X-ray techniques applied to surface paintings of ceramic pottery pieces from Aguada Culture (Catamarca, Argentina)

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X-ray diffraction (XRD), energy dispersive spectrometry (EDS), x-ray imaging (XRI) and scanning electron microscopy (SEM) techniques were applied to characterize and differentiate surface paintings of archeological pottery from the Aguada Ambato and Portezuelo styles (Catamarca, Argentina). Standard procedures are not always appropriate for such samples (paint layers are porous, nonplanar and discontinue). Image processing is necessary when chemical contrast is not discriminated. Soft x-ray lines (e.g. Fe L) are more revealing because those detected come from shallower depths, clearly depicting the composition of the paint layer.

These styles differ in mineralogy and chemistry suggesting that they are two distinctive entities not only on their designs but also on the materials chosen and the technology used. Aguada Portezuelo paints contain Ca (white), Fe–Mn (black), Fe–Mn–Ca (dark reddish) and Fe–Ca (reddish). The white ones correspond to gehlenite, a firing product (possible firing temperature $\geq 900-1000\,^\circ C$); calcite and CaO occur in cases of firing temperatures $<900\,^\circ C$.

Aguada Ambato presents difficulties for paint discrimination; only EDS spectra show slight differences. White paint from Tricolor Ambato contains mainly Pb-phases (hatchite, anglesite, plumalsite), reddish paint resembles the paste ($\sim$Fe, hematite); reddish surfaces may have not been painted but polished. Black paint has scarce Mn–minerals. On Black Incised sherds no particular phase was identified suggesting possible organic pigments or resulting from the firing technique.

The chemistry and mineralogy of the paste almost always overlap that of the paints; painted layer is irregular and partially worn by years of burial. Copyright © 2008 John Wiley & Sons, Ltd.

Introduction

X-ray nondestructive analytical techniques and scanning electron microscopy (SEM) are common tools of clay mineralogists and physicists, who can contribute with archeologists providing information to typify ceramics, paints, pigments and raw materials. The interdisciplinary study of ancient pottery by means of these techniques has lately proved to be of great help in understanding and solving some archeological problems such as provenance of ceramic pieces and raw materials, and technologies used by potters.[1–3]

X-ray diffraction (XRD) applies to minerals and other crystalline phases identification; energy dispersive spectrometry (EDS) and x-ray imaging (XRI) to chemical composition determinations while secondary electron imaging (SEI) and backscattered electron imaging (BEI) are used to textural, topographic and chemical contrast analyses of ceramic pastes, surfaces, paints and pigments. Although quantification is usually unreliable on nonpolished samples by SEM-EDS spectra, it is preferred over x-ray fluorescence for which the sample must be ground.

These valuable data, correlated with studies of technology of production, are used in the interpretation of social, political, economic and cultural contexts of pre-Inca societies and the interaction among different sites. The identification of paints and pigments is not only useful in archeological studies but also in art history and restoration.

Although various combinations of these techniques are lately, commonly used and discussed in archeometric studies (in surface analyses, are mostly devoted to enamels and glazes[4–7]) there is still a lack of detailed information regarding their suitability and experimental conditions to be considered when applied, particularly when the standard procedures are not always enough to characterize this kind of samples. This is particularly important if thin layers (nonglassy paints) or micro granular phases (new phases or contaminants) are to be analyzed, and even more, quantified.

This work focuses on the mineralogical and chemical characterization by x-ray and SEM techniques of the external surfaces treatments and paintings of pot sherds from Ambato and Portezuelo styles of the Aguada Culture, Ambato and Catamarca valleys respectively (Catamarca, Argentina).

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This culture emerged as a consequence of a social and ideological change that occurred in the forth to twelfth centuries of the Christian era, in the Ambato Valley,[8] and progressively spreading out regionally. It was a process of deepening and consolidation of social inequalities, which was based on the preeminence of a solar cult, long distance exchange of luxury and symbolic goods and the establishment of hereditary social hierarchies. Local ceramic styles developed within each cultural region (Ambato, central Catamarca and Hualfin valleys, and northern La Rioja). Ambato and Catamarca are the two contiguous valleys that, although not separated by any net geographical barriers, show two very different and peculiar Aguada styles that are understood as an evidence of two autonomous political units.

The occurrence of ceramics of one style along with the other one (Ambato pieces are found at archeological sites in Catamarca and other Valleys, while Portezuelo ones barely appear at some sites in the Ambato Valley), poses the question of the kind of relationships established between these two political units: Are we in front of a regional system of circulation of particular goods or both ceramic styles were locally produced in both valley? Were they made in the same way and/or using the same materials? Neither their relationships and the materials used nor their technology has yet been well understood.

No previous comparative archeometric studies of this kind regarding the pottery paints have been done on these styles; only few papers from each one can be recalled.[2,3,9–11] The information reported here will not only help to characterize the paintings and to understand the technology used by potters but also to compare and to differentiate both styles. On the other hand, the measurement conditions and techniques suitability will also be discussed in an attempt to define the best methodology to apply in such cases.

Experimental

Materials

The Aguada Ambato pot sherds samples were collected from Piedras Blancas (*ca* 600–1000 A.C.) site, in the Ambato Valley, while the Aguada Portezuelo ones from Portezuelo and Tiro Federal South (radiocarbon age *ca* 600–900 A.C.) sites within the Catamarca Valley, about 80-km south of Piedras Blancas.

