Compositional study of prehistoric pigments (Carriqueo rock shelter, Argentina) by synchrotron radiation X-ray diffraction

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In this work synchrotron radiation X-ray diffraction technique was successfully applied for the analysis of pigments found in excavation at Carriqueo rock shelter, Neuquén, Argentina. The pigment samples of orange, red, and brown shades were collected from different levels of this archaeological site and compared with a suspected source of provenance (La Oficina creek). X-ray diffraction patterns of several yellowish, reddish, and red pigments showed the presence of haematite, goethite, kaolinite, and quartz. The majority of Carriqueo collected samples belonged to the same group of the suspected source, having haematite and quartz as main crystalline phases. The results indicate that the raw material from La Oficina is the source of most of the pigments found at Carriqueo. The present work helps us to understand the strategy of supplying raw materials by human groups in the North Patagonia region. © *2010 International Centre for Diffraction Data.* [DOI: 10.1154/1.3478884]

Key words: prehistoric pigments, synchrotron radiation X-ray diffraction, minerals

I. INTRODUCTION

Natural earths have been used as colour pigments since prehistoric times. They have been detected in works of art everywhere and in any historical period probably due to their availability, high colouring capacities, and stabilities to light and a variety of weather conditions. Ochres are natural earth pigments varying from yellow to red and brown shades. The colour shade of ochre depends on the type of the iron oxide chromophore. The red ochres contain mainly haematite (Fe_2O_3), while the yellowish ochres are rich in hydrated iron oxide (goethite, $FeO \cdot OH$) (Cornell and Schwertmann, 1996; Helwig, 1997, 2007; Fiore *et al.*, 2008).

Most often the red ochre was detected as a main component of rock paintings and human funerals (Mortimore *et al.*, 2004; Bikiaris *et al.*, 2000). Red colour plays an important role in human behavior. Studies and opinions on the mechanisms of colour preference can be found in such fields as anthropology, psychology, and linguistics (Leach, 1976). The presence of other minerals, such as clay minerals or metal oxides, can also influence the colour of the ochres. It is well known that clay materials and iron oxides were adopted as mineral pigments along the history (Hradil *et al.*, 2003). They were used for ethnic or social marks expressed as rock art, burial ceremonies, paintings or engravings, and also body paintings or exhibition of adornments or sumptuary objects such as engraved plates. The marks with colour, generally red, were not hidden but, on the contrary, there are evidences they were intentionally shown (Gradín *et al.*, 2003; Albornoz, 1996). To a large extent, red pigments were selected for rock paintings (Hajduk *et al.*, 2004; Podestá, 2003; Wainwright *et al.*, 2000). Red pigments were also found colouring valves of molluscs (British) or mollusks (American) (*Diplodon patagonicus*) intentionally or unintentionally (Parada and Peredo, 2008; Trubitt, 2003; Bar-Yosef Mayer, 1997).

Mineral pigment colours varying from yellow to red are given by the presence of different iron oxyhydroxides and oxides, mainly goethite and haematite. Their structural and

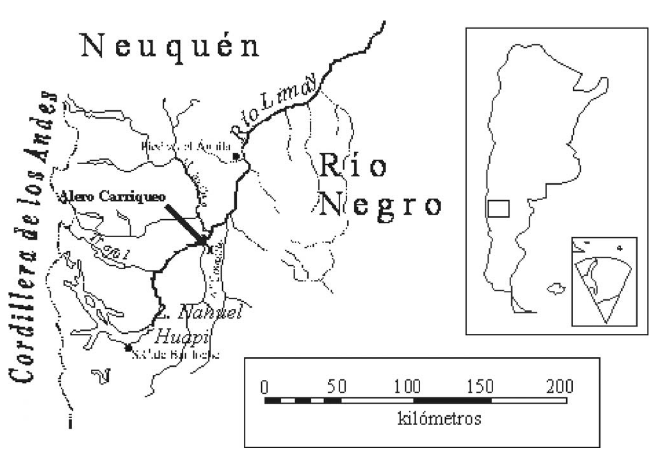

Figure 1. Map of the site location (by Mabel Fernández).

