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Historical Pigments

Insights into the Maya Blue Technology: Greenish Pellets from the Ancient City of La Blanca**

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Since its discovery by Merwin in 1931,[1] Maya Blue, an ancient nanostructured material resulting from the attachment of indigo, a blue dye extracted from leaves of añil or xiuquitlitl (*Indigofera suffruticosa* and other species), to the clay matrix of palygorskite, a fibrous phyllosilicate, has received attention not only for its considerable archaeological and ethnohistoric value[2] but also for its peculiar structure that predates contemporary organic–inorganic hybrid materials.[3] The latter idea was first proposed by Shepard,[4] whereas Arnold and Bohor identified sites for palygorskite extraction in the Yucatán peninsula and recognized the use of palygorskite in Mesoamerican ceramicware.[5]

Elucidation of the nature of the indigo–palygorskite association as well as the reasons for its peculiar hue, subject to prolonged controversy,[6] is a difficult analytical task owing to, among other reasons, the high dilution of the organic component in the inorganic host and lack of documentation relating to Maya Blue preparation.[6b,e,f,g,7] This latter aspect is particularly intriguing if we consider that Maya Blue was used in mural paintings, pottery, sculptures, luxury art, and even as a therapeutic agent by ancient Mayas and other populations in Mesoamerica. In this context, Arnold et al. have provided evidence that Maya Blue could be prepared ritually by burning incense using a mixture of copal (called ′pom′ in the Yucatec Maya language) from tree sap (*Protium copal*), palygorskite, and some part of the indigo plant.[8] This discovery suggests that Maya Blue could be a 'sacred' material handled by a restricted social group. In this context a view has emerged that Maya Blue was a unique material, the ritual preparation and sociocultural value of which remained essentially invariable during pre-Columbian times. In previous reports, we have provided reasons for questioning this view;[9] thus, the presence of variable amounts of dehydroindigo as an accompaniment of indigo could explain the variability in the pigment hue,[10a,b] whereas the chemometric analysis of the electrochemical and spectral data of genuine Maya Blue samples have indicated that the preparation of the pigment probably underwent significant variations throughout Mayan times.[10c,d] Lastly, we have detected an association between indigoid compounds and palygorskite in "Maya Yellow" samples from different archaeological sites.[11]

Herein, we provide both chemical and historical insights into Maya Blue, as a result of the analysis of a set of greenish clayed noduli discovered in Structure 4H1 of the La Blanca archaeological site (Peten Department, Guatemala). La Blanca was an important Mayan town in the lower basin of the Mopan River. La Blanca′s highest political, social, economic, and cultural splendor existed between the Late Classic (ca. 600–800 AD) and the Terminal Classic (ca. 800–950 AD) periods.[12] The set of noduli discovered in 2008 consisted of four sphaeoridal agglomerates fractioned into 32 irregular pellets (BV01 to BV32, see Figure 1) of 4–8 mm in diameter presenting a light greenish hue. The pellets were found in La Blanca Great North Plaza, on the south façade in

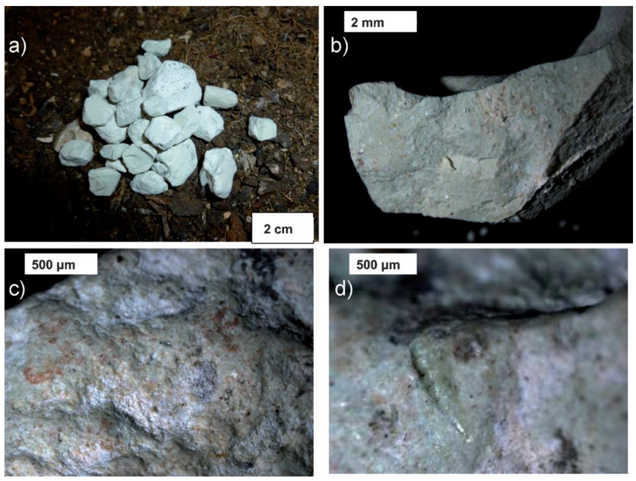

Figure 1. Photographs of the greenish noduli from La Blanca. a) In situ image of the discovery, b) cross section of pellet BV31 that shows a characteristic uniform greenish hue, c) detailed image of the external surface of pellet BV09 showing small iron oxide rich grains, d) microphotograph of the surface of pellet BV10 showing the print of a mollusk.

