Journal of Archaeological Science: Reports 12 (2017) 553–560

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

Compositional variability of pigments of Belén-style prehispanic ceramics from El Bolsón Valley, Catamarca Province, Argentina

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ARTICLE INFO

Article history:
Received 3 November 2016
Received in revised form 24 February 2017
Accepted 3 March 2017
Available online xxxx

Keywords:
Pigments
Belén pottery
XRD
Raman spectroscopy
Compositional variability
Argentine Northwestern region

ABSTRACT

This paper presents the first studies on the compositional characterization of the pigments used on Belén-style prehispanic pottery from El Bolsón valley (Catamarca, northwestern Argentina). The integrated analyses using micro-Raman spectroscopy and XRD revealed variability in the precursors used to generate the black paints: manganese oxides, magnetite, titanomagnetite, carbon and calcined bone. This variability of compounds, and their use in various combinations, had not been previously documented for a particular ceramic style, and provides evidence of the coexistence of different recipes for the elaboration of paints. It is also noted that this is the first case in which the use of calcined bone as a component in black paint is registered. From these results, and those previously obtained from ceramic pastes, it is proposed that the Belén-style pottery manufacture from El Bolsón valley was not standardized, but developed with low intensity in small-scale workshops.

1. Introduction

Ceramics are among the principal material items remaining as evidence of the societies living in the Argentine Northwestern region (NWA) during the pre-Hispanic period. Their study has generated valuable information regarding several social practices in which this kind of objects were involved. The compositional studies on the paintings of surfaces of ceramics covering different styles, regions and chronologies performed during the last decades, resulted in significant progress on the understanding of knowledges, resources and elaboration methodologies of ancient potters (Baldini et al., 2005; Cremonte et al., 2003; De la Fuente and Pérez Martínez, 2008; De la Fuente et al., 2010; Centeno et al., 2012; López et al., 2012; Freire et al., 2016). The combined application of analytical techniques such as x-ray diffraction (XRD) and Raman spectroscopy (RS), has been of great importance in this process. Also, scanning electron microscopy-microprobe analysis (SEM-EDS) has been recently used in order to confirm the presence of Mn in some of the samples. This paper discusses new results obtained on a ceramic set of Belén style samples from the El Bolsón valley, Belén Dept., Catamarca Province, Argentina.

The Belén pottery style has been found in the valleys area of NW Argentina, mainly at El Bolsón, Hualfín, Tafí and Abaucán valleys and Antofagasta de la Sierra in the Argentine southern Puna (Fig. 1). This style is entailed to human agricultural occupations established in groups of settlement of different hierarchies, dating approximately between XI and XVII centuries, (Olivera and Vigliani, 2000–2002; Quiroga, 2003; De la Fuente, 2007; Quiroga and Puente, 2007; Basile, 2009; Wynveldt and Iucci, 2009; Páez, 2010). The people who developed this style were both previous and contemporary to the Inka presence in the region. Traditionally it was considered that this ceramic style was developed under directions prescribed by ruling elites, in a chiefdom-type sociopolitical organization. On this basis, it was proposed that the pottery production was done by specialists, controlled and sponsored by these rulers (Núñez Regueiro, 1974; Tarragó, 2000). This form of socio-political organization has been largely assumed for most of NWA during the period known as "Regional Developments"(AD 1000 - 1480), as originated by transformations from previous periods, such as higher population densities, the apparition of fortified communities (pukaras), and regional ceramic styles. However, recent investigations question the traditional model, suggesting that communal or corporative organizations could be responsible of the observed changes (Nielsen, 2006; Acuto, 2007).

The Belén pottery shows limited morphological variability, and is characterized by urns, bowls and pitchers, the surfaces of which were decorated with figurative and geometric designs, painted in black color over a red base (Quiroga and Puente, 2007; Puente and Quiroga, 2007). They were used as containers of liquids and solids and food service in domestic contexts and as grave goods in burial contexts. In recent times, technological and compositional studies on ceramic pastes

