

## Multi-Analytical Characterization of Rupestrian Precolonial Paintings of Inhuma, Piauí, Brazil

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The chemical-mineralogical characterization of rupestrian paintings in red, white, black and yellow colors, which decorate the rocky walls from the archaeological sites of Ema and Furna dos Índios (Inhuma, Piauí, Brazil) was performed. The chemical analyses were performed *in situ* by the non-invasive analytical technique X-ray fluorescence spectrometry (XRF) as well as in laboratory using a non-destructive approach, without previous sample preparation, and Raman microscopy, and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) techniques. The results, when together, allowed unequivocal identification of the main substances responsible for the color pigments, namely, hematite (red pigment), gypsum (white pigment), amorphous carbon from charcoal (black pigment) and goethite (yellow pigment).

**Keywords:** rupestrian pigments, chemical-mineralogical characterization, iron oxides, gypsum, charcoal

### Introduction

The State of Piauí, as well as the entire Brazilian Northeast, holds a rich archaeological archive,<sup>1,2</sup> distributed in nearly 100 municipalities, where there are around 2,000 archaeological sites registered on the National Registry of Archaeological Sites (CNSA) from Institute of National Historical and Artistic Heritage (IPHAN).<sup>3</sup> These are mostly rocky formations which served, for thousands of years ago, as shelters for human groups whose permanence was recorded quite expressively through paintings and engravings, and also by other time-persistent remains, such as lithics, ceramics, fires, and human skeletons, among others.<sup>4,5</sup> The dating carried out on precolonial anthropic bonfire remains points to a human occupation in the State of Piauí for at least 50,000 years.<sup>6</sup>

The studies of archaeological remains, specially rupestrian paintings, allow us to know about the activities

developed over thousands of years, since much is revealed on the culture of past communities, where and how they lived, and which technologies they used. The rupestrian art found on rocky blocks and walls, grotto ceilings, caves, and slabs, brings considerable information on the environmental and social-cultural scenario from a distant time, because beyond stands out by the aesthetics and interpretation that come from human consciousness, can bring important indication of how or what were the festive and daily activities, the beliefs, the intimate desires, the practice and behavior of theirs authors, through interpretative scenes.<sup>7,8</sup>

The paints used to produce the rupestrian paintings were prepared from a mixture of organic or inorganic pigments, binders (whose function was to give plasticity to the mixture) and fixatives, for better adherence to the rocky surface. Due to the easy degradation of organic pigments over time, their identification in archaeometric studies is limited.<sup>9,10</sup> On the other hand, ochre, a complex mixture of clay, silica and iron oxides, are the most common pigmentation agents of precolonial paints, since their

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Editor handled this article: Jaísa Fernandes Soares

inorganic nature gives them high chemical and thermal stability, allowing the conservation of many paintings until the current days.<sup>11</sup> To have a notion of their coloring potential, are necessary only 1.0-1.5% (m m<sup>-1</sup>) of iron (Fe) to use it as a rupestrian dye, which explain the preference of this raw material by the precolonial artists.<sup>12</sup>

There are several iron chromophores responsible by the ocher color shifting, being the most commons: hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), which has different shades of red, and eventually, the violet (caput mortuum), goethite ( $\alpha$ -FeOOH), with a yellowish appearance, limonite (Fe<sub>2</sub>O<sub>3</sub>.H<sub>2</sub>O) from yellow to brown, and black magnetite (Fe<sub>3</sub>O<sub>4</sub>).<sup>1,13-15</sup> The nuances observed in these colors can be obtained by mixing or heating the pigments.<sup>13</sup> Thus, it is necessary, many times, to use more than one analytical technique to characterize rupestrian pigments, as part of a micro-analysis based approach. Finally, there are also white paintings due to the presence of calcite (CaCO<sub>3</sub>), gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O) or kaolinite (Al,Mg,Fe)<sub>4</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>8</sub>, and black, due to the presence of manganese oxide (MnO<sub>2</sub>), or animal or wood charcoal.<sup>1,10</sup>

In the last decades, the interest in knowing the chemical-mineralogical composition of rupestrian pigments, aiming origin studies, as well as the need to establish intervention parameters for the conservation of these remains, has narrowed the interdisciplinary between archaeology

and chemistry. Regarding to the conservation aspects, precolonial rupestrian art, due to its exposition to bad weather, is subject to constant exchange actions with the environment, which cause the appearance of alteration deposits, such as: saline efflorescence, nests of building insects, climbing plants and/or anthropic actions, among others. Such deposits need to be studied in order to assess their effects on the rupestrian panels.

Numerous analytical techniques have been used for the morphological, elemental, and mineralogical characterization of rupestrian pigments, thus, allowing to advance the knowledge of how lived the human groups that inhabited Brazil in past times, being the most commons: energy dispersive spectroscopy coupled with scanning electron microscopy (SEM-EDS),<sup>7</sup> Mössbauer spectroscopy,<sup>7</sup> Fourier transform infrared spectroscopy (FTIR),<sup>13</sup> Raman spectroscopy,<sup>14</sup> X-ray fluorescence spectroscopy (XRF),<sup>15,16</sup> and X-ray diffractometry (XRD).<sup>17</sup>

Although the State of Piauí has a significant amount of archaeological sites registered and others to be discovered, there are still many of them that have not been object of multidisciplinary studies, for example, the archaeological sites of Ema and Furna do Índios (Figure 1), located at Ema and Jabuti locations, respectively, in the municipality of Inhuma, 240 km distant from the state Capital, Teresina. They were recently added at the IPHAN registry and

