Four-Color Polychrome Pottery from the Coclé Region of Panama: Investigating the Production of the Purple Colorant

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Abstract: A unique purple slip exists on pottery of Panama from approximately 500-1100 AD. Gettens identifies the slip as a hematite in the 1942 excavation report of Sitio Conte but there is no explanation for the purple hue of the hematite, a color not achieved through the use of hematite alone. No further studies into the production of this purple slip appear to have been conducted. Continuing Gettens' work, this research investigates the composition of the purple slip, using complementary analytical techniques as well as experimental archaeology.

Keywords: Panama, Coclé, Sitio Conte, XRF, XRD, SEM, PLM, Experimental Archaeology, Hematite, Slips

INTRODUCTION

During the years 500-1100 AD, a polychrome slip design with three or four colors was being used in the Coclé region of Panama. The distinctive slip color of this period is a purple. Although other areas in Central and South America have purple hues in their pottery, these other purples are more maroon. The Panamanian examples have a grey hue. This purple slip color only existed in Panama for a relatively brief period of time. While there are numerous sources that discuss the designs on these ceramics, there are no recent studies on their production technology. As stated by Karen O'Day, "Despite the availability of a sound analytical method, the symmetry of Sitio Conte ceramic painting never has been the subject of a comprehensive analysis (O'Day, 2003, p. 39)." Many suggestions about the materials in these Panamanian ceramics have been stated as fact, but none of these suggestions are supported with analytical evidence. The following study was conducted to better define the production technology of these ceramics.

CERAMICS FROM THE COCLÉ REGION

These Panamanian ceramics have an orange body with fine particles of quartz, specular hematite, and large nodes of hematite as temper. The ceramic has no core; the same color is seen throughout the thickness of the sherd **(Figure 1).** This homogeneity of color is likely due to a long firing in order for the core to become fully oxidized (Orton et al., 1993, p. 69). The hematite nodules are rounded and thus may be from a water source and/or ground. There are no voids, which indicate a lack of organic inclusions. The surfaces of these ceramics were coated with a white slip, decorated with red, black, brown, and purple slips, and highly burnished. Each ceramic is decorated with a geometric design, typically depicting a human transformation to an animal or an insect. These ceramics typically have no use wear, which could indicate that the ceramics were made for special purposes, such as rituals or burial practices (Briggs, 1989, p. 42).