There are two typical Aguada Ambato ceramics: the Aguada Ambato Black Incised pottery (B4, B7, B11, B27, B52) and the Aguada Tricolor ware (B2, B22, B33, B39, B44, B49, B53, B54, C1). The first is a fine ware of very good quality, detailed engraved or incised decoration depicting animal, human and fantastic motives; it is found at many places outside the Ambato Valley, pointing toward its value as exchange good.[12,13] The second one is a more rough finish ware, of large vessels used for storage and beer processing, which can be plain or decorated with human and fantastic motives painted in white, red and black.[14–16] These tricolor vessels are related to an older technological tradition, which acquired a new meaning within the Aguada context. Along with these two types, there are others with different finishing, from which samples B32, B36 and B37 were chosen.

The Aguada Portezuelo style (A11, A12, Gui1, Gui2, GP1, GTF5, GTF6), from the Central Catamarca Valley, characterizes by a very fine ware, with very complex and highly variable manufacturing and decorative techniques.[9,17–19] One of the most outstanding characteristics is its noticeable polychromy. Decorative motives are painted in red purple, reddish, black and yellow (a very atypical

color in other Aguada ceramics of Northwest Argentine[19]) over a white slip and combining an elaborated background and figure interplay depicting motives either in negative or positive. In some cases, the colors have not been fixed by the firing and appear smooth and without brightness, also displaying pre- and postfiring paintings. Another decorative technique poorly studied for this ceramics is the existence of resistant negative painting.[19]

Techniques

Mineralogical and chemical analyses were carried out on ceramics painted surfaces, combining XRD, SEM and EDS. SEI, BEI, XRI and x-ray spectra were collected to determine the elemental distribution and composition of painted surfaces.

These techniques have different strengths and weaknesses when applied to the case studied. Archeological ceramic pieces and sherds have been buried for over 1000 years, suffered weathering and partial removal of the paints, so the paint layer thickness is not homogeneous and the surfaces are rough and not plane.[20] In addition, the amount of pigment that can be extracted is too small for conventional analyses (i.e. XRD). Nevertheless, considering all data together, they give a good characterization of both the paint and the paste.

XRD

Samples scraped from the surface of selected sherds prepared in random mounts were analyzed on a Philips X'Pert PRO PW 3040/60 difractometer, with Cu Kα x-ray radiation, Si monochromator, at 40 kV y 30 mA, step scan at $\sim$1°/min and step size of 0.02° 2θ. In most cases, samples were mounted on an Si holder of low background, where small amounts (few milligrams) can be studied.

SEM and EDS

Natural fragments of samples were coated with Au (11 nm thick) and/or C (25–30 nm thick, when Au interferes the sign of elements of interest) and analyzed with a LEO 1450VP scanning microscope, coupled with EDAX energy dispersive spectrometers, at the Laboratorio de Microscopía Electrónica y Microanálisis (LABMEM, UNSL). Measurement conditions were 20 to 15 kV, 0.5 nA; all spectra were normalized to Si for a better comparison of relative intensities of present elements, because Si is a major component in all samples.

SEI

The images are produced by the secondary electrons emitted very close to the surface of the sample making the topographic information contained in such images easy to interpret. Secondary electron (SE) emission is not strongly composition-dependent and in any case with coated samples is governed mainly by the properties of the coating, but they may still reflect atomic number variation mainly due to the production of secondary electron by backscattering.[21]

BEI

These images, produced by backscattered electrons emitted from an intermediate zone close to the surface of the interaction volume, yield the information of chemical contrast allowing the distinction of small variations in the mean atomic number. In very low noise

images BEI may discriminate eventually up to $\Delta Z \approx 0.1$, but this is not the regular case for ceramics. With the working conditions used, beam current of 300–400 pA and ~25 to 40 sec of scan frame time, the minimum contrast percent discriminable is lower than 4%, which will provide a good quality image. They clearly depict the different pigments of painted surface, being particularly useful in specimens with pigmented surface too thin to be characterized by x-ray spectra.

EDS spectra

X-ray spectra acquire information on global composition from an interaction volume[22] area 3- to 4-μm deep; they were collected from a 100 μm^2 area. The results may contain information not only from the painted surface but also from the paste. The surfaces are rough and may have any tilt angle in the scanned area so that the elemental composition obtained is usually only qualitative. In the studied case (painted surfaces), the spectra can contain information from the paste, particularly if dealing with hard x-ray emission lines that may come from deeper zones of the specimen; on the contrary, soft x-ray emission lines come from shallower zones thus it may better reflect the composition of the thin layer of paint.[23]

XRI

X-ray images provide information about the distribution of selected elements concentration within an area. Like in the case of x-ray spectra, if the paint layer is too thin, the images are not sensitive enough to show changes in concentrations of the selected element.

Results and Discussion

Chemical and mineral composition of Aguada Portezuelo

Topographic (SEI) and chemical contrast (BEI) images (Fig. 1) obtained from the surface of sherds show the compositional differences of white (slip) and black paints. As explained in the Section Techniques, SEI, though mostly topographic, in this case, slightly reflect the chemical contrast. This is clearly seen on the BEI, where it is possible to distinguish not only the design contours but also the differences in mean atomic number (Z) of paints, therefore black paint is seen in lighter color because it has higher Z.

