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ORIGINAL PAPER

Combining TXRF, FT-IR and GC–MS information for identification of inorganic and organic components in black pigments of rock art from Alero Hornillos 2 (Jujuy, Argentina)

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Abstract Archaeological samples are complex in composition since they generally comprise a mixture of materials submitted to deterioration factors largely dependent on the environmental conditions. Therefore, the integration of analytical tools such as TXRF, FT-IR and GC–MS can maximize the amount of information provided by the sample. Recently, two black rock art samples of camelid figures at Alero Hornillos 2, an archaeological site located near the town of Susques (Jujuy Province, Argentina), were investigated. TXRF, selected for inorganic information, showed the presence of manganese and iron among other elements, consistent with an iron and manganese oxide as the black pigment. Aiming at the detection of any residual organic compounds, the samples were extracted with a chloroform–methanol mixture and the extracts were analyzed by FT-IR, showing the presence of bands attributable to lipids. Analysis by GC–MS of the carboxylic acid methyl esters prepared from the sample extracts, indicated that the main organic constituents were saturated ($C_{16:0}$ and $C_{18:0}$) fatty acids in relative abundance characteristic of degraded animal fat. The presence of minor $C_{15:0}$ and $C_{17:0}$ fatty acids and branched-chain *iso*-$C_{16:0}$ pointed to a ruminant animal source.

Keywords Prehistoric rock art · Inorganic and organic components · TXRF · FT-IR · GC–MS

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Introduction

Chemical analyses of rock art paintings have focused principally on identification of inorganic components such as pigments, mainly iron and manganese oxides, and extenders (clay, gypsum, calcite, bone, talc, potassium feldspar) mixed with them [1–3]. It is probable that in many cases water or organic natural products (blood, vegetable oil, or animal fat) were added to enhance the adhesive properties and facilitate the application of the prepared paints. Human blood [4], beeswax [5], and plant residues [6] have been identified in rock art from Australia while lipids present in pictograph paints from southwestern Texas were native to the rock coating [7]. Studies on rock art have an outstanding role in the development of Argentine archaeology, but only a few attempts have been made to analyze the chemical composition of the paints

used. The scarce literature on this subject is limited to inorganic component analysis by X-ray diffraction, scanning electron microscopy, and FT-IR, which have shown that hematite, goethite, manganese dioxide, and green earth were the main inorganic pigments used [8–16]. Recently, the first chemical analysis of organic components of rock art samples and painting residues from archaeological sites in Argentina have been performed, identifying the presence of lipids of vegetable and animal origin in samples from Northern Patagonia [10, 13] and of 5-methoxy-*N*,*N*-dimethyltryptamine in rock art paintings from Catamarca [17].

Following these studies on the components of prehistoric rock paintings, the inorganic and organic components of two black rock art samples from the archaeological site Alero Hornillos 2 were investigated. Hornillos 2 (23° 13′ 47″ S, 66° 27′ 22″ W) is a little cave associated with a rock shelter located in the large Puna ignimbritic plateau, reaching a 42 m^2 surface. It is located in the Quebrada Agua Dulce about 20 km North of the town of Susques (Jujuy Province, Argentina), 4020 m above sea level (Fig. 1). The cave lies at the bottom of a Neogenic ignimbritic farallon of dacitic–riodacitic composition, in the Zapaleri Formation, and it has been continuously filled by the lateral supplied materials. In general, this regional ignimbritic rock has irregular surface micro-topography accentuated by important weathering processes, mostly thermoclastism. Until now, eight grid squares have been excavated and nine levels of human occupation have been determined. The eight radiocarbon dates from these stratigraphic levels pointed out its chronology between 11150±270 cal BP and 7085±70 cal BP [18]. The archaeological record is mainly composed by stone tools, for example projectile points, scrapers, mortars and pestles, and bone tools, for example needles and faunal remains. The occupations of the site can be attributed to hunter-gatherer groups that lived in the region since the Pleistocene–Holocene boundary and which used the location as a residential base that gave shelter to small domestic units.