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http://dx.doi.org/10.1016/j.jasrep.2017.03.007
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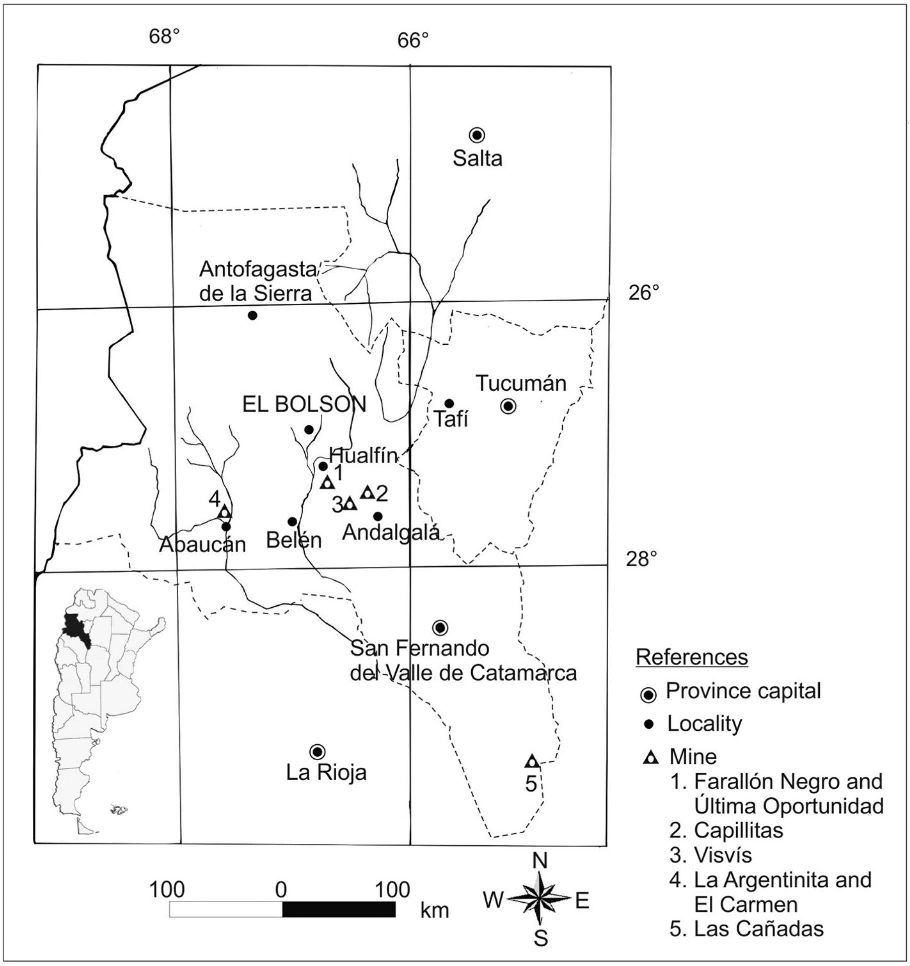

Fig. 1. Regional map: locations of the valleys and mineral deposits mentioned in the text.

have considerably increased, revealing different areas and elaboration methodologies (De la Fuente, 2007; Páez, 2010; Zagorodny et al., 2010; Puente, 2012; Puente et al., 2014). However, the chemical and mineralogical composition of the pigments used to develop color have not been previously studied.

The aim of this work is to present the results of compositional analysis of the colors that define the style obtained through the joint application of RS and with XRD. The final goal is to determine whether the potters who painted the ceramics used the same precursors to produce the paints, and in this way to advance our understanding of the manufacture technology of this widespread pottery style.

2. ARCHAEOLOGICAL BACKGROUND: Pottery production at the El Bolsón valley

The El Bolsón valley lies between 2500 and 2900 m asl in Belén Department, Catamarca Province, Argentina. Due to its transitional location between Puna (3400 m asl) and valleys (1800 m asl), it provided a transit zone between well-differentiated productive regions, while also being occupied on a permanent basis for the exploitation of varied resources (Aschero and Korstanje, 1993). In our period of study (*ca.* AD 1000 - 1600) this is shown by the coexistence of archaeological sites related to farming and housing practices, and also by the existence of temporary residential places associated to interregional mobility activities (Quiroga, 2002; Korstanje, 2007).

The pottery studied in this work was recovered in the two main permanent settlements of the region, named La Angostura and El Duraznito. While these sites were contemporarily occupied, they played different roles in the dynamics of the valley, as shown by their architectural and placement characteristics. La Angostura is located at the lower edges of an alluvial fan with fertile lands suitable for farming and near water sources. This site includes residential and agricultural architectures, and its planned layout indicates that it aimed at securing access to resources critical for an agricultural society in a semi-arid environment (Quiroga, 2002). About 9 km to the north is El Duraznito, a settlement located over the top of a hill without vegetation, surrounded by cliffs that make its access difficult. This setting has been interpreted as part of defensive strategies related to regional or interregional conflicts that characterized the period (Quiroga and Korstanje, 2013).

As a result of the localization of the sites, and the erosion processes having place after their abandonment, most of the archaeological evidence remains on surface, which makes the preservation of organic material suitable for absolute dating difficult. Until the time of this publication only two radiocarbon dates, from La Angostura site are available dating the occupations between AD 1460 - 1600 (Quiroga, 2011). However, the architectural features and recovered material remains allow, from comparisons at a macro-regional scale, to associate both settlements within the *ca.* AD 1000 - 1600. This limitation for the identification of more precise occupations has also been observed in nearby valleys (Tarragó and Nastri, 1999). For this reason, and until more dates become available, we consider the analyzed pottery within this broad temporal block.

Previous studies of the production practices of this style of pottery have taken into account aesthetic, technological and archaeometric analyses, and also compositional analyses of the raw materials available in the region, which were adequate for pottery fabrication. With this purpose, the chemical correspondence (elemental and mineralogical) of ceramic samples with clays and sands from the valley was determined through neutron activation analysis (NAA) and petrography. These analyses allowed to conclude that the Belén ceramics found in these sites were locally manufactured (Puente, 2012; Puente et al., 2014).