Their chemical composition was identified by XRI and EDS spectra (Fig. 2). In all the samples white paint has a high Ca content, black one, Fe and Mn (plus minor Ca), while reddish brown Fe, Mn and Ca and reddish Fe and Ca. Comparing with the composition of the paste, it is evident that paints always contain the same major elements such as Si, Al, minor Mg, K, Na and traces of Ti, in similar proportions than the paste. This may be caused by the irregular thickness and distribution of the paint layer as observed in Fig. 3. Ca is present in all paints; in the EDS spectra, peaks of typical elements for nonwhite paints (Mn, Fe) are generally weak. Colored paints are very thin layers and irregularly sparse on the surface; these might be reflected on the low intensity of EDS spectra which are also overlapped by the components (Ca) of the white paint used as a substratum.

The observations in cross-section (Fig. 3) also show that the white paint has diffused in the paste voids probably while being painted by the potters.

XRD was applied to most of the white paints but only in few black ones, due to the scarce amount found in black and other non-white paints. In all cases, the extracted materials also contained some grains from the paste, which is reflected in the bulk mineralogy mainly by the presence of quartz, feldspars, hematite, micas (as traces) and sometimes spinel (Fig. 4).

Calcium minerals are the main components in all white paint samples from Portezuelo. Gehlenite is always present, along with subordinate analcime (Gui1) and/or calcite (Gui2>Gui1) and sometimes traces of CaO. Sample GTF6 only contains analcime.

Gehlenite is an aluminosilicate that forms from mixtures of calcite with clay minerals (paste) at temperatures between 850 and 900 °C[24] or 1050 °C.[25] Beyond that temperature it reacts and forms anorthite.[18] Buxeda i Garrigós and Cau Ontiveros[25] described the reactions and new Ca-rich phases (CaO, gehlenite) produced in calcareous ceramics and paid attention to the fact that they strongly depend on the structure of the firing, the maximum firing temperature, calcite grain size, etc. During this reaction, if the dissociation of calcite was not completed (usually at <750 °C), the reaction sequence of gehlenite, calcite and CaO may coexist in the range of 700–900 °C. After firing, free metastable CaO may transform to portlandite (with atmospheric water) and this mineral to secondary calcite, with the addition of CO_2 from the atmosphere.

The mineralogy found, dominated by metastable Ca phases, suggests that the original white pigment used by potters was
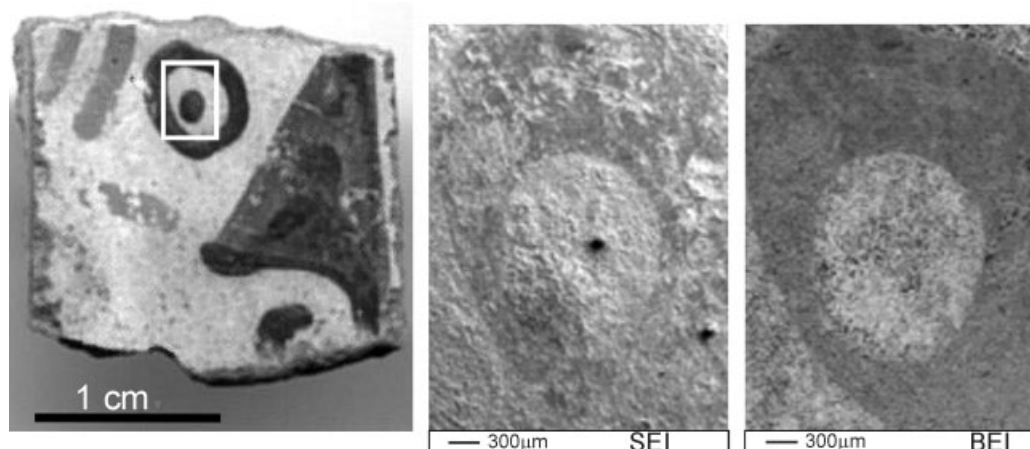

