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The use of FT-IR spectroscopy and SEM/EDS characterization of slips and pigments to determine the provenances of archaeological ceramics: the case of Guanacaste ceramics (Costa Rica)

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Summary

In this paper, the red and black pigments and slips of 63 Guanacaste ceramics were analyzed by Scanning Electronic Microscopy and infrared spectroscopy. All the pigment layers were made by dilution of a pure pigment in the slip layer. Red pigments were made using hematite, sometime in association with maghemite, mixed in the slip geomaterial. Black pigments were made of manganese oxide, sometime in association with magnetite.

Methodologically speaking, we clearly showed that the FT-IR analysis of the slip layer could allow a fast and pertinent discrimination of different sites of ceramic production according to their chemical compositions. Such approach could allow easier, cheaper and faster analytical analysis to answer to provenance study of archeological ceramics. In fact, the different ceramic types shared similar slip compositions with no correlation with the excavation site, showing that slip ceramics are relevant to trace Guanacaste ceramics in their exchanges or trades up to the Central Valley. Moreover, no local reproduction of Guanacaste styles in the central valley was noticed in this study. Meta-kaolinite and meta-smectite, different types of tectosilicates as quartz and cristobalite, hematite and feldspar were notably detected in slip layers. The Agglomerative Hierarchical Clustering and Principal Component Analysis of slip infrared spectra showed the presence of three distinct clusters in great accordance with actual knowledge on the ceramic production in the area. Finally, the heating temperatures were estimated between 670 and 870°C during the fabrication processes, with almost no significant difference due to school or ceramic types.

Keywords

Slips, Infrared spectroscopy, Provenance, Ceramics, Pigments

Introduction

Color always had an important role in human societies for symbolic [1] or aesthetic [2] aspects. In many civilizations, specific colored materials were created from natural materials in order to improve art and representations on a large palette of supports.

Pre-Columbian cultures settled in Guanacaste (north of Costa Rica), in the archeological area of Greater Nicoya [3], developed an important production of fine bichrome and monochrome ceramics until the arrival of Mesoamerican groups around 500 CE. After 500 CE, the ceramic production was expanded with polychromy and different designs of Mesoamerican origin [4–6]. These ceramics stand out for their white and cream slip layers with the use of red, orange, and black pigments in vessels with shaped like bowls, cups, plates and anthropomorphic and zoomorphic figurines [7].

The most important study about the production and distribution patterns of the pottery of Greater Nicoya was made by Ronald L. Bishop and Frederick W. Lange [4,8,9]. In their publications, the elemental (Instrumental Neutron Activation Analysis) and petrographic compositions of more than 3000 ceramic pastes were analyzed in order to find geochemical and mineralogical patterns associated to their types and varieties. Bishop and Lange [4] proposed the existence of 30 compositional groups linked to the existence of possible ceramic schools in Greater Nicoya, with three of them located in Guanacaste. According to these authors, Guanacaste Polychrome School II, (GN-04) was most probably located at the east of Guaitil, and was related to the production of Altiplano Polychrome, Birmania Polychrome, Mora Polychrome Chircot, and late Mora Polychrome Mora varieties. Near the coastal zone at the height of Tamarindo Bay, Middle Tempisque School (GN-05) most probably produced all the varieties of the Jicote Polychrome type [4]. The location of the different schools proposed by Bishop and Lange is given in figure 1.

Guanacaste ceramics were clearly important goods in exchange and trade networks all over Costa Rica and Nicaragua. Indeed, the presence of such Guanacaste ceramics was documented in domestic and funeral contexts in many archeological sites located in the Central Valley of Costa Rica [10–13]. The ceramic trade even increased from approximately 700 CE to 1520 CE, with Mora, Birmania, Papagayo, Altiplano and Jicote as the most frequent polychrome ceramic types [7,14–16].

Another central question raised in the scientific literature is whether there was an exchange of polychrome ceramics from Guanacaste to the Central Region or whether there could have been local copies of this ceramic production [8,17]. In order to answer such scientific issue, physicochemical analyses are a truly pertinent solution as various studies showed the differences between elemental compositions of Gran Nicoya and Central Valley ceramics [18,19].

In this way, the production techniques of Guanacaste ceramics, and especially the materials used in the slip and pigment layers, could allow finding new fabrication patterns in order: (i) to assess the presence of copies of the Guanacaste types in the Central Valley, (ii) to strengthen, question or precise the theory of the schools of ceramic productions.

Lastly, Guanacaste ceramics are famous for their colored patterns and decorations. However, with the exception of our preliminary work [20], no research ever characterized the colored geomaterials used in slip and pigment layers. These colored materials are often slightly dependent on the local geology. In Costa Rica, clay materials can be composed, for example, of various mixtures of kaolinites, smectites, allophanites, iron oxohydroxides (Hematite, goethite), halloysite, gibbsite, feldspars [21–23].

In this project, we analyzed 63 fragments of Guanacaste polychrome ceramic types from: (i) two Guanacaste archeological sites were selected: Palo Blanco (MNCR-G-800 PB) and Las Pilas (MNCR-G-850-LP), (ii) four sites in the Central Valley: Cariari (MNCR-H-134-CR), Chaparral (MNCR-A-359-CH), Barranca (MNCR- A-372-BA) and Alto del Cardal (MNCR- C-304-AC), (iii) one in the Central Caribbean: Nuevo Corinto (MNCR-L-72-NC). The selected ceramic types were Mora Polychrome with the varieties Guapote, Mono and Chircot, Altiplano Polychrome, Birmania Polychrome, Jicote Polychrome and Jicote variedad Felino, all of them produced between 800 CE to 1520 CE.

The Palo Blanco site is located in the lower basin of the Tempisque River, in the Palo Verde National Park in Guanacaste. The samples were taken from funerary contexts [24]. The Las Pilas site, located in the Abangares area, is a multi-component site with funerary contexts. The analyzed samples come from burial 6 and stratigraphic excavations [25]. In the western sector of the Central Valley, the Chaparral site is located, the samples come from the excavation of garbage and the Barranca site, the samples were obtained from test pits as a result of intensive prospecting. In the central sector of the Central Valley, the Cariari site is located; the samples were obtained from the excavation of burials and surface collections [26]. The Alto del Cardal site is in the eastern portion of the Central Valley, the samples came from a funeral and domestic context [27]. Finally, in the Nuevo Corinto site, the samples were obtained from domestic and funeral contexts [28]. The locations of all archeological sites are given in figure 1.



Figure 1: Map of the different archeological sites and possible locations of ceramic school as proposed by Bishop and Lange (2013).

