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X-ray diffraction and Raman spectroscopy study of white decorations on tricolored ceramics from Northwestern Argentina

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ABSTRACT

White virgules, commas, and dot designs on tricolored ceramics are sporadically found in different archaeological sites located in Northwestern Argentina area, as *Puna* and *Quebrada de Humahuaca*. This decorating style has been reported in several articles, but few previous archaeometric studies have been carried out on the pigment composition.

Fragments from *Puna* and *Quebrada* archaeological sites, belonging to Regional Development Period (900–1430 AD), were analyzed by X-ray diffraction and Raman spectroscopy in order to characterize the pigments employed. Red and black pigments are based on iron and manganese oxides, as it has been extensively reported for the NW Argentina area. White pigments from white virgules, comma, and dot designs have shown different composition. Hydroxyapatite was found in samples from *Doncellas* site (*North Puna* region), and calcium and calcium–magnesium containing compounds, as vaterite and dolomite, along with titanium containing compounds were detected on samples from *Abralaite* (*Central Puna* region) and *Gasoducto* (*Quebrada de Humahuaca* region). It has been concluded that pigment composition is not characteristic of a unique region.

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1. Introduction

In the Northwestern (NW) region of Argentina, some archaeological sites in *North Puna*, *Central Puna* and *Quebrada de Humahuaca* present ceramics artifacts with a particular type of decorative design usually named as *virgulas* (virgule) or *comas* (commas). This decorative style is usually associated to the so-called *puntos blancos* (white dot) style [1–5]. The use of different layers in order to obtain a polychrome effect is characteristic of this tricolor-decorated ceramics. These ceramics have been observed in this area from Regional Development Periods (900–1430 AD), through Inca domination time (1430–1536 AD) to Spanish colonization [1–3,6].

In the past, the inhabitants of these geographical adjacent regions kept a fluent communication; however, their identities were clearly different. Considering that these potteries had been transported around these regions through prehispanic time until after Spaniard contact, many questions have arisen about the social practices concerning the manufacture [2,7].

In North and Central *Puna* regions these tricolor-decorated ceramics present different shapes, sizes and designs. In *Quebrada de Humahuaca* region, these decorations are present on smaller pieces and usually associated to a black-over-red local style [2,3]. Because of this, some authors have presented tricolored decorations as a variety of black-over-red style, however, it is also considered as a group itself. According to 20th century typical classifications, these decorations have also been labeled with local names as *Alfarcito* polychrome, *Isla* polychrome, *Peña Colorada* tricolored and *Puna* tricolored [8–10]. Typological and stylistic studies have been carried out on these decorations [3,4]; however, few physicochemical analyses were performed [2,11].

Considering the design pattern similarity on fragments from different sites in the *North Puna*, *Central Puna* and *Quebrada de Humahuaca* regions, the aim of this study is to determinate whether there is a unique pigment-composition associated to them.

As multi-technique studies proved to be a powerful tool to characterize pigments, mineralogical and compositional analysis by powder X-ray diffraction (XRD) and Raman spectroscopy (RS) were carried out on archeological ceramic fragments to determine the elemental composition and to identify the crystalline phases present in pigments employed in the decorating external surface.

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2. Experimental

2.1. Site and fragment description

Fragments coming from three different archaeological sites in NW Argentina were analyzed: *Doncellas* and *Santa Ana de Abralaite* sites are located in Jujuy's *Puna* and *Gasoducto* is located in *Quebrada de Humahuaca*. Jujuy's *Puna* is found at around 3400 m elevation. *Doncellas* archaeological site is placed in *Cochinoca* Department, *Guayatayoc-Miraflores* watershed, *North Puna*. *Santa Ana de Abralaite* site is situated on the west side of *Sierra de Aguilar*, *Central Puna*. *Quebrada de Humahuaca* is a ravine found over 2000 m elevation at *Río Grande de Humahuaca* watershed. It is flanked by high hills which separate it from *Puna* region to the West and from valleys to the East. *Gasoducto* is close to *Humahuaca* Town and it was found during a gas line excavation.

