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Pre-Columbian estucado pottery from El Salvador: A multi-technique investigation

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Summary. — Pottery is one of the main productions of the pre-Columbian cultures in the Mesoamerican area. Among the others, the estucado pottery represents a very particular type of ceramic, widespread in Maya territory but still never investigated systematically. The peculiarity of this ceramic lies in the unusual application of the color decoration and in the excellent conservation conditions. Seventeen ceramic fragments from El Salvador have been analysed by Raman spectroscopy, SEM/EDS and XRPD, both as fragments and in cross-sections, in order to investigate the manufacturing technique and to understand the good and unexpected conservation state. In both cases, the presence and the chemical nature of a thin white layer (engobe) between the ceramic bulk and the colored decorations seems to be determinant.

1. – Introduction

Historical ceramics, due to their large amount in each archaeological excavation, can be considered important clues to investigate the evolution of both technological skills and aesthetic taste of the ancient civilization that had produced them. For these reasons, several archaeometric investigations on archaeological pottery are reported in the literature, often following a different analytical approach [1-5]. Pottery are heterogeneous materials made of cooked clay, in many cases decorated. Scientific investigations can contribute to characterize the raw materials and the ceramic bulk, to investigate the firing temperature and the nature of firing atmosphere and to identify pigments and binders used for the decoration. A complete characterization of these materials helps to know ancient civilization, to date and authenticate, and to assess a suitable conservation and restoration treatment [6-10]. Estucado ceramics are the most representative and less investigated pottery from Meso-American Maya culture, a variegated civilization that occupied a large territory (from the Southern Highland regions of Mexico to Costa Rica) during a broad chronological period, dating from the 2nd to the 16th century AD [11]. In the literature [12] it is reported that estucado pottery is characterised by an unusual and particular cold-working technology, but this assessment has never been demonstrated by

scientific investigations. This cold-working technique is particularly uncommon. Interestingly, the conservation state of the estucado artefacts is excellent, possibly due to the used binders or to the manufacturing process. Estucado pottery is generally decorated with a very rich palette (yellow, orange, red, green, different tones of blue and brown) and the colors were applied after pottery firing, above a white preparatory layer (engobe) realised by cold immersion of the object in a white material. The presence of an engobe layer (also called stucco) gives the name to this kind of ceramics (estucado). Seventeen decorated ceramic fragments have been sampled by six estucado ceramic objects from El Salvador and have been investigated in order to identify the used materials and to contribute to the historical and archaeological studies of the ancient civilization of El Salvador. A detailed Raman, Scanning Electron Microscope coupled to Energy-Dispersive Spectrometer (SEM/EDS) and X-Ray Powder Diffraction (XRPD) investigations have been performed to completely characterize the pigment and engobe composition and the results have been reported in [13]. In this paper we present and detail our results on one of the most interesting aspect of this work: the engobe and white pigment composition, discussing the presence of TiO2, its relevance and giving a contribution to understand the unusual good state of conservation of these art objects.

2. – Experimental

2˙1. *Samples.* – Seventeen different colored fragments have been sampled by El Salvador experienced staff from six different estucado objects dated back to the Classic Period (200–250 AD to 900 AD). These pieces belong to the National Museum of Anthropology "Dr. David J. Guzman" in El Salvador. In fig. 1 we report the macrophotographs of the ceramic objects, the points of sampling (labelled with numbers from 1 to 17) and the differently colored investigated fragments.

2˙2. *Raman spectroscopy.* – Raman measurements have been performed by using a Labram Micro-Raman spectrometer by Horiba, equipped with a He-Ne laser source at 632.8 nm (nominal output power 18 mW). The illumination and collecting optics of the system consist in a microscope in confocal configuration. The system achieves the high contrast required for the rejection of the elastically scattered component by an edge filter. The backscattered light is dispersed by a 1800 line/mm grating and the Raman signal is detected by a Peltier cooled (−70 °C) 1024 × 256 pixel CCD detector. Nominal spectral resolution is about 1 cm^{-1}. In order to avoid sample degradation, neutral filters have been used to reduce laser power on the samples. Spectral acquisitions (3 accumulations, 30 s each, in the range 100–2000 cm^{-1}) have been performed with 20×, 50× and 100× objectives. LabSpec software has been used for spectra acquisition and Origin 8 software for spectra elaboration (baseline correction to remove background fluorescence).

