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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Micro-chemical characterization of surface paintings

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Introduction

- Ceramic sherds belonging to two archaeological sites dated from the Early and Middle Post-classic periods (900-1450 AD) and situated on the Malpaís of Zacapu, in the Mexican state of Michoacán (Fig. 1), have been investigated by a combined multi-analytical approach.
- The ceramic material has been excavated within the framework of the Uacúsecha project (directed by G. Pereira, CNRS/MAE/CEMCA) and belongs to two historical phases: the Palacio phase (900-1200 AD) and the Milpillas phase (1200-1450 AD).
- They represent a long period of cultural changes which led to the creation of the centralized Tarascan state, in the middle of the 14th century. While at the Palacio period painting decoration on ceramics was rare (Fig. 2), the Milpillas pots regularly exhibited a polychrome white and red painting associated to negative decoration (Figs. 4 and 5).

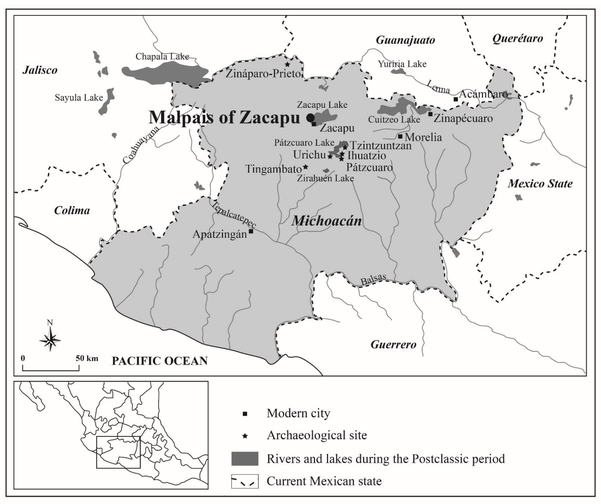

Fig. 1 - Location of Malpaís of Zacapu at Michoacán, Mexico.

Objectives

A multi-analytical approach has been applied to the ceramics under study to shed light on the technological production technique, as far as the choice and the use of raw materials intended for the surface covers (slips and paintings), as well as the master's skill during the firing process (temperature, atmosphere, smudging) are concerned.

Experimental

- µ-XRF was performed using Tornado M4 from Bruker, equipped with a Rh tube with a poly-capillary lens and a SDD detector with energy resolution of 142 eV for Mn-Kα. Analysis were carried out at 50 kV, 300 µA under 20 mbar vacuum conditions.
- BSEM-EDS using a HITACHI S3700N 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/MnKα). 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 µA emission current. The detection limits for major elements (>Na) were in the order of 0.1 wt%.
- Raman analyses were undertaken using a Horiba-Jobin Yvon XploRA spectrometer operating at 785 nm. Scattered light was collected by a 100 x objective with a pinhole of 300 µm and an entrance slit of 100 µm, and dispersed onto an 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}. The identification of pigments was made with Spectral ID ™.