Regarding manufacture techniques, the observed variability in paste preparation methods, and in the forming of objects of similar objects of similar geometry and size, indicated that pottery manufacture in this valley was not standardized, and was probably carried out by different small-scale production units (Puente, 2012). It is likely that pottery manufacture was embedded within a broader set of daily tasks, as it has been documented in some Andean societies (Druc, 2005; Sillar, 2000). In this way, it is proposed that the production in each unit was of low intensity: each individual artisan made few pieces, which could be intended for personal use or for exchange with other members of the community.

Earlier researchers (Núñez Regueiro, 1974) have proposed that Regional Developments decorated pottery (*e.g.* Belén, Abaucán and Sanagasta styles) were status goods elaborated by full-time artisans under the direction and sponsorship of a governing élite. More recently, studies at the Abaucán valley (Tinogasta Department, Catamarca province), have drawn upon this earlier hypothesis to propose that the archaeological site Batungasta operated during the Regional Developments and Inka periods as an intensive production center specialized in the manufacture of these decorated wares at supra-domestic scale (De la Fuente, 2007). However, the Bolsón Valley data contradict this interpretation, given the demonstrated coexistence of variability in organization forms and magnitude scales for the relevant temporal period (Puente, 2011).

On this basis, it is hoped that the compositional study of the paints used on the pieces will contribute to a better understanding of the technical choices behind the ceramic production of Regional Development period pottery in this study area.

3. Experimental

3.1. Samples

The ceramic sets found in both sites came from stratigraphic excavations and systematic superficial recollections, both inside and outside of rooms and yards. Belén pottery is found mainly as fragments but comparison with whole pieces of museum collections allowed us to reconstruct the morphological profile of the vessels. In order to perform the compositional study of red and black colors, 21 samples were selected; three of them from bowls and 18 from urns (Fig. 2).

3.2. Instrumentation

3.2.1. Raman spectroscopy (RS)

Raman spectra on red and black pigments were acquired on a Renishaw inVia Reflex microscope with two laser lines: 785 nm (300 mW) and 514 nm (50 mW). To avoid sample damage, filters were applied to reduce the laser power on the sample to values typically <10 mW. The spectrometer, equipped with a Peltier-cooled CCD detector, is coupled to a Leica DM2500M optical microscope. A 50× long working distance objective (NA = 0.5) was used to focus the laser beam on the sample and to pick up the backscattered Raman signal. Regular confocality (6 pixels of the CCD, 65 μm slit width) was used. In those conditions, the spot size has a diameter of about 15 μm (lateral). Gratings of 1200 lines/mm (785 nm laser) and 2400 lines/mm (514 nm laser) were used, which deliver a spectral resolution below 4 cm^{-1}. Acquisition time was set between 30 and 60 s per accumulation; the maximum number of accumulations was typically below 20. The pigments were identified through comparison with the reference spectra in the literature. The recorded spectra were baseline-corrected to eliminate the background signal.

3.2.2. X-ray diffraction (XRD)

The analyses were carried out with a PANalytical X-Pert Pro diffractometer at 40 kV–40 mA, using CuKα radiation (1.5418 Å) and a graphite monocromator, over a 570°2θ angular range, with 0.02° step size and 0.5 s reading time.

In order to respect their integrity, the samples were analyzed as macroscopic pieces without any treatment, except a gentle rubbing, which was performed in order to eliminate dust. The mounting of the specimens was done selecting planar zones of the decorated surfaces,

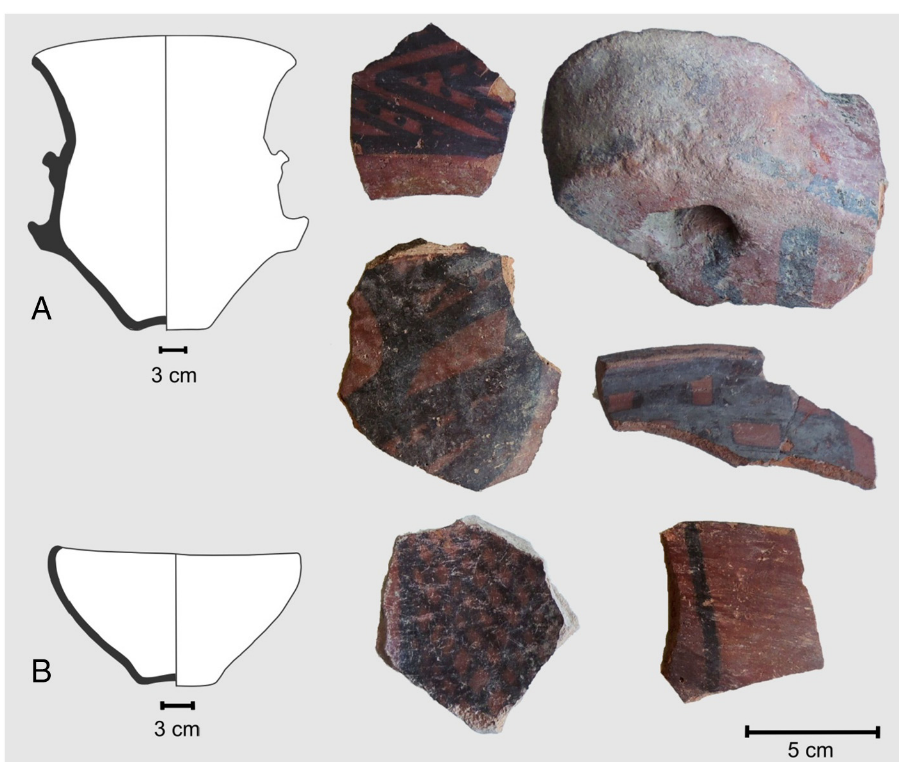

Fig. 2. A sample of the studied ceramic fragments and full morphological referent. A: urn; B:bowl.

