



The ceramics of Malpaís of Zacapu, Michoacán, Mexico, during the Early and Middle Postclassic periods (900–1450 AD): Micro-chemical characterization of surface paintings

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ABSTRACT

Tarascan ceramic sherds from two Postclassical archaeological sites (900–1450 AD) at the Malpaís of Zacapu, Michoacán, Mexico, were investigated by combining Back-Scattered Scanning Electron Microscopy and Energy Dispersive Spectroscopy (BSEM-EDS), μ -X-Ray Diffractometry (μ -XRD), μ -X-ray Fluorescence Spectroscopy (μ -XRF) and μ -Raman Spectroscopy. These sherds are famous for their forms and decorations although the composition of its raw materials remains so far unknown and focused only on the composition of the ceramic paste. For the purpose of surface decoration characterization, the pigments used in slips and paintings were identified as hematite, magnetite, amorphous carbon, graphite and lignite. Furthermore chemical and molecular structure determination allowed the identification of technological aspects such as the firing temperatures and atmospheres used in ceramics production.

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1. Introduction

The Tarascan state in Pre-Columbian Mexico, roughly covered the geographic area of the present-day Mexican state of Michoacán (Fig. 1). At the time of the Spanish conquest (1521 AD), it was the second-largest state in Mesoamerica. In the lake Zacapu basin, two archaeological urban sites situated on the volcanic complex of the Malpaís of Zacapu, El Palacio (Mich.23) and El Malpaís Prieto (Mich.31), were excavated within the framework of the Uacúsecha project (dir. G. Pereira, CNRS—Centre National de La Recherche Scientifique). The investigations in a ceremonial area (near a pyramid and a ball-court) in Mich.23, and in domestic structures, funeral area and ceremonial zone (near a pyramid and an altar) in Mich.31, allowed the discovery of numerous pottery sherds of the Postclassic period belonging to the Palacio phase (900–1200 AD) and the Milpillas phase (1200–1450 AD).

These two phases represented a long period of socio-cultural changes which led to the emergence of the centralized Tarascan state,

in the middle of the 14th century. Pottery decorations in the two phases are distinct: during the Palacio phase, the majority of the adorned ceramics has plastic decoration; whereas during the Milpillas phase the decorated ceramics show polychrome motives painted in white and red, often associated with a negative decoration, which appears greyish-black [1]. Although Tarascan ceramics are famous for their forms and decorations, the composition of the raw materials remains so far unknown with the few studies available being focused only on the composition of the ceramic paste [2,3].

Studies on surface coatings (slips and paintings) in Mexican ceramics have been mainly concentrated on Maya and Aztec artefacts. Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and X-ray diffraction (XRD) studies have confirmed the use of hematite (Fe_2O_3), pyrolusite (MnO_2), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and calcite (CaCO_3) respectively used as red, black, brown and cream pigments in Mayan potsherds from 300–1400 AD found at the archaeological site of Lagartero (Chiapas, Mexico). The main mineral components of the orange pigment were identified as hematite and calcite, whereas those of the grey pigment were calcite and pyrolusite [4]. Previous studies by photoacoustic spectroscopy in Aztec ceramics from 1325 to 1521 AD revealed an absorption peak around 530 nm characteristic of earth sienna pigment ($\text{Fe}_2\text{O}_3 \cdot (n\text{H}_2\text{O}) + \text{MnO}_2 \cdot (n\text{H}_2\text{O}) + \text{Al}_2\text{O}_3$). This study was carried out in combination with EDS technique

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Fig. 1. Localisation of the Malpaís of Zacapu, at Michoacán state, Mexico.

that confirmed the presence of iron in the pigment under analysis [5]. Other analytical studies were carried out on Maya ceramics from Guatemala and Honduras neighbouring countries, but none has been conducted on Tarascan ceramics [6,7].

The technology involved in the application of pigments and paintings in archaeological pottery is one of the most interesting aspects of ancient ceramic processing. The use of elemental and molecular structure analytical techniques on archaeological pottery research can provide information about the chemical composition of pigments, paintings and clays, as well as on the technological aspects (firing temperature and redox state of the firing atmosphere), and can define the nature and the provenance of the raw materials used in its production [8].

