

Characterization of Archaeological Ceramic from Lagartero, Chiapas, Mexico, by Nuclear and Conventional Techniques

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Abstract. Ceramic potshards collected at the archaeological Mayan site of Lagartero, Chiapas, Mexico were analyzed by NAA and data were statistically studied. The ceramics were of local manufacture and from other sites of the Upper Grijalva Basin and Guatemalan Lowlands and Highlands. XRD indicated that quartz, feldspars, montmorillonite and calcite are the main components of pastes. Pigments were analyzed by means of SEM and XRD, and hematite, pyrolusite, maghemite and calcite were identified. A discussion is presented in the context of the Mayan region.

Keywords: Ceramics, Lagartero Chiapas, NAA.

Resumen. Fragmentos de cerámica recolectados en el sitio arqueológico de Lagartero, Chiapas, México fueron analizados mediante AAN y los datos fueron tratados estadísticamente. Las cerámicas fueron de manufactura local y de otros sitios de la Cuenca Superior del Grijalva y de las Tierras Bajas y Altas de Guatemala. DRX indicó que cuarzo, feldespato, montmorillonita y calcita son los componentes principales de las pastas. Los pigmentos fueron analizados mediante MEB y DRX, fueron identificadas hematita, pirolusita, maghemita y calcita. Se presenta una discusión en el contexto de la región maya.

Palabras clave: Cerámicas, Lagartero, Chiapas, AAN.

Introduction

The archaeological site of Lagartero (Chiapas, Mexico) is a Classic Period Mayan site, on the border between Mexico and Guatemala (Figure 1) with a particular ecological environment in the Upper Grijalva Basin (UGB). It is surrounded by swamps which cover 8.6 km² of swiftly flowing streams and lakes (Lagos de Colón) [1,2] fed by springs and the backed-up water of the Lagartero and San Lucas Rivers diverted by natural travertine barriers. The ceremonial architecture is found mainly on Limonar Island whereas the habitation area is located on other smaller islands. The site has pyramids that form a large plaza, a ball-court, several interconnected platforms, on which are structures and 160 archaeological mounds of different sizes. The most important period for Lagartero was from the Late Classic Period (750 to 900 A.P.) to the Early Post-Classic Period (900 to 1200 A.P.) [1-4].

The main component of ceramic pastes is clay, but there are others which are commonly called tempers (like volcanic ashes, calcite, etc.). In addition, the outer layer is often painted for decorative or identification purposes [5]. The study of these materials allows to the archaeologist to establish the origin of the pottery recovered at the site and obtain relevant information about the kind of raw material which was used in the manufacturing process of these pieces and to determine their possible source. This reconstruction may be quite a task because of the influence of many factors, among which are the origins of raw materials, the firing temperatures and the burial conditions. However, the study of ceramic provides information on the subsistence, population, social organization, cultural boundaries, trade networks, alliances and the cosmovision of ancient civilizations.