2˙3. *Scanning Electronic Microscopy coupled to Energy-Dispersive Spectrometer (SEM/EDS).* – All samples have been placed on an aluminum SEM stub and sputtered with gold under vacuum using K550 unit (Emitech Technologies Ltd., Kent, England) and then observed with a XL30 SEM microscope (FEI Company, Eindhoven, The Netherlands) with back-scattered electrons detectors, equipped with an energy-dispersive spectrometer (EDS analysis). Backscattered electron (BSE) images have been acquired in order to obtain information about the elemental composition of the samples, using an accelerating voltage of 20 kV and a working distance of 11 mm. In order to identify the elemental composition of the points of interest, EDS microanalysis has been performed

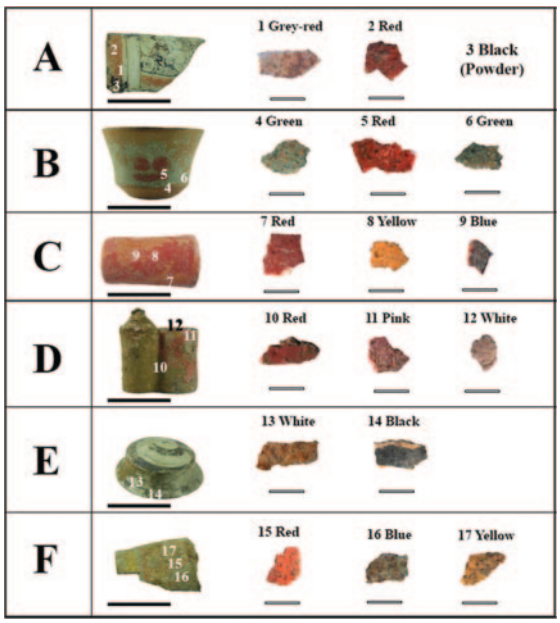

Fig. 1. – Photographs of the six investigated estucado ceramic artifacts (named A, B, C, D, E, F). For each object, experienced staff sampled different colored fragments (labelled with numbers from 1 to 17). The numerical labels are located in the exact point of the sampling. The black bar corresponds to 10 cm, the white one to 2 mm.

on single spots or on small areas using an accelerating voltage of 25 kV and a working distance of 11 mm.

2˙4. *X-ray Powder Diffractometry (XRPD).* – The X-ray diffraction analyses have been performed using a Scintag mod X1 with Cu K radiation, 45 kV acceleration voltage and 40 mA tube current. Scans have been performed in 2 steps of 0.05, with a recording time of 1 s per step. Pictures of all samples have been taken by a Olympus SZX16 stereomicroscope, digital pictures have been taken with a Color View II (Soft Imaging System GmbH, Münster, Germany) digital camera coupled to a Cell^{B} software.

3. – Results and discussions

3˙1. *Engobe layer.* – The six investigated ceramic object have a thin white layer (engobe) between the ceramic bulk and the colored decoration. Depending on the thickness of the sampling, only some fragments show on the rear side the estucado layer. The estucado layer is observable on twelve samples, namely samples 1, 2, 7, 9–17. In order to identify the composition of the engobe, a multi-technique approach (Raman spectroscopy, SEM-EDS and XRPD investigations) has been used. Measurements have been performed both directly on fragments and on polished cross-sections, thus allowing a complete characterization of the engobe layer. Polished cross-sections were obtained by inclusion in a polyester resin according to UNI 10922 [14]. The thickness of the engobe layer has been measured in the cross-section samples and it spread from 120 to 280 μm. The measured values are 120 μm for sample 1; 130 μm for samples 2, 12 and 17; 140 μm

