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ARCHAEOMETRICAL CHARACTERIZATION OF PIGMENTS AND PAINTINGS ON PREHISPANIC POTTERY FROM THE REGIONS OF FIAMBALÁ AND CHASCHUIL (CATAMARCA, ARGENTINA).

ABSTRACT

We present the results of analysis of pigments used in slips and designs deployed in ceramic assemblages recovered from archaeological sites located in different environments, expressing the socio-historical process developed in the regions of Fiambalá and Chaschuil during the last 1500 years (Catamarca, Argentina). The sample, formed by fragments of different ceramic styles and natural pigments, was analysed via Raman spectroscopy and X-ray diffraction. Results indicate the continuity in the use of certain pigments (mainly hematite for the red hues, and manganese oxides in combination with magnetite for the black paints), within the different socio-political organizations that inhabited the region from I to XVI centuries, in spite of the diverse shades of colour, which suggests an intentional search linked with their cultural conventions. For the Inca Period, this scenery of continuities in minerals employed for reds and blacks is complemented by the use of new compounds (titanium oxide, apatite, and gypsum) in order to generate the "cream" tones applied as slips, all of which have not been identified for previous moments.

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INTRODUCTION

Archaeology, as a social discipline of collective practice, it demands the development of several and complementary research lines. Combined results enable us to trace and propose models for the different ways of life of past societies. The labor of an inter-disciplinary team (from humanistic and natural sciences) should not be merely declarative, but rather executive: techniques and methods of each discipline are involved. On the one hand, the recovery and selection of samples for specific analysis oriented to solving archaeological problems and questions and, on the other, the election of the most adequate analytical techniques. In this sense, the application of archaeometric techniques must be based on questions, problems, and theoretical views that guide the archaeological research projects.

According to this conception, we present and discuss the results of the pigments' analysis carried out by an inter-disciplinary team composed by archaeologists, chemists, and physicists. The present work is focused on the study of pigments employed in the preparation of images on ceramic vessels recovered from archaeological sites located in the last 1500 years, in the regions of Fiambalá and Chaschuil (western Tinogasta Department, Catamarca, Northwest Argentina). Pigments were analysed by X-ray diffraction (XRD) and Raman spectroscopy (Freire et al. 2016; Vandenabeele 2013). It must be stressed that no archaeometric results can be straightforwardly deduced from X-ray diffractograms and Raman spectra; it is mandatory to analyse these data under the light of an archaeological perspective.

In recent years, the number of archaeometric studies of pigments in archaeological ceramics of the North-West Catamarca area (Argentina) has increased. The different analytical techniques were focused on determining the composition of surface pre and post firing paints used on the pottery of specific ceramic styles or chronologies (see, e.g., Cremonte et al 2003; Puente et al 2017, 2019; Bugliani et al 2012; De la Fuente et al 2018, 2019; Centeno et al 2012). The main contribution of our work is to offer a broader look by focalizing not only within each specific style but also on a wide regional spatiotemporal scale. With this goal, a set composed by 26 samples, representing 22 fragments of painted ceramic vessels and four of natural pigments were selected. The whole set was analysed by Raman spectroscopy, while 20 samples were also tested by XRD. The selection was designed to fulfil two requirements. The first one is the diversity of decorative styles, in order to represent different moments in the regional cultural development before Spaniard conquest. The second one: analysed fragments should belong to sites located in different and contrasting environments (eco-zones) from the wide study area, particularly, valleys, pre-mountain range, transitional Puna, and mountain range, in altitudes between 1200 and 4700 meters above sea-level. These sites had diverse functions from permanent residences to seasonal occupation and present radiocarbon dates that place them in different stages of the regional cultural development, from the development of the first pottery-making societies (ca. I century) until the Inca conquest (ca. XVI century) despite the fact that there are no samples between XI to XIII centuries as the valley of Fiambalá was not inhabited in that lapse due to processes of environmental instability (Ratto et al. 2013).

The archaeological question is focused on identifying which pigments were selected to prepare the paintings in order to determine the changes and continuities in those elections throughout time. These paints were used in the configuration of visual languages expressed in pre-Hispanic pottery. Those visual languages are characterized by presenting particular theme repertoires (types of motifs), spatial compositions and forms of resolution (techniques, sizes, colours) (Basile 2013).

GEOLOGY OF WESTERN TINOGASTA: REGIONS OF CHASCHUIL AND FIAMBALA

According to the Fiambalá 13c (González Bonorino 1972) and Fiambalá 2769-IV (Rubiolo *et al.* 2001) geological sheets, this region presents low mining development and some mineral deposits such as skarn-types (lead, zinc, and copper), metasomatic replacement with potassium presence (tungsten), greisen (lead-zinc and uranium), pegmatitic (mica) and metamorphic (asbestos) can be distinguished. The associated minerals correspond to different types, but magnetite, hematite, manganese compounds, gypsum, carbonates, and calcite can be found. On the other hand, in the region of Chaschuil and Andes mountain range, the *Paso de San Francisco* 2769-II geological sheet, also reports that mining deposits are scarce, and mainly polimetalliferous, such as La Hoyada (Ag-Pb-Zn-Cu-Au) or Cerro Azul (Pb-Zn-Ag-Au), both in the San Buenaventura mountain range, where co-magmatic mineralization is represented by magnetite, hematite, ilmenite, rutile, pyrite, and chalcopyrite. Furthermore, iron mineralization (specular hematite and magnetite) has been reported in Chaschuil's transitional puna. Based on what has been stated here, the regions of Fiambalá and Chaschuil present a geological diversity and high presence of ferromagnesian minerals.

The coloration of geological strata is multi-causal, considering that some intervening factors are the intrinsic colour of minerals and grains composing the rocks, the iron content and its oxidation state, the organic matter content, and the prevailing environment in the formation of the deposit (Dana and Hurlburt 1960). Therefore, ferromagnesian minerals, some oxides, and organic matter are the main rock coloration factors. Siddall (2018) intensively studied the relation between pigments, geology, and archaeology, based on a previous piece of research which resulted in an optical microscopy compendium of pigments (Eastaugh *et al.* 2018). Thus, reddish colours are produced by the presence of oxidized iron, for example, taking the form of hematite (α-Fe_2O_3), which also indicates an oxygen-rich formation environment, as in the case of rivers. Nonetheless, iron can also generate yellow to reddish-brown colours when hydrolysed as oxides, for example, limonite - $FeO(OH).nH_2O$- that provides yellowish or ochre colours, or goethite -$FeO(OH)$- with brownish and reddish colours. Another cause for yellow colour in sediments is the presence of manganese-rich limestone. On the other hand, light colours such as white and whitish, are produced by the presence of abundant quartz or calcium carbonates. Although the easiest way to obtain black is through charcoal, the use of minerals such as manganese is well known, considering its use since the Palaeolithic (Siddall 2018).