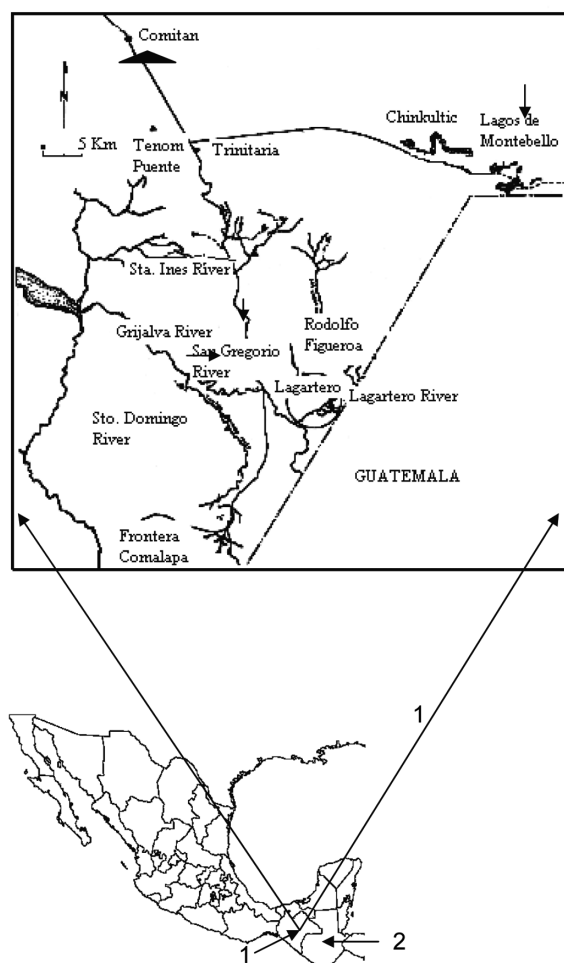


Fig. 1. Map of the Lagartero region (1) Chiapas State, Mexico, (2) Guatemala

In order to obtain a general panorama of the ceramic of Lagartero, forty-two shards were chosen for this research; they represent the temporalities and typologies of the ceramic of Lagartero. Table 1 includes a description of these shards, all of which were collected at the ball-court of Limonar Island [1-4] and were dated according to their stratigraphic contexts and morphologies from the Early Classic Period to Late Post-Classic Period (300-1400 A.P.). Since the Late Classic Period was the most relevant period of occupation, nearly half of the shards are of this period. Considering the ceramic types described elsewhere [3,4,6], their typologies correspond to Bon Polychrome: variety Bon, Complex Mix, Group Bon (L1 ad L30); Tang Polychrome: variety Guajilar, Complex Mix/Nichim, Group Red Tasajo (L2, L3, L4); Musaraña, variety Musaraña (L23); Yol brown, variety Yol and Danta Brown incised: variety Danta (L5, L13); Sasben Black: variety Sasben (L6-7, L15-19) and Kash Polychrome (L31). According to their typologies, three samples were typified as coming from the Upper Grijalva Basin (UGB, black on orange), the Lowlands of Guatemala (LLG, black and brownish red-on-cream) and the Highlands of Guatemala (HLG: Tohil Plombate: variety Tohil), respectively. Un-slipped ceramics were analyzed as well (L14, L32-39).

The main purposes of this research were to gather information about the Mayan ceramic of Lagartero and provide insights into their provenance. The pastes of these forty-two ceramic shards were analyzed by instrumental Neutron Activation Analysis (NAA), and the data were subjected to statistical methods in order to discriminate among different composition by groups. Moreover, mineralogical compositions of several pastes and pigments were identified by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). This study is a contribution for the understanding of ancient Mayan cultures.

Results and discussion

NAA of pastes and statistical treatments

Seventeen elements were quantitatively determined (Sc, Cr, Fe, Co, Rb, Sb, Cs, La, Ce, Sm, Eu, Tb, Yb, Lu, Hf, Th and U), iron being the most abundant (between 56 ± 0.3 and 16.8 ± 0.5 mg/g) and lutetium the scarcest (between 1.2 ± 0.1 and 0.2 ± 0.01 µg/g). The precision of the analytical data obtained by NAA was satisfactory because the standard deviations of iterated analyses of the samples were not usually higher than 10% of the mean values. Although alumina and silica are the two major chemical constituents of clays [5] and obsidians [9], they are not useful in their differentiation because of overlapping concentration ranges; therefore, statistical discrimination usually takes into account other elements [5].

Statistical treatments were carried out by taking into consideration all the elemental concentration data and using the MURR procedures for statistical analysis of multivariate archaeometric data written in GAUSS language by Dr. Hector

Neff (2008) [10]. Figure 2 shows the resulting principal-component diagram. Two main groups were formed, one of which (13 specimens) is chemically similar to the shard typified as coming from other sites of the UGB and the second group (23 specimens) was considered as manufactured at the site of Lagartero. It is interesting to remark that red-on-orange ceramic (samples L4 and L23 and Figure 3) has not been found in other sites of the UGB and that this kind of ceramic is considered as typical of Lagartero. The main chemical differences between those groups were found in their Cr and rare earth element (from La to Lu) concentrations. Samples L8, L13, L34 and those ichnographically typical of LLG and HLG were chemically different from both mentioned groups. Table 2 shows the analytical results of both groups and other specimens.