The general aim of the current study is to extend scientific research on the technology of production of ceramics from Michoacán contributing with the identification of the pigments and firing parameters used in their decoration. We focus our analysis on two main purposes. The first concerns the composition of the paintings and slips, and the firing temperature of the ceramics from the Milpillas phase. Another technical question arises about a black slip from the Palacio phase: it is characterized by a particularly brilliant, almost metallic lustre, resembling the so-called Plumbate surface appearance, originally known in the Maya material culture in the region of Soconusco, in the Pacific slope of southwest Guatemala [9–11]. Instrumental Neutron Activation Analysis proved that it may represent in fact a locally produced imitation of the Maya Plumbate type (H. Neff and M.D. Glascock, personal communication, February 10, 2015). In order to better understand the transfer of technological know-how in pottery manufacturing between these two

cultural areas it is fundamental to determine whether the potters could perfectly mimic the original Maya ceramics or if they had to adapt their “recipe” for the local production and the consumption in Zacapu. The second main question concerns the negative technique: how was it made? According to the commonly accepted hypothesis, it would involve, after a first firing, a surface application of a thin layer of clay of the parts of the motif not to become blackened. A second firing of the pottery would then be carried out in order to obtain a carbon smudging of the unprotected areas [2]. This technique is being currently used in pottery workshops of Michoacán using a mixture of clay, water and beeswax. To achieve these aims, μ -X-ray fluorescence (μ -XRF), BSEM-EDS, μ -XRD and μ -Raman techniques were used. The investigation of organic and inorganic pigments is the dominant issue in the ceramic analysis using Raman spectroscopy. This technique allows the identification of crystalline and amorphous compounds, and the discrimination of the mineral phases without the interference of matrix signal [6,12–14]. Nevertheless the fluorescence effect in Raman spectroscopy may hamper the identification of the pigments characteristic bands and in these cases XRD could represent a good complementary tool although limited to the identification of crystalline compounds. X-ray fluorescence technique is a common technique used in the determination of pigments elemental composition and trace elements that can provide relevant information on the provenance of raw pottery materials [15,16]. SEM-EDS provides morphological characterization and elemental distribution maps of the decorated surfaces. The non-destructive high resolution and sensibility in the identification of trace elements and organic and inorganic compounds strongly recommend the application of these techniques in the archaeological field.

2. Materials and methods

2.1. Materials

Selected sherds for analysis are shown in Fig. 2 while the whole set is described in Table 1. Concerning the study of the composition of the paintings and slips and the firing temperature, seven sherds (1, 2, 5, 9, 10 and 7, 8) plus an imported one (4) were selected. The selected sherds are well preserved and representative of the range of decorations and colours (Malpaís Negative on Red Polished and Malpaís Negative on Polychrome Polished types) used during the Milpillas phase to analyse the white and red colours, and 2 undecorated sherds to study the slips (Milpillas Polished type). One extra sherd of the same phase was also analysed in order to verify if the pigments are the same or not as it represented a fragment of an imported ceramic (Toro Red and Orange Polychrome type). Concerning the study of the negative technique, four of the polychrome sherds were analysed (1, 2, 5, 10). Finally, one sherd of the local Plumbate was selected as well as one fragment of a jar discovered in the same context and which presented a brilliant black deposit that could have been used to prepare the slip (3 and 6).

2.2. Methods

Analyses were carried out directly on ceramics surfaces combining μ -XRF, BSEM-EDS, μ -XRD and μ -Raman techniques.

2.2.1. μ -X-ray fluorescence analysis

Bruker's M4 Tornado μ -XRF spectrometer was used. The excitation of fluorescence radiation is performed by a Rh side window X-ray tube with a polycapillary lens offering a spot size down to 25 μ m combined with high excitation intensity. Detection of fluorescence radiation was performed by an energy-dispersive silicon drift detector with 30 mm² sensitive area and energy resolution of 142 eV for Mn-K α . The X-ray generator was operated at 50 kV and 300 μ A. Analyses were carried

out under 20 mbar vacuum conditions. Spectra acquisition and evaluation were carried out using Esprit software from Bruker.