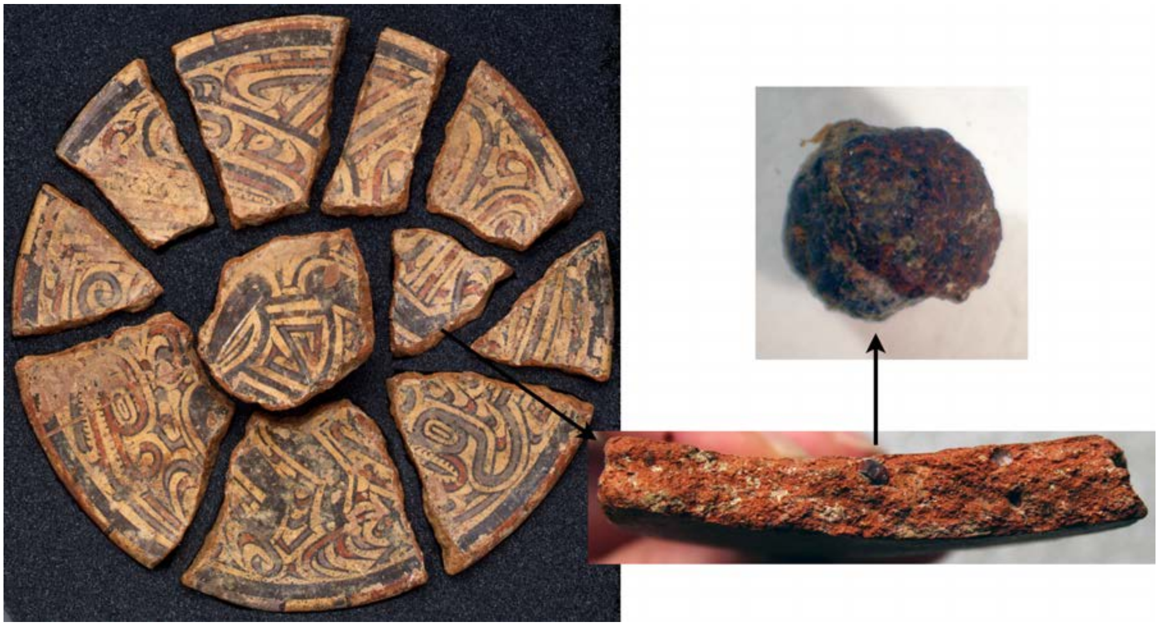

Figure 1: Killed ceramic used for sampling (left) with a view of the body of the ceramic without a core (right bottom) and the vesicular hematite temper (right top)

The Michael C Carlos Museum of Emory University has nineteen ceramics from the Coclé region with this purple slip. These ceramics are in various states of preservation, differ in size, and display varying imagery. Some of these ceramics are whole, while others have been broken and restored. Many of these ceramics have been varnished during their collection history – altering the appearance of the slips. Additionally, some of these ceramics have been ritually killed. Most of the analysis for this study was conducted on a killed pot, which provided easy access to break edges as well as worn slip for sampling **(Figure 1)**. Three additional pots with worn slips (and unvarnished) were selected for sampling of the purple pigment.

FIRING TEMPERATURE

Since firing temperature can affect the color of the slip, it was important to determine the firing temperature. Different crystalline structures, which can be studied by X-ray Diffraction (XRD), will develop or disappear depending on the firing temperature. Unfortunately, the analysis could not be conducted non-destructively because the inclusions (quartz and hematite) in the ceramic interfered with identifying the peaks for the clay minerals. Instead, a small sample (0.25ml) was removed from the break edges of the killed ceramic and then ground. Large inclusions were removed by floating the sample in water. The sample was then glycolated (suspended over ethylene glycol for 1 hour at 80°C) to identify expanding clays –smectite, bentonite, and montmorillonite. The body of the ceramic is predominately made of bentonite, a volcanic soil (**Figure 2)**. El Valle, the closest volcano, last erupted in

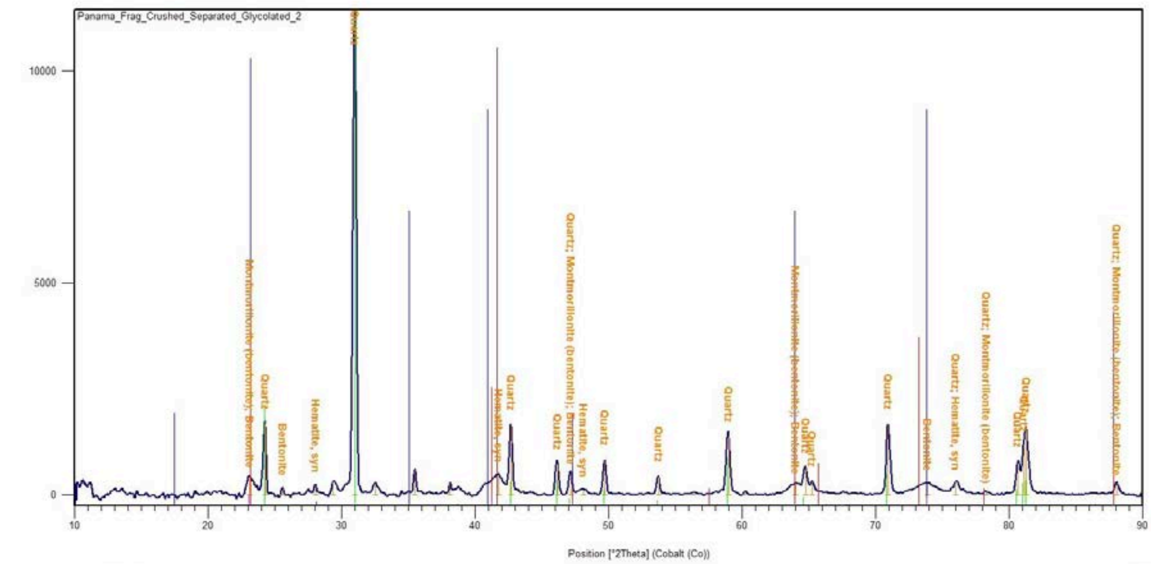

Figure 2: XRD spectra of the ceramic body, showing peaks of montmorillonite, bentonite, hematitite, and quartz