Methodologically speaking, ceramic provenance studies are principally based on mineralogical and elemental analysis of ceramic pastes and raw materials. In this study, we clearly showed that FT-IR analysis of slip layer could allow a fast and pertinent discrimination of different sites of ceramic production according to their chemical compositions. Such approach could allow easier, cheaper and faster analytical analysis to answer to provenance study of archeological ceramics.

The different objectives of this work are (i) to produce the first analyses of pigments and slip layers in Costa Rica and assess the material and techniques used, (ii) to use multivariate statistics in order to Group samples by similar chemical composition in order to find patterns of fabrication of Guanacaste ceramic found in Guanacaste and Central Valley sites using slip chemical compositions, (iii) to trace Gran Nicoya ceramics in the central region in order to validate the presence of a ceramic trade between the different archeological sites, (iv) to compare the group of similar composition to the ceramic school theory in Guanacaste.

Materials and methods

Archeological samples

All 63 Samples were part of the collection of the Archeology Laboratory of the Costa Rica university. The table 1 describe the distribution of the samples among the different archeological sites. The pictures of different samples are given in figure 2.

Ceramic types	Acronyms	Archeological sites and associated samples
Altiplano Polychrome	AP	(Palo Blanco) 17, (Barranca) 29, (Chaparral) 20, (Cariari) 3,6,8, (Alto del Cardal) 109, 110, 111, 112, 114, 115, (Nuevo Corinto) 55, 56
Birmania Polychrome	BP	(Las Pilas) 34, (Barranca) 27, 31, (Chaparral) 23, (Alto del Cardal) 113, 119
Jicote Polychrome	JP	(Palo Blanco) 12,13,16,18, (Las Pilas) 39, 40, 41, 42, 43, 44, 46
Jicote Polychrome Felino	JF	(Las Pilas) 45
Mora Polychrome	MP	(Palo Blanco) 14, 15, (Las Pilas) 35, 36, (Barranca) 26, (Chaparral) 19, 22, (Alto del Cardal) 104, 105, 106, 107, 108, 117, (Nuevo Corinto) 54
Mora Polychrome Chircot	MCh	(Cariari) 1,4, (Alto del Cardal) 116, 118
Mora Polychrome Guabal	MGb	(Chaparral) 25
Mora Polychrome Guapote	MGp	(Nuevo Corinto) 51
Mora Polychrome Mono	MMono	(Las Pilas) 37, 38, (Cariari) 9, (Nuevo Corinto) 49, 52
Mora Polychrome Mora	MMora	(Chaparral) 24, (Cariari) 5, (Nuevo Corinto) 47, 48, 50, 53


Table 1: Ceramic types and archeological sites of the samples analyzed in the present study. 



Figure 2: Pictures of different samples analyzed in this paper: a) 49, b) 51, c) 25, d) 47, e) 34, f) 109, g) 1, h) 40, i) 45.

Infrared spectroscopy

Micro-sampling was performed with 0.55 mg of pigment, after lightly and carefully scraping the pigmented surface. The pigment mass was homogenized with 100 mg KBr and compressed to 7.5 T.cm^{-2} to form pellets.

The FT-IR spectrometer used was Perkin Elmer Frontier model, coupled to Spectrum software, which belongs to the Materials Science and Engineering Research Center (CICIMA). In addition, it was used in transmission mode. The spectra were collected in the range of ($4000\text{-}400 \text{ cm}^{-1}$), with a resolution of 4 cm^{-1} and 30 scans. The samples were directly analyzed with FT-IR.

All spectra were treated using the R software with the Chemospec packages. These spectra were baseline corrected using the Fillpeak algorithm, smoothed using Savitzky-Golay algorithm and normalized. Furthermore, the second derivative of infrared spectra were performed to improve the identification of minerals.

Scanning Electron Microscopy

Micro-fragments of the samples were used in order to prepare cross-sections of pigment and slip layers. An encapsulation in Epoxy Mount resin was performed using PLA sample holders made by 3D printing and silicone molds. The cross-sections were polished with aluminum oxide polishes ($15 \mu\text{m}$ and $3 \mu\text{m}$) and aqueous suspension of $0.25 \mu\text{m}$ diamond powder using the EcoMet 30 equipment belonging to the Central American School of Geology. The cross-sections were cleaned during 20 min in distilled water in an ultrasonic bath. Gold coating of 10 nm was applied to cross sections in order to improve the image resolutions in scanning electron microscopy.

The cross-sectional analyses were performed with Hitachi S-3700 N scanning electron microscopy equipment which belongs to Microscopic Structures Research Center (CieMIC). The backscattered electron technique was used in COMPO Std. mode to choose the

measurement areas of the elemental composition. Energy-Dispersive-X-ray Spectroscopic (EDS) was performed with 120 s of measurement and the results were obtained using the Iridium Ultra software. The analysis conditions were 15 kV, 10-12 mm working distance, and high vacuum.

Results and discussion

All ceramic sherds included 2 distinct layers: white slips and red or black pigments. All the pigment layers presented a similar infrared signal as their associated slip layer with new infrared absorption specific to the red or black geomaterials used as coloring agent, as shown for sample 5 (Mora Mora type, found at Cariari site) in figure 3. Such result revealed the use of a similar technique for the confection of the pigment layer: the dilution of a pure pigment in the slip layer.

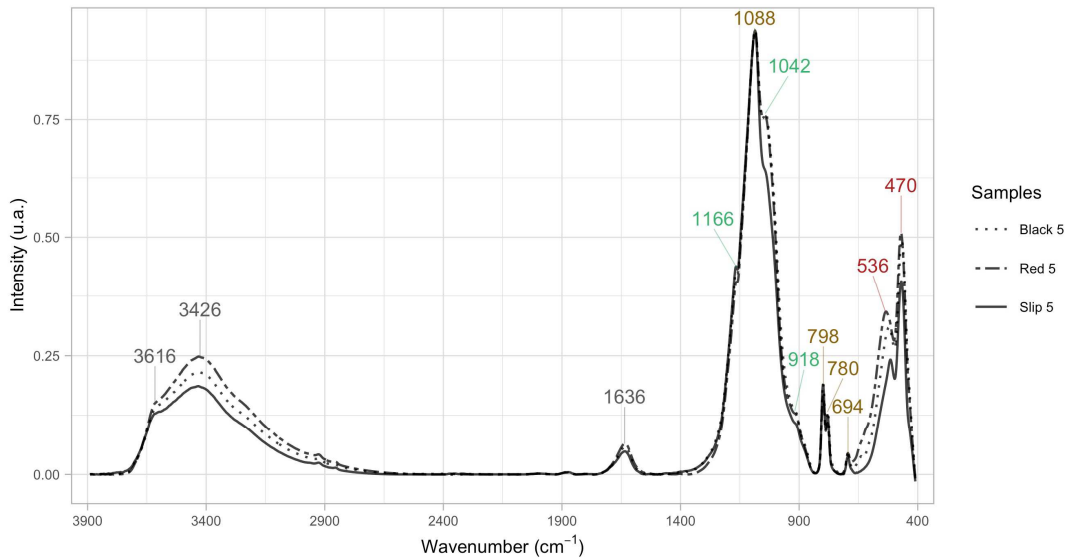


Figure 3: Infrared spectrum of slip and pigments layers of sample 5 (Type Mora Mora, Cariari).