Results

Palacio phase (900-1200 AD) – El Palacio archaeological site

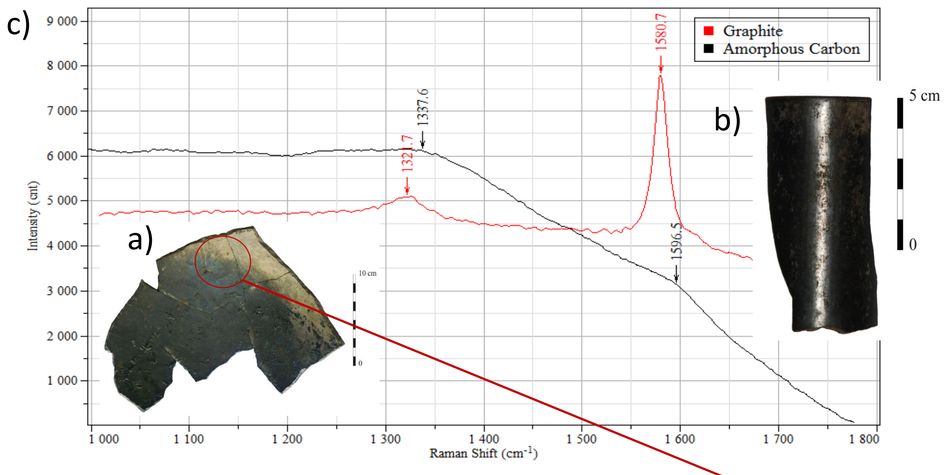

Fig. 2 - (a) Ceremonial jar. Unknown type. (b) Ceremonial jar? *Plumbate* type. (c) Raman spectra obtained pottery sherds. Amorphous carbon was identified in both sherds. Graphite was found in *Plumbate* type jar.

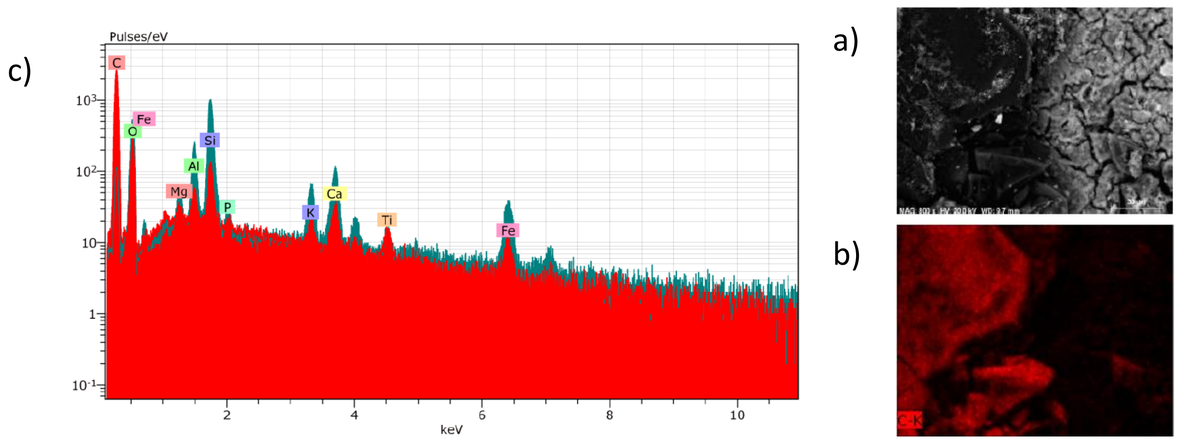

Fig. 3 - (a) Surface observation obtained by SEM. (b) C-Kα elemental mapping obtained by EDS. (c) Comparison of EDS spectra revealing the presence of a higher amount of carbon on the darkest region of the sherd.