to avoid angular errors brought about by superficial curvature. Even so, the alignment of the pieces on the sample holder was not always perfect, due to slight irregularities in the surface of the specimens. To correct for eventual resulting angular deviations, the angular position of the (101) peak of quartz (present in all the samples) was taken as a reference, which in all cases led to corrections smaller than 0.4°. In three of the samples the lack of planar surface regions of acceptable size made impossible their XRD analysis.

3.2.3. Energy dispersive electron spectroscopy (SEM-EDS)

The analyses were performed with a Jeol JSM-6460LV scanning electron microscope, equipped with a EDS EDAX Genesis XM4-Sys 60 probe, and software EDAX Genesis *v*.5.11.

4. Results

4.1. Red pigments

Raman spectra were collected in different points of the red pigment of all the samples, and Fig. 3 shows a typical spectrum. The analysis of this spectrum reveals a set of various peaks at *ca*. 226, 294, 411, 498, 612 and 1293 cm^{-1} which show that the pigment used to produce the red color was always hematite, α-Fe_2O_3. These wavenumbers are in good agreement with those reported in the literature (De Faria et al., 1997; Parras et al., 2010; De Benedetto et al., 2011).

The difractograms of all the samples showed that the red color of the superficial or underlying red paint is due to hematite (ICDD File 33-0664). When no other colored phase is present in the pigment, even low hematite concentrations (few percents by weight) may result in the red coloring of the paint.

4.2. Black pigments

The black chromophore components identified (Table 1) are: manganese oxides (MO), magnetite (Fe_3O_4) (M), titanomagnetite ($Fe_{3-x}Ti_xO_4$) (TM), and graphite (G) among the black pigments; also, the presence of hematite (H), phosphates, and sulphates was observed. The results from different experimental techniques show remarkable consistency, and the eventual differences registered derive from the different characteristics and capabilities of these techniques, mainly the size of the analyzed region (~20 mm^2 for XRD and ~800 μm^2 for RS) and the detected feature (crystal lattice periodicity for XRD, vibrations of chemical bonds for RS).

MO were detected by RS in 18/21 samples, by the bands at *ca*. 340, 455 and 630–640 cm^{-1}, corresponding to jacobsite ($MnFe_2O_4$) (J) (*e.g*. Fig. 4) (Clark et al., 2007; Bugliani et al., 2012; Centeno et al., 2012; Lafuente et al., 2015). Their identification by XRD was difficult, due to the simultaneous presence of M, TM and J. These three pigments are isostructural (cubic crystals, S.G. Fd3m); consequently, their diffractograms are similar, showing only slight differences in the crystal cell dimensions; the proximity of the ionic radii of Fe and Mn results in relative shifts of the peaks amounting few tenths of °2θ. Also, since TM is a solid solution of variable composition, the angular positions of its peaks are not constant from one sample to another, but depend on the Fe/Ti ratio in each sample. Furthermore, the poor crystalinity of MO affects the efficiency of the diffraction. In spite of these inconvenients, this technique allowed to differentiate some of these compounds, and eventually to estimate their relative concentrations.

For these reasons, SEM-EDS was used as a complementary technique to confirm the presence of Mn-containing phases.

The most intense Raman bands of M and TM (observed in 17 of 21 samples) appear at *ca*.670 cm^{-1} (Shebanova and Lazor, 2003; Rodríguez Ceja et al., 2009), superimposing one another, and are habitually recognized as a shoulder on the higher wavenumber side of the jacobsite band; this makes impossible the determination of the precise nature of the present oxides. For this reason, in Figs. 4 and 5, and in Table 1, they are identified as "M/TM".

By XRD, M was identified in 11/17 samples, and TM in 8/17 samples (*e.g*. Fig. 6). In the ICDD database (ICDD, 2008), a series of TM with different Ti concentrations are included]; for our samples, a stoichiometry of about $Fe_{2.5}Ti_{0.5}O_4$ gave the best fit for the analyzed samples (PDF File N° 75–1375).

In Figs. 7 and 4b, the broad Raman bands at *ca*.1390 and 1598 cm^{-1} are the D band (graphitic disorder-induced, A_{1g} symmetry vibration involving the disordered network of C_{sp2} coordinated clusters), and the G band (graphite-like carbon, E_{2g} symmetry attributed to vibrations within the polyaromatic structure), respectively (Tuinstra and Koenig, 1970; Beyssac et al., 2003; van der Weerd et al., 2004; Ospitali et al., 2006). Its presence was observed in 6/21 samples.