PIGMENTS AND VESSELS THROUGHOUT TIME

Paint application was one of the expressive techniques frequently employed for the configuration of designs on pre-Hispanic ceramic surfaces of the regions of Fiambalá and Chaschuil. The selected sample of ceramic assemblages finds correspondence with the different decorative styles that characterize distinct moments within the I and XV century of the Era in western Tinogasta (Catamarca).

Decorated ceramic materials from the beginning of the first millennium are associated with Saujil style (Sempé 1977), characterized by presenting non-figurative designs exclusively solved through incisions and polished lines that, in some cases, are combined with the application of red paints, and are always fired in reducing atmosphere. These designs are distributed mainly on the external surfaces of open and closed vessels. Saujil style has been chronologically located in western Tinogasta between 200 and 800 AD in the archaeological locality of Palo Blanco (see, e.g., González and Sempé 1975; Sempé 1977; Feely and Ratto 2009). It is worth mentioning that the use of paint as an expressive technique is not the prevailing form in the pottery of the first millennium of the Era in western Tinogasta, but the most frequent is the execution of designs through incisions or polished lines. The designs displayed on the scarce painted ceramics of this time are of red colour.

By the middle of the first millennium, new shapes of vessels begin to be incorporated to the repertoire, mostly closed sub-globular, fired in oxidizing atmospheres; the selected expressive technique is fundamentally black and red paint, sometimes over a cream background. These materials are ascribed to Aguada style (González 1998), that, independently of their regional varieties, in our region is characterized by presenting non-figurative designs, felines and felinized animals. Absolute dates obtained by different investigators have widened the chronological frame formerly thought for this material style and suggest a chronological frame between 600 and 1200 years of the Era (Gordillo 2007).

The first half of the second millennium, the visual scenery is diversified, considering the co-existence of distinct contemporaneous decorative styles: Belen and Sanagasta (see, e.g., Serrano 1941, González 1955). In general terms, these are characterized by presenting open and closed vessels, exclusively fired under oxidizing atmospheres. In these vessels' surfaces, non-figurative and figurative designs are displayed through the application of red and black paints, sometimes combined with incisions, excisions, or models (see, e.g., Sempé and García 2007). In this region, these materials are registered in contexts dated after XIII century and extend towards moments of the Inca conquest in the region (*circa* XV century). From that moment on, the new social scenery linked to this conquest is materialized trough decorative styles which are characterized by presenting a combination of local and Inca elements in terms of morphology (*aryballous* and *aryballoids*), compositional structure, type of design and greater diversity of colours (Bray 2000; Orgaz *et al.* 2007).

In sum, the analysed pigments' samples were recovered from vessels' fragments that correspond to different ceramic styles that had relevance and prominence between I and XVI centuries of the Era. In these expressive forms black and red paints stand out, and less frequently creams or whites, which present different shades and were always applied before being fired, indistinctly if they use a reducing or oxidizing atmosphere. Therefore, the selected ceramic assemblage is representative of ceramic vessels that circulated in diverse contexts, environments, and times.

METHODOLOGY: PHYSICOCHEMICAL ANALYTICAL TECHNIQUES

Raman spectroscopy and X-ray diffraction analyses were applied to characterize the samples. These experimental techniques provide complementary information about crystalline compounds on the surface. However, not all compounds have a Raman signal or a diffraction pattern, or signals are not strong enough to identify them. Furthermore, the analysed area by XRD is about 0.5 cm^2 while by Raman spectroscopy is about 10^{-6} cm^2. Samples do not require prior preparation and they are not damaged during the analysis. Neither of these techniques gives quantitative information about the composition.

Raman spectra were acquired on a LabRAM HR Raman system (Horiba JobinYvon), equipped with two monochromator gratings and a charge coupled device detector (CCD). A 1600 g/mm grating and 100 μm hole resulted in a 1.5 cm^{-1} spectral resolution. A He-Ne laser line at 632.8 nm and an Ar laser line at 514.5 nm were used as excitation sources. Laser fluence was adjusted in order to avoid overheating on the sample (around 5 mW). The spectrograph is coupled to an imaging microscope with 10X, 50X and 100X magnifications giving as result a laser spot of 20 to 1 micrometer of diameter on the sample.

X-ray powder diffraction patterns were taken on a Panalytical Diffractometer (Empyream) with a PIXCEL3D detector, using graphite monochromatized Cu Kα radiation (1.54184 Å), at room temperature (1° divergence slit; 1° detector slit and 0.1 mm receiving slit). X-ray measurements were performed using the step mode (0.02° per step) with a 15 s counting time per step, in the range $10° \leq 2\theta \leq 70°$. Phases were identified with the JCPDS-ICDD

Powder Diffraction Database (International Centre for Diffraction Data, PA, USA). The samples were directly mounted, using an Al holder to fix them; the analysis was performed on different areas.

It is worth clarifying that on this occasion we did not analyse natural backgrounds (original ceramic paste) but rather focused the analyses on pigments employed in traces, designs, and slips that homogeneously and completely coloured the vessels. Nonetheless, every colour, both in natural backgrounds as in traces, designs, and slips, was classified in accordance with its tone and nomenclature in the Munsell Soil Colour Chart.

