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COMPOSITION OF PIGMENTS ON HUMAN BONES FOUND IN EXCAVATIONS IN ARGENTINA STUDIED WITH MICRO-RAMAN SPECTROMETRY AND SCANNING ELECTRON MICROSCOPY

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Results on analysis of prehistoric pigments from excavations and pigments on coloured child bones from North Patagonia, Argentina, are reported. To analyze their composition we used two micro-analytical techniques: micro-Raman spectrometry (MRS) and scanning electron microscopy coupled with X-ray micro-analysis (SEM/EDX). Most investigated excavated pigments show red or yellow ochres consistent with reddish or yellow minerals, such as α- and γ-goethite, haematite, erdite, haapalaite and jarosite. Raman spectra show also evidence of calcium oxalate monohydrate and calcite indicating lichen activity.

Pigments covering human bones were identified as hematite and magnetite. This study allows us to infer that pigments found in excavation were employed for burial ceremonies, even though distances between excavated pigment archaeological site and buried remains are quite far, more than 50 km in a straight line.

1 Introduction

Analyses of ancient paint pigments components could cast a light on ancient ritualistic ceremonies and pigment preparation technologies, applied by early social groups for their art.[1-4] The hypothesis of their peculiar life style demands evidence lines in order to draw out their variety and differences among them. One of the ways to reconstruct the life style of this ancient society is investigation of prehistoric pigments.

The objects of investigation presented here are excavated prehistoric pigments and coloured child bones found in North Patagonia, one of the six archaeological regions of Argentina. This region is located to the South of the Colorado river, including Río Negro and El Neuquén provinces (Figure 1). The North Patagonia archaeological region is traditionally considered as a transition or interchange zone for social groups coming there from north-west to south on the one hand and from east to west on the other hand crossing the Andes mountains.

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The pigment powders were collected in the Carriqueo rock shelter archaeological site and the colored bones of newborn come from Traful I cave. This cave (S 43º; W 71º 07) is placed on the south side of Traful river near the Cuyín Manzano river exit in the El Neuquén province.[5-8] The Carriqueo rock shelter (S 40º 37' 27"; W 70º 31' 42") is located on the west side of La Oficina canyon, a tributary of the Limay river, Pilcaniyeu area, in the Río Negro province.[9,10]

The buried remains (Figure 2) of a baby have been found in the archaeological layer corresponding to the period of about 8000 - 9000 years ago. The skeleton was laid on its back. All bones, including the ribs, were completely articulated[5]. Significantly, the head and the first cervical vertebra were missing. Additionally, on both scapulas, some vertebrae and ribs and one humerus (upper arm bone), reddish-brown spots, dark blue and black areas were observed. These facts can suggest a secondary funeral or some type of a ritual ceremony.

Any other similar findings in the region have not been registered, so no comparison could be made.

Double burial of two newborns (excavated in 2005) and a single one (excavated in 2006) were found in a camping at Krems-Wachtberg in Lower Austria.[11] Radiocarbon dated these findings at 27000 years before present. The bodies were covered with a thick layer of red ochre and decorated with ornaments and were probably ritually buried.

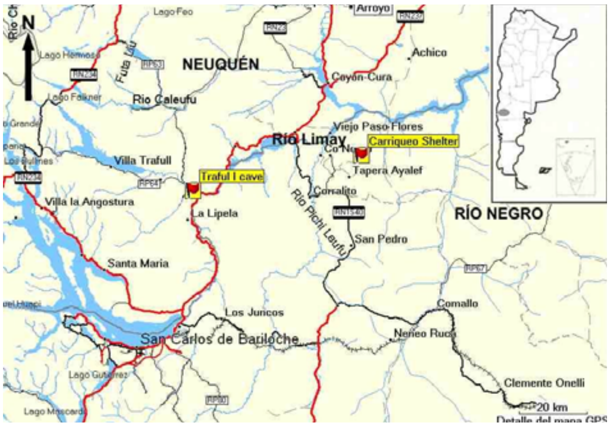


Fig. 1. Map of North Patagonia with the site locations.

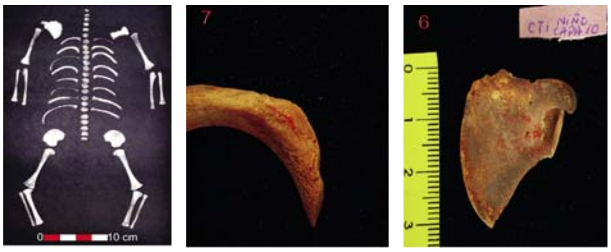


Fig. 2: Skeleton (black-white photo) and pictures of coloured child bones.