the Holocene Epoch (NMNH, 2013) and would provide a local source of volcanic soils such as the bentonite. The main mineral component of bentonite is montmorillonite, which degrades at 860°C (Kayani and Siddiqui, 2011, p. 71). Typical clay particles illite, kaolinite, and smectite degrade between 550°C to 650°C. The absence of these clay minerals and the presence of montorillonite indicate a firing temperature between 650°C and 860°C (Rasmussen et al., 2012, p. 1710; Moropoulou, 1995, p. 744, and Grattan-Bellew and Litvan, 1978, p. 493-4). Hematite develops between 800°C and 900°C. It is uncertain but likely that the hematite seen in the XRD spectra of the clay body is due to the temper (the specular and vesicular hematite) rather than the firing conditions. These hematite inclusions are nodules of vesicular hematite that show iridescence and bubbling (vesiculation)**(Figure 1).** This appearance indicates that the hematite was heated enough to vesiculate, which occurs at approximately 700°C, but was not heated enough to release all the oxygen - leaving the air bubbles present on the surface (Size pers. comm., 2012, 16 November). The presence of the vesicular hematite may narrow the firing temperature to between 700**°**C-860**°**C. Some unidentified d-spacing peaks at 3.53, 3.20, 1.98, 1.90, and 1.79 Å in the XRD spectra of the ceramic could possibly help to narrow the firing temperature. These unidentified d-spacing peaks could identify other crystalline structures that develop or degrade at a temperature within the 700 -860 °C range.

Dr. John Basca, Director of the X-Ray Crystallographic Center at Emory University, collected the XRD spectra. D8 Discover Powder Diffractometer and a Bruker D8 Diffractometer with an APEX II CCD detector were used.

PURPLE SLIP

The only scientific analysis of the slips on these ceramics was conducted by Rutherford Gettens - the father of conservation science, and reported in Lothrop's 1942 *Coclé: An Archaeological Study of Central Panama*. Gettens identified the slips of these ceramics, but his analytical methods are not reported. Red is identified as red ochre, purple as violet hematite, brown as brown hematite, black as manganese, and white as kaolin or another white clay mineral (Lothrop, 1942, p. 13). Preliminary XRD analyses at Emory University confirm the red is a mixture of hematite and goethite as seen in red ochre, the black is manganese, and the purple is iron based. These elemental results are further confirmed by X-ray Fluorescence (XRF) and Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM-EDX), both revealing significant peaks for iron in both the red and purple pigments as well as manganese in the black **(Figure 3).** None of the Panamanian ceramics with a purple slip at the Carlos Museum have a brown slip.

SEM analysis was conducted at the Center for Advanced Ultrastructural Research at University of Georgia by Dr. John Shield, co-Director on a *Zeiss 1450EP*. The author collected the XRF data, using a *Bruker Tracer III-V* at 40KeV and 14µamps with a green filter (0.006"Cu, 0.001"Ti, and 0.012"Al), for 180 seconds.

Figure 3: Overlay of XRF spectras of the purple, red, and black slips

There are very few purple mineral colorants (FitzHugh and Zycherman, 1992, p. 145) and even fewer containing iron. These iron-containing purple minerals are purpurite (iron manganese phosphate), vesuvianite (iron manganese silicate), crocus martis (Iron Sulfate), and natural violet hematite. Purpurite, vesuvianite, and viviante ((iron phosphate) the blue mineral turning purple upon heating) can all be discounted as neither manganese or phosphorous occur in the spectra of the purple pigment on the Coclé ceramics. Although the sulfur in crocus martis could have been burned off during firing of the ceramic, crocus martis becomes maroon when fired instead of maintaining the purple hue.