SAMPLES: PIGMENTS, ARCHAEOLOGICAL SITES, AND ENVIRONMENTS

Pigments of painted ceramic vessels represented through 22 fragments recovered in archaeological installations and/or localities where analysed, plus other four samples composed in two cases by natural pigments from the area of La Troya and Palo Blanco's village; and the other two cases by natural grinded pigments contained within non-decorated ceramic vessels. These ceramic assemblages correspond to distinct styles that characterize the different moments of the cultural development in western Tinogasta approximately between I and XVI centuries of the Era (Figure 2 A and B); in addition, the analysed set evidence the diversity of archaeological contexts (villages, temporary sites, burial and agricultural sites) and provenance environments (valley, transitional puna, and mountain environments) in which these circulated. On the other hand, the acquisition of pigment samples was conducted accordingly to the specified methodology of recording. In Table 1 we present the different types of sample, identification acronym, provenance data, and colours sample's) according to the Munsell Soil Colour Chart registered at the moment of recollection (use Figure 1 as support). In the following section we present a brief description of each one of the samples' provenance sites:

1) The archaeological locality of Palo Blanco (#1, Figure 1 and Table 1) is composed by six residential areas (RA) presenting a disperse distribution, and part of them were identified and/or re-defined using geophysical methods and techniques (Ratto et al. 2019). Radiocarbon dates obtained in these RA indicate that they were inhabited in different moments of the first millennium of the era, some in the beginnings and some towards the end of this stage. The 10 analysed samples were recovered from RA 1, 3, 4, 5, 6, and 7, and correspond to decorated vessels (7:10), to natural pigments (1:10) and to undecorated vessels used for grinding pigments (2:10). In Table 1 we present the ceramic styles of the analysed Saujil and Aguada vessels (cases 1-01, 1-02., 1-03, 1-06, 1-07, 1-08 and 1-09 in Table 1), as well as natural pigments (1-04, 1-05 and 1-10) (Figure 2A). Aguada style vessels are mostly recovered after V century associated to engraved and not painted Saujil style vessels.
2) The archaeological site 1 of Cuesta de Zapata (#2, Figure 1 and Table 1) was intervened by González and Sempé (1975) and is a small residential site. Analysed samples correspond to two painted Aguada composed *pucos*, most likely post V century, and an Inca *aryballous*, XVI century (cases 2-11, 2-12, and 2-22 respectively, Table 1).

3) The archaeological site of Punta Colorada (#3, Figure 1 and Table 1) was intervened by Sempé (1983) characterized as a temporary residential site. The two fragments from this site correspond to painted Aguada *pucos* (cases 3-13 and 3-14, Table 1, Figure 2A), whose radiometric dates place them approximately during the VIII century.

4) The archaeological site of Ojo de Agua (#4, Figure 1 and Table 1) is a temporary residential site where pastoral activities were carried out. Radiometric dates placed this site, approximately near the end of the X century (Feely and Ratto 2009). The analysed sample corresponds to a fragment recovered from a painted Aguada composed *puco* (case 4-15, Table 1, Figure 2A).

5) The archaeological site of Canchones de Guanchincito (#5, Figure 1 and Table 1) is an agricultural field on the river terrace of the Guanchin river. It occupies approximately 60 hectares, and the size of each *canchón* is approximately 10x14 meters. Within this agricultural space we have registered sepulchres in circular rock chambers (*cista*) and 22 engraved rocks (Basile and Ratto 2009). This site is chronologically situated in XIV-XV centuries, and the analysed sample corresponds to a Belén *puco* emulating a *quirquincho* (Andean armadillo) (case 5-16, Table 1, Figure 2B).

6) The archaeological site of Las Champas (#6, Figure 1 and Table 1) is a burial site within a circular rock chamber from the XIV century of the Era (Ratto *et al.* 2014). The analysed fragment corresponds to a Belén urn (case 6-17, Table 1, Figure 2B).

7) The archaeological locality of Mishma (#7, Figure 1 and Table 1) comprehends temporary residences and is chronologically set towards the early XV century; it presents material evidence related to the Inca period and mobilized populations (Orgaz et al. 2007). The two analysed fragments correspond to Sanagasta and Belén style simple contour *pucos* (cases 7-18 and 7-19, respectively, Table 1, Figure 2B).

8) The area of La Troya (#8, Figure 1 and Table 1) is a large muddy area (*barreal*) occupied throughout time by productive societies with different types of socio-political organization, from first village societies to the Incas and mobilized populations in the

frame of a domination strategy implemented in western Tinogasta near the end of XIV century. Particularly, the analysed fragment corresponds to a Belén style urn registered in the outskirts of Batungasta, an Inca archaeological site (Orgaz *et al.* 2007) (case 8-20, Table 1). Case 8-21, a sample of natural mud, was also recovered in this area (Table 1).

9) The Inca site of San Francisco (#9, Figure 1 and Table 1) is a *tambo*, a seasonal residential site related to the high-altitude shrine of Incahuasi, in the XV century (Orgaz *et al.* 2007). The three analysed samples correspond to Mixed Inca and Provincial Inca *aryballous* (cases 9-23, 9-24, and 9-25 respectively, Table 1, Figure 2B).

10) The archaeological site of San Francisco-05 (#10, Figure 1 and Table 1) is a seasonal site, and its location is related to the ascent to San Francisco Volcano in Inca times, XV century (Ratto *et al.* 2012). The analysed fragment corresponds to an Inca Provincial *aryballous* (case 10-26, Table 1).

RESULTS

In Table 2 we present archaeometric results of the 26 analysed samples.

In the red tones, hematite (Fe_2O_3) is the main observed compound; ilmenite ($FeTiO_3$) is also present, mostly detected by XRD. Some examples can be seen in Figure 3a (Raman spectra) and 4 (XRD). Hematite Raman spectrum has been extensively reported. However, the complete assignment and understanding are still uncertain. According to its crystalline structure, vibrational modes have been assigned: two A_{1g} modes (224 and 499 cm^{-1}) and five E_g modes (245, 292, 299, 410 and 610 cm^{-1}). But, other two peaks are sometimes present at c.a. 656 and 1320 cm^{-1}, with variable intensity and width. The origin of these forbidden peaks is still controversial. One recent study on a single pure crystal of hematite, attributes the 1320 cm^{-1} band to a two-phonon scattering process, which is an overtone of the longitudinal optical (LO) mode at 660 cm^{-1} (Marshall et al. 2020). However, in some cases, this peak has been attributed to the mineral phase of magnetite (Rosina et al. 2019). Considering XRD results for the samples studied in this paper, we attribute the band around 660 cm^{-1} to hematite. It should be highlighted here the case of sample 2-11 where XRD results detect the combination of hematite and magnetite to obtain a dusky red that could be the result of an impurity of the mineral source. It is interesting that the same combination is registered on the natural pigment (sample 1-10) and the red pigment contained on domestic ceramics (sample 1-05, Table 2).

In summary, hematite and ilmenite were used to obtain the five registered variants of red, both in traces as in slips, through the whole temporal sequence, and including several shades such as reddish brown, dusky red, dark red, weak red, and red (Table 1).