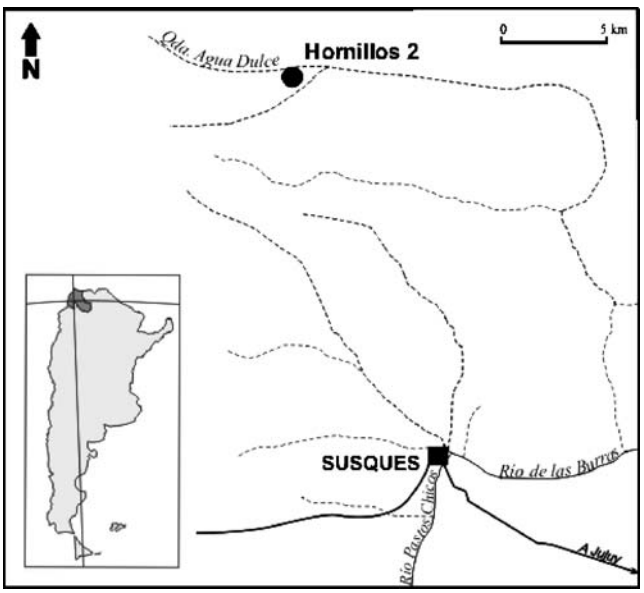

Fig. 1 Location of the cave Hornillos 2 in the Susques region (Argentine Puna)

The complete rock art represented on these cave walls is painted in black and in red colours (from reddish yellow to dark red). These plain paintings constitute a simple panel with seventeen almost complete figurative camelid figures and five schematized human figures. There are, at least, three types of camelid—two legs black, four legs black, and four legs red. All representations are stylized, non-schematized small figures. The paintings show superposition of black and red figures, suggesting two manufacturing events. The first would be the four-legged red camelids associated with the red anthropomorphic figures, and the second the four-legged black camelids. The two-legged camelids are not superimposed on any red figure, but their execution could be associated with the other black motifs. The execution of some black figures, like the two-legged camelids, shows very thin lines that have sharp boundaries between painted and unpainted areas (Fig. 2), suggesting that the pigments were applied using some kind of instrument, perhaps a paintbrush, and that a binder was added to enhance paint's fluidity. Nowadays, these paintings are very deteriorated, as a result of weathering processes affecting the rock wall, so it was necessary to be very careful during sampling. In this study, two painting samples were collected from two of the six distinguishable black camelids. Samples M10 (Munsell Gley 3/1) and M15 (Munsell Gley 4/1) were taken from two legs (ca. 12 cm) and four legs (ca. 17 cm) camelids, respectively (Figs. 2 and 3). The pigment layers were thin and very firmly bound to the rock beneath, so it was not possible to separate them completely from the substrate. Preliminary analyses using XRD, SEM-EDX, and FT-IR showed the presence of large amounts of gypsum; nevertheless, the black pigment could not be identified. TXRF was then selected as a micro-analytical technique for inorganic characterization of the pigment [19]. This technique is specially recommended, considering the small amount of sample (a few micrograms) required for the analysis and the low detection limit achieved (in the parts per billion range).

There is chemical evidence that in some cases organic substances were used in the paints to suspend the inorganic pigments and the extenders and bind them to the rock surface [6, 20]. A variety of analytical methods have been used to study the organic composition of archaeological samples. FT-IR helps in a preliminary identification of the main molecular constituents present in organic residues and in the selection of conditions of sample preparation for further analysis by a more informative technique, for

