What is that Pigment? Surface Analysis of Early Ceramics from Kuntur Wasi, Andes of Peru, by Way of Raman Microscopy and Portable X-Ray Fluorescence Spectroscopy

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ABSTRACT
Preliminary analyses using Raman microscopy and portable X-ray fluorescence spectroscopy (pXRF) were conducted on 21 ceramic fragments to assess the composition of the pigments used by the ancient potters producing for the ceremonial center of Kuntur Wasi (950-50 BC), Department of Cajamarca, in the northern Peruvian highlands. The chemical and mineral analyses evidenced the manipulation of iron oxides to provide for most of the surface colors and painted designs observed. In addition, titanium oxides and calcium were used for obtaining white. Only one sample showed the presence of cinnabar and azurite, as post-firing pigments on a bottle that is suspected to be nonlocal.

Keywords: pigment analysis, Raman, pXRF, archaeology, Andes, Peru.

INTRODUCTION
We present the preliminary results of pigment analysis of 21 ceramic fragments from the Formative ceremonial center of Kuntur Wasi (950-50 cal. B.C.) in the Cajamarca highlands of Peru (Figure 1). The analysis included low-power digital microscopy to assess paste composition, as well as Raman microscopy and portable X-ray fluorescence spectroscopy (pXRF) to identify the pigments used for the slip or the paints enhancing the designs on the vessels' surface. These techniques are non-destructive and complement each other.

Although we had conducted extensive mineral and chemical paste analysis using petrographic analysis, X-ray diffraction and LA-ICP-MS to understand ceramic production and distribution at or for this site ([1] Druc and Inokuchi 2016, [2] Druc et al. 2013, [3] 2017), no pigment analysis had been performed. This analysis was initiated to further our understanding of the technological knowledge the ancient potters had at the time and to possibly identify rare pigments indicative of special productions or long-distance distribution. Pigments can easily be traded over long distances, but our initial analysis showed that most wares were locally produced. So, identifying nonlocal pigments on a local vessel would inform us about the extent to which the potters had access to pigments and from where they could possibly originate, unless the whole vessel was proven non-local.

We will first briefly present the archaeological context, the corpus of analysis, and the methodology for the analysis. This is followed by a presentation of the results, which are then discussed and placed in a wider perspective of ceramic technology and possible pigment or ware distribution with neighboring regions.

Archaeological Context and Ceramic Styles
Kuntur Wasi is located at 2300 m asl in the northern highlands of the Cajamarca Department, Peru (Figure 1). The Japanese Kuntur Wasi Archaeological Project excavated the site from 1988 to 2002, and again in 2012, 2013, and 2019. The site is contemporaneous in part with the famous ceremonial site of Chavin...
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de Huantar some 330 kilometers to the south and in part with the site of Pacopampa 90 km to the north, Huacaloma in the Cajamarca basin 40 km east, and with the site of Las Huacas in the Middle Jequetepeque Valley 45 km west.

Figure 1. Location of Kuntur Wasi and area of study. Original map drawn by Kinya Inokuchi, Eisei Tsurumi and Yuko Ito, modified with permission to show the main sites mentioned in the text.

Four archaeological phases were identified: Idolo (ID; 950-800 cal. B.C.), Kuntur Wasi (KW; 800-550 cal. B.C. including the Sangal Complex), Copa (CP; 550-250 cal. B.C.) and Sotera (ST; 250-50 cal. B.C.) ([4] Inokuchi, 2010; [5] Onuki and Inokuchi, 2011; [6] Onuki et al., 1995). A shift in architecture happens during the second phase, the Kuntur Wasi phase, with a new large-scale architectural complex, stone monoliths, water canals, special burials, and stylistic changes in the ceramic repertoire ([4] Inokuchi, 2010, [7] 2014; [6] Onuki et al., 1995). The next phase (Copa phase) witnessed an intensification of building activity, and a larger population, with more people involved in activities related to the temple, including probably ceramic manufacture. During the final architectural subphase of the Copa phase the major part of the ceremonial architecture was abandoned, and during the Sotera phase Kuntur Wasi ceased to function as a ceremonial center.