The three varieties of black registered in the analysed samples' designs include dark grey, very dark grey and black tones (Table 1). Iron and manganese oxides were the main compounds used in order to obtain these colours (Figure 3b and Figure 4): magnetite (Fe_3O_4), jacobsite (Fe_2MnO_4), hausmannite (Mn_3O_4), bixbyite (Mn_2O_3), ramsdellite (MnO_2), and hollandite ($BaMn_8O_{16}$). From Fig. 3b, it can be seen that magnetite, jacobsite and hausmannite present similar Raman spectra: only one wide band in the region 600-700 cm^{-1}. Even today identification of the minerals in many Mn oxide samples is not straightforward. In general, powder x-ray diffraction is diagnostic for well-crystallized, monophasic samples. Unfortunately, the crystal structures, and consequently, the powder diffraction patterns are also similar for many of the Mn oxide minerals. In these cases, the combined analysis by Raman spectroscopy and XRD is decisive to obtain a certain assignment. Bixbyite, ramsdellite and hollandite were only detected by XRD.

According to the literature ramsdellite can be formed from groutellite at low temperature (c.a. 250 °C). For further temperature increase, pyrolusite is formed at 330 °C and bixbyite at 450 °C. Finally, hausmannite is formed at 1030 °C. However, thermal stability of Mn oxides has been shown to depend on the grain size, and the crystallinity, among others (Bernardini et al. 2020).

The presence of hausmannite, in Aguada style samples, could indicate a high temperature technology. In some cases, Raman spectroscopy has detected the presence of hausmannite while XRD detected ramsdellite: this apparent discrepancy could be attributed to laser heating during Raman measurements. Carbon based black pigments were not detected in any sample.

Finally, some of the samples presented cream tones in designs and slips. In these cases, titanium oxide (TiO_2), apatite ($Ca_5(PO_4)_3(Cl,F,OH)$), calcite ($CaCO_3$) or gypsum ($CaSO_4 2H_2O$) were detected. They could have been employed to achieve the two registered variants of cream tones (very pale brown and pink) used in the slips, mainly from the second millennium (Table 1).

The results of the natural red pigments' analyses (1-04, 1-05, 1-10, and 8-21, Table 2), which were used in the preparation of paints, indicate the presence of most of the minerals found in the above mentioned decorations: mainly hematite, although ilmenite was also identified. As it was observed for the paints, identified compounds in natural pigments gave as result a diverse set of colours within a wide spectrum of different shades of red: reddish yellow, dark red, red, light reddish brown (Table 1). We have not obtained samples from white or cream natural pigments, but gypsum and calcite, the main compounds of the last ones, can be found in the regional geology. Samples of possible red and black pigments were taken from the de Narváez Mountain range; they are currently under study.

From the above, we can assume that contrasting environments from western Tinogasta offered different raw materials for the preparation of colouring substances that were used in the painting of ceramic vessels, given that the minerals identified through Raman and XRD were registered both in paints as in natural pigments.

DISCUSSION: PIGMENTS, COLOURS, AND SOCIO-HISTORICAL CONTEXTS IN TIME

First millennium pigment samples were recovered from archaeological sites located at different heights in the valley and pre-mountain range. Here, the year 500 of the Era behaves as a temporal node reflecting changes in the colour palettes used by village societies of the first millennium. This diversity decreased once again in the first half of the second millennium. In this section, we explore this journey of 1500 years except for a lapse with environmental instability (XI - XIII centuries).

At the beginning of the first millennium (Temporal range A1, Table 2), the use of paint as an expressive technique on ceramic vessels from the valley and pre mountain range of the region is not dominant; it was limited to red painted designs (Munsell red) on Saujil style vessels, with polished lines on surfaces fired in reducing atmospheres based on the colouration of the resulting paste. This expressive mode continues to be documented in sites of this period. However, from around 500 years of the Era, painting became dominant. It is from this moment onwards, for Aguada style ceramic assemblages, that painted designs started to be documented showing a wide variety of reddish shades, complemented by designs in black and very dark grey tones, and over surfaces fired in oxidizing atmospheres (Temporal range A2, Table2). In order to obtain a large variety of reddish tones of diverse intensity (weak red, dusky red, dark red, and reddish brown), the use of iron oxides as hematite and ilmenite was necessary. Magnetite, another iron oxide, was predominant in black and grey designs, even for the case of vessels fired in oxidizing atmosphere (see below), fundamentally associated to iron-manganese oxides in the form of jacobsite, although we also identified manganese oxides (hausmannite and hollandite). The presence of hausmannite could indicate high firing temperatures (around 1000 °C). On the other hand, it is interesting to highlight the record of a combination of hematite with magnetite to achieve the dark red observed in one Aguada style sample (2-11), also documented on natural pigments analyzed, that could explain the presence of impurities in local sources.

The Sanagasta and Belén style samples from the first half of second millennium, placed within the temporal range B (XIV-XV centuries, Table 2), were recovered in the valley. From this point onwards, the variety of red hues identified in designs and slips notably decrease Only one black hue and two of the five shades of red (red and dark red) documented in previous moments were identified during this period. The Red tones employed for the slips were achieved mainly with hematite, while black designs used magnetite and jacobsite. Although the tones of the employed colours tended to standardize, the identified minerals are the same ones as those in the first millennium (Temporal range A1 and A2, Table 2). On the other hand, Inca style samples dated between XV and XVI centuries (Temporal range C, Table 2), were recovered in the valley, Puna, and mountain range. In all cases, for slips and designs, iron oxides were employed as well as red and dark-red pigments. Jacobsite, magnetite, as well as ramsdellite and bixbyite were detected for black tones. Finally, during the same lapse, several compounds were registered related to the "cream" tones applied as slips in the Inca ceramics of the sample: titanium oxide, apatite, calcite, and gypsum.

We did not find any relation between the ecozone and altitudinal value of the samples' recovery site on the one hand, and detected minerals and compounds on the other. The same compounds (hematite only in one sample mixed with magnetite) are used throughout time to generate the red hues employed both on the designs as on the whole cover. Identical behaviour is observed for black tones, where magnetite and jacobsite were detected all along the studied temporal sequence. Nonetheless, there seems to be a greater variety of compounds for obtaining black hues in samples from the second half of the first millennium and also in vessels recovered from Inca contexts (post XV century), considering the appearance of hausmannite and hollandite, and ramsdellite and bixbyite, respectively.

