Artistic Expressions in Maya Architecture: Analysis and Documentation Techniques

Expresiones artísticas en la arquitectura maya: Técnicas de análisis y documentación

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Abstract: *The recent use of electrochemical techniques, combined with microscopy and spectroscopic techniques, have led to considerable advances in the study of Maya Blue. These advances include the detection of pigment in wall paintings at the Substructure IIC of Calakmul, dated as the Late Preclassical period, and notably bringing forward the use of the pigment. Chemometric analysis of Maya Blue samples from different sites suggest that the preparation procedure of Maya Blue probably changed over time following a branched pattern. More recent analysis on yellow samples from wall paintings in several archaeological sites in Yucatán and Campeche has shown the presence of indigoid compounds, including isatin and dehydroindigo, attached to palygorskite, forming a 'Maya Yellow' material. Analytical studies on a set of spherical pellets discovered at Structure 4H1 of La Blanca (Petén, Guatemala) confirm the presence of indigo and its alteration products associated with palygorskite and suggest that the ancient Mayas could prepare indigo, Maya Blue and related green and yellow pigmenting materials in different stages from a common preparative procedure. This process, which would undergo local variations during the different periods of the Maya culture, show a command over Maya Blue technology of great significance throughout time.*

Resumen: *El uso reciente de técnicas electroquímicas, junto con la microscopía y el empleo de técnicas espectroscópicas, ha permitido avanzar notablemente en el estudio del color azul Maya, incluyendo la detección del pigmento en pinturas murales de la Subestructura IIC de Calakmul, fechadas para el periodo Preclásico Tardío, anticipando así significativamente la fecha de uso de este pigmento. El análisis quimiométrico de muestras de azul Maya procedentes de diferentes sitios arqueológicos ha permitido sugerir que muy probablemente el procedimiento de preparación del azul Maya ha cambiado a lo largo del tiempo siguiendo un patrón ramificado. Los más recientes análisis de muestras de color amarillo procedentes de las pinturas murales de diversos sitios arqueológicos de Yucatán y Campeche han permitido detectar la presencia de compuestos indigoides, incluyendo isatin y dehydroindigo, unidos a palygorskita, formando una materia colorante 'amarillo Maya'. Estudios analíticos en un conjunto de bolas de pigmento verde halladas en la Estructura 4H1 de La Blanca (Petén, Guatemala) confirman la presencia de índigo y sus productos de alteración asociados a palygorskita, sugiriendo que los antiguos Mayas podían preparar índigo, azul Maya y otros colorantes derivados verdes y amarillos en diferentes etapas a partir de un plan de preparación común. Este proceso, que habría experimentado variaciones locales a lo largo de los diferentes periodos de la cultura Maya, puede considerarse como el dominio de una tecnología del color azul Maya con un importante significado a través del tiempo.*

Introduction

The Maya culture has received considerable attention because of its obvious historic importance and extraordinary architectural and artistic productions. In the context of the Maya culture, a material of surprising chemical properties, the Maya Blue, has received an increasingly growing interest due to its peculiar nature as hybrid organic-inorganic material resulting from the combination of a dye, indigo, to a phyllosilicate, palygorskite[1]. The term Maya Blue was coined by Gettens and Stout[2] several years after the discovery of the pigment by Merwin[3], to denote a pigment widely used by the ancient Mayas and other Mesoamerican peoples in mural paintings. This material, that possesses an exceptional archaeological and ethnohistoric value, was also used in pottery, sculptures, luxury art, thus appearing as a technological material[4].

In contemporary chemistry, the Maya Blue has claimed attention because of its high resistance to chemical and biological degradation (being highly resistant to acids, alkalis, organic solvents and biodeterioration), its peculiar

1 GÓMEZ-ROMERO and SÁNCHEZ 2005.
2 GETTENS and STOUT (Eds.) 1946.
3 MERWIN 1931.
4 MILLER and MARTIN 2004.

brightness and hue. In fact, the Maya Blue palette ranges from a bright turquoise to a dark greenish blue. Just its colour imparts to Maya Blue an important symbolic value in the Maya culture, being associated to sacrifice and the gods of rain and water, as well as to the sky. In the Maya highlands, the Maya Blue was associated to one of the cardinal directions, a symbolism, however, which was apparently absent in the Maya lowlands[5].

Along time, the study of Maya Blue has motivated different controversies dealing with the reasons for its peculiar hue, the nature of the indigo-palygorskite association and the location of indigo molecules in the palygorskite framework[6]. The absence of historical sources describing the method(s) used by the ancient Mesoamerican people to prepare Maya Blue has contributed to maintain the view of the pigment as a mysterious material.

Recently, the use of solid state electrochemical techniques, combined with microscopy and spectroscopic ones, leaded to introduce new pieces into the Maya Blue scenario[7]. These include the detection of the pigment in wall paintings of the Substructure IIC in the archaeological site of Calakmul, dated in the Late Preclassical period, thus anticipating significantly the date of use of the pigment with regard to the currently accepted period[8], and the presence of dehydroindigo, the oxidized form of indigo, which could be formed by aerobic oxidation of the palygorskite-associated indigo complex, accompanying indigo, recently confirmed from chromatographic/mass spectrometric techniques[9]. The presence of different dehydroindigo/indigo ratios would permit to justify the variability in the colour of the pigment. Temperature variation of voltammetric data allow to determine thermochemical parameters for dye attachment to palygorskite and provide information on the spatial distribution of topological isomers of indigo and dehydroindigo in palygorskite crystals[10].