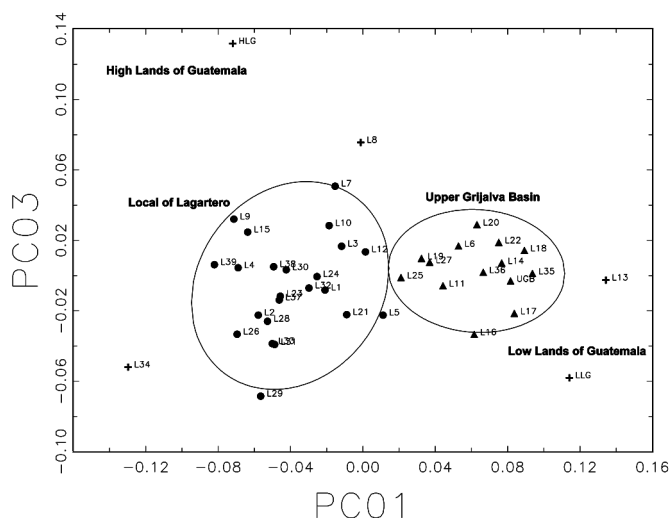


Fig. 2. Principal component diagram of ceramic shards from Lagartero Chiapas, Lowlands of Guatemala (LLG), Highlands of Guatemala (HLG), and Upper Grijalva Basin (UGB). Confidence interval for ellipses: 0.9.



Fig. 3. Ceramic red-on-orange (Group Musaraña, variety Musaraña).

Table 1. Description of the ceramic shards L: Lagartero. UGB: Upper Grijalva Basin; HLG: Highlands of Guatemala and LLG: Lowlands of Guatemala.

Sample	Pigment colour, surface	Stratigraphic context	Chronology ^(*)	Origin ^(*)
L1	Red, black, and orange-on-cream	I-3, N-4	Late Classic	L
L 2	Red and black-on-orange	C-3, N-3	Late Classic	L
L 3	Red and black-on-natural colour of clay	Surface	Early Post-Classic	L
L 4	Red-on-orange	J-3, N-2	Early Classic	L
L 5	Dark brown exterior surface	P-SC-18, N-1	Late Classic	L
L 6	Black, smoothed	C-4, N-1	Late Classic	UGB
L 7	Black, smoothed	V-8, N-1	Late Classic	L
L 8	Dark red	D-2, N-1	Early Post-Classic	Unknown
L 9	Red	C-20, N-2	Late Classic	L
L 10	Brown and orange	T-2, N-4	Late Classic	L
L 11	Light brown	Shaft-20, N-5	Late Classic	UGB
L 12	Orange	N-3	Late Classic	L
L 13	Dark brown	V-1, N-1	Late Classic	(*)
L 14	Without coat	Surface	Early to Late Classic	UGB
L 15	Black, smoothed	Surface	Early to Late Classic	L
L 16	Black, smoothed	Surface	Early to Late Classic	UGB
L 17	Black, polished	Surface	Late Classic	UGB
L 18	Black, polished	H-2, N-1	Late Classic	UGB
L 19	Black, polished	I-3 and J3, N-2	Late Classic	UGB
L 20	Reddish-orange	N 5	Late Classic	UGB
L 21	Orange, polished exterior surface	L-5, N-8	Late Classic	L
L 22	Orange, polished interior surface	Surface	Early Classic	UGB
L 23	Red-on-orange, polished	V-3 N-6	Late Classic to Early Post-Classic	L
L 24	Orange exterior surface and black interior surface	L-21, N-4	Late Classic	L
L 25	Red-on-cream and orange, polished	Surface	Late Classic	UGB
L 26	Black-on-cream exterior surface and orange interior surface	Q-4, N-5	Late Classic	L
L 27	Brownish-red, smoothed	Shaft-3 N-3	Late Classic	UGB
L 28	Red-on-black, polished	J-3; N-1	Late Classic	L
L 29	Red-on-black, polished	J-3; N-1	Late Classic	L
L 30	Red, black and orange-on-cream, polished	Lagartero 93, group S3, N-6	Late Classic	L
L 31	Brown-on-cream exterior surface and black and polished interior surface.	L-6, 1-3, N-7	Late Classic	L
L 32	Monochrome without slip	Surface	Late Classic to Early Post-Classic	L
L 33	Monochrome without slip	Surface	Late Classic to Early Post-Classic	L
L 34	Monochrome without slip	Surface	Late Classic to Early Post-Classic	Unknown
L 35	Monochrome without slip	Surface	Late Classic to Early Post-Classic	UGB
L 36	Monochrome without slip	Surface	Late Classic to Early Post-Classic	UGB
L 37	Monochrome without slip	Surface	Late Classic to Early Post-Classic	L
L 38	Monochrome without slip	Surface	Late Classic to Early Post-Classic	L
L 39	Monochrome without slip	Surface	Late Classic to Early Post-Classic	L
UGB	Black on orange, polished	M-2, N-3	Late Pre-Classic to Epi-Classic	Upper Grijalva Basin
HLG	Plumbate gray	Est-5, C-C-19, Surface	Early Post-Classic	Highlands of Guatemala
LLG	Black and brownish red-on-cream, smoothed	Surface	Early Post-Classic	Lowlands of Guatemala