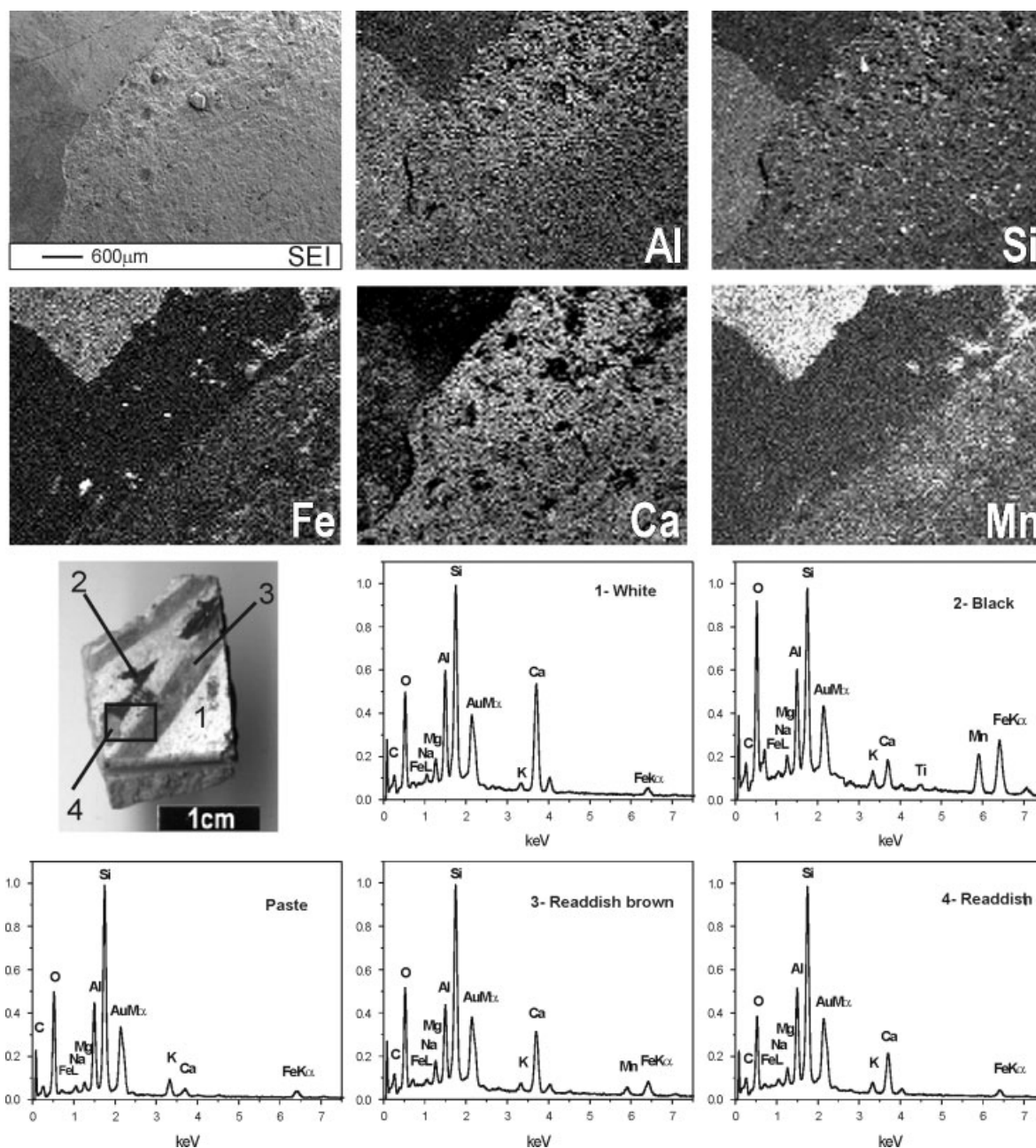**Figure 1.** Comparison of SEI and BEI of sherd A11, Aguada Portezuelo; Au coating.

Figure 2. SEI, XRI and EDS spectra of sherd A12, Aguada Portezuelo showing the chemical composition of different pigments; Au coating.

calcite (except GTF6). It also makes clear that at least the white pigment was painted before firing. The occurrence of solely gehlenite (GP1, GTF5) points out that the firing temperatures may have reached or overcome 900–1000 °C, as previously reported by Bertolino *et al.*[10]; those that contain CaO and/or calcite seem to have been fired at temperatures possibly lower than 900 °C. These temperatures are in agreement with those suggested by the pastes characteristics.[26] It is not possible to be certain on the origin of calcite detected by XRD. A secondary origin is more likely since CaO occurs in trace and one would expect higher CaO and less calcite contents if the reaction would have been stopped before complete dissociation of calcite. It should be considered that in samples with calcite, micas are present in higher proportions than in the other ones; micas tend to disappear with increasing firing temperatures

(at about 900 °C its structure will be lost[27]) supporting the idea that these samples were fired at lower temperatures.

Black paints contain hematite, titanomagnetite (GTF5) and traces of hollandite and lithiophorite (Gui1).

Chemical and mineral composition of Aguada Ambato

The SEI of Aguada Ambato Tricolor sherds reveals textural and grain-size differences resulting from the pigments used and the treatment given to their surfaces. Figure 5 shows the smooth and even finish of the reddish paint (1), while white paint (2) exhibits coarser grains and a rough surface; black paint (3) has intermediate features.[10] There seems to be a parallel trend of reddish material distribution suggesting that the surface could have been polished with a smoothing tool. In this case, it is evident that the black
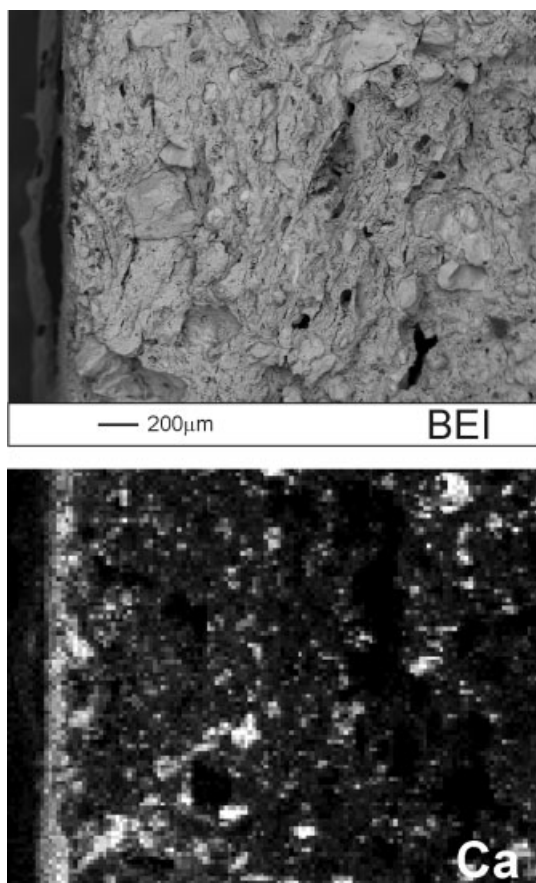
Figure 3. BEI and Ca XRI of a cross-section of sherd Gui1, Aguada Portezuelo; Au coating. The paint layer is distinguished from the paste and become evident in the Ca mapping (light colors, left).

