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Identification of pyroxene minerals used as black pigments in painted human bones excavated in Northern Patagonia by Raman spectroscopy and XRD

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A B S T R A C T

The skeletal remains of seven individuals were excavated in a secondary burial context in the site of Cima de los Huesos, in the San Matías Gulf (Río Negro, Argentina). AMS dating of two samples for this site to 1173 ± 45 and 1225 ± 47 years BP make it one of the earliest burials of its kind uncovered so far in the Patagonian region. Among the findings, the skeleton of a male painted with parallel lines alternating red and black colors was uncovered. SEM-EDS elemental analysis of microsamples removed from the red and the black pigments showed the presence of Mn and Fe as the main components, respectively. Raman microspectroscopy combined with micro-X-ray diffraction analysis showed that the red pigment contains hematite and that the black pigment is composed of members of the pyroxene mineral group, ferrosilite ($FeSiO_3$) and enstatite ($MgSiO_3$) along with kanoite ($MnMgSi_2O_6$). This is, to our knowledge, the first report on the use of pyroxenes as black pigments to decorate human remains or archeological artifacts in South America. No organic compounds that could have been used as binders for the paints were detected by FTIR-ATR. Contamination due to quartz and aluminosilicates, mainly microcline and albite, from the burial environment did not allow determining whether clay minerals were used in the paints as binders and/or extenders. The multitechnique approach used was crucial to overcome the limitations of the individual techniques to firmly identify Mn-containing black pigments.

1. Introduction

The occupation by hunter–gatherer groups of the San Matías Gulf coast, in the Argentinean province of Río Negro (Patagonia), dates back to about 6000 years ago. During the period, primary burials in which all the bones of skeletons were placed in an anatomical articulated position were the most common. However, since about 1200 years ago, another mortuary practice called secondary burial emerged. In this case, the skeletons were unearthed by members of the social group and reburied in a different place, arranging the bones in particular ways. During the excavation of the *Cima de los Huesos* site, in the Bajo de la Quinta locality (BQ-CH) (Fig. 1a), the human remains of at least seven individuals, two sub-adults (with indeterminate sex) and five adults (two males, two females and one with indeterminate sex), were discovered. In this burial, long bones were placed parallel, oriented predominantly East–West (Fig. 1b). Among these remains, the bones of an adult male, including all the long bones, the ribs, tarsal bones, pelvis, and skull, were found to be carefully painted. In the long bones, alternating red and black lines approximately 3 mm wide are observed, while more irregular lines are found in the ribs (Fig. 2).

The BQ-CH site lies in a low terrain covered by sand dunes. A temporary freshwater pool that developed in the area must have attracted the human populations which inhabited the semiarid coast of the Northern Patagonia in the past. This is evidenced by the fact that several human burials, along with diverse archeological artifacts have been uncovered by archeologists in the area [1]. The human bones examined and analyzed in this study correspond to a unique secondary burial, located on a Pleistocene marine terrace, about 40 m above the sea level and about 1000 m from the sea. Two samples (a skull fragment and a tooth) corresponding to different individuals from the site were dated by AMS to 1173 ± 45 and 1225 ± 47 years BP [2], respectively. Therefore, this is one of the earliest burials of its kind so far uncovered in the Patagonian region.

Bones painted with red and black pigments were previously discovered in San Blas, Province of Buenos Aires [3], although no chronological