Slip layers

In the slip layers, several geomaterial were identified by FT-IR spectroscopy (cf table 2 for main geomaterials): (i) Two distinct types of meta-clays: meta-kaolinite and meta-smectite, (ii) different types of tectosilicates as quartz and cristobalite, (iii) iron oxides, (iv) other types of minor minerals as anorthite, feldspar and calcite. All identifications were done according to the existent literature [29–32] and comparison with standards from the laboratory as described in table 2.

Meta-clays were detected in all samples according to their main absorption band around $1040 \pm 10 \text{ cm}^{-1}$ for meta-smectite (cf figure 4) and $1080 \pm 10 \text{ cm}^{-1}$ for meta-kaolinite due to asymmetric stretching of Si-O bonds. Other characteristic bands were found around 1168 cm^{-1} ($\nu_{as}(\text{Si} - \text{O} - \text{Si})$), and between 465 and 475 cm^{-1} ($\delta_{as}(\text{Si} - \text{O} - \text{Si})$).

Three types of tectosilicates were identified: (i) quartz thanks to its characteristic doublets at 778 and 798 cm^{-1} ($\nu_s(\text{Si} - \text{O})$), main absorption band at 1084 cm^{-1} ($\nu_{as}(\text{Si} - \text{O})$), and confirmatory band at 694 cm^{-1} , (ii) cristobalite thanks to its main absorption band at 1098 cm^{-1} ($\nu_{as}(\text{Si} - \text{O} - \text{Si})$), its single band centered at 796 cm^{-1} , and other confirmatory bands around 1200 cm^{-1} , (iii) feldspar thanks to infrared bands at 1140 , 1008 , 642 and 586 cm^{-1} . Water adsorbed in slip and pigment layers induced a broad band around 3426 cm^{-1} and

another around 1636 cm⁻¹ respectively linked to H₂O stretching and bending modes. It is important to point out that cristobalite is naturally present in the volcanic area of Guanacaste [20] and, thus do not come from the thermic degradation of quartz, occurring at high temperatures.

The presence of hematite was revealed in almost all ceramic slips with its characteristic band around 520-570 cm⁻¹ which maximum vary in function of the percentage of substituted Al [33]. Confirmatory bands were taken at 634 cm⁻¹ ($\nu(Fe - O)$) and 470 cm⁻¹ ($\nu(Fe - O)$). The last one was often overlapped by meta-clays or tectosilicates signals.

Mineral	Wavenumber (cm ⁻¹)	Acronym	Color used in graphics	References
<i>Meta-clays</i>				
Meta-clays	465-475, 1169, 1235	MC	Black	[31]
Meta-kaolinite	1070-1090	MK	Blue	[31]
Meta-smectite	1030-1050	MS	Green	[31]
<i>Oxide minerals</i>				
Hematite	430, 470, 520-560, 634	Hem	Red	[30,34]
Maghemite	444, 486, 556, 624	Mgh	Orange	[36]
Magnetite	570	Mgn	Grey	[30]
Manganese oxide	454, 606, 640	MnO ₂	Black	[30,31]
<i>Tecto silicates</i>				
Cristobalite	480, 618, 695, 795, 1099, 1176, 1200	Cr	Yellow	[31,35]
K-Feldspar	430, 586, 642, 1008, 1139	Feld	Purple	[31,35]
Quartz	460, 513, 694, 778, 798, 1084, 1180	Qz	Brown	[31,35]
Mineral	Wavenumber (cm ⁻¹)	Acronym	Color used in graphics	References
<i>Meta-clays</i>				
Meta-clays	465-475, 1169, 1235	MC	Black	[31]
Meta-kaolinite	1070-1090	MK	Blue	[31]
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<i>Oxide minerals</i>				
Hematite	430, 470, 520-560, 634	Hem	Red	[30,34]
Maghemite	444, 486, 556, 624	Mgh	Orange	[36]
Magnetite	570	Mgn	Grey	[30]
Manganese oxide	454, 606, 640	MnO ₂	Black	[30,31]
<i>Tecto silicates</i>				
Cristobalite	480, 618, 695, 795, 1099, 1176, 1200	Cr	Yellow	[31,35]

K-Feldspar	430, 586, 642, 1008, 1139	Feld	Purple	[31,35]
Quartz	460, 513, 694, 778, 798, 1084, 1180	Qz	Brown	[31,35]

Table 2: Infrared characteristic frequencies (cm^{-1}) of identified geomaterials

The presence of meta-clays was strengthened by the SEM/EDS elemental analysis, characteristic of silicate minerals, showing that: (i) Si relative molar concentration varied between 23.2 and 31.3 %, and (ii) Al relative molar concentration varied between 5.5 and 8.7 %. Quartz and cristobalite crystals were also detected thanks to their characteristic elemental composition (as shown for a quartz microstructure of samples 48 in appendix C).

An impressive homogeneity of the infrared spectra of the slips of Jicote type ceramics (Jicote Polychrome and Jicote Polychrome Felino) was observed as shown in figure 4 and table 3. Indeed, most slips were made of a geomaterial composed of meta-smectite, cristobalite, hematite and feldspar. Some traces of quartz were observed in many Jicote samples. The figure 4 was made by calculating the mean of all infrared spectra, the low distribution of slip chemical compositions was underlined by the very thin interval of the mean confidence limits based on the t-distribution.

As detailed in table 3, slips from Mora Polychrome Mora, Guabal and Guapote, and different Mora Polychrome ceramics were made of meta-kaolinite with quartz in more than 80% of analyzed samples, sometimes in association with minor levels of meta-smectites. Moreover, more than 70% of Altiplano Polychrome, Birmania Polychrome and Mora Polychrome Chircot ceramic slips included meta-smectite, meta-kaolinite with quartz.