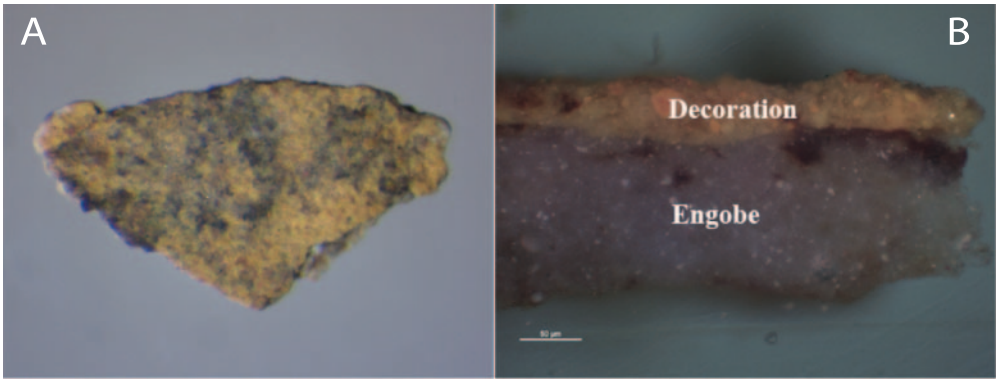

Fig. 2. – (A) Stereomicroscope image of sample 17; (B) Optical microscope image (20×) of the cross-section of sample 17 (engobe layer 130 μm).

for sample 13; 170 μm for samples 7 and 9; 190 μm for sample 16; 210 μm for sample 15; 220 μm for sample 14; 280 μm for samples 10 and 11. In fig. 2, we report the stereomicroscope images of sample 17 and the optical microscope image of its cross-section, in which the engobe layer is well visible below the yellow decoration.

In our analytical approach, Raman spectroscopy has been used to identify the molecular composition of the investigated samples, while SEM/EDS investigations allowed to determine their elemental distribution. This has been done by EDS, after the selection of an area of the sample on its SEM image. XRPD analysis permitted to have access to the mineralogical composition of the investigated samples and, due to its destructive approach, it has been used only in ambiguous cases that were not completely characterized by the other techniques. These three techniques, due to their complementarity, are often used together to investigate decorated archaeological ceramics. In all the Raman spectra collected from the twelve investigated samples it was possible to detect only the presence of anatase, a titanium dioxide. The Raman spectrum of anatase is characterized by a very strong band at 147 cm^{-1} and by three weak bands centered at 400, 519, 641 cm^{-1} [15]. In all our spectra the band at 147 cm^{-1} is always visible, with a variable intensity depending on the investigated sample, while the other three bands are detectable only on some samples. In fig. 3, we report the Raman spectrum of samples 7, 11, 12, 14, 15 in the range 120–180 cm^{-1}, where the presence is easily recognizable of the most intense Raman band of anatase centered at 147 cm^{-1} even if with different Raman intensity.

In nature, titanium dioxide is present in three different polymorphs: anatase, rutile (the most common) and brookite, the rarest. These mineral forms can easily and unambiguously be distinguished, by Raman spectroscopy, since they have well distinct lineshapes and peaks. In particular, brookite has Raman bands at 125, 152, 194, 246, 323, 366, 412, 492, 461, 542 and 640 cm^{-1} and rutile at 237, 442, 610 cm^{-1} [15]. The presence of anatase in estucado pottery can give important information. First of all, anatase and rutile are spread constituents of many soils, sediments and clays and their identification can give geological information about the clay sources [16]. Then, it is well known that anatase transforms irreversibly to rutile in air at about 600 °C [17], for this reason the presence/absence of the two titanium dioxide polymorphs is often used as a thermometer to investigate the firing temperature of ceramics. Several works have demonstrated that the transformation temperature is influenced by many factors, such

