ELECTRON MICROPROBE ANALYSIS OF RED PAINTED AND SLIPPED CERAMICS FROM CHOCOLA, GUATEMALA – AN INITIAL INVESTIGATION OF THE PIGMENTS AND METHODS OF APPLICATION

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Introduction

The site of Chocolá is located to the west of Guatemala City in the Central Pacific highlands in what historically was the Southern Maya Zone. It is an area still occupied by the Quiché Maya and has been the subject of research since Robert Burkitt discovered evidence of the Maya there in the 1920's (Kaplan 2004, 7). Recent research on Chocolá has been undertaken under the direction of Dr Jonathan Kaplan (University of Pennsylvania) and Dr Juan Antonio Valdez (University of San Carlos, Guatemala). This paper presents the analysis of decorative pigments on Early to Late Formative period ceramics from Chocolá.

Early Mayan ceramics were hand-formed, low-fired earthenware vessels with different types of surface decoration that included polishing, burnishing, slipping and painting (Coe 1997, 140-1). Whilst slipped and burnished wares are more common, red paint appears on several known trade wares of the Middle/Late Formative period (400BC – 600AD) (James 2001, 18). The use of red paint on vessels could have a symbolic significance since the colour red (*Chac*) was associated by the Maya with the East (*Likin*), with the rising sun, blood, fire, the sap of the sacred ceiba tree and with roasted corn, all of which were connected to the concept of life and vital force (Morley 1946, 245).

Research aims

The main aims of this research were to identify the pigments used in the red paint and slips forming the surface decoration on the different ceramic wares and the possible methods by which they were applied. It also attempted to identify whether the differences in colour were due to a difference in the raw material utilised or due to technological reasons such as the method of application and firing conditions.

While visually similar surface decoration may have been produced using different techniques (inter alia McGovern 1989, 63; Day et al. 2006, 49-57), it is equally possible that typologically distinct traditions may have been produced by the same potters using similar decorative techniques (Rye 1981, 5). Compositional analysis can help identify the materials used and help establish if well known trade wares, based on typological studies, may in fact be imitations or copies with distinctly different chemical profiles (Pollard and Heron 1996, 105). Pigments may have been obtained from more distant sources than clay or temper raw materials (Arnold 1985, 47-53), and thus the identification of the materials used for paints and surface decoration may be important in the study of trade, exchange and distribution networks (Beudray 1989, 84; Rice 1987, 119). However, it is also possible that similar materials may have been used as constituents of paint and slips by widely separate communities of potters (Arnold 1985, 50).

Traditional methods of application of the paints and slips

There is a variety of methods that can be used to apply slip and/or pigment decoration. Slips can be applied using a wiping or brushing motion, which may be more suitable on smooth surfaces and on a completely dry pot because the moisture is absorbed immediately and the slip dries quickly and evenly (Rye 1981, 24). In contrast, dipping the vessel into the slip will penetrate recesses, grooves and incisions and may give a more even cover. The identification of slip decoration can be confused due to 'self-slipped' vessels, where the surface has an even, smooth finish of similar colour to the body that is achieved by wiping or smoothing the surface while the clay is still damp (Rye 1981, 57), or by 'washes' where a very thin coating of pigment/slip is applied before or after firing (Rye 1981, 41). Paints or pigment decoration are created from a mixture of a pigment, a medium in which the compound dissolves or is suspended, and possibly a binder, which allows the pigment particles to adhere to each other and the surface (Beudray 1989, 90).

A microstructural analysis of the decorative surface of the samples can help in identifying the possible methods by which the surface decoration has been applied by clarifying the nature of the join between slip/pigment and the body.

Analytical methodology

The samples were analysed using the JEOL JXA8200 electron microprobe in the Department of Archaeology at the University of Nottingham. The pottery samples were prepared as polished cross-sections to allow microstructural and compositional analysis of the decorative pigments. The analytical set-up used a 15kV accelerating voltage, a 50nA beam current and a 1µm diameter focused beam for quantitative analysis, while a 500pA beam current was used for backscattered electron (compositional) imaging. The compositions of eleven elements were analysed using WDS with the results presented as oxides: Na₂O, MgO, Al₂O₃, SiO₂, P₂O₅, SO₃, K₂O, CaO, TiO₂, MnO and FeO. The microstructures observed in the backscattered electron (BEI) images were used along with the chemical results to help identify possible production techniques utilised to apply surface decoration and to look at the interaction zone between the decorative surface and paste.