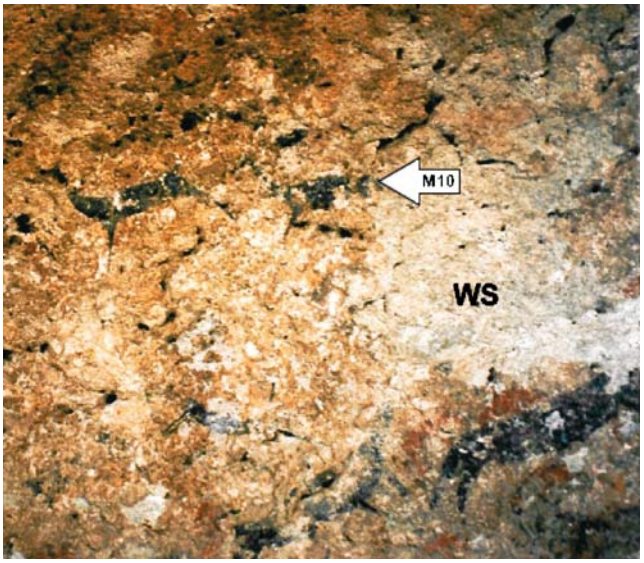

Fig. 2 Black camelid figures. The *arrow* indicates the site of extraction of black painting sample M10 from one of the two legs camelids. *WS* indicates rock weathered sector

example GC–MS [21]. In order to search for the presence of organic compounds as potential binders, a combination of these spectroscopic and chromatographic techniques was employed for both black painting samples.

The purpose of this work was to determine the nature of the black pigment, painting preparation, and application in order to enlarge understanding of the artistic practices and technological knowledge of the early inhabitants of this area in the northern region of Argentina. Although the number of samples analysed here is small, this is consistent with rock art studies in which the first concern has to be the conservation of the archaeological site.

Experimental

Solvents and materials

All chemicals were analytical grade (Merck, Argentina). The methanolic HCl was prepared by adding 0.5 mL acetyl chloride to 5 mL anhydrous methanol in a water–ice bath.

Sampling and sample preparation

The two black samples (M10 (973 mg) and M15 (213 mg)) were collected with a tungsten carbide tool from the wall painted motifs, scraping from the most deteriorated areas, and placed in plastic bags. The colour of both samples was described according to Munsell Soil Colour Charts [22]. For TXRF analysis, a minute piece was carefully scraped off the paint layer from each sample and was directly attached to the TXRF quartz reflector. For the organic analyses, the samples were crushed to a powder using a porcelain mortar and pestle and extracted three times with chloroform–methanol (2:1 *v*/*v*, 15 mL, 15 min sonication) at room temperature. The total lipid extracts were centrifuged (15 min, 3,200 rpm), decanted, and filtered through celite under vacuum. The filtrates were then dried under a stream of nitrogen and analysed by FT-IR prior to derivatization. Fatty acid methyl esters (FAMEs) were prepared by treating 1 mg of each extract with 2% HCl in methanol (0.5 mL) at 60 °C for 2 h. After cooling, water (0.5 mL) was added. The mixture was extracted with chloroform (3×0.5 mL) and the solvent evaporated under nitrogen. The FAMEs were stored at −25 °C until GC–MS analysis. After adding 500 μL chloroform, 2 μL of the solution was analysed by GC–MS. Peak assignment was based on comparison with analysed reference compounds, with library mass spectra, and on interpretation of mass spectra.

Instruments

For TXRF measurements, an X-ray fluorescence spectrometer, comprising a Philips generator, equipped with a fine-focus Mo X-ray tube was employed. Total reflection was achieved by a TXRF module designed by the Atominstitut der Österreichischen Universitäten. The acquisition data system consisted of an Ortec fast amplifier and an Ortec multi-channel analyzer (MCA) associated with a Maestro-32 emulator computational program. For X-ray detection, a Canberra Si(Li) detector with a Be window (80 mm^2 area, 0.008 mm thickness) with a 160 eV FWHM at 5.9 keV was used. Excitation conditions were 50 kV and 30 mA, and the acquisition time for each spectrum was 500 s. For spectra deconvolution the AXIL program was employed. All the measurements were made in air.

Infrared spectra were obtained on a Nicolet Magna 550 Fourier transform spectrometer. For each sample 32 scans

Fig. 3 Location of M15 sample from one of the four legs camelids. The photograph shows the superposition of the paintings where the red fragmented figures are beneath the four legs black camelids

were recorded in the 4,000 to 400 cm^{-1} spectral range in transmittance mode with a resolution of 4 cm^{-1}. Spectral data were collected with Omnic 7.3 (Thermo Electron Corporation) software. The KBr pressed disc technique (1% sample in KBr) was used. As background, the spectrum of the KBr pellet was used.