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Structure 4H1 (Suboperation 141), and were accompanied by other remains (mainly pottery shards), which allowed them to be dated back to the Terminal Classic period. Under the optical microscope the surface of the fragments was irregular and locally showed a decay of the blue-greenish hue, whereas an uniform greenish hue was observed in cross sections. Some prints of small organisms such as mollusks can be seen on the surface of some pellets, thus indicating their original paste constitution. The possibility of the pellets being the remains of a decorative plaster filling that incorporated indigoid compounds was the crucial aspect to be elucidated: apart from constituting a novel Mayan material, this discovery could provide the first evidence of the use of Maya Blue components in a quotidian, non-sacred preparative context, which in turn could be consistent with the possible use of wet routes to prepare Maya Blue.[11]

Backscattered electron images obtained by scanning electrochemical microscopy (SECM) and transmission electron microscopy (TEM) on finely powdered microsamples from the green pellets show elongated crystals with fibrous features that are characteristic of palygorskite clay (Figure 2). The surface pores that are frequent in palygorskite in Maya

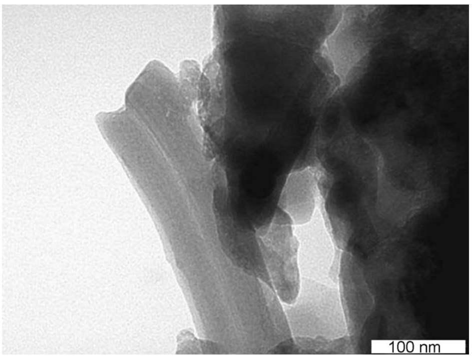

Figure 2. TEM image of palygorskite crystals from greenish noduli BV03 from La Blanca.

Blue samples and attributable to water evacuation[10] are entirely absent in the observed images. This last feature, denoting lack of heat treatments, would be consistent with the use of the green noduli as a plaster. Palygorskite appears to be the major component of the studied pellets, as determined by the scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDX), X-ray diffraction, and attenuated total reflection FTIR spectroscopy data. Interestingly, when comparing the IR spectra of our samples with the IR spectrum of palygorskite from the Sak lu'um mine, one of the classical palygorskite sites,[5] several different features can be observed in the OH-stretching and OH-bending regions, where IR bands are ascribed to vibrations of structural, coordinated, and zeolitic water (Figure 3). Thus, relative to palygorskite, green pellets display an IR spectrum in which a slight shift of the band at 3613 to 3602 cm^{-1} is observed, and a noticeable increase in the intensity of the band at 3380 cm^{-1} is accompanied of a general broadening of the bands in this region. Bands at 1652 and 1631 cm^{-1} become overlapped, as

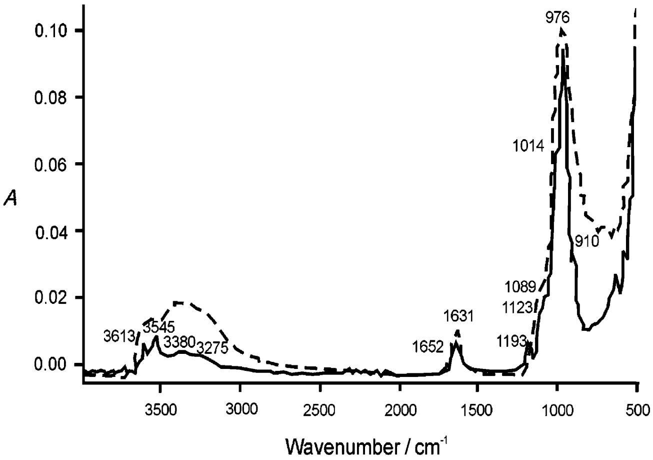

Figure 3. ATR-FTIR spectra for palygorskite from Sak lu'um (solid line) and the greenish noduli BV05 (dashed line) from La Blanca.

do the bands in the 900 to 1200 cm^{-1} region. All these features are close to those reported for synthetic Maya Blue specimens[13] and suggest the existence of an interaction between palygorskite and an organic dye.

