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Short communication

First use of portable system coupling X-ray diffraction and X-ray fluorescence for *in-situ* analysis of prehistoric rock art

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ABSTRACT

Study of prehistoric art is playing a major role in the knowledge of human evolution. Many scientific methods are involved in this investigation including chemical analysis of pigments present on artefacts or applied to cave walls. In the past decades, the characterization of coloured materials was carried on by taking small samples. This procedure had two main disadvantages: slight but existing damage of the paintings and limitation of the number of samples. Thanks to the advanced development of portable systems, *in-situ* analysis of pigment in cave can be now undertaken without fear for this fragile Cultural Heritage.

For the first time, a portable system combining XRD and XRF was used in an underground and archaeological environment for prehistoric rock art studies. *In-situ* non-destructive analysis of black prehistoric drawings and determination of their composition and crystalline structure were successfully carried out. Original results on pigments used 13,000 years ago in the cave of Rouffignac (France) were obtained showing the use of two main manganese oxides: pyrolusite and romanechite.

The capabilities of the portable XRD–XRF system have been demonstrated for the characterization of pigments as well as for the analysis of rock in a cave environment. This first *in-situ* experiment combining X-ray diffraction and X-ray fluorescence open up new horizons and can fundamentally change our approach of rock art studies.

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1. Introduction

Study of prehistoric art is playing a major role in the knowledge of human evolution. Many scientific methods are involved in this investigation including chemical analysis of pigments present on artefacts or applied to cave walls.

In the last decades, collaborative studies between archaeologists and chemists show a growing interest in prehistoric rock art such as identification of source materials [1–7], working technologies [8–10] and dating [11,12].

Based on these joined efforts in the analysis of the archaeological remains, it is possible to comprehend the behaviour of the past humans for pigment procurement strategy as well as for art production. In the last two decades, chemical analysis has given information on the "chaîne opératoire" followed by artists for producing Paleolithic paintings and drawings [8,10,14–16] and on the origin of the pigments [2–7,13]. The majority of these results have been obtained from laboratory analysis based on the whole block of pigment or from small samples taken from coloured blocks or from rock paintings. In the first case, the object has to be transportable and the instrumentation has to be suited for unprepared materials. In the second case, the procedure has two main disadvantages: slight but existing damage of the paintings and limited number of samples. One way to overcome these limitations is to benefit of the recent advances of the portable analytical systems which enable non-destructive analysis of materials on site.

A first portable XRF experiment [17] has been undertaken in a prehistoric cave in 2005 providing chemical composition of pigments

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but no information on the crystalline structure. Conversely, Raman spectrometry is sensitive to chemical structure. It has been recently used in different prehistoric rock art sites: in an open-air shelter in South Africa [18] and in underground caves in France and Spain [19–21]. This technique is well adapted to carbon and organic products [18,22], but it is less efficient for low-crystallised pigments such as manganese oxides. In order to access to the crystalline structure of manganese based pigments, XRD seems to be more suitable [23,24].

To better know about the materials used in prehistoric times to paint and draw figures, elemental and structural information on pigments are necessary. For that purpose, we have used a portable system combining XRD and XRF [25] in the cave of Rouffignac (Dordogne, France). The XRF technique allows elemental analysis (qualitative and/or semi-quantitative) and XRD gives information about compounds present in a crystalline form.

This paper reports the first XRD–XRF experiment ever undertaken in an underground and archaeological environment for prehistoric rock art studies.

2. Materials and methods

2.1. Prehistoric figures in the cave of Rouffignac

The Cave of Rouffignac, also known as the *Cave of the hundred mammoths*, is situated in South-West France, in Périgord (Dordogne). This prehistoric cave is decorated with more than 200 animal representations, mainly mammoths (70% of all depicted animals). Four human figures are also present. The prehistoric pictures were mainly executed as engravings or black contour drawings. The drawings consist of a thin layer of black pigment on cave wall (Fig. 1).

The Rouffignac cave has not yet been dated directly because of the general lack of archaeological artifacts. Nevertheless, according to the style of the representations, this art is attributed to the Upper Paleaolithic, about 13,000 years Before Present (Middle Magdalenian).

