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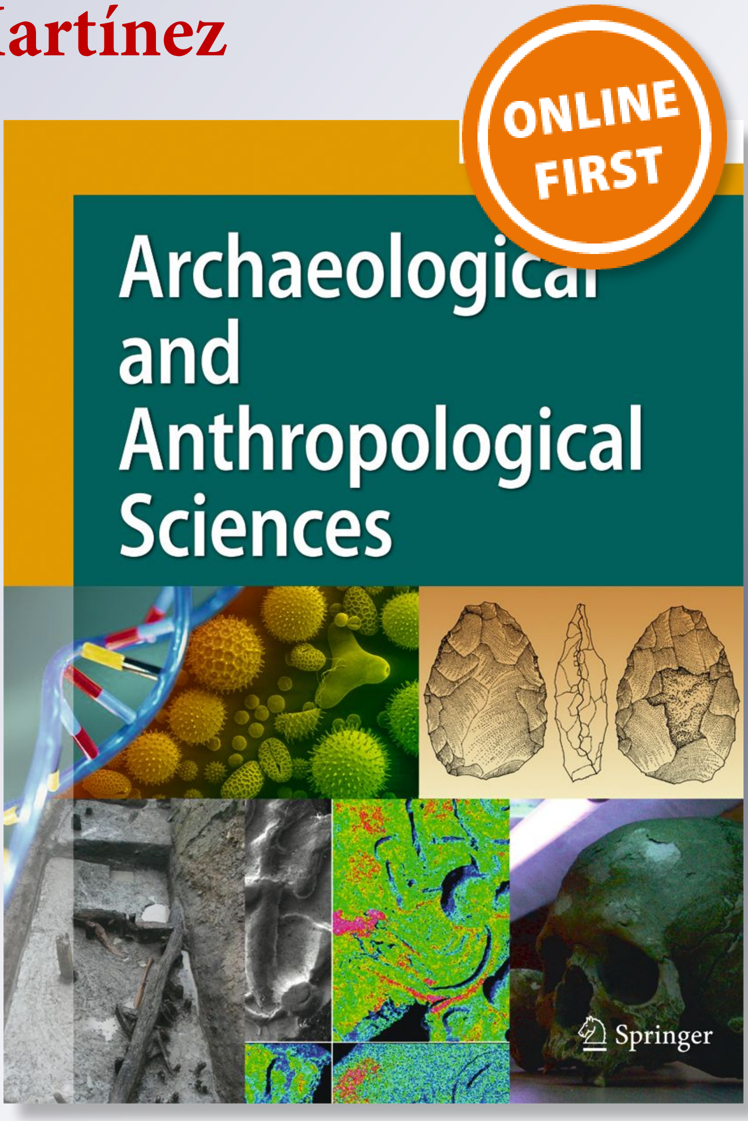

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ORIGINAL PAPER

Ancient potters, paintings and craft specialization in northwestern argentine region: new data through Raman characterization of pre- and postfiring ceramic paintings on Aguada Portezuelo Ceramics from Middle Period (Catamarca, Argentina)

Guillermo A. De La Fuente[1] · Juan Manuel Pérez Martínez[2]

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Abstract

Raman micro-spectroscopy (RMS) is nowadays a very well established analytical technique for the pigment identification in archaeological pottery which allows the study of art and museum objects through a totally non-destructive approach. Data on the chemical nature of the different pigments used by the ancient potters to decorate ceramic vessels can be obtained directly throughout the application of this analytical technique. In this paper, we explore the technological choices done by potters in the past to select, process and apply different natural pigments to decorate the Aguada Portezuelo vessels. The technological process itself is approached through the analytical results obtained from the study of pre- and postfiring paintings in Aguada Portezuelo archaeological ceramics, Middle Period (ca. AD 600–AD 900), Northwestern Argentine region. With the aim to explore the origin of the pigments (inorganic versus organic) used in the past by the potters, several paintings of red, black and brown colours were analyzed by Raman microspectroscopy. Additionally, the chemical nature of the white coloured prefiring slip characteristic of most of this ceramic type was studied, and we explored the molecular structure of the black plumbed coloured internal surfaces of these ceramic bowls.

Keywords Ramán microspectroscopy · Pigments · Ceramics · Aguada Portezuelo · Catamarca · Argentina

Raman microspectroscopy (RMS) is nowadays a very well established analytical technique for pigment identification in archaeological pottery which allows the study of art and museum objects through a totally non-destructive analytical approach (Dufilho and Coupry 1992; Clark 1999; Coupry 2000; Ciliberto and Spoto 2000; Edwards 2001; Smith and Clark 2001, 2004; Bersani and Lottici 2016). Applying this technique, data and information about the chemical nature of the different pigments used by ancient potters to decorate the ceramic vessels might be obtained (Clark and Gibbs 1997; Clark et al. 1997a, 1997b; Clark and Curry 1998; Jian et al. 1998; Edwards 2001; David et al. 2001; Pérez and Esteve-Tébar 2004; van der Weerd et al. 2004; Chaplin and Clark 2006; Bersani and Lottici 2016). Raman microspectroscopy has recently appeared in archaeometry laboratories as a powerful technique in the field of analysis of art objects basically due to the several advances in the analytical equipment, mainly referred to microspectroscopy (Smith and Clark 2004). This situation has allowed to eliminate the destructive phase in the analytical procedure, keeping the integrity of the art object, and also gather very good analytical results (Pérez and Esteve-Tébar 2004: 607–609). Thus, to obtain a Raman spectrum, it does not require any kind of sample preparation, special atmospheres or coatings—like for instance SEM-EDS (Pérez and Esteve-Tébar 2004: 607). The resulted spectrum gives information about the molecular composition, the structure and the environment of the sample, being analogous, although not identical, to that recorded in infrared spectroscopy (IR)

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(van der Weerd et al. 2004). Many minerals of importance to archaeological pottery (e.g. iron oxides, carbonate, quartz, feldspars and so on) are good Raman scatterers, and they are very well characterized by their Raman spectra. The Raman spectrum is unique to each material and can be interpreted as a "fingerprint", thereby allowing characterization of that material. The identification procedure needs a Raman database, and several have been published concerning pigments and minerals (Bell et al. 1997; Burgio and Clark 2001; Bouchard and Smith 2003; Bersani and Lottici 2016). The main aim of this paper is to explore the technological choices done by potters in the past to select, process and apply different natural pigments to decorate the Aguada Portezuelo vessels. The technological process as a whole is approached through the results obtained by Raman microspectroscopy (RMS) analytical technique applied in pre- and postfiring paintings from Aguada Portezuelo archaeological pottery, belonging to the Middle Period (ca. AD 600–AD 900) from Northwestern Argentine region. Pre- and postfiring external and internal surface paintings of red, black, brown (ochers) and white colours were analyzed by RMS to explore the pigment origin used by ancient potters as well as their chemical nature. Additionally, we carried out both an exploratory analysis on the white prefiring slip applied in the external surface of the vessels, a feature very characteristic in this ceramic type, and a deep exploration to study the molecular structure of the black polished internal surfaces, a feature so-called "graffited" in these vessels (González 1998; De La Fuente and Pérez 2008).

Geographical and cultural context

The *Aguada Portezuelo* style was given to know for the first time through several pottery sherds collected at the beginnings of XX century by Lafone Quevedo at Las Garrochas dunes, near to Andalgalá, Catamarca (Lafone Quevedo 1892). Serrano (1958) gave it the name of "Huillapima fondo Crema" style. Barrionuevo (1971) pointed out the presence of ceramic of this style in the Nanahuasi locality, Dept. of Ancasti. Afterwards, in 1972, Petek and collaborators carried out test pits in several settlements of this locality recovering an important number of Aguada Portezuelo sherds (cited in Haber 1992). Latterly, Kriscautzky y Togo (1996) carried out an archaeological prospection at Catamarca valley surveying several archaeological sites in which they found sherds of this style. Also at Catamarca valley, Haber (1992) found new archaeological sites with Aguada Portezuelo sherds.

In 1997, at the Choya locality, Dept. of Capayán, to the southwest of Catamarca valley, a ceremonial site belonging to this cultural phase was detected, consisting in a troncoconical plain-top and circular base shaped ceremonial mound with approximately a 25 m diameter (González 1998).

This group of studies allowed knowing the geographical distribution of the Aguada Portezuelo ceramic style, which is very well defined into the Catamarca valley, with material manifestations at the eastern slope of Ancasti sierra and the north of La Rioja province (Fig. 1a). It is almost totally absent at the western of Ambato sierra, and the finding of pottery of this style in the proximity of Andalgalá is very difficult to interpret mainly due to the lack of field studies (González 1998).