Several adult graves (covered by red ochre) from the Stone Age (Upper Palaeolithic period) have been found[12] but child burials seem to be rare. Maybe this fact demonstrates different hierarchy of infants and adults.

The task of our investigation was to determine and to compare the composition of prehistoric pigments from excavated layers and pigments covering child bones to assess origin and production techniques, as well as to investigate the recurrence of the pigments used in the region.

We used two micro-analytical techniques, micro-Raman spectrometry (MRS) to look for molecular composition and scanning electron microscopy coupled with energy-dispersive X-ray analysis (SEM/EDX) to detect the average elemental composition of the investigated samples. For the study of cultural heritage objects, MRS is one of the most informative methods.[13,14] Usually the laser beam does not cause any damage of the samples, so it is possible to continue the investigation of the same sample with another laser wavelength or with another technique. Also we can focus the excitation laser beam on a very small spot, which area depends on the laser wavelength and the objective aperture. Typically the laser beam diameter is about 1 μm.

SEM/EDX analysis is adequate for elemental identification of pigment and bone samples, providing quantitative information of relative elemental abundance.

2 Materials and Methods

Prehistoric pigment samples were collected from different layers of an excavation. First of all the specimen were divided into several colour groups according to different shades of yellow, orange, red and brown; one pigment was green. When looking at the red pigment samples, different shades could be distinguished, ranging from orange to dark red (Figure 3). Colour indices were assigned according to Munsell Soil Charts.[15]

MRS measurements were carried out by a Renishaw InVia unit with laser excitation at 785 nm, in the range between 100 and 3200 cm^{-1} with a spectral resolution of 2 cm^{-1}. Spectrum accumulation was used to improve the signal-to-noise ratio.

Elemental analysis of the prehistoric pigments was performed on a JEOL JSM 6300 SEM (JEOL, Tokyo, Japan) equipped with a backscattered electron detector (BSE), a secondary electron detector (SE) and an energy dispersive X-ray detection system. A Si (Li) X-ray detector PGT (Princeton Gamma Tech, Princeton, NJ, USA) was employed for acquiring the X-ray spectra. The analysis was carried out on several (5-7) single pigments grains. An accelerating voltage of 20 kV and current of 1 nA was applied during the measurements. Each spectrum was integrated and the relative intensities of each element presented were calculated using AXIL software.[16] Then the sum of relative intensities was standardised to 100% and the average relative abundance of each element (%) for certain type of pigment was obtained. It should be emphasised that only qualitative analysis was performed and the values can only be treated as an estimated and not as an absolute one.

3 Results and Discussion

The Raman spectra of the coloured child bones are presented in Figure 3. The spectra collected from reddish spots show a weak haematite (iron(III)oxide, α-Fe_2O_3) band at 296 cm^{-1} and a typical band of magnetite (Fe_3O_4) at 680 cm^{-1}. Usually red ochre has been found in adult burials as a sign of special funeral ceremony. This natural mineral consists of hematite (Fe_2O_3) as a red pigment.

Strong sharp bands in the spectral region appear at 500-600 cm^{-1} and 1300-1600 cm^{-1}; bands at 520 cm^{-1} and 550 cm^{-1} correspond to calcium oxalate (whewellite $CaC_2O_4{\cdot}H_2O$ and weddellite $CaC_2O_4{\cdot}2H_2O$). The intense band at 1460-1490 cm^{-1} is the result of overlapping of three bands: 1464, 1477 and 1490 cm^{-1} and can be assigned to the C=O symmetric stretching mode of whewellite and weddellite. These detected calcium oxalates could be explained by the reaction of calcium carbonate with oxalic acid produced by lichens present in this site with a humid atmosphere on the surface of the child bones. The appearance of calcium oxalates in prehistoric pigments as a result of metabolic activity of lichen invasion and colonisation is well documented[17]. Calcium oxalates were often identified in rock paintings on calcareous and sandstone surfaces in Argentina, California, Utah and Australia.[18-22]

The Raman shift at 964 cm^{-1} is ascribed to the phosphate stretching mode of hydroxyapatite. Bone tissue is represented by apatite material that contains also carbonate components - carbonate hydroxyapatite, with an approximate formula $Ca_{10}(PO_4)_6(OH)(CO_3)$. The strong shift at 1590 cm^{-1} belongs to graphite. Some of the shifts present in the spectral region 1300 - 1600 cm^{-1} were not recognized. This region is typical for organic compounds but it would be doubtful to expect the presence of organic substances because of their relatively fast decay.