Milpillas phase (1200-1450 AD) – Malpaís Prieto archaeological site

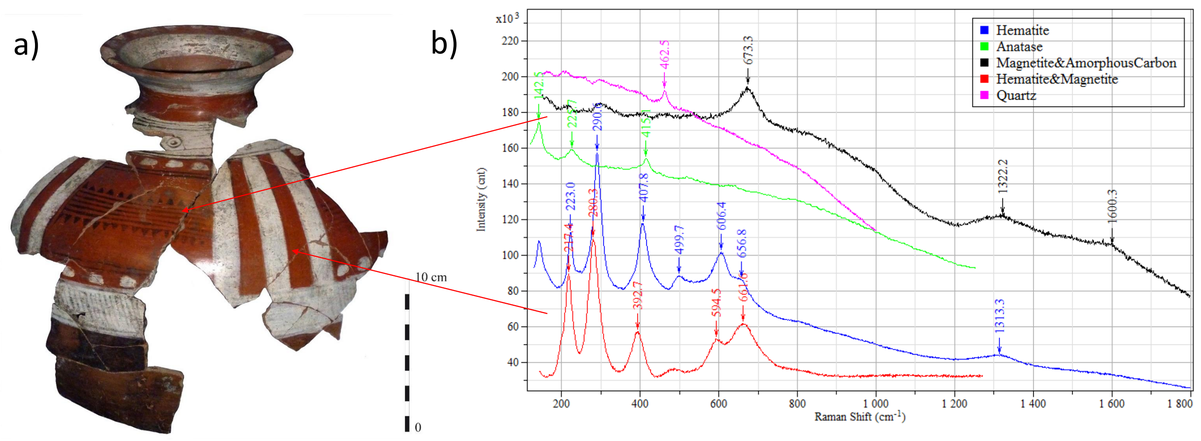

Fig. 4 - (a) Jar used in an elite funeral context. *Malpaís negative on polychrome polished* type. Malpaís Prieto archaeological site. (b) Raman spectra obtained from different colored areas. Hematite was identified on red paint, with dark particles of magnetite dispersed throughout the red material. A small band at 660 cm^{-1} is assigned to Magnetite in the Hematite. Magnetite and amorphous Carbon were detected in greyish black negative decoration. Individual particles of Quartz and Anatase appear to derive from the underlying ceramic paste in the pigment layers.

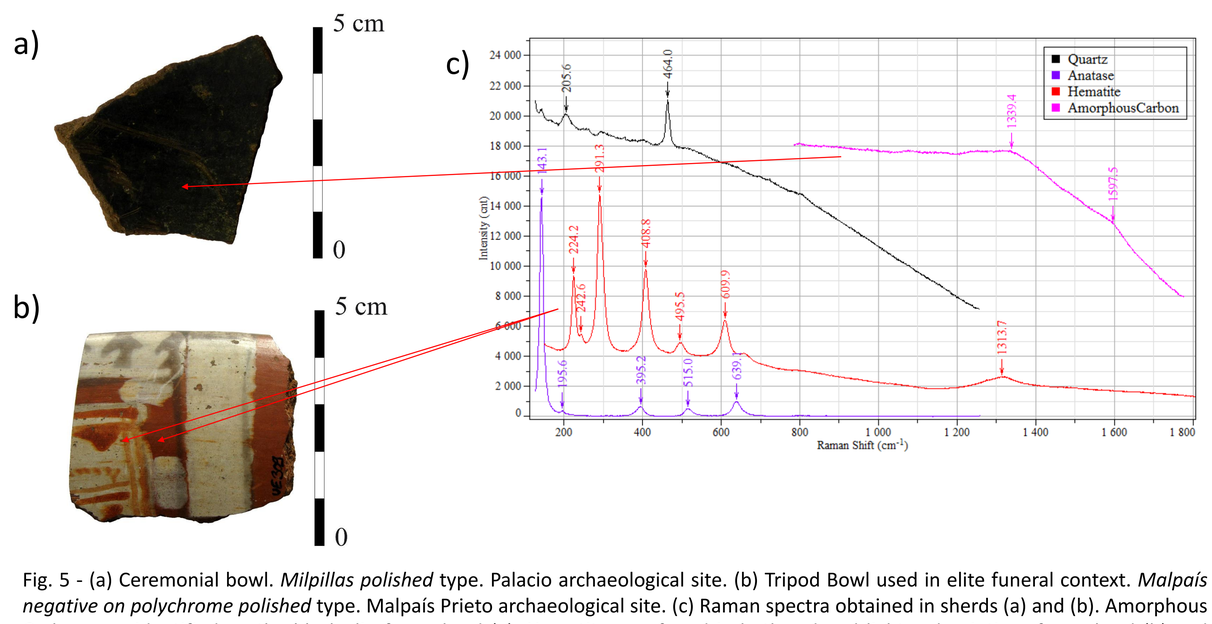

Fig. 5 - (a) Ceremonial bowl. *Milpillas polished* type. Palacio archaeological site. (b) Tripod Bowl used in elite funeral context. *Malpaís negative on polychrome polished* type. Malpaís Prieto archaeological site. (c) Raman spectra obtained in sherds (a) and (b). Amorphous Carbon was identified on the black slip from sherd (a). Hematite was found in both red and light red paintings from sherd (b) and Anatase and Quartz are probably originated from its ceramic paste.