It is worth highlighting that the persistence of magnetite in black over red designs constitutes a question yet to be answered, considering that this compound is expected to turn red under oxidizing fire conditions. There is no univocal solution to this question. Some authors have proposed a causal factor: a double firing process or a strict control of firing atmospheres in order to induce an intentional change in firing conditions from oxidizing to reducing, in the last minutes of the process (Botto et al. 1998; Lopez 2007, Acevedo et al. 2012; De La Fuente and Pérez Martínez 2018). In contrast, recent experimental pieces of research argue that the persistence of magnetite in black paints could be related to the particle size in the mineral pigment employed, or even that it could indicate particular characteristics of the fire atmosphere, specifically: "*This atmosphere was not sufficiently oxidizing to transform M /magnetite/ in H /hematite/, nor sufficiently reducing to provoke H reduction in the red paint and in the ceramic paste, therefore behaving as a 'neutral' atmosphere*" (Puente *et al.* 2019: 12). This enables them to suggest that pre-Hispanic potters could have developed specific techniques to get finely milled pigments, such as separation by flotation and decantation, in order to obtain the desired shades. In this case, a process of double firing to achieve the persistence of black (magnetite) and red (hematite) colours, would not have always been necessary (Puente et al. 2019). Our results do not enable us to solve this issue but contribute to a discussion that requires the development of experimental research. The experimental design, now in process, should help us to clarify the combination of hematite and magnetite registered in one Aguada style piece (2-11, Table 2) that can be the result of some mineral impurities in local sources as can be deduced from the analyses of the natural pigment samples (1-10, 1-05, Table 2).

On the other hand, the presence of jacobsite may be related to the use of minerals rich in Fe and Mn treated at high temperature before its application or fired at temperatures above

900°C. Or perhaps, considering that it is present in metamorphic geological environments, it was applied directly to the vessels before cooking (Bugliani et al. 2012).

As regards the samples analysed here, jacobsite was registered throughout the whole sequence in vessels fired in oxidizing atmosphere at temperatures above and below 900°C, therefore, we consider that it must have been available in the region as a mineral for direct application

In summary, iron oxides in the form of hematite were the compounds used for the manufacture of red pigments, employed both for slips and designs, and generating diverse tonal ranges (very pale and reddish brown to dark red). These were used within the different socio-political organizations that inhabited the region from I to XVI centuries and were detected in vessels recovered in archaeological sites located in every altitudinal environment (valley, pre-mountain range, puna, and mountain range). On the other hand, manganese oxide in the form of jacobsite in combination with magnetite, were the main compounds employed in the generation of black paints. In Inca times, this scenery of continuities in minerals employed for reds and blacks that transcend the variety of designs, social, and temporal contexts, is complemented by the use of new compounds such as titanium oxide, apatite, and gypsum in order to generate the “cream” tones applied as slips. None of which has been identified for previous moments. The presence of apatite could indicate the use of ground bones. Although it is a component that has been found in other ceramic samples of North-Western Argentina (De La Fuente and Pérez Martínez 2008; Palamarczuk 2007, Acevedo 2011, Marte et al 2012) in our region and, so far, apatite is detected only in Inca style samples.

This first approximation to the use and employment of pigments in western Catamarca managed to answer some questions and generate new inquiries. The first contribution comes from the use of a wide scale, both in the spatial and temporal scope, considering that it enables us to affirm that the use of certain pigments is maintained through time, but presenting changes in their intensity, the way of combining them, and the generated colour palettes, independently of the diverse recovery environments.

First village societies prioritized engraving over painting, which was limited to the use of red, but this situation is reversed in the middle of the first millennium, where Aguada ceramic styles present a diversity of colours, especially red in association with blacks and creams. This chromatic expansion faded during the first half of the second millennium. Owing to the fact that Belén and Sanagasta styles were limited to the use of highly standardized reds and blacks there is a loss of chromatic diversity. With the incorporation of new styles during Inca moments, we observe a large diversity of colours (reds, blacks, creams) again, but keeping a standardization of the achieved shades.

In this way, hematite, magnetite, and manganese oxides, available in local geology and/or in muddy clays, are used throughout time for the generation of “reds” and “blacks”, but tonal varieties, especially for reds, differ with the passing of time. Similarly, white/cream shades are mostly due to the presence of calcite, also available in the environment and used on the cover of vessels of both the first and second millennia of the Era.

We consider that the different shades, obtained by the use of the same mineral, are not only related to different ways of doing and technical choices, but rather with the importance of colour in an Andean worldview, both in current and past communities (Siracusano 2005). In this sense, changes of “colour palettes” in time are in relation to the ways of expressing, communicating, and sharing exercised by societies in the past (Ávila 2011). It is in this point where technology, understood as a social phenomenon, articulates both technical decisions and elections, and those from the supernatural world (1992; Pfaffenberger 1999). Therefore, we argue that the use of the same set of minerals for the generation of diverse or standardized colours responds to different ways of seeing the world, ways that are related to social, political, and religious aspects of societies in the past. These aspects must be thoroughly studied, but raise new questions related to labour organization at different scales, familiar and non-controlled versus specialized and controlled, and their ways to communicate and control. We think that experimentation is a way of approaching the universe of colours for paint preparation, considering that pigment's grinding, use of binders, and firing temperatures, for mentioning some examples, could provide insight to some of the technical processes employed for the obtainment of certain colours, while the articulation of that information with other research lines may enable us to investigate the prevailing cultural conventions along time.