The spectra of dark-blue and black bone areas contain only two broad bands typical for amorphous carbon (Figure 3). These colours are not attributed to pigments but some bacterial activities on bones surfaces.[23,24]

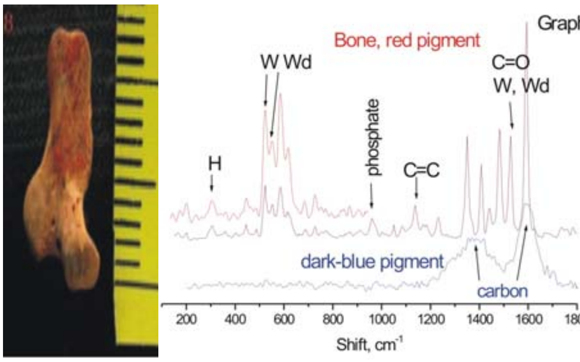


Figure 3: Picture of piece of child bone and Raman spectra of bone pigments, Wd – weddelite, W – whewellite, and H – haematite.

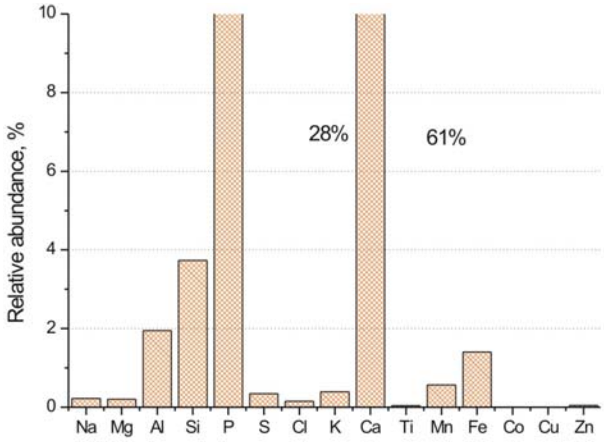


Figure 4: Diagram of reddish bone pigment elementary composition (relative abundance of elements).

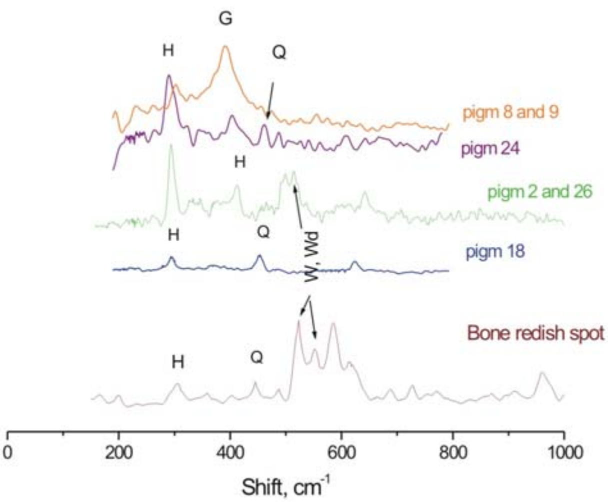


Figure 5: Raman spectra of prehistoric pigments, Wd – weddelite, W – whewellite, H – haematite, G- goethite, Q - Quartz.