To detect organic components of greenish pellets, voltammetry of microparticles (VMP), an electrochemical technique developed by Scholz et al. for analyzing sparingly soluble solids[14] and applied to the analysis of works of art,[15] was used. The most relevant results were obtained from extracts that were prepared by exposing the green pellets to 0.10 M Bu_4NPF_6/DMSO overnight; the voltammetric profile of these extracts was close to that of indigo dissolved in the same electrolyte.[16] Upon the adsorptive transfer of the DMSO extract onto a glassy carbon electrode, the voltammogram obtained with aqueous acetate buffer as the electrolyte shows a main peak at +0.45 V vs. AgCl/Ag, matching with the response obtained for a wet mixture of indoxyl (1 % w/w) and palygorskite (see Figure 4), a system resulting in high dehydroindigo yields.[11] This finding suggests that dehydroindigo and possibly other indigoid products coexist with indigo, presumably the original organic component of the paste. Such products could be formed as a result of the degradation of palygorskite-associated indigo.

In agreement with the voltammetry results, the ^{1}H NMR spectrum of the DMSO extracts from the green pellets (see Figure 5) exhibits signals (overlapping doublets between $\delta =$ 7.0 and 7.4 ppm) attributable to the aromatic protons of indigo[17] and a multiplet centered at $\delta = 7.6$ ppm, attributable to the aromatic protons of dehydroindigo.[18] Also consistent with these findings, the optical spectrum of the powdered green pellets displays significant common features with the spectra of Maya Blue type samples (see the Supporting Information).

The above analytical data suggest that: 1) the studied green pellets mainly consist of palygorskite agglomerates resulting from original clay-plus-water pastes; 2) indigo and/or its alteration products are present in the studied green pellets; 3) these indigoid components are extractable with organic solvents, thus indicating that there is no strong attachment to the palygorskite. All these results suggest that

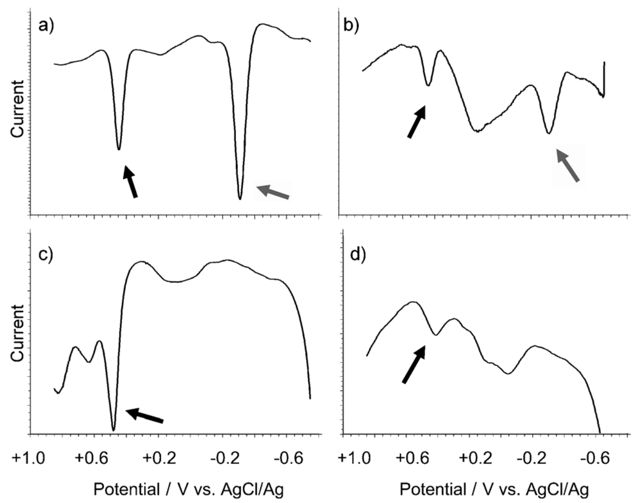

Figure 4. Square wave voltammograms for: a) indigo paste (Kremer 36003), b) Maya Blue sample from Chichén Itza, c) wet mixture of indoxyl (1% w/w) and palygorskite attached to paraffin-impregnated graphite electrodes, and d) glassy carbon electrodes modified with the extract of a green pellet (BV32) 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; gray arrow: indigo/leucoindigo couple.

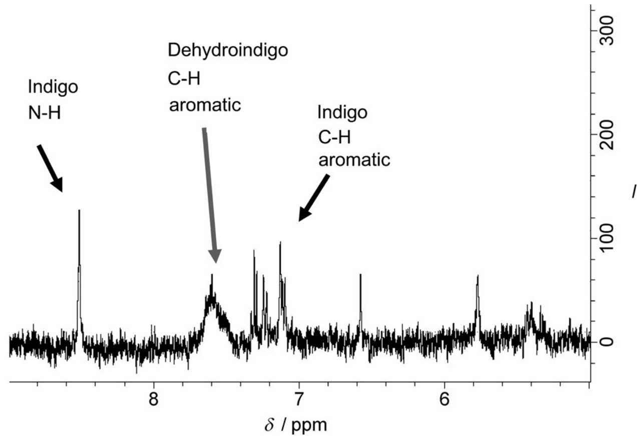

Figure 5. ^{1}H NMR spectrum for the extract of a fragment of green pellet BV05 after being in contact with deuterated DMSO overnight.