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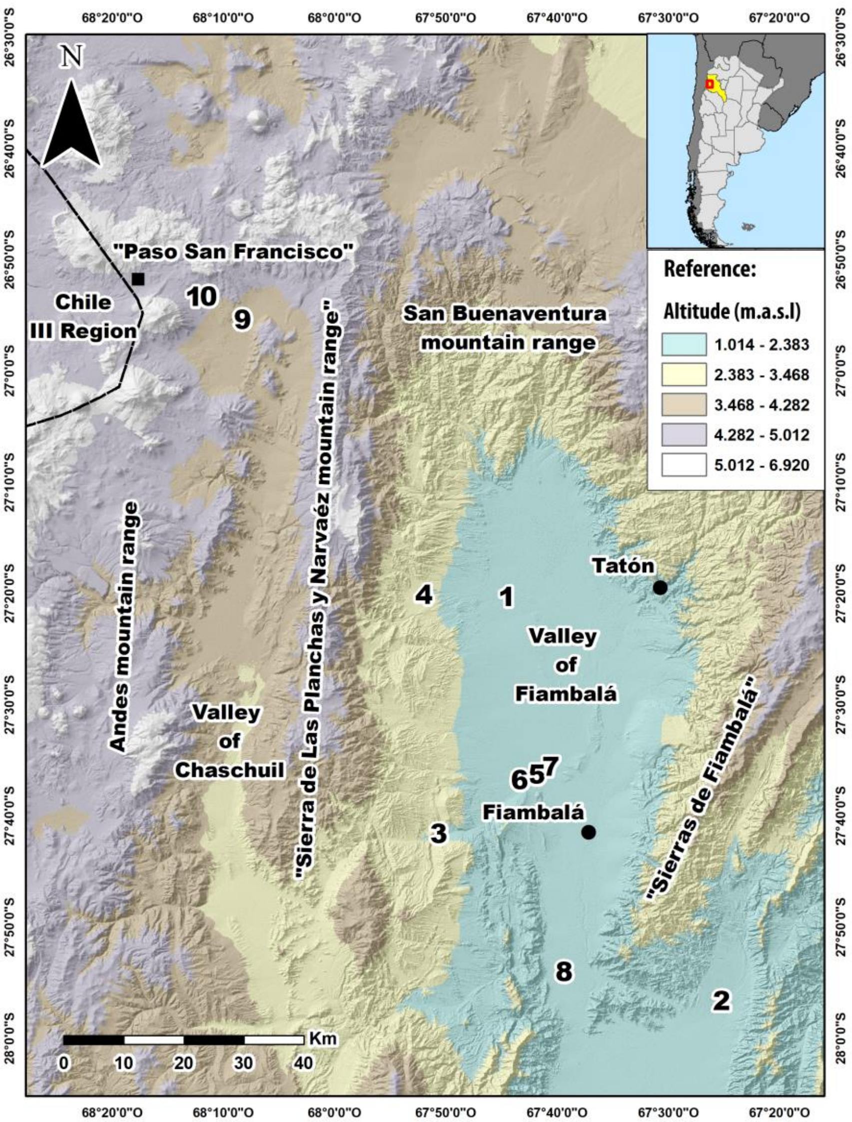

Figure 1: The location of the samples' provenance sites under study. References: (1) Archaeological locality of Palo Blanco; (2) Site 1 of Cuesta de Zapata; (3) Punta Colorada; (4) Ojo de Agua; (5) Canchones de Guanchincito, (6) Las Champas, (7) Archaeological locality of Mishma; (8) area of La Troya; (9) San Francisco; (10) San Francisco-05.

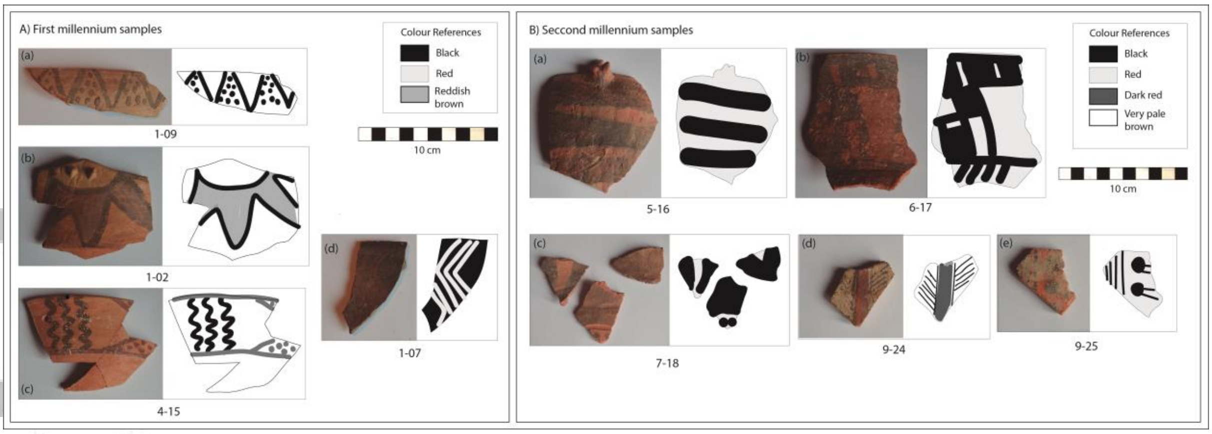

Figure 2: Examples of pottery analysed corresponding to (A) first millennium styles: (a)-(c) Aguada style; (d) Saujil style: (B) second millennium styles: (a)-(b) Belén style; (c) Sanagasta style, (d)-(e) Inca style.