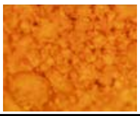
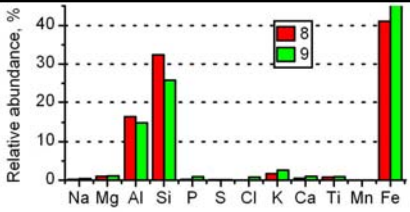
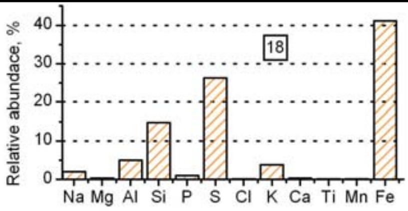
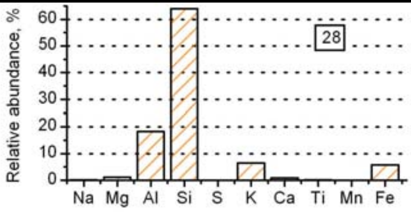
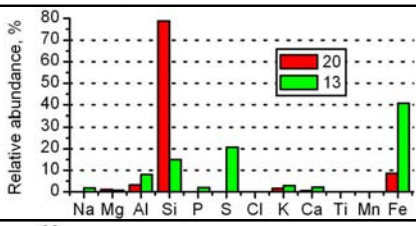
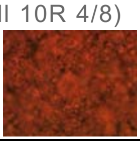
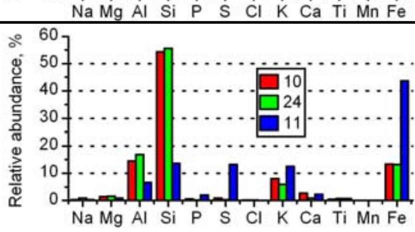
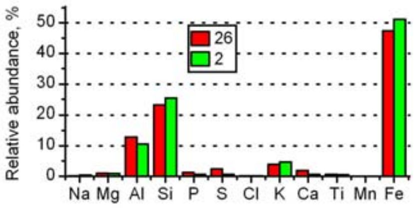
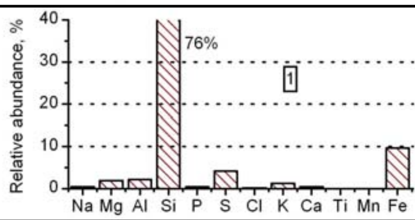
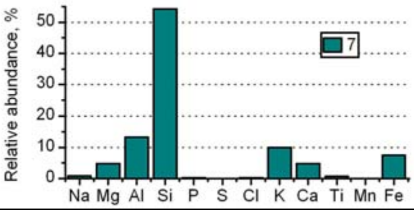
Samples, Munsell colour index	SEM/EDX results	M-Raman results
8 (Munsell 10YR 7/8), 9 (Munsell 10YR 6/8) 		Goethite
18 (Munsell 5YR 6/6) 		Gypsum
28 (Munsell 2.5YR 5/8) 		Haematite, Quartz
13 (Munsell 5YR 5/6), 20 (Munsell 2.5Y 7 5/8) 		Intensive fluorescence
10 (Munsell 10R 4/8), 24 (Munsell 2.5YR 4/8), 11 (Munsell 10R 4/8) 		10 – Haematite, quartz 11 – intensive fluores- cence 24 – Haematite, quartz
2 (Munsell 2.5 R 3/6), 26 (Munsell 2.5 YR 3/6) 		Haematite
1 (Munsell 54R 4/6) 		Quartz
7 (Munsell Gley 1 6/5G) 		Intensive fluorescence

Figure 6: Colour shade and elemental composition (relative abundance) of pre-historic pigments by SEM/EDX analysis.

The elementary composition of the coloured child bone surface (Figure 4) revealed by SEM/EDX shows a high content of Ca and P corresponding to bone hydroxyapatite, whewellite and weddellite. SEM analysis also demonstrates the presence of elements such as Fe, Al, Si, K, Na, Mg and Mn, which are the main components of the visible reddish spots on the bone.

As a rule, the natural yellow, orange or red natural pigments are represented by yellow and red ochre. It is a mixture of iron oxide + clay + silica. These ochres are detected frequently in prehistoric pigments, probably because they are very resistant to light (they do not get bleached) and were easily accessible, even in the prehistoric times.

Raman spectra of the most investigated pigments are shown in Figure 5. The reddish ones (2 (Munsell 2,5 YR 3/6), 28 (Munsell 2,5 YR 5/8), 24 (Munsell 2,5 YR 4/8) and 26 (Munsell 2,5 YR 3/6)) show Raman shifts corresponding to haematite α - Fe_2O_3 at 230, 295, 410, 611 and 658 cm^{-1}.

Raman spectra of the yellowish pigments (8 (Munsell 10 YR 7/8) and 9 (Munsell 10 YR 6/8)) demonstrate the presence of bands at 299 cm^{-1}, ascribed to α-FeO(OH) (α-goethite) and two others at 250 and 376 cm^{-1} ascribed to γ-FeO(OH) (γ-goethite).

Samples 18 (Munsell 5 YR 6/6), 24 (Munsell 2,5 YR 4/8) and 28 (Munsell 2,5 YR 5/8) contain also the band at 465 cm^{-1} that belongs to quartz (α-SiO_2) and the band at 1010 cm^{-1} which is typical for gypsum ($CaSO_4$•$2H_2O$).