The identification of graphite by XRD is particularly difficult due to its laminar structure, since the preferred orientation of the particles along the basal plane results in a very intense diffraction from the (001) plane, with the rest showing a very low intensity. Furthermore, the (001) peak of graphite overlaps with the most intense peak of quartz (always present in the ceramic paste), making its determination doubtful. However, in the particular case of sample 43–2, the calcination at 1000 °C in air atmosphere and subsequent XRD analysis of a tiny portion of the pigment, made possible the confirmation of the presence of graphite in the pigment, corroborating the RS results (Fig. 8a and b).

In 4 of the carbon-containing samples, the presence of phosphates was also determined by RS (band at *ca*.960 cm^{-1}). When this band is present together with the two carbon bands, the black pigment is called "ivory black" or "bone black", generally obtained by burning bones which contain hydroxyapatite [$Ca_{10}(PO_4)_6(F,OH,Cl)_2$] (HA) (*e.g*. Fig. 4a and b) (Smith et al., 1999; Smith and Clark, 2004).

The detection of HA by XRD is a difficult task, due to the presence in the ceramic paste of feldspars, which have particularly complicated diffractograms, with many peaks, some of which hinder the smaller peaks of HA; and also to the usually low diffraction intensity of the HA peaks caused by its low concentration and poor crystallinity (organic HAs are usually non-stoichiometric [Ca/P molar ratio < 1.67]). In one case (sample 45–317) a very weak band was observed by XRD at the angular position corresponding to the most intense peak of hydroxyapatite (31.8°2θ).

RS measurements performed at different points of the surfaces also revealed, in 7/21 samples, the presence of a peak at 1007 cm^{-1} which is characteristic of gypsum, $CaSO_4.2H_2O$ (Edwards et al., 2000), probably present as a product of postdepositational processes.

Finally, in almost all samples of black pigments, and in coincidence with previous studies, corresponding to other styles of NWA pottery, *e.g*. Vaquerías (300 BC - 1000 AD), Aguada Portezuelo (*ca*. AD 600 -

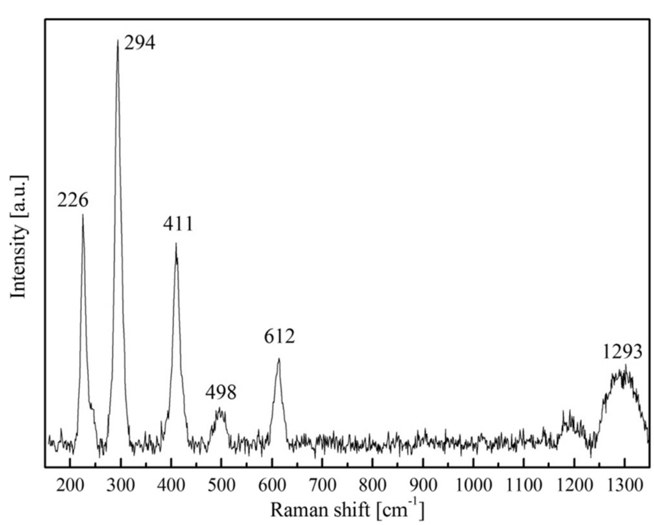

Fig. 3. Raman spectrum of the red paint.

Table 1
Results of the compositional analyses of black color: + = present; +? = doubtful; − = not present; (1) LA = La Angostura, ED = El Duraznito; (2) $MnFe_2O_4$ (RS); Mn_2O_3 (EDS); (3) Expressed as % by weight Mn_2O_3; (4) Raman: as M and TM are superimposed, the 670–700 cm^{-1} band is reported as magnetite/titanomagnetite; (5) HA: Hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$.

Sample	Site[(1)]	Mn[(2)]			Magnetite	Magnetite/titanomagnetite	Titanomagnetite	Carbon		Hematite		PO_4^{-3}(HA)[(5)]		$SO_4^{=}$
		RS	XRD	EDS[(3)]	XRD	RS[(4)]	XRD	RS	XRD	RS	XRD	RS	XRD	RS
1-3b Urn	LA	+		16.5		?		−		+		−		−
1-4 Urn	LA	+		5.0		+		−		+		+		+
5-127 Bowl	LA	+		5.9		+		−		+		−		−
5-10 Urn	LA	+	−	6.0	+	+	−	−	−	−	+	−	−	−
32-1 Bowl	LA	+	+	16.8	+	+	−	−	−	+	+	+	−	+
32-4 Urn	LA	+	+?	5.2	+?	+?	+	−	−	+	+	−	−	−
32-40 Urn	LA	+	−	12.1	+	+	+	−	−	+?	+	−	−	−
43-2 Urn	LA	+	−	14.5	+	+	+	+	+	−	+	−	−	−
45-296 Urn	ED	+	−	12.8	−	+	+	+	−	+	+	+	−	?
45-317 Urn	ED	+?	−	1.3	+	+	−	−	−	+	+	+	+?	+
45-366 Bowl	ED	+	−	5.1	+	+?	−	+	−	+?	+	+	−	+
45-415 Urn	ED	+	−	7.5	−	+	+	−	−	−	+	+	−	+
45-680 Urn	ED	+	−	5.1	+?	+	+	−	−	−	+?	+?	−	−
45-1438 Urn	ED	+	−	1.4	+	+	+?	−	−	+?	+	+	−	+
46-562 Urn	ED	−	−	16.5	+?	+	−	−	+?	+	+	+	−	+
46-947 Urn	ED	+	−	10.3	−	+	+	+	−	+	+	+	−	+?
47-185 Urn	ED	+	+?	10.5	+	+?	+?	−	−	−	+?	−	−	−
47-663 Urn	ED	+?	−	3.8	+	+	+	−	−	+	+	−	−	−
47-735 Urn	ED	+	−	9.2	+?	+	+?	+	−	−	+	+	−	−
47-930 Urn	ED	+	−	8.3	+	+	+?	−	−	+?	+	+	−	−
47-1061 Urn	ED	+	−	2.0	+	+	+?	+	+?	−	+	−	−	−