Since cinnabar was used by the Maya as a pigment (Beudray 1989, 176; Shepard 1980, 43), a qualitative EDS assessment of the pigments was undertaken prior to quantitative analysis to identify whether mercury (Hg) was present and should be included in the analysis. There was no evidence for the presence of mercury within the pigments and thus the red pigment on these vessels could not be cinnabar.

KUCH sample no.	site	ware	context	decoration	sherd	form	period*		
1	Chocolá	Xuc	PACH 4-53-4	red paint	rim	cuenco (bowl)	MF		
2	Chocolá	Xuc	PACH 4-81-6	red paint	rim	cuenco	MF		
3	Kaminal- juyú	Xuc	RND 601A-2	red paint	rim	cantaro (jar)	MF		
4	Chocolá	Semetabaj Cafe	PACH 4-62-5	red paint and punching	body	cantaro	M/LF		
5	Chocolá	Semetabaj Cafe	PACH 4-72-4	red paint and punching	body	cantaro	M/LF		
6	Chocolá	Semetabaj Cafe	PACH 4-72-6	red paint and punching	rim and handle	cantaro	MF		
7	Chocolá	Chocolá local ware	PACH 4-72-9	red paint	rim	cantaro	E/MF		
17	Chocolá	Chocolá local ware	PACH 4-91-7(a)	red slip	rim	unknown	M/LF		
18	Chocolá	Chocolá local ware	PACH 4-91-7(b)	red slip	rim	cuenco or plato (plate)	M/LF		
* Period : MF = Middle Formative; E/MF = Early/Middle Formative; M/LF = Middle/Late Formative									

Table 1. Stylistic and contextual information of the sherds from Chocolá.

Sampling and wares

The samples selected for analysis were representative of three ware types from the Middle to Late Formative period present at the site: Xuc, Semetabaj Cafe and Chocolá local wares (Table 1). The Xuc ware and Semetabaj Cafe ware samples were chosen as possibly representing links with other sites based on their identification as distinctive trade wares.

Three sherds of Xuc wares were sampled: two were from the Chocolá excavations (KUCH 1 and-2) and one from excavations at Kaminaljuyú, where it is common during the Middle Formative (KUCH 3). All three are characteristically 'white' in colour, and unslipped but with the surface of KUCH 3 appearing smoother than the two from Chocolá. This may have been burnished and polished which is common of this type (de Hatch 1997, 150) or the clay may have had a natural lustre. Xuc wares are only common in the Middle Formative and the brighter red paint is thought to be earlier than darker and more purple painted wares (de Hatch pers. comm. 2005). The two Chocolá sherds have a limited amount of red paint present due to weathering but this appears to extend from the rim onto the body and may have been applied to the whole vessel after firing. KUCH 3 has the paint applied on the exterior lip and over onto the interior surface of the everted rim for around 20mm. The two Chocolá samples have thicker walls and a slightly concave form, suggesting they are from *cuencos* (bowls) whilst the sherd from Kaminaljuyú has an everted rim and could be from a small cantaro-shaped (jar) vessel. The paint on the inner lip also suggests this as it is common on vessels used for pouring liquids.

The Semetabaj Cafe samples (KUCH 4-6) are from an utilitarian ware thought to be a trade ware dominant in the Middle to Late Formative, and originating at Semetabaj near Lake Atitlán in the Highlands (de Hatch 1997, 140). This ware is recognised by its red band of paint below the neck accompanied by punched decoration (Figure 1). KUCH 5 has a band of paint below the collar and all have evidence of a slip or further painting on the exterior of the body.



Figure 1. KUCH 6, A Semetabaj cantaro with characteristic strap handle and punched decoration.

The samples identified as Chocolá Local Ware included sherds with decoration that appears to be either painted (KUCH 7 and 17) or slipped (KUCH 18). The most common form appears to be a *cantaro* which may be copies of Semetabaj cafe vessels, but usually these are undecorated. The surface finish on KUCH 7 is similar to that of Semetabaj cafe, characteristically bearing a thick polished matt red 'slip'. In the Late Formative period, some vessels are perhaps self-slipped, with the surface appearing almost the same colour as the paste.