For the green-grey sample 7 (Munsell Gley 1 6/5G) and for part of reddish and yellowish samples (11 (Munsell 10 R 4/8), 13 (Munsell 5YR 5/6) and 20 (Munsell 2.5 Y7 5/8)) we did not obtain informative spectra because of the huge fluorescence caused by the presence of clay in the prehistoric pigments.

Elemental analysis of the prehistoric pigments was fulfilled by SEM/EDX. For yellowish, reddish, brown, beige pigments we detected Ca, C, O, Mg, Fe, Si, K and Na (Figure 3). Several pigments contain S and Mg. This set of elements can form the following minerals: haematite, jarosite, magnetite and, additionally, phosphate compounds.

Elementary composition analysed by SEM/EDX demonstrated strong similarity among pigments with the same colour shade, e.g. vinous – brown 2 and 26 or yellow – gold 8 and 9 (see Figure 6). For two groups of pigments (pigments 13 and 20 and pigments 10, 11 and 24) the different elemental composition was detected, although these pigments have the same colour shade. They were probably prepared and used by different ancient social groups because North Pathagonia region was a transition zone of ancient tribes.

Mineral	Colour	Hardness
Red ochre Fe_2O_3	red	1,5-2 as talc-gypsum
Yellow ochre FeO(OH)	yellow	1,5-2 as talc-gypsum
Erdite $NaFe^{2+}S_2$•$2H_2O$	copper-red, red, black	2 as gypsum
Haapalaite 2(Fe, Ni)S•1,6(Mg, Fe^{2+}) $(OH)_2$	bronze red	1 as talk
Sideronatrite $Na_2Fe^{3+}(SO_4)_2$ (OH) •$3H_2O$	yellow, yellow-brown, paleorange	1,5-2 as talc-gypsum
Metahohmannite $Fe^{3+}_2[O(SO_4)_2]$•$4H_2O$	orange-yellow	1,5-2 as talc-gypsum
Palygorskite (Mg, $Al)_2Si_4O_{10}(OH)$•$4H_2O$	red-yellow	2-3 as gypsum -calcite
Vashegyite $Al_{11}(PO_4)_9(OH)_6$•$38H_2O$	red-brown	2-3 as gypsum -calcite
Jarosite $KFe_3(SO_4)_2(OH)_6$	amber yellow or brown	2,5-3,5 as calcite
Whewellite CaC_2O_4•H_2O	white	3 as calcite
Weddellite CaC_2O_4•$2H_2O$	white	3 as calcite

Table 1: Minerals with the suitable composition and hardness for prehistoric pigments consistency.

The results of elementary investigation allow us to suppose that green-grey pigment may be formed by glauconite (terre-verte) (K, Na)(Fe, Al, Mg)(Al, $Si)Si_3O_{10}$•$(OH)_2$ - (coloured components – iron hydrates, magnesium oxide hydrate) and aluminosilicates.

The chemical composition of the pigment 24 was compared to the element content of the pigment visible on the child bone as reddish spots. It revealed a similar Al/Fe/Mg ratio: 17/13/2 for pigment 24 and 19/14/2 for the reddish bone spots. It is very likely that the same pigment was used for funeral ceremony of the child. In case of the other investigated pigments, the concentration of iron is higher than that of aluminium.

As a result of SEM/EDX analysis we can conclude that their basic component is yellow (colouring mineral is goethite) or red ochre (colouring mineral is haematite). They also contain inclusions of some minerals, such as jarosite, magnetite and oxalates (see Table 1). These minerals have suitable hardness to be powdered and used for paint pigments.

4 Conclusions

The basic component of the investigated prehistoric pigments is yellow or red ochre containing iron oxides, which can give yellow, red or brown colours. The elements determined as major components (Fe, Al, Si, K, Na, Mg, P) can form hematite, goethite, jarosite, magnetite, and phosphates compounds.

Several groups of prehistoric pigments have the same colour shade but different elemental and molecular compositions, which suggests that they were prepared and used by different ancient groups.

Based on the chemical composition of the investigated pigments we selected one red-brown pigment which was characterised by a similar elemental content ratio obtained for the pigment covering the prehistoric child bones. This information suggests us to conclude that this pigment was employed for some ritual burial ceremony by ancient social groups living in this region. In addition, considering that the Carriqueo rock shelter and Traful 1 cave are more than 50 km away and separated by the Limay river, these results demonstrate that this geographical situation was not a barrier for inhabitants of the North Patagonian region. On the other hand, evidences of the use of similar pigments for rock paintings and drawings in this area have been mentioned by several authors.[18,25,26]

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