GC was performed on a Hewlett-Packard 5890A chromatograph equipped with a flame-ionization detector and an Ultra 2 column (30 m × 0.25 mm i.d., 0.25 μm film thickness). Temperature program: 1 min isothermal at 100 °C and then 100 to 290 °C at 10° min^{-1}, followed by a 10-min hold at 290 °C. GC–MS was performed on a Trio-2 VG mass spectrometer (electron impact 70 eV, ion source temperature 180 °C, interface temperature 250 °C) coupled to a Hewlett–Packard 5890 chromatograph. Chromatographic conditions were the same as for GC analysis. Helium was used as the carrier gas and inlet pressure was 7 psi.

Results and discussion

The TXRF spectrum of sample M10 is shown in Fig. 4. Both sample spectra showed the presence of manganese (120 μg kg^{-1} for M10 and 180 μg kg^{-1} for M15) and iron (300 μg g^{-1} and 250 μg g^{-1} for M10 and M15, respectively) among other major elements (sulfur and calcium). Further elements detected (potassium, vanadium, titanium, rubidium, strontium, and zinc), arising from the rock support, were always present in the samples. The high calcium and sulfur content confirm the presence of gypsum, also identified by FT-IR analyses; this is commonly used in rock paintings as an inorganic extender of the pigment [8, 9, 13]. The manganese content of both samples could be ascribed to manganese dioxide used as a black pigment in rock art [1, 7, 23] or to the presence of an umber, that is, a dark earthy pigment containing manganese oxides in addition to iron oxides [24, 25]. The association of iron and manganese in mineral phases is very common in nature and, in the region of Susques where the archaeological site Hornillos 2 is located, there are numerous sources of this kind [26–28]. This information together with the detected presence of manganese and iron in both samples suggest that the black pigment is an iron and manganese oxide.

To look for any lipidic residual organic compounds, fragments of both black samples were extracted with chloroform–methanol 2:1. Both samples contained appreciable quantities of organic compounds—962 μg g^{-1} (M10) and 36,780 μg g^{-1} (M15). The extracts were analysed by FT-IR, revealing the presence of organic components, most likely lipids. The most important features were the presence of a broad carbonyl absorption band at 1729 cm^{-1} together with bands attributable to C–H stretching of CH_3 and CH_2 groups at 2934–2861 and 1466–1387 cm^{-1}. The carbonyl band at 1729 cm^{-1} could arise from fatty acids or from acylglycerol groups. FT-IR spectra of vegetable oils and animal fats contain a strong, sharp carbonyl band at 1750–1740 cm^{-1} due to the ester group [29] while fatty acids from these sources show the carbonyl band at around 1715 cm^{-1} [13]. Therefore, broadening of the carbonyl band at 1729 cm^{-1} in the spectra of the organic extracts of samples M10 and M15 indicates the presence of acylglycerides of plant and/or animal provenance together with the formation of free fatty acids by hydrolysis.

Analysis by GC–MS of the carboxylic acid methyl esters prepared from the lipids extracted from the black painting samples (M10 and M15) showed that the main organic