Chemometric analysis of Maya Blue samples from different sites suggested that the preparation procedure of Maya Blue probably changed along time following a ramified pattern[11]. The most recent analysis on yellow samples from wall paintings in several archaeological sites in the Maya lowlands in Yucatán and Campeche (Mexico) permits to detect the presence of indigoid compounds, including isatin and dehydroindigo, attached to palygorskite, forming 'Maya Yellow' materials[12]. Analytical studies on a set of spherical pellets discovered in the Structure 4H1 of the ancient Maya urban settlement of La Blanca (Petén Department, Guatemala), dated in the Terminal Classic period, confirm the presence of indigo and its alteration products associated to palygorskite and suggests that the ancient Mayas could prepare indigo, Maya Blue and related green and yellow pigmenting materials in different stages from a common preparative scheme[13]. The current work is devoted to present a comprehensive view of such recent findings in the context of contemporary studies of Maya Blue and related materials.

The origin and preparation of Maya Blue

Currently, it is accepted that Maya Blue results from the attachment of indigo (3H-indol-3-one, 2-(1,3-dihydro-3-oxo-2H-indol-2-ylidene)-1,2-dihydro), a blue dye extracted from leaves of *añil* or *xiuquitlitl* (*Indigofera suffruticosa* and other species), to palygorskite, a fibrous phyllosilicate clay whose ideal composition is $(Mg,Al)_4Si_8(O,OH,H_2O)24.nH_2O$. Shepard[14] and Shepard and Gottlieb[15] first introduced the idea of Maya Blue as a material consisting of a dye attached to certain Yucatán clays. This proposal, however, was not immediately accepted. Gettens[16] hypothesized about the existence of a blue form of the palygorskite mineral, an idea further supported by Littmann[17], who hypothesized montmorillonite being the possible source of the pigment, although subsequently recognized the validity of the indigo-palygorskite model[18]. Arnold[19] first discovered use of palygorskite in Yucatán and that the contemporary Maya were using it for pottery temper and for medicinal purposes[20]. Different contemporary locations where palygorskite has been found are known[21].

Van Olphen[22] prepared synthetic Maya Blue-type specimens using three procedures: embedding palygorskite with a solution of indoxylacetate, vat dyeing soaking leucoindigo, the reduced form of indigo, in a water suspension of palygorskite, and crushing indigo with powdered palygorskite. Importantly, the prepared materials must be heat-treated during a certain time. Temperatures between 90 and 300ºC can be found in literature[23], the time duration of the heating process varying between few minutes to hours and days but, in all cases, relatively low proportions of indigo (1-3 % wt) have to be used. Similar specimens have been prepared from indigo and sepiolite, another phyllosilicate[24]. Details of the above preparation procedures

5 REYES-VALERIO 1993.
6 DOMÉNECH *et al*. 2009a; SÁNCHEZ DEL RÍO *et al*. 2011.
7 DOMÉNECH *et al*. 2006.
8 VÁZQUEZ DE ÁGREDOS *et al*. 2011.
9 DOMÉNECH *et al*. 2013.
10 DOMÉNECH *et al*. 2009c, d.
11 DOMÉNECH *et al*. 2007a, 2009b.
12 DOMENECH *et al*. 2011a.
13 DOMÉNECH *et al*. 2012; DOMÉNECH *et al*. 2014.
14 SHEPARD 1962.
15 SHEPARD and GOTTLIEB 1962.
16 GETTENS1962.
17 LITTMANN 1980.
18 LITTMANN 1982.
19 ARNOLD 1967a,b.
20 ARNOLD 1967a,b, 1971, 2000, ARNOLD and BOHOR 1975, 1976.
21 ARNOLD 2005; ARNOLD *et al*. 2007; SÁNCHEZ DEL RÍO *et al*. 2009a.
22 VAN OLPHEN 1966.
23 *Idem*; KLÉBER *et al*. 1967; REYES-VALERIO 1993.
24 VAN OLPHEN 1966; HUBBARD *et al*. 2003; OVARLEZ *et al*. 2006, 2009; SÁNCHEZ DEL RÍO *et al*. 2006; YASARAWAN and VAN DUIJNEVELDT 2008.

have been discussed by Cabrera Garrido[25], Littmann[26], Torres[27], Reyes Valerio[28], Vandenabeele *et al*.[29] and Sánchez del Río *et al*.[30] In particular, Cabrera-Garrido[31] proposed several other possible recipes to prepare Maya Blue, including direct dyeing of palygorskite using the colorant juice from *Indigofera* plant, heating indigo with water vapor and further fixation on palygorskite, burning *Indigofera* leaves and mixing the ashes with other ingredients, and ritual ceremonies burning ingredients like copal. In this context, Arnold[32] have provided evidence that Maya Blue could be prepared ritually by burning incense using a mixture of copal (called *pom* in Yucatec Maya language) coming from the sap of a tree (*Protium copal*), palygorskite and some part of the indigo plant. This discovery reinforced the view of the Maya Blue as a 'sacred' material whose preparation and handling would be a restricted to a sacerdotal class (*vide infra*).