Likewise, the socio-political and economic complexity of Aguada culture, without precedents in this region of the argentine northwestern, is also present in the degree of complexity impressed in the organization and structuration of the iconographic repertory, production system, ceremonial centres, technological features in pottery production, metallurgy and a great social hierarchy materialized in the funerary practices (González 1998).

The most represented motifs and designs in all the characteristic styles of this culture were anthropomorphous, felines, ophidians, monkeys, batrachians and birds (Kusch 1996–1997; Nazar and De La Fuente 2016). Nevertheless, the best represented and most important motifs belong to the anthropomorphous figures, the "Lord of the Walking Stick", the "Sacrificer" and the Feline (jaguar) (González 1998). The iconographic richness, as well as the unique treatment of the common themes in Aguada allowed the characterization of Aguada Portezuelo ceramic style (González 1977, 1998; Kusch 1996–1997, 2000). González (1998: 213), in reference to this ceramic style, has said: "The Portezuelo style together with that from Ambato, for the imaginative unfolding, is the most extraordinary, not only of Aguada but of all the prehispanic cultures at the Northwestern Argentine." Besides, not only is the excellence of the utilized materials, but also the equilibrium in the colours used in the designs, the configuration of the themes and the abstraction of the fantastic images. But, together, these expressions are the nitid and clear representations of deities/divinities, which are represented in a very realistic way and with easily recognizable human or animal features. Probably, this style reflects with major similitude the iconographic themes of the medium horizon at the Andes (Nazar and De La Fuente 2016).

Kusch (1996–97), studying the designs of Aguada Portezuelo ceramics has identified four structural design patterns: continue band pattern, rhombus and triangle pattern, stepped pattern and rim wide band pattern; the later associated exclusively with human-felinic figures. In reference to these patterns, this author points out the existence of functional modalities, thinking in a differential use not determined by the potential form of a container, but for the figurative referent that explicitly would be remitting to a cultic or ceremonial function, suggesting a broader form of some institutionalized cult (Kusch 1996–97: 246; Kusch and Abal 2005). The ceramic morphology in Aguada Portezuelo is still not well

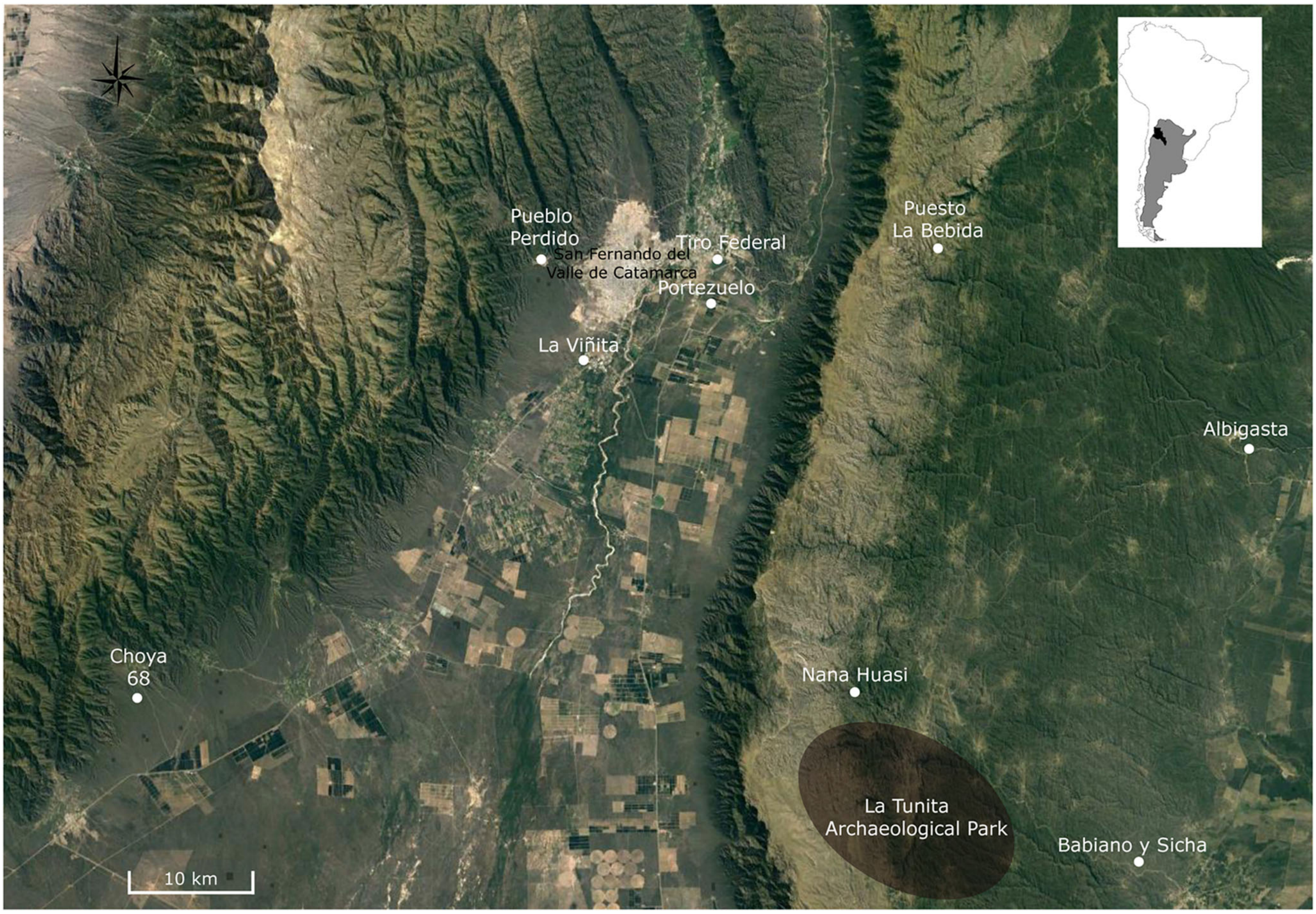


Fig. 1 **a** Catamarca valley and archaeological sites mentioned in the text. **b** Aguada Portezuelo archaeological pottery analysed by Raman. Pre- and postfiring black, red, brown, ocher and white paintings (*N* = 14)

defined. Ceramic material recovered mainly coming from surface collections is characterized by its high degree of fragmentation, thus making a good definition of the vessel shape difficult (Kusch 1996–97). However, from rims, bases, handles and body fragmented sherds, it appears that forms such as bowls, vases, jars and globular and semi-globular vessels are present (Nazar and De La Fuente 2016: 162–176, Figs. 2, 3, 10, 11, 13, 20, 21, 22, 23, 24 and 25). Also, for the globular and semi-globular forms, we are in presence of very large vessels in size (Nazar and De La Fuente: 172, Figs. 20–22).

Aguada Portezuelo pottery style: main technological characteristics and previous analytical studies

The Aguada Portezuelo ceramic style (ca. AD 600–AD 900) from Northwestern Argentine region presents a highly stylistic variation and complexity in the forming techniques used by ancient potters concerning surface treatments and the decoration applied to ceramic vessels (Kusch 1991, 1996–1997, 2000; González 1998; Cremonte et al. 2003; Baldini et al. 2005; De La Fuente and Pérez 2008; Nazar 2012; Nazar and De La Fuente 2016). One of the most important features in these ceramics is its highly marked polychromy (Fig. 1b). The main decoration technique applied in this pottery is painting, presenting both pre- and postfiring paints (González 1998; De La Fuente and Pérez 2008). Motifs are elaborated in negative and positive, and the colours used by ancient potters to decorate the external surfaces range among burgundy—or purple red—reddish, ocher, black, white and yellow; being this later colour unique to Northwestern Argentine region (Kush 1996–1997, 2000; González 1998; De La Fuente and Pérez 2008; Nazar and De La Fuente 2016). Sometimes, colours have not been very well fixated by firing mainly due to the amount of pigment added by the potter; thus, they appear as light and brightless (see for instance Fig. 1b, samples MN°1 and MN°4) (De La Fuente et al. 2005a). Postfiring paintings are mainly of black, red and brown (ocher) colours, and they are basically on the external surfaces (Nazar and De La Fuente 2016) (Fig. 1b). Prefiring paintings are of white, black and red colours, and they are displayed both at internal and external surfaces of the vessels (Nazar 2012; Nazar and De La Fuente 2016) (Fig. 1b). Another decorative aspect in this pottery very less known