The ceramic styles, production and distribution patterns reflect the changes observed in the site. 61 ceramic types were recognized ([4] Inokuchi, 2010), with changes in technological traditions and resources used over time. During the first two archaeological phases (Idolo and Kuntur Wasi) foreign ceramics are found along with local productions. During the third phase (Copa) foreign imports decreased, and a new potting community worked close to the ceremonial center. Production degraded during the fourth phase (Sotera), when the site ceased to function as a ceremonial center. The interaction networks involved the Middle Jequetepeque Valley and the Cajamarca basin ([1] Druc and Inokuchi 2016; [3] Druc et al. 2017; [4] Inokuchi, 2010; [8] Inokuchi and Druc 2019).

Prior Ceramic Studies

Prior petrographic studies identified different paste groups and atypical pastes for the ceramics found in Kuntur Wasi ([2] Druc et al., 2013; [1] Druc and Inokuchi, 2016; [8] Inokuchi and Druc 2019). Comparison with local geology, geological samples, and modern ceramics allowed us to see that 1) most of the ceramics were local productions, 2) different potting traditions co-existed, and 3) ceramic production and distribution evolved, with a peak of foreign vessels in the early archaeological phases at the site, and intensive, local production later. The local tradition, continuing throughout the existence of the site, is characterized by the use of volcanic pyroclastic material mined from deposits in the nearby mountain, 8 km north of the site. The other main potting community appears later and is very active during the third archaeological phase (Copa), using subvolcanic material as temper from possible sediments less than 5 km from the archaeological site. Another paste group represents ceramics with inclusions of mix compositions, which could derive from the use of local quaternary sand deposits. The nonlocal pastes present material which outcrop in the middle coastal Jequetepeque Valley below or from the Cajamarca basin, east of the site. The LA-ICP-MS confirmed the diversity of compositions and presence of multiple production units ([3] Druc et al. 2017).

Materials and Methods

The 21 fragments analyzed come from excavations conducted between 1988 and 2013, under the direction of Dr. Yoshio Onuki, Dr.
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Yasutake Kato, and Prof. Kinya Inokuchi. They were chosen from the site laboratory to represent the range of pigments found on the ceramic surfaces, as slip or paints, applied in incisions, grooved or simply directly over the surface or the slip. The samples were examined in Peru, in the laboratory of the archaeological site, for the initial, mineral analysis, and in Lima, for pXRF and Raman analyses. The mineral analysis was done with a portable digital microscope (DinoLite) in reflective light looking at a cross section without damaging the piece. This allowed us to assess paste composition and texture whenever possible, classifying the samples according to the petrographic groups identified in the prior analyses briefly described above. All of the ceramic samples are rather coarse, with fine to coarse nonplastic inclusions, have a compacted paste, and are oxidized to incompletely oxidized with superficial oxidation at the end of the firing. Many present local, volcanic or subvolcanic compositions. A few others seem to have intrusive rock fragments, a material identified in our earlier analysis as indicative of foreign provenance ([1] Druc and Inokuchi 2016; [3] Druc et al. 2017) as such rock type foreign provenance (Table 1).

As the fragments are usually small, rare, or of museum value, it was important to choose analyses techniques for pigment study that would not require damaging the sample. Portable X-ray fluorescence allows one to identify chemical elements in an area that is later analyzed with Raman microscopy which yields information about the minerals and oxides present in the sample.

In both techniques, the ceramic fragment is simply laid on a surface or deposited in the chamber of the instrument. The samples were analyzed at the laboratories of the Pontificia Universidad Católica del Perú. pXRF analyses were performed with a Bruker Tracer II-SD portable XRF spectrometer, equipped with a rhodium tube. The experimental conditions were 40 kV, 10.3 µA, and 30 s live time. Raman analyses were carried out with a Renishaw Invia Raman spectrometer (785nm diode laser or 514nm argon ion laser) in conjunction with WiRE 3.4 software, with extended scan from 100-2200 cm⁻¹, 50X objective lens, exposure time of 10 and 20 seconds/scan for 1 to 5 accumulations, and 0.05 to 5% laser power.

Table 1 gives the list of samples studied with Raman and pXRF, while figure 2 illustrates these fragments and their paste composition as seen in reflexive light microscopy.