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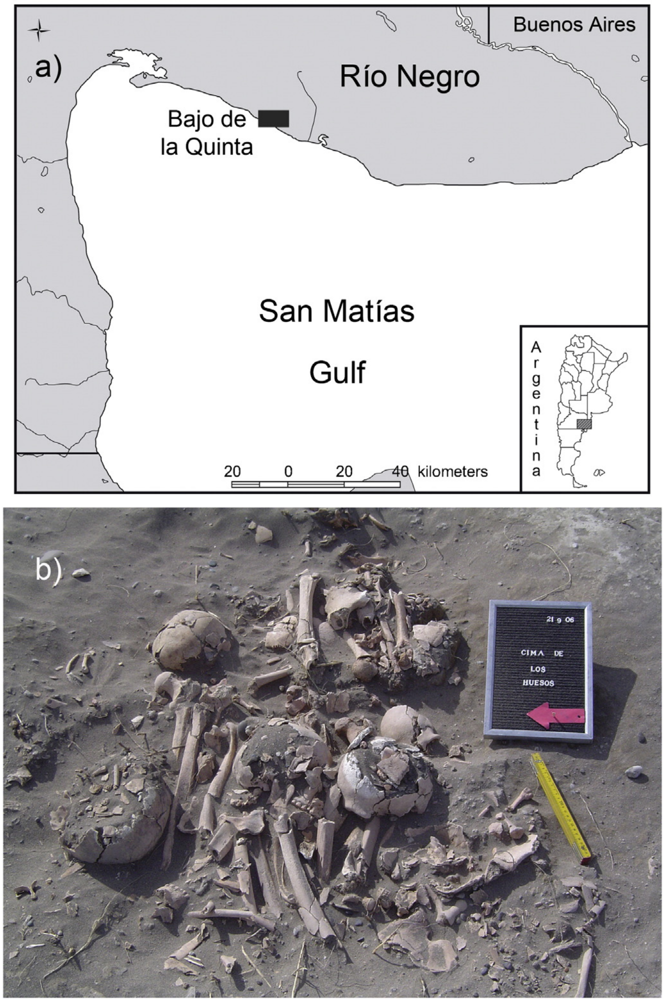

Fig. 1. a) Location of the *Bajo de la Quinta* locality, in the Northern Patagonian Atlantic coast. b) Photograph of the ground excavation of BQ-CH, where it can be observed the arrangement East–West of the long bones and the fragmented state of the material (the red arrow indicates the North). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. a) Ribs painted with alternating red and black lines. b) Photomicrograph of a rib surface taken with a stereomicroscope. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

information is available for this finding. In secondary burials of the Pampa and Patagonia regions, the most frequent practice consisted in sprinkling pigments or applying a uniform paint film over the bones. Therefore, the discovery of alternating colored lines carefully adorning all the bones of a single individual in the *Cima de los Huesos* burial is unusual, and suggests that the deceased had a very special status among the individuals of the group.

Most prehistoric paintings found in rock art sites, decorated archeological ceramics and, as in this case, bone remains in ritual contexts, contain red and black pigments as the main colorants [4–7]. Physicochemical analyses have shown that, in their great majority, the red paints in these artifacts are based on Fe oxides/hydroxides, and that the black pigments are either carbon-based, such as charcoal, or Mn oxides/hydroxides [4–15]. Raman spectroscopy is a well established and powerful technique for the non-invasive identification of materials in cultural heritage objects. However the variety of oxidation states and polymorphic forms of Mn oxides and hydroxides presents a challenge to their firm identification [16–19]. These and other difficulties involved in the identification of Mn-based black pigments by Raman spectroscopy have been previously discussed [9,12,15,19]. Nevertheless, the combination of vibrational spectroscopic techniques and X-ray diffraction has proved to be a powerful methodology to unambiguously identify Mn-based black pigments [12,15,17]. In this work, Raman spectroscopy, X-ray diffraction, FTIR spectroscopy, and SEM-EDS elemental analysis were used to identify the components of the red and black paints.

Our study aims to shed light onto burial practices of ancient hunter–gatherer groups living in the Argentinean Patagonia.

2. Experimental

2.1. Painted bone samples

The skeletal remains examined in the present study are in a fragmentary state. Microscopic paint samples were removed from rib fragments by scrapping them with a stainless steel scalpel, and also some bone fragments were non-invasively analyzed in situ, without removing any samples.

2.2. Instrumentation

The samples were observed under a Leica MZ6 stereomicroscope and photographed with a Canon S50 camera. A Carl Zeiss Axio Imager equipped with Z2m sources in visible and ultraviolet light polarized normal modes were used. Images were taken with an AxioCam HRc camera using the Axio Vision software for acquisition and processing.

Information on the surface morphology of the samples and elemental composition were obtained using a field environmental scanning electron microscope (FE-SEM) Zeiss:Supra 40 coupled with an energydispersive X-ray spectrometer (SEM-EDS) INCA X Sight (Oxford Instruments).