2.2.2. Back-scattered scanning electron microscopy with energy dispersive spectroscopy

BSEM-EDS using a Hitachi S-3700 N interfaced with a Quanta EDS microanalysis system. The Quanta system was equipped with a Bruker AXS XFlash® Silicon Drift Detector (129 eV Spectral Resolution at FWHM/Mn K α). Standardless PB/ZAF quantitative elemental analysis was performed using the Bruker ESPRIT software. The operating conditions for EDS analysis were as follows: BSEM mode (BSEM), 20 kV accelerating voltage, 10 mm working distance, 120 μ A emission current. The detection limits for major elements (>Na) were in the order of 0.1 wt.%.

2.2.3. μ -X-ray diffraction analysis

μ -XRD was used to identify crystalline phases. A Bruker AXS D8 Discovery XRD with the Da Vinci design with a Cu K α source operating at 40 kV and 40 mA and a Lynxeye 1-dimensional detector was used. Scans were run from 3 to 75° 2 θ .

2.2.4. μ -Raman analysis

μ -Raman analyses were undertaken directly on the ceramics surface using a Horiba-Jobin Yvon XploRA confocal spectrometer, operating at wavelength of 785 nm, with maximum incident power of 0.2 mW to avoid structural modification due to overheating. Using a 100 \times – magnification objective with a pinhole of 300 μ m and an entrance slit of 100 μ m, the scattered light collected by the objective was dispersed onto the air-cooled CCD array of an Andor iDus detector by a 1200 lines/mm grating. Raman microscopy was performed in a range of 100–1800 cm^{−1}. Spectra deconvolution was performed using LabSpec (V5.78). The identification of pigments was made with Spectral ID™. Spectra obtained from ceramic samples may present small shifts to the wavenumber and/or larger widths of the bands because of the firing process, which causes a partial loss of crystallinity and mineralogical transformations.

3. Discussion and results

3.1. Palacio phase (900–1200 AD)

In sherds 3 and 6 μ -Raman spectroscopy revealed the presence of two broad bands at 1320 and 1570 cm^{−1} and at 1338 and 1597 cm^{−1} respectively (Fig. 3). Carbon characteristic bands are at 1320 and 1600 cm^{−1}. The band at 1320 cm^{−1} has been shown to broaden and shift to higher wavenumbers as the material becomes less crystalline, and in highly disordered carbon the band at 1600 cm^{−1} can disappear completely. The very broad nature of the bands recorded on this sample indicates the presence of amorphous carbon [17]. The lack of the phosphate Raman band at 961 cm^{−1} [18] and of a phosphorus peak in the EDS spectra, indicates that the carbon used is derived originally from charred plant material instead of charred bone. In sherd 3 the characteristic band of graphite at 1580 cm^{−1} was also identified accompanied of the 1323 cm^{−1} band (Fig. 3). The presence of the second band is an indication of a less crystalline carbonaceous material since highly crystalline graphite has only one band at 1600 cm^{−1}. This mineral is certainly responsible for the particularly brilliant appearance, almost metallic of the black slip in sherd 3, characteristic of the Plumbate type ceramics, originally known in the Maya area [9–11]. In this area, this slip is composed by iron and alumina [10]. μ -XRD investigation of the surface slip of sherds 3 and 6 confirmed the presence of poorly crystallized graphite together with quartz and feldspars of albitic composition.

3.2. Milpillas phase (1200–1450 AD)

Red pigments were found on samples number 1, 2, 4, 5, 9, 10. The red decorated areas were identified as hematite (Fe₂O₃) from the distinct



Fig. 2. Representative Tarascan ceramic sherds under study.