The chemical structure of Maya Blue

The attachment of the dye to the clay has promoted an extensive debate. Van Olphen[33] suggested that indigo molecules attaching to surface channels of the clay, while Kleber *et al.*[34] suggested that indigo penetrates (at least partially) into the clay tunnels. These authors also suggested that the indigo attachment to the clay is related to loss of zeolitic water. This process occurs at temperatures between 150 and 200 ºC whereas externally adsorbed, hygroscopic water is lost near 100 ºC. Structural water molecules in the palygorskite framework are released at temperatures between 375 and 425 ºC.

The insertion of indigo molecules into the palygorskite channels has been advocated by different research groups[35] while the surface channels model has been supported by others[36]. Chiari *et al.*[37] proposed that indigo attachment to palygorskite is restricted to the grooves (half channels cut along their axis) present in the exterior crystal surfaces of the clay. Hubbard *et al.* [38] has proposed that indigo molecules block the entrance of the palygorskite channels, a model further supported by Sánchez del Río *et al.* [39].

With regard to the specific interaction governing the attachment of indigo molecules to the clay, it has been proposed the formation of hydrogen bonds between indigo C=O units and structural water of the clay[40] accompanied by hydrogen bond between N-H and structural water[41]; formation of hydrogen bonds between the C=O and N-H groups with edge silanol units of the clay[42], direct bonding between the clay octahedral cations and the dye molecules[43]; specific bonding to Al-substituted Si sites in tetrahedral centers[44]. The possibility of significant Van der Waals interactions was introduced by Fois *et al.* [45] and further considered by Doménech *et al.* [46]. It is pertinent to note that the emphasis made by several authors on the direct Al^{3+}-indigo binding is in contradiction with the recognized feature that indigo forms materials analogue to Maya Blue with sepiolite, another phyllosilicate clay where Al^{3+} is absent.

The hue of Maya Blue

The Maya Blue has a characteristic blue-greenish hue, with different tonalities ranging from greenish to turquoise blue. José-Yacamán *et al.* [47] reported the presence of iron metal and iron oxide nanoparticles in Maya Blue and suggested that Mie-type light dispersion in nanoparticles could be responsible for the characteristic hue and brightness of the pigment[48]. This hypothesis was later discarded so that there was general agreement in which the peculiar hue of Maya Blue results from the bathochromic shift of the indigo absorption bands as a consequence of the dye attachment to the palygorskite host[49].

This bathochromic effect would be accompanied by the presence of dehydroindigo, the oxidized form of indigo, as a minority compound attached to the palygorskite matrix. The crucial role played by dehydroindigo is supported by electrochemical and spectral data in the VIS-UV and infrared regions[50], further supported by fluorescence[51] and Raman spectral data[52].

Literature data can be re-examined in the light of the dehydroindigo hypothesis. Thus, Figure 1 compares the VIS-UV spectra for indigo and dehydroindigo taken

25 CABRERA GARRIDO 1969.
26 LITTMANN 1982.
27 TORRES 1988.
28 REYES VALERIO 1993.
29 VANDENABEELE *et al*. 2005.
30 SÁNCHEZ DEL RÍO *et al*. 2006, 2007.
31 CABRERA-GARRIDO 1969.
32 ARNOLD *et al*. 2008.
33 VAN OLPHEN 1966.
34 KLEBER *et al*. 1967.
35 CHIARI *et al.* 2003; FOIS *et al.* 2003; GIUSTETTO *et al.* 2005; TILOCCA and FOIS 2009.
36 CHIANELLI *et al.* 2005; MANCIU *et al.* 2007; POLETTE-NIEWOLD *et al.* 2007; FUENTES *et al.* 2008.
37 CHIARI *et al*. 2008.
38 HUBBARD *et al*. 2003.
39 SÁNCHEZ DEL RÍO *et al*. 2009b.
40 FOIS *et al.* 2003.
41 GIUSTETTO *et al*. 2005.
42 HUBBARD *et al*. 2003.
43 CHIARI *et al*. 2008; TILOCCA and FOIS 2009.
44 CHIANELLI *et al*. 2005; FUENTES *et al*. 2008; POLETTE-NIEWOLD *et al*. 2007.
45 FOIS *et al.* 2003.
46 DOMÉNECH *et al.* 2007b.
47 JOSÉ-YACAMÁN *et al*. 1996.
48 FERNÁNDEZ *et al.* 1999; POLETTE *et al.* 2002.
49 CHIARI *et al.* 2003; FOIS *et al.* 2003; HUBBARD *et al*. 2003; REINEN *et al*. 2004; SÁNCHEZ DEL RÍO *et al*, 2004; GIUSTETTO *et al*. 2005; SÁNCHEZ DEL RÍO *et al.* 2005; OVARLEZ *et al*. 2006.
50 DOMÉNECH *et al.* 2006, 2007a,b, 2009a-c.
51 RONDAO *et al.* 2010.
52 DOMÉNECH *et al*. 2011b.

from Klessinger and Lüttke (1963) with those for Maya Blue samples reported by Reinen *et al.* [53] (MB-1) and García-Moreno *et al.* [54] (MB-2). Clearly, the spectra of Maya Blue samples display spectral features able to be described in terms of the superposition of those for indigo and dehydroindigo, including spectral shifts due to the dye-palygorskite association.