Fig. 1 (continued)

nowadays is the existence of resistant negative paintings (González 1998). Previous microanalysis studies carried out through ESM-EDS and XRD on postfiring black, red and brown colour paintings allowed to chemically characterize the chemical composition of these pigments and to detect the presence of certain mineral phases, establishing that the mineral origin of the source pigments as several oxides minerals (Cremonte et al. 2003; De La Fuente 2005: Table 1; Baldini et al. 2005; De La Fuente et al. 2005a: Table 3; Bertolino et al. 2009; De La Fuente and Pérez 2008). These paintings are *matte* pigments, not glazed, and they must adhere to the vessel surfaces, retaining the colour after the adsorption and fixation process, and ultimately after the firing process itself. Pigments are incorporated to a colloid (alumino-silicate clay mineral), which forms the vehicle of the pigment and it must reach specific conditions to get its adsorption into the surface of the ceramic matrix (De La Fuente et al. 2005a). Black pigments, which present high concentration on iron (Fe), and lesser concentration of manganese (Mn), do have their inorganic source in minerals like hematite (α-Fe_2O_3), pirolusite ($Mn^{+4}O_2$) and psilomelane ($BaMn^{+2}$ + Mn_8O_{16} $(OH)_4$). Red pigments do have high concentrations in iron (Fe) with the inorganic source of hematite (α-Fe_2O_3) (De La Fuente et al. 2005a:76). These black and red pigments were added to colloidal solutions (clay minerals, e.g. illite) after a technical preparation. White slip, which is a colloidal solution with high concentrations of calcium (Ca), generally does not fix well in the external surface of the vessels producing cracks and lately exfoliation (De La Fuente 2005). Baldini et al. (2005) analyzed by FT-IR, SEM-EDS and XRD the composition of several pigments (black, white and red) and their ceramic pastes in Aguada Portezuelo sherds from Catamarca valley. Results obtained confirmed those reached by us in different analytical stages by SEM-EDS (De La Fuente 2005: Table 1; De La Fuente et al. 2005a: Table 3), with the exception of the indirect determination of powered bone (hydroxyapatite) to elaborate the white pigment in an Aguada Portezuelo ceramic pipe (Baldini et al. 2005: 97–99, Figs. 5 and 6). Presence of hydroxyapatite in the white slip was inferred by the anomalous presence of P and Ca values, which together with bone texture are comparables to organic apatite (Baldini et al. 2005:98). Bertolino et al. (2009) through the application of SEM-EDS, EPMA and XRD on Aguada Portezuelo paintings obtained the same compositional results concerning the source of black, red, brown and white pigments, establishing that bowls belonging to Aguada Portezuelo ceramic styles reached 900–1000 °C firing temperatures, inferred by the presence of ghelenite, the lack of anorthite and the low intensity reflection of micas (cf. Cremonte et al. 2003:13–14; Baldini et al. 2005:99, for different results in estimating firing temperatures). XRD of prefiring white slip identified ghelenite as the main mineral phase, formed by the reaction between the ceramic paste and calcite (CO_3Ca) (Bertolino et al. 2009). Additionally, in the back scattered electron images (BEI), the diffusion of Ca into the porous ceramic matrix was observed (Bertolino et al. 2009, Figs. 3 and 4). Raman microspectroscopy was performed in pre- and postfiring paintings on Aguada Portezuelo style sherds (De La Fuente and Pérez 2008). Sherds with paintings of red, black, brown (ocher), yellow and white colours were analyzed by RMS. Additionally, black internal polished surfaces were analyzed to explore the "graffited" visual effect on bowl forms of Aguada Portezuelo vessels. Red postfiring paintings were characterized by the presence of hematite (α-Fe_2O_3) (De LaFuente and Pérez 2008: 177–178, Figs. 5a and 6). Black postfiring paintings gave manganese oxide (MnO_2) as the main chromofore for this colour, while white prefiring slip was characterized by the presence of calcite (De La Fuente and Pérez 2008: 179–181, Figs. 7, 8 and 11). Yellow brownish prefiring paint on the external surface of a sherd produced for the first time an interesting discover: the use of mineral *tungstite*, hydrous tungsten–wolfram oxide ($WO_3{\cdot}H_2O$) to obtain the yellow colour (De La Fuente and Pérez 2008:179–180, Fig. 9). *Tungstite* is naturally present in nature and its colour ranges from yellow to yellowish. The origin source of this mineral is still unknown. Concerning the internal surfaces of the Aguada Portezuelo bowls, black-plumbed coloured, which do have this visual effect so-called "graffited", RMS confirm the presence of *carbon black* (biogenic charred material). Raman spectra showed up the presence of strong adsorption bands: the G-band at 1585 cm^{-1} and the D-band at 1350 cm^{-1}, well characteristic of disordered graffito structures derived from biogenic material (De La Fuente and Pérez 2008: 182, Fig. 12; van derWeerd et al. 2004: 1433–1434). According to this data, ancient potters added vegetable materials inside of these bowls and charred them during the firing process diffusing the black colour into the ceramic matrix and producing this visual effect (De La Fuente and Pérez 2008: 182; see also Adams et al. 2002; Jehlîcka et al. 2003; Kay 1994; Speakman and Neff 2002; Stewart and Adams 1999; Stewart et al. 2002; van der Weerd et al. 2004; Centeno et al. 2012 for further discussion).

Materials and methods

Fourteen Aguada Portezuelo ceramic samples containing red, black, brownish (ocher), white and yellow pre- and postfiring paintings on the external and internal surfaces of the vessels were analysed through Raman microspectroscopy (Fig. 1b). Additionally, several black and plumbed coloured polished internal surfaces were also explored by Raman microspectoscopy. Ceramic sherds belong at least to two form categories: (1) bowls and (2) globular vessels (Table 1). All fragments analysed are coming from different archaeological sites geographically located at Catamarca valley (De La Fuente et al. 2005b; Kriscautzky 1996–1997; Kristcautzky and Lomaglio 2000; Kristcautzky and Togo 1996; Lomaglio and Kristcautzky 2005; Kristcautzky et al. 2005) (Fig. 1a). Ceramic sherds labelled TFS are coming from stratified archaeological contexts excavated at Tiro Federal Sur (TFS) archaeological site (Dept. Capital, Catamarca valley, Catamarca, Argentina) (Kriscautzky 1996–1997; Kristcautzky and Togo 1996), whereas the MN-labelled sherds are coming from the archaeological type site of Aguada Portezuelo (Dept. Valle Viejo, Catamarca, Argentina) (Fig. 1a). Table 1 presents the main characteristics of analysed sherds. Additionally, the chemical nature of prefiring white slip was studied, and the molecular structure of the black and plumbed internal surfaces of the bowls was explored.

Raman spectra were obtained with two different types of spectrometers: Raman dispersive and FT Raman, both coupled with a microscope, located at Department of Chemistry-Physics, University of Alicante, Spain. Most spectra were obtained with a dispersive LabRAm spectrometer (Jobin-Ivon Horiba). The system has a high detecting sensitivity and uses a single spectrograph equipped with a notch filter in order to filter the Raylegh scattering and holographic gratings (1800 and 600 grooves mm^{-1}). The slit and pinhole employed were 300 and 500 μm, respectively. The excitation

Table 1 Aguada Portezuelo pottery analysed in this research. Main morphological and technological characteristics ($N = 14$)

