the natural colouring matter due to the presence of other phases.

“Internal standard” procedure

This protocol is applied to the experimental data obtained on the mock-ups. The obtained element intensities present a wide range of accuracy (Table 3, sum spectra are shown in Figure 3 of SI). The Mn intensity is always well estimated by this protocol. The accuracy of this protocol for the other elements, including Ba, can be very variable, but no clear systematic tendency between different elements can be observed. Light elements (Si, P, S) are totally out of the range. This could be due to their high sensitivity to physical effects or to the fact that they can be linked to Ca (such as Si, which is present in significant amounts in the substrate). Despite the good accuracy of some elements, it is not constant between the different samples.

Table 3: Difference of peak intensity between pure material and the corresponding mock-up determined with the Internal Standard protocol.

Mock-up sample	Al	Si	P	S	K	Ti	V	Mn
MP-3	50%	927%	298%	72%	46%	79%	74%	3%
MP_1	41%	574%	439%	505%	36%	50%	61%	0%
MP_2	45%	303%	427%	90%	13%	100%	4%	5%
Mock-up sample	Fe	Ni	Cu	Zn	As	Sr	Zr	Ba
MP-3	12%	26%	5%	22%	33%	14%	94%	84%
MP_1	8%	1%	102%	11%		61%	24%	5%
MP_2	45%	14%	72%	27%	53%	41%	55%	19%

We conclude that this protocol, in its current state of development, is not well adapted to the complex analytical system of prehistoric paintings. Therefore, it will not be considered for the data evaluation of the black Mn-oxide based colouring matter of the Font-de-Gaume cave.

In-situ analyses

About 50 in-situ pXRF measurements on black paintings in the cave have been evaluated. Some points were eliminated due to their low Mn intensity. The measured points with sufficient Mn intensity were evaluated by the linear regression method of the Ba/Mn elemental ratios. The determined Ba/Mn experimental data points performed in-situ in the cave are much less aligned than those on the mock-ups in the laboratory (Figure 4). Indeed, the system analysed in-situ is also less ideal than the mock-ups, although they are made of natural Mn oxides. In the case of the mock-ups, the heterogeneity of the raw Mn oxide was reduced by a fine grinding and homogenization. On the contrary, a heterogeneity typical of unprocessed geological materials can be seen in the in-situ data. However, straight correlation lines can still be identified by simple linear regression showing the robustness of this method.

The determined slopes cannot be directly compared to those determined in the lab for mock-up samples. Indeed, the materials used in the lab were geological Mn oxides, each one was constituted by a particular Mn oxide phase (except psilomelane samples, which were natural mixtures) in a mineral matrix. Thus, the influence of the latter on the Ba/Mn slope is unknown. It will also be the case of the colouring matters used in the cave. In addition, hollandite could also be present and it can have a non-negligible range of Ba content, as showed in its formula ($Ba_{1-2}Mn_8O_{16}, xH_2O$). We can then only indicate that high value of Ba/Mn is linked to the important presence of romanechite, while low Ba/Mn slopes indicate a high content of pyrolusite. In all cases, a mixture between hollandite, romanechite and pyrolusite is possible, and only phase-sensitive techniques like Raman spectroscopy allow to determine it.