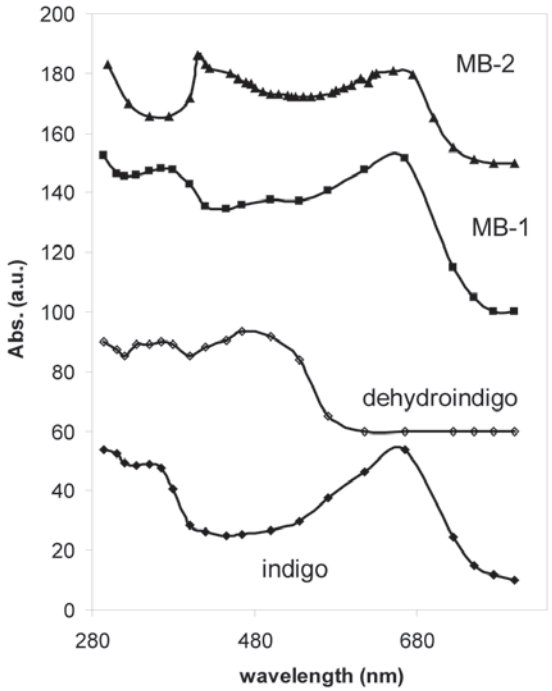

Fig. 1. VIS-UV spectra for indigo and dehydroindigo from Klessinger and Lüttke, 1963 and Maya Blue samples reported by Reinen *et al.* (2004) (MB-1) and García-Moreno *et al.* (2008) (MB-2).

Remarkably, the presence of variable amounts of palygorskite-associated dehydroindigo accompanying palygorskite-associated indigo could explain the relatively large hue variability of the Maya Blue. Thermochemical data indicate that the formation of palygorskite-associated dehydroindigo from palygorskite-associated indigo would be spontaneous under the usual heating conditions[55] so that the formation of Maya Blue could be formally represented by two consecutive (or simultaneous) reaction processes:

$$\{\text{hydr. palyg.}\} + \{\text{indigo}\} \rightarrow \{\text{dehydr. palyg.} \cdots \text{indigo}\} + x\text{H}_2\text{O} \quad (1)$$

$$\{\text{dehydr. palyg.} \cdots \text{indigo}\} + \text{O}_2 \rightarrow \{\text{dehydr. palyg} \cdots \text{dehydroindigo}\} + 2\text{H}_2\text{O} \quad (2)$$

where { } denote solid materials. Then, the dehydroindigo/indigo ratio, and ultimately, the tonality of the Maya Blue, could be controlled by varying the temperature of the thermal treatment applied during the process of preparation of the pigment[56].

The 'uniqueness' paradigm

In the context of research on the nature of Maya Blue there has emerged a view of this material as a unique product with regard to three basic aspects that one can formulate in terms of three uniqueness hypotheses[57]:

i) Indigo is the unique organic component in Maya Blue.

ii) There is a unique type of attachment between indigo and palygorskite.

iii) A unique preparation recipe which remained invariable during the pre-Columbian times was used by the ancient Mayas.

Such hypotheses remain implicit and even explicit[58] in recent literature. In previous works, however, we have provided reasons for questioning this extended paradigm. First of all, as previously noted, there are experimental evidences supporting the coexistence of both indigo and dehydroindigo in Maya Blue. By the second token, electrochemical and spectral data suggest that several topological isomers of indigo (and dehydroindigo) can exist in the Maya Blue, such isomers corresponding to dye molecules located in different positions in the clay framework, presumably with different coordinative arrangements[59]. Finally, chemometric analysis of voltammetric and spectral signatures for Maya Blue samples from different archaeological sites in Yucatán and Campeche covering the Late Preclassical-Early Postclassical period, suggested that the preparation procedure of Maya Blue probably changed along time, the data fitting to a ramified, evolutionary pattern[60].

53 REINEN *et al*. 2004.
54 GARCÍA-MORENO *et al*. 2008.
55 DOMÉNECH *et al*. 2006.
56 *Idem.*
57 DOMÉNECH *et al*. 2009a.
58 TSIANTOS *et al*. 2011.
59 DOMÉNECH *et al*. 2009a, c, d.
60 DOMÉNECH *et al*. 2007a, 2009b.