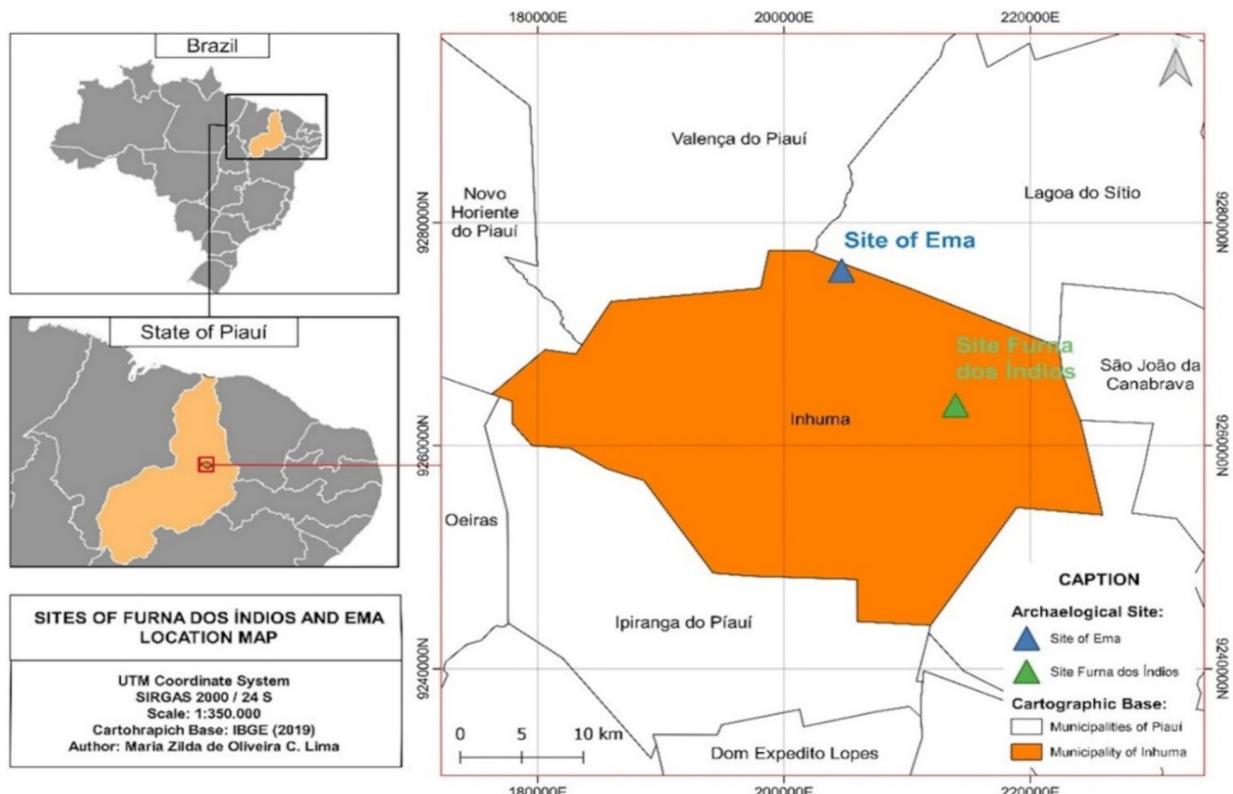


Figure 1. Location of the archaeological sites of Ema and Furna dos Índios, Inhuma, Piauí, Brazil.

are undergoing the first investigation studies on the chemical composition of their paintings, in order to obtain information about the occupation processes of these places, which assist in the construction of the history of the first Brazilian people, before the arrival of colonizers, and to contribute with essential information to execute future conservation works in these sites, since they had serious degradation problems from natural origin.

This work aims, therefore, to carry out the chemical-mineralogical characterization of the archaeological sites of Ema and Furna dos Índios, using a multi and micro-analytical non-destructive approach, through the techniques of energy dispersive X-ray fluorescence spectroscopy (ED-XRF) using a portable equipment, Raman microscopy and SEM-EDS.

## Experimental

### Description of sites and samples

The rupestrian art sites of Ema and Furna dos Índios (Figure 1) are located in the rural area of the municipality of Inhuma-PI and are 12.5 km distant. Both have a sandstone rock formation, typical caatinga vegetation in their surroundings, such as medium-sized trees and bushes, and conservation problems of natural origin. The choice for these sites as research object had as motivation: the absence of studies about the physicochemical characterization of their pigments, using a multi-analytical approach, the beauty and diversity of paintings, regarding to colors and styles, and the archaeometric contribution on the technological aspects that help to clarify the man way of living in precolonial Brazil. In addition to the necessity in obtaining archaeochemical data about the rupestrian paints to support conservation works.

### Archaeological site Furna dos Índios

The archaeological site Furna do Índios is located at the coordinates UTM 24 M 213942E and 9267616N (Sirgas 2000), 463 meters above sea level. It is a rocky shelter, 15 meters large, 10 meters deep, and nearly 1.52 meters high, East/West oriented, opened to the North. All the rupestrian paintings are non-figurative (lines, zigzag lines, concentric circles and circles with lines around them), that is, they do not allow an immediate interpretation of the intention of graphic representations.<sup>18</sup> They are present in yellow and red colors (in different shades), with few cases of overlapping. The technical assessment of paint application on the support reveals thick lines, which can indicate that fingers or other thick and hard tools were possibly used, whose pressure on the rocky support ensured good adhesion of the paint. The

degradation state of the paints is due to natural factors such as nests of building insects, saline efflorescence, termite galleries and animal waste.

### Archaeological site of Ema

The archaeological site of Ema is located at coordinates UTM 24 M 204675E and 9275688N (Sirgas 2000), 422 meters above sea level, Northwest/Southeast oriented and opened to West. It is a big rocky block 58 m large, where there are non-figurative rupestrian paintings (lines and zigzags) and figurative ones (zoomorphs, anthropomorphs, star) in red, white, and black colors. Regarding to the paintings style, they present coarse features resembling the Agreste Tradition, a classification given to Brazilian Northeast rupestrian art in which the figures do not transmit the notion of movement and show little concern with the elaboration of the art.<sup>18</sup>

Some graphic representations were elaborated using the technique of contour and filling, bichromatic in red and white, and preference using this last color in the inner region. The macroscopic examination revealed that due to the color overlapping on the same figure, the red paint was initially applied, followed by white paint. In this site, there are also rupestrian paintings that were elaborated using only the contour and filling technique, and these paintings are monochromatic (red or black). The paintings in red have thicker lines, which indicates that the way the paints were applied can be similar to the one used in the site of Furna dos Índios. Regarding to conservation problems, were found in the site nests of building insects, saline efflorescence, termite galleries and animal waste, detachment, climbing trees, deposits of anthropogenic contaminants (e.g., soot) and direct sunlight on the graphics in the afternoon, as a result of its West-oriented opening.