	Ceramic Form	Vessel form	Internal colour	External colour	Core colour	Texture	Firing	Surface treatment	Decoration
MN°1/TSF 354	*globular vessel*	*lip/neck*	*4/N black*	*2.5YR 5/6 red* *10YR 3/1 black* *2.5Y 8/2 white*	*6/N gray*	*fine*	*reduced*	*smoothed-polished internal /external surface*	*postfiring painting external surface*
MN°2/TFS 1570 (23)	*bowl*	*body*	*4/N black*	*5YR 4/4 red* *10YR 3/1 black* *7.5YR 5/4 brownish*	*3/N internal surface* *4/N core* *7.5YR 5/4 slip*	*fine*	*reduced*	*smoothed-polished internal /external surface*	*postfiring painting external surface* *polished*-graffited *internal surface*
MN°3/TFS1015(26)	*globular vessel*	*body*	*4/N black*	*2.5Y 8/1 white* *7.5YR 6/6 yellow*	*6/N gray* *7.5YR 5/4 brownish*	*fine*	*oxidized*	*smoothed-polished internal /external surface*	*postfiring painting external surface* *polished*-graffited *internal surface*
MN°4/TFS 4(26)	*globular vessel*	*lip*	*7.5YR 5/4 brownish* *10R 4/3 red* *2.5Y 3/1 black*	*10R 4/3 red* *2.5Y 3/1 negro* *2.5Y 8/1 white*	*7.5YR 5/4 brownish*	*fine*	*oxidized*	*smoothed-polished internal /external surface*	*postfiring painting internal / external surface*
MN°5/TFS28	*vessel*	*body*	*4/N black*	*2.5Y 3/1 black* *10R 4/3 red* *7.5YR 5/4 brownish*	*7.5YR 5/4 brownish*	*fine*	*reduced*	*smoothed-polished internal /external surface*	*pre- and postfiring painting internal / external surface*
MN°6/TFS 11	*vessel*	*body*	*4/N black*	*2.5Y 8/1 white* *10R 4/3 red*	*6/N gray*	*fine*	*reduced*	*smoothed-polished internal /external surface*	*postfiring painting external surface* graffited *internal surface*
MN°7/TSF 6 (27)	*globular vessel*	*lip*	*4/N black*	*2.5Y 3/1 black* *2.5Y 8/1 white*	*6/N gray*	*fine*	*reduced*	*smoothed-polished internal /external surface*	*postfiring painting external surface* graffited *internal surface*
MN°8	*globular vessel*	*body*	*4/N black*	*2.5Y 3/1 black* *2.5Y 8/1 white*	*7.5YR 5/4 brownish*	*fine*	*oxidized*	*smoothed-polished internal /external surface*	*postfiring painting external surface* graffited *internal surface*
MN°9	*globular vessel*	*body*	*4/N black*	*2.5Y 8/1 white* *7.5YR 6/6 yellow* *2.5Y 3/1 black*	*7.5YR 5/4 brownish*	*fine*	*oxidized*	*smoothed-polished internal /external surface*	*postfiring painting external surface* graffited *internal surface*
MN°10/TFS 048 (25)	*bowl*	*body*	*4/N black*	*2.5Y 3/1 black* *7.5YR 5/4 brownish*	*6/N gray*	*fine*	*oxidized*	*smoothed-polished internal /external surface*	*prefiring painting external surface* graffited *internal surface*
MN° 11	*globular vessel*	*body*	*4/N black*	*2.5Y 3/1 black* *7.5YR 5/4 brownish*	*6/N gray* *7.5YR 5/4 brownish*	*fine*	*reduced/oxidized*	*smoothed-polished internal /external surface*	*prefiring painting external surface*

Table 1 (continued)

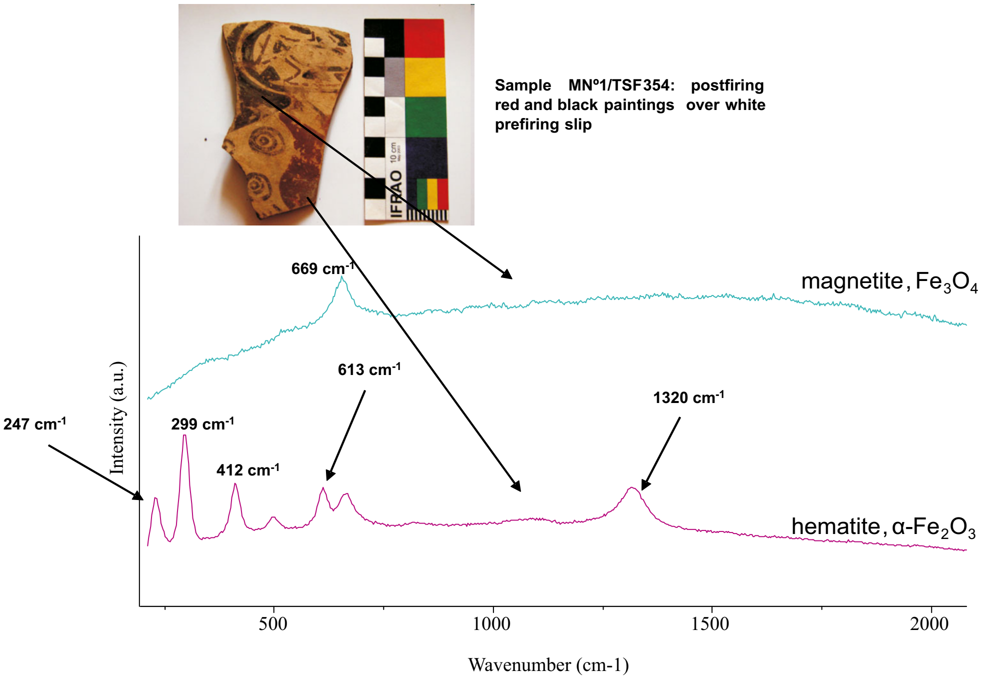
	Ceramic Form	Vessel form	Internal colour	External colour	Core colour	Texture	Firing	Surface treatment	Decoration
									graffited internal surface
MN°12	*globular vessel*	*body*	*4/N black*	*2.5Y 3/1 black* *2.5Y 8/1 white*	*7.5YR 5/4 brownish*	*fine*	*oxidized*	*smoothed-polished internal /external surface*	*postfiring painting external surface* *graffited internal surface*
MN°13/TFS 1570 (23)	*bowl*	*body*	*4/N black*	*10R 4/3 red* *2.5Y 3/1 negro*	*6/N gray*	*fine*	*reduced*	*smoothed-polished internal /external surface*	*prefiring painting external surface* *graffited internal surface*
MN°14/TFS 336	*globular vessel*	*body*	*4/N black*	*2.5Y 3/1 black* *7.5YR 5/4 brownish*	*6/N gray*	*fine*	*reduced*	*smoothed-polished internal /external surface*	*prefiring painting external surface* *graffited internal surface*

line was provided by a 17 mW He-Ne laser at 632.8 nm, and the laser power delivered at the sample ranged from 0.12 to 1.2 mW (the laser power was kept at a minimum value in order to prevent sample degradation). The laser beam was focused through a 50× long-working objective (0.5NA). The diameter of the laser beam spot on the sample surface was 2 μm. The sample viewing system consisted of a colour television camera attached to the microscope. After each spectrum had been recorded, a visual inspection was performed in order to detect any superficial change caused by the laser. The spectrometer resolution was better than 3 cm^{-1} and the detector was a Peltier-cooled charge-couple device (CCD) (1064 × 254 pixels). The time needed for the analysis (including data acquisition and averaging) ranges from 20 to 120 s depending on the efficiency of the Raman scattering and the interference of the fluorescence that could also occur in the sample. When fluorescence occurred at a sample, a Bruker RFS/100 model FT Raman spectrometer was used to analysis coupled microscope. This equipment possesses an excitation line with a laser in the near infrared, 1064 nm, Nd-YAG and a Ge detector cooled with liquid N_2.

Analytical results and discussion

Red colour in ceramic paintings has been characterized mainly by inorganic chromophores such as iron oxide bearing minerals (Pérez and Esteve-Tébar 2004; De La Fuente and Pérez 2008;Tuñon López et al. 2012; Acevedo et al. 2012; Bugliani et al. 2012; Centeno et al. 2012; Puente et al. 2017). The spectra recorded from the red surface of several samples are shown below (Figs. 2, 3, 4, 5, 6, 7 and 10). The red pigment here is mainly hematite, α-Fe_2O_3 (Figs. 2, 3, 4, 5, 6, 7 and 10, Table 2). According to the crystal space group to which hematite belongs ($D^6{}_{3d}$), seven phonon lines are expected in the Raman spectrum (Porto and Krishnan 1967): two A_{1g} modes at 225 and 498 cm^{-1} and five Eg modes at 247, 293, 299, 412 and 613 cm^{-1}, respectively. Hematite is an antiferromagnetic material and the interaction of two magnons yields the strong broad feature at 1320 cm^{-1} (Hart et al. 1976, Pérez and Estéve-Tébar 2004). These results are in accordance with previous analytical research done by SEM-EDS, XRD and Raman (De La Fuente 2005a; De La Fuente and Pérez 2008). All these red paintings analyzed here are postfiring paints applied mainly on a white prefiring slip, as seen in Fig. 1b. Postfiring paintings usually are not well fixed into ceramics porous matrix, and much of these paints are poorly preserved (samples MN°1/TSF 354 (29), MN°2, MN°4 TSF 4 (26) and MN°6 TFS 11) (see Figs. 2 and 5); thus, they tend to disappear with time causing a conservation problem in

Fig. 2 Postfiring black and red paintings over white slip. Raman spectra (632 nm) of hematite (red) and magnetite (black). Observe the poorly preserved paintings in the external surface



many of these ceramic vessels (De La Fuente 2005; De La Fuente and Páez 2007).

