Enhanced identification of trace element fingerprint of prehistoric pigments by PIXE mapping

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Enhanced identification of trace element fingerprint of prehistoric pigments by PIXE mapping

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ABSTRACT

The elemental composition of Fe rich rocks used as pigment during prehistoric periods can provide valuable information about the type of material used and their geological origin. However, these materials present several analytical constraints since their patrimonial value involve using non-invasive techniques maintaining a high sensitivity of the detection and the quantification of trace elements. Micro-beam techniques also require to take into account the heterogeneity of these geomaterials from the macroscopic to microscopic scales. Several previous studies have demonstrated that PIXE analysis satisfies these analytical conditions. However, application of micro-PIXE analysis is still complex when thin and discontinuous layer of pigment is deposed on the surface of other materials such as rocks or bones. In such case, PIXE imaging could improve the ability to take into account the high heterogeneity of such archaeological objects. In study, we used PIXE imaging system developed at the NewAGLAE facility in order to visualize distribution of elements associated with iron-rich pigment phase. The results obtained show that PIXE maps can improve the identification of the main trace elements specific to the iron mineral phase. By grouping pixels of iron-rich areas and performing quantitative treatment, it was possible to reveal additional trace elements associated to pigment. This study highlights the contribution of PIXE imaging to the identification of elements associated with mineral phases of interest and to use them as proxies to discriminate different geological materials used in archaeological context.

1. Introduction

Elemental composition of rocks and mineral found in archaeological context can provide valuable information to identify their nature and, in some cases, to determine their geological and geographical origins [1]. These information can then help to establish territories of past populations, displacement and migration, or trade between them. For prehistoric periods it is well known that the composition of the obsidian tools can make it possible to identify, sometimes very precisely, the origin of these materials [2]. As shown by previous studies, it can be also the case for iron-rich pigments such as hematite and ochres. Different analytical techniques have been applied to these materials, including XRF, LIBS, ICPMS, NAA and PIXE [3–14]. The latter has various advantages which are crucial for materials with a significant heritage value [15,16]. Pigment materials have the specificity to be particularly heterogeneous at the macroscopic and microscopic scales. This is the case for raw pigments, but above all, for pigments covering objects, more or less thick and more or less discontinuous. It is then necessary to take into account this heterogeneity by using techniques allowing to carry out analyses with a spatial resolution in the range of few tens of micrometers, or even to have imaging facilities. The patrimonial nature of these objects also requires the use of non-invasive techniques while maintaining high sensitivity and accuracy of the quantitative data. Among the above mentioned analytical techniques, PIXE mapping seems to be the best suitable technique to meet these requirements. In this paper, we propose to use the imaging system – including multi-detector, systematic imaging system, visualization and processing software dedicated to data treatment – recently developed at the A-GLAE accelerator (Accelerateur Grand Louvre d'Analyse Elementaire; C2RMF – Paris) [17–19]. This article presents, through the example of the analysis of prehistoric pigments of Abri Pataud, the capability of the new analytical procedure combining mapping and data treatment to enable the identification of elements associated with mineral phases of interest and to use them as proxies to discriminate different kinds of geological materials.

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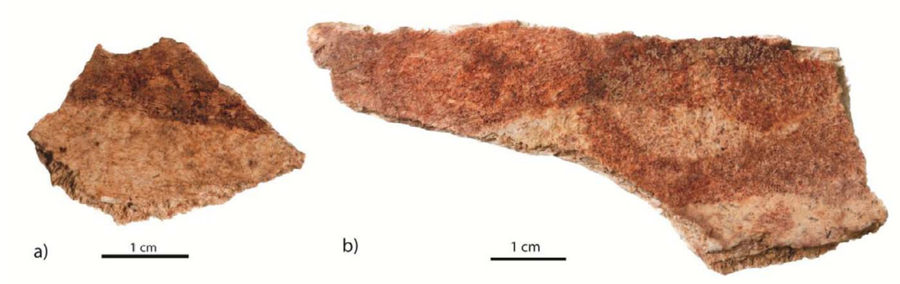

Fig. 1. Archaeological decorated bones from Abri Pataud: (a) Scapula 1 (Ref: V75B-159), (b) Scapula 2 (Ref: V76B-5741).