Table 1
Sample description.

| Sherd | Phase | Site (context) | Form | Ceramic type | Colours |
|-------|-----------|-----------------------------------|---------------------|---|--|
| 1 | Milpillas | El Malpaís Prieto (elite house) | Tripod bowl | Malpaís negative on red polished | Red slip Greyish-black negative |
| 2a/b | Milpillas | El Malpaís Prieto (elite funeral) | Jar | Malpaís negative on polychrome polished | Red painting White painting Greyish-black negative Lustrous black slip |
| 3 | Palacio | El Palacio (ceremonial area) | Miniature jar? | Plumbate | |
| 4 | Milpillas | El Malpaís Prieto (elite funeral) | Bottle with handles | Toro red and orange polychrome | Red painting Orange slip |
| 5 | Milpillas | El Malpaís Prieto (elite funeral) | Tripod bowl | Malpaís negative on polychrome polished | Red painting Light red painting White painting Greyish-black negative Lustrous black deposit |
| 6 | Palacio | El Palacio (ceremonial area) | Jar | Unknown | |
| 7 | Milpillas | El Palacio (ceremonial area) | Bowl | Milpillas polished | Red slip Black slip |
| 8 | Milpillas | El Malpaís Prieto (common house) | Bowl | Milpillas polished | Brown-red slip Black slip |
| 9 | Milpillas | El Malpaís Prieto (elite funeral) | Bowl | Unknown | Red painting White painting |
| 10 | Milpillas | El Malpaís Prieto (elite funeral) | Tripod bowl | Malpaís negative on red polished | Red slip Greyish-black negative |

Raman bands at 225, 290, 405, 500, 610 cm^{-1} [19]. μ -Raman analyses of individual dark red particles in the red matrix show strong bands of hematite. Thin coatings of paint matrix give weak spectra and are identified from the major bands at 225, 290 and 405 cm^{-1} only.

In the hematite spectra of samples 1, 2b, 5 and 10 a small band at 660 cm^{-1} is clearly visible in Fig. 4 and can be assigned to the strongest band of magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) [20].

According to Gosselain, ceramics fired in open fires or basic pit kilns achieved maximum temperatures of 850–900 °C and oxidizing conditions [21]. At or below these temperatures most iron oxides are converted to hematite, thus creating the red colour seen on the ceramic samples. Temperatures exceeding 1000 °C are required to convert hematite back to magnetite [22,20]. Even under controlled conditions, temperatures would not have exceeded 950 °C and would not be high enough to convert hematite into magnetite. The magnetite particles still remaining in the red paint of samples 1, 2b, 5 and 10 must hence be part of the original paint mixture.

In the imported sherd 4, XRF spectra has shown the presence of iron and bromine peaks in red painting and orange slip areas respectively (Fig. 5). Bromine presence has been recently detected in archaeological materials such as Roman glass [23]. In natural systems, bromine is usually bonded to alkaline metals such as calcium in salts and is abundant (still as a trace element) in modern seawater, where it can reach concentrations up to 70 $\mu\text{g/g}$ [23]. μ -XRD results confirms the association of Br as detected by μ -XRF with crystalline calcite in sherd 4. It is interesting to note that with SEM investigation we could find abundant well preserved remains of marine microfossils (foraminifera) in the same sample (Fig. 6). Elemental EDS mapping of red and orange areas in the surface slip of sample 4 also confirmed Fe-enrichment in the red bands.

In sherd 5 hematite was found in both red and light red paintings.

Raman spectra obtained in the monochrome sherd 7 revealed the presence of amorphous carbon on the black slip.

In the case of the negative and polychrome decoration, the question of a preparatory drawing was laid because of the complexity of the technique. The sherds were examined under grazing white light to look for variations in the microtopography, then under infrared light

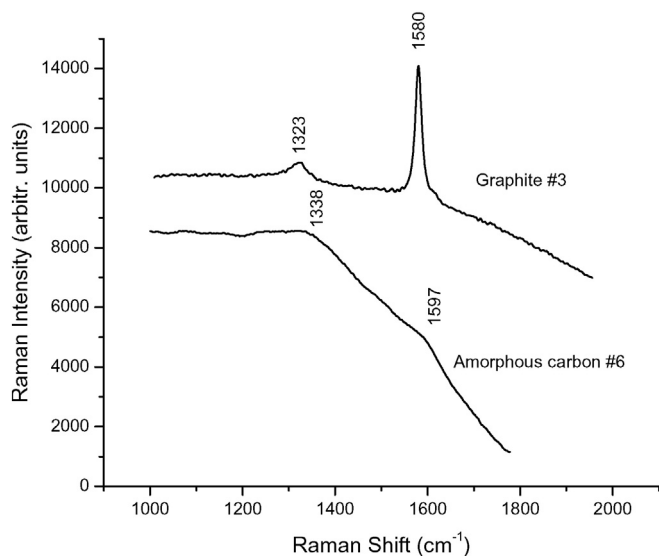


Fig. 3. Raman spectra obtained from pottery sherds number 3 and 6. Amorphous carbon was identified in both sherds. Graphite was found in Plumbate type jar number 3.