Figure 4. XRD patterns of paints from Aguada Portezuelo. Qz, quartz; Mi, micas; Ge, gehlenite; Cal, calcite; Feld, feldespars; Plag, plagioclase; Ana, analcime; Ilm, ilmenite; Hem, hematite; Sp, spinel; Tima, titanomagnetite; Holl, hollandite; Lith, lithiophorite.

and white pigments were painted over the reddish base, probably before firing the pieces.

BEI and XRI show no differences among paints either coated with Au (with higher production of backscattered electrons) or with C (to avoid overlap of Au-M and Pb-M lines) at the selected working conditions, except for one case with a very slight but visible contrast (B7). EDS spectra are quite similar but let identify the colors (Fig. 6). Unlike Portezuelo, in almost all sherds white paints are not Ca-rich; this element is actually slightly more abundant in the reddish ones. Weak Pb-M lines were detected in white surfaces; these lines are absorbed by lighter elements such as Si and Al that are the major components, so higher proportions of these elements could be suspected considering the identification of Pb minerals by XRD on this paint. It is well known that even small proportions of Pb mixed in a translucent media result in a good white pigment. The composition of black paints is not clearly distinguishable as it was in Portezuelo sherds. Only Fe peaks change more visibly (Fig. 6). As expected, in reddish ones, Fe is more abundant than in the others but it is always present in considerable amounts. The Fe content in white paints may suggest contamination from the bottom paste. Differences are more pronounce when analyzing the FeL lines (soft x-ray); only superficial FeL photons will come out from the sample so they would reflect better compositional variations (Fig. 6).

The sameness among paints by BEI, XRI and EDS is may be due to lack of chemical contrast. If so, it may be explained by the proximity in mean atomic number Z that all materials have; but if
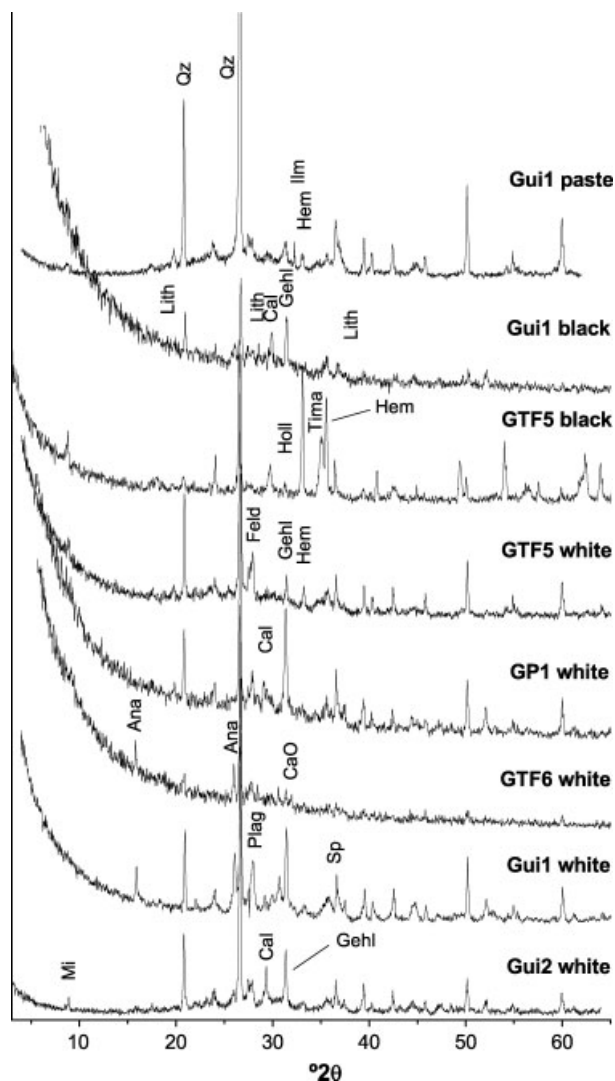
not, the lack of image contrast could be produced by noise or a poor peak/background rate. The porosity of these materials would generate considerable sign fluctuation pixel to pixel, more than Portezuelo surfaces where the base white paint was recrystallized by firing and possibly became more compact.