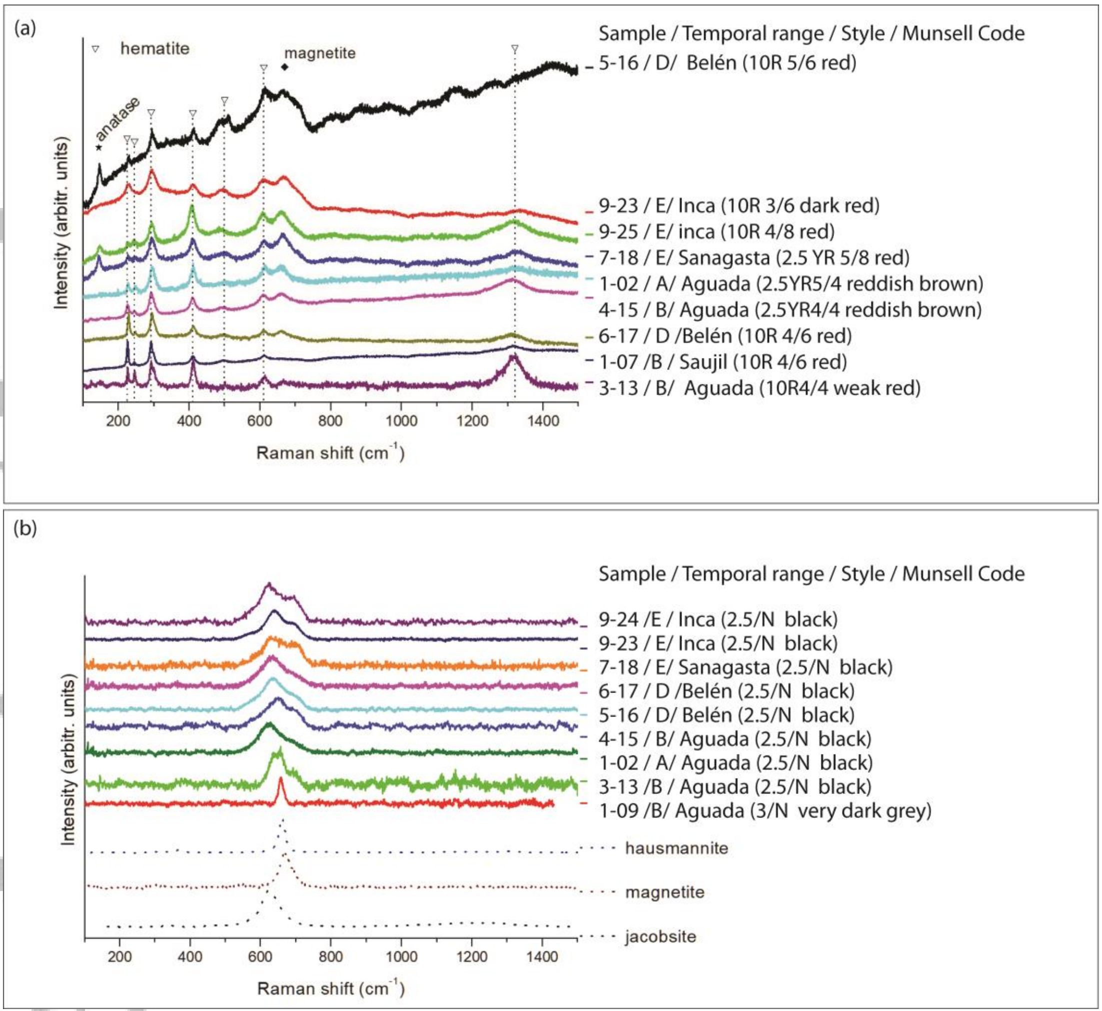

Figure 3: Micro-Raman spectra of the (a) red tones and (b) black tones from some of the archaeological samples analysed.

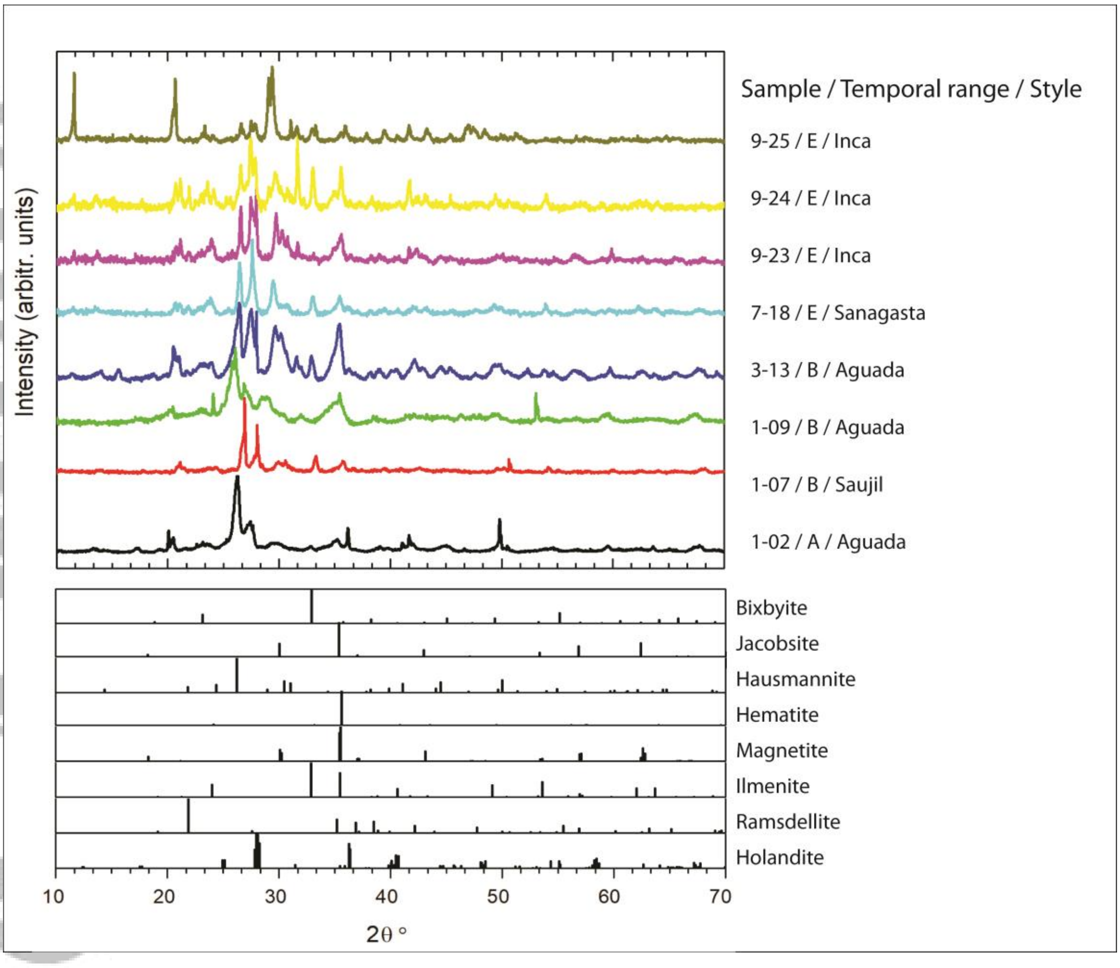

Figure 4: Diffractograms of the red tones and black tones from some of the archaeological samples analysed.

Table 1: Sample presentation including provenance, classification and Munsell colour codes of the original ceramic paste, designs, and slips. References: APB archaeological locality of Palo Blanco; (CZ) Site 1 of Cuesta de Zapata; (PC) Punta Colorada; (OA) Ojo de Agua; (Cch-Gch) Canchones de Guanchincito, (LCh) Las Champas, (Msh) archaeological locality of Mishma; (ALT) area of La Troya; (SF) San Francisco; (SF-05) San Francisco-05.