As Gettens identified, the purple pigment appears to be a violet hematite. The question is why is the hematite purple rather than the expected red? The color of hematite particles is dependent on their size and grouping of particles– bright red between 0.1µm-0.2µm and purple between 1-5µm. However, this optical affect –appearing purple- is destroyed through grinding (Torrent and Schwertmann, 1987, p. 685). Under PLM (Polarized Light Microscopy) at 40X, the particles of this purple pigment are homogenously purple and between 0.5µm to 0.1µm in diameter **(Figure 4)**. This homogeneity shows that this purple pigment cannot be a mixture of red and blue minerals, but rather is a purple pigment itself. The purple particles in the slips studied are much smaller (0.5-0.1µm) than the size of particle necessary (1-5 µm) to be purple

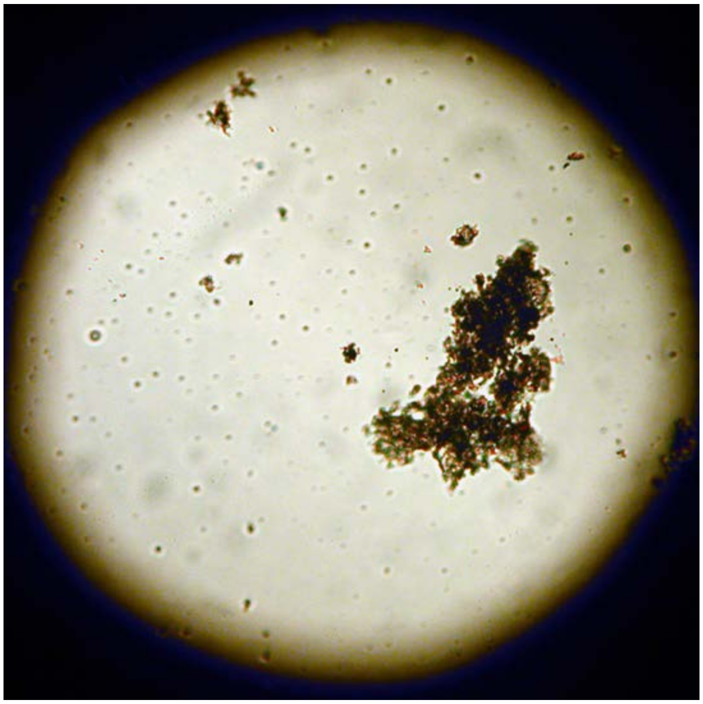

Figure 4: Purple slip particles at 40X

naturally and the size of the particle would not account for the partially dehydrated state of the purple pigment as identified by Gettens. Gettens mentions that the violet hematite may derive from red hematite but does not explain how it derived. The dehydrated state of the violet slip, as noted by Gettens, could be created by two different processes – heating under high heat or heating under a reducing atmosphere and then reheating under an oxidizing atmosphere.

The alteration of this hematite pigment must occur separately from the formation of the pottery itself. Although the white slip is applied first, then the colored slips, and finally the black outlining, there is no consistency on the application of the purple and red pigments. If the purple slip was always added first or last, a change in the firing conditions, such as seen in Greek red and black ware, could be possible. However, when the overlap of the various slips is examined, sometimes the red pigment is seen applied over the purple and sometimes the purple overlaps the red. If the alteration of the purple pigment occurred during final firing of the pot, the red slip, also composed of iron oxide, would become purple under these conditions as well. Therefore, the hematite first must have been turned purple, then applied as a slip to the pot.

Briggs found pockets of colored powders in graves at Sitio Conte (Helms, 2000, p. 75) and a nodule of a purple mineral found with excavation materials from the Coclé region at the University of Pennsylvania Museum of Archaeology and Anthropology (Grant, pers. comm., 2014, 18 June). The presence of a concentration of these pigments could be evidence of manufacture of these pigments for the polychromy.

The Coclé purple slip is in actuality **not** purple. Munsell color charts place all of the purple slips within the gray red range. This placement may support the idea that red hematite contains less oxygen to produce the grey tinge. The Munsell colors of the four ceramics analyzed are: 10RP 5/1 (two objects), 7.5RP 4/2, and 5R 4/2. The rest of the Coclé ceramics at the Carlos Museum fall within this range.

An artificially produced iron purple, Mars Purple (most commonly called caput mortuum) was used at the end of the eighteenth century (FitzHugh and Zycherman, 1992, p. 145). Dossie stated that an aqueous precipitation of iron salts with alkalis could be roasted to produce dark purple shades of iron (III) oxides (Dossie, 1764, p. 53-4) and George Field claimed a purple colorant could be created by calcining red ocher or heating it with ammonium chloride (Field, 1835, p. 69). However, caput mortuum has been identified on Roman wall paintings (de Oliveira et al., 2002). A purple colorant has also been found on Theban Archaic pottery. This colorant is a hematite with no magnetite in the XRD spectra. The lack of magnetite is evidence that a reducing stage is unnecessary and the formation of the purple is due to high heats (Mastrotheodoros and Beltsios, 2012; Mastrotheodoros et al., 2010; Mirti, 1998). However, technological similarities between the Old and New World seem to be commonly suspect.