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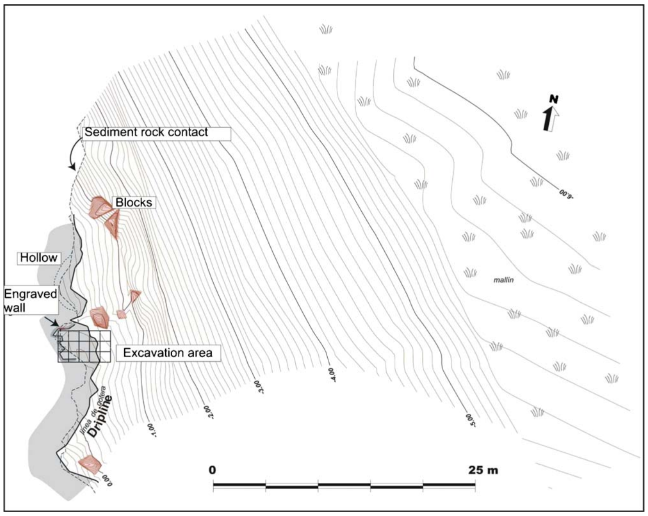

Figure 2. (Color online) Flat view of Carriqueo shelter (by Luis Teira).

mineralogical compositions are related with their natural genesis and provenance. Compositional characterization helps archaeologists and anthropologists to reconstruct ancient society life style as well as to hypothesize the group's peculiar mobility and to infer different uses.

The purposes of this research were to determine the mineralogical compositions of prehistoric pigments from excavated layers collected at the Carriqueo rock shelter archaeological site and to compare them with a suspected provenance source, La Oficina. Carriqueo shelter (S 40°37′27″; W 70°31′42″) is located on the west side of La Oficina creek, a tributary of the Limay river, Pilcaniyeu area, in the Río Negro province (Figure 1) (Palacios and Ramos, 2009; Crivelli Montero *et al.*, 2007).

From an archaeological point of view, Carriqueo is a small specialized site with a doubtless hunting activity and, to a less extent, a sedentary living site (Crivelli Montero *et al.*, 2007). This area is also archaeologically related with other sites such as La Divisoria, a chert lithic manufacturing area located 350 m away on the other side of the creek. Several surface sites that seem to have been active at the same time in the neighborhoods had been detected. Radiocarbons analysis $[^{14}C]$ reveals two dates: 2620 ± 110 BP and 610 ± 50 BP. From November to December 2006, the archaeological Carriqueo shelter site was investigated (Crivelli Montero *et al.*, 2007). A flat view of this site is shown in Figure 2. During the excavations, several pigment samples,

Figure 3. (Color online) La Oficina site, suspected source of red pigments.

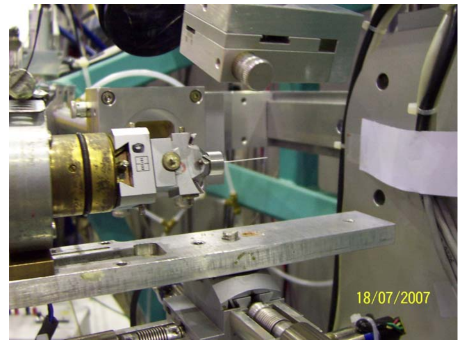

Figure 4. (Color online) Pigment sample sizes.

deposited in layers in the sedimentary pile, were collected. The environs of the Carriqueo shelter were also prospected discovering, 200 m away, a probable source of pigments: two blocks of raw material for red pigment production. The site was denominated La Oficina. Figure 3 shows a partial view of 0.80 m^3 of the La Oficina rock, the suspected main pigment source.