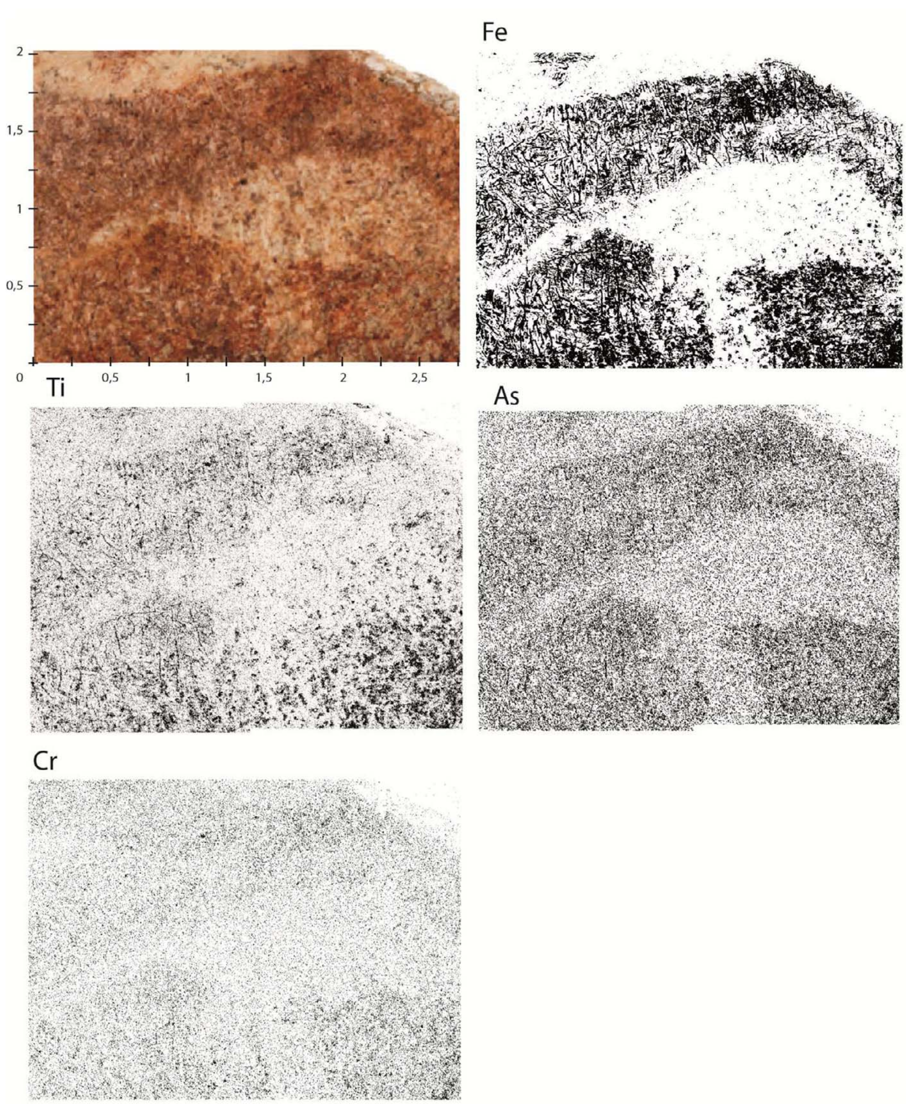

Fig. 2. Elemental distribution of Fe, Ti, As and Cr obtained by PIXE mapping on decorated scapula bone from Layer 2 of Abri Pataud (sample Scapula 2; Ref.: V76B-5741).