(*) Periods: Late Post-Classic (ca. 1400-1500 A.P.); Early Post-Classic (ca. 1100-1200 A.P.); Late Classic to Early Post-Classic (ca. 800 – 1200 A.P.); Late Classic (ca. 800-900 A.P.); Early Classic to Late Classic (ca. 300-900 A.P.); Early Classic (ca. 300-600 A.P.); Late Pre-classic to Epi-classic (ca. 300 – 1000 A.P.).

(*) According to the statistical methods.

(*) Unknown, possibly Seibal.

Table 2. Elemental composition of the ceramics samples from Lagartero Chiapas, México. The values are in $\mu\text{g/g}$, unless otherwise indicated. Mean \pm standard deviation. The sub-groups are: L-L: Local of Lagartero and L-UGB: Ceramic found at Lagartero and having a similar chemical profile to other sites of the Upper Grijalva Basin; UGB, LLG and HLG: Samples found at Lagartero with typical typologies of Upper Grijalva Basin, Lowlands of Guatemala and Highlands of Guatemala, respectively.

Element	L-L <i>n</i> = 23	L-UGB <i>n</i> = 14	UGB	L13	LLG	L34	L8	HLG
Sc	9 \pm 1	9 \pm 2	8.6 \pm 1	13.6 \pm 0.01	11 \pm 2	10.1 \pm 0.01	11.2 \pm 0.3	21.3 \pm 0.4
Cr	30 \pm 11	63 \pm 32	86 \pm 6	268 \pm 43	368 \pm 57	34 \pm 2	22 \pm 1	15.2 \pm 0.1
Fe (mg/g)	24.8 \pm 0.3	25.7 \pm 0.4	24 \pm 2	48 \pm 0.2	33 \pm 0.5	36 \pm 0.7	36 \pm 1	56 \pm 0.3
Co	7 \pm 2	7 \pm 2	15 \pm 2	25.5 \pm 0.9	19 \pm 3	4.5 \pm 0.2	10 \pm 0.03	16.8 \pm 0.1
Rb	80 \pm 20	122 \pm 25	97 \pm 3	76 \pm 3	78 \pm 11	61 \pm 0.5	46 \pm 3	23 \pm 4
Sb	1.4 \pm 1.0	1 \pm 0.5	1.1 \pm 0.1	1.2 \pm 0.2	1.1 \pm 0.5	1.2 \pm 0.2	1.1 \pm 0.07	0.8 \pm 0.1
Cs	5 \pm 1	4.7 \pm 0.9	4.3 \pm 0.01	4.1 \pm 0.1	5 \pm 0.2	1 \pm 0.1	3.8 \pm 0.4	2.4 \pm 0.3
La	27 \pm 7	41 \pm 9	41 \pm 3	47 \pm 2	38 \pm 7	10.7 \pm 0.8	39 \pm 1	30 \pm 4
Ce	54 \pm 11	85 \pm 21	85 \pm 3	101 \pm 5	88 \pm 2	25 \pm 6	70 \pm 2	49 \pm 0.1
Sm	5 \pm 2	9 \pm 4	8.4 \pm 0.1	8.6 \pm 0.8	11 \pm 6	2.1 \pm 0.1	6.8 \pm 0.1	2.3 \pm 0.4
Eu	0.7 \pm 0.2	1.1 \pm 0.3	1.1 \pm 0.01	1.6 \pm 0.01	0.9 \pm 0.2	0.4 \pm 0.01	1.3 \pm 0.1	2 \pm 0.1
Tb	0.7 \pm 0.2	1 \pm 0.1	0.9 \pm 0.01	0.8 \pm 0.01	0.7 \pm 0.1	0.5 \pm 0.01	0.9 \pm 0.01	0.6 \pm 0.01
Yb	2.4 \pm 0.4	3.5 \pm 0.6	3.2 \pm 0.3	3.3 \pm 0.3	3.3 \pm 0.4	1.3 \pm 0.1	4.3 \pm 0.2	3.2 \pm 0.3
Lu	0.29 \pm 0.08	0.43 \pm 0.08	0.4 \pm 0.01	0.4 \pm 0.01	0.3 \pm 0.01	0.2 \pm 0.01	0.6 \pm 0.02	0.4 \pm 0.01
Hf	5 \pm 1	7 \pm 2	9.4 \pm 0.4	5.7 \pm 0.01	4 \pm 0.5	5.5 \pm 0.3	2 \pm 1	6.7 \pm 0.2
Th	13 \pm 5	16 \pm 3	17.1 \pm 1.7	12.3 \pm 0.2	11 \pm 2	8.8 \pm 0.1	12 \pm 0.1	8.7 \pm 0.2
U	3 \pm 1	4 \pm 1	4.7 \pm 0.2	4.9 \pm 0.6	3 \pm 1	4 \pm 1	3.3 \pm 0.08	1.8 \pm 0.1