Changing the working conditions to a beam current of 600 pA and to 340 seg scan time for frame (Fig. 7) does not improve the BEI really much. Images 1 and 2 in Fig. 6 show scan line profiles crossing the diverse colors. It is clear that the signs from each colored surface differ in fluctuation; white surfaces are rougher and, consequently have more fluctuations while reddish ones are smoother, as explained before (Fig. 5). The profiles were very stable when repeated, discarding the chance of being under the effect of noise. Thus, the fluctuation changes are only due to variations on the topography of each surface (Fig. 7 image 1): major oscillation in white areas (roughest), while the reddish ones (smoother) are quite steady. There is also a complete agreement between the higher fluctuations and major topographic accidents (holes, cracks, etc.). This effect of topography blurs the chemical
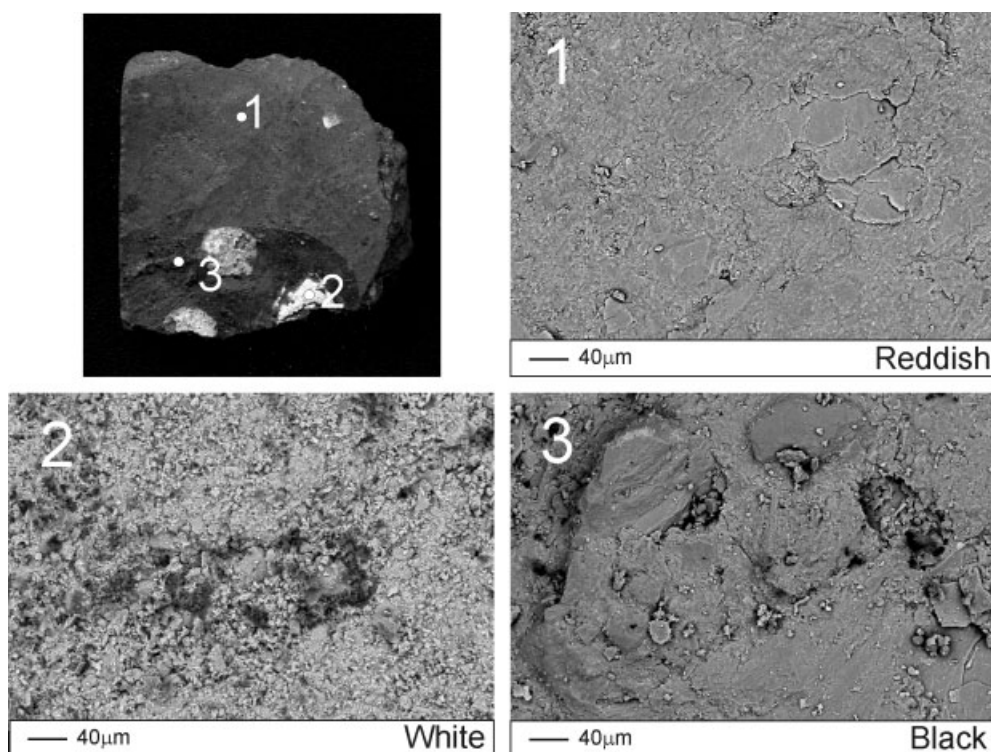
Figure 5. BEI from Aguada Ambato; Au coating. Grain size and textures are different in 1-reddish (smooth), 2-white (grainy), and 3-black areas.
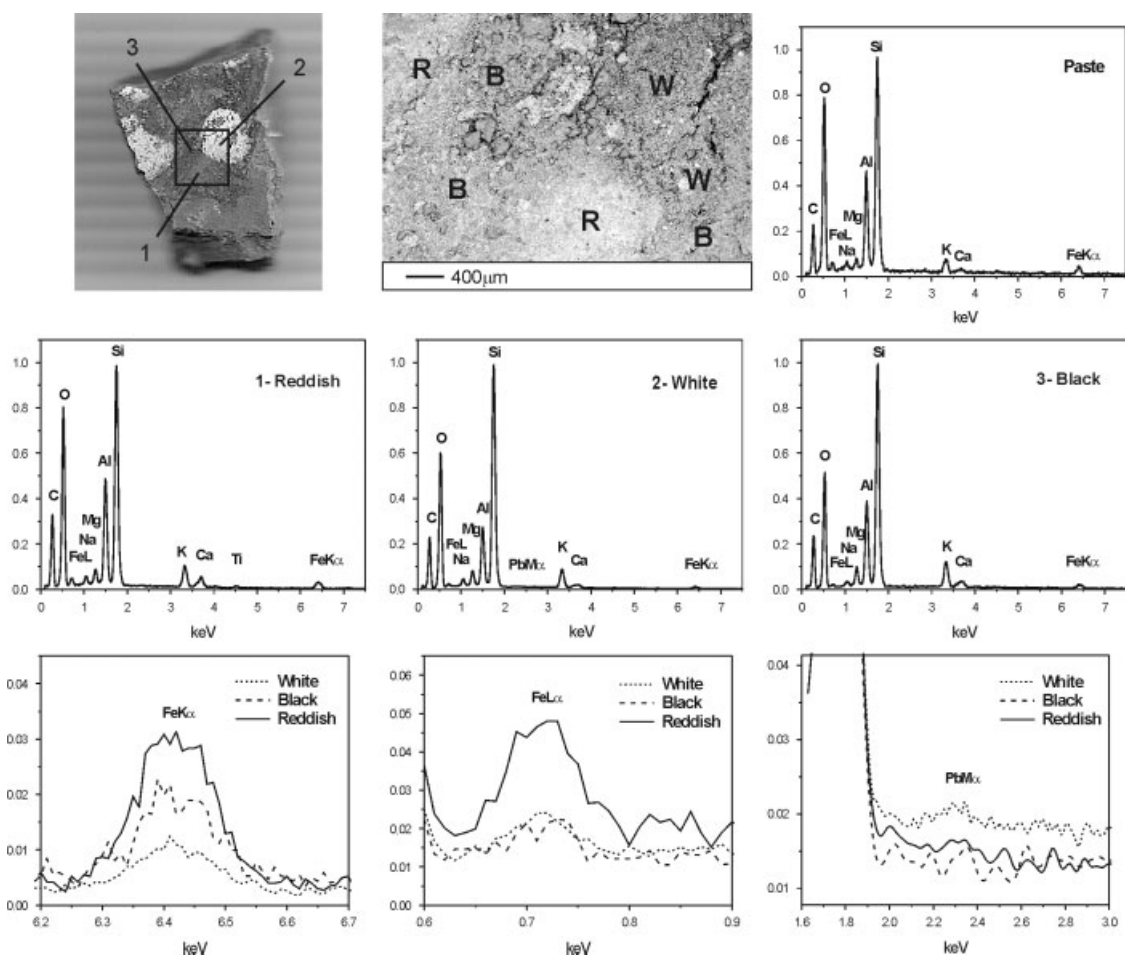