The origin of black colour to decorate the vessels presents more than one possibility to be obtained by ancient potters according to the following: (1) first to the type of chromophores used in the past (inorganic versus organic) and (2) second, if the pigment poses a mineral precursor, because there are many ways to obtain a black colour depending on the mineral itself and the reactions occurred in the pottery kiln during firing (Noble 1960; Maggeti et al. 1981; Tite et al. 1982; Maniatis et al. 1993). Manganese oxides—jacobsite, pyrolusite, bixbyite—

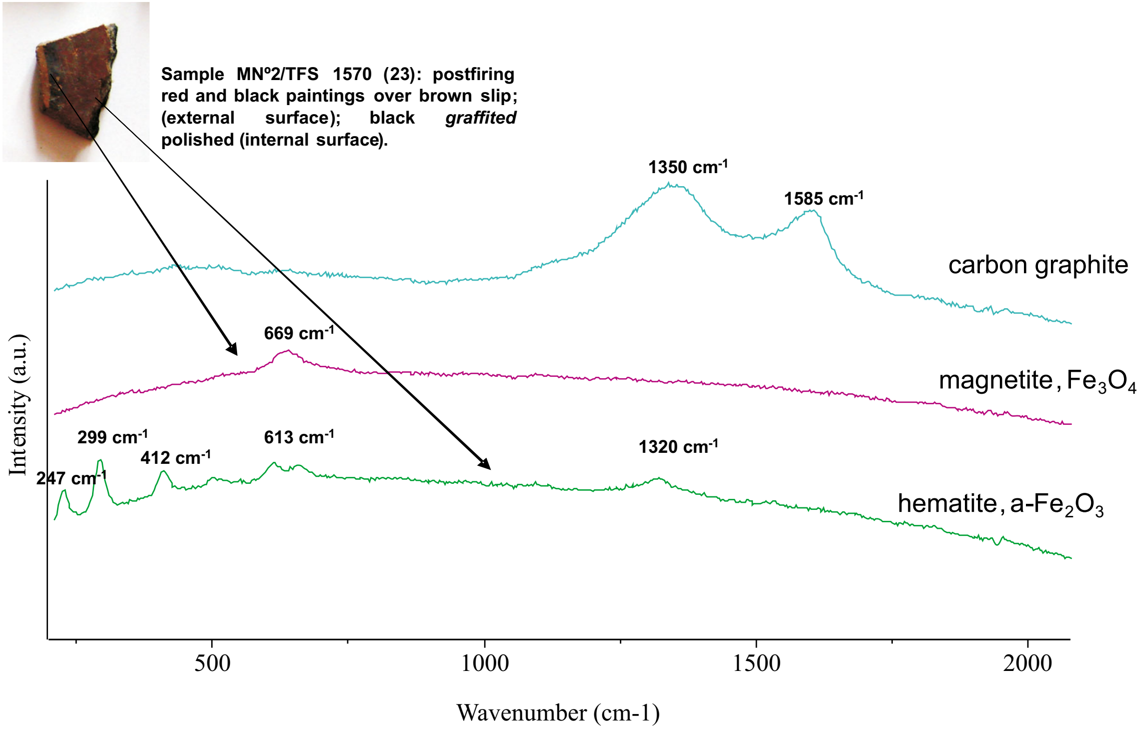


Fig. 3 Postfiring black and red paintings over brown slip. Raman spectra (632 nm) of hematite (red) and magnetite (black). Raman spectrum for *graffited* (carbon graphite) internal surface of the bowl

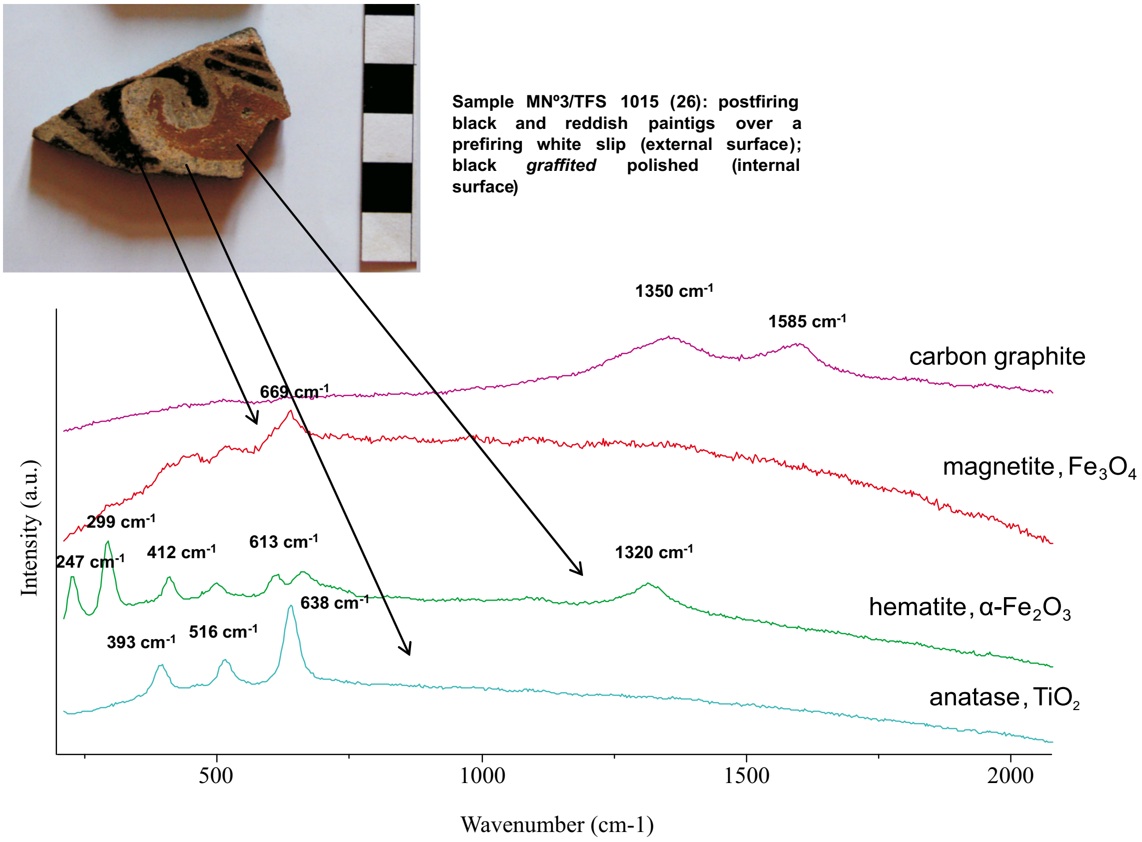


Fig. 4 Postfiring black and reddish paintings over white slip. Raman spectra (632 nm and FT) showing hematite (reddish), magnetite (black), anatase for white prefiring slip and carbon graphite for black internal surface

magnetite, titanomagnetite, carbon and hydroxyapatite have been reported as common mineral precursors for black paintings used at Northwestern Argentine region during all most prehispanic cultural development (De La Fuente and Pérez 2008; Acevedo et al. 2012; Bugliani et al. 2012; Marte et al. 2012; Centeno et al. 2012; Freire et al. 2016; Puente et al. 2017). Previous analytical research on these black paintings have shown MnO_2 (pyrolusite) as the main inorganic precursor for this colour (De La Fuente and Pérez 2008: 179). Surprisingly to expected, the analyses by Raman of all samples containing pre- and postfiring black paintings on the external surface of vessels indicate that the black pigment is magnetite, Fe_3O_4. Figures 2, 3, 4, 5, 6, 7, 8 and 9 show the spectra recorded from black areas on the surface of all samples analysed. Most of the samples present the typical band of magnetite centred at 669 cm^{-1} (samples MN°1/TSF354 (29), MN°2, MN°4 TSF 4 (26), MN°7/TSF6 (27), MN°8, MN°9, MN°11, MN°12 and MN°13/TFS1570 (23) (Table 2). Sample MN°3/TSF 1015 (24) shows three bands for magnetite centred at 300, 534 and 669 cm^{-1} (Fig. 4), whereas sample MN°12 shows the strongest band at 669 cm^{-1} (Fig. 10). This spectrum is in agreement with that reported in the literature (de Faria et al. 1997; Shebanova and Lazor 2003). Black pigment, magnetite (F_3O_4) has a spinel structure in which one third of the metal is Fe (II) and the remainder is Fe (III); thus, it is alternatively represented as Fe^{III} (Fe^{II} Fe^{III}) O_4. Ferruginous clays containing iron oxides and hydroxides can form spinel phases that are mainly black in colour under reducing atmospheres in the kilns. Variations in kiln atmospheres can produce, in iron oxide-rich clays, alternatively red or black surfaces (Noble 1960; Pérez and Estéve-Tebar 2004). In prefiring paintings, such colours depend exclusively of the kiln atmosphere, its internal atmosphere variations, the exact position of the vessel inside the kiln, the maximum firing temperature reached, and the presence or absence of oxygen (de Waal 2004; Cecil and Neff 2006; Cornell and Schwertmann 1996; Shepard 1976). Magnetite can be naturally obtained or by reducing hematite (Cornell and Schwertmann 1996). Most of natural iron oxides bearing minerals (such as hematite and magnetite) contain other iron oxides as impurity contaminants. Hematite is naturally formed from magnetite by metamorphism, thus is very common that particles of original magnetite are still present in the final hematite formation (Cornell and Schwertmann 1996). Hematite is converted to magnetite under reducing