A good comparison was found for the concentration of ten coincident elements (Sc, Cr, Fe, Co, Rb, Cs, Ce, Eu, Hf, Th) between our data and those from the ceramic literature for Seibal [11] and Palenque [12]. According to these statistical treatments, no difference was found among the samples L13 and LLG, and those of Late Classic Period of Seibal. Regarding the paste of the plumbate specimen (HLG), the \log_{10} values of iron and chromium concentration are in good agreement with the values reported previously [13] for the Tohil Plumbate pastes.

XRD of pastes

The analyzed pastes were mainly of the ceramic group of Lagartero (L1-5, L7-12, L-24, L28, L30, L32, and L37). Pastes L17 and L19 from the group UGB and the sample HLG were analyzed as well.

Quartz (SiO_2) and one or more feldspars (such as albite ($\text{NaAlSi}_3\text{O}_8$), anorthoclase ($(\text{NaK})\text{AlSi}_3\text{O}_8$), and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) were identified virtually in all samples. Montmorillonite ($(\text{NaCa})_{0.33}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$, and calcite (CaCO_3) were found in the pastes of the group of Lagartero and particularly in the L32 dolomite ($\text{CaMg}(\text{CO}_3)_2$) was identified as a main component. A similar mineralogical composition was found for ceramics of

Calakmul [14], and indeed this composition is very common for Mesoamerica, pottery. For the sample L17 (UGB group), the boggsite zeolite ($\text{NaCa}_2(\text{Al}_5\text{Si}_{19}\text{O}_{48}) \cdot 17(\text{H}_2\text{O})$) was found. For the paste of plumbate ceramic (HLG), both cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) and calcite (CaCO_3) were identified.

The presence of calcite indicates that possibly limestone and/or shells of marine organisms were used for the paste preparation. The aragonite of marine shells becomes calcite at 470 °C and calcium oxide at 800-900 °C [5,15]. Therefore, the finding of calcite indicates that firing temperatures of these pieces were lower than 800 °C. On the other hand, samples L11 and L12 were not crystalline. Pastes do not vitrify when the firing temperature is between 800 and 1200 °C; whereas, amorphous materials are obtained at higher temperatures [5,15]. The lack of crystallinity could then be due to the position of these ceramics in the kiln, in which firing temperatures were high enough to vitrify them.