Type of material	**Archaeological site/ ambient/ altitude**	**Code (archaeological site/ sample n°)**	**Classification of painted vessel or containing pigment (Style and colours)**	**Munsell Soil Colour Chart Codes**				
				Natural or ground pigment	**Ceramic vessel**			
					original ceramic paste	**Painted surface**	**Painted strokes and designs**	
Fragments of painted ceramic vessels	APB, valley, 1900 m.a.s.l.	1-01	Aguada red on original ceramic paste		7.5YR6/8 reddish yellow		2.5YR4/4 reddish brown	
		1-02	Aguada black and red on original ceramic paste		5YR6/6 reddish yellow		2.5YR5/4 reddish brown	C1FG/2.5/N black
		1-03	Aguada black and red on surface painted white			10YR8/3 very pale brown	10R3/4 dusky red	C1FG/3/N very dark grey
		1-06	Aguada blackon original ceramic paste		2.5YR 5/6 red			C1FG/2.5/N black
		1-07	Saujil red on polished lines				10R4/6 red	
		1-08	Aguada black on original ceramic paste		7.5YR6/4 light brown			C1FG/2.5/N black
		1-09	Aguada black on original ceramic paste		5YR6/4 light reddish brown			C1FG/3/N very dark grey
	CZ; valley; 1200 m.a.s.l.	2-11	Aguada red on original ceramic paste		7.5YR6/4 light brown		10R3/4 dusky red	
		2-12	Aguada black and red on original ceramic paste		7.5YR6/4 light brown		10R3/6 dark red	C1FG/3/N very dark grey
		2-22	Inca black and red on surface painted white			7.5YR7/4 pink	2.5YR4/8 red	C1FG/2.5/N black

	PC; valley; 2295 m.a.s.l.	3-13	Aguada black and red on original ceramic paste		7.5YR6/4 light brown		10R4/4 weak red	C1FG/2.5/N black
		3-14	Aguada red on original ceramic paste		5YR6/6 reddish yellow		2.5YR4/4 reddish brown	
	OA, pre-mountain range, 2400 m.a.s.l.	4-15	Aguada black and red on original ceramic paste		5YR6/6 reddish yellow		2.5YR4/4 reddish brown	C1FG/2.5/N black
	Cch-Gch, valley; 1734 m.a.s.l.	5-16	Belén black on surface painted red			10R 5/6 red		C1FG/2.5/N black
	LCh, valley, 1862 m.a.s.l.	6-17	Belén black on surface painted red			10R4/6 red		C1FG/2.5/N black
	Msh, valley, 1750 m.a.s.l.	7-18	Sanagasta black on original ceramic paste		2.5YR5/8 red			C1FG/2.5/N black
		7-19	Belén black on surface painted red			2.5YR5/6 red		C1FG/2.5/N black
	ALT, valley, 1380 m.a.s.l.	8-20	Sanagasta red on original ceramic paste				10R5/6 red	
	SF; puna; 4000 m.a.s.l.	9-23	Inca black and red on surface painted white			10YR7/3 very pale brown	10R3/6 dark red	C1FG/2.5/N black
		9-24	Inca black and red on surface painted white			10YR7/3 very pale brown	10R3/6 dark red	C1FG/2.5/N black
		9-25	Inca black on surface painted red			10R4/8 red		C1FG/2.5/N black
	SF-05; mountain range; 4700 m.a.s.l.	10-26	Inca surface painted red			10R3/6 dark red		
Natural pigment	APB, valley, 1900 m.a.s.l.	1-04	Saujil polished lines containing red pigment	7.5YR6/8 reddish yellow 10R3/6 dark red				
		1-05	Domestic containing red pigment	2.5YR4/8 red				
		1-10	Natural pigment	10R4/6 red				

	ALT, valley, 1380 m.a.s.l.	8-21	Natural clay	2.5YR light reddish brown				

Table 2: Archaeometrical results of the 26 samples analysed according to analytical technique. References: A1 = I-V centuries; A2= VI-X centuries; B=X-XIV centuries; C= XV-XVI centuries; X = not relevant (natural sample); a = Raman; b = XRD; * = no data in XRD.

Code (archaeological site/ sample n°) Table 1	**Classification of painted ceramic vessel or containing pigment (style and colours)**	**Quantity of colours**	**Temporal range**	**Minerals identified in paints according to analytical technique and tones**											
				Red		**Black**						**Cream**			
				ilmenite	hematite	magnetite	jacobsite	hausmannite	bixbyite	ramsdellite	hollandite	titanium oxide	apatite	calcite	gypsum
				$FeTiO_3$	Fe_2O_3	Fe_3O_4	Fe_2MnO_4	Mn_3O_4	Mn_2O_3	MnO_2	$BaMn_8O_{16}$	TiO_2	$Ca_5(PO_4)_3(Cl,F,OH)$	$CaCO_3$	$CaSO_4.2H_2O$
1-07	Saujil red on polished lines	1	A1		**a,b**										
1-01	Aguada red on paste	1	A2	**b**	**a,b**										
1-03	Aguada black and red on white paint	3	A2	**a,b**	**a,b**	**a,b**	**a**							**b**	
1-02	Aguada black and red on paste	2	A2		**a,b**	**a,b**	**a,b**	**b**							
2-11	Aguada red on paste	1	A2		**a,b**	**b**									
2-12	*Aguada black and red on paste	2	A2		**a**	**a**	**a**								
3-13	Aguada black and red on paste	2	A2	**b**	**a,b**	**a,b**	**a**				**b**				
3-14	*Aguada red on paste	1	A2		**a**										
1-09	Aguada black on paste	1	A2			**a,b**	**b**	**a**							
1-06	Aguada blackon paste	1	A2			**a**	**a,b**	**b**							
1-08	Aguada black on paste	1	A2			**a**	**a,b**				**b**				
4-15	*Aguada black and red on paste	2	A2		**a**	**a**	**a**								
5-16	*Belén black on red paint	2	B		**a**	**a**	**a**								
6-17	*Belén black on red paint	2	B		**a**	**a**	**a**								
8-20	Sanagasta red on paste	1	B	**b**	**a,b**										
7-18	Sanagasta black on paste	1	B			**a,b**	**a**			**b**					

7-19	Belén black on red paint	2	B		**a,b**	**a,b**	**a**		**b**						
2-22	Inca black and red on white paint	3	C		**a,b**	**a,b**		**a**		**b**			**a**		
9-23	Inca black and red on white paint	3	C		**a,b**	**a,b**	**a**								
9-24	Inca black and red on white paint	3	C		**a,b**	**a,b**	**a**			**b**		**a**	**a**	**a**	**b**
9-25	Inca black on surface painted red	2	C		**a,b**	**a,b**	**a**		**b**						
10-26	Inca surface painted red	1	C	**b**	**a,b**										
1-10	Natural pigment	1	A1	**b**	**a,b**	**b**								**b**	
1-04	*Saujil polished lines containing red pigment	1	A1		**a**										
1-05	vessel containing red pigment	1	A1		**a,b**	**b**									
8-21	Natural clay	1	X		**a,b**									**b**	**a**