Two locations have been selected to perform the analyses: the “Great Ceiling” chamber and the “Henri Breuil” gallery. These sites gather about one hundred drawings representing five animal species: horse, bison, ibex, woolly rhinoceros and mammoth. The Great Ceiling shows 65 images distributed without significant organization, whereas the Henri Breuil gallery with the “ten mammoths frieze” and the “rhino frieze” is well structured. The mean size of the drawings is 1 m^2 approx. They are present on various types of surface: flat and horizontal on the ceiling, concave and vertical in the gallery. The substrate is the limestone composing cave walls or secondary deposit of calcite. Instrumental access to the figures is sometimes not possible due to the presence of large flint blocks.

A total of 16 figures were investigated with the XRF–XRD portable system: the ten mammoths of the frieze in the Henri Breuil gallery, forming a stylistically homogeneous group that it has been relevant to compare to the rhino in the same gallery and to five drawings of the Great Ceiling.

2.2. The XRD–XRF portable system in cave environment

The portable system is a home-made device combining XRD and XRF analysis, initially developed for work art investigation in museums [25]. It is regularly used for collection examination [26,27] or in churches and ancient buildings [28]. Some difficulties were expected in a prehistoric cave environment: access to the cave, lack of power supply and installation of the apparatus close to the figures drawn on very irregular walls. For the first reasons, the Rouffignac cave was a good candidate to test the system: it is a large site well equipped to welcome visitors, it is supplied with electricity and a small train allows the transport of public to the decorated areas which are located at about 1 km far from the cave entrance. Water condensation on electronics was also expected due to the low temperature (13 °C) and high humidity (95%) [personal communication of the authors of ref. 17].

In order to get close to the figures, the portable equipment was mounted on a hydraulic crane which enables the system to be at a few centimetres from the cave walls. Because XRD and quantitative XRF require careful alignment, the components of the system are assembled on a frame that can be moved along the surface to be analyzed (Fig. 2). Two laser pointers intersect at the analysis position, where the X-ray beam impinges the surface to be analyzed. A X–Y table, mechanically interdependent with the frame, is used to finely adjust the position spot with lasers. The combination of this table and the crane was very useful to carry out the experiment in well controlled geometrical conditions for analytical accuracy as well as for preservation of the prehistoric figures. Measurements were carried out without any contact neither with the figures nor with the cave walls. The distance between the analyzed point and the X-ray detector is 15 mm.

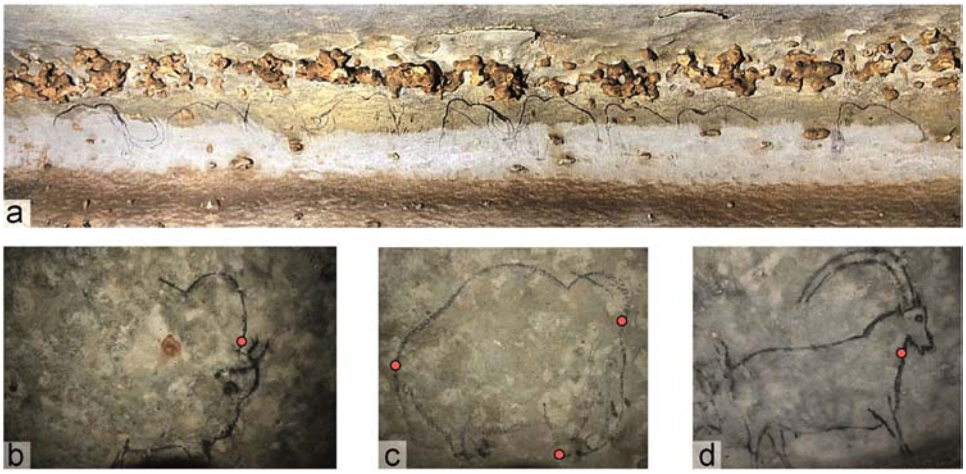

Fig. 1. Some drawings of the prehistoric cave of Rouffignac (France) analyzed in this study. (a) Frieze of the ten mammoths (from right to left: MAM190 to MAM199) in the Henri Breuil gallery. (b) Figures of the Great Ceiling chamber: bison (BISON100), mammoth (MAM66), ibex (BOUQ102). The size of each animal is 0.8 × 0.8 m^2 approx. In red, the analyzed point. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