Results: chemical composition and microstructure of the paints and slips

Xuc ware

The pigment used for the red paint on the three Xuc wares (KUCH 1-3) is characterised by inclusions of iron oxide mostly of around 1µm, but with occasional larger up to c. 15µm, and thus may have been derived from haematite (Figure 2). The quality of the adhesion between the pigment and the body is suggestive of prefiring application (Figure 3). KUCH 1 has an applied paint layer of around 10-15µm though the paint on this sherd was highly abraded and did not cover the whole sample and it is likely it was originally thicker. KUCH 2 likewise, has a very thin surface layer of around 10µm though it is a more sharply defined layer than KUCH1. KUCH3, the sherd from Kaminaljuyú has a much thicker layer of finer material at around 30-40µm but appears less uniform in application. The chemical compositions exhibit a lower concentration of silica and a higher concentration of iron oxide and potassium oxide in the paint compared to the body (Table 2), and the matrix of the pigment appears to be finer grained than the clay body, suggesting that an iron pigment was ground and applied in a fine clay suspension. The paint on KUCH 3 appears more likely to have been applied by painting as it has a slightly uneven line on the inner lip. It is difficult to tell exactly how the decoration was applied on KUCH 1 and 2 as both sherds are very abraded but as it appears to cover the outer body and does not extend over the rim, the whole vessel could have been dipped or brushed with a thick red slip.



Figure 2. Backscattered electron micrograph of the red paint on KUCH 3 Xuc ware from Kaminaljuyú characterised by varying sizes of large iron oxide inclusions (over $15\mu m$ in length) and dispersed iron oxide particles in a clay medium.

JEOL COMP 15.0kV x500 10µm WD11mm

Figure 3. Backscattered electron micrograph of XUC ware KUCH 2 showing the strong adhesion between the pigment and body.

	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	K2O	CaO	TiO2	MnO	FeO
KUCH 1	0.14	0.49	26.32	43.98	0.36	0.10	3.22	0.40	0.29	0.05	24.65
KUCH 2	0.23	0.59	27.86	47.77	0.54	0.26	3.91	0.39	0.42	0.08	17.95
KUCH 3	0.19	0.70	17.45	40.65	0.43	0.19	4.09	0.62	0.38	0.05	35.25
KUCH 4	0.17	0.19	25.47	25.78	1.74	0.55	0.28	0.42	0.79	0.91	43.70
KUCH 5	0.03	0.22	34.33	32.42	1.33	0.40	0.31	0.61	1.73	0.02	28.61
KUCH 6	0.31	0.70	17.77	30.09	0.38	0.25	0.46	0.42	0.73	0.10	48.81
KUCH 7	0.08	0.19	27.55	28.85	1.52	0.25	0.24	0.87	1.96	0.03	38.45
KUCH 17	0.14	1.27	24.72	31.27	0.79	0.18	0.59	1.02	1.51	0.04	38.46
KUCH 18	0.09	0.31	36.06	38.77	1.11	0.80	0.27	1.41	2.25	0.07	18.87

Table 2. Average chemical compositions of the red pigment or slip on the samples from Chocolá, n = 3 - 5 spot analyses.

Semetabaj ware

The paint on the Semetabaj sherds was also characterised by high levels of iron oxide in the surface treatment (Table 2) and a visibly higher concentration of dispersed particles of around 1-2 μ m diameter in a fine grained matrix, again suggestive of the use of a fine grained clay suspension for the pigment. Several large inclusions proved to consist of iron oxide, including one which was almost 20 μ m in size (Figure 4).

In the Semetabaj wares there is also a strong adhesion between the pigments of the surface treatments and the body. The pigment layers vary in thickness between 10 μ m on KUCH 4 (Figure 5) and 30 μ m on KUCH 6 (Figure 4). Since the decorative band on KUCH 6 extends under the strap handle, it seems likely that it was painted on rather than dipped. The decorative layer on KUCH 5 appeared less clear and more abraded.





Figure 4. Backscattered electron micrograph of KUCH 6 with the pigment clearly seen as a layer of up to $20\mu m$ against the paste including a large inclusion of iron oxide.