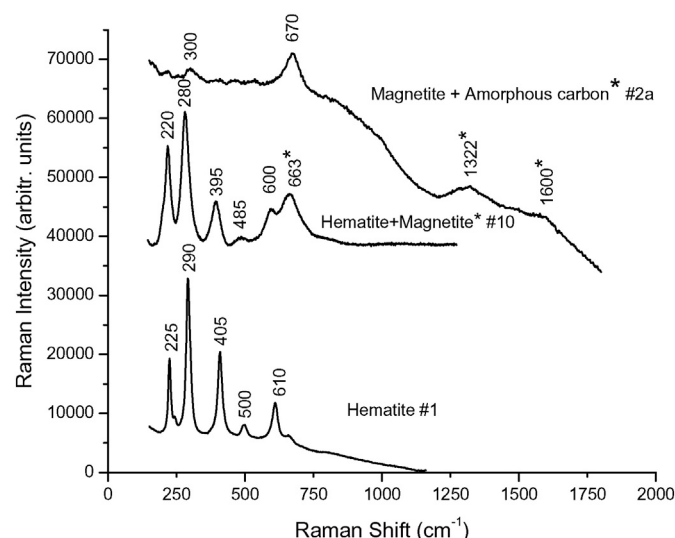


Fig. 4. Raman spectra obtained from pottery sherds number 1, 2a and 10.

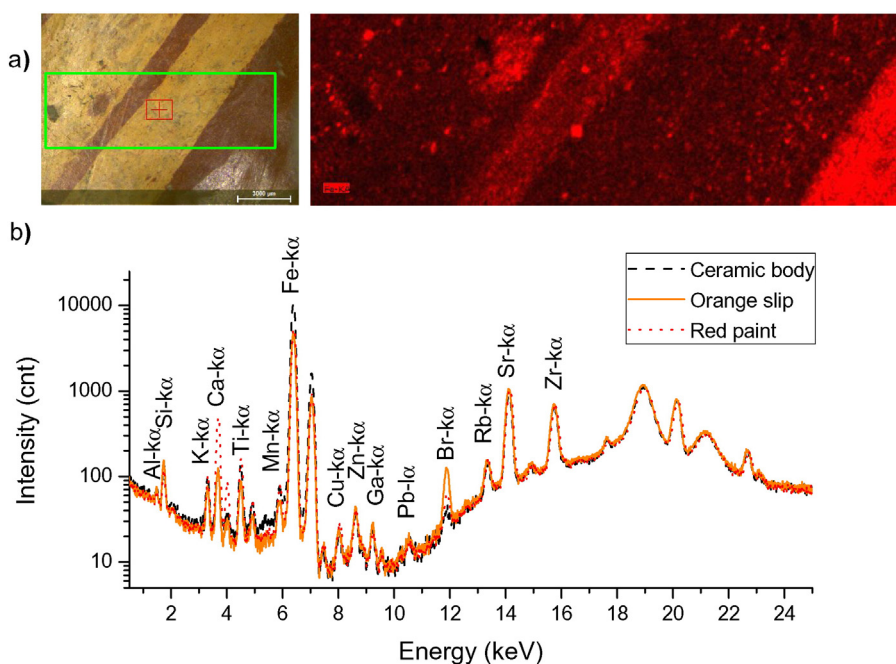


Fig. 5. (a) Sherd 4 and respective Fe- α mapping obtained by XRF. The presence of iron is marked in red (b) Spectra comparison of ceramic body, red paint and orange slip obtained at sherd 4 by XRF.

(940 nm) but no evidence of underlying drawings in decorations could be observed.