the greenish pellets consist of aged palygorskite-plus-indigo pastes. Although the origin and function of the pellets remains uncertain, their location and composition suggest that they could have originally been a plaster filling used during the construction of the palatial complex. From the chemistry point of view, the composition of La Blanca greenish pellets suggests that wet procedures were used by ancient Mesoamerican people to handle materials related to Maya Blue, which is in agreement with a previous report.[11]

To our knowledge, although it is not Maya Blue, this discovery corresponds to the first occurrence of a 'Maya Blue like' material, which contains the Maya Blue components, in a context not related to the actual end use in pottery, murals, sculpture, and copal, or the religious context. This discovery reveals an additional context for creating Maya Blue other than heating a combination of indigo and palygorskite during ritual ceremonies. It appears that ancient Mesoamerican people developed a technology in which the Maya Blue pigment was a part, and that they established a relatively complex preparative chemical method, the knowledge of which could be of interest not only from the historical but also from a contemporary chemical viewpoint. With this mind, it should be emphasized that the Maya people might have prepared a variety of materials, ranging from yellow, green, and blue pigments to plasters, which combined few natural products: palygorskite and parts of the *Indigofera* plant. This rich and unexpected chemistry, based on the modulation of the type of attachment between organic and inorganic components, was likely accomplished with subtle variations in the preparation recipe.

Experimental Section

Palygorskite, collected from the Sak lu'um classical site in Yucatan,[5] synthetic indigo (Fluka) and indoxyl β-D-glucoside (Sigma), were used as reference materials. The instrumentation and procedures were described in previous reports[10,11] and details are given in the Supporting Information.

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[1] H. E. Merwin, *Chemical analysis of pigments in Temple of the warriors at Chichén-Itzá, Yucatán* (Eds.: E. H. Morris, J. Charlot, A. A. Morris), Carnegie Instit, Washington, **1931**, pp. 355–356, 406.
[2] C. Reyes-Valerio, De Bonampak al Templo Mayor: el azul Maya en Mesoamérica, Siglo XXI, México, **1993**.
[3] P. Gómez-Romero, C. Sanchez, *New J. Chem.* **2005**, *29*, 57.
[4] A. O. Shepard, *Am. Antiq.* **1962**, *27*, 565.
[5] a) D. E. Arnold, *Am. Antiq.* **1971**, *36*, 20; b) D. E. Arnold, B. F. Bohor, *Archaeology* **1975**, *28*, 23; c) D. E. Arnold, B. F. Bohor, *Katunob* **1976**, *8*, 25; d) D. E. Arnold, *Ancient Mesoam.* **2005**, *16*, 51.
[6] a) M. José-Yacamán, L. Rendón, J. Arenas, M. C. Serra Puche, *Science* **1996**, *273*, 223; b) B. Hubbard, W. Kuang, A. Moser, G. A. Facey, C. Detellier, *Clays and Minerals* **2003**, *51*, 318; c) E. Fois, A. Gamba, A. Tilocca, *Microporous Mesoporous Mater.* **2003**, *57*, 263; d) D. Reinen, P. Köhl, C. Müller, *Z. Anorg. Allg. Chem.* **2004**, *630*, 973; e) M. Sánchez del Río, P. Martinetto, A. Somogyi, C. Reyes-Valerio, E. Dooryhée, N. Peltier, L. Alianelli, B. Moignard, L. Pichon, T. Calligaro, J.-C. Dran, *Spectrochim. Acta Part B* **2004**, *59*, 1619; f) R. Giustetto, F. X. Llabres-i-Xamena, G. Ricchiardi, S. Bordiga, A. Damin, R. Gobetto, M. R. Chierotti, *J. Phys. Chem. B* **2005**, *109*, 19360; g) M. Sánchez del Río, P. Martinetto, C. Reyes-Valerio, E. Dooryhée, M. Suárez, *Archaeometry* **2006**, *48*, 115.
[7] a) H. Van Olphen, *Science* **1966**, *154*, 645; b) J. M. Cabrera-Garrido, El "*Azul Maya*", Informes y Trabajos del Instituto de Conservación y Restauración de Obras de Arte, Arqueología y Etnología 8, Madrid, **1969**; c) L. M. Torres, *Proc. Mater. Res. Soc.* **1988**, *123*, 123–128.
[8] D. E. Arnold, J. R. Branden, P. R. Williams, G. M. Feinman, J. P. Brown, *Antiquity* **2008**, *82*, 152.