Types	Slip layers					Red pigments		Black pigments	
	Hem	MK	MS	Qz	Cr	Hem	Mgh	MnO ₂	Mgn
AP	80	60	87	100	7	100		100	
BP	57	71	71	100		100		100	
JP/JF	100		100	67	100	100		100	100
MCh	75	75	75	100		100		100	
MGb		100		100		100	100	100	
MGp		100		100		100	100	100	
MMono	60	60	60	100		100	80	100	
MMora		100		100		100	83	100	
MP	20	80	27	100		100	15	100	

Table 3: For each ceramic type, percentages of detection of every geomaterials identified by FT-IR spectroscopy and SEM/EDS (number of samples with detection of the mineral divided by the number total of sample for a specific ceramic type or variety).

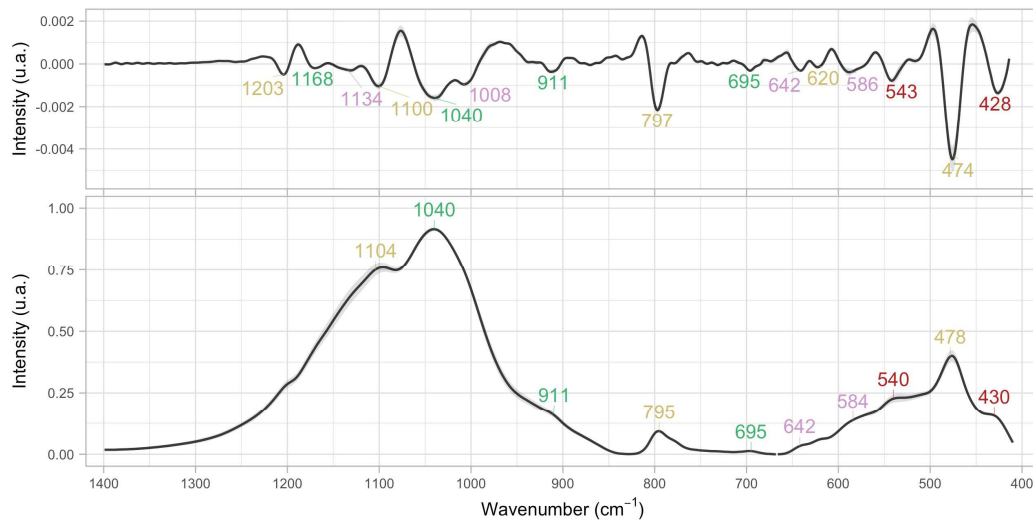


Figure 4: Mean infrared spectrum (*bottom*) and its second derivative (*above*) for all JP y JF analyzed. The gray area represents the lower and upper Gaussian confidence limits based on the t-distribution.

Multivariate statistic analysis of slip FT-IR spectra

The Agglomerative Hierarchical Clustering (AHC) dendrogram presented in figure 5 (b) showed the presence of three distinct clusters, associated with three distinct slip compositional groups (cf appendix A). This observation nicely fitted the 3 groups of samples observed on the graph of individuals of Principal Component Analysis (PCA) using the first two Principal Components (PC1 and PC2) representing 85.7% of total variance (cf figure 5 a)). The different clusters included the following ceramic types and varieties and main identified geomaterials (the mean FT-IR are presented in figure 4 and in appendix A) :

- *Cluster 1*: containing all MGp and MGb, 5 MMora, 1 MMono, 11 MP mostly composed by meta-kaolinite, quartz and the highest concentrations of hematite.
- *Cluster 2*: containing all JP and JF, composed of meta-smectite, cristobalite, feldspar and the lowest concentrations of hematite.
- *Cluster 3*: containing all the AP, BP and MCh, 4 MMono, 1 MMora, 3 MP mostly composed by a mix of meta-kaolinite and meta-smectite, quartz and variable concentrations of hematite.

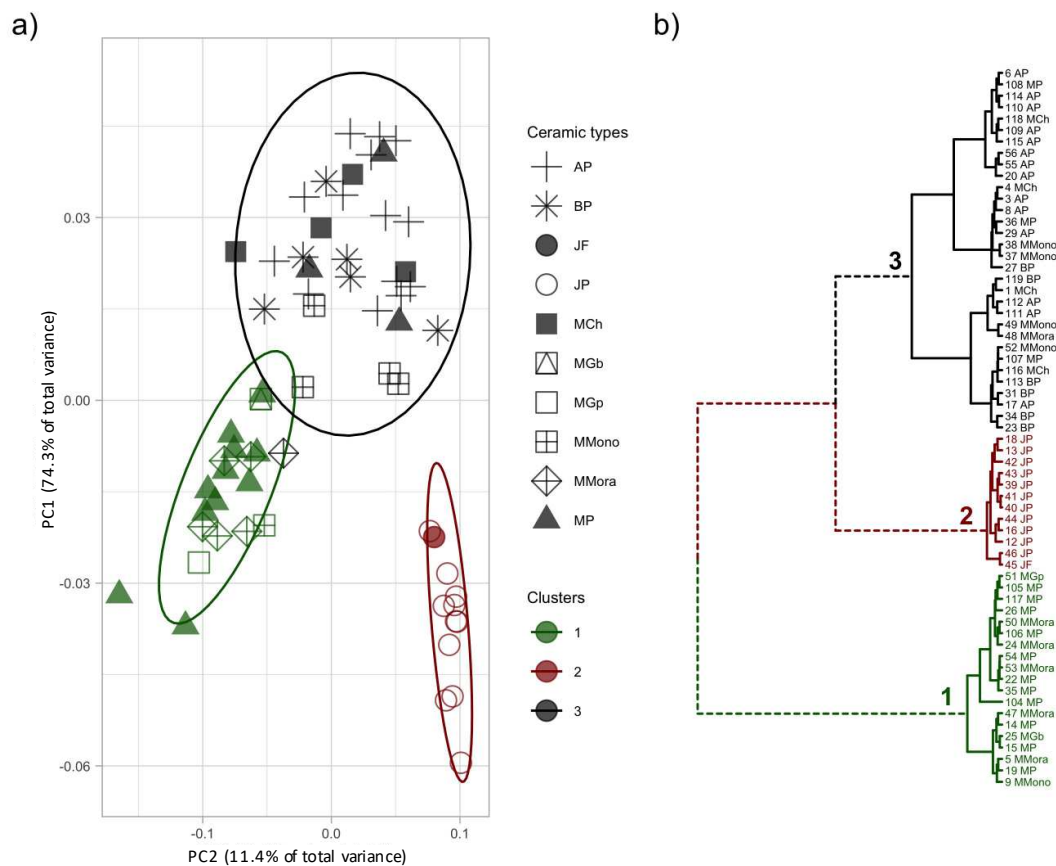


Figure 5: a) Principal component analysis of the first derivative of slip infrared spectra with 95% confidence ellipse of the clusters identified by Agglomerative Hierarchical Clustering. b) Agglomerative Hierarchical Clustering of the first derivative of slip infrared spectra (Euclidean distance, Ward's method).