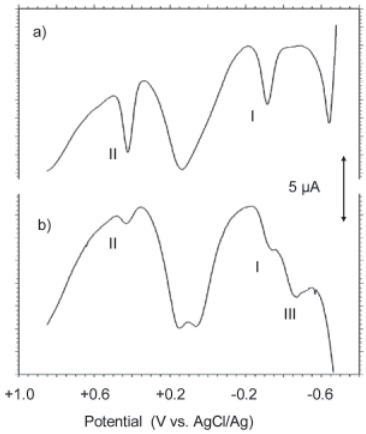

Fig. 2. Square wave voltammograms of synthetic Maya Blue-type specimens prepared by crushing indigo (1% wt) with palygorskite and tretating at 130 ºC for a) 0, and b) 15 min. Potential scan initiated at -0.65 V in the positive direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

In fact, the appearance of other indigoid dyes can result from the evolution of indigo upon attachment to the palygorskite framework. This can be seen in Figure 2, where square wave voltammograms of synthetic Maya Blue-type specimens prepared by crushing indigo (1% wt) with palygorskite and tretating at 130 ºC for 0 and 15 min are compared. In the pristine indigo plus palygorskite specimen the voltammogram is close to that of solid indigo, consisting of two indigo-centered signals at -0.30 (I) and +0.40 V (II) vs. AgCl/Ag. Such peaks can correspond to the solid-state electrochemical reduction of indigo to leucoindigo (LI, process I) and the solid state electrochemical oxidation of indigo to dehydroindigo (DI, process II), processes that can be represented as[61]:

$$\{H_2IN\} + 2H^+(aq) + 2e^- \rightarrow \{LI\} \quad (3)$$

$$\{H_2IN\} \rightarrow \{DI\} + 2H^+(aq) + 2e^- \quad (4)$$

In the thermally treated specimen, peaks I and II become wider while an additional peak at *ca*. -0.40 V (III) is recorded. This peak can be assigned to the reduction of palygorskite-associated indirubin (2H-indol-2-one, 3-(1,3-dihydro-3-oxo-2H-indol-2-ylidene)-1,3-dihydro) and/or isatin (indole-2,3-dione), other well-known indigoid pigments, thus showing the existence of significant dye reactivity under these experimental conditions.

The electrochemical features displayed by Maya Blue samples and indigo plus palygorskite specimens attached to graphite electrodes in contact with aqueous electrolytes differ from those recorded for indigo as a result of the dye-clay association[62]. Interestingly, the voltammetric response exhibits subtle, but significant variations from one archaeological site to another, as can be seen in Figure 3. Chemometric analysis of electrochemical parameters alone[63] and combined with spectral features[64] by means of multivariate clustering methods, permits to propose an evolutionary, ramified scheme based on the idea that different preparation procedures of Maya Blue were used[65]. Figure 4 shows one of the possible schemes relating the studied sites on the basis of the classification of samples in different 'electrochemical types' using voltammograms such as in Figure 3. Obviously, entirely conclusive results can only be extracted by using a more representative set of samples.

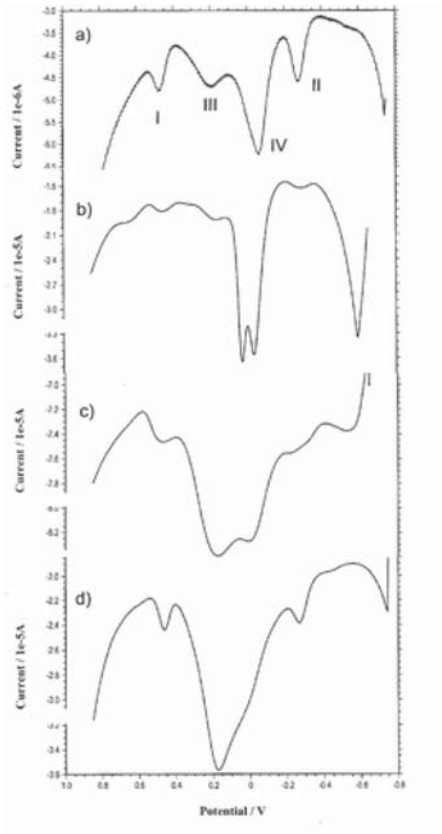

Fig. 3. Square wave voltammograms of PIGEs modified with Maya Blue samples from (a) Chacmultún (type A3), (b) El Tabasqueño (type B), (c) D'zula (type C), and (d) Mayapán (type D), immersed into 0.50 M acetate buffer, pH 4.85. Potential scan initiated at −750 mV in the positive direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz. Adapted from Doménec*h et al.* 2007a. *Anal. Chem.* 79: 2812-2821, with permission, copyrightACS(2007).

61 BOND *et al.* 1997.

62 DOMÉNECH *et al.* 2006, 2007a, b.
63 DOMÉNECH *et al.* 2007a.
64 DOMÉNECH *et al.* 2009b.
65 DOMÉNECH *et al.* 2007a, 2009b.