### Samples

The research was approved by IPHAN, process No. 01402.000504/2019-88.<sup>19</sup>

The *in situ* microscopic and elemental chemical analyses of three rupestrian paintings from the Site Ema and two of the Site Furna dos Índios (Table 1), chosen according to the color palette used by the precolonial artists, were carried out. Rocky fragments were also collected from these five samples analyzed *in situ*, in order to be measured by Raman and SEM-EDS microscopy. For the collections, priority was given to respect the integrity of archaeological remains with actions such as removal of a limited amount of rock fragments (only one *per* rock

painting analyzed *in situ*) in the order of  $\mu\text{m}$ , carried out with the aid of micro-surgical instruments, only in areas that were already degraded. All samples were labeled with the initial letters of the site (SE-Archaeological Site of Ema; SFI-Archaeological Site Furna dos Índios), the last two digits of the year of collection (19-2019) and the sampling sequential number. The rocky blocks, without the paint layer, were taken as a reference sample and received the codes SE19R and SFI19R to the archaeological sites of Ema and Furna dos Índios, respectively.

For the color shades identification of rupestrian paintings under study, the Munsell international color code was used. According to this code, color can be classified by combining three codes called hue, value and chroma, which represent the dominant spectral color, the shade and saturation, respectively.<sup>20</sup> The definitions of the pigment colors presented in Table 1 were carried out *in situ* by the same person and under ambient light, overlapping the colored insert of the Munsell code directly on the rupestrian paintings.

**Table 1.** Classification of sample colors belonging to Furna dos Índios and Ema sites, according to the Munsell Code

Sample/origin	Munsell color observed (Munsell code)
SE1901/Site of Ema	red (2.5YR 5/6)
SE1902/Site of Ema	white (10YR 8/1)
SE1903/Site of Ema	black (10YR 2/1)
SFI1901/Site Furna dos Índios	light red (2.5YR 6/8)
SFI1902/Site Furna dos Índios	yellow (10 YR 7/8)

### Experimental procedure

#### Image treatment

In order to obtain highlights that could provide a better visualization of the colors observed in the rupestrian paintings, different image treatment filters were applied to the photographs taken from the rupestrian art panel. It was used the Dstretch® plugin from Image J software.<sup>21</sup> This action was necessary since some rupestrian paintings were overlapped or even discolored due to the action of natural processes, such as rains and solar radiation.

Among the various filters available in DStretch®, LDS was chosen because when used with a customized 15 dpi image density scale, it showed better results regarding sharpness and noise.

#### *In situ* microscopic analysis

In order to verify the morphological characteristics of the rupestrian paintings, *in situ* micrographs were

obtained. The microscopic examinations, in different spots of each painting under study, were carried out using a CCD (charge coupled device) camera present in portable optical microscopy (ProScope, HR5, Oregon City, USA), and objective with 50 $\times$  magnification.

#### Analysis by ED-XRF

A portable ED-XRF spectrometer (Thermo Fischer, Scientific Niton XL3t ultra, Waltham, USA) was used for elemental analysis of the pictorial layers and rocky support. This equipment has an X-ray tube (with silver anode), a silicon drift detector (SDD), maximum voltage of 50 kV, current of 200  $\mu\text{A}$  and power of 2 W. It also has a coupled CCD camera, whose function is to visualize and record the exact area of the sample where the measurement will be performed. The portable ED-XRF spectrometer has four filters called: main, low, high and light, and each one of them operates sensitively to a set of chemical elements. In order to obtain a sample screening, all four measurement filters were used. The analytical measurements were carried out directly over the rupestrian paintings, at different points and, in triplicate, with a measurement time of 120 s (30 s for each filter), using the irradiation area of 7  $\text{mm}^2$  and the Cu/Zn Mining calibration mode. To compare the results obtained for the two sites, a data normalization was performed, in which the spectral values were divided by the intensity of the analytical signal of argon (Ar), taken as a reference value.

#### Analysis by Raman microscopy

Samples were analyzed directly on glass plates without prior preparation or special handling on a Renishaw inVia Reflex Raman microscope (Wotton-under-Edge, UK). This equipment has a CCD detector (600  $\times$  400 pixels, Renishaw) thermoelectrically cooled to  $-70\text{ }^\circ\text{C}$  and is coupled to a Leica DM 2500 M microscope, and an objective of numerical opening of numerical aperture (NA) 0.75 was used both to focus the exciting laser radiation on the desired area of the sample (ca. 1  $\text{m}^2$ ) and to collect the radiation inelastically scattered over this area. The Raman spectra were obtained using 632.8 and 785 nm radiation, whose power was adjusted in order to minimize the possibility of degradation of the analyzed areas and to optimize the signal/noise ratio of the spectra; the exposure time to obtain each spectrum was defined according to the same criteria. At least three readings were performed in each area with similar characteristics to obtain a better representation of the results. The spectral range assessed was between 100 and 1800  $\text{cm}^{-1}$  with spectral resolution ranging from 3 to 6  $\text{cm}^{-1}$ , depending on the wavelength used.

### SEM-EDS

The morphology of the samples, which were preliminarily attached to the double carbon tape, was investigated using a field emission gun scanning electron microscope Quanta FEG 250 (FEI, Thermo Fisher Scientific, Hillsboro, USA) in low vacuum mode to enable the observation of the non-conductive samples without coating. The microscope was operated at 200 Pa using a pressure limiting aperture and acceleration voltage of 20 kV and images were obtained using a large field detector (LFD). Element chemical composition of the surface was investigated using an energy dispersive spectrometer (EDS) (Oxford Instruments, X-Max50, Abingdon, UK).