With the aim to look for chemical compositional analogies between Carriqueo and La Oficina sites, a set of 34 specimens was analyzed. Synchrotron radiation X-ray diffraction (SR-XRD) was selected as the instrumental technique used in this study (Bugoi *et al.*, 2008; Welcomme *et al.*, 2007; Calza *et al.* 2008; Sánchez del Río *et al.*, 2008). Remarkable reasons are the higher flux which improves the signal to noise ratio and the polarization of the incident beam in relation to the sample, increasing in this way the sensitivity. The detection limit by conventional laboratory X-ray diffraction is in the range of a few weight percent, limiting the required amount of sample. SR-XRD improved the detection limit allowing the analyses of minute samples. Elemental analysis is widely applied for this kind of study. However, an appreciable amount of sample is required for most of the analytical techniques. In addition, phase identification is mandatory since the colour could depend not only on the element amount but also on the crystalline composition of the pigment (Dillmann *et al.*, 2002; Artioli, 2008; Simova *et al.*, 2005). Then, the use of X-ray fluorescence, inductively coupled plasma, atomic emission spectrometry, and neutron activation analysis is limited. It is expected that SR-XRD would provide valuable information about the phase composition without compromising the integrity of the archaeological information.

II. EXPERIMENTAL

A. Sampling and sample preparation

Carriqueo samples were obtained during excavation at different levels. Figure 4 shows three examples of the ana-

Figure 5. (Color online) Rotating capillary containing the pigment sample in the X-ray path.

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TABLE I. SRDRX results, site, stratigraphic level, stratum, and identified colour according to Munsell chart for the 34 analyzed samples.

#	Identified phase	Site	Grid	Level (cm)	Stratum	Munsell index	Colour
1	Q	Carriqueo	F13	70-75		5YR 4/6	
2	Q, Htt, Zeo	Carriqueo	G13	90-95	8	2,5YR 3/6	
3	Q, Mi, Htt	Carriqueo	G13	90-95	8	2,5YR 3/6	
4	Q, Mi, Htt	Carriqueo	G13	90-95	8	10R 5/6	
5	Q, Mi, Htt	Carriqueo	ED 12-13-14-15	Looting cleaning		10R 3/6	
6	Q, Htt	Carriqueo	F13	105-110	7	10R 3/3	
7	Q, Mi	Carriqueo	F13	105-110	5	GLEY 1 6/5G	
8	Q, K, Ght	Carriqueo	H12	0- 50		10YR 7/8	
9	Q,Ght	Carriqueo	F14	60-65		10YR 6/8	
10	Q, Htt	Carriqueo	G13	90-95		10R 4/8	
11	Q, Htt	Carriqueo	G13	90-95		10R 4/8	
12	Q, Mi, Htt	Carriqueo	G13	90-95		10R 5/8	
13	Q, Mi , Htt	Carriqueo	G13	85-90		5YR 5/6	
14	Q, Htt	Carriqueo	G13	85-90		2,5 YR 4/8	
15	Q, Htt	Carriqueo	F13	100-105	13	2,5 YR 5/8	
16	Q, Mi, Htt	Carriqueo	G12	85-90		10R 4/6	
17	Q, Mi, Htt	Carriqueo	F13	0- 70		10R 4/6	
18	Q, Ght	Carriqueo	F12 - G12	Sheep feces		5YR 6/6	
19	Q, Mi , Ght,	Carriqueo	H12	0- 50		5YR 7/3	
20	Q, Htt	Carriqueo	H12	105-110		2,5 Y R 5/8	
21	Q, Mica, Htt	Carriqueo	G12	90-95		5YR 5/6	
22	Q, Mi	Carriqueo	F13	95-100		5YR 7/4	
23	Q, Mi	Carriqueo	F12 G12	Sheep feces		GLEY 1 /5G	
24	Q, Mi, Htt	Carriqueo	G12	110-115		2,5 YR 4/8	
25	Q, Mi, Htt	Carriqueo	G13	105-110		10R4/6	
26	Q,Htt, Zeo	Carriqueo	G13	105-110		2,5 YR 3/6	
27	Q, Mi, Htt	Carriqueo	G13	105-110		2,5 YR 4/6	
28	Q, Mi, Htt	Carriqueo	G13	105-110		2,5 YR 5/8	
29	Q, Mi, Htt	Carriqueo	G13	115-120		2,5 YR 5/6	
30	Q, Mi, Htt	Carriqueo	F13	100-105	5	2,5 YR 4/6	
31	Q, Mi, Htt	Carriqueo	F13	100-105	5	2,5 YR 4/6	
32	Q, Mi, Htt	Carriqueo	F13	100-105	5	2,5 YR 4/6	
33	Q, K, Htt	La Oficina Canyon 1/06	Red block			2,5 YR 6/6	
34	Q, K, Htt	La Oficina canyon 1/07	Red block			2,5 YR 6/6	