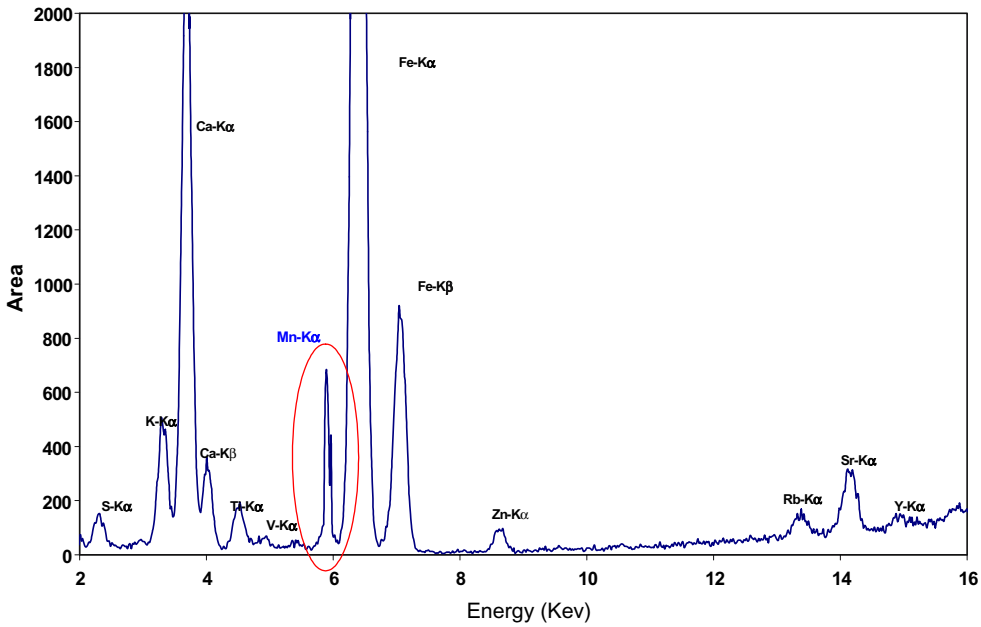

Fig. 4 TXRF spectrum of sample M10

constituents were palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) acids together with minor saturated ($C_{14:0}$, $C_{15:0}$, *iso*-$C_{16:0}$, $C_{17:0}$) and unsaturated ($C_{16:1}$ and $C_{18:1}$) fatty acids. The fatty acid distribution in both samples (Fig. 5), with a greater abundance of palmitic acid ($C_{16:0}$) than stearic acid ($C_{18:0}$), is typical of degraded animal fats [30]. The small amounts of odd-carbon-numbered, straight-chain compounds, specifically $C_{15:0}$ and $C_{17:0}$, and the presence of branched-chain *iso*-$C_{16:0}$ point to a ruminant animal source due to microbial activity in their digestive system [13, 31]. Recently, we have determined the fatty acid composition of the marrow lipid of a guanaco from Patagonia (*Lama guanicoe*) [13] showing the presence of large amounts of palmitic ($C_{16:0}$) and oleic ($C_{18:1}$) acids together with minor myristic ($C_{14:0}$), pentadecanoic ($C_{15:0}$), palmitoleic ($C_{16:1}$), and margaric and stearic ($C_{18:0}$) acids. The presence of bone remains of South American camelids, for example vicuna (*Vicugna vicugna*) and guanaco (*Lama guanicoe*), in the archaeological record of the site reinforces this assumption. These bone remains show evidence of having been processed in order to extract the marrow content and the fat of the trabecular tissue. Triacylglycerols are character-