## Results and Discussion

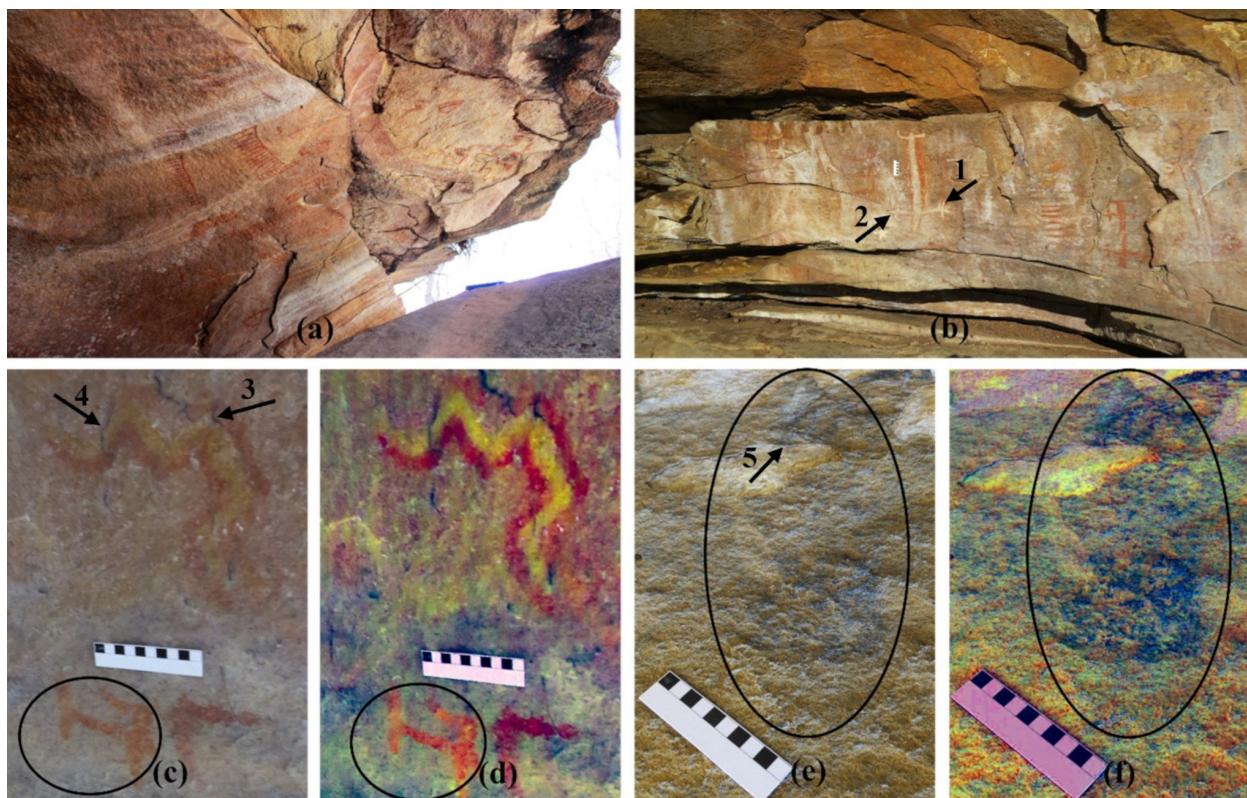
The colors observed in the rupestrian art are reference in chemical mineralogical studies of rupestrian pigments, since they can suggest the origin of the raw material used in the preparation of paints.<sup>13,22</sup> In this study, for example, the site of Ema presents red, white, and black pigments; while the site Furna dos Índios presents yellow and red (light) pigments, Figure 2, and each of them is associated

to a type of chromophore or material used to prepare these precolonial paints.

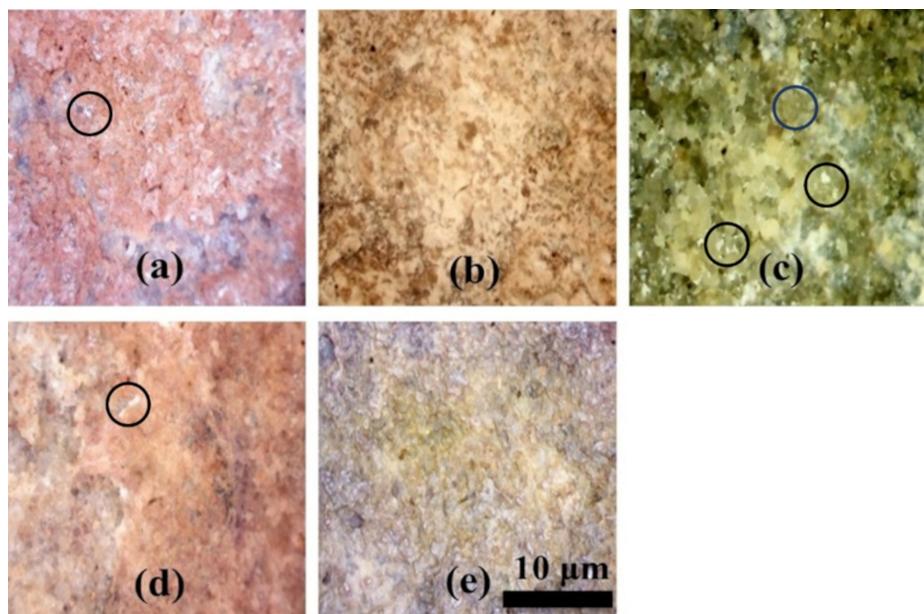
As observed in the Figure 2, the image treatment performed by applying the DStretch® plugin filter of the ImageJ software<sup>21</sup> showed important highlight in the rupestrian paintings, which allowed a more clear observation, mainly the occurrence of paints overlapping (Figure 2c, rupestrian painting with superposition of the colors yellow and red), what make us to presume that their application occurred in different moments or by different human groups, or, that is a shift of paint caused by the flow of rain water on the rocky support and the presence of more deteriorated rupestrian paintings, example of Figure 2e.

### Optical microscopy

The morphological and chemical analyses performed in different colors of rupestrian art can help to trace the cultural-historical profile, the daily life and technology used in past times. Figure 3 shows the results of examination performed *in situ* by optical microscopy in red (Figure 3a), white (Figure 3b), black (Figure 3c), light red (Figure 3d) and yellow (Figure 3e) pigments, which revealed a heterogeneous and irregular surface with the presence of



**Figure 2.** General view of rupestrian painting panels from the Sites Furna dos Índios (SFI) (a) and Ema (SE) (b) and rupestrian paintings, belonging to each one of these sites, in light red and yellow (c, SFI), and black colors (e, SE) before and after (d and f) image treatment. Points 1, 2, 3, 4 and 5 correspond, respectively, to the removal locations of the original samples SE1901, SE1902, SFI1901, SFI1902 and SE1903. The scale used to size the cave paintings is 10 cm.



**Figure 3.** Optical micrographs obtained *in situ* of the (a) red, (b) white and (c) black pictorial layers from the site of Ema and (d) red and (e) yellow from the site of Furna dos Índios, with 50 $\times$  magnification.

white spots (saline deposits adhered) in Figures 3a, 3c and 3d, and quartz grains crusted in the pictorial layer (bright spots), Figure 3c.

The micrographs revealed that the rock porous morphology allowed the rupestrian pigments to fix in the interstices of the support, ensuring continuous spreading of the paint, therefore, suggesting that there was a careful application of the pictorial material, or that the paints could be applied as a suspension. It was also possible to observe that the rupestrian paintings showed a thin layer of paint dispersed on the rocky matrix, specially the black and yellow ones (Figures 3c and 3e, respectively), which indicates that the paints could be intentionally applied in this mode or be the result of physical deterioration over time, due to exposure of paintings to local weather.