Figure 6. Aguada Tricolor Ambato; C coating. BEI taken at 600 pA and 350 seg acquisition time. W, white; B, black; R, reddish; T, transition zone.
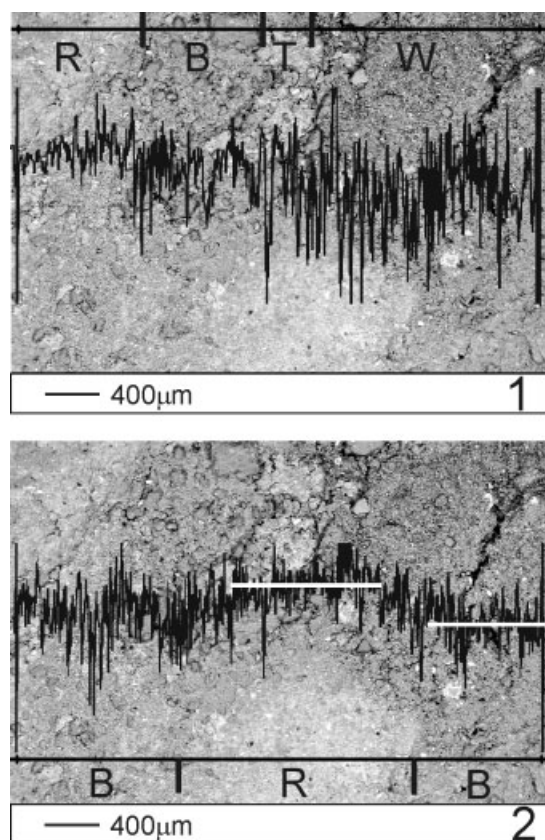
Figure 7. Aguada Tricolor Ambato; C coating. BEI, same as Fig. 6. Scan line profiles crossing two different areas. White lines in image 2 represent the approximate mean fluctuation values for reddish and black paints respectively; their different heights reflect the ΔZ.

contrast, but nevertheless, a change in mean Z may occasionally be distinguished when the mean value of the scan line profile differs in height from one area to another (Fig. 7, image 2).

Like in Portezuelo analyses, Si, Al, minor Mg, K, Na and traces of Ti are always found which are from the paste.

As expected, no Ca minerals were found in white paintings from Ambato Tricolor except in sample B49 which contains calcite and traces of this mineral in B2; the main components (Fig. 8) are Pb minerals such as hatchite (B2, B49, B53, C1) and/or anglesite and traces of plumalsite (B2). The mineralogy of reddish paints is similar to that of the paste but with differences on quartz and feldspars content; this may suggest that the pieces were only polished (without addition of a slit) so that the coarse grains were removed; Fe-rich minerals present are hematite and traces of goethite. Black paints of Tricolor type are composed of hollandite, magnetite and hematite, while the black surfaces of Incised type (B4, B11) hardly show any mineral used as black; it is likely that the color of these surfaces was given by organic dyes or by the firing technique. All samples also contain quartz, feldspars and micas like the paste.

Figure 8. XRD patterns of paints from Aguada Ambato. Qz, quartz; Mi, micas; Feld, feldespars; Anor, anortite; Alb, albite; Hat, hatchite; Angl, anglesite; Plum, plumalsite; Hem, hematite; Magn, magnetite; Holl, hollandite; Phyll, phyllosilicates; Sp, spinel.

Conclusions

The strengths and weaknesses of EDS, XRI, XRD, BEI, SEI, nondestructive techniques and their procedures have been discussed when applied to this challenging case of archeological ceramic pieces. These techniques are complementary, since individually, they may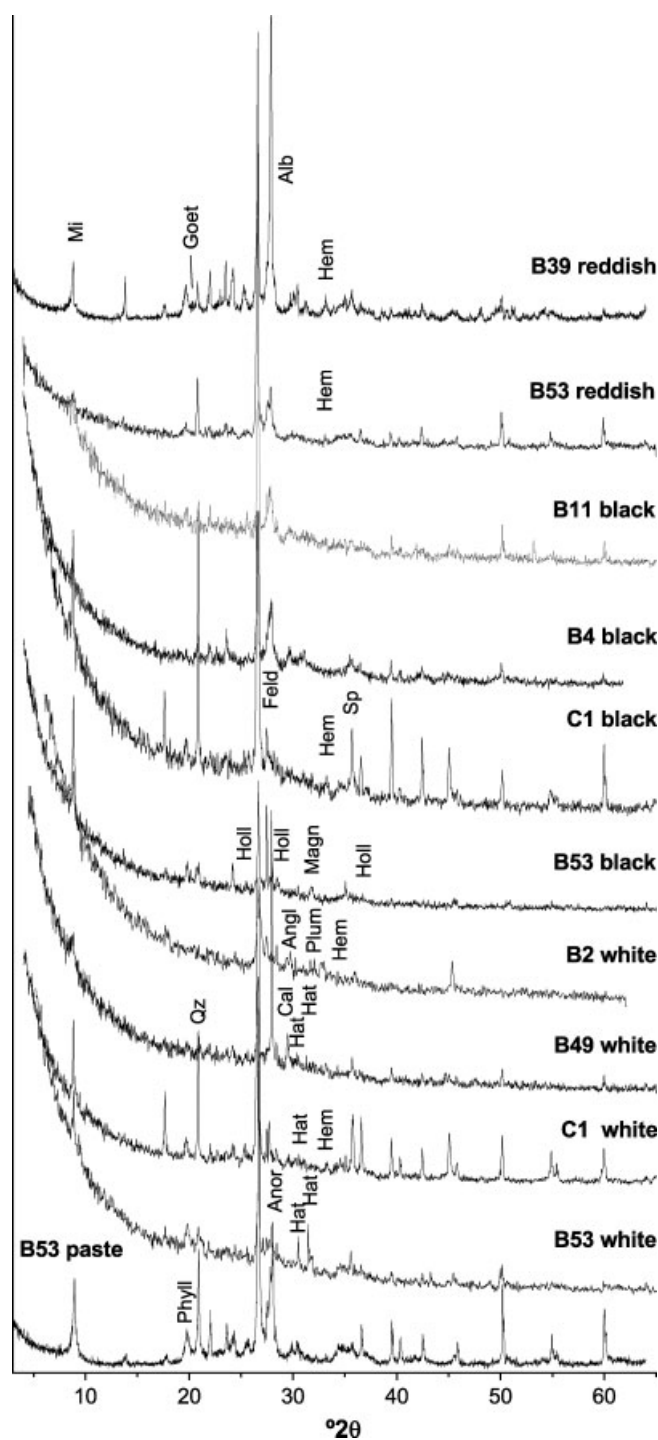 lead to confusing interpretations, but combining them and considering all data together they give a good characterization of both the paint and paste.

It is always a compromise to decide whether to use Au or C coating or to choose the adequate working conditions to apply, particularly if acquisition times are too long; this is not only time and money consuming but also the instrument stability cannot be warranted in long periods of time providing uncertainty on the results

obtained. Eventually, other coating elements with lower *Z* than Au could be considered, such as Ti, Cu, etc., to improve the BEI and SEI and to avoid absorption of lower energy photons and peak interferences, but each element has its own specific problems to attend.

Low energy lines (e.g. Fe L) on EDS spectra are more sensitive to the surface composition because those detected come from shallower depth; this is particularly useful when the thickness of the layer analyzed (the paint) is porous, heterogeneous and unknown.

Aguada Portezuelo paints (Au coated) are easily recognized and distinguished in their chemical contrast and chemical and mineralogical composition by all means used. Even SEI shows some chemical contrast. White paints contain predominantly Ca in the form of gehlenite, sometimes associated with calcite and traces of CaO. Some sherds contain analcime instead of Ca minerals. This mineralogy suggests that: (1) the possible original pigment was calcite; (2) the surfaces were painted before firing (gehlenite is a metastable firing product); (3) sherds with only gehlenite may have been fired at temperatures $\geq 900–1000\,^{\circ}$C while those with calcite and CaO at temperatures lower than $900\,^{\circ}$C (mica XRD reflections are larger than in the other ones). Reddish paints characterize by Fe and Ca, reddish brown by Fe, Mn and Ca and black ones by Fe and Mn (with minor Ca). The mineralogical composition of the latter was hard to detect in most samples, hematite and titanomagnetite along with traces of hollandite and lithiophorite were identified in some cases.

Unlike Portezuelo, in Aguada Ambato sherds, BEI and XRI do not show differences among paints even when working conditions are changed, but testing in this way and processing the images would eventually highlight the variations in mean *Z* of each painted area or define if the sameness is due to the low quality imaging, topographic effects or lack of chemical contrast. The EDS spectra reveal changes in composition. Ca is always low; it is present in all the cases more or less in the same proportions. Weak Pb-M lines were detected in white paints of Tricolor Ambato type, in agreement with the mineralogy found by XRD and represented by predominant hatchite, or anglesite and plumalsite. These mean that the white paint was obtained from a Pb-based pigment. Because of the occurrence of Pb, the samples were also coated with C to avoid Au interference, although Au will give better images. Reddish areas were distinguished by the higher Fe content, which was better observed in the FeL lines. Hematite and traces of goethite were identified by XRD on this paint. In any case, reddish chemical and mineralogical composition is similar to that of the paste; it seems to be that these surfaces were just polished without any further addition of material. No characteristic elements for black paints were identified by EDS spectra or XRI; only XRD revealed the occurrence of Mn and Fe minerals such as hollandite, magnetite and hematite in Tricolor sherds but not in the Incised type; this might suggest that their surfaces were treated with organic dyes or the black color was produced by the firing technique used.

Contamination from the paste is unavoidable in XRI, EDS and XRD spectra because the paint layer is heterogeneously distributed.

The chemical and mineral composition of paintings from Aguada Ambato and Portezuelo is clearly different, particularly regarding whites. There is some heterogeneity within these groups too, but it does not affect the compositional characteristics identified on each style. It can be concluded that the ceramic pieces of Aguada Ambato and Portezuelo are two dissimilar entities that were made in very distinct way; they not only differ on their designs but also on the chosen materials and the production technology applied by ancient potters.

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