[9] a) A. Doménech, M. T. Doménech, M. Sánchez, M. L. Vázquez, E. Lima, *New J. Chem.* **2009**, *33*, 2371; b) A. Doménech, M. T. Doménech, M. Sánchez, M. S. Goberna, E. Lima, *J. Phys. Chem. C* **2009**, *113*, 12118.

[10] a) A. Doménech, M. T. Doménech, M. L. Vázquez, *J. Phys. Chem. B* **2006**, *110*, 6027; b) A. Doménech, M. T. Doménech, M. L. Vázquez, *J. Solid State Electrochem.* **2007**, *11*, 1335; c) A. Doménech, M. T. Doménech, M. L. Vázquez, *Anal. Chem.* **2007**, *79*, 2812; d) A. Doménech, M. T. Doménech, M. L. Vázquez, *Archaeometry* **2009**, *51*, 1015; e) A. Doménech, M. T. Doménech, M. Sánchez, M. L. Vázquez, *J. Solid State Electrochem.* **2009**, *13*, 869.

[11] A. Doménech, M. T. Doménech, M. L. Vázquez, *Angew. Chem.* **2011**, *123*, 5859; *Angew. Chem. Int. Ed.* **2011**, *50*, 5741.

[12] a) *La Blanca. Arqueología y Desarrollo* (Eds.: G. Muñoz, C. Vidal), UPV, Valencia, **2005**; b) *La Blanca, Arquitectura y Clasicismo* (Eds.: G. Muñoz, C. Vidal), UPV, Valencia, **2006**; c) *La Blanca y su entorno. Cuadernos de arquitectura y arqueología maya* (Eds.: C. Vidal, G. Muñoz), UPV, Valencia, **2007**.

[13] a) M. Suárez, R. García-Romero, *Appl. Clay Sci.* **2006**, *31*, 154; b) M. Sánchez del Río, E. Boccaleri, M. Milanesio, G. Croce, W. Van Beek, C. Tsiantos, G. D. Chyssikos, V. Gionis, G. H. Kacandes, M. Suárez, E. García-Romero, *J. Mater. Sci.* **2009**, *44*, 5524.

[14] a) F. Scholz, B. Meyer, *Electroanalytical Chemistry, A Series of Advances*, *Vol. 20*, Marcel Dekker, New York, **1998**, p. 1; b) F. Scholz, U. Schröder, R. Gulabowski, *Electrochemistry of Immobilized Particles and Droplets*, Springer, Berlin, **2005**.

[15] a) A. Doménech, M. T. Doménech, V. Costa, *Electrochemical Methods in Archeometry, Conservation and Restoration*, Springer, Berlin, **2009**; b) Electrochemistry for Conservation Science (Ed.: A. Domenech Carbo), *J. Solid State Electrochem.* **2010**, *14*, No.3.

[16] a) A. M. Bond, F. Marken, E. Hill, R. G. Compton, H. Hügel, *J. Chem. Soc. Perkin Trans. 2* **1997**, 1735–1742; b) A. Doménech, M. T. Doménech, M. L. Vázquez, *J. Phys. Chem. C* **2007**, *111*, 4585.

[17] R. C. Hoffman, R. C. Zilber, R. E. Hoffman, *Magn. Reson. Chem.* **2010**, *48*, 892.

[18] R. Rondao, J. S. de Melo, V. B. D. Bonifácio, M. J. Melo, *J. Phys. Chem. A* **2010**, *114*, 1699.