The white pigment (Figure 3b) showed microscopically covered by a black soot layer, probably from recent anthropogenic fires that occurred in the place, since there were carbonized fragments nearby the rocky wall. Finally, it was observed greater sharpness in the red shades (Figures 3a and 3d), which may be associated with the use of a diluent for the preparation of precolonial paint, or even the diversity of raw material used for the production of rupestrian art.

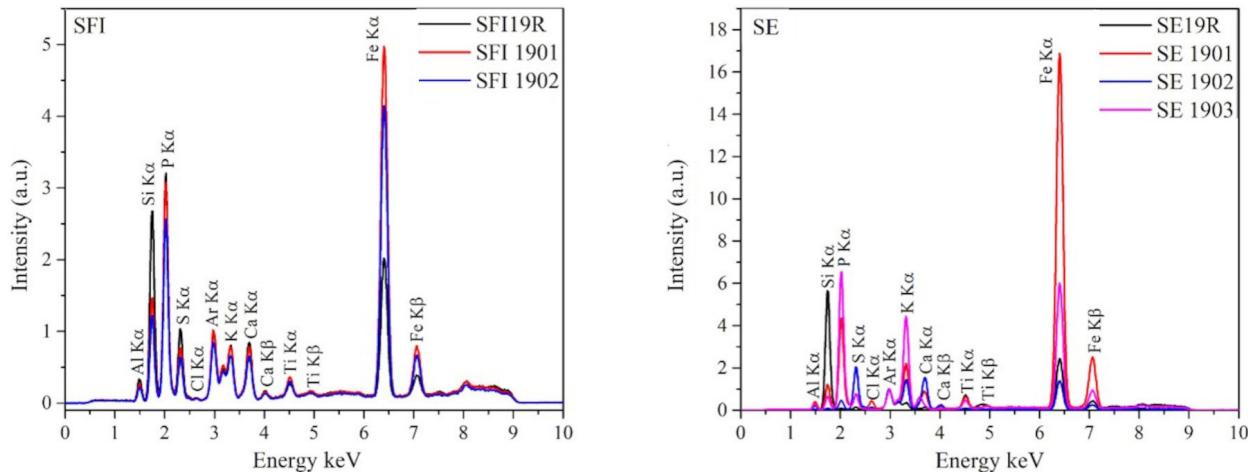
#### ED-XRF

The results of chemical elemental analysis of rupestrian paintings and the rocky support from the sites of Ema and Furna dos Índios, performed *in situ* by portable X-ray fluorescence spectrometry, are presented in Figure 4. These

results and additional information about the qualitative analysis carried out by ED-XRF can be found at the literature.<sup>23</sup>

The elements silicon (Si), aluminum (Al), potassium (K), sulfur (S), calcium (Ca) and phosphorus (P), present in all spectra of Figure 4 were attributed, partly, to silicate minerals (of the sandstone rocky support itself) and partly to saline efflorescence, that many times are present in different compositions and contents<sup>7,24-28</sup> in the pictorial surface layer, where they chemically attack it. Phosphorous (P) can also indicate the presence of alteration deposits, attributed to organic material from the decomposition of small-sized building insects or their excrements.<sup>7,29</sup> The occurrence of these deposits is quite common in open-air sites, as in the case of the archaeological Site of Ema, since they are more vulnerable to problems of natural origin. Perhaps, for this reason, the SE1901 sample presented the highest signal intensity for this element.

The sample SE1901 (red pigment) showed the highest intensity analytical signal for Fe, when in comparison to the signal of samples SFI1901 and SFI1902 (red and yellow pigments, respectively), in which this element is the chromophore responsible for the color. So, there is the suspicion that the precolonial paints of these samples have been applied in a previous period of time, therefore undergoing a greater deterioration over time, which would justify a lower signal intensity. Or also can be the result of the influence of the thin thickness of the paint layer or their preparation mode. The analytical signal of Fe contained in the white rock painting has lower intensity than that for this element present in the rock support, which makes us



**Figure 4.** Elemental spectra, obtained by portable ED-XRF, of rupestrian pigments and the analytical blank (rocky support, SFI19R and SE19R) belonging to archaeological sites: SFI-samples SFI1901 (red pigment) and SFI1902 (yellow pigment), and SE-samples SE1901, SE1902 and SE1903 (red, white, and black pigments, respectively).

believe that the peak in the spectrum of this sample may be due only to its presence in the chemical composition of the rock matrix. The low intensity of analytical signal of Fe in the black pigment was already expected, and its presence in the sample can be attributed to a possible addition of some raw material in which it was contained, when the paints were drawn up (since it is not the chromophore responsible for this color) or, also, due to the presence of this element in the rock matrix, in which the paint layer was finely dispersed, and may have facilitated the interaction of radiation with the matrix.

The presence of the element calcium (Ca) in all spectra, can be attributed to saline efflorescence over the rupestrian paintings or the use of some chemical additive, a component used to improve the quality of paints, such as fixatives. However, it was observed that for the sample SE1902 (white pigment), the intensities of analytical signals of this element and of sulfur (S), were much higher than those of the analytical blank (rock support) and other samples under study, indicating that it can be resulting from the raw material, such as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and/or anhydrite ( $\text{CaSO}_4$ ), used in the manufacture of white precolonial paint.<sup>1,10</sup> As a source of gypsum was not found nearby the site, the hypothesis that the rupestrian art was made from pigments based on this mineral and then taken to Ema Site by precolonial painters cannot be discarded, since they maintained a nomadic lifestyle (hunter-gatherers), and the Araripe sedimentary basin, rich in this mineral, is located just over 200 kilometers from the city of Inhuma.<sup>30</sup>

Although the literature<sup>1,17,29,31,32</sup> indicates pyrolusite ( $\text{MnO}_2$ ) as one of the substances responsible for the black coloration of natural mineral pigments, observed in some rupestrian paintings, this possibility was discarded, due to the absence of an analytical signal for manganese (Mn) in

the sample SE1903. This suggests that this pigment may have been prepared from carbonized organic materials (bones or vegetables).<sup>10</sup> The other chemical elements observed in this sample were attributed to the constitution of the rock itself, since the radiation applied to the sample during the analysis may have reached the rock matrix, to the existence of saline efflorescence or impurities brought in by the air.<sup>4</sup>