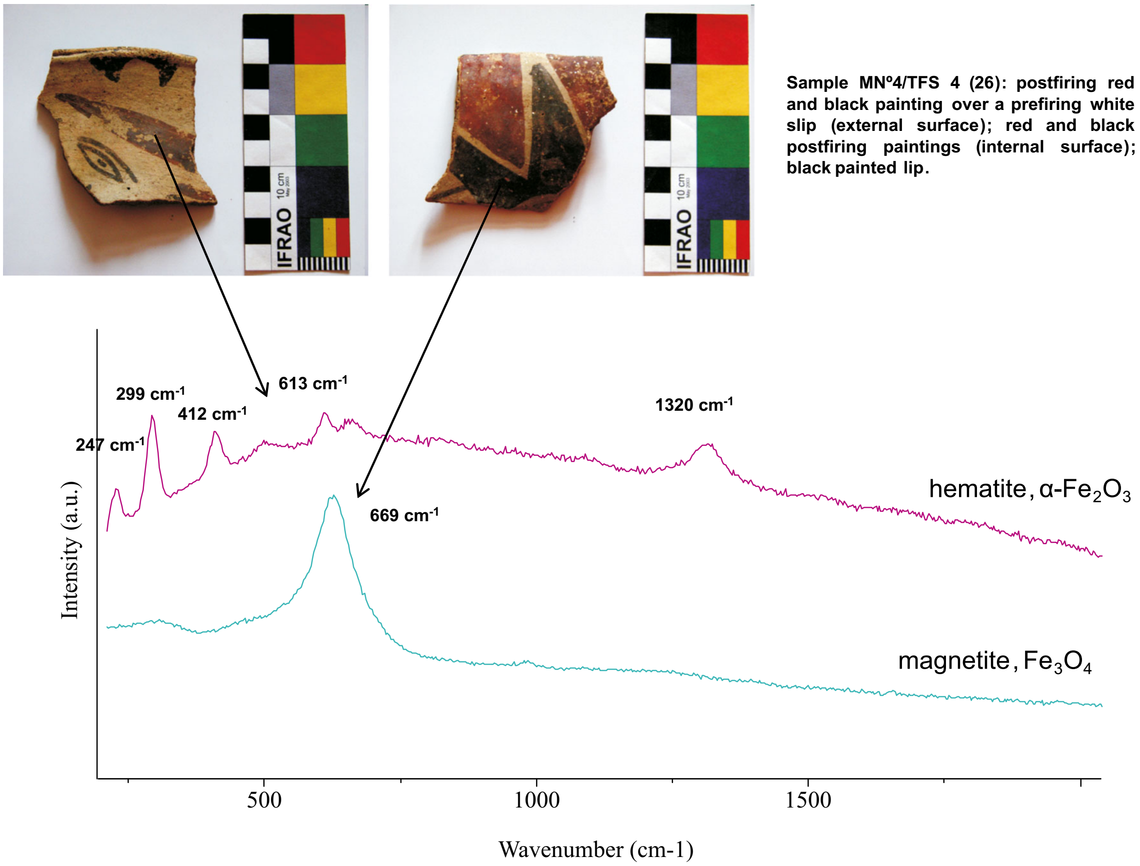

Sample MNº4/TFS 4 (26): postfiring red and black painting over a prefiring white slip (external surface); red and black postfiring paintings (internal surface); black painted lip.

Fig. 5 Postfiring red and black paintings over white slip. Raman spectra (632 nm) of hematite (red) and magnetite (black). Observe the poorly preserved paintings in the external surface

conditions between 650 and 900 °C (Ramdohr 1980; Zuo et al. 1999; Goodall et al. 2009), usually the temperatures achieved in firing Aguada Portezuelo ceramics. After this conversion, magnetite would remain stable and produce a dark or black pigment (Cornell and Schwertmann 1996). Sometime, this conversion is not fully achieved and original hematite can be observed in the Raman spectra (Fig. 8, sample MN°8 external surface and Fig. 9, sample MN°11 external surface). In previous papers, we proposed that this polychrome Aguada Portezuelo pottery was produced in a two-step process (De La Fuente 2005a, 2005b; De La Fuente and Pérez 2008). During the first reducing step of firing done at ca. 800–900 °C, both paste and some pigments such as hematite turned gray and black (generating magnetite), respectively. In the next oxidizing step at a lower temperature than 800 °C, a white slip with different mineralogy (mainly biotite) (De La Fuente et al. 2005a: 66–67, Fig. 4) and the remaining pigments like hematite (red) and ochers (iron oxides) are fixed, turning red the paste into the matrix (~ 1 mm), and keeping white the external surface (see for instance Fig. 1b, sample MN°1/TSF354 (29), also see De La Fuente and Pérez 2008:181, Figs. 10 and 11). After that, postfiring paintings were added to the external surfaces (black, red, ochers and yellow) (De La Fuente and Pérez 2008). Thus, black paintings in Aguada Portezuelo pottery have been obtained at least by three ways by ancient potters: (1) prefiring black pigment (magnetite) was obtained by reducing hematite during the first firing step (see Figs. 8 and 9); (2) postfiring black paintings also were obtained alternatively by processing manganese oxides (MnO_2), pyrolusite (De La Fuente and Pérez 2008: 179, Figs. 7 and 8); and (3) postfiring black pigments (magnetite) were obtained by processing naturally occurring magnetite. The presence of residual hematite on the final black surface, as indicated above, highlights the fact that the reducing step sometimes was not a complete process (see Fig. 8, sample MN°8, peak at 299 cm^{-1}, and Fig. 9, sample MN°11, peak at 299 cm^{-1}). Goodall et al. (2009: 96–97) have excellently summarized the different mineralogical and physical changes iron oxides overcome through different heating temperatures during the process of ceramic production.

The spectra recorded from the black plumbed coloured internal surfaces (a smoothed process so-called *graffited*) of the Aguada Portezuelo bowls are shown in Figs. 3, 4, 6 and 7. The black colour of the internal surfaces present here is characteristic of carbon (disordered graphitic structures) with two bands