SEM and XRD of pigments

The pigments analyzed in this research were red, black, brown, cream, orange, and gray. The photo-micrographies obtained showed granular aggregates measuring between 10 and 140 μm (Figure 4). EDS analyses showed that Si, Al, Fe, Ca, K, C,

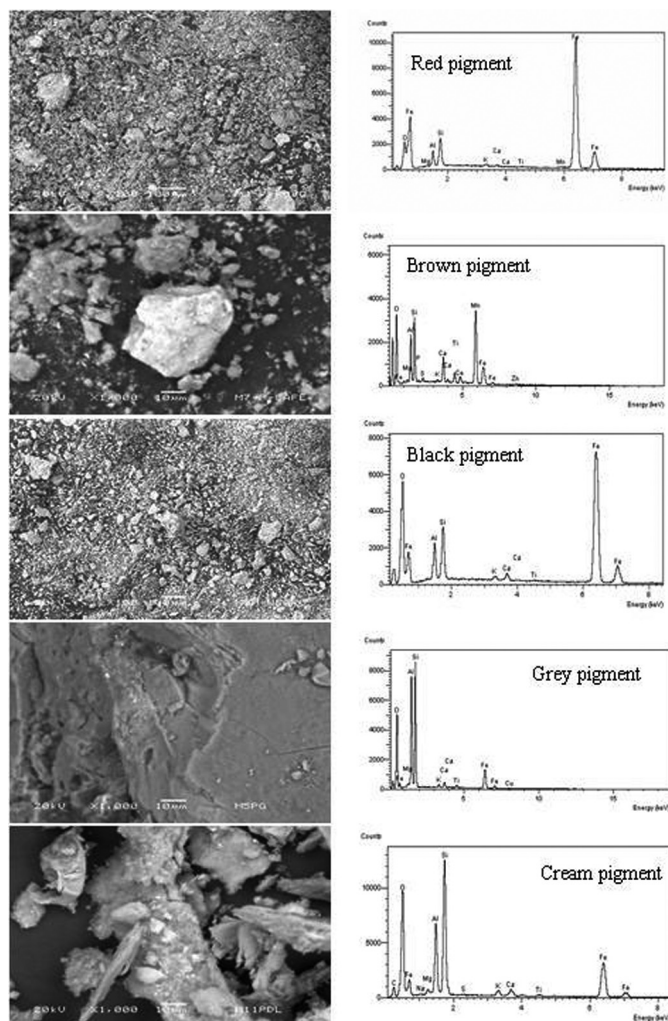


Fig. 4. SEM images of red, brown, black, grey, and cream pigments and their EDS analyses.

O, Ti, and Mg; were the most abundant elements followed by Mn, S, Cu, Na, and P, whereas V, Cr, Cl, Zn, Ce, La, Ba, and Ag were found in <10%. Several of these elements are common in clays and feldspars such as those reported by XRD. Therefore, the main elements considered for each pigment are the following: For the red, Fe, for the black, Mn and Fe, for the brown, Fe and to a lesser extent Mn, Cu, Cr or Zn, for the cream, Ca, C, Fe, and Mn, for the orange, Fe, Ca, C, and to a lesser extent Mn, Cu, or Cr, and finally for the gray, Ca, C, Mn and to a lesser extent Ti and Fe.

XRD analyses showed that the primary phase for the red pigment is hematite (Fe_2O_3), for the black it is pyrolusite (MnO_2), for the brown maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and for the cream calcite (CaCO_3). Calcite and hematite have been found in Mayan pigments of ceramic and stucco (see for example reference 16). The main components of the orange pigment are hematite and calcite, whereas those of the gray pigment are calcite and pyrolusite.

Conclusions

It has been demonstrated here that the codex style ceramic was made at Lagartero with a paste that is chemically different from the ceramic from other sites of the Upper Grijalva Basin (see Table 1 and Figure 2).

The ceramic found at Lagartero is basically of local manufacture, but the ceramic from other sites of the Upper Grijalva Basin was found as well. Certainly both domestic and ceremonial potteries were made at specialized ceramic manufacturing centers, Lagartero being one of the most important because of the quantity of shards found on the surface and in the excavations.

It is difficult to determine if the ceramic vessels were used as barter articles; however, it is certain that the inhabitants of Lagartero were in contact with people of the Upper Grijalva Basin region and of the Chiapas Central Highlands, as well. On the other hand, there is not much evidence of Mayan polychrome glassware imported from the Southern Lowlands or from the Guatemalan Highland; therefore, trade and contact with the Peten area (Guatemala) must have been limited during the Late Classic Period.