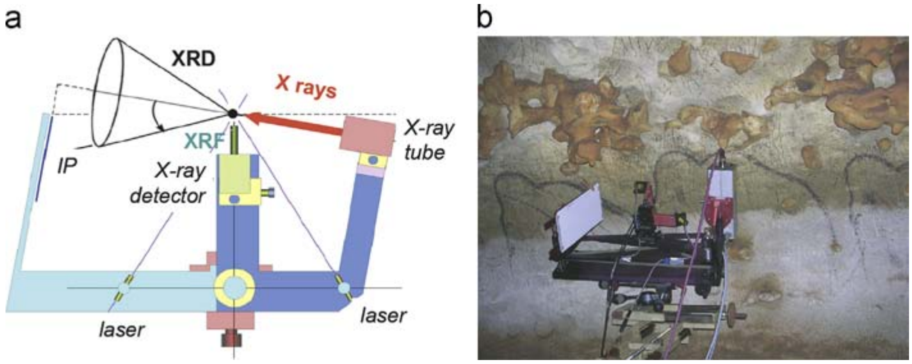

Fig. 2. The XRD–XRF system. (a) Schematic view of portable device. (b) During measurement in front of MAM194 in the Frieze of ten mammoths.

The XRD–XRF portable system is composed of an air-cooled iMOXS-MFR X-ray tube (30 W, 40 keV at 700 μA) with a copper anode (E=8.05 keV). In order to increase the photon flux, the source is equipped with a polycapillary semi-lens that provides a 3-mm diameter high intensity parallel X-ray beam. With such a parallel beam, there is less alignment constraint, compared with the conventional focusing diffraction geometry. The incident angle is 10° to the specimen surface. Grazing incidence of the incident X-rays is particularly suitable for layered samples such as painting or drawing on support. In the case of rock art, it offers the possibility to increase the number of X-rays coming from the pigment material compared to those coming from the limestone substrate. The drawback of this configuration is that the horizontal size of the beam becomes 6 times larger ($1/\sin 10^\circ \approx 6$) than the actual beam size and slits have to be used to obtain a 3 mm × 3 mm XRD measurement on the wall [25].

XRD diffraction patterns are recorded on imaging plate (IP) detector (dimensions 15 cm by 30 cm) in 20 min. The read-out procedure is done on site and requires less than 3 min. The image is then analyzed by using the Free Share software Fit2D [29]. The radial profiles over an arc-shaped region of interest are linearized and summed, giving rise to typical XRD diagrams (Fig. 3).

During exposure, XRF signal (Fig. 4) is collected by a 7 mm^2 Silicon Drift Detector located on the axis perpendicular to the analyzed surface [30]. Elemental concentrations are extracted using the software PymCa [31].

Finally, no problem has been encountered by the high humidity environment.

3. Results and discussion

3.1. XRD

26 diffractograms were recorded on the black drawings: 15 in the Henri Breuil gallery and 11 in the Great Ceiling chamber. Due to the low amount of pigment, only 17 imaging plates were readable. Fig. 3 shows typical XRD diagrams collected on prehistoric drawings and on rock walls of the cave of Rouffignac. Different compounds have been observed: calcite, quartz and manganese oxides.

Before the pigment characterization, several diffractograms were recorded on the same wall as the figures, but at a few centimeters, in an area without pigment. As shown in Fig. 3a, calcite is the main phase of the cave rock. Diffractograms presented in Fig. 3b–d were measured on the prehistoric drawings. Two types of manganese oxides were identified: pyrolusite (MnO_2) and romanechite ($Ba_2Mn_5O_{10}$). These two components were found almost pure or naturally mixed. Pure compounds were observed in the Great Ceiling chamber: romanechite for one ibex (BOUQ102) (Fig. 3b) and pyrolusite for one mammoth (MAM66) and one bison (BISON100) (Fig. 3d). Pyrolusite was also observed for one rhinoceros (RH185) of the Henri Breuil gallery. Conversely, mixture of the two phases was systemically measured in all the figures of the mammoths frieze in the Henri Breuil gallery (Fig. 3c). Relative intensities of each phase slightly vary from a mammoth to another with the predominant presence of romanechite for MAMs 190, 191, 192, 193 and predominant presence of pyrolusite for MAMs 195, 197.

Quartz was observed for all the figures and not for the calcite substrate, showing that quartz grains belong to the pigment. On the other hand, calcite peaks are not visible on the diffraction pattern when pigment is thick enough to mask the substrate (Fig. 3b). We can deduce that the pigment contains quartz but not calcite (at least, less than 5%).

In summary, two manganese oxide compounds giving three different mixtures were found for the black pigments in Rouffignac: pure pyrolusite (MnO_2), pure romanechite ($Ba_2Mn_5O_{10}$) and mixture of pyrolusite and romanechite. Pure compounds were found in the Great Ceiling chamber whereas mixtures were observed for the mammoths of the Frieze in the Henri Breuil gallery. Quartz is systematically associated with the manganese oxides, suggesting that the pigment is naturally composed of quartz and manganese black.