2. Material and method

Archaeological material comes from Abri Pataud (Dordogne, France), a prehistoric rock-shelter occupied repeatedly between about 34,000 and 20,000 years ago, by people representing the Aurignacian, Gravettian and Solutrean archaeological cultures. Over the nine metres depth of the dig, 14 archaeological levels are observed, corresponding to 40 successive occupations [20–22]. The analyses were focused on imaging pigment distribution of two fragments of decorated bone coming from the recent excavation of the Layer 2, a Gravettian layer dated from to 28,000 to 26,000 cal. BP. (Fig. 1a – Scapula 1 [Ref. V76B-159] and 1b – Scapula 2 [ref V76B-5741]).

Analyses were performed after the improvements of the AGLAE facility and the implementation of a multi-detector and fast imaging system (NewAGLAE) [19]. In this upgraded system, two Peltier-cooled SDD detectors (50 mm^2) covered by 50 µm-thick aluminum filter were used to collect high X-ray energy. A systematic magnetic deflection of the beam allows scanning continuously a vertical area of 640 µm by 40 µm (beam size). This beam scanning is coupled to a horizontal/vertical mechanical movement of sample stage allowing mapping large areas. Dose detector was used to adjust mechanical movement speed in order that each pixel of the map received the same beam charge during acquisition. The large scale area map, covering a surface of 2.5 by 2.75 cm^2, was acquired in 7 h on bone sample Scapula 2.

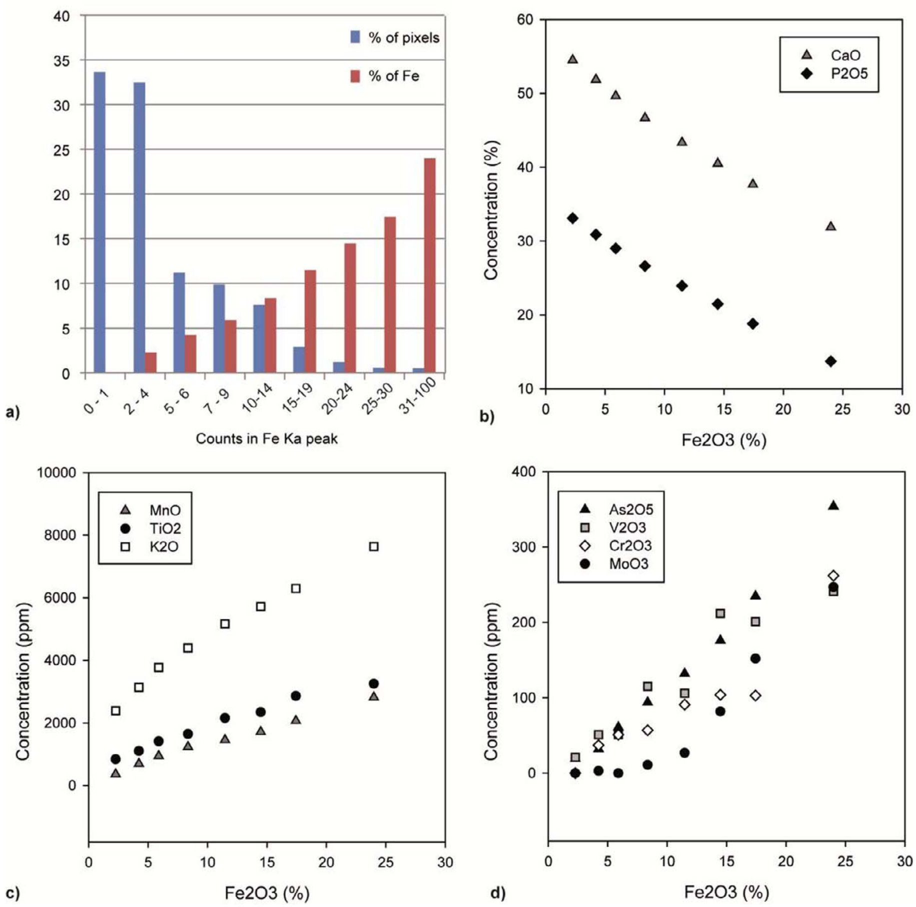

Fig. 3. a) Histogram of the summed spectra according to the Fe Kα peak intensity. Each category is composed of a% of pixels (in blue) which is used to calculate the elemental concentrations from the Scapula 3 PIXE map (% of iron is reported in red for each category). b) to d): major, minor and trace element concentrations extracted from the summed spectra a function of the Fe_2O_3 concentration.(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