#### Raman

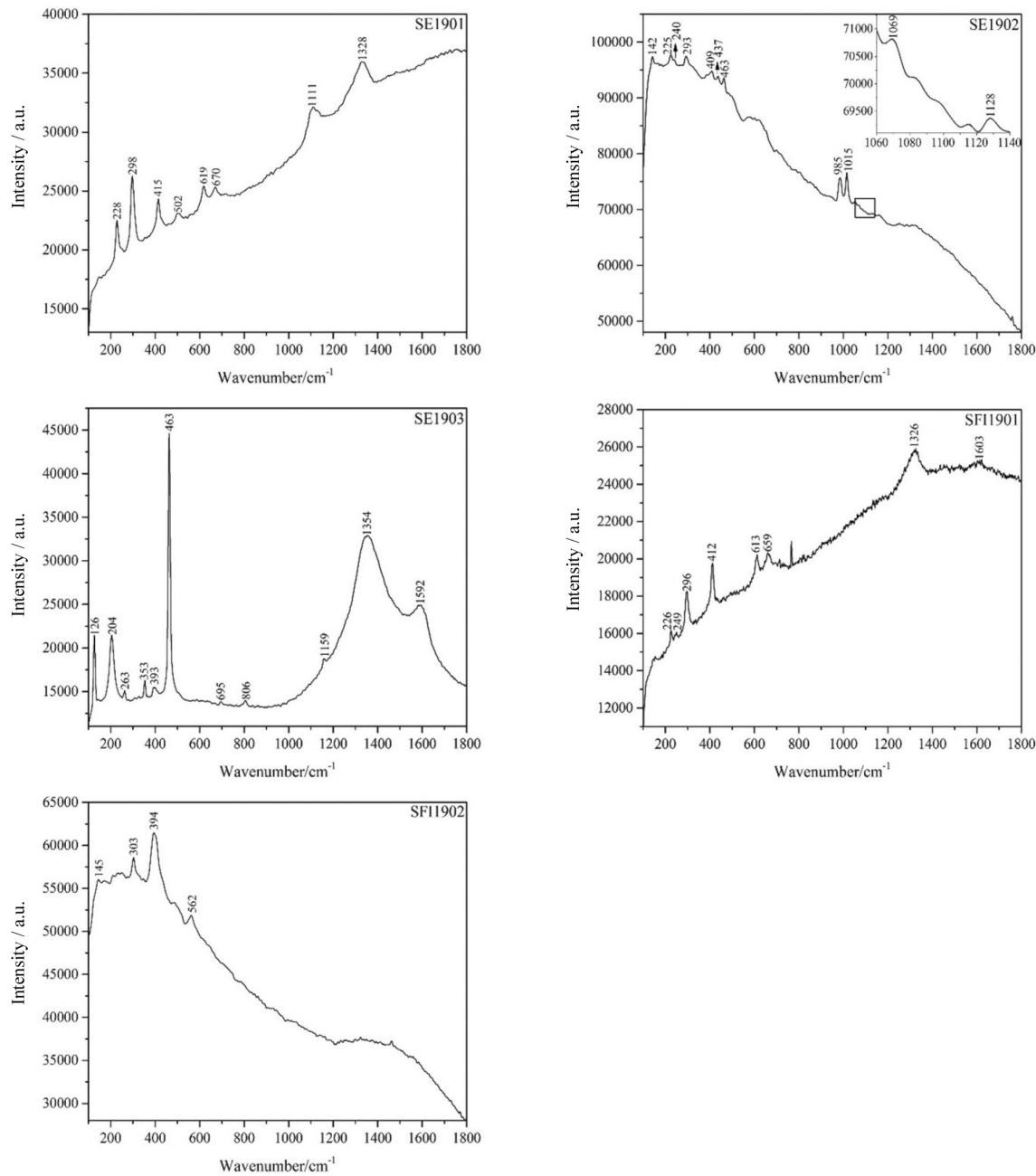
Figure 5 shows the spectra obtained by Raman spectroscopy for the samples presented in Table 1. The structural chemical description, as well as the characteristic bands of the pigment samples, are found in Table 2.

For the sample SE1901, red pigment, it can be observed a typical spectra profile of the hematite chromophore, since the bands identified are characteristic of this oxide, compatible with active vibrational modes of  $\text{A}_{1g}$  and  $\text{E}_g$  symmetry. The band at  $1328 \text{ cm}^{-1}$  is considered an overtone related to the longitudinal optical phonon (LO) observed ca.  $670 \text{ cm}^{-1}$ , prohibited by selection rules.<sup>37</sup> Generally, that band occurs at  $1320 \text{ cm}^{-1}$ , so it is suspected that some accidental degeneracy may have contributed to change its profile, making it more asymmetrical and enlarged, in addition to causing a small displacement. On the other hand, the band at  $1111 \text{ cm}^{-1}$  is not related to hematite and is possibly related to some component of the rocky matrix. Finally, the broad luminescence background observed can be related with aluminosilicates of the sandstone rocky support, although its organic origin cannot be discarded.

The sample SE1902, with white pictorial film, has its band at  $1015 \text{ cm}^{-1}$  attributed to the presence of anhydrous form of calcium sulfate (anhydrite,  $\text{CaSO}_4$ ), probably due

to the dehydration of gypsum over time, as a result of its excessive exposure to solar intensity, a condition favored by

the site location. Other bands of this salt, located ca. 415, 497, 608, and 1039  $\text{cm}^{-1}$ , were not observed, probably



**Figure 5.** Raman spectra of rupestrian pigment samples SE1901 (632.8 nm), SE1902 (785 nm), SE1903 (785 nm), SFI1901 (632.8 nm), and SFI1902 (785 nm), whose colors are red, white, black light red, and yellow respectively.