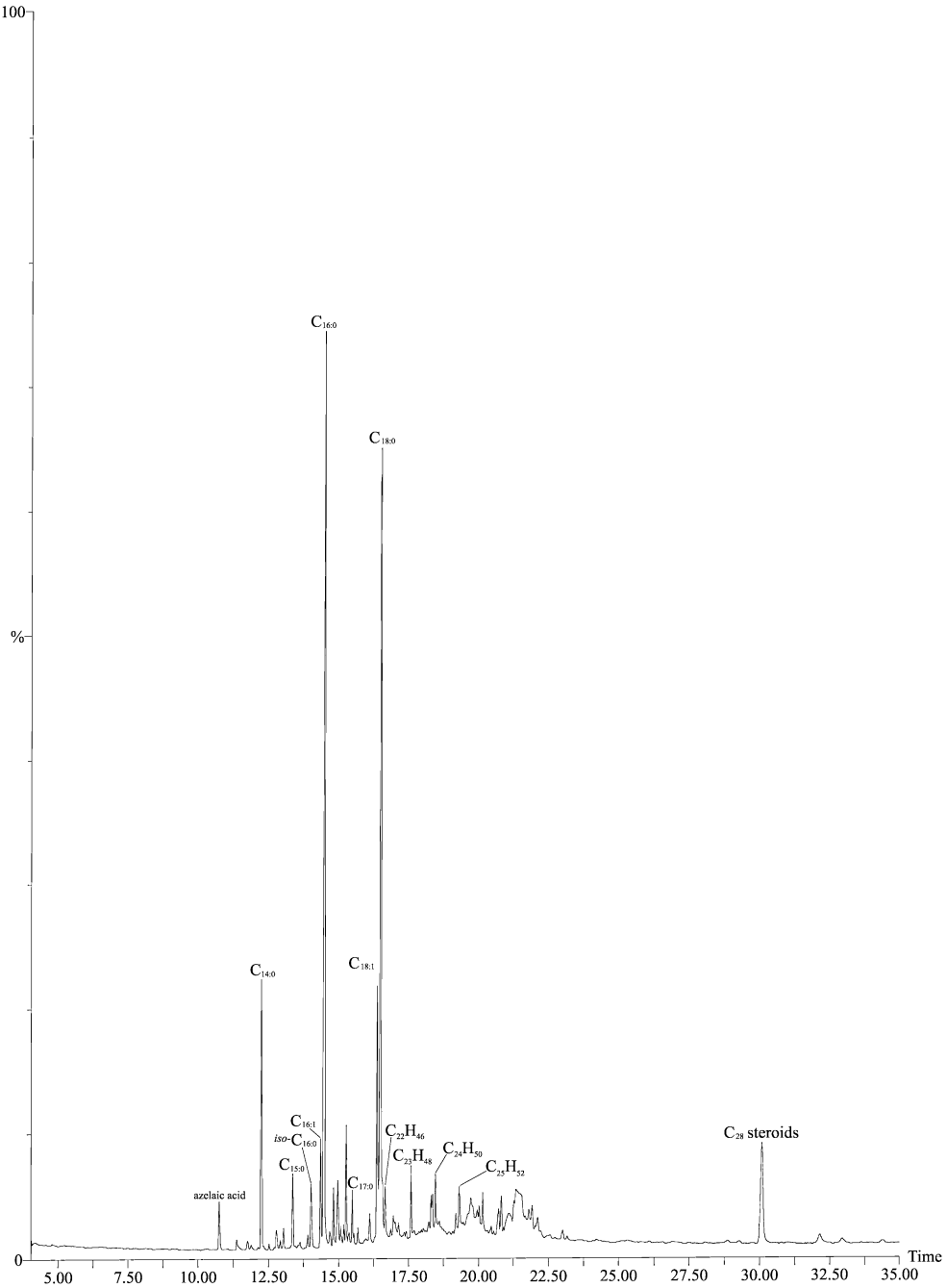

Fig. 5 GC–MS total-ion chromatogram of the fatty acid methyl esters in lipids extracted from archaeological sample M10

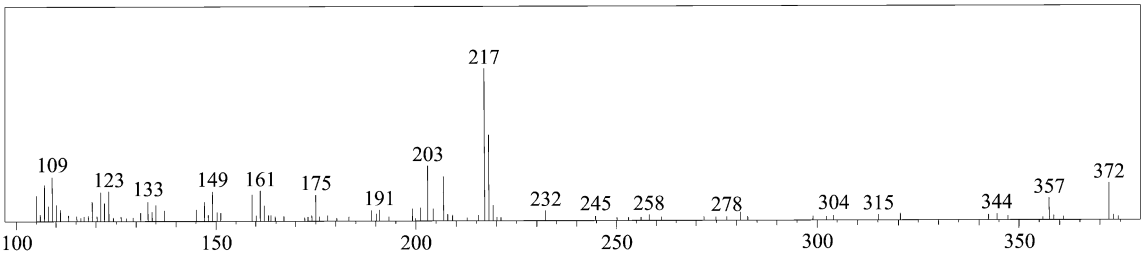

Fig. 6 Mass spectrum of cholestane detected in the lipid extract of sample M15

istic biomarkers of vegetable oils and animal fats [32, 33]. Comparison of their composition and distribution in reference contemporary samples with those found in archaeological pottery has enabled the discrimination of dairy and subcutaneous fats from sheep, cows, and goats [34]. However, there are no reports on the triacylglycerol composition of American camelids fats. Therefore, further studies on their identification will be useful to assess the origin of animal fats in remains from archaeological sites in Argentina.