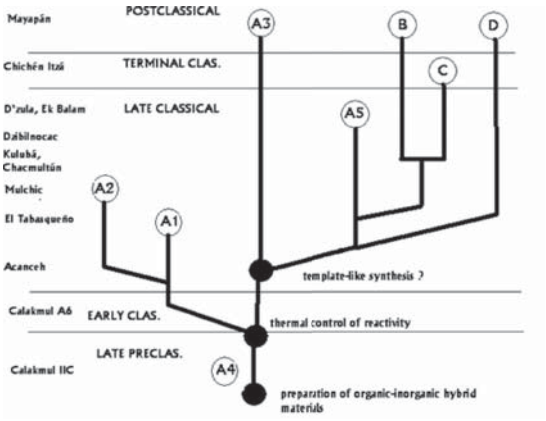

Fig. 4. Possible Chronological Scheme for the Evolution of MB in the Late Preclassical−Postclassical Maya Periods. Adapted from Doménech *et al.* 2007a. *Anal. Chem*. 79,: 2812-2821, with permission, copyright ACS (2007).

'Maya Yellow'

It is known that the Mayas and other Mesoamerican cultures used a variety of vegetal pigments. In its *Florentine Codex*, Fray Bernardino de Sahagún[66] mentions only two yellow vegetal pigments used by the aztecs: *zacatlaxcalli* (*Cuscuta tinctorea*) and *xochipalli* (*Cosmos sulphureus*), but Wallert[67], Haude[68] and Magaloni[69] have provided more extensive lists. These involve carotenoids and xantophiles (*zacatlaxcalli*, *cempaxóchitl*), naphtoquinonics (*guachupin*), and flavonoids (fustic, *caco de nance*), among others.

In this context, we explored the possibility of existing yellow pigments resulting from a dye plus clay association similar to that of Maya Blue. In fact, Vandenabeele *et al.* [70] on analyzing the Raman spectra of a series of yellow, green and blue Maya Blue samples from the site of Ek' Balam, suggested that possibly leucoindigo accompanied indigo in yellow samples.

Examination of a series of five yellow samples from Yucatán by means of microscopy (SEM/EDX, TEM) and voltammetric techniques revealed the presence of palygorskite associated, in several cases to isatin[71] (indole-2,3-dione). Interestingly, SEM and TEM images of palygorskite crystals in such archaeological samples evidenced the presence of typical elongated crystals where gross pores associated to the loss of zeolitc water, a feature observed in genuine Maya Blue samples[72], were absent. These features, which suggested that such 'Maya Yellow' samples consist of a palygorskite-dye complex in whose preparation no, or smooth thermal treatment was used, can be reconciled with the possible preparative schemes for indigo and Maya Blue. Fray Bernardino de Sahagún[73] described in detail the preparation of indigo for dyeing purposes. The pigment was extracted from leaves and twigs of *Indigofera* species by preparing a maceration of the vegetal materials in a quick-lime suspension in water. The coarse material was further removed and the suspension was submitted to intensive aeration by stirring during several days (a process called *batido*). An alternative *sancochado* procedure was also used; here, one or two intermediate steps in which the suspension was boiled and cooled preceded the ending *batido* step[74]. Upon reproducing *in situ* the preparation of indigo using such recipes, it was observed that the suspension changes from yellow to green and finally blue during its progressive aeration[75]. This observation suggests the possibility of extracting aliquots of the suspension in order to prepare different dyes. Additionally, the addition of palygorskite could result in the preparation of different dye plus clay materials, so that not only indigo but also different dyes and pigmenting materials could be obtained following a common preparative scheme[76].

The foregoing set of considerations can be adduced in support of the idea that the ancient Mayas used not only blue-green Maya Blue but also yellow pigments with comparable indigo plus palygorskite association. Figure 5 shows the voltammograms for several 'Maya Yellow' samples illustrating (compare with Figure 3) their differences with the voltammetric response of Maya Blue. The more significant feature is the presence of a voltammetric signal at -0.55 V, attributable to isatin, an indigoid pigment which could be also involved in the synthesis of indigo from their precursors in plants, mainly indicant and isatans A and B[77]. Differences between the 'Maya Yellow' samples from Acanceh, D'zula and Mayapán suggested that local variants of such yellow pigment were prepared[78]. Such variants can in principle be correlated with the corresponding varieties of Maya Blue previously described[79].

66 SAHAGÚN 1950:82
67 WALLERT 1994.
68 HAUDE 1997.
69 MAGALONI 2001.
70 VANDENABEELE *et al.* 2005.
71 DOMÉNECH *et al.* 2011a.
72 DOMÉNECH *et al.* 2007a.
73 SAHAGÚN 1950:82
74 DOMÉNECH *et al.* 2007c.
75 *Ídem.*
76 DOMÉNECH *et al.* 2011a.
77 OBERTTHÜR *et al.* 2004; DOMÉNECH *et al.* 2007c.
78 DOMÉNECH *et al.* 2011a.
79 DOMÉNECH *et al.* 2007a, 2009b.