Raman microspectroscopy analyses were carried out with a Renishaw System 1000 configured with a Leica DM LM microscope, notch filters, and a thermoelectrically cooled charged-coupled device (CCD) detector. A 785 nm laser line was used for excitation and was focused on different areas of the sample fragments using the 50× objective lens of the microscope attached to the spectrometer, achieving a lateral resolution of ~2–3 μm. In order to avoid changes of the sample materials due to overheating, neutral density filters were used to set the laser power at the sample to values between 0.2 and 1.0 mW. A 1200 lines/mm grating was used and integration times were set between 10 and 300 s. The wavenumber stability and the accuracy were checked by recording the Raman spectrum of a silicon wafer (520 cm^{-1}).

Micro-X-ray diffraction (XRD) patterns were obtained using a Rigaku D/Max Rapid Diffractometer. Microscopic sample scrapings were mounted on glass fibers using Elmer's® glue and the instrumental parameters used were as follows: Cu Kα ($\lambda = 1.542$ Å) radiation (50 kV accelerating voltage and 40 mA current), chi (χ) fixed at 45°, omega (ω) fixed at 0°, and phi (φ) spun from 60° to 120° at 1°/s, 0.8 mm collimator, 10 min exposure time.

FTIR-ATR spectra were obtained using a Nicolet iS50 FTIR spectrometer with a diamond single-bounce ATR crystal. For each reference sample, 64 scans were recorded in the 4000–400 cm^{-1} spectral range in the reflectance mode with a 4 cm^{-1} resolution. Spectral data were collected with the Omnic v9.2 (Thermo Electron Corp.) software without post-run processing. The spectrum of air was used as background.

3. Results and discussion

The painted bones analyzed in the present study are shown in Fig. 2a and photomicrographs of the bone areas with red and black paints are presented in Fig. 2b. Table 1 shows the results of the SEM-EDS analysis carried out of the surface of red and black paints in bone fragments and in an unpainted bone area. Mn was found to be present in the black paint only, while Fe was identified both in the red and black paints, in relatively larger amounts in the former. All samples showed Ca and P from the bone hydroxyapatite along with relatively large amounts of Al and Si, together with minor amounts of K, Mg, and Na, that indicate the presence of silicates.

Raman analysis performed on sample scrapings of the red paint gave peaks characteristic of hematite (α-Fe_2O_3) at ca. 223, 291, 408 and 610 cm^{-1} [7] (Fig. 3 spectrum a), consistently with the results of the elemental analysis. In many of the spots analyzed, bands at ca. 960 cm^{-1} that are characteristic of the P–O symmetrical stretching were observed, along with features due to carbonate present in hydroxyapatite at ca. 281, 712, and 1086 cm^{-1} (Fig. 3, spectrum b) [20].

The main bands observed in the Raman spectra acquired on sample scrapings of the black paint are consistent with the presence of pyroxenes, with characteristic bands below 700 cm^{-1} and above 1000 cm^{-1} (Fig. 4) [21]. Minerals of the pyroxenes group ($MSiO_3$) are one of the most abundant rock-forming minerals on Earth. The spectrum presented in Fig. 4a corresponds to a member of the enstatite–ferrosilite (En–Fs) series [21–23]. Ferrosilite ($FeSiO_3$) forms a solid solution with enstatite ($MgSiO_3$) and the positions of the Raman bands for this solution depend on the Fe content, which partially replaces the sites occupied by the Mg atoms, whose orthorhombic structure includes it in the orthopyroxenes group [21,22]. Raman spectra recorded in other particles of the black paint revealed the presence of kanoite ($MnMgSi_2O_6$) (Fig. 4 b), a clinopyroxene with a monoclinic structure [24,25]. Although kanoite is a mineral found in different geographical areas, scant spectroscopic information has been published about it [26,27]. The Raman spectra of pyroxenes share general features according to Wang et al. [21]. However, differences in symmetries between orthopyroxenes and clinopyroxenes make the number, position, and relative intensities of the peaks in each spectral range different, allowing to identify them. For example, in the range between 800 and 600 cm^{-1}, orthopyroxenes usually present a strong doublet, and for clinopyroxenes, such as kanoite, an asymmetric single peak near 670 cm^{-1} is expected instead. In Table 2, the assignments of the various Raman spectral ranges for En–Fs and for kanoite are presented. XRD patterns obtained for different microsamples of the black paint match