It is possible that nodes of hematite were buried in coals to produce an oxygen deprived, or reducing, atmosphere. Once the purple color was reached, the nodules could be ground to produce pigment for the slip. In this way, a purple color could be achieved without necessitating a high temperature. Although an appropriate color was achieved using this technique, magnetite was present in these samples under XRD **(Figure 5)**. None of four examples from the four color polychrome ceramic from the Carlos Museum's collection had any magnetite in the XRD spectra **(Figure 6**). The samples appear to be solely hematite, iron oxide, and quartz.

Hematite can turn maroon at 800°C for 5 hours and gray at 900°C for 5 hours or at higher temperatures for a shorter time (Mastrotheodoros and Beltsios, 2012; Mastrotheodoros et al., 2010; Legodi and de Waal, 2007, p. 15; Mirti, 1998). However, scholars have doubted that Pre-columbian Panamanians could achieve such a temperature during firing due to the lack of evidence of kilns. The lack of a kiln, however, does not necessarily mean that such kilns did not exist (Orton and Hughes, 2013, p. 136). Such evidence could have been destroyed by the people who abandoned the site, exist below sites still populated, been destroyed by the Conquistadors, or by the large scale mining operations in the area. However, use of a brazier as in metal production seems more likely.

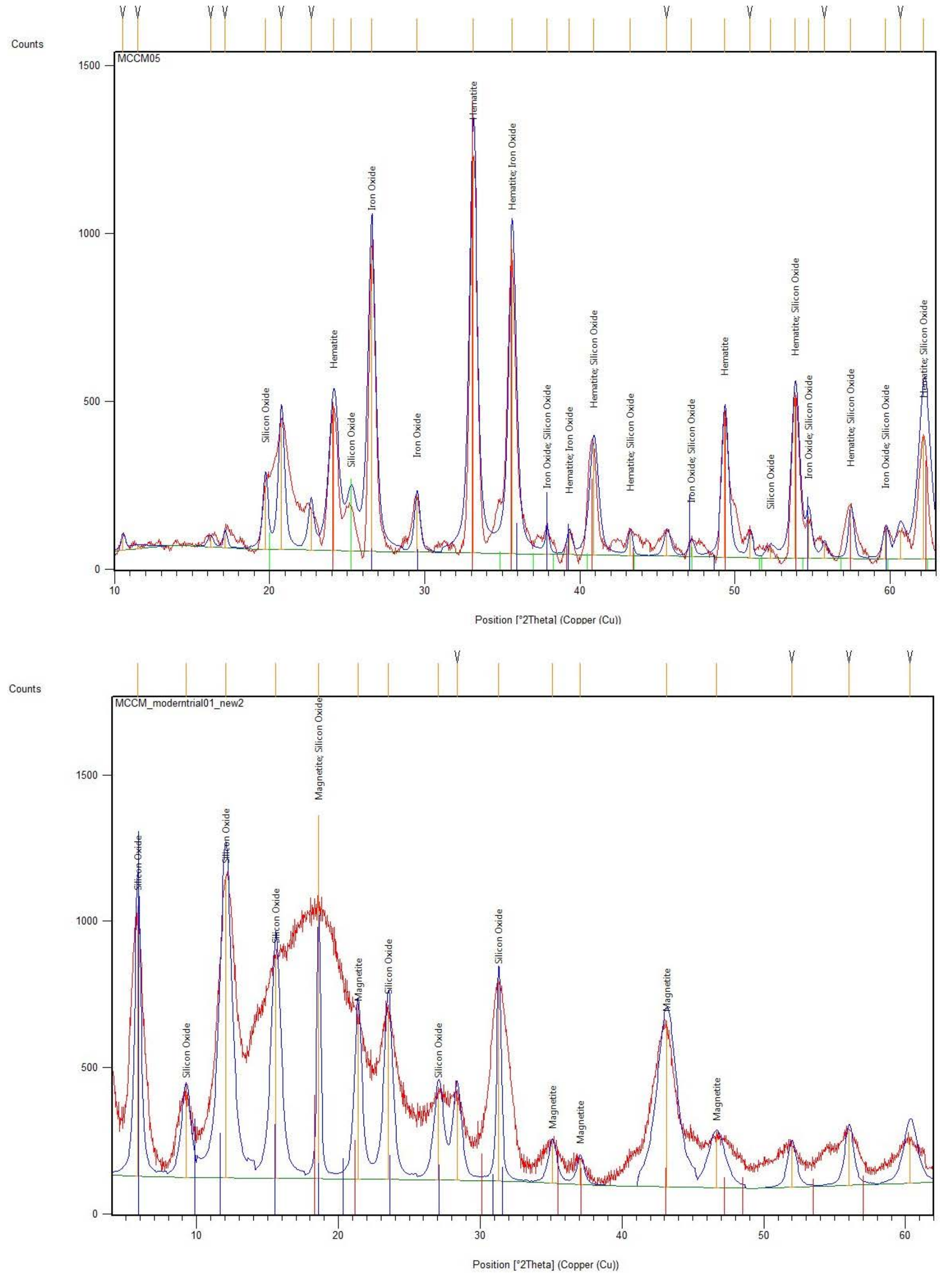

Figure 5: Comparison of the XRD spectra of the original purple slip (top) and the hematite fired under a reducing atmosphere (bottom)