Table 1. List of samples analyzed with Raman and pXRF

<table>
<thead>
<tr>
<th>Sample</th>
<th>Code</th>
<th>Phase</th>
<th>Style</th>
<th>Form</th>
<th>Pigments visible</th>
</tr>
</thead>
<tbody>
<tr>
<td>99KW-C229</td>
<td>RA1</td>
<td>ID</td>
<td>Rojo Grafitado</td>
<td>bottle</td>
<td>black and red</td>
</tr>
<tr>
<td>99KW-A789</td>
<td>RA2</td>
<td>ID</td>
<td>Rojo Grafitado</td>
<td>bottle</td>
<td>black and graphite</td>
</tr>
<tr>
<td>90KW-309</td>
<td>RA3</td>
<td>ID</td>
<td>Policromo</td>
<td>bottle or cup</td>
<td>white and brown</td>
</tr>
<tr>
<td>7KW-L161</td>
<td>RA4</td>
<td>ID</td>
<td>Pintura post-cocción en zona</td>
<td>bowl</td>
<td>red-yellow-white</td>
</tr>
<tr>
<td>4KW-225</td>
<td>RA5</td>
<td>ID</td>
<td>Pintura post-cocción en zona</td>
<td>bowl or plate</td>
<td>red-white-yellow-black</td>
</tr>
</tbody>
</table>
| 4KW-2746  | RA6     | ID    | Pintura post-cocción en zona | sculpted? bottle | red-white-yellow-
| 7KW-A556  | RA7     | ID    | Rojo & Blanco A (sub A) | bowl | white   |
| 4KW-2642  | RA8     | ID    | Rojo & Blanco A (sub B) | cooking pot? | white   |
| 4KW-647   | RA9     | ID    | Rojo & Blanco A (sub B) | cooking pot | white   |
| 4KW-2507  | RA10    | KW    | Rojo Grafitado         | bowl? cooking pot? | black   |
| 6KW-1976  | RA11    | KW    | Rojo Grafitado         | bottle sculpted | black |
| 6KW-2930  | RA12    | KW    | Blanco                 | bowl | white   |
| 7KW-A342  | RA13    | ST    | Rojo s/ Blanco         | bowl | white   |
| 6KW-104   | RA14    | ST    | Rojo s/ Blanco         | bowl | white   |
| 6KW-1691  | RA15    | CP    | Marrón inciso B        | bowl | red     |
| 3KW-371   | RA16    | CP    | Blanco s/ Rojo         | bowl | white   |
| 9KW-369   | RA17    | CP    | Rojo y Blanco          | bowl | white   |

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<table>
<thead>
<tr>
<th>Sample Code</th>
<th>RA18</th>
<th>KW</th>
<th>Feature</th>
<th>Paint Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>4KW-B-57</td>
<td>RA18</td>
<td>KW</td>
<td>uncl post-firing paint</td>
<td>bottle</td>
</tr>
<tr>
<td>7KW-G-S27</td>
<td>RA19</td>
<td>KW</td>
<td>uncl post-firing paint</td>
<td>bowl</td>
</tr>
<tr>
<td>9KW-1621</td>
<td>RA20</td>
<td>KW</td>
<td>uncl post-firing paint</td>
<td>bottle?</td>
</tr>
<tr>
<td>99KW-C116</td>
<td>RA21</td>
<td>KW</td>
<td>uncl post-firing paint</td>
<td>bottle</td>
</tr>
</tbody>
</table>

Ra1 ID bottle Rojo Grafitado  
Ra2 ID bottle Rojo Grafitado  
Ra3 ID bottle or cup, Pólicromo

Ra4 ID bowl Pintura post cocció in zonas  
Ra5 ID bowl pintura post cocció in zonas  
Ra6 ID bottle Pintura post cocció in zonas

RA7 ID bowl Rojo & Blanco A m/A  
RA8 ola® ID Rojo & Blanco A m/A  
RA9 ola® ID Rojo & Blanco A m/A
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RESULTS OF THE pXRF AND RAMAN PIGMENT ANALYSES

Table 2 presents the chemical elements detected with pXRF and minerals identified with Raman microscopy. Not all pigments could be identified as their Raman signal was not strong enough. In other cases, only pXRF analysis could be done. Also, pXRF easily picks up signals from the surface or slip beneath the pigment if the pigment layer is too thin. This would explain the differences between the pXRF and Raman results; iron in particular is frequently detected by pXRF even for whites, but this signal may rather relate to the ferruginous, oxidized paste or slip underneath.