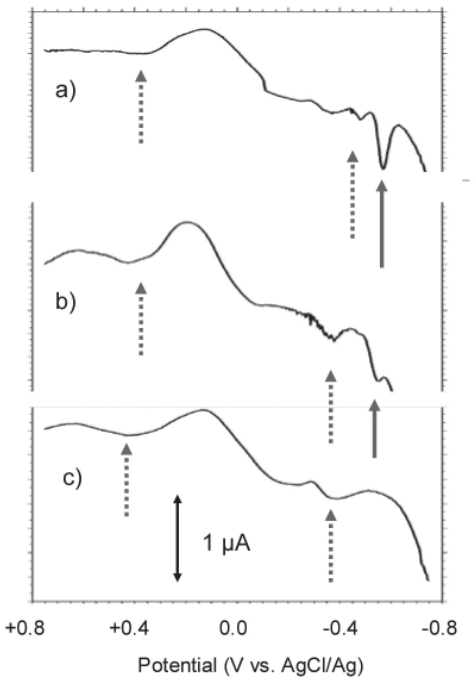

Fig. 5. Square wave voltammograms for samples from: a) Acanceh, b) D'zula and c) Mayapán attached to paraffin-impregnated graphite electrodes immersed into 0.50 M acetic acid/sodium acetate aqueous buffer, pH 4.75. Potential scan initiated at -0.75 V in the positive direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz. Peaks for isatin (continuous arrows) and the dehydroindigo/indigo/leucoindigo system (dotted arrows) are marked. Adapted from Doménech *et al.* 2011 *Angew. Chem. Int. Ed.* 50: 5741-5744, with permission, copyright Wiley(2011).

La Blanca green pellets

A recent discovery can be added to the corpus of the Maya Blue-type materials. The discovery consisted of four spheroidal agglomerates of light greenish hue which were fractioned into 32 irregular pellets, 4-8 mm diameter sized, in the Suboperation 141 of the Structure 4H1 south façade of La Blanca Great North Plaza. La Blanca was one of the many Mayan urban settlements formed in the lower basin of the Mopan River during the pre-Hispanic period. Its most important period of occupation was between the Late Classic (c. 600-800 AD) and the Terminal Classic[80] (c. 800-950 AD) periods. The greenish pellets were accompanied by other remains of material culture (pottery sherds, mainly) that allowed to date them in the Terminal Classic period. In this time La Blanca knew a period of prosperity, as reflected in the decoration of the palatial residences, just some years before of the Classic Maya civilization "collapse" and the site overgrown by the jungle[81]. The greenish pellets would be part of the plaster filling used in constructive works, as suggested by the appearance of some print of small organisms such as mollusks which can be seen in the surface of several fragments[82].

SEM and TEM examination of samples, combined with infrared spectroscopy and X-ray diffraction permitted to detect the presence of palygorskite as an essential component of the pellets. Importantly, the infrared spectra of the greenish pellets displayed features (weak bands at 2928 and 2860 cm^{-1}) attributable to the stretching vibrations of CH bonds from indigo or other organic matter present in the samples while palygorskite bands at 1652 and 1631 cm^{-1} become overlapped, a feature appearing in Maya Blue. As observed in the spectra for synthetic Maya Blue specimens re-equilibrated in ambient conditions after to be submitted to thermal treatment[83], overlapping and a general broadening of the bands in the 900 to 1200 cm-1 region was also observed. The above spectral features suggested that there is an organic dye associated to the palygorskite.

This idea was confirmed by electrochemical data on glassy carbon electrodes adsorptively modified with the extracts of the green pellets obtained after contact overnight with 0.10 M Bu_4NPF_6/DMSO. Now the voltammograms obtained upon immersion of the modified electrodes into aqueous acetate buffer become close to that obtained for the Maya Blue. Detailed analysis of such voltammetric curves[84] suggests that indigo plus dehydroindigo and, possibly, any other indigoid products can be extracted from the studied pellets, as confirmed by ^1H NMR spectra of green pellets extracts in deuterated DMSO. Such extracts display features (overlapping duplets between 7.0 and 7.4 ppm) attributable to aromatic protons of indigo[85] and a multiplet centered at 7.6 ppm, attributable to the aromatic protons of dehydroindigo[86]. In fact, the voltammetric response of such extracts adsorptively transferred onto glassy carbon electrodes in contact with aqueous electrolytes shows the voltammetric signatures of indigo plus dehydroindigo mixtures, as can be seen in Figure 6[87].

80 MUÑOZ and VIDAL (Eds.) 2005, 2006; VIDAL and MUÑOZ (Eds.) 2007.

81 VIDAL and MUÑOZ 2009.
82 DOMÉNECH *et al.* 2012.
83 SÁNCHEZ DEL RÍO *et al.* 2009b.
84 DOMÉNECH *et al.* 2012.
85 HOFFMAN *et al.* 2010.
86 RONDAO *et al.* 2010.
87 DOMÉNECH *et al.* 2012.