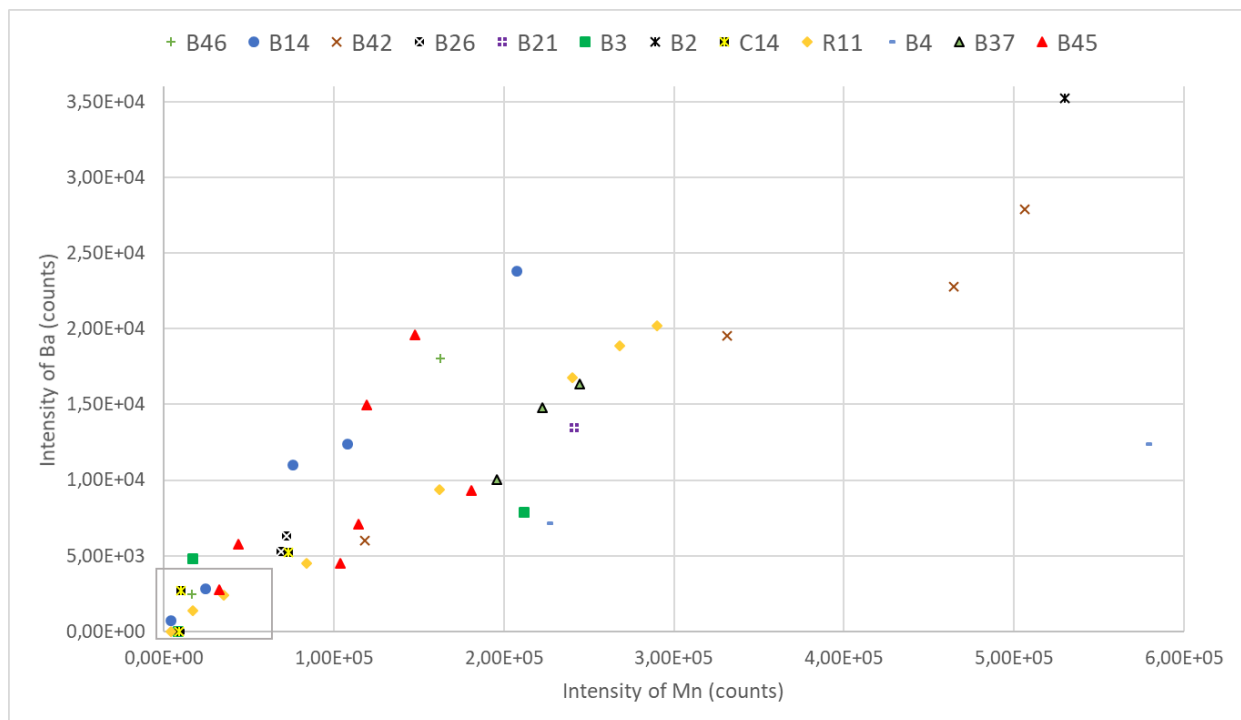


Figure 4: Ba/Mn intensity ratios of the in-situ pXRF spectra collected in the cave. The grey rectangle defines the limit of the ratios, where figures that have only points in it cannot be attributed to any group.

The criteria adopted to attribute a set of points to a group is that there must be at least two series of points in one group and the correlation coefficient r must be above 0.8 while being significant at 0.01

at least. With this method, three groups can be distinguished among the prehistoric figures at Font-de-Gaume cave (Figure 5, Table 4), namely the bisons B14, B45 and B46 for group I, the figures R11, B21, B37, B42, B45 for group II and the bisons B3 and B4 for group III. Several outliers, namely the figures B26 and C14 show a too low amount of colouring matter to be attributed to a group or their Ba/Mn intensity ratio lies above the uncertainty range defined for a grouping. The points of the prehistoric bison B2 could not be attributed to a group because they show a very high Ba content out of the range of the Ba-containing Mn oxides. Its Ba/Mn ratio does not fit any group possibly because it likely contains other Ba-based minerals such as barite²⁰. The presence of such a mineral could also explain the positive offset of the straight lines. The bison B2 has been attributed to the undetermined group X as B26 and C14.

The $1-R^2$ value is an interesting data to report as it represents the scattering of the experimental points around the linear regression (Table 2). Thus, for the same number of points it could be used to compare the parameters limiting the analysis (such the heterogeneity of the material) between two different figures or sites. The scattering of the points has also been directly estimated as the difference of Ba intensity between the model (simple linear regression) and the experimental points (see SI). The maximum value amounts to $3,7 \cdot 10^3$ counts.