lyzed samples. As shown in this figure, the amount of samples is extremely small, less than 100 mg in all the cases. Two representative samples from La Oficina were taken for the comparison. An agate mortar and pestle were used to crush and grind each specimen into powders to ensure better homogeneity. The powders were passed through a plastic sieve with mesh of 0.074 mm and carefully introduced in a 0.3 mm diameter Mark-Rohrchen boron capillary sample holder; this procedure minimises preferential orientation (Piszora *et al.*, 2008). The use of the capillary method allows the use of small amounts of sample material and preserves the sample for further microanalysis. Finally, a set of 34 samples was measured.

B. XRD Instrument

The obtained samples were characterized in the D12A-XRD1 beamline at the Brazilian Synchrotron Light Laboratory (LNLS). The beamline is equipped with a three-circle Huber diffractometer $(\theta, 2\theta, \varphi)$, which permits the rotation

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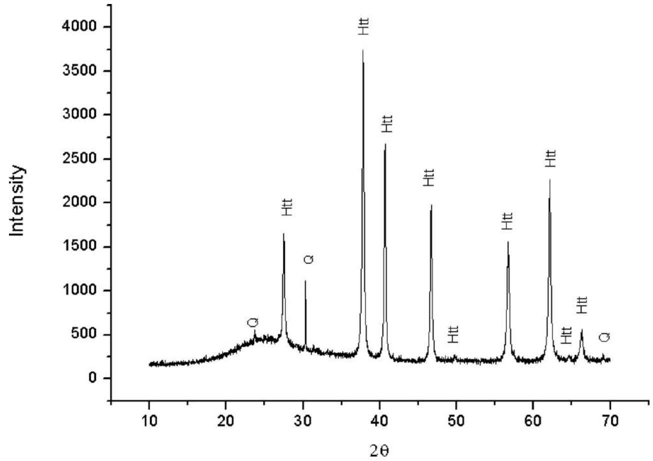

Figure 6. Synchrotron powder diffraction pattern of sample 6 corresponding to group I showing the presence of haematite.

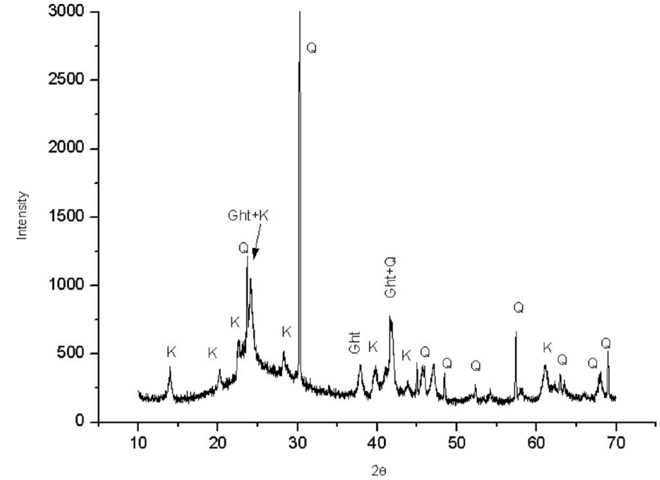

Figure 8. Synchrotron powder diffraction pattern of sample 8 corresponding to group II showing the presence of goethite.