First of all, the ceramics were grouped by types or varieties either if they were excavated in Guanacaste or Central Valley sites, showing that they shared similar slip compositions with no correlation with the excavation site. These results indicated that slip ceramics are relevant to trace Guanacaste ceramics in their exchanges or trades up to the Central Valley. Moreover, no local reproduction of Guanacaste styles in the central valley was noticed in this study.

As noticed in figure 5 (a), the ceramics included in the clusters 2 and 3 nicely fitted the associations between ceramic types and varieties of the Middle Tempisque (GN-04) and Guanacaste Polychrome II (GN-04) ceramic schools described in introduction and proposed by Bishop and Lange [4]. Moreover, in the cluster 2, all samples had an important level of similarity. In the cluster 1, all slip compositions only showed the presence of meta-kaolinite as meta-clay.

The different compositional groups shown in figure 5 (a) were discriminated according to the type of meta-clay, the concentrations of hematite and feldspar, and the presence of quartz or cristobalite, as noticed on the loading spectra of PC1 and PC2 presented in figure

6. Indeed, PC1 is highly correlated with the infrared bands of meta-smectite (1034 and 918 cm^{-1}), hematite (430 and 544 cm^{-1}) and quartz (1180, 1088, 800, 780 and 694 cm^{-1}). The PC2 is linked to the FT-IR signal of cristobalite (1114 and 484 cm^{-1}), feldspar (1002, 586 and 642 cm^{-1}) and meta-kaolinite (1062, 1228, 452 cm^{-1}).

Mora Polychrome of unknown varieties were named MP in this study. Using AHC clustering, 11 samples were associated to the clusters 1, and 3 samples were associated to the cluster 3. Linear Discriminant Analysis (LDA) was also used in order to validate these attributions using a supervised statistical model. The LDA was realized on the first four principal component (PC, cf figure 5) of the 49 ceramics from AP, BP, JP, JF, MCh, MGb, MGp, MMono, MMora types (cf table 1). We used the AHC clusters previously described as predictive class. This allowed us to model the linear combinations between PC and clusters in order to predict the group attribution (1, 2 or 3) of all MP samples. As previously discussed, these AHC groups contain specific ceramic types and varieties attributed to the presence of different workshops of fabrication in the area [4]. Thus, in order to homogenize the types and varieties inside the different clusters, the MMono of cluster 1 was attributed to cluster 3 and the MMora of cluster 3 was attributed to the cluster 1 before the LDA analysis. The LDA model was then validated by Leave One Out Cross Validation (LOOCV) which matrix (appendix B) showed a 96% of correct predictions. The confusion matrix (data not shown) led to 100% of correct predictions. LDA predictions and AHC clustering led to the attribution of samples: (i) 104, 105, 106, 117, 14, 15, 19, 22, 26, 35, 54 to cluster 1, (i) 107, 108, 36 to cluster 3. This result is in perfect accordance with the good grouping of these samples with corresponding clusters in PCA analysis (5 a).

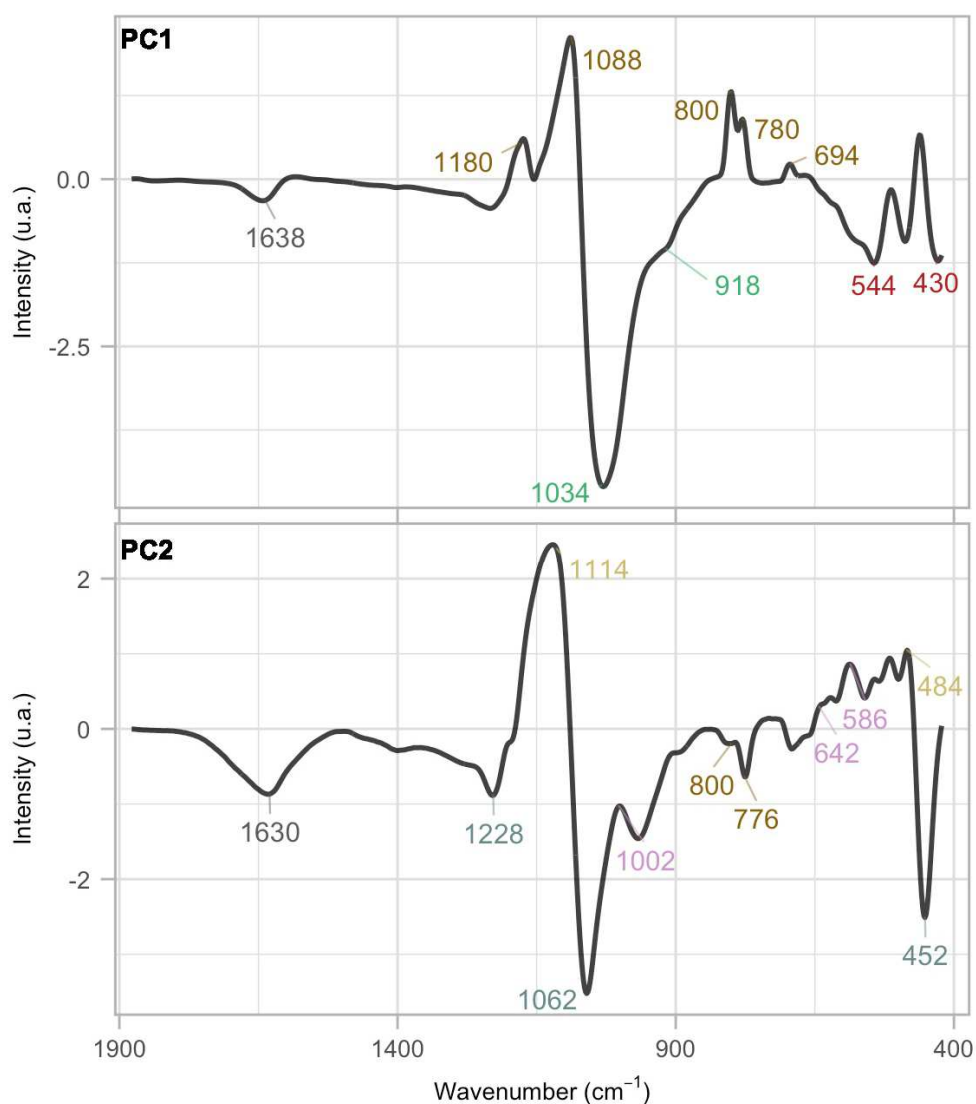


Figure 6: Loading spectra of Principal Components 1 and 2 of the PCA presented in figure slip infrared spectra. The presented spectra are the non-derivative spectra obtained by the integration of the original loading spectra using R software using the cumsum function from base package.