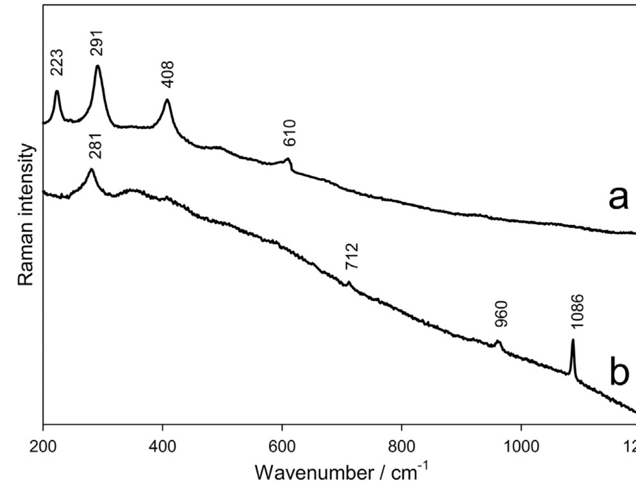

Fig. 3. Raman spectra representative of those acquired in a sample of the red paint: in red pigment particles (spectrum a) and in white particles in the same sample (spectrum b), respectively.

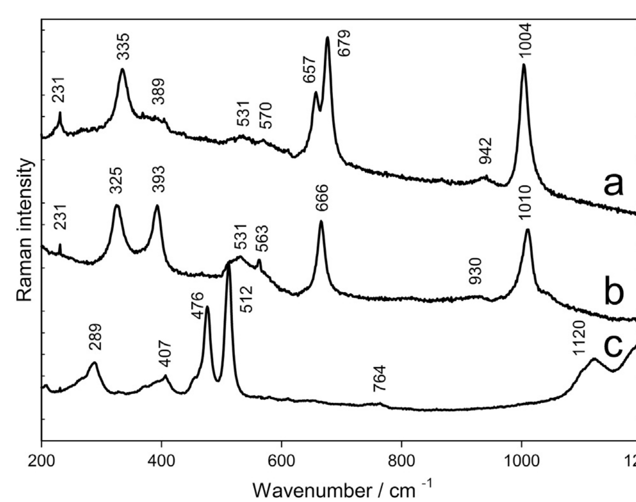

Fig. 4. Raman spectra representative of those recorded in different particles in the black paint: black particles (a and b) and white particle (c), respectively.

Table 1
Results from the SEM-EDS elemental analysis of the red and black paints expressed as % of the total atomic content.

Element	Unpainted bone	Black paint	Red paint
Fe	0.2	1.8	6.9
Mn	–	0.8	–
Ca	5.5	5.6	6.2
P	3.3	2.8	3.3
Mg	0.5	0.8	0.6
Al	1.0	2.3	1.9
Si	2.4	6.6	5.8
Na	0.3	0.4	0.4
K	0.1	0.3	0.3
C	29.3	16.9	17.5
O	57.5	61.8	59.1

Table 2
Tentative assignments of the Raman bands observed for the pyroxenes En–Fs and kanoite based in Wang et al. [22] (*) Fig. 4a, (+) Fig. 4b.

ν (cm^{-1}) En–Fs*	ν (cm^{-1}) kanoite+	Assignments
231	231	M–O strech/bend
335	325	M–O strech/bend
389	393	
531	531	O–Si–O bend
570	563	
657sh	666	Si–O–Si stretch
677		
942	930	Si–O strech
1004	1010	

reference patterns of ferrosilite and estantite (Fig. 5a), and of kanoite (Fig. 5 b), respectively, however no reference patterns for the solid solutions En–Fs were available in our libraries.