3.2. XRF

26 XRF spectra were recorded on the black drawings together with the XRD measurements. For each point analyzed on the black drawings, a measurement was done on the wall, at one centimetre of the figure. This procedure is made to verify that the collected X-rays mainly come from the pigment and are not significantly biased by the substrate.

Pigment of the black drawings is composed of manganese, barium, iron, potassium and silicon. The wall in calcite mainly contains calcium and low amounts of titanium, manganese and iron. The ratio in counts between the wall and the figure is 0.001, 0.007 and 0.03 for manganese, barium and iron respectively (Fig. 4). We consequently consider that the Mn and Ba contributions of the substrate can be neglected and that the Fe contribution has a little impact on the pigment results.

The analysis was done in atmosphere without He flux. Even if light elements (Al, Si, P, S, K) were detected, concentrations in silicon and potassium cannot be extracted accurately due to the uncertainty in X-ray attenuation. In addition, to compare our results with the previous study of de Sanoit et al. [17], we have calculated the concentrations in the main oxides MnO_2, Fe_2O_3 and BaO and normalized them to 100%. Results are presented in Table 1. MnO_2 content varies from 36% to 68%, Fe_2O_3 from 18% to 57% and BaO from 5% to 19%. Three main compositions are showed: high amounts of manganese and barium for the ibex (BOUQ102), high