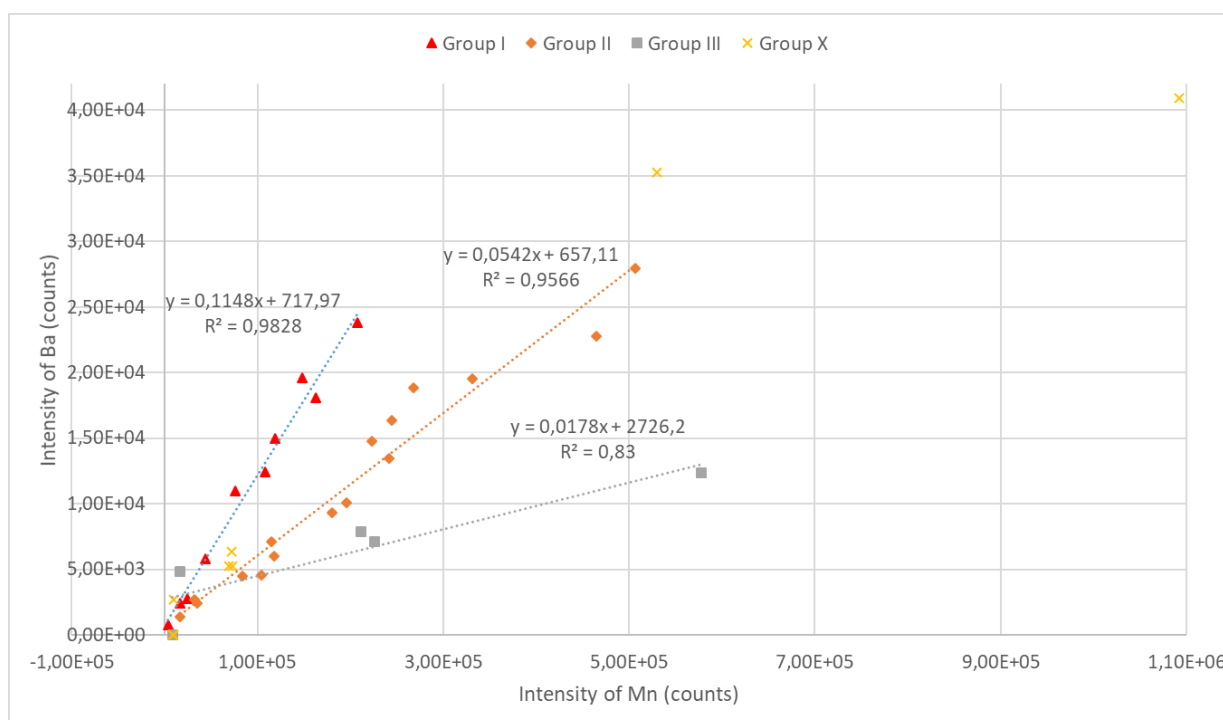


Figure 5: Ba/Mn intensity ratio in the spectra collected in-situ presenting three different groups of colouring matter with the corresponding simple linear regression equation.

Table 4: Classification of the analysed figures depending on their Ba/Mn intensity ratio.

Group	Associated figures	Experimental slope of Ba/Mn intensities determined by linear regression	Correlation coefficient r	Scattering $1-R^2$
I	B14, B45, B46	0.11480 ± 0.00005	$0.9914 (N=10)$	0.0172
II	R11, B21, B37, B42, B45	0.0542 ± 0.0008	$0.9781 (N=16)$	0.0434
III	B3, B4	0.018 ± 0.004	$0.9110 (N=4)$	0.17
X	B26, C14, B2	X	X	X