It is important to note that some bands in the Raman spectra acquired for the black paint match those previously reported for manganese oxides such as Mn_2O_3 [18]. These comprise features in the 300–350, 500–550, and 650–700 cm^{-1} ranges [16–19]. However, bands at ca. 1000–1050, 800–600, and 450–300 cm^{-1} have not been reported for manganese oxides, so our results are strongly suggesting the presence of pyroxenes as discussed above. No Mn oxides were identified by XRD analysis, however these compounds can also be amorphous [28].

Raman spectra recorded from white particles present in the black paint samples showed the presence of quartz and the feldspars microcline ($KAlSi_3O_8$) and albite ($NaAlSi_3O_8$) (Fig. 4, spectrum c) [29]. The presence of aluminosilicates is also inferred from the results of the SEM-EDS elemental analysis for all the samples, including the unpainted bone (Table 1). These compounds are most likely due to contamination from the burial environment.

FTIR-ATR measurements performed in-situ on painted and unpainted areas of the bone fragments showed bands due to hydroxyapatite, with PO_4^{-3} characteristic frequencies at ca. 1087, 962, 599, 557 and 468 cm^{-1} [30,31], and CO_3^{-2} modes at ca. 1418, 873, and 713 cm^{-1} (Fig. 6, spectra a, b and c). These results are consistent with those of the Raman analysis discussed above. Similar features were observed in the spectra acquired in a sample removed from the inner zone of the bone (Fig. 6, spectrum d), strongly suggesting that the presence of CO_3^{-2} observed in the