Concerning the greyish negative decoration characterization, lignite was detected by μ -XRD in sample 1 (Fig. 7) while amorphous carbon was identified by μ -Raman in samples 2 and 10. Magnetite large broad Raman band at 670 cm^{-1} [24] was also detected on sherd 2b.

Furthermore, individual mineral grains of TiO_2 in the form of anatase on samples 1, 2, 4, 5 and 9, and less frequently in the form of rutile in sample 5 and quartz (SiO_2) on samples 2 and 4 appeared to derive from the ceramic paste underlying the pigment layers (Fig. 8). The presence of anatase was confirmed by μ -XRD in samples 1, 2a and 9. At low temperature, anatase is the most common polymorph of titanium dioxide, stable in $600\text{--}900\text{ }^\circ\text{C}$ range, whereas above this temperature threshold anatase converts into rutile, depending on grain size, atmosphere and nature and amount of impurities [25]. Therefore, the presence of anatase may indicate a firing temperature lower than $900\text{ }^\circ\text{C}$. The finding of rutile could suggest that the firing of sherd 5

may have been carried out at a higher temperature close to the anatase/rutile transition temperature.

Samples of the Milpillas phase show strong peaks of well-crystallized cristobalite, which is a high temperature quartz polymorph. In ceramic manufacturing, conversion of quartz to cristobalite is indicative of firing temperatures exceeding $1100\text{ }^\circ\text{C}$ for long periods of time in the kiln. This would not be compatible with the simultaneous detection of calcite and of well preserved remains of calcitic microfossils in the ceramic paste of many sherds under study. Cristobalite minerals, though, are common in sediments and soils derived from volcanic rocks which are common in the geology of the investigated region. It is therefore likely that the detected cristobalite represents a detrital component of the pottery rather than a product of firing processes bearing in mind also that firing temperature exceeding $1000\text{ }^\circ\text{C}$ were not typical of pre-hispanic pottery technology in central America.

Results obtained by μ -Raman and μ -XRD techniques are summarized on Table 2.

4. Conclusions

This study is the first one investigating the colouring materials of the ceramics from Michoacán. The combined analytical approach using atomic spectrometry (μ -XRF) with electron microscopy + EDS, μ -XRD and μ -Raman spectroscopy brings valuable information at various levels.

For the Palacio phase (900–1200 AD), μ -Raman spectroscopic analysis indicates the use of graphite to give the lustrous aspect to the slip of the local version of Plumbate ceramic (sherd 3). The amorphous carbon also found in this sherd was certainly originated in the smudging at the end of the firing process. The other jar (sherd 6) contains no graphite, only amorphous carbon, so it cannot be associated to the production of this type of decoration. Hitherto, it is not possible to determine if there was a technical transfer from the Maya region of Soconusco to Michoacán, or it represents a simple imitation of products from commercial trade involving the two regions. In both cases, we need to consider that contact could be established in stages, for example via the Toltec people inhabiting central highlands.

For the Milpillas phase (1200–1450 AD), the combined μ -XRF, SEM-EDS, μ -XRD and μ -Raman analysis indicate the use of amorphous

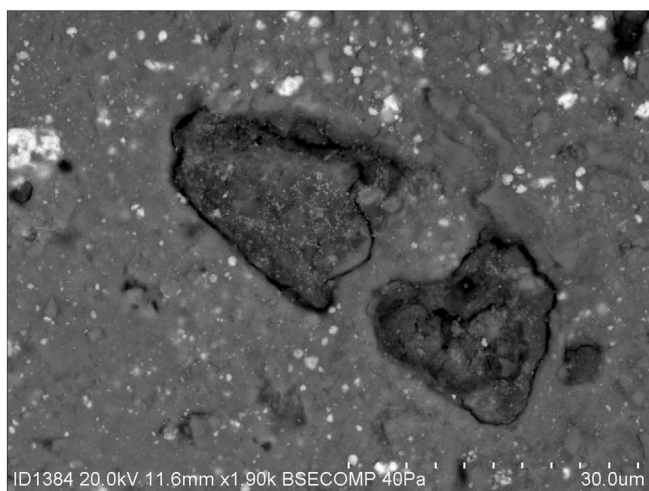


Fig. 6. BSEM image of ceramic paste with well preserved relics of Foraminifera marine microfossils obtained from sherd 4.