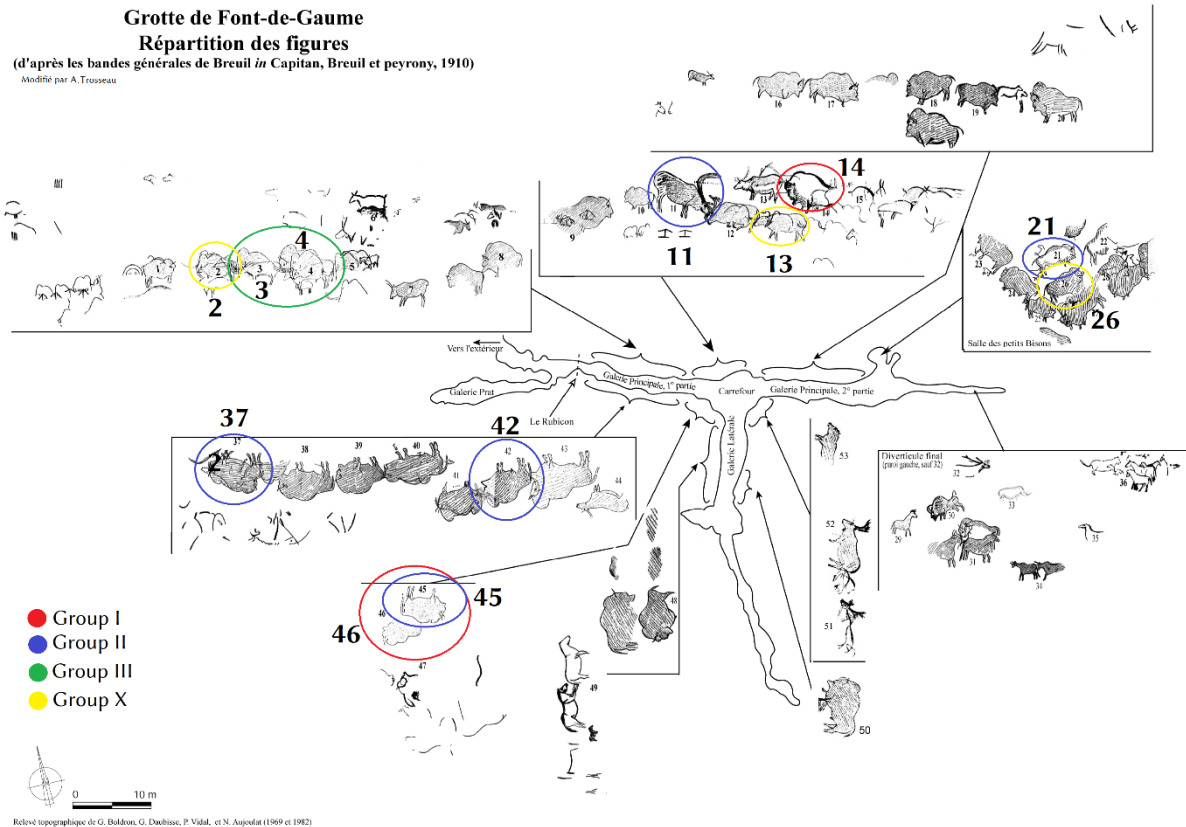


Figure 6: Localization of the analyzed figures in the Font-de-Gaume cave.

Homogeneity of the colouring matter used for each figure

Generally, one type of colouring matter can be determined for each figure, except for the measuring points of the bison B45, which shows colouring matters belonging to two different groups. It means that the colouring matter found for one figure is generally homogeneous enough to be attributable to a group. In the exceptional case of the bison B45 the colouring matter falls in the range of the defined groups but seems more heterogeneous than one of the defined groups (Figure 6).

Different groups

Group I is corresponding to a high Ba/Mn ratio and was determined for two bisons, B45 and B46, that are situated very close, one above the other on the cave wall on the right of the principal gallery at the corner of the Carrefour. The third figure, also a bison B14, belonging to this group is drawn right in front of the Carrefour at the opposite cave wall. A possible link of a similar execution phase of the three bisons can be established.

Group II corresponding to an intermediate Ba/Mn ratio concerns the majority of the analysed prehistoric figures distributed in the gallery: R11, B21, B37, B42 and B45. One of the figures is a reindeer and the others are bisons. Nevertheless, the determined Ba/Mn slope has a good correlation coefficient and match the composition of a balanced mixture of romanechite and pyrolusite, with a possible presence of hollandite.

Group III with a low Ba/Mn ratio is found in the black colouring matter of the bisons B3 and B4. One can notice the fact that they are also located very close on the same wall, at the beginning of the

principal gallery on the left-hand side and that they are faced to each other. An analogous link of a similar execution phase of the two bisons can be established as for those of the first bison group B14, B45 and B46.

Considering these results, one can observe that the same type of colouring matter can be found for prehistoric graphical entities that are located very close to each other and that are monothematic (such as those corresponding to the groups I and III). Concerning the largest intermediate group II, it can be found all over the cave décor and it is difficult to make correlations concerning execution sequences. In this case the grouping based on linear regression of elemental ratios is not discriminative enough.

We can conclude that the pXRF data evaluated with the linear regression method is efficient for the discrimination of several chemical signature groups corresponding to different colouring matter. However, inside these groups it is at this time not possible to determine precisely with pXRF, which phases are presents and in what extent they are. To achieve this, other characterization techniques are needed. Yet, the attribution of the figures to different groups is sufficient to make an archaeological interpretation.