of a sample in three axes (Figure 5) (Lima *et al.*, 2007). The energy of the beam was 7.100 keV and the intensities were monitored with a detector perpendicularly located. The scan speed was 0.02° min^{-1} for the 2θ range of 10 to 70°.

C. Analysis

After the beamline was adjusted, the capillary containing the sample was mounted and located in the X-ray path. This operation was controlled using an external screen. Once the samples were measured, the collected data were analyzed using the CRYSTALLOGRAPHICA free software package (Oxford Cryosystems, Inc., 2007).

III. RESULTS AND DISCUSSION

Table I shows the SR-XRD results as well as the site, stratigraphic level, stratum, and identified colour according to the Munsell chart (*Munsell Soil Colour Charts*, 1994) for the 34 analyzed samples. In order to group the samples, the presence of haematite (Htt, α-Fe_2O_3) was used as one of the references. Following this criterion, four groups were formed:

I. Presence of Htt corresponding to samples 2 to 6, 10 to 17, 20 to 21, and 24 to 34;
II. Presence of goethite (Gtt, FeOOH) and no Htt corresponding to samples 8, 9, 18, and 19;
III. Nonreddish samples corresponding to samples 7 and 23; and
IV. Reddish samples but no chromophores detected corresponding to samples 1 and 22 (Q, quartz).

In order to assess the validity of the classification based on the presence or absence of haematite, the following remarks based on the SR-XRD results can be made.

Group I shows similar diffraction patterns: the peaks of quartz (JPCDS, ICDD, Card No. 46-1045) and haematite (JPCDS, ICDD, Card No. 33-0664) are intense and well defined indicating good crystallinity. The presence of haematite is associated in some samples also with a zeolite. Natural zeolites could come from volcanic ashes and crystallize in postdepositional environments over large periods of time in marine basins, which are the case of Los Andes mountains

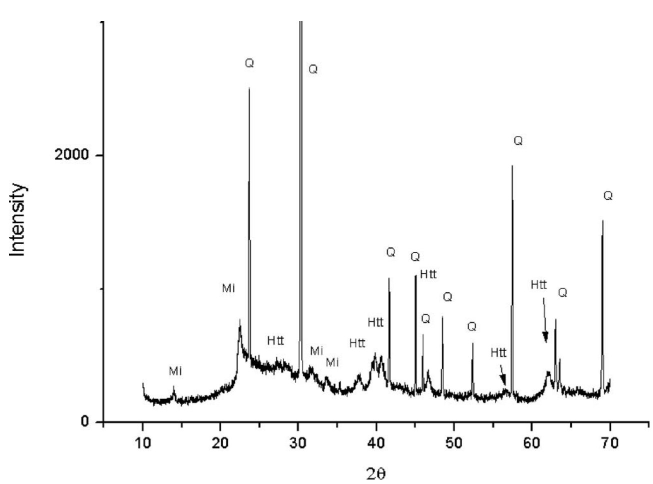

Figure 7. Synchrotron powder diffraction pattern of La Oficina creek sample corresponding to group I showing the presence of haematite.