900) and Sanagasta (AD 900 - 1200) (Baldini et al., 2005; De la Fuente et al., 2010; Bugliani et al., 2012), hematite was detected in variable quantities; this should be attributed to its presence in the clay used as vehicle in the paint, in the ceramic paste, as independent mineral phase, and/or in the red paint under the black pigment.

5. Discussion and conclusions

Red and black colors have been used to paint pottery surfaces in a variety of styles throughout NWA's prehistory. Recent studies coincide with our results in identifying iron oxides, hematite in particular, as the source for red paint (Cremonte et al., 2003; Baldini et al., 2005; De la Fuente and Pérez Martínez, 2008; De la Fuente et al., 2010; Acevedo et al., 2012; Bugliani et al., 2012). Our studies of black paint, however, have produced more diverse results: the black paint utilized in Belén ceramics of the El Bolsón valley was elaborated from a variety of inorganic precursors (manganese oxides, magnetite and/or titanomagnetite), which in some of the samples were combined with organic raw materials (vegetal carbon and/or charred bone).

The origin of magnetite and titanomagnetite in black pigment is an aspect still under discussion in regional investigations (Botto et al., 1998; De la Fuente et al., 2010; Acevedo et al., 2012). In the case of Belén pottery, the consideration of the firing conditions (maximum reached temperatures, time of treatment at these temperatures, atmosphere composition) and the survey of ore deposits in the zone under study, suggests that these minerals are present as precursors in the generation of the pigment, and not as a consequence of the firing process (Puente et al., 2015, unpublished results).

The use of Mn oxides -jacobsite, bixbyite, pirolusite, *etc*.- together with magnetite and/or vegetal carbon has been documented in ceramic paints of NWA for a prolonged period in the region's prehistory (*ca*. BC 300 - 1500 AD) (Cremonte et al., 2003; Baldini et al., 2005; De la Fuente and Pérez Martínez, 2008; De la Fuente et al., 2010; Acevedo et al., 2012; Bugliani et al., 2012; Centeno et al., 2012; Tuñón López et al., 2012). Also, the use of vegetal carbon was registered in black internal surfaces of Aguada Portezuelo style bowls from Catamarca valley (De la Fuente and Pérez Martínez, 2008), as well as a main component of the paint in some Viluco style vessels (Mendoza Province) and Black over White style vessels from Jujuy Province (Baldini et al., 2005; Tuñón López et al., 2012). However, there are few reported cases of the use of bone to generate white paint involving some Aguada Portezuelo pieces and tricolored ceramics from sites located in the North Puna region (Baldini et al., 2005; De la Fuente and Pérez Martínez, 2008; Marte et al., 2012; Freire et al., 2016).

In this way, the Belén ceramics results are the first case in the NWA in which the use of calcined bone is detected in black pigment mixtures, probably scraped from bone surfaces containing charred organic matter. It should be mentioned here that the petrography analysis of fabrics of our samples did not show the presence of bone (Puente, 2012), thus corroborating that the phosphates are contained in the pigment.

Vegetal carbon and calcined bone are raw materials which were readily available for the potters on a daily basis, and are commonly observed as remainders in archaeological hearths. However, manganese oxides and iron and titanium minerals are scarcely distributed, and found at different distances as superficial and stratified deposits (Fig. 1), some of which have been industrially exploited (Angelelli, 1984). At the time of this study there are no reports of nodules of these minerals dispersed in the valley, neither are antecedents known for the neighboring valleys. The manganese deposits near the area under study are "Farallón Negro" and "Última Oportunidad" (Dpt. Belén), located 32 km west, and "Capillitas" (Dpt. Andalgalá) at 53 km southeast. Hematite deposits free of magnetite are found at the "Visvís" mines (Dpt. Andalgalá) at about 50 km south. At greater distances -*ca*. 140 km southwest- superficial and sub-superficial hematite with magnetite deposits in "La Argentinita" and magnetite in "Carmen", Tinogasta Dept., are found. Finally, the presently known ferrotitaniferous deposits are located at 230 km southeast in "Las Cañadas", at the Sierra de Ancasti (Dpt. El Alto) (González Bonorino, 1950; Angelelli, 1984). It is also relevant to mention here that reports of the existence of other non-hematite red-colored pigments in the region are inexistent. Though hematite and manganese oxides sources are the nearest to the El Bolsón valley, the more distant mineral raw materials could have circulated from these mentioned sources. Many investigations about interaction mechanisms in the NWA document the active circulation of goods and raw materials -mainly obsidian- through long distances (*e.g*. Escola, 2007; Lazzari et al., 2009; Lazzari, 2010; Sprovieri, 2011). However, since there are neither studies reporting pigments circulation, potential use of the known deposits, nor methodologies of extraction and/or