Three potsherds from *Doncellas* site were analyzed (Fig. 1). All of them present a reddish slip on the background with black and white designs over it. From the stylistic point of view, all of them were included in *Puna Tricolor* style [3,4]. Sample DO502 is about $4 \times 5 \text{ cm}^2$ decorated with white opened-circles with a black dot inside. Sample DO517 is about $2.5 \times 4 \text{ cm}^2$ decorated with a black wide line over the reddish background and white off centered opened circles which are partially overlaid on the black line. Sample DO1096, about $5 \times 5.5 \text{ cm}^2$ size, is painted with two black lines and some vanished white opened-circles.

Sample AB, from *Abralaite* site, is about $3 \times 4 \text{ cm}^2$ size. Two black V-shaped lines and white thick opened circles are clearly visible over a reddish slip.

Sample GA, from *Gasoducto*, is about $3 \times 4 \text{ cm}^2$ size. One black line, several white thick opened circles and one thick dot are noticeable over a dark red slip.

All the analyzed fragments belong to the time period called Regional Development in NW Argentina (from 900–1430 AD). All potsherds were analyzed by different techniques directly onto the surface, and no previous preparation was needed. As archaeological fragments are unique, valuable and scarce the use of non-destructive methods is particularly important.

2.2. Instrumentation

X-ray powder diffraction patterns were taken on a Philips X'Pert PW3020 diffractometer (Philips, The Netherlands), using graphite monochromatized $\text{Cu K}\alpha$ radiation (1.54184 \AA), at room temperature

(1° divergence slit; 1° detector slit and 0.1 mm receiving slit). The generator was operated at 40 kV and 30 mA. X-ray measurements were performed using the step mode (0.02° per step) with a 15 s counting time per step, in the range $5^\circ \leq 2\theta \leq 70^\circ$. Phases were identified with the JCPDS-ICDD Powder Diffraction Database (International Centre for Diffraction Data, PA, USA). In most cases, the potsherds were directly mounted, using an Al holder to fix them; the analysis was performed on different areas (size $\sim 0.5 \text{ cm}^2$) of interest of the decorated fragments.

Raman microscopy analyses were performed on a LabRAM HR Raman system (Horiba Jobin Yvon), equipped with two monochromator gratings and a charge coupled device detector (CCD). An 800 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 was used as an excitation source. Laser fluence was adjusted in order to avoid overheating on the sample (around 5 mW). The spectrograph is coupled to an imaging microscope with $10\times$, $50\times$ and $100\times$ magnifications. Typically, the laser spot on the sample was about 10 and 3 μm diameter for $10\times$ and $50\times$ magnifications, respectively. An advantage of the microscopic facility is the possibility of separately analyzing different pigmented areas.

For wavelength dispersive X-ray fluorescence (WDXRF) analysis a Analytical Venus 200 MiniLab was used, with a Sc X Ray tube operating at fixed excitation conditions of 50 kV and 5 mA.

3. Results

XRD technique was applied to most of the white decorations but in all cases, some materials from the slip were also analyzed.

The analysis of X-ray diffractograms obtained on samples DO502 and DO1096 from *Doncellas* site showed hydroxyapatite which could be associated to the white pigment. On GA and AB samples the presence of calcium and calcium-magnesium containing compounds, such as vaterite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$), together with titanium oxides (TiO_2), as rutile and anatase, was confirmed by XRD results. Many other minerals were detected, however they are not related to white colorations (see Table 1).

Fig. 2 shows as an example, a comparison between the XRD pattern of one of the samples from *Doncellas* (DO502), AB and GA samples. The more intense peaks of some relevant compounds are indicated according to powder diffraction files: hydroxyapatite, vaterite, dolomite, anatase and rutile.



Fig. 1. Ceramics fragments analyzed from *Doncellas*: a – DO502, b – DO517, c – DO1096, d – *Abralaite* (AB) and e – *Gasoducto* (GA) sites.

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