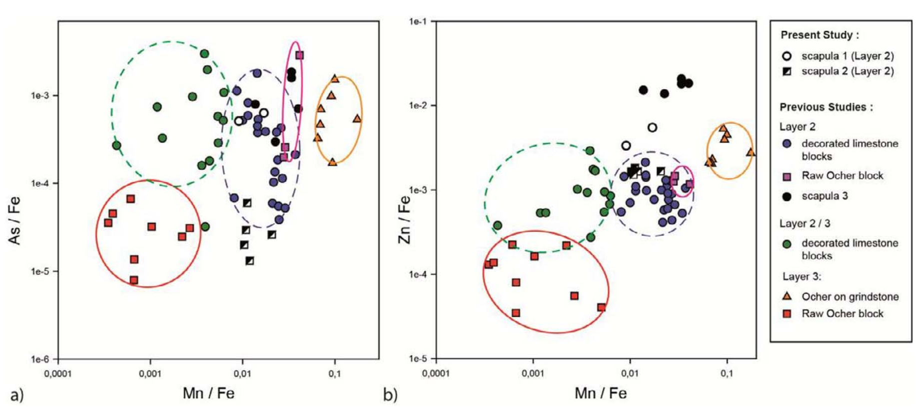

Fig. 4. Bivariate plots of Mn/Fe ratio compared to As/Fe and Zn/Fe for Abri Pataud pigments coming from Layer 2, Layer 3 and "Eboulis" 2/3.

AGLAEMAP software [17] was used to visualize elemental maps by using peak integration from EDF output data files. Due to the heterogeneity of ochre thickness and distribution, pigment-rich areas were selected to perform local mapping (640 µm × 640 µm). Afterward, the AGLAEMAP software was used to select pixels displaying high iron content in order to export cumulative low and high energy spectra. Finally, GUPIX software [23] was used to calculate elemental concentrations. This selection aimed to limit the contribution of the bone substrate composition in the pigment concentration calculation.

Pigments deposited on Scapula 1 and Scapula 2 were then compared to other decorated materials from the same layer and from underlying Gravettian layers (Layer 3 and "Eboulis" 2/3). These samples were previously studied by PIXE spot analysis using the AGLAE facility before the implementation of the new imaging system [5,24].

3. Results and discussion

The NewAGLAE system was used to visualize elemental distributions. Pigments are mainly composed of Fe, Si and Al suggesting mixture of iron oxide mineral (hematite) with quartz and/or aluminosilicates. The largest map was performed on the scapula 2. Iron map points out the heterogeneity of pigment distribution on the bone surface and its accumulation in the small cracks (Fig. 2). The distributions of As, Ti and Cr are similar to the Fe one, thus showing that these elements are correlated with the iron oxide mineral phase. The Elemental concentrations in the Fe-rich areas selected from the maps were calculated by GUPIX [23]: $\%Fe_2O_3$ 15.7 ± 0.7, $\%As_2O_5$ 0.36 ± 0.015, $\%TiO_2$ at 0.11 ± 0.05, and $\%Cr_2O_3$ at 0.35 ± 0.05. The maps allow to visualize minor and trace element distributions at concentration levels from 0.1 to 1%. Trace element distributions make much easier the identification of the elements associated with mineral phases of interest and the use of these elements as proxies for the origin of materials. However, in some case, elemental maps do not show all the elements associated with the pigment phase. This is the case of trace elements for which the counts in a single pixel are lower than or close to the background, and when concentrations are too close to the LOD to observe a contrasting element distribution. In order to calculate the concentrations of these trace elements, we propose to group pixels of the iron rich areas to sum spectra.