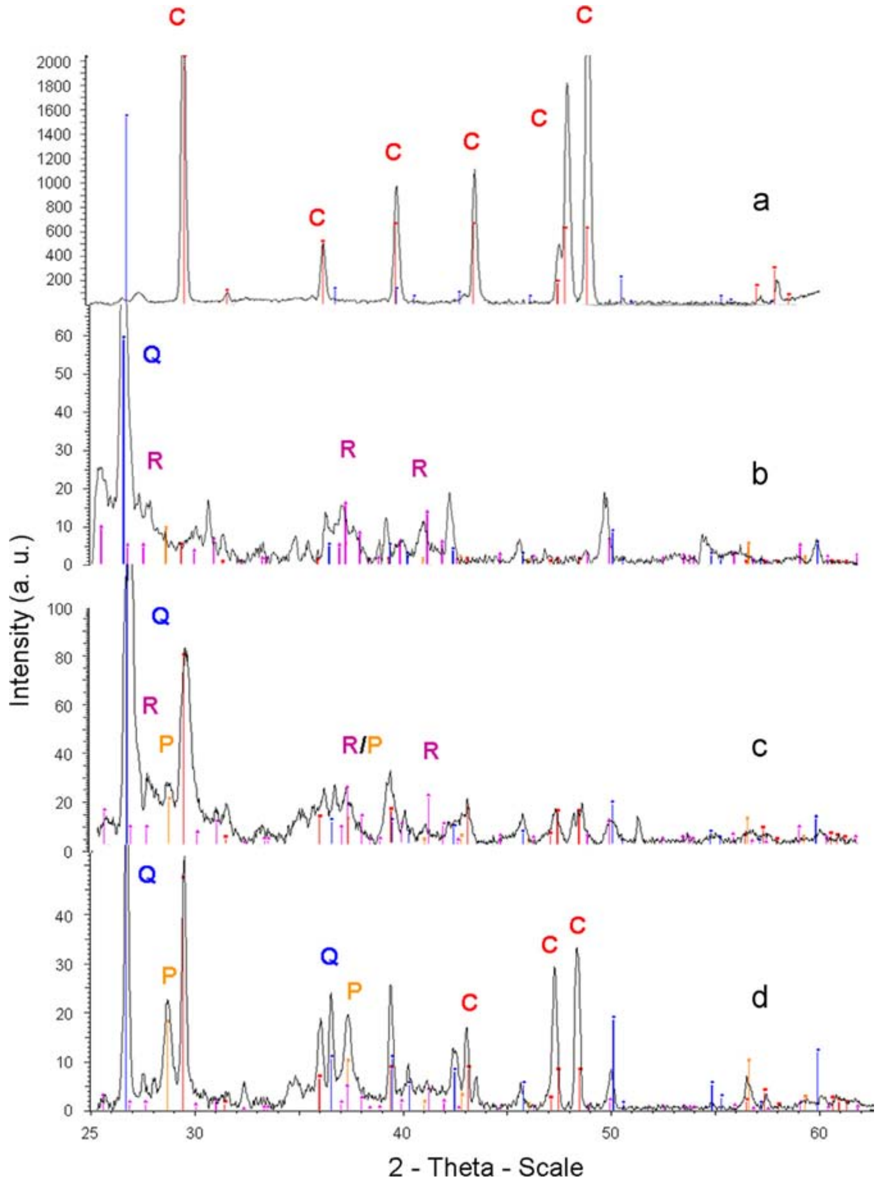

Fig. 3. X-ray diagrams collected on (a) cave rock and (b–d) prehistoric figures: (b) ibex (BOUQ102, see Fig. 1d), (c) mammoth (MAM197, see Fig. 1a), (d) bison (BISON100, see Fig. 1b). *C*=Calcite, *Q*=Quartz, *R*=Romanechite, and *P*=Pyrolusite.

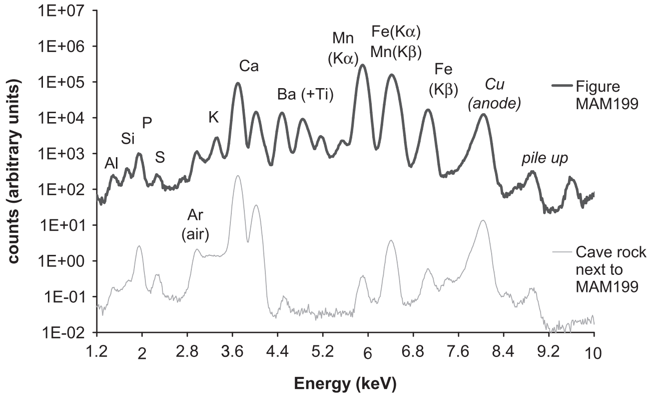

Fig. 4. X-ray spectra collected on one mammoth of the Frieze (MAM199, see Fig. 1a) (black line) and on cave rock next to the drawing (grey line).

amount of manganese and low amount of barium for the other figures of the Great Ceiling chamber and for the rhinoceros of the Henri Breuil gallery and, lower amount of manganese, higher amount of iron and intermediate values of barium for the 10 mammoths of the Henri Breuil gallery. For this group, we observe a global composition of $MnO_2=(49\pm7)\%$, $Fe_2O_3=(41\pm10)\%$ and $BaO=(10\pm3)\%$. Despite relatively large standard deviations, we can consider this group as homogeneous and different from the other figures. The mammoths and the bison of the Great Ceiling chamber as well as the rhinoceros of the Henri Breuil gallery have very close compositions forming together another group characterized by low amount of barium (5–6%). Finally, the ibex shows particular composition with high value of barium. Complementary analyses are planned for the other ibexes to verify this particular feature.

3.3. *Pigment characterization and correlation with the drawing location*

Black pigments used for rock art are commonly issued from combustion (carbon black, soot, bone black *etc.*) or occur in nature, such as manganese oxides or oxihydroxides. Pigments containing carbon are especially interesting because they can allow the direct dating of drawings or paintings. Manganese oxides are also

Table 1
XRF results for black pigments of the prehistoric drawings in the Rouffignac cave (France). MnO_2, Fe_2O_3 and BaO concentrations (in w%, normalized to 100%). Relative uncertainties are 10% approx.

Location	Figure-point#	% MnO_2	% Fe_2O_3	% BaO	Mean and standard deviation (1σ)
Henri Breuil gallery					
10 mammoths frieze	MAM190-01	59	29	12	**MnO_2 49 ± 7 Fe_2O_3 41 ± 10 BaO 10 ± 3**
	MAM191-01	46	45	9	
	MAM192-01	54	36	10	
	MAM192-02	46	46	8	
	MAM193-02	53	32	15	
	MAM193-03	47	41	12	
	MAM194-00	50	39	11	
	MAM195-01	44	49	7	
	MAM195-02	48	43	9	
	MAM196-01	41	50	9	
	MAM197-01	51	42	7	
	MAM197-03	49	43	8	
	MAM198-01	36	57	7	
	MAM199-01	67	18	14	
3 rhinoceros frieze	RH185-01	66	29	5	
Great ceiling chamber					
Ceiling	MAM-66-back	63	33	5	**MnO_2 64 ± 4 Fe_2O_3 30 ± 5 BaO 6 ± 1**
	MAM-66-tusk	56	39	5	
	MAM-66-head	68	24	7	
	MAM-66-foot	66	26	8	
	MAM107-01	66	28	6	
	MAM107-02	61	34	5	
	Bison100-01	67	27	6	
	Bison100-04	63	29	7	
	Bouq102-01	63	18	19	**MnO_2 62 ± 1 Fe_2O_3 19 ± 1 BaO 19 ± 1**
	Bouq102-02	62	20	18	
	Bouq102-03	61	20	19	