The GC–MS total ion chromatogram of the fatty acid methyl esters of the lipids extracted from sample M10 also showed the presence of minor saturated hydrocarbons with 22, 23, 24 and 25 carbon atoms and a mixture of coeluting 24-methylcholestane (M^+=386) and 24-methylcholestene (M^+=384) (Fig. 5). Sample M15 contained, in addition to fatty acid methyl esters, minor hydrocarbons and cholestane (M^+=372), characterized by its molecular ion and an intense peak at *m/z* 217 in its mass spectrum (Fig. 6). The presence of *n*-alkanes together with steranes and sterenes, presumably derived from sterols in higher plants [35], is not easy to explain. These compounds are characteristic components of bitumens, mixtures of complex natural hydrocarbons, and oxidized products that have been used as adhesives [36], embalming materials [37], and as black pigments [38]. However, the presence of these compounds in both samples could be either because of their use as a black pigment in combination with iron and manganese oxides, or as components of biogeological organic matter. A similar steroid hydrocarbon composition was found in a reddish pigment (not treated here) also obtained from this archaeological site. Therefore, instead of bitumen, one possible origin of these components could be the organic matter mixed during the formation of evaporitic deposits (salt-lakes) which could be the sources of gypsum detected in both samples [39].

Conclusions

This paper has demonstrated that the combination of these three analytical techniques (TXRF, FT-IR, GC–MS) allowed complete characterization of the inorganic and organic components of both black rock paintings. In nature, the geochemical affinity relating iron and manganese elements enhances a variety of earthy pigments or rich clay materials, where the dark colour is due to manganese oxides. This combination of oxides was frequently used in rock art as black pigments. Their natural occurrence in mineral ores and different kinds of Earth's crust deposits is common in this region [26, 28]. The large gypsum content of the two painting samples is consistent with the ancient mode of making these wall representations. In the Susques area, there are vast evaporitic basins that could be the source of this gypsum material [26, 27]. However, one of the most significant results of this investigation is the fact that the inorganic phase of these paintings contains measurable amounts of organic components. The presence of lipids in the organic residues associated with the rock paintings and the fatty acids distribution suggest an animal source as a potential binder in the preparation of the paints. The presence of unsaturated fatty acids ($C_{16:1}$ and $C_{18:1}$) in the archaeological samples from Hornillos 2 indicates that the lipids were preserved under the favourable dry environmental conditions of the Puna region.

The results obtained in this investigation induce us to suggest that the early inhabitants of this region employed at least three principal components to prepare their black painting mixtures:

1. iron and manganese oxide (the pigment);
2. gypsum (the extender); and
3. an animal fat (the binder).

Apparently, the paint recipes of these cave-wall figures were the same for both black camelid types, suggesting that both types were painted in a short period of time. Identification of gypsum in both samples also allowed us to infer that the painting pigment preparation consisted in grinding and mixing the iron and manganese oxides and gypsum with a fluid animal fat as binder to perform the paintings shown in Figs. 2 and 3 on a rock wall not completely adequate as a painting support. This preparation could enhance the adhesive properties and texture of paints [1]. The use of gypsum as an extender in rock paintings of this region has been reported from another archaeological site of similar chronology. This site was also occupied by hunter-gatherers and the designs are very different, because

they are only geometric motifs [8, 9, 14]. This may indicate a common technique of pigment preparation in different localities, and represent distinct styles of paintings as far as 200 km from Hornillos 2, indicating some kind of information flow between different groups of hunter-gatherers population.

The results of this research are the first report on the inorganic and organic components of rock paintings in Northwestern Argentina and they contribute to enlarging the archaeological knowledge of this region.

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