Using AGLAEMAP, pixels that did not present any traces of Fe were discarded and the remaining pixels were gathered in 8 groups according to the relative intensity of the Fe Kα peak at 6.4 keV (Fig. 3a). Then, element concentrations were calculated from the summed spectra of each group of pixel using GUPIX. The comparison of Fe with Ca and P (Fig. 3b), the main components of the bone mineral, shows that the influence of the substrate can be limited by selecting pixels with high iron content.

Quantitative data reveal several additional elements correlated to Fe which were not identified on elemental distribution maps, such as K, V, Mo (Fig. 4c and d), or Mg and Rb. For Mn, Ti and K, a high correlation is observed between their concentrations and the Fe content. For As, V, Cr, and Mo, the relationship between iron and these elements in very low concentrations is less well defined. For Mo, the correlation with iron is clearly observed for iron concentration higher than 12%. It seems that when iron concentration is too low (under 12%), the quantitative data obtained for the low traces elements may be distorted by the contribution of the substrate or by sediment contaminations.

Concentrations extracted from the maps as well as point analysis carried out in the iron-rich area identified on maps were compared to the elemental composition of other archaeological objects of Layers 2, 2/3 and 3 previously analyzed by spot analysis [5,24]. These previous studies had highlighted correlations between Fe and Mn, As and Zn concentrations that have been used as fingerprints to discriminate different pigment compositions (Fig. 4). Fig. 4a shows that values of Mn/Fe and As/Fe for scapula 1 and scapula 2 are similar to the previous results obtained for pigments from Layer 2. For Zn/Fe ratio, the previous study had pointed out that the Zn content was higher for pigment on decorated bone (scapula 3) than for the other samples [24]. This high Zn concentration was explained by the contribution of the fossil bone substrate which contains Zn. The localisation of the pigment was based only on visual aspect and it was thus difficult to evaluate the pigment thickness. As the penetration depth of a 3 MeV proton beam is ≈100 µm in bone and the pigment is not sufficient neither to stop the particle nor to absorb the Zn X-rays, the contribution of the substrate can not be neglected in the spectra obtained bombarding the pigment areas. For data extracted from imaging, Zn/Fe ratio values are slightly higher for scapula 1 than the other samples from Layer 2 suggesting a small contribution of bone substrate but to a lesser extent than for scapula 3 analyzed with spot analysis. On the contrary, for scapula 2, Zn/Fe ratio is quite similar to that of the decorated wall fragments and raw pigment from Layer 2 showing that the pigment layer is sufficiently thick to avoid an effect of the bone substrate. This lower influence of the substrate may also be due to the lower Zn content (170–190 ppm) in scapula bones 1 and 2 than in scapula 3 (190–350 ppm), but also to a better identification of the Fe rich areas using the NewAGLAE imaging system.

4. Conclusion

PIXE analysis and imaging have been used to analyze decorated bones from the prehistoric site of Abri Pataud (Dordogne, France). These materials dating from 28,000–26,000 cal. BP constitute valuable patrimonial objects and must be analyzed with non-invasive techniques. Previous studies have shown that PIXE meets the requirement of both non-invasive analysis and good sensitivity for quantifying trace elements used to discriminate ochres from different origins. However, due to the heterogeneity at the macroscopic and microscopic scales of Fe-rich pigments, in particular when applied on archaeological objects, PIXE point analysis is sometimes limited by the difficulty to localize pigment-rich areas. To overcome this difficulty, the NewAGLAE system was used to map bone artifact covered by pigment in order to visualize elemental distributions. The maps show that it is possible to detect some trace elements (up to 1000 ppm) associated with the pigment phase. By grouping pixels of Fe-rich area, it has been possible to increase statistics, reduce LOD by a factor 10, calculate low concentrations and reveal several additional trace elements correlated to Fe in the range of 100 ppm. This study shows that for such ancient and valuable objects, PIXE imaging enhances the ability to identify the elements of interest associated with mineral phases and to use these elements as proxies for the origin/provenance of materials.

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