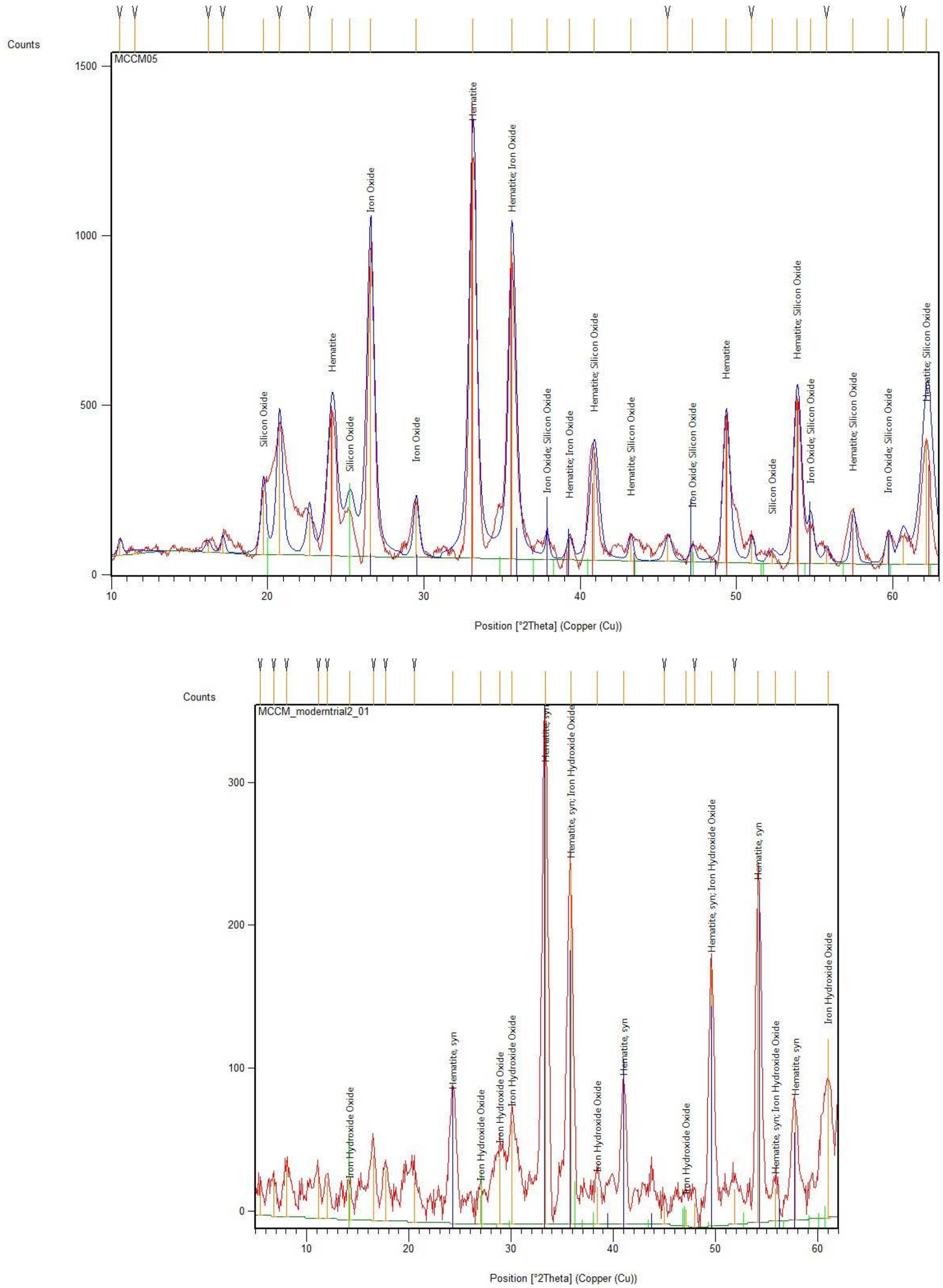

Figure 6: Comparison of the XRD spectra of the original purple slip (top) and the hematite fired at a high temperature (bottom)

High temperatures could be created in a brazier, especially the temperature needed to melt gold. Metalwork appears to have been burgeoning at the time of the introduction of the four-color polychrome scheme on Panamanian pottery (Cooke et al., 2000, p. 165) perhaps suggesting a link between the production of purple and metalwork. Gold melts at 1063°C and cast objects from Panama could have a high percentage of gold, up to 97% (Harrison and Beaubien, 2010; Scott, 1995, p. 502-3; Linares, 1977, p. 41; Biese, 1967, p. 208). Although the addition of copper will lower the melting point of gold, such high purity gold as used in Panamanian cast gold objects will need a higher temperature to melt – no lower than 1000°C (Fleming, 1992, p. 56). Spaniards mentioned the ability of Panamanians to melt gold, both to torture captives and to adorn chieftains (Cooke et al., 2003; Hearne, 1992, p. 19). Ralegh wrote that Panamanians increased the temperature in a small crucible “so with the breath of men they increased the fire till the mettell ran (Ralegh, 1848, p. 96)”. “Such temperatures [needed to melt high purity gold] can be obtained locally by means of a brazier-type hearth and a blow pipe blown by human lungs (Tylecote, 1981, p. 108).” A tomb of goldsmith gold was found near El Caño with furnaces and molds (Cooke and Bray, 1985, p. 35), indicating that gold production as described above did occur. The temperatures needed to melt high purity gold are within the range necessary to turn hematite purple. Hematite could well have been heated in a brazier such as those used for metal production, especially since in braziers, the temperature needed to melt gold was reached.