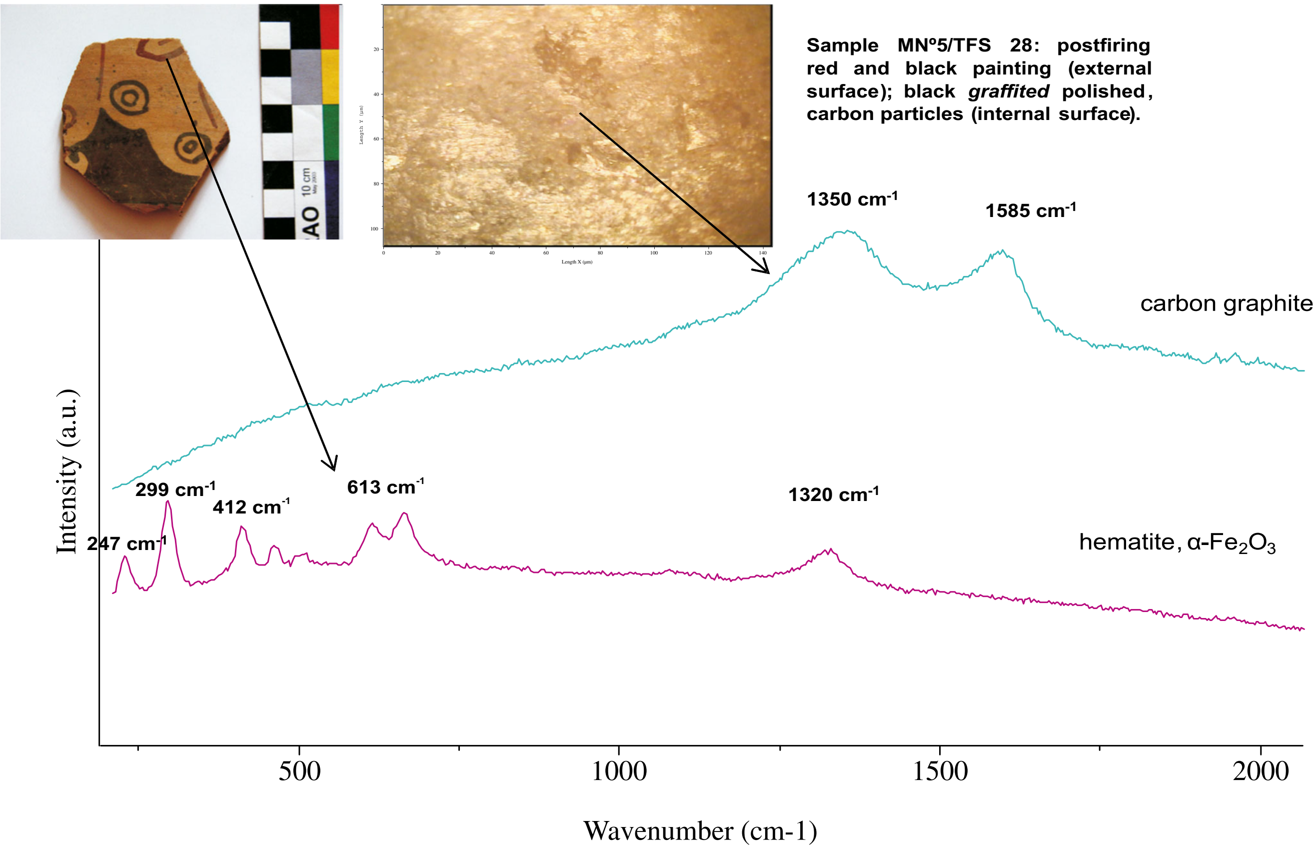


Fig. 6 Raman spectra (632 nm) of hematite for red postfiring paintings and carbon graphite for the internal black plumbed surface of the bowl

centred at 1350 and 1580 cm^{-1}. These bands are commonly called the G and D bands of carbon (van der Weerd et al. 2004). The G band, at 1584 cm^{-1}, is related to polycyclic bonds in the graphite structure and is typical of highly crystalline graphite, whereas the D band, at 1350 cm^{-1}, is typical of less crystalline carbonaceous material (van der Weerd et al. 2004). The broad nature of these bands indicates that the material is amorphous carbon, and the lack of a band at 961 cm^{-1} (Edwards et al. 2000), characteristic of bone, indicates that the carbon is derived from originally charred plant material (see van der Weerd

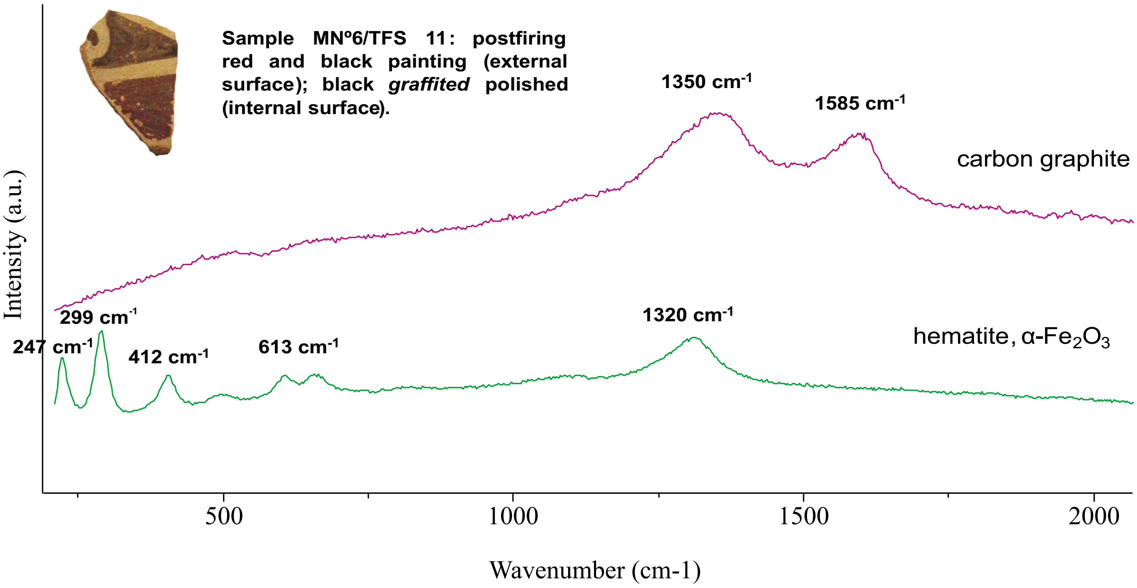


Fig. 7 Raman spectra (632 nm) of hematite for red postfiring paintings, and carbon graphite for the internal black plumbed coloured surface of the bowl

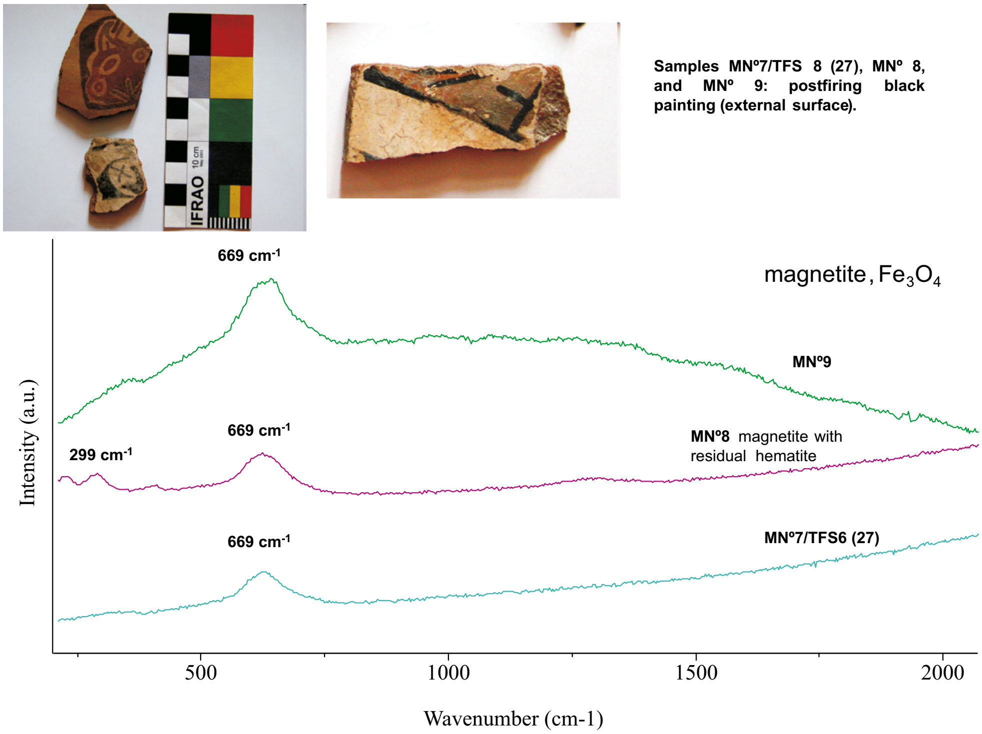


Fig. 8 Raman spectra (632 nm and FT) of magnetite for black postfiring paintings on the external surface of samples MN°7and MN°9. Sample MN°8 shows magnetite for the black prefiring paintings, but also, it presents residual hematite at 299 cm^{-1}

et al. 2004). These results are in accordance with previous analytical research and strongly suggest that this visual "graffited" effect achieved by ancient potters is due to the firing of plants in the interior of these bowls in the kilns (De La Fuente and Pérez 2008). This produces a black plumbed coloured surface, which is finally smoothed and polished by potters, a technical practice carried out by the American southwest Tewa potters in the first of XX century (Adams et al. 2002; Colton 1953; Colton and Hargrave 1937; Kay 1994; Simon