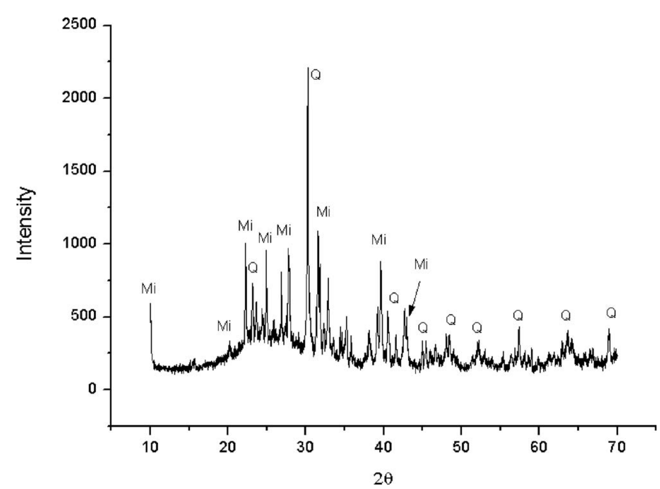

Figure 9. Synchrotron powder diffraction pattern of sample 23 corresponding to group III with nonreddish evidences.

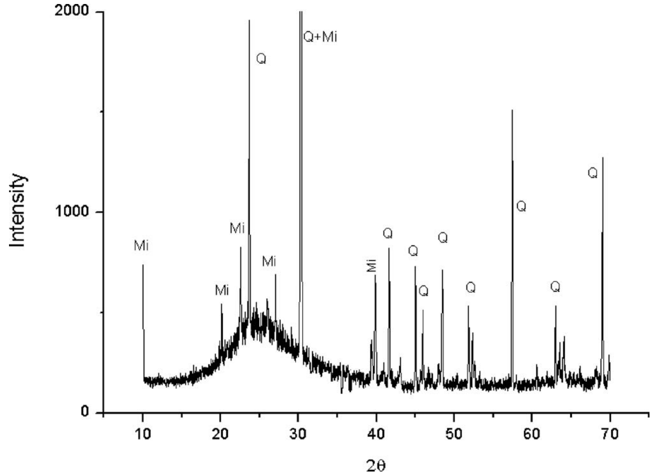

Figure 10. Synchrotron powder diffraction pattern of sample 22 corresponding to group IV with no evidences of chromophore substances.

(Bouza *et al.* 2007) (Figure 6). It must be noted that La Oficina samples belong to group I, as the majority of the red coloured samples, and have similar diffraction patterns regarding the phases and crystallinity (see Figures 6 and 7).

Group II shows the presence of goethite (JPCDS, ICDD, No. 29-0713) associated with kaolinite (K) and quartz. The samples exhibit high crystallinity, similar to those of group I (Figure 8).

Only two green samples correspond to group III. The phase found in both samples was mica (Mi). The green-grey colour leads to associate samples 7 and 23 with green earths. There are several green earth mica minerals such as celadonite, glauconite, etc., which have been used as green pigments since ancient periods (Murray, 2000). Identification of green earth mica minerals is complicated because of the similarities in their powder patterns (Tamburini *et al.*, 2003). In this case the results show the presence of mica but they are inconclusive about the nature of the source of the green colour (Figure 9). Finally, group IV corresponding to reddish samples presents the sharp peaks of quartz but no evidence of red pigments. This could be the result of the presence of a noncrystalline pigment or of its low concentration (Figure 10).

IV. CONCLUSIONS

It has been demonstrated the potential of SR-XRD in the archaeometry field and its suitability as an analytical technique for provenance studies. In this work, it was successfully employed for explaining chemical compositional analogies between samples coming from Carriqueo and La Oficina sites . In this way, it could be concluded that La Oficina site seems to be the provenance source for red pigment samples found at Carriqueo archaeological site. Although four different groups have been identified, the provenance of them would still need to be investigated using complementary techniques such as microanalysis by total-reflection X-ray fluorescence spectrometry. In terms of archaeology, the importance of this work is to confirm that the human groups in the surroundings of Limay river had a strategy of supplying of raw material based on the use of the closest resource. This research helps us to increase the understanding of the human group mobility in the North Patagonia area of Argentina using pigment information as an archaeological evidence. Data published in this research contribute to interested archaeologists and archaeometrists as a reference for further studies.

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