A sample of hematite was heated in an oxygen-rich environment at a high temperature and the hematite turned purple. After being ground, painted on a test tile, and refired at 784°C (cone 14), the mid-range of the 700-860°C range mentioned previously, the purple color remained (5R 2.5/1 and 5R 2.5/2) and was closer to the range of Munsell Colors of the four-color polychrome pot at the Carlos Museum than the sample of pigment which was reduced (7.5R 4/4 and 10R 4/2). More significantly, the XRD spectra of the recreated purple pigment showed no peaks for magnetite, similar to the XRD patterns of the four Panamanian pots tested **(Figure 6)**. However, it is uncertain whether the Panamanians may have used a chemical, such as ammonium chloride, as a flux as mentioned by Field, to quicken the reaction.

CONCLUSION

Purple has been equated with luxury and power in many cultures due the rarity of purple in nature as a colorant and the amount of time necessary to produce purple artificially.

The time and resources needed to achieve at least 900°C for a length of time and the possible association with gold production places extra significance on the use of purple on Coclé ceramics. Ancient Panamanians had the ability to produce this artificially purple hematite. A temperature of around 1000°C is needed to melt the high purity gold used in cast gold objects from the Coclé region well within the temperature needed to turn the hematite the hue seen on Coclé ceramics. As evidenced by this gold manufacture, ancient Panamanians could reach the temperatures necessary to turn hematite purple and the deposits of purple minerals/pigments found in archaeological sites suggest ancient Panamanians did so.

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