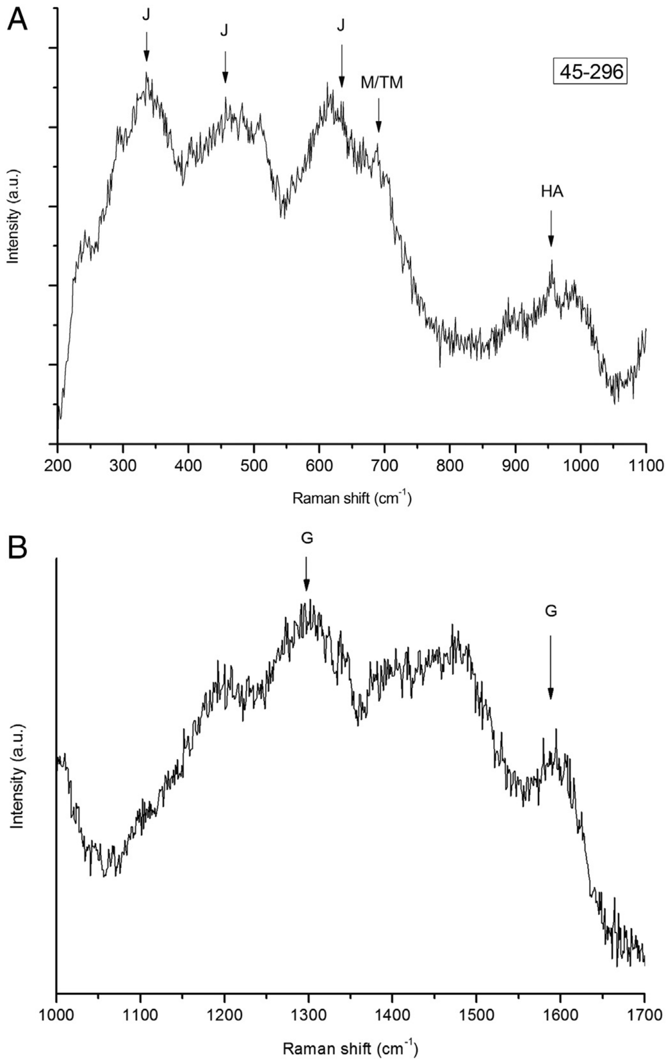

Fig. 4. a–b. Raman spectrum of black paint from sample 45–296: J = jacobsite, M/TM = magnetite/titanomagnetite, HA = hydroxyapatite, H = hematite, G = graphite.

processing of those pigments, this aspect should be confirmed through future provenance studies combining compositional information of both mineral deposits and archaeological paints.

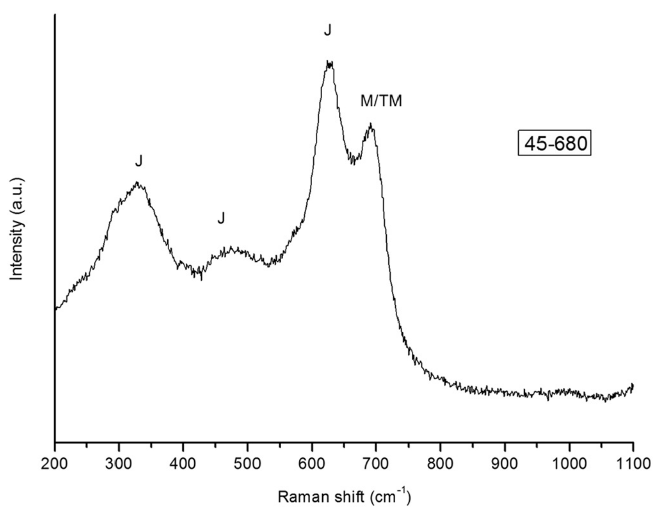

Fig. 5. Raman spectrum of black paint from sample 45–680: J = jacobsite, M/TM = magnetite/titanomagnetite.

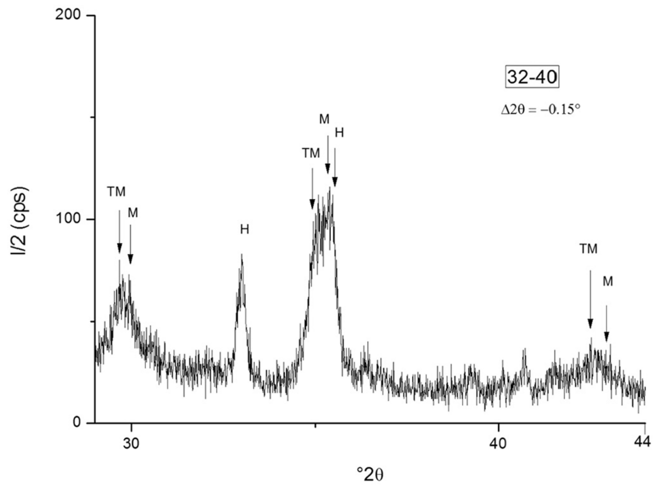

Fig. 6. XRD pattern of black paint from sample 32–40: M = magnetite, TM = titanomagnetite, H = hematite.