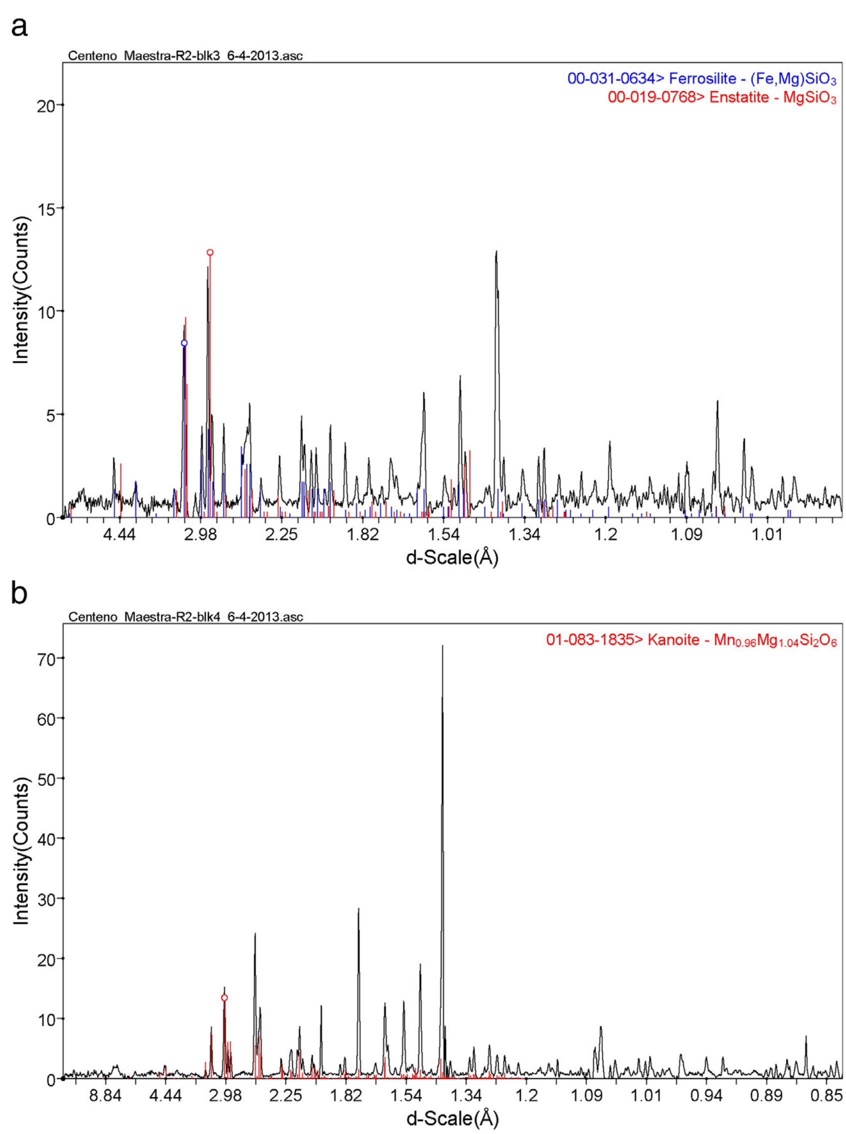

Fig. 5. Micro-XRD patterns representative of those acquired in samples removed from the black paint in the bones, showing the presence of ferrosilite and enstatite (a) and of kanoite (b). Peaks that do not fit to the patterns of the minerals indicated cannot be assigned with certainty.

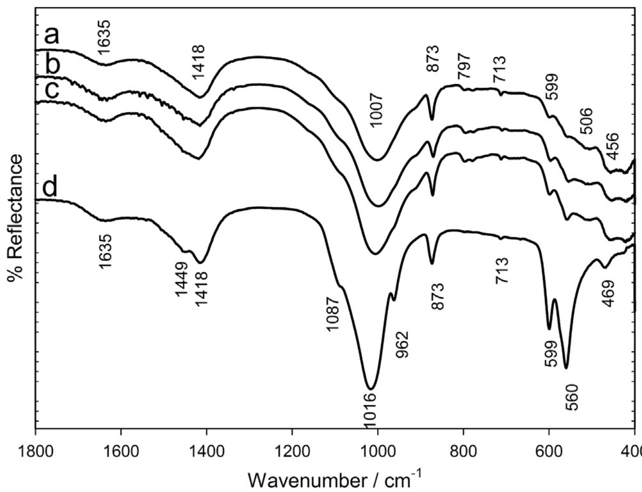

Fig. 6. FTIR-ATR spectra acquired in situ in the black paint (a), in the red paint (b), in a bone surface area with no paint visible (c), and in a spot in the interior of the bone (d), respectively.

painted areas by FTIR is most likely due to the replacement of PO_4^{-3} in bone [31,32], and not to the use of calcite mixed in the paint or applied in a preparatory layer.

In the FTIR-ATR spectra recorded on painted and unpainted areas on the outer surface of the bone, the most intense band occurs near 1007 cm^{-1} together with two very weak doublets around 780–800 and 420–460 cm^{-1}, respectively, which are assigned to feldspars [33], and that were also observed by Raman. These bands are not observed in the spectra recorded in the samples removed from the inner zone of the bone.

All the samples analyzed by FTIR-ATR showed a weak band around 1636 cm^{-1} and a group of weaker features in the 1520–1560 cm^{-1} range. The first band could be assigned to the C=O stretching (Amide I) and the second to the N–H deformation (Amide II) originating in residues of collagen from the bone [31]. The FTIR-ATR spectra show no bands due to the red or black pigments in the paints. It is possible that the bands due to feldspars and hydroxyapatite overlap the bands expected for ferrosilite [34], in the ranges around 735 and 1010 cm^{-1}, and at ca. 950 and 875 cm^{-1}. No bands that could be assigned to organic compounds used as binders in the paints were detected in the FTIR spectra either.

4. Conclusions

This is, to our knowledge, the first report on the use of black pigments containing the pyroxene minerals enstatite, ferrosilite, and kanoite in South American painted bones, most likely because in most studies carried out previously only elemental analyses were performed. Therefore, this work highlights the importance of the use of complementary microanalytical techniques to properly identify Mn-containing minerals in archeological black paints. The Raman spectra obtained can be used as references to non-invasively identify the compounds in objects of cultural significance.

Even though the possible use of clays has been previously reported as binders and/or extenders for paints in some archeological objects, the results presented above show the challenges presented when the artifacts are contaminated by the soil in the burial environment.

As the correct identification of minerals allows researchers to locate the potential sources and learn about the artistic techniques used in their application, our study provides new information on this particular burial practice of hunter–gatherer groups in the Argentinean Patagonia about 1200 years ago.

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