Red pigments

All red pigments were made using hematite mixed in the slip geomaterial, as noticed by the presence its specific identified infrared bands (540 and 430 cm^{-1}) as shown in figure 8. As shown in figure 7, SEM/EDS analysis confirmed these identifications and detected up to 36% (relative molar concentration) of iron and significant amounts of silicon, oxygen and aluminum.

In addition to hematite, maghemite was detected in all MGb, MMora and MGp red pigments of the cluster 1. Maghemite could be detected thanks to its characteristic bands at 446 ($\nu(\text{Fe} - \text{O})$), 486 ($\nu(\text{Fe} - \text{O})$), 558 ($\nu(\text{Fe} - \text{O} - \text{Fe})$) and 624 ($\nu(\text{Fe} - \text{O} - \text{Fe})$) cm^{-1} (cf figure 8). It is worth noting that maghemite was also identified in the MMora present in the cluster 3.

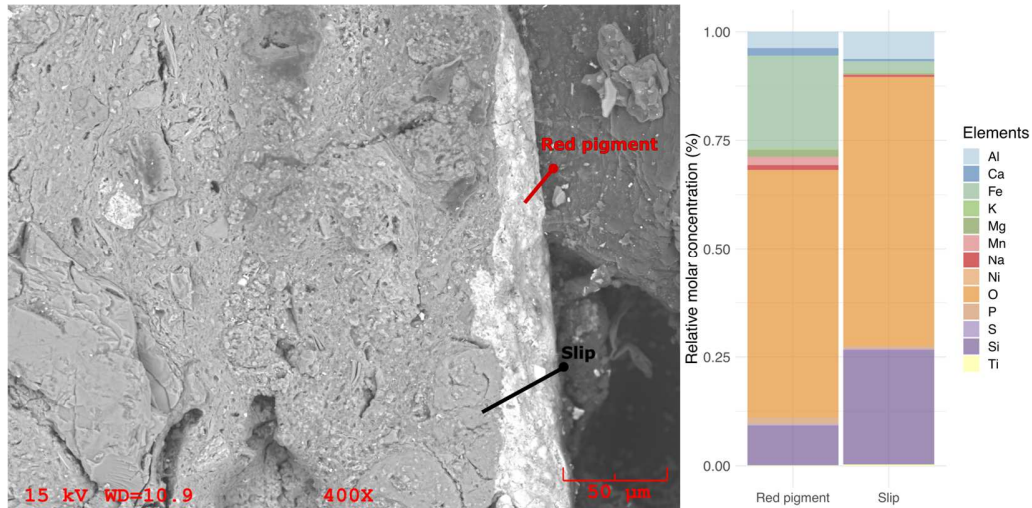


Figure 7: (left) Photography of the red pigment layer of sample 14 (MP, Palo Blanco) using Scanning Electron Microscopy with backscattering electron detector (400x). (right) Associated elemental compositions of slip and red pigment of sample 14 measured by the Energy Dispersive X-ray detector.

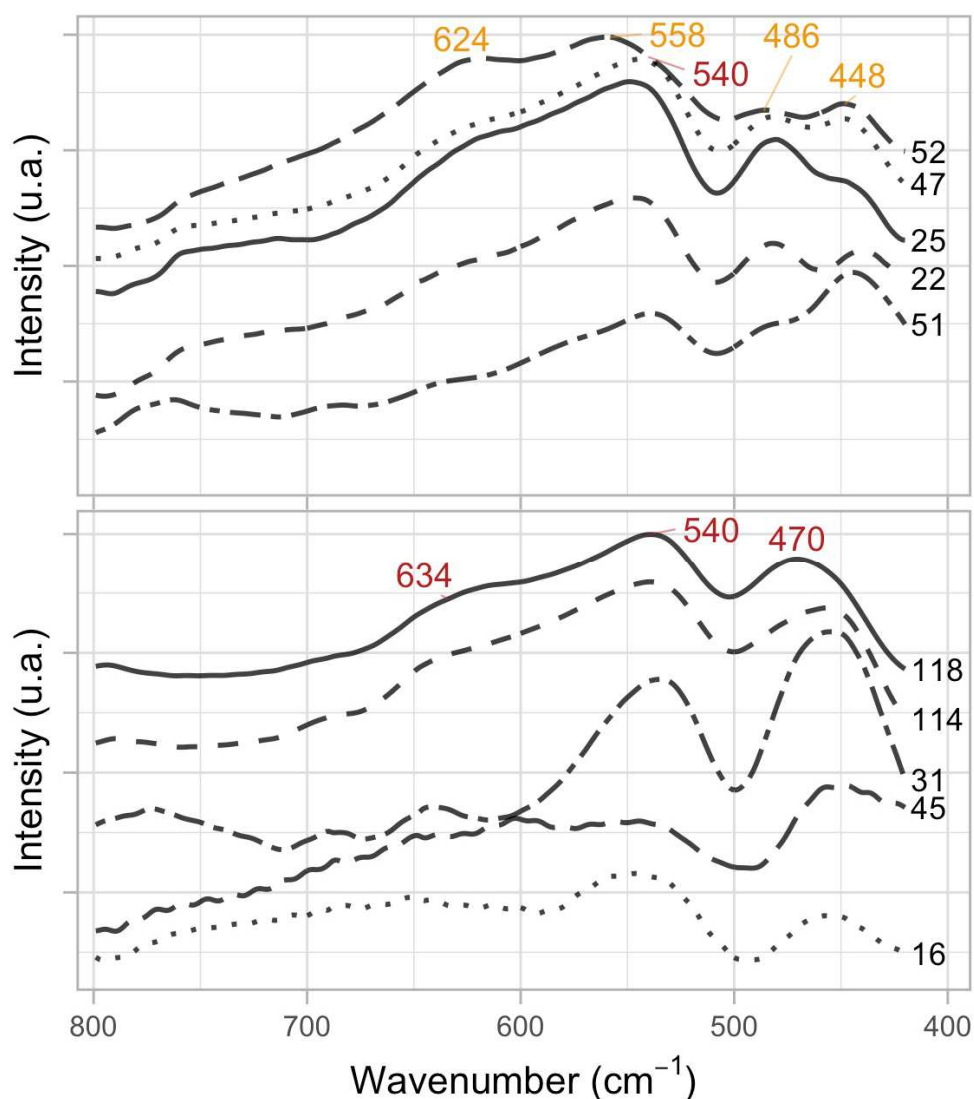


Figure 8: *(above)* Results of the subtraction of the red pigment spectra by the above slip layer for samples 22 (MP, Chaparral), 25 (MGp, Chaparral), 47 (MMora, Nuevo Corinto) 51 (MGp, Nuevo Corinto) and 52 (MMono, Nuevo Corinto) with characteristic infrared bands of hematite and maghemite. *(bottom)* Results of the subtraction of the red pigment spectra by the above slip layer for samples 16 (JP, Palo Blanco), 31 (BP, Barranca) and 45 (JF, Las Pilas), 114 (AP, Alto del Cardal), 118 (MCh, Alto del Cardal) with characteristic infrared bands of hematite.