The red-on-orange bi-chromes (such as specimens L4 and L23), which seem to be a variant of polychrome ceramic (red and black-on-orange, such as specimens L2 and L3) were also almost restricted to Lagartero. This means that the potters at Lagartero did not commonly exchange their fine bi-chrome and polychrome vessels for articles from their neighbors. The domestic pottery was available through a regional market, but ceremonial pottery was not. Population pressure, boundary problems and friction between capitals might have prevented the smooth exchange of luxury ceramic.

Although the rough un-slipped Late Classic Period pottery from Lagartero is similar to the ceramic from the Comitán Valley, there is virtually no correspondence between the Late Classic Period ceramic from Lagartero and that from the Chiapas Central Highlands. The ceramic of Late Classic Period from the downriver region, near Chiapas de Corzo, the Mixe-Zoque or Chiapanec, is very different as well. Since the forbidding escarpment along the west edge of the Guatemalan Cuchumatán Mountains is practically unknown archaeologically, a comparison with that area at present can not be made. The Lacandon jungle to the northeast is similarly unknown.

The Epi-Classic Period occupation at Lagartero (900 – 1200 A.P.) marked a decline until nearly the end of this period. Ceramic evidence suggests that contact with the Guatemalan Highland increased throughout the Post-Classic Period.

The Early Post-Classic Period ceramic inventory is a mixture of domestic types carried over from the Late Classic Period to a range of new decorated and imported wares. Fine orange and plumbate trade wares appeared during this period but they were relatively uncommon. This suggests that contact with the Guatemalan Highland was quite infrequent during the Early Post-Classic Period. The bulk of Early Post-Classic Period pottery is local, domestic and rather poorly made. For this period there was also a marked reduction in the number of

forms. Vessels became smaller, less attention was paid to producing even surface finishes, paste became softer and potters switched from volcanic ash temper to crystalline calcite temper. The Late Post-Classic Period type is small and dominated by domestic wares. The major ceramic influence was from the Guatemalan Highland; nevertheless, the chemical compositions of the pastes are quite different.

Experimental

Sample preparation

Since the majority of pottery samples were decorated, their pigmented slips had to be removed before analyses by means of a drill with a tungsten bit. In order to obtain the pigments, the shards were scraped with a razor, first to eliminate the slip and then to obtain a sufficient quantity for analysis, an optical microscope being used for this purpose. The pastes and the pigments were then ground with an electric agate mortar and these powdered samples were dried at 353 K for 24 h.

Material Characterization

Nuclear Activation Analysis (NAA) of pastes.

Irradiation was performed in a TRIGA MARK III nuclear reactor at a neutron theme rate of $1 \times 10^{13} \text{ cm}^{-2}\text{s}^{-1}$. Samples of 200 mg of pastes, irradiated for 2 h, were allowed to decay for 12 - 14 days, γ -ray spectra being recorded for 2 h. All radioactivity values were corrected taking into account half-life and decay times. Soil-7 of the International Atomic Energy Agency (IAEA) was the reference material used in our research to calculate elementary concentrations. Nuclear data of the isotopes identified on the γ spectra are given elsewhere [7].

X-ray Diffraction (XRD)

A mineralogical analysis by X-Ray Diffraction (XRD) was performed for pastes and pigments at room temperature by using a Siemens D-5000 diffractometer with Cu K_{α} radiation with a graphite monochromator; the diffraction pattern was collected from 2.5 to $70^{\circ} 2\theta$ with a step size of $0.02^{\circ} 2\theta$ in order to acquire X-ray patterns with sufficiently high intensities to identify the minerals present. For the qualitative identification of the mineralogical composition the data file JCPDS [8] was used.

Scanning Electron Microscopy (SEM)

The morphology of the pigments was analyzed on a scanning electron microscope Phillips XL-30 at 25 KeV. The samples were mounted on an aluminum holder with a carbon conductive tape and later covered with a gold layer approximately 150 Å thick in a Denton Vacuum Desk II sputtering system. In

all cases, the images were taken with a backscattered electron detector. The elemental composition of the same samples was determined by Energy Dispersion Spectroscopy (EDS) with an EDAX DX-4 spectrometer; to obtain the X-ray spectra, a count rate of 2000 to 2500 cps, dead times of 25-30 %, and a 150 sec acquisition time was used.

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