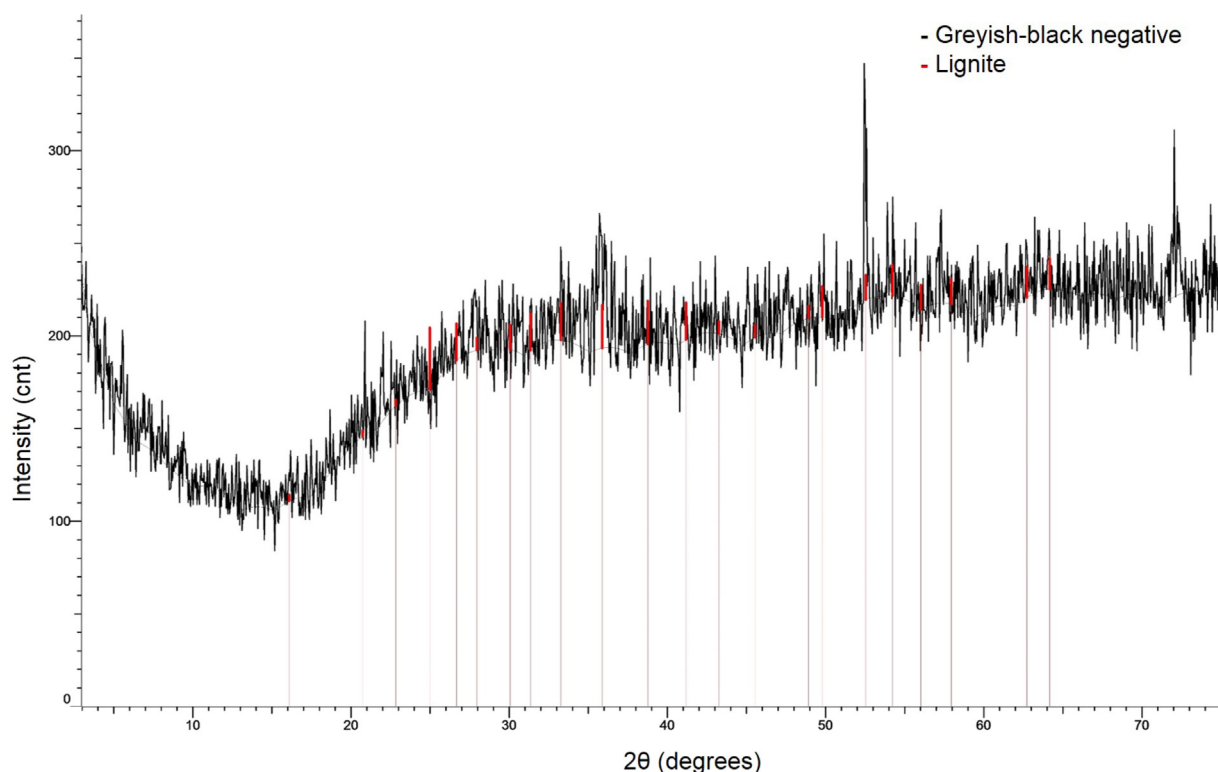


Fig. 7. XRD Pattern from greyish-black negative showing lignite obtained in sherd 1.

carbon, hematite and magnetite based pigments. Back-scattered Electron Microscopy with EDS mapping revealed how the pigments are not evenly distributed within the painted slip but occur in grains and patches.

All the red colours are due to a hematite-based pigment. Thus, the light red painting appears to be obtained from the same preparation as the one used for red paintings and slips but it is certainly diluted to obtain a more fluid texture, giving it a lighter and more transparent aspect. Nevertheless the frequent presence of the Raman band of magnetite in the hematite spectra of the red paint suggests that magnetite was used as raw material and that firing was carried out at low temperatures (600–1000 °C) and oxidizing conditions. The presence

of titanium dioxide in the form of anatase again indicates a firing temperature below 900 °C.