For nearly all samples, the red and black tones come from an iron oxide, possibly in the form of ochre applied on the surface as slip or paint (Fig. 3). We do not know which medium or adhesive was used with these oxides, be it a clay or an organic one. In sample RA10, the red contains both iron and manganese (Mn), which is fairly common. Iron oxides can also yield yellows. This depends upon firing and the type of iron oxide used. In two cases, calcite appears to have been preferred or used for obtaining a white color (samples RA16 and RA17). These are two bowls of the Copa phase (third archaeological phase at the site). For the production of white, titanium oxide in the form of anatase is the most frequent mineral used. Graphite to produce black was identified in four samples (RA1, RA2, RA10, RA11). Even so pXRF detected Fe, we are confident that the Raman identification of graphite is correct in view of the style of the vessels (Rojo Grafitado). These are traditionally decorated with graphite lines over a shiny red slip (Druc et al. 2019). Ochre and calcite are local minerals.

Table 2. Pigment composition in the samples studied. ns: no useful Raman signal was obtained, na: the sample could not be analyzed.

<table>
<thead>
<tr>
<th>Samples</th>
<th>pXRF</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>RA1</td>
<td>red: Fe black: Fe</td>
<td>red: ns black: graphite</td>
</tr>
<tr>
<td>RA2</td>
<td>red: Fe black: Fe</td>
<td>red: ns black: graphite</td>
</tr>
<tr>
<td>RA3</td>
<td>red: Fe black: Fe</td>
<td>red: hematite black: ns</td>
</tr>
<tr>
<td>RA4</td>
<td>red: Fe black: Fe yellow: Fe white: Fe S</td>
<td>red: hematite black: ns yellow: ns white: ns</td>
</tr>
<tr>
<td>RA5</td>
<td>red: Fe black: Fe yellow: Fe white: Fe</td>
<td>red: hematite black: ns yellow: ns white: ns</td>
</tr>
</tbody>
</table>
The only sample showing a different pattern from these common mineral pigments is the bottle fragment from the Kuntur Wasi phase RA18 (Figure 4). The red in this sample was identified as cinnabar (HgS), while the blue is azurite. The green pigment in this sample is not copper-based, but it could not be further identified for now. In some cases, due to the colored area being too narrow, XRF analyses could not be conducted.
**DISCUSSION AND INFERENCES ABOUT TECHNOLOGICAL KNOWLEDGE IN PIGMENT USE**

Mineralogy and chemical composition of the raw materials to build a ceramic vessel are usually related to the geology of the area where the potters work, at least in the Andes and for the time period and area of study. However, pigments can come from further away ([9] Rice, 1985) and can easily be traded. To apply them, the potters also need a good understanding of their behavior upon drying and firing to obtain the intended color. Some of the vessels recovered at Kuntur Wasi were also decorated with post-firing paint. These were not common and not for everyday use.

Our analysis of the pigments on the ceramic fragments studied show that the potters providing Kuntur Wasi manipulated iron oxides to obtain a wide range of colors to coat and decorate their wares. The hues vary from yellow to red, brown and black. It testifies to a good control of firing to achieve the intended colors.

The usual pigments included iron oxides such as hematite and ochre to obtain reds and blacks, and titanium oxides and calcite for white. Graphite was used occasionally and only for certain ceramics, to produce the Rojo Grafitado style for example. All these pigments could have been found locally and the wares produced and decorated in the area or region around the ceremonial center.

The only exception to the pigments mentioned above is cinnabar (mercury) for red and azurite for blue as a post-firing paints on a sculpted bottle (sample RA18, Figure 4), from the Kuntur Wasi Phase. Note that it is during this phase and the precedent Idolo one that nonlocal vessels were more often brought to the site ([1] Druc and Inokuchi, 2016, [3] Druc et al., 2017, [8] Inokuchi and Druc, 2019).

Due to its rarity, no thin section could be made out of this sample, but the paste seems coarse and possibly with volcanic material, based on optical microscopy. Volcanic outcrops are found throughout the Andes and as such the vessel could have been manufactured in different...
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places, including Kuntur Wasi. However, the paste does not display the usual volcanic fragments seen in Kuntur Wasi ceramics and the rarity of the azurite and cinnabar pigments leads us to believe that this is a nonlocal bottle.

The use of azurite as pigment is reported in Pacopampa, an important ceremonial site from the same time period, 90 km north of Kuntur Wasi, in the Cajamarca department ([10] Seki et al., 2019). Azurite was probably part of the copper smelting and production activities at this center, and was found nearby in a mine of secondary copper minerals, along with chrysocolla and malachite ([10] Seki et al., 2019; [11] Shimizu et al., 2012). In Pacopampa, at least two tombs contained azurite and cinnabar as powder pigments. In one, the pigments were deposited as offerings along with other pigments close to a young boy while cinnabar covered part of his body; in the other case azurite and cinnabar powder covered the upper left and right (respectively) skull of the woman buried ([10] Seki et al. 2019). Similar burial customs are witnessed in Kuntur Wasi with all eight special tombs displaying cinnabar on the skull and face of the individuals (but no azurite) ([12] Onuki, 1995; [5] Onuki and Inokuchi, 2011).