**Table 2.** Substances identified by Raman microscopy as responsible for the pigment color samples of Ema and Furna dos Índios Sites

Sample	Substance identified/formula	Observed bands / $\text{cm}^{-1}$	Reference
SE1901	hematite/ $\alpha$ - $\text{Fe}_2\text{O}_3$	228, 298, 415, 502, 619, 670 and 1328	33
SE1902	anhydrite/ $\text{CaSO}_4$	1015	34
SE1903	amorphous carbon/C	1354 and 1592	35,36
SFI1901	hematite/ $\alpha$ - $\text{Fe}_2\text{O}_3$	226, 249, 296, 412, 613, 659 and 1326	33
SFI1902	goethite/ $\alpha$ - $\text{FeOOH}$	303, 394 and 562	33

because of their low intensity and intense luminescence background of the spectrum.<sup>38</sup> It was also identified the presence of magnesium sulfate in epsomite ( $MgSO_4 \cdot 7H_2O$ ) form, confirmed for its main band ca.  $985\text{ cm}^{-1}$ .<sup>27</sup> After spectral amplification, as done by Apopei *et al.*,<sup>39</sup> it was possible to identify other characteristic bands of this salt at ca.  $1069$  and  $1128\text{ cm}^{-1}$ . The band of low intensity at  $142\text{ cm}^{-1}$  indicates the presence of anatase ( $TiO_2$ ),<sup>40</sup> because even in very low concentration, it can generate analytical signals, as it is a good light scatter. The band at  $463\text{ cm}^{-1}$  is indicative of the presence of  $\alpha$ -quartz.<sup>41,42</sup>

For the black pigment (related to the sample SE1903), the Raman spectra revealed two broad bands (typical of disordered material), one at  $1354\text{ cm}^{-1}$ , high intensity, and another at  $1592\text{ cm}^{-1}$ , called D and G bands, respectively, which are related to the stretching vibration of C–C bond from amorphous carbon, which suggests charcoal as origin.<sup>35,36</sup> The band at  $463\text{ cm}^{-1}$  is attributed to the presence of  $\alpha$ -quartz in the sandstone matrix of rocky support, or can also indicate the addition of sand as load or thickener. Other silicate bands were also observed at  $126$ ,  $204$ ,  $263$ ,  $353$ , and  $393\text{ cm}^{-1}$ .<sup>10,42</sup>

Regarding the red pigment (sample SFI1901) from the Furna dos Índios archaeological site, the Raman spectrum showed bands at  $226$ ,  $249$ ,  $296$ ,  $412$ ,  $613$ ,  $659$  and  $1326\text{ cm}^{-1}$ , compatible with hematite. The small band ca.  $1603\text{ cm}^{-1}$  suggests the presence of amorphous carbon in low concentration.<sup>35</sup> However, the other representative band of this substance, around  $1354\text{ cm}^{-1}$ , may be overlapping the one of hematite, which is in this spectral region. It may have been used as an additive or even be of current anthropic origin (burnings) or ancient, from the use of bonfires to meet the daily needs of precolonial human groups.

The Raman spectrum obtained for the sample SFI1902 revealed goethite as the pigment responsible for the yellow color observed, with characteristic bands ca.  $303$ ,  $394$  and  $562\text{ cm}^{-1}$ . The presence of an intense band at  $145\text{ cm}^{-1}$  was attributed to anatase ( $TiO_2$ ).<sup>40</sup>

Although the presence of binding substances, such as blood, animal fat, beeswax, egg, resin, among others, has not been confirmed by Raman microscopy, it is always prudent not to discard their use in the preparation of paints, even if they are not easily identified, since they can disappear as a result of the long air exposure time.<sup>10</sup> According to Faria *et al.*,<sup>14</sup> these substances are generally detectable in the spectral range from  $800$  to  $1700\text{ cm}^{-1}$ , due to the presence of bands at  $1245$ ,  $1450$  and  $1670\text{ cm}^{-1}$  referring to the vibrations  $\nu(C=O)$  of amide I,  $\delta(NH)$  of amide III and  $\delta(CH_2)$ , respectively.