Figure 5. Backscattered electron micrograph of KUCH 4 showing strong adhesion between the body and surface treatment at the bottom of the image.

Chocolá local wares

The Chocolá wares with red painted decoration, KUCH 7 and 17 have high levels of iron oxide in the pigment, which is reflected in the microstructure as small (<1 μ m), evenly dispersed grains (Figure 6), although there are several larger inclusions of iron oxide that are between 5 μ m and 30 μ m in size. KUCH 7 shows a relatively fine-grained layer of iron rich pigment around 10 μ m in thickness (Figure 3) although the sherd is abraded and this may have been thicker originally. This pigment layer appears to have been applied as a paint in a clay matrix. The surface layer of KUCH 17 appears to have been as thick as 30 μ m. Both samples have grains of iron oxide suspended in a fine-grained matrix, which is well adhered to the body, again strongly suggesting the use of a fine-grained clay base that was applied pre-firing.



Figure 6. Backscattered electron micrograph of KUCH 7 from a red painted Chocolá cantaro rim sherd showing red pigment containing small particles of iron oxide.

The surface layer on KUCH 18 is thin (around 5μ m) and uneven, suggesting smoothing or perhaps wiping, to create a smooth surface in a slightly darker clay, although without the strong alignment of the clay particles that would be indicative of burnishing. The concentration of iron oxide in the surface is slightly higher than in the body, but there are no visible inclusions (Figure 7). The decorative materials in all three examples of Chocolá local ware have high levels of Ti and Ca (Table 2) which may suggest that these reflect differences in the fine-grained clay raw material used to bind the iron pigment (in KUCH 7 and 17) or used as a slip (KUCH18).



Figure 7. Backscattered electron micrograph of KUCH 18 from a red painted Chocolá cuenco or plato rim sherd showing the red pigment containing no visible particles of iron oxide.

Discussion: evidence of trade and diffusion of techniques

The Xuc sherds from Chocolá could be local copies of unusual trade vessels from Kaminaljuyú or may just have been obtained from a different source. Without study of further sherds from Chocolá and other sites it is difficult to reach a conclusion. Visually the two sherds from Chocolá are certainly different to many of the Xuc sherds viewed in the reference collections at the Universitie de Valle and IDAEH (The Institute of Anthropology and History). It is clear from both the visual and analytical examinations that while the two Chocolá Xuc sherds are similar in style, form and paste to each other, they appear different to the sherd from Kaminaljuvú. As there are no secure dates for any of them, it is difficult to postulate whether this is due to a refinement/development of techniques, a different place of manufacture or a different clay source. The presence of a thick but even paint on the Xuc wares implies that care appears to have been taken to prepare the pigment to ensure a bright, even colour (especially in the Kaminaljuyú sherd). Their presence on the site suggests Chocolá was an important site, whether they were imports or imitations.

It has been assumed that the local wares being produced during the Middle Formative period, were possibly imitating trade wares. The analysis of the pigments suggests the use of different raw materials (perhaps in terms of the clay used to suspend the pigment) between the 'Chocolá' and 'Semetabaj' sherds. It is difficult to say whether the local wares are imitations of Semetabaj ware, or whether they represent the movement of potters from Semetabaj to Chocolá, who then continued their potting tradition with slightly different raw materials. There are differences even within the Semetabaj sherds, since KUCH 5 appears different to KUCH 4 and 6, both chemically, in its method of application of surface treatment (in that it has no distinct layer as the other two) and stylistically (in terms of the shape of its punched decoration) despite being contemporary with the other two sherds. This might imply that there was a variety of sources or production sites for this ware.

Conclusions

The major component in the pigments used for the decorative treatments was iron oxide. However, the compositions vary as do the methods by which the paints were applied. The obvious care taken to prepare the pigments for use in some of the paints, such as the careful preparation of small, evenly dispersed particles of iron oxide in a fine-grained clay suspension, suggests these ceramics were of high quality and value.

Whilst there is a difference between the pigments used on the Kaminaljuyú Xuc sherd and the two Chocolá Xuc samples, it is difficult to hypothesise the relationship between these since none are associated with secure dates and thus the chronological relationship is unclear. Although stylistically similar, the techniques and materials used to decorate the local Chocolá and Semetabaj sherds are clearly differentiated, perhaps suggested the presence of several production centres.

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