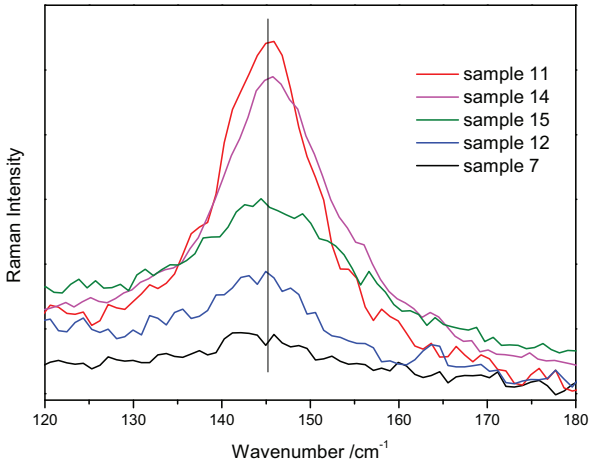

Fig. 3. – Raman spectra of the rear side (engobe layer) of sample 7, 11, 12, 14, 15. In all the samples the most intense characteristic band at 147 cm^{-1} is evidenced by a black line.

as chemical environment, association with different mineral phases, size and purity of the starting oxides [17, 1] and that when anatase is associated with clay materials, the transformation temperature between the two titanium dioxide forms (anatase to rutile) increases up to 1100 °C [18]. To completely characterize the composition of the engobe white material we performed EDS/SEM investigation that revealed the presence of silicon, aluminium, titanium and a small amount of iron, thus suggesting the presence of a clay. This could explain the Raman results that showed only the presence of anatase. It is well known, in fact, that titanium dioxides, especially anatase, have a huge Raman sensitivity and they are detectable although present in small quantity. Several works reported in the literature [19-21] demonstrate that the presence of anatase, also in low quantity, can completely mask information on low-scattering clay minerals. To identify the nature of the clay associated to anatase, we performed XRPD measurements that revealed, together with traces of anatase and quartz, the presence of a phyllosilicate clay mineral, in particular kaolinite ($Al_2Si_2O_5(OH)_4$), the most abundant and widespread white clay in Central America. The presence of kaolinite has been determined by main peaks at about 12.3 ($d = 7.2$) and at 24.9 ($d = 3.6$).

3˙2. *White pigment.* – Historical white pigments used to decorate ceramics are calcite, biacca and gypsum. So far, only one paper on the characterization of color pigments in pre-columbian pottery [22] has been published and the authors report as a remarkable result that the white pigment was prepared with some titanium compounds, possibly oxides. The possible presence of a white titanium pigment is extremely remarkable. In fact, the literature reports a vivid debate concerning whether and when natural mineral TiO_2 has been used as a pigment in ancient artifacts [16, 23-25]. On the other hand, it is known that synthetic titanium dioxide is the most widely used modern white pigment, since its synthesis in 1920. As a consequence, nowadays, the presence of titanium oxide as a white pigment in artworks is used to date and authenticate pieces of art. For this reason, a possible use of TiO_2 as a white pigment in the estucado productions deserves a deeper investigation, as a this could be the first experimental evidence of an early application of natural TiO_2. Only two fragments (samples 12, 13) present a pure white