Finally, it should be remarked that the compositional variability observed in the studied set of samples had not been previously reported for a set of pieces with common style and provenience. Furthermore, this variability does not depend on the type of vessel nor its provenience (Table 1). Having said this, the observed diversity of compounds indicates the absence of standardization in the raw materials and methodologies of generation of the paints characteristic of this ceramic style, and coincides with the variability of the pastes elaboration forms previously identified (Puente, 2012). In this way, this study allows us to conclude that the local potters manufactured the pottery through diverse technical procedures, but with the aim of obtaining stylistically similar specimens. We consider that this variability is a consequence of the existence of different small scale production units, and of the absence of a close external control on the potters about the elaboration modalities employed.

The combination of analytical techniques for the color studies, together with the compositional analyses of pastes and raw materials previously realized, constitutes a complementary analytical corpus that revealed fundamental information for the knowledge of ceramic production practices in the El Bolsón valley.

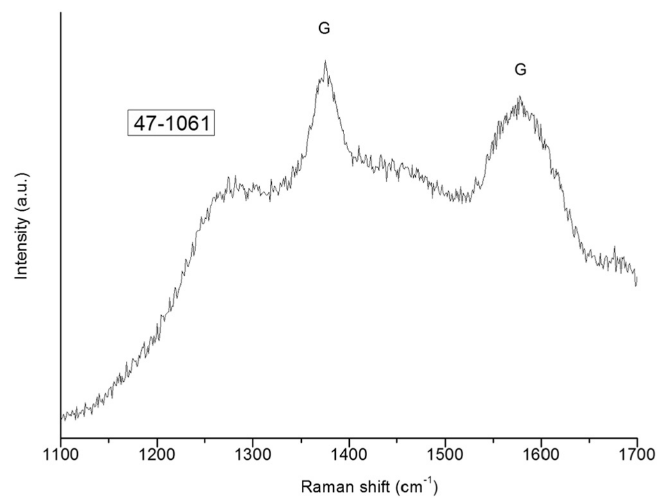

Fig. 7. Raman spectrum of black paint from sample 47–1061: G = graphite.

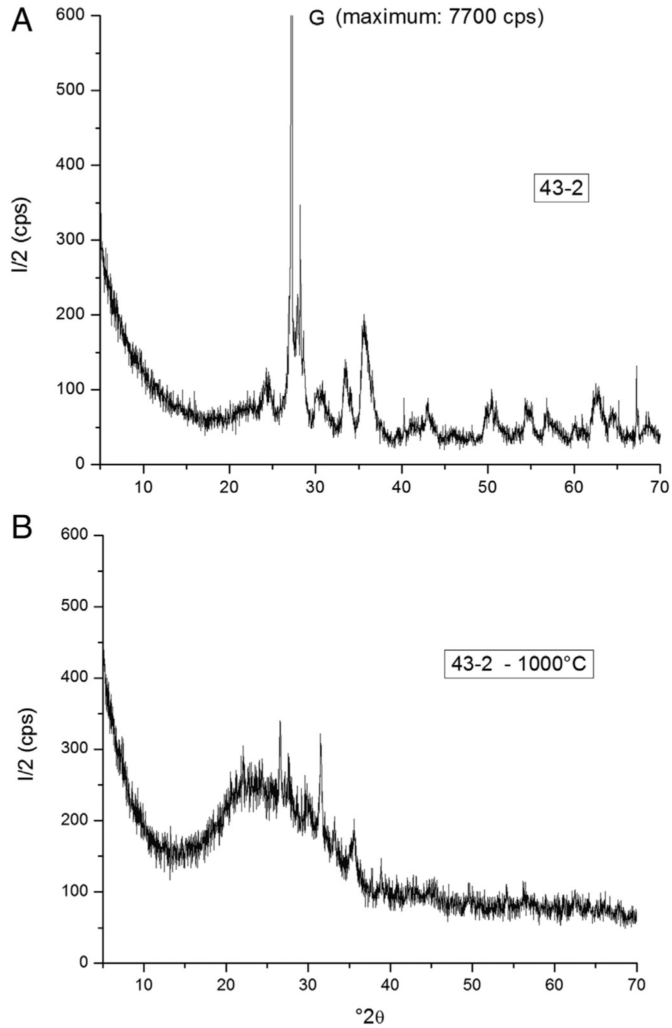

Fig. 8. a–b. XRD pattern from sample 43–2: a- black pigment; b- black pigment heated at 1000 °C. G = graphite.

Acknowledgements

This work was supported by Universidad de Buenos Aires [UBACyT 2014-2017]. The collaboration of Dr. Marisa Lazzari in the english redaction is gratefully acknowledged.

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