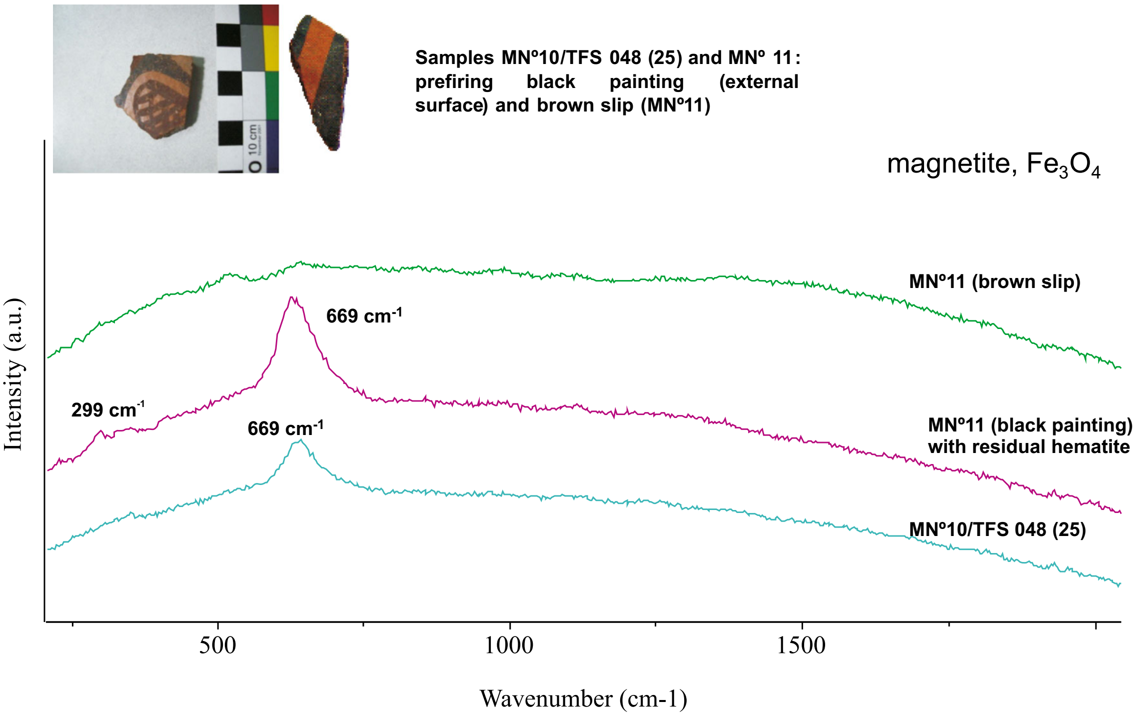


Fig. 9 Raman spectra (632 nm) of magnetite for prefiring black paintings, samples MN°10 and MN°11. MN°11 shows the Raman spectrum for the brown slip with some iron oxide identified (hematite). Sample MN°11 shows some residual hematite in the spectrum at band 299 cm^{-1}

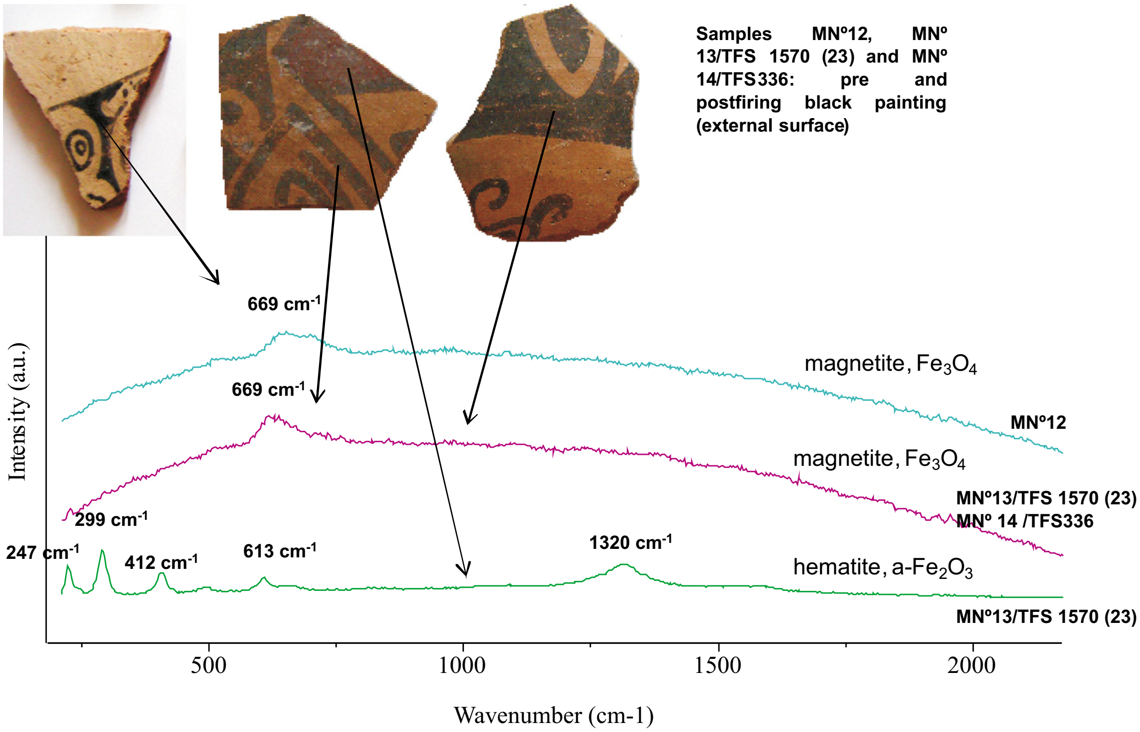


Fig. 10 Raman spectra (632 nm) for magnetite for pre- and postfiring black paintings; also, it is observed for red painting the hematite spectrum in sample MN°13

1996; Speakman and Neff 2002; Stewart and Adams 1999; Stewart et al. 2002; van der Weerd et al. 2004).

Most common white pigments reported in the literature used as chromophores in ceramic decoration are lead carbonate, chalk (calcite), bone white (calcium phosphate) and gypsum (Burgio and Clark 2001; Baldini et al. 2005; Marte et al. 2012; Freire et al. 2016). In a previous paper, results for this white prefiring slip produced calcite ($CaCO_3$) as the main pigment (De La Fuente and Pérez 2008: 181, Fig. 11). An exploration on the white prefiring slip was carried out on sample MN°3/TSF 1015 (24), which gave anatase (titanium dioxide, TiO_2) as the main pigment characterizing this white slip. Figure 4 shows the spectrum recorded for this sample, and Table 2 gives the whole information for the pigments recorded in the whole analyzed pottery sample.

Table 2 A summary of the results obtained by micro-Raman analysis (*N* = 14)

Sample number	Sample type and pigment colour	Ceramic form	Mineral type (Raman)
MN°1/TSF 354	black, red	globular vessel	magnetite, hematite
MN°2/TFS 1570 (23)	black, red, *graffited*	bowl	magnetite, hematite, carbon
MN°3/TFS1015(26)	black, red, white, *graffited*	globular vessel	magnetite, hematite, anatase, carbon
MN°4/TFS 4(26)	black, red	globular vessel	magnetite, hematite
MN°5/TFS28	red, *graffited*	vessel	hematite, carbon
MN°6/TFS 11	red, *graffited*	vessel	hematite, carbon
MN°7/TSF 6 (27)	Black	globular vessel	magnetite
MN°8	Black	globular vessel	magnetite
MN°9	Black	globular vessel	magnetite
MN°10/TFS 048 (25)	Black	bowl	magnetite
MN°11	Black, brown	globular vessel	magnetite
MN°12	black	globular vessel	magnetite
MN°13/TFS 1570 (23)	black, red	bowl	magnetite, hematite
MN°14/TFS 336	black	globular vessel	magnetite

Conclusions

Raman microspectroscopy provides a non-destructive and highly selective analysis of pottery paintings because of its spatial and spectral resolution and it is a key technique for the identification of pigments in archaeological pottery. Aguada Portezuelo archaeological pottery has a complex technical elaboration process, involving at least two different firing steps during which several pigments were used by ancient potters as chromofores to obtain different coloured pre- and postfiring paintings (Nazar and De La Fuente 2016). Attention was given by potters to the marked polychrome and how pigments were prepared, applied to the vessel surfaces and fixed by firing (De La Fuente and Pérez 2008). In this paper, the chemical nature of black, red and white pigments of 14 ceramic samples of Aguada Portezuelo ceramic style has been explored. Pigments are the precursors of pre- and postfiring paintings applied by ancient pottery to these ceramic vessels. Several pigments and its chromophores were inequivocally identified by Raman. The black prefiring pigment if found to be magnetite (Fe_3O_4), mainly produced from hematite and reached during the first firing step by reducing atmosphere in the kiln, whereas postfiring black pigment is fresh magnetite processed by potters and applied directly to the external surface. It is interesting to observe that this is the first time we recorded magnetite for this black pigment, showing the high compositional variability for this colour. The red pigment is hematite (α-Fe_2O_3), obtained both by applying an oxidative atmosphere in the kiln, reached during the second and last firing step, and by directly applying this pigment together with a colloidal solution after firing the vessels. The black plumbed coloured visual effect so-called "graffited" is obtained by firing plants inside the Aguada Portezuelo bowls during the first reducing firing in the kiln. This gives a unique Raman signal of two bands (the G and D bands) very well characteristics of the presence of crystalline and amorphous carbon. Finally, the white prefiring slip is shown to be anatase (TiO_2), again cautioning about the compound variability observed for this pigment.

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