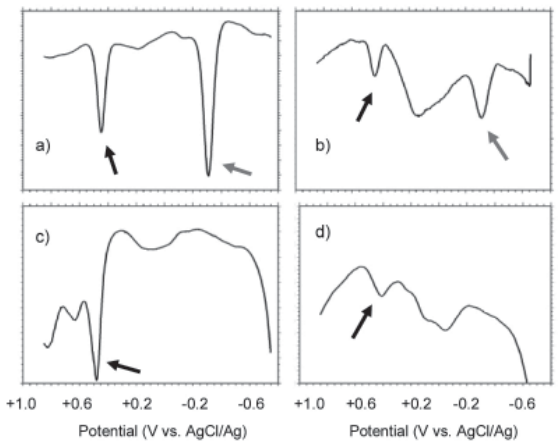

Fig. 6. Square wave voltammograms for: a) indigo paste (Kremer 36003); b) Maya Blue sample from Chichén Itza; c) indoxyl (1 % w/w) plus the palygorskite wet mixture attached to paraffin-impregnated graphite electrodes and d) glassy carbon electrodes modified with the extract of a green pellet (BV32) in contact with DMSO overnight. Electrolyte 0.50 M HAc/NaAc, pH 4.85. Potential scan initiated at -0.75 V vs. AgCl/Ag in the positive direction; potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz. Black arrow: dehydroindigo/indigo couple; grey arrow: indigo/ leucoindigo couple. Adapted from Doménech *et al.* 2012. *Angew. Chem. Int. Ed.* 51: 700-703, with permission, copyright Wiley(2012).

Consistently with the above results, the UV-VIS diffuse reflectance spectra of the green pellets exhibited a profile having significant common features with the spectra of Maya Blue-type samples, consisting of reflectance minima at 660 and 350 nm, associated to indigo and Maya Blue specimens, accompanied by spectral features at 400 and 528 nm, attributable to dehydroindigo[88]. Ochre and other indigoid compounds could also be present in the samples which can be described as aged palygorskite plus indigo mixtures[89].

A Maya Blue technology?

The above analytical data can be viewed within the context of current tendencies on materials-based analysis, focused not only on the description and characterization of the material properties of the archaeological objects, but also on the role of such materials in the social lives of people[90]. In this sense, the technology surrounding Maya Blue-type materials would be permeated by religious significance, symbolism and practice[91]. The 'Maya Yellow' and green pellets from La Blanca discoveries described in the precedent sections suggest the existence of a (pre)technology based in the combination of indigoids (and/or other organic components extracted from plants) and clays which was not limited to Maya Blue. In the case of La Blanca greenish pellets, although their origin and function is uncertain, their location and composition is consistent with their attribution to residuals during the preparation of decorative pigmenting materials. This is relevant because the green pellets would be an evidence for the use of the materials constitutive of the Maya Blue in a quotidian, non-sacred context.

As previously noted, the discovery of the Maya Blue pigment on a ball of copal from Tikal and one from the Cenote of Scrifice at Chichén Itzá[92], among others, led to Arnold *et al.*[93] to consider that Maya Blue could be prepared ritually by burning incense using a mixture of copal and some part of the *Indigofera* plants. There are reasons, however, to assume that, apart from a 'sacred' Maya Blue circuit, there was a non-sacred one, where Maya Blue and related materials were used:

i) The use of combinations of palygorkiste with other indigoids as pigmenting materials ('Maya Yellow? and 'Maya Green', greenish pellets) whose preparation could follow common schemes[94].

ii) The extended use of the Maya Blue in ceramics[95]. In fact, most objects relating to practical scale like fishing, medicine, or sacrifice were often painted blue by the Mayas[96].

iii) The plausible existence of different preparation recipes for Maya Blue, with local variations and evolving with time[97].

This non-sacred version of Maya Blue can be viewed on the basis of the notion of material metaphor, widely used in interpretative archaeology[98]. The central idea is that there exists a dynamic interdependence between the signs and their physical embodiment[99]. Then, the variety of symbolisms associated to the blue color by the Mayas[100] may have parallel with different technological blue products. In particular, it is conceivable that local/regional differences in symbolism could be related with concomitant differences in the applications and/or preparation of the Maya Blue-related materials.

88 RONDAO *et al.* 2010.
89 DOMÉNECH *et al.* 2012.
90 JONES 2004.
91 SILLAR and TITE 2000; SAUNDERS 2002.
92 CABRERA GARRIDO 1969; SHEPARD 1962; SHEPARD and GOTTLIEB 1962; SHEPARD and POLLOCK 1971.
93 ARNOLD *et al.* 2008.
94 DOMÉNECH *et al.* 2011a, 2012, 2014.
95 ARNOLD 1967a,b, 1971, 1991, 2000, ARNOLD and BOHOR 1975, 1976.
96 REYES-VALERIO 1993.
97 DOMÉNECH *et al.* 2007a, 2009b.
98 RAY 1987; PLUCIENNIK 2002; BRAY 2008.
99 HAYLES 2002.
100 REYES-VALERIO 1993.

It should be emphasized that, to some extent, the Maya Blue technology roughly described here would possess several aspects of 'modern' technology, namely, the flexible utilization of the disposable materials, the possibility of innovation and competence and the systematic control of the production schemes. In fact, several aspects of the preparation of the Maya Blue would anticipate those used by contemporary chemistry[101].

Conclusions

Analytical data on yellow pigments from different Mayan sites and a series of green pellets discovered in the site of La Blanca (Petén, Guatemala) indicate the presence of indigoid compounds accompanying palygorskite. Textural and compositional data suggest that these materials were possibly produced within a technological frame based on the combination of organic and inorganic components. In this technological context, different procedures of preparation of Maya Blue were probably developed by the ancient Mayas along their history, the pigment and related 'Maya Yellow', 'Maya Green' materials would be handled not only in a sacred, ritual circuit, but also in a quotidian context.

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