Like for Pacopampa, cinnabar is not known in the area of Kuntur Wasi and must be acquired. A well-known and important source of cinnabar for that time period is near Huancavelica in the southern highlands of Peru, which was widely distributed as confirmed by in-depth sourcing analysis conducted by Burger and Matos ([13] 2002) and Cooke and colleagues ([14] 2013). Isotope analysis confirmed that the cinnabar found in Gramalote, an early fishing village near Trujillo on the northern coast ([15] Prieto et al., 2015) came from there. Thus, it would not be surprising that Kuntur Wasi and Pacopampa also obtained their cinnabar from Huancavelica. However, smaller sources are reported for the northern and central Andes ([15] Prieto et al., 2015, [16] Burger et al., 2016).

Del-Solar and other colleagues have studied ceramics and pigments for San José de Moro in the Lower Jequetepeque Valley (e.g. [17] Del-Solar, 2014, [18] 2015, [19] Del-Solar et al., 2017, [20] 2019; [21] Rohfritsch, 2006). Nino Del-Solar also used pXRF and Raman to study pigments on Moche and Cajamarca vessels, ceramic styles and cultures following the period when the Kuntur Wasi center was in use. Del-Solar and colleagues observe, as we do for Kuntur Wasi, that iron oxides are the primary minerals responsible for the pigments analyzed ranging from red to black. They also report hematite and magnetite, as well as other pigments, like manganese (see [20] Del-Solar et al., 2019 for a literature review about pigments’ use in Peru). We know manganese is available in the Cajamarca area and used by a modern ceramist ([22] Druc 2011), but this mineral was rarely found in ceramic pigments during Kuntur Wasi time.

Our results suggest long-distance distribution, not of the pigments but of this particular painted bottle (RA18). It also testifies to highlands relationships, possibly with Pacopampa, based upon the importance of cinnabar and azurite found at that site. While this can be due to the hazards of excavations and research, until cinnabar and azurite are found elsewhere in this area, this is the strongest ‘material’ link we can propose between Kuntur Wasi and Pacopampa. In addition, vessels with post-firing paint of similar colors (red-blue-green-yellow) as found in Kuntur Wasi are known in Pacopampa, and some styles of the Kuntur Wasi ceramics of the Idolo phase show similarities with contemporary sites among which figures Pacopampa. As for the Rojo Grafitado Idolo bottles RA1 and RA2, they seem to show intrusive rock fragments (to confirm with petrography). This points to a provenance from one of the coastal northern valleys, in comparison with similar bottles of this style analyzed before ([1] Druc and Inokuchi 2016; [23] Druc 2015; [24] Druc et al. 2019). Without more detailed mineral and chemical analyses it is hard to propose provenances for the other possible nonlocal pastes. Their pigments are common and found throughout the Andes, coast and highlands.

Conclusion

The preliminary pXRF and Raman analyses of the pigments of ceramics found in the ceremonial center of Kuntur Wasi, Peru, showed that the potters used iron oxides such as hematite and ochre for the yellow, red, brown and black colors to decorate their wares. It testifies to a good control of firing to achieve the intended colors. Titanium oxides and calcite were used to obtain a white color. All these oxides and pigments could have been found locally, and applied on wares produced in the area around the ceremonial center. Graphite was also identified in four fragments from three bottles and one bowl, to produce Rojo Grafitado style vessels. These ceramics are often nonlocal
and widely distributed. This is probably the case for the three Rojo Grafitado bottles we analyzed (as fragments). Finally, one bottle fragment showed the presence of cinnabar for the red and azurite for the blue post-firing paints, none of which local to Kuntur Wasi. One hypothesis for the provenance of this bottle could be that it came from the ceremonial site of Pacopampa, where azurite was mined, and cinnabar was also used (but not extracted there). Cinnabar, although found only in a few places in the Andes, was distributed throughout ancient Peru at that time period and later. We hope to be able to continue these analyses in more details, as much information could still be acquired.

ACKNOWLEDGMENTS

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