The presence of carbon in the greyish black negative decorations and black slip suggests a second firing under a reducing atmosphere, which did not last long enough to transform the hematite in magnetite within the ceramics paste. Negative decoration was obtained through smudging. The same technique was also used in the production of the monochrome ceramics (sherds 7 and 8).

The imported pottery sample (sherd 4) (foreign origin confirmed by petrographic analyses) revealed the presence of bromine in the orange slip. This result could support a hypothesis of a possible origin of the clays from marine sedimentary deposits which explains the widespread presence of relics of marine foraminifera microfossils in the ceramic paste observed by SEM [26]. It raises questions on the variability of supply of raw materials between the region of origin of this sherd and those produced near the Malpaís of Zacapu.

These results are the first step in understanding the techniques used for pigment preparations and ceramic decorations of the Palacio and Milpillas phases, but also in identifying the origin of the raw materials used in pottery production. Indeed, while iron and titanium oxides are very common in magmatic rocks of volcanic regions such as the lake Zacapu basin, the same cannot be said for bromine, which is found mainly in marine environment, nor for graphite presence. The continuation of the study of the origin of these raw materials is expected to highlight exchanges between the Zacapu area and other regions in Early and Middle Postclassic periods, at the moment still unknown.

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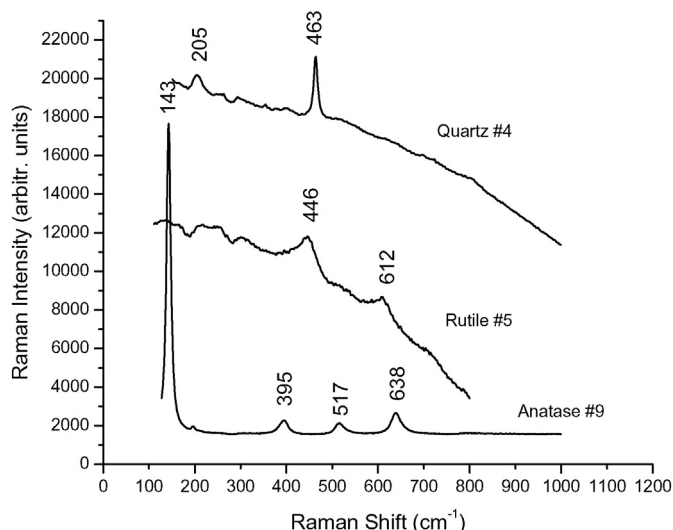


Fig. 8. Raman spectra obtained from pottery sherds 4, 5 and 9.

Table 2

Mineralogical phases detected by μ -Raman spectroscopy and μ -XRD on the samples. Albt: albite; Amorph: amorphous; Ant: anatase; Cal: calcite; Car: carbon; Crn: corundum; Crist: cristobalite; Dis: disordered; Enst: enstatite; Graph: graphite; Hem: hematite; Ilm: ilmenite; Lign: lignite; Mag: magnetite; pyroxene: Pyrx; Qtz: quartz; Rt: rutile; Sil: silica.

| Samples | Colours | XRD | Raman |
|---------|--------------------|-----------------------------------|---|
| 1 | Red | Hem Mag Pyrx Ant Albt | Hem Ant |
| | Greyish-black | Lign | Hem Mag |
| 2a | White | Crist | Hem Ant |
| | Greyish-black | Dis Graph Crist Ant | Amorph Car |
| b | Red | Hem Mag | Hem Mag Qtz |
| | Greyish-black | | Amorph Car Mag Qtz Graph Amorph Car |
| 3 | Black | Graph Qtz Albt | Graph Amorph Car |
| 4 | Red | Hem Qtz Cal | Hem |
| | Orange | | Qtz Ant |
| 5 | Red | | Hem Mag Rut |
| | Light red White | | Hem Ant |
| 6 | Black | Dis Graph Albt Qtz Enst | Amorph Car |
| 7 | Black | | Amorph Car |
| 8 | Black | | Amorph Car |
| | Brown | | |
| 9 | Red | | Hem |
| | White | | Ant |
| 10 | Red | | Hem Mag Sil |
| | White | | Hem Mag |
| | Greyish-black | | Amorph Car |

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