Chemical grouping confirmed by mineralogical determination using Raman spectroscopy

Portable micro-Raman spectroscopy is applied in addition to pXRF at Font-de-Gaume in order to compare mineralogical data with elemental data. It has to be kept in mind that Raman spectroscopy is sensitive to fluorescence phenomena²², has a Laser probe which is several orders of magnitude smaller than the millimetric x-ray beam of pXRF and not always produce an interpretable spectrum under the cave measurement conditions². There are several reasons for this. Some spectra show too weak Raman signals because the small Raman laser spot in the range of some micrometers does not hit perfectly the colouring matter. Another reason can be the high Raman fluorescence induced other compounds present in the cave environment creating a very strong background signal in the spectrum so that it hides the Raman peaks of the colouring matter. Additionally, certain Mn-oxides share the same peak positions but with different relative intensities that can be modified due to the complex measurement conditions so that it is not always possible to determine exactly which phase or which phase mixture is detected. Therefore, even when measuring very similar spots on a prehistoric figure it does not mean that the spectral information is directly comparable. Two types of Mn oxides could be identified using portable Raman spectroscopy, corresponding to a Ba-bearing Mn oxide phase that could be either romanechite or hollandite, and also a Mn-oxide phase without Ba identified as pyrolusite (Figure 7). Moreover, both Mn oxide phases (Ba bearing and without Ba) were identified together in most of the analyzed prehistoric figures. It could be interpreted as the fact that the used raw materials are indeed naturally mixed phases of these different Mn oxides with different Ba contents. Proportions of romanechite and pyrolusite content have been estimated in the Raman spectra (Table 5). It can be seen that the colouring matters containing more romanechite are corresponding to those that have been attributed to the groups of high Ba content using the linear regression protocol with pXRF analysis. Analogously, the group with the low Ba content corresponds to a low romanechite content. These data validate the use of the linear regression model based on elemental ratios as a differentiation criterion of the colouring matter of prehistoric figures and show the possibility to establish such groups with portable Raman spectrometry as a complementary method.

Table 5: Detected phases in the Raman spectra of the figure 7.

Spectra	Figure	Group	wt % of romanechite, hollandite or birnessite	wt % of pyrolusite	Other minerals
#54	Bison 4	III	10% to 20%	80% to 90 %	calcite