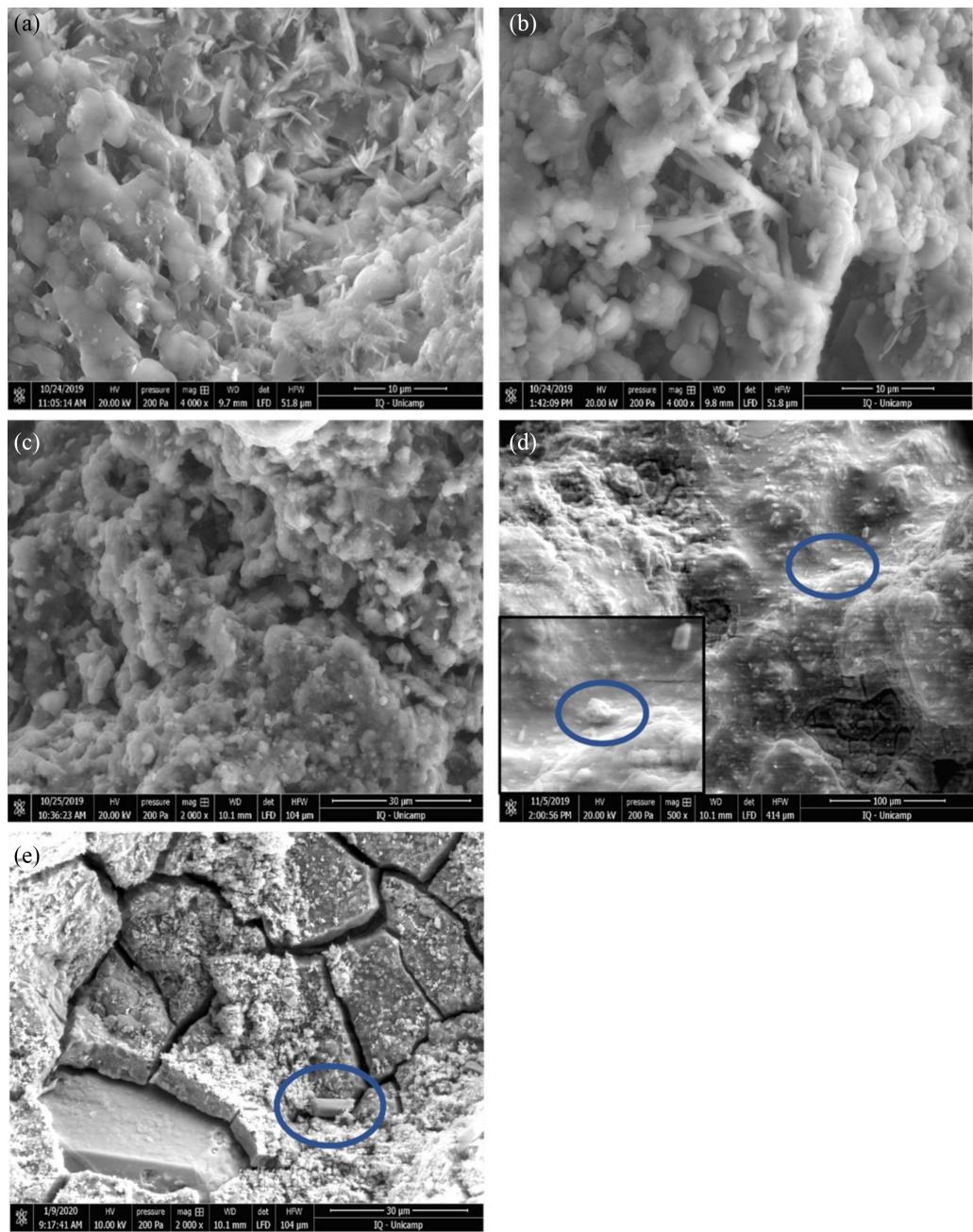
## SEM-EDS

Figure 6 illustrates the morphology, obtained by SEM, of the pictorial layers of the 5 samples under study. Micrographic analysis of sample SE1901 (Figure 6a) showed the presence of hematite in the form of thin plates (rosette petals).<sup>43</sup> Microscopy of the pictorial surface of the sample SE1902 (Figure 6b) revealed little occurrence of calcium sulfate crystals in the hydrated form (gypsum), whose standard morphology is acicular, similar to those of prismatic needles.<sup>44,45</sup> The changes observed regarding the size and shape are, in part, explained by Middendorf<sup>46</sup> as a change that occurs when gypsum is exposed to prolonged wet-dry cycles during natural weathering, therefore undergoing crystallization and recrystallization processes, since its porosity, combined with the rocky support, facilitates the penetration of water into the microstructure of this highly soluble crystal, as well as its dissolution and precipitation. Another observation is the presence of anhydrite (anhydrous form of gypsum), already shown by Raman spectroscopy, whose observed morphology showed similarity to the one presented by Kronbauer<sup>47</sup> for this mineral. Figure S1 (Supplementary Information (SI) section) presents the chemical map, obtained by SEM-EDS, of the spots with the highest concentration of calcium (Ca) and sulfur (S). It is possible to verify that both are uniformly distributed over the same area, which suggests that these are regions with calcium sulfate.

Figure 6b also points out to the presence of epsomite ( $MgSO_4 \cdot 7H_2O$ ) as saline efflorescence, whose morphology is similar to the aggregate obtained by Del Lama *et al.*<sup>48</sup> Epsomite, such as anhydrite, was also observed in the results collected by Raman microscopy, for sample SE1902.

The morphology of the pictorial film of the sample SE1903 (Figure 6c) proved to be homogeneous and the microanalysis of this sample performed by SEM-EDS (Figure S2, SI section) confirms that the paint is rich in carbon, which corroborates the result obtained by Raman microscopy. The other elements presented in the spectrum are in agreement with the results obtained by ED-XRF and were attributed to the presence of saline efflorescence, impurities brought in by the air<sup>4</sup> or to the rock constitution itself since the volume of interaction of the electron beam can have reached a small fragment of it, which is usually stuck to the sample, and generated part of the signal obtained by EDS. This may have been caused by the presence of microcracks in the sample.

The morphology of the sample SFI1901, Figure 6d, revealed the presence of hematite particles with different shapes and sizes, similar to those reported by Espin,<sup>49</sup> and



**Figure 6.** SEM micrographs of the red (a), white (b), black (c), light red (d) and yellow (e) pictorial layers of samples: SE1901, SE1902, SE1903, SFI1901 and SFI1902, respectively.

different from the classic occurrence in thin plates, such as rosettes.<sup>43</sup> However, the absence of hematite in the rosettes form has already been reported in other works in the literature, such as Mortimore *et al.*,<sup>50</sup> who found disk-shaped hematite particles. Superficial microcracks were also seen. Figure S3 (SI section) shows the chemical map of the distribution of iron (Fe) in the hematite present in Figure 6d and, from the highlight, it is observed that the morphology of this mineral does not present in the form of rosette petals, corroborating what had been observed in Figure 6d (for the same point).

The micrograph obtained from the yellow pictorial layer (sample SFI1902, Figure 6e) showed the presence of acicular goethite (in its classic needle shape, with elongated length) and also of superficial microcracks.

## Conclusions

The physicochemical and morphological study of the samples, through a combined multi-analytical approach, allowed the unequivocal identification of the main substances responsible for the colors of the rupestrian

pigments of the archaeological sites of Ema and Furna dos Índios, located in Inhuma, Piauí, Brazil. For the red, yellow, white and black samples, the pigments were hematite, goethite, gypsum/anhydrite and amorphous carbon from charcoal, respectively. It was not possible to detect the presence of organic binders, probably because they disappeared over time or, perhaps, because it is necessary to use another set of analytical techniques for such detection.

Finally, the integrated spectroscopic and morphological results in this study provided information about the technologies and natural resources used for the elaboration of rupestrian art, which are important aspects for understanding the expansion of precolonial human groups in Brazilian lands.

## Supplementary Information

Supplementary information (chemical map of distribution of elements Ca and S, chemical map of distribution of element Fe and EDS spectrum of black pigment in the samples SE1902, SFI1901 and SE1903, respectively) are available free of charge at <http://jbcs.sbrq.org.br> as PDF file.

## Acknowledgments

The authors are thankful to Federal Institute of Education, Science and Technology of Maranhão (IFMA) for supporting the author Jacira I. Moura so that she could dedicate herself, full-time, to the development of the research project, to the Federal University of Piauí (UFPI), to the laboratory GIA- Group of Instrumentation and Automation in Analytical Chemistry/IQ - Unicamp for the support to the development of this work, to the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) funding agency for granting the research productivity grant to Maria Conceição S. Meneses Lage (process 304915/2014-9), to the Fundação de Amparo a Pesquisa do Estado do Piauí - FAPEPI (process 033/2019) for the financial support and to the Institute of National Historic and Artistic Heritage (IPHAN) for supporting the development of the research.

## Author Contributions

Jacira I. de Moura was responsible for conceptualization, data curation, formal analysis, investigation, methodology, resources, writing original draft, review and editing; Maria Conceição S. M. Lage for conceptualization, formal analysis, project administration, supervision and writing review; Benedito B. Farias Filho for conceptualization,

formal analysis, project administration, supervision, writing-review and editing; Dalva Lúcia A. de Faria for conceptualization, data curation, investigation, review and editing; Wilkins O. de Barros for data curation, investigation, methodology; Hugo C. Loureiro for data curation, investigation, methodology and editing.

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Submitted: July 19, 2022

Published online: December 9, 2022