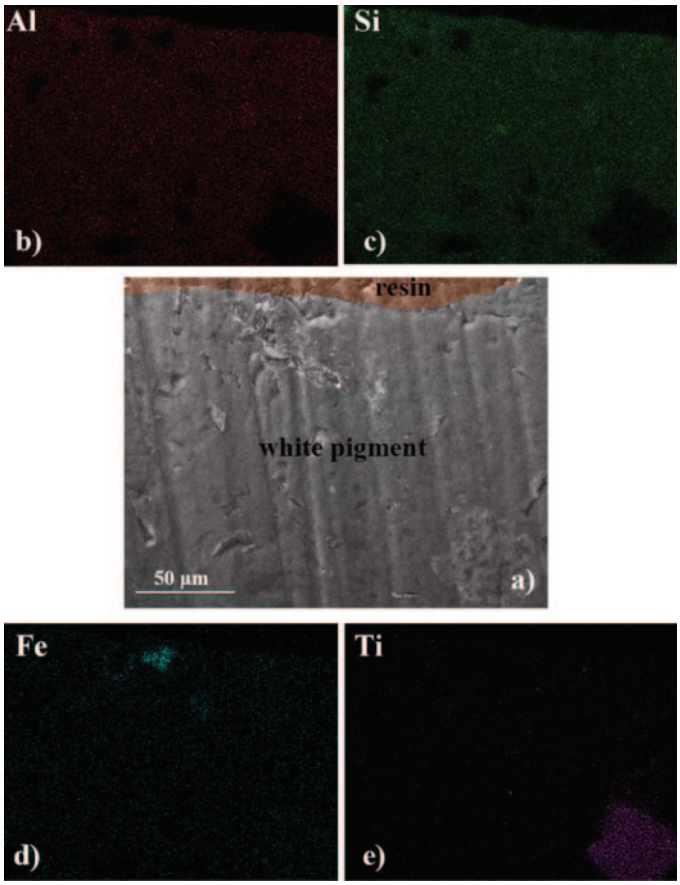

Fig. 4. – EDS maps showing the spatial distributions of Al, Si, Ti, and Fe element of the cross-section of sample 13.

pigment, but after a microscope investigation, we noticed that several colored samples (namely 4, 5, 7, 9, 10, 11, 14, 16) contain a white pigment mixed with other colors with the aim of obtaining a paler tone, as pinkish or grayish tonality. Raman investigation on the two pure white samples shows the characteristic strong band at 147 cm^{-1}, ascribable to anatase and already observed in the stucco layer. The elemental SEM/EDS analysis has shown the presence of silicon, aluminium, titanium and iron that suggests a clay but due to the fact that under the layer color the engobe is present, we cannot exclude that the signal we detected came from the engobe layer and not only from the white-colored layer. Moreover, a XRPD investigation could not help us to discriminate between the stucco and the color layer due to their thickness. Thus, the question is whether here we are facing the first application of natural anatase as a white pigment, or the application of the same clay, containing anatase, in the engobe layer and as a pigment. To answer this question we performed SEM/EDS maps on the cross-sections. In fig. 4 we report, in the middle panel, the SEM photograph of sample and on the four small panels at the top and bottom the maps showing the spatial distributions of Al, Si, Fe and Ti in the investigated cross-section. The two maps in the top panels demonstrate that Al and Si

are homogeneously distributed over all the cross-section. At the same time, Ti and Fe are present in spots distributed over all the cross-section, suggesting that these elements are present as impurities of the homogeneous material that has been used both in the preparation layer and as coloring agent. Since Al and Si are the main components of the kaolinite clays, we assert that the white pigment used in estucado ceramics is the same mineral (kaolinite containing anatase) used for the engobe.

Anatase has been identified by Raman spectroscopy in the other colored samples in which a white pigment was observed (samples 4, 5, 7, 9, 10, 11, 14, 16), suggesting that the white clay containing anatase was used in mixture with other pigments in order to obtain different tones, as pinkish or grayish tonality.

4. – Conclusions

Thanks to a multi-technique approach (Raman spectroscopy, SEM/EDS and XRPD investigations), it has been possible to identify the chemical composition of the engobe layer and of the white pigment used to decorate six pieces of estucado pottery from El Salvador. Both the engobe and the white pigment have been realized by the same compound: a white clay, kaolinite, rich of quartz and anatase. This finding is important for two different aspects. The first is that we can contribute to the debate about the application of anatase as a pigment in ancient artifacts, having established that in the pre-Colombian estucado production analysed in this work, the anatase has not been used by itself as a pigment as assessed in previous works [16, 23, 25, 26] but it is a minor component of the white clay used as a pigment. Moreover, the presence of kaolin and anatase can help us to investigate the firing temperature of estucado pottery since these two compounds modify at high temperature. Kaolinite transforms in metakaolinite at about 500 °C and then in mullite at 1200 °C [18] while anatase transforms into the most stable form rutile when heated over 1100 °C [17, 18]. This information confirms that engobe layer and decorative elements were realized by cold-working or low-temperature technique. Since no presence of any binder has been detected, we can hypothesize that kaolin has been used both as a coloring agent and as a binder. This, along with the cold or low-temperature technology, may be the secret of the surprising good conservation state of this pottery production, as hypothesized by Striova *et al.* 2006 [27] about Prehistoric Native Americans ceramics.

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