Black pigments

All black pigments presented manganese oxides with its characteristic infrared bands at 456 ($\delta(Mn - O)$), 606 and 634 cm^{-1} ($\nu(Mn - O)$) as shown on figure 9. Indeed, black

pigment layers from all ceramic types presented relative molar concentration up to 9.6% of Mn when analyzed using SEM/EDS. All black pigments, with the exception of those from Jicote ceramics, presented significant amount of hematite (band around 540 cm^{-1}).

All black pigments of the cluster 2 (all JP and JF) presented a particular composition with mix of manganese oxide and magnetite. Magnetite could be identified by its characteristic band at 570 cm^{-1} (cf figure 9). Such result could be related to: (i) an anthropic origin, with a intentional mix of these two geomaterial, which could be specific of the black pigments of cluster 2, or (ii) a geological origin, with the use of geomaterial containing both pigments. Nevertheless, Mapping of Mn and Fe concentrations in Jicote black pigment layer showed the presence of different microstructures: (i) ones rich in Fe, (ii) other rich in Mn (cf figure10). Moreover, in a previous study [20], we characterized a black geomaterial from the nearby Guaitil area, which was traditionally used by indigenous local potters from ages to nowadays, and only detected manganese oxide as black pigment. All these data allowed to hypothesize an anthropic origin for the mix between magnetite and manganese oxide for Jicote ceramics. It is worth noting that, for the black pigments of Jicote ceramics, characteristic infrared bands of hematite could be hidden by magnetite and manganese oxides infrared signals.

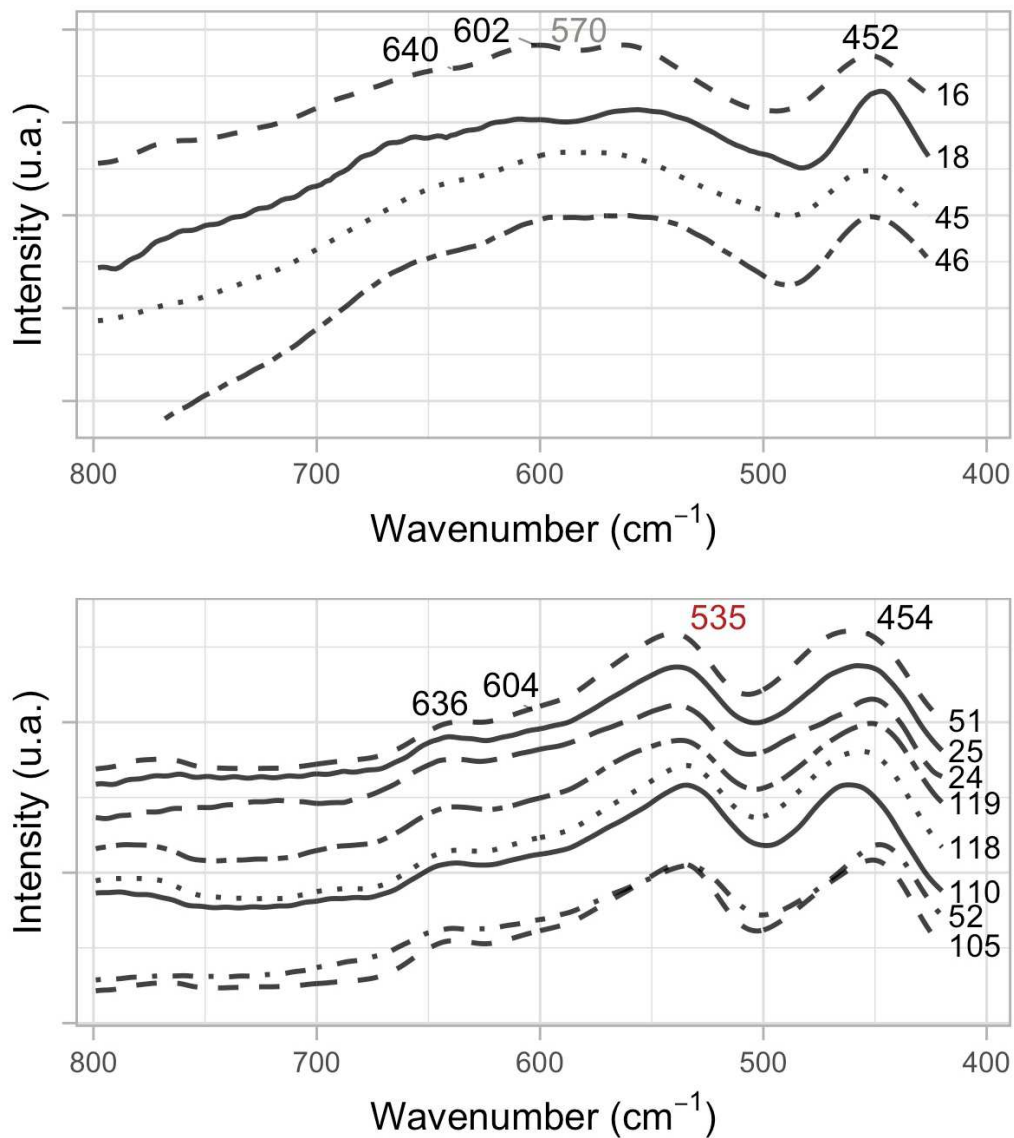


Figure 9: *(above)* Results of the subtraction of the black pigment spectra by the above slip layer for samples 16 (JP, Palo Blanco), 18 (JP, Palo Blanco), 45 (JF, Las Pilas) and 46 (JP, Las Pilas) with characteristic infrared bands of manganese oxide and magnetite. *(bottom)* Results of the subtraction of the black pigment spectra by the above slip layer for samples 24 (MMora, Chaparral), 25 (MGp, Chaparral), 51 (MGp, Nuevo Corinto) 52 (MMono, Nuevo Corinto), 105 (MP, Alto del Cardal), 118 (MCh, Alto del Cardal) and 119 (BP, Alto del Cardal) with characteristic infrared signal of manganese oxide and hematite.