important since their nature and microstructure can provide information on the provenance of the supplying sites, and therefore give clues about different aspects of prehistoric human behaviours. Manganese oxides are reported for some caves decorated during the Paleolithic period [32]. In the cave of Lascaux, many crystalline structures were found: cryptomelane (KMn_8O_{16}), todorokite, pyrolusite (MnO_2), romanechite ($Ba_2Mn_5O_{10}$) and hollandite ($BaMn_8O_{16}$) [9]. In Pech-Merle, hollandite and romanechite were identified in the Black Frieze [23].

In the cave of Rouffignac, all the pigments analyzed on the figures are composed of manganese oxides. Two crystalline structures, pyrolusite (MnO_2) and romanechite ($Ba_2Mn_5O_{10}$) have been observed by XRD. Elemental analysis by XRF shows that the manganese oxides contain also various amounts of potassium, iron, barium and silicon. K and Ba can be present in the different structures of manganese oxides such as cryptomelane, hollandite and romanechite. In this survey, only romanechite as barium manganese oxide has been identified. From the XRD and XRF results, three groups of composition can be derived.

Group 1 consists of 4 figures of the Great Ceiling (MAM66, MAM107, BISON100, MAM121 [17]) and of one rhino (RH185) of the Breuil Gallery. These figures are composed of manganese oxides with low amount of Ba (6 ± 1%). The crystalline structure for this group was found to be pyrolusite (MAM66, BISON100) which theoretically does not contain Ba. Barium content is probably due to minor phases of barium manganese oxides. Group 2 has the highest content of Ba (19%) measured for the ibex (BOUQ102) of the Great Ceiling. This result is in perfect agreement with the identification of romanechite as the unique compound of this pigment. Group 3 is composed of the 10 mammoths of the Frieze in the Henri Breuil gallery. For this group, romanechite and pyrolusite were identified together in the figures. This result is consistent with intermediate values of Ba (10 ± 3%).

From this first experimental survey, we can draw some preliminary conclusions. First, the 10 mammoths of the Frieze in the Henri Breuil Gallery have similar chemical composition in agreement with the homogeneous style of the drawings. The results confirm that the set of the 10 figures may have been carried out in a short period of time, in a single artistic act.

For the Great Ceiling chamber, another type of manganese oxide – pyrolusite – has been used for 4 drawings on 5 analyzed figures. It is surprising to find the same pigment for the rhino which is located at the entrance of the Breuil Gallery. Finally, one figure of the Great Ceiling was found to be drawn with romanechite. The figure is an ibex which composes a group of 5 ibexes stylistically different from the other animal figures. This result suggests that the ibex group could have not been made at the same time as the other drawings or by other prehistoric "artists".

4. Conclusion

For the first time, a portable system combining XRD and XRF was used in an underground and archaeological environment for prehistoric rock art studies. *In-situ* analysis of black prehistoric drawings and determination of their composition and crystalline structure were successfully carried out. Original results on pigments used 13,000 years ago in the cave of Rouffignac were obtained showing the use of two main manganese oxides: pyrolusite and romanechite. Based on these preliminary results, it is possible to propose correlations between chemical composition and location of the figures in the cave: the Frieze of the 10 mammoths in the Henri Breuil gallery has a chemical fingerprint in agreement with the homogeneous style of the drawings whereas the analyses in the Great Ceiling chamber show at least two other chemical compositions for the pigments: mainly pyrolusite and, for one figure, romanechite.

The capabilities of the portable XRD–XRF system have been demonstrated for non-destructive *in-situ* characterization of pigments as well as for analysis of rock in a cave environment. The availability of an instrument able to determine both elemental and structural compositions of paintings and drawings provides new information for the identification of the pigments and contributes to a better knowledge of art production in the prehistoric period. This instrumental advance open up new horizons and can fundamentally change our approach of rock art studies. It offers the possibility to develop new strategies for this field and paves the way for future investigations.

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