#65	Reindeer 11	II	60% to 70%	30% to 40%	hematite
#105	Bison 14	I	>90%	<10%	-

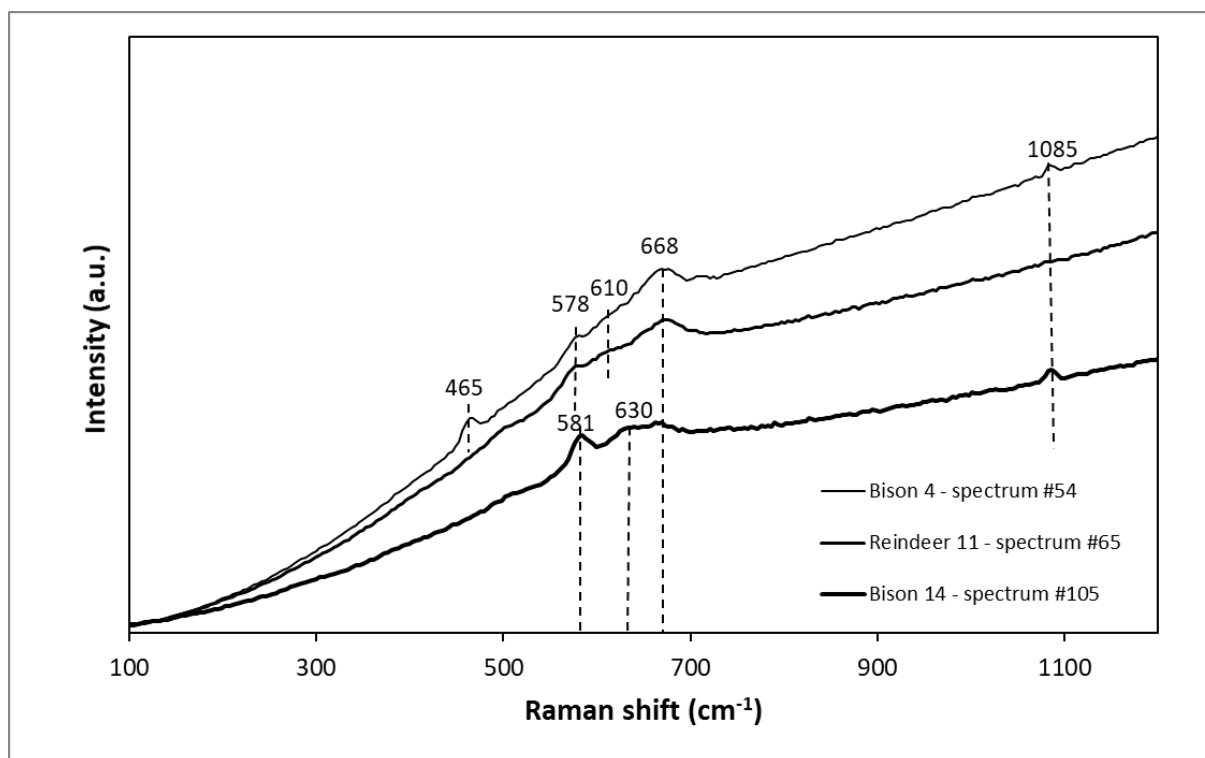


Figure 7: Treated Raman spectra acquired on the B4, the R11 and the B14.

Comparison with other regional prehistoric sites

The cave of Font-de-Gaume is located in Dordogne (France), a region that concentrates a lot of decorated prehistoric sites. In addition, several studies have been conducted on the colouring matter used at these sites. A similar *in-situ* approach was adopted at the cave of Rouffignac¹¹, less than 10 km away. In contrast, the colouring matter of the famous cave of Lascaux, which is located 20km away from Font-de-Gaume, was studied on microsamples^{23,24}. Font-de-Gaume and Lascaux as both caves with polychrome paintings dating to the Magdalenian period are often considered as a stylistically comparable, at least for the part of the polychrome figures of Font-de-Gaume. However, the black colouring matter of Font-de-Gaume is closer to that found of Rouffignac than that of Lascaux. Indeed, the Mn oxides of the black drawings of Rouffignac are mixtures of pyrolusite and romanechite or either phases, whereas those of Lascaux are more complex phases that also contain K^{23,24}. As in Rouffignac cave, three chemical groups of Ba-bearing Mn oxides were evidenced at Font-de-Gaume. The current similarities between the colouring matter of Font-de-Gaume and Rouffignac tend to show a certain regional coherence in consistence with local sources of Mn oxides²⁵.

Conclusion

Despite the difficult analysis conditions, the differentiation of black colouring matters used in prehistoric paintings at the cave of Font-de-Gaume was achieved by semi-quantitative data evaluation of pXRF data. For this purpose, two spectrum evaluation protocols were tested on appropriate mock-ups samples. However, only the model using linear regression of elemental ratios was applied to *in-situ* data, due to its robustness and better reliability than the model based on an internal standard.

In practice, this linear regression protocol seems to be adapted to the problem, although the *in-situ* data are noisier than the laboratory data. Three groups of Ba-containing Mn oxides have been determined among the colouring matter of the figures of Font-de-Gaume. The majority of the black colouring matter analysed are attributed to an intermediate Ba/Mn group and can be found in every studied part of the cave. On the other hand, the colouring matters attributed to the groups I (high Ba content) and III (low Ba content) can be correlated with their location in the cave, suggesting different execution phases of these two monothematic groups of figures (bisons). The linear regression protocol will continue to be improved, particularly on the aspect of quantification of the different Ba-bearing phases.

In a regional archaeological perspective, the phases and groups determined at Font-de-Gaume cave are consistent with the Mn oxide groups determined at the Rouffignac cave, a cave situated geographically very close to Font-de-Gaume. The cave art of Font-de-Gaume will continue to be studied with further analyses using a combined approach as this approach was revealed to be successful. This combined approach is very promising to better understand the complex cave art of Font-de-Gaume.

Author contributions

Project concept and preparation of field trips: I.R., Conducting of pXRF analyses: I.R., A.T., Conducting of Raman analyses: Y.C., Conducting of photography: A.M., Data treatment of pXRF results: A.T., Data treatment of Raman results: Y.C., Discussion of results: A.T., Y.C., I.R., Editing of the article: A.T., I.R., Proofreading: A.T., I.R., A.M., Y.C.

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