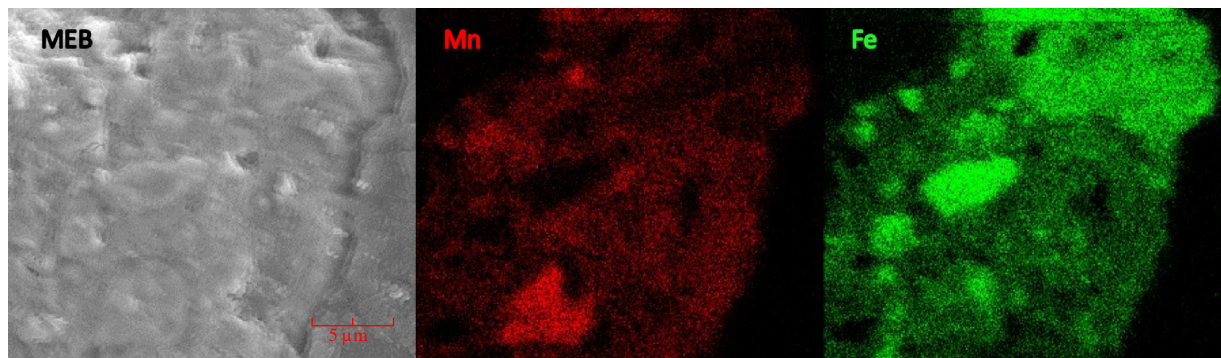


Figure 10: (*SEM*) Photography of the black pigment layer of sample 39 (JP, Las Pilas) using Scanning Electron Microscopy with Secondary Electrons detector, (*Mn - Fe*) Associated mapping of Mn and Fe measured by the Energy Dispersive X-ray detector.

Heating temperatures

Shoval & al [37] showed the existing relation between wavelength position meta-clay principal absorption band and the heating temperature of associated clay. This relation is $\bar{\nu}_{maximum} = 0.074 \times T_{heating} + 1032$ with $\bar{\nu}_{maximum}$ in nm and $T_{heating}$ in °C. For meta-smectite, we used their data to build a new model using R software: $T_{heating} = ((\bar{\nu}_{maximum} - 1028)/(1.23 * 10^{-22}))^{0.125}$ with $\bar{\nu}_{maximum}$ in nm and $T_{heating}$ in °C (p-value = $6 * 10^{-4}$, Adjusted $R^2 = 0.983$). These equations allowed us to establish direct correlations between meta-smectite and meta-kaolinite Si-O asymmetric stretching bands and heating temperatures.

According to our results (cf table 4), Guanacaste ceramics were most probably heated between 670 and 870°C during the fabrication processes, with almost no significant difference between school or ceramic types. Heating temperatures were calculated for all slip and pigment samples. It is important to point out the good level of similarity between the values calculated with meta-smectite and metakaolinite Si-O asymmetric stretching bands, showing the good reliability of the method.

On the archeological point of view, such range of temperature is coherent with the pre-Colombian ovens, open and buried, found in the Vidor Bahía Culebra site in Guanacaste [38]. According to the authors, such technology could allow reaching temperatures up to 900°C, in good agreement with the values given by other experimental archaeology experiments [39,40].

Clusters	Min (MK)	Min (MS)	Max (MK)	Max (MS)
1	676	650	730	730
2		684		775
3	676	684	757	807

Table 4: Minimum and maximum heating temperatures estimated from the wavelength of Si-O asymmetric stretching band for AHC cluster. The values were calculated thanks to the data from Shoval and al (2011) for meta-kaolinites (MK) and meta-smectites (MS).

Conclusion

In this paper, the red and black pigments and slips of 63 Guanacaste ceramics were analyzed by Scanning Electronic Microscopy and infrared spectroscopy. Red pigments were made using hematite, sometime in association with maghemite, mixed in the slip geomaterial. Black pigments were made of manganese oxide, sometime in association with magnetite.

All the pigment layers were made by dilution of a pure pigment in the slip layer. Meta-kaolinite and meta-smectite, different types of tectosilicates as quartz and cristobalite, hematite and feldspar were notably detected in slip layers. Impressive homogeneity of the compositions of the slips of Jicote type ceramics was observed with all 12 samples composed of meta-smectite, cristobalite, hematite and feldspar.

We clearly showed that slip layer could allow to discriminate different sites of ceramic production according to their chemical compositions. Indeed, the different ceramic types shared similar slip compositions with no correlation with the excavation site, showing that slip ceramics are relevant to trace Guanacaste ceramics in their exchanges or trades up to the Central Valley. Moreover, no local reproduction of Guanacaste styles in the central valley was noticed in this study. Meta-kaolinite and meta-smectite, different types of tectosilicates as quartz and cristobalite, hematite and feldspar were notably detected in slip layers. The Agglomerative Hierarchical Clustering and Principal Component Analysis of slip infrared spectra showed the presence of three distinct clusters in great accordance with actual knowledge on the ceramic production in the area.

The cluster 1 was composed of slips made of meta-kaolinite, quartz and the highest concentrations of hematite, and contained almost all Mora Polychrome Guapote and Mora Polychrome Guabal and Mora Polychrome Mora samples. Moreover, all red pigments of this cluster were composed of maghemite and hematite, which strengthen a common fabrication techniques, and potentially a common workshop, for all sherd of this cluster.

Meta-smectite, cristobalite, feldspar and hematite were found in cluster 2 slips in all ceramics from Jicote Polychrome and Jicote Polychrome Felino Their black pigments were the only one made of manganese oxide and magnetite, unlike all the black pigments of all other clusters. The ceramic varieties in this cluster were in good accordance with the Middle Tempisque proposed by Bishop and Lange [4].

The slips from the cluster 3 were composed of a mix of meta-kaolinite and meta-smectite, quartz and variable concentrations of hematite, and included all Altiplano Polychrome, Birmania Polychrome and Mora Polychrome Chircot ceramics Interestingly, four FT-IR spectra of M Mono slips were statistically attributed to this cluster. Such materials could be characteristic of the Guanacaste Polychrome II (GN-04) ceramic schools [4].

For the slips of Mora Polychrome of unknown varieties (MP) eleven could be associated to the clusters 1, and three to the cluster 3 thanks to Agglomerative Hierarchical Clustering and Linear Discriminant Analysis. Two of the three MP samples associated with the cluster 1, also presented a mix of maghemite and hematite as red pigment.

Finally, the existing relation between the wavelength position of meta-clay principal absorption band and the heating temperature of associated clay allowed us to estimate heating temperature between 670 and 870°C during the fabrication processes, with almost no school or ceramic types significant difference.

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