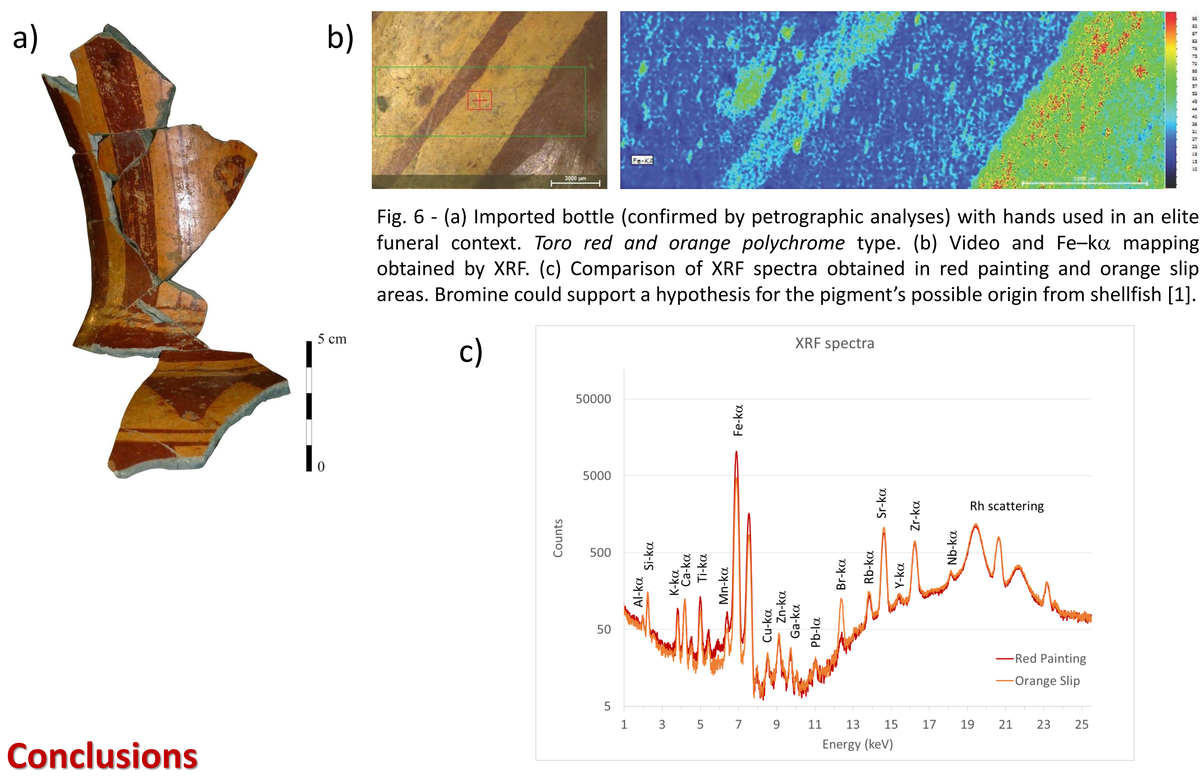

Fig. 6 - (a) Imported bottle (confirmed by petrographic analyses) with hands used in an elite funeral context. *Toro red and orange polychrome* type. (b) Video and Fe–kα mapping obtained by XRF. (c) Comparison of XRF spectra obtained in red painting and orange slip areas. Bromine could support a hypothesis for the pigment's possible origin from shellfish [1].

Conclusions

- This study is the first one taking into account material from Michoacán. It brings valuable information on various levels. Energy dispersive (XRF and SEM+EDS) and Raman spectroscopic analysis indicate the use of amorphous Carbon, Hematite and Magnetite based pigments. The presence of Magnetite and Carbon black suggests a firing under a reducing atmosphere (which confirms the characteristics of the paste that indicate a reducing firing and an oxidizing cooling for the Milpillas phase).
- Titanium oxides in the form of Anatase were also detected on the ceramic surface from Milpillas phase, evidencing the use of a firing temperature below 900° C [2].
- Back-scattered Electron Microscopy EDS mapping revealed how the pigments are not evenly distributed within the painted slip but occur in grains and patches.
- In comparison, the imported ceramic is different: a Bromine-based pigment could have been sourced from the sea. 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.

References

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