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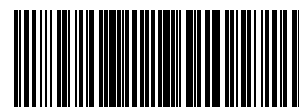
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**PERSPECTIVE**

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# Maya Blue as a nanostructured polyfunctional hybrid organic–inorganic material: the need to change paradigms

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Maya Blue, an ancient nanostructured organic–inorganic hybrid material resulting from the attachment of indigo, a natural dye, to a phyllosilicate clay, palygorskite, has received considerable attention of late. Despite intensive research, several aspects remain unsolved, in particular the nature of the indigo–palygorskite association. Recent results suggest that the Maya Blue pigment is a complex system in which different topological isomers of various indigoid molecules attached to the palygorskite matrix coexist.

## 1. Introduction

Maya Blue (MB) is a famous pigment which is widely used in murals (Fig. 1), pottery, codices and sculptures by the ancient Mayas and other people in Mesoamerica from at least the 8th century. The peculiar MB palette, ranging from a bright turquoise to a dark greenish blue, and its enormous stability with regard to attack of acids, alkalis, organic reagents as well as biodegradation, have claimed considerable attention in recent decades.

The attention paid to the chemistry of MB has been considerably reinforced in recent years because of the characteristics of this pigment as it is a nanostructured material resulting from the attachment of indigo, a blue dye extracted from the leaves of both *Indigofera suffruticosa* and other species, to

the clay matrix of palygorskite, a fibrous phyllosilicate. Gómez-Romero and Sanchez<sup>1</sup> underlined that a combination of organic and inorganic components at the molecular level is a crucial aspect for the modern synthesis of hybrid organic–inorganic nanocomposites, and, therefore, consider Maya Blue a seminal example of this kind of materials.

MB was widely used in Prehispanic Mesoamerica for religious altarpieces during the first century of the Conquest.<sup>2</sup> Its use declined considerably, and even disappeared since 1580. However, a similar pigment, identical in composition, has been reported<sup>3</sup> in civil decoration in Colonial Cuba, and its use may have survived until recent times in isolated communities.

This pigment was rediscovered by Merwin in 1931 at the archaeological site of Chichén Itzá.<sup>4</sup> Gettens provisionally called it Maya Blue, a term which was soon to be adopted universally.<sup>5</sup> Due to the excellent resistance of MB to chemical attack and bioaggression, it was initially thought to be made from an unknown blue mineral. In the 1950s a particular clay in Maya Blue was identified, called at the time attapulgit, now officially known as palygorskite. It was the first breakthrough in the problem of Maya Blue composition.<sup>5,6</sup> However, this clay is not blue, and the problem of its coloration origin was traced by Shepard, who first introduced the idea of MB being an unusual

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Antonio Doménech-Carbó works on supramolecular electrochemistry, electrochemistry of porous nanostructured materials, and electroanalytical methods applied to conservation and restoration of cultural heritage. María Teresa Doménech-Carbó is interested in the development of new analytical methods in the heritage conservation context for characterization of the constitutive materials of art pieces and their condition, alterations and biodeterioration, control and assessment of conservation treatments, etc. The professional activity of Manuel Sánchez del Río is devoted to synchrotron radiation instrumentation and research. María Luisa Vázquez de Agredos Pascual participated in different Archaeological Research Projects in the Maya Area in Mexico and Guatemala. Enrique Lima's research interests concern hybrid pigments, new catalytic materials and characterization by spectroscopic techniques.





**Fig. 1** Wall paintings in Chacmultún (Yucatán, Mexico, Late Classical period) show an intense blue hue due to MB pigment. Photograph from M. L. Vázquez.

material consisting of a dye attached to certain Yucatán clays.<sup>7</sup> Van Olphen<sup>8</sup> prepared synthetic specimens analogue to MB from both palygorskite and sepiolite, a related phyllosilicate, and indigo, thus verifying the resistance of such materials to acid attack. Arnold identified palygorskite in Yucatán clays and recognized the use of this clay in Mesoamerica ceramicware,<sup>9</sup> after having identified several sites for its extraction.<sup>10</sup> Doubts about the composition of MB, however, persisted for years.

In spite of intensive research, MB remains a challenging material in terms of both historic and chemical aspects. First, the preparation procedure used by the ancient Mayas remains unknown; and, the nature of the indigo–palygorskite association in Maya Blue and its relation to the hue and durability of the pigment have become controversial.

In this context, we should be emphasise that a considerable part of the current research appears to be implicitly (and often explicitly) based on an ‘uniqueness’ paradigm which can be summarised by three hypotheses: (i) there is a unique organic component in MB, (ii) there is an unique type of attachment between indigo and palygorskite, and, (iii) there was an unique preparation recipe used by the ancient Maya people. There are reasons, however, for questioning this paradigm. The current report aims to provide a general view of the problems in terms of the structure and properties of MB and a review of recent literature about its different physico-chemical aspects, in particular the interesting debate on the exact nature of the indigo–palygorskite bonding. We expect more investigations will converge in a model over the next few years that will explain the exceptional MB properties. Interest will not only lie in this historic pigment, but also in learning how to use this knowledge to engineer new composite hybrid materials which could have great technological impact.<sup>1</sup>

## 2. The ingredients of the Maya Blue

### 2.1 Indigo

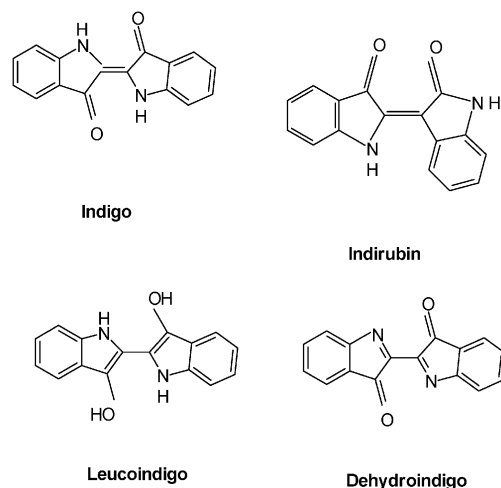
Indigo is a natural blue dye formed by a mixture of colouring species of which indigotin (3*H*-indol-3-one, 2-(1,3-dihydro-3-oxo-2*H*-indol-2-ylidene)-1,2-dihydro) is the primary species

responsible for the distinctive blue colour. From this point onwards, the term indigo will be used to designate indigotin, which is general practice in current literature. The indigo (strictly, indigotin) molecule has a slightly elongated central C=C bond and two elongated C=O bonds, as illustrated in Chart 1. This is a quasi-planar molecule whose approximate dimensions are  $4.8 \times 12$  Å, small enough for penetrating the channels of palygorskite (*vide infra*).

Indigo is a dye that many ancient civilizations have used so the dyeing technique with indigo was probably discovered independently in several geographic places.<sup>11</sup> Different plants of the *Indigofera* family have been used by different civilisations: India (*Indigofera tinctoria*), China (*Indigofera indigotica* or *tein-cheing*) and the Far East (*Polygonum tinctorium*). In Europe, growing woad (*Isatis tinctoria*) and obtaining indigo played an enormous economical, political and cultural role from the 12th to the 17th century.<sup>11</sup> The fact that the woad plant produces much less dye than the *Indigofera* plants, together with lower prices of indigo imported from India and America brought about a decline in the European woad industry in the late 17th century. This market continued until the industrial production of synthetic indigo which was first prepared from isatin by Baeyer in 1870.<sup>12</sup> Its industrial production, based on a method devised by Heumann in 1890,<sup>13</sup> was shortly initiated and displaced indigo production from plants in the late 1890s.

The Mayas obtained indigo from a group of plants generically termed *añil* or *xiuquitlil* (mainly *Indigofera suffruticosa*). The dyeing recipes based on plants used by the ancient Mesoamericans always related to water solutions. They are described in different historical sources<sup>14</sup> and they are similar to those used by other civilizations.<sup>11</sup> It is believed that a similar method, but one that include the addition of clays in the dye suspension was used by the ancient Mayas for MB production.<sup>2</sup> However, there is no historical documentation available to prove this.<sup>15</sup>

The formation of indigo parallels the reaction scheme proposed in plants.<sup>16</sup> The indigo precursors found in leaves, indican and isatans A and B, are first hydrolyzed to hydroxyl which is subsequently oxidized to indigo. Electrochemical monitoring of indigo preparation following traditional



**Chart 1** Main indigoid compounds involved in MB chemistry.

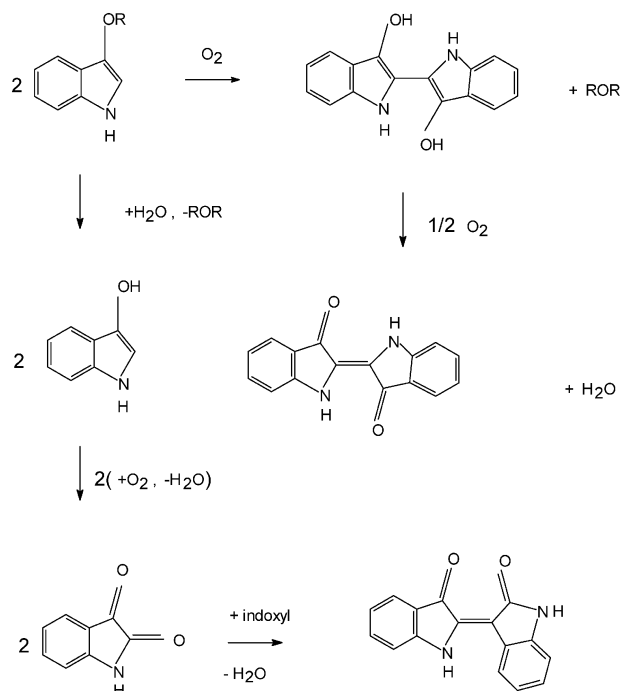
procedures (see Fig. 2) suggests that two competing reaction pathways are involved.<sup>17</sup> In the first, leucoindigo, the reduced form of indigo (see Chart 2) is produced and is subsequently oxidised to indigo. This is favored by the alkaline quick-lime suspension, because leucoindigo, unlike indigo, is slightly soluble in alkaline media. A second reaction pathway involves the formation of isatin by the aerobic oxidation of indoxyl, which yields indirubin as a secondary product.

## 2.2 Palygorskite

Palygorskite (or attapulgite), locally known as *sak lu'um*, is a material still used by the indigenous communities of the Yucatán Peninsula for several applications ranging from domestic and art craft ceramic production to medical treatments.<sup>18,19</sup> Although several locations have been identified,<sup>19</sup> it appears that the most important source<sup>10</sup> was the *cenote* in the village of Sacalum (a Yucatán village whose name possesses an obvious etymology).



**Fig. 2** *Indigofera* leaves and preparation of indigo using traditional materials and methods. Photograph from M. L. Vázquez taken in Yucatán in 2004.



**Chart 2** Possible scheme for the formation of indigo and indirubin from isatin/indican precursors from ref. 17.

Palygorskite is a fibrous clay, and was first described in 1860 in the mineral basin of Palygorsk.<sup>20</sup> Bradley firstly proposed its crystallographic structure in 1940<sup>21</sup> and it was later refined by several authors.<sup>22</sup> The structural model for palygorskite which is mostly accepted today consists in a mixture of two polymorphs: monoclinic and orthorhombic of an ideal composition  $\text{Si}_8(\text{Mg}_2\text{Al}_2)\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4 \cdot 4\text{H}_2\text{O}$ . The palygorskite structure can be described as a pile of layers, each one formed by an octahedral sheet surrounded by two tetrahedral sheets. However, the tetrahedra in each sheet present a periodic inversion of the apical oxygen, resulting in a discontinuous octahedral sheet, or, in other words, the production of structural tunnels of  $6.4 \times 3.7 \text{ \AA}$ . Such clays are therefore crossed by zeolite-like channels which are filled by weakly bound, non-structural (zeolitic) water. Magnesium and aluminium cations complete their coordination with tightly bound water molecules (structural water). Recently, Sánchez del Río *et al.*<sup>23</sup> established that all Yucatán palygorskites present a significant compositional and structural homogeneity, whose 'mean' compositional formula is  $(\text{Si}_{7.96}\text{Al}_{0.07})\text{O}_{20}(\text{Al}_{1.59}\text{Fe}_{0.20}\text{Mg}_{2.25})(\text{OH})_2(\text{H}_2\text{O})_4\text{Ca}_{0.02}\text{Na}_{0.02}\text{K}_{0.04} \cdot 4\text{H}_2\text{O}$ . Differentiating palygorskites from other sources can be done with chemometric analysis using elemental composition data.

## 3. Preparation, color and chemistry of Maya Blue

### 3.1 Preparation recipes

Unfortunately, there is no historical source to describe the ancient recipe of MB. Based on some interpretations of historical documents, Reyes-Valerio<sup>2</sup> made numerous syntheses of stable pigments using leaves of the *Indigofera suffruticosa* plant (which the Mayas called *ch'oo*) and applying some processes that are compatible with the Mayan technology.

Among the vast literature on MB, only a few references describe and analyse samples produced using *Indigofera* leaves.<sup>1,17,24</sup> Today, the preparation of synthetic analogues to MB using synthetic indigo is easy. The three main preparation methods follow those initially proposed by Val Olphen:<sup>8</sup> embedding palygorskite with a solution of indoxyl acetate, vat dyeing, and crushing indigo with powdered palygorskite. The vat dyeing procedure is a 'wet' method where *Indigofera* leaves are soaked in a water suspension of palygorskite and are further submitted to a prolonged aerobic stirring (a process termed *batido*). Alternatively, dry crushing of indigo with palygorskite can be used. In all cases, a heating phase is required after the ingredients have been combined and dried. This phase has a variable duration (from a few minutes<sup>2</sup> to hours or even days<sup>8</sup>) with different temperature ranges (90–100 °C,<sup>2</sup> 190 °C,<sup>25</sup> or even 250–300 °C<sup>7</sup>). The preparation of MB pigments from indigo and sepiolite<sup>8,26–28</sup> has been also reported.

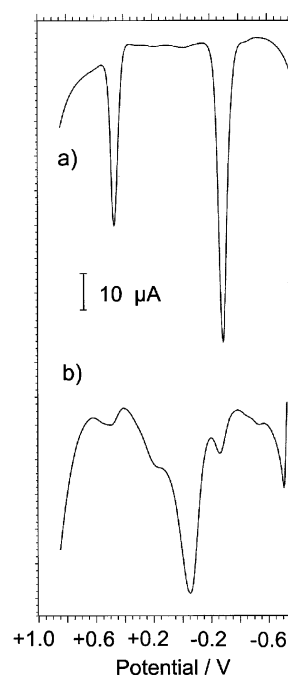
Interestingly, Arnold *et al.*<sup>29</sup> reported that burning copal incense (called *pom* in Yucatec Maya) with palygorskite and indigo was one way by which the ancient Mayas made MB in the context of ritual ceremonies. This possibility has a definite ethno-historical implication: MB would be the result of the ritual combination of three materials (*sak lu'um*, *pom* and *ch'oo*) used for healing and, consequently, the preparation itself and use would be of a high symbolic value.<sup>29</sup>

### 3.2 The hue of Maya Blue

As previously mentioned, the peculiar hue and brightness of the MB pigment has claimed considerable attention. Different hypotheses were first proposed: attribution to a blue mineral form (palygorskite, montmorillonite), and indigo molecules associated with a mineral support. In 1996, José-Yacamán *et al.*<sup>30</sup> proposed the existence of a superlattice in palygorskite crystals forming a periodic feature of 14 Å, about three times the lattice spacing, attributable to the presence of indigo molecules. These authors also reported that iron metal nanoparticles encapsulated in an amorphous silicate substrate exist which are accompanied by iron oxide nanoparticles upon the surface of that substrate. Based of these observations, they suggested that Mie-type light dispersion in nanoparticles could produce the characteristic hue of MB. This hypothesis was further re-assessed, and led to the report of the presence of iron oxide and an amorphous phase of FeO(OH) in authentic MB samples.<sup>31,32</sup>

Subsequent studies reported by Sánchez del Río *et al.*<sup>33,34</sup> neither found iron in a metallic form nor goethite in archaeological MB. In the most recent literature it is commonly accepted that MB coloration is mainly due to the bathochromic shift of the indigo absorption bands as a result of the association of the dye with the inorganic support.<sup>26–28,33,34</sup>

In this context, Doménech *et al.* placed a new piece into the MB puzzle.<sup>35</sup> Application of voltammetry of microparticles approach, a technique developed by Scholz *et al.*,<sup>36</sup> to analyse sparingly soluble, nonconducting solids, supported by visible and infrared spectroscopies and nuclear magnetic resonance data, led to the proposal that dehydroindigo accompanies

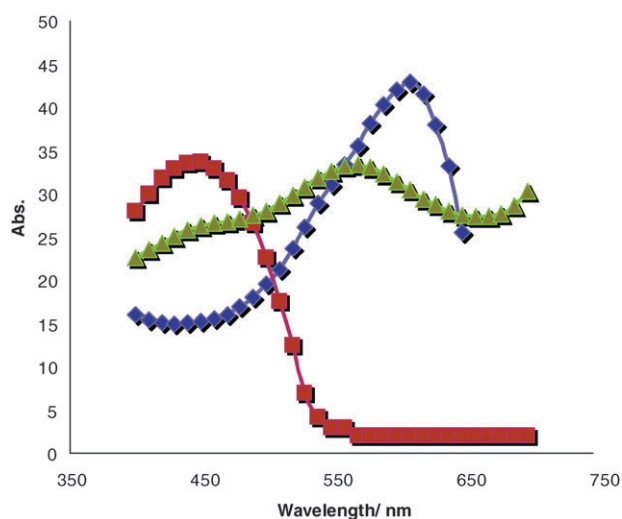


**Fig. 3** Square-wave voltammogram for: (a) indigo microparticles, (b) MB sample from the Substructure II-C in the archaeological site of Calakmul, in contact with 0.50 M acetate buffer, pH 4.85. Potential scan initiated at  $-0.75$  V vs. AgCl/Ag in the positive direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 10 Hz. The sample, dated in the Late Preclassical period, may be the most ancient sample of MB currently detected.<sup>35</sup>

indigo in the palygorskite system and is responsible for the peculiar hue of MB. Fig. 3 shows square-wave voltammograms for indigo microparticles and an MB sample, from the Substructure II-C at the archaeological site of Calakmul, in contact with aqueous acetate buffer. The sample, which dates back to the Late Preclassical period, is the oldest MB sample currently studied.<sup>35</sup> Peaks at  $+0.45$  and  $-0.30$  V vs. AgCl/Ag correspond, to the proton-assisted oxidation of indigo to dehydroindigo and to the reduction of indigo to leucoindigo, respectively. A detailed analysis of such electrochemical processes indicate that: (i) dye molecules firmly attach to the palygorskite matrix, and, (ii) dehydroindigo accompanies indigo in MB.<sup>35,37</sup>

Dehydroindigo, the oxidised form of indigo (see Chart 1) was prepared by Kalb in 1909.<sup>38</sup> The spectral properties of indigo compounds were first studied exhaustively by Klessinger and Luettker in 1963<sup>39</sup> and have been recently revised.<sup>40</sup> With regard to MB it is convenient to note that, in ethanolic solution, indigo yields an absorption band in the visible region of the spectrum with  $\lambda_{\text{max}}$  located at 605 nm, while dehydroindigo produces a unique band with  $\lambda_{\text{max}}$  at 440 nm. The corresponding spectra, superimposed with that of a MB sample from Kulubá, in the Late Classical period are shown in Fig. 4. Clearly, the spectrum of MB can be described in terms of the superposition of absorption bands corresponding to indigo and dehydroindigo, the former showing a bathochromic shift ( $\lambda_{\text{max}}$  ca. 570 nm) attributable to the interaction with the palygorskite framework. Essentially, the idea is





**Fig. 4** Visible spectra for indigo (rhombs), dehydroindigo (squares) and MB sample from Kulubá (triangles). The spectra are vertically translated for clarity.

that the hue of MB can be modulated by varying the dehydroindigo/indigo ratio in the palygorskite. As indicated by the thermochemical parameters for the attachment of indigo, dehydroindigo and leucoindigo to palygorskite,<sup>35,37</sup> the dehydroindigo formation by aerobic oxidation of indigo is favoured by increasing temperature. Therefore, controlling the temperature of the thermal treatment should control the color of MB specimens.

All these approaches outline a view of the MB hue problem where three main factors can be superimposed: (i) shift of indigo absorption bands due to the interaction of indigo guest molecules with the palygorskite host; (ii) light dispersion associated to the eventual presence of iron nanoparticles; and (iii) the presence of dehydroindigo associated to the palygorskite framework. In this line of reasoning, the presence of secondary indigoid products, namely leucoindigo, the reduced form of indigo, in yellow MB samples<sup>41</sup> and indirubin in several greenish-blue MB samples has also been proposed.<sup>17,42</sup>

### 3.3 Ethno-historic and archaeological implications

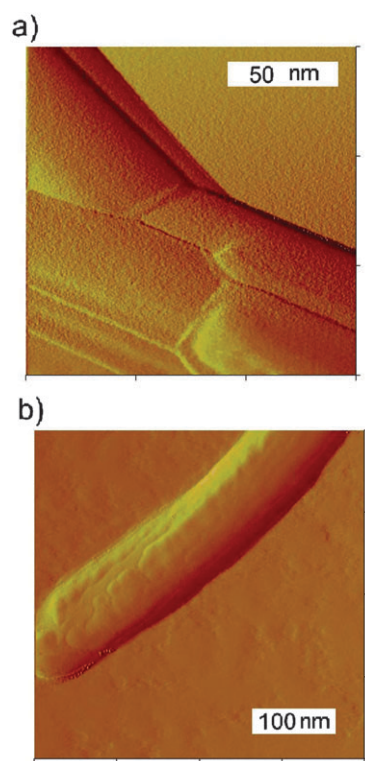
The analysis of archaeological objects may provide information on past technologies, materials used, manufacturing techniques, origin of the materials and, implicitly, peoples' migration as well as trade routes. Therefore the analytical methods play an important role in the study of archaeological materials, and the obtained results may be used to formulate, validate or refute hypothesis about the life of our ancestors. They are also fundamental for the understanding of the degradation mechanisms of art objects, which are of great interest for curators and restorers.<sup>43</sup>

From the ethno-historic point of view, the key question is to elucidate whether the ancient Mayas obtained MB as a result of an inadvertent discovery, if they prepared and used the pigment in a ritual, 'static' way for centuries, or if there was a certain MB 'culture' in which the pigment was a 'technological' material whose preparation and applications underwent modifications and advances.

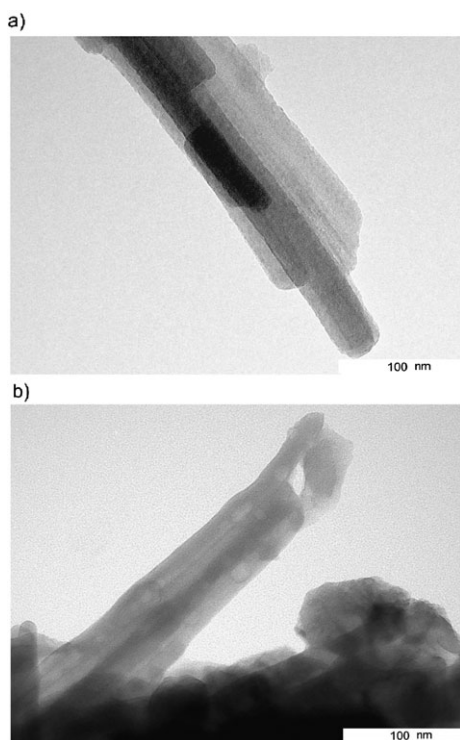
In recent studies, Doménech *et al.*<sup>42,44</sup> compared the electrochemical and spectral responses of a set of samples from 12 different archaeological sites of Yucatán and Campeche using the voltammetry of microparticles approach. The relevant point to emphasise is that electrochemical and spectral data provide complementary information on the chemical composition (dehydroindigo/indigo ratio, in particular), mineralogy and textural properties of MB samples. These results, compared with those obtained for synthetic MB specimens suggest that the 'uniqueness' hypothesis of MB preparation by ancient Mesoamerican civilisations should be seriously questioned. Application of multivariate chemometric methods, in particular the hierarchical cluster analysis, allows the studied samples to be grouped into a few 'electrochemical types' and to establish a series of linkages between different sites which can be rationalised on assuming that:<sup>42,44</sup> (i) different MB preparation procedures were used by the ancient Mayas; (ii) these procedures evolved probably from a primordial procedure involving no thermal (or moderate) treatment to procedures with (more) energy thermal treatments; (iii) ochre and other minerals were used as *in situ* additives to MB to vary the hue of the paint layers; however, such additives were probably used eventually during the crushing/thermal treatment process for preparing several types of MB; (iv) the variation of such MB types over time can be fitted to a ramified scheme, into which new MB types are progressively incorporated, thus suggesting the possibility of establishing a more detailed chronology of certain Maya periods.

Transmission electron microscopy (TEM) and atomic force microscopy (AFM) examination of genuine MB samples support the foregoing set of considerations. Fig. 5(a) and 6(a) depict pristine palygorskite showing elongated 0.5–1  $\mu\text{m}$ -sized crystals with fine 30–60 nm-spaced fibre structures. Several MB samples consist of irregularly shaped palygorskite crystals divided into almost square domains of irregular texture, as shown in the AFM image of Fig. 5(b). The TEM images of the MB samples vary significantly; irregular-shaped palygorskite crystals are observed in many cases, while the crystals exhibit a dense array of fine 2–5 nm-sized pores covering the surface of the crystals in others and, in several cases, 10–20 nm-sized pores are irregularly distributed on the surface of the palygorskite crystals (see Fig. 6(b)). Since such pores can unambiguously be attributed to the segregation and evacuation of physisorbed and zeolitic water, the differences in their shape, size and distribution on the surface of palygorskite crystals is indicative of the use of different MB preparation procedures, and can be correlated with the observed variation of electrochemical parameters.<sup>44</sup>

With a radical reading of these results, one can draw a picture in which the ancient Mayas successively anticipated some of the modern chemistry methods; namely: solid-to-solid reaction and hybrid organic–inorganic synthesis, thermal control of chemical processes and coupled physico-chemical properties; as well as the possible use of reactivity-modulating additives or, *sensu lato*, catalysts, whose successive development over time allows to speak, to some extent, of 'technological revolutions' within the Mayas' culture.<sup>44</sup>



**Fig. 5** AFM images for: (a) pristine palygorskite crystals from Sacalum and (b) an MB sample from Mayapán.



**Fig. 6** Micrographs obtained by TEM for: (a) pristine palygorskite from Sacalum (12000 $\times$  magnification) and (b) MB sample from D'zula (15000 $\times$  magnification).

Obviously, this does not mean that the ancient Mayas developed a technology based on a rational formulation and

design of materials and processes; *i.e.*, a 'Maya chemistry'; nor does it mean that the ancient Mayas developed a technology in the currently accepted sense. However, the possible variability in the preparation of MB could be indicative of the existence of a certain degree of 'research' and its concomitant cultural patterns: innovation, competence between local workshops, *etc.* Therefore, MB could be viewed not only as an important component of rituals but also as a (pre)technological product. While further studies into more representative MB samples is needed to properly establish a complete scene for MB in the Maya culture, the above methodology can, in principle, be used to establish a reliable chronology of Mayan sites and to also define commercial and cultural relationships between different centres, *etc.*

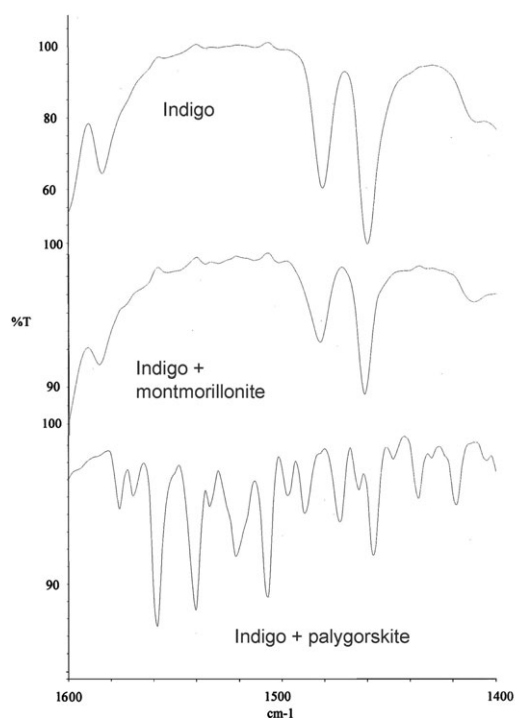
From the archaeological, historic and ethnographic viewpoints, the existence of such technological evolution in MB suggests that the 'static' view of Maya civilization as an exclusively tradition-based culture needs to be revised. While the development of (scientific-technological?) advances on MB technology does not imply a radical change in the essential patterns of the Mayas' culture, nonetheless, such advances suggest that a more complex view of this ancient civilisation is needed.

### 3.4 The nature of the palygorskite–indigo association

The nature of the indigo–palygorskite association has been the centre of considerable research in recent years. Proposed models include formation of hydrogen bonds between the carbonyl and amino groups of indigo with edge silanol units of the clay,<sup>26</sup> formation of hydrogen bonds between the C=O and N–H groups of indigo molecules and structural water molecules,<sup>45</sup> and the hydrogen bonds between indigo carbonyl and structural water.<sup>46</sup> More recently, bonding between cationic aluminium and dye molecules,<sup>47</sup> and indigo adsorption in the grooves which cover the faces of the palygorskite fibres,<sup>48</sup> have been proposed. This last hypothesis, however, has been contradicted by experimental data on sepiolite–indigo specimens.<sup>49</sup>

It should be noted that the proposed models, in general, assume that the loss of physisorbed and zeolitic water from the palygorskite matrix is an essential condition for MB formation, thus requiring a heating process. However, a total loss of zeolitic water occurs at temperatures higher than the temperature required to stabilize palygorskite–indigo powder. Therefore, the palygorskite channels are not completely evacuated from zeolitic water in MB.

It is generally acknowledged that hydrogen bonding is required for MB formation. However, discrepancy exists between the computational methods applied to the refinement of the indigo–palygorskite structure, which indicate that structural water is associated only with carbonyl groups of indigo,<sup>45</sup> and molecular modeling coupled to spectroscopic data, suggesting that both C=O and N–H indigo groups are involved in hydrogen bond formation with structural water.<sup>45</sup> In this context, the electrochemical data indicate that the oxidation of indigo to dehydroindigo in the palygorskite framework implies the release of two molecules of water per molecule of indigo.<sup>37</sup> As pointed out by Fois *et al.*,<sup>46</sup> apart



**Fig. 7** ATR-FTIR spectra of indigo, indigo-montmorillonite, and indigo-palygorskite, specimens in the 1400 to 1600  $\text{cm}^{-1}$  region.

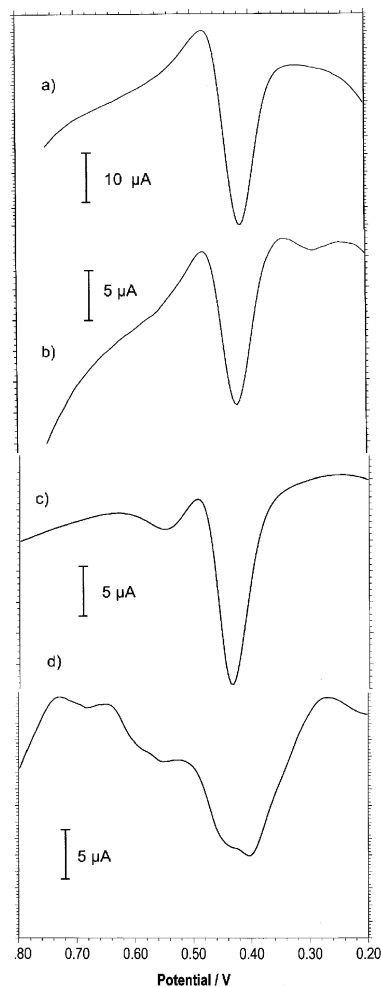
from hydrogen bonding, the van der Waals interactions and a direct interaction between indigo and clay octahedral cations, not mediated by structural water, could also play an important role in anchoring indigo molecules, as suggested by the thermochemical data.<sup>35,37</sup>

In this context, the most recent electrochemical and spectroscopic data suggest that different topological redox isomers, *i.e.*, dye molecules located in different sites of the palygorskite framework, can be discerned.<sup>50,51</sup> An illustration of this possibility is presented in Fig. 7, where the ATR-FTIR spectra of indigo is compared with those of the MB-like specimens prepared by crushing indigo with montmorillonite and palygorskite and heating in a furnace at 180 °C for 24 h. Spectra are confined to the region between 1400 and 1600  $\text{cm}^{-1}$ , where only dye bands which are not interfered by the clay bands are recorded. We may see that the absorption bands are essentially the same for both the pristine dye and the montmorillonite specimen. In contrast, the number of indigo bands increase as a result of the association of dye with palygorskite. The complicated, multiple-band spectra recorded for the MB-like specimens prepared from indigo and palygorskite clearly suggests the presence of different topological isomers of indigo, and possibly, of other indigoid molecules attached to different sites in the palygorskite matrix.

Similarly, the voltammetric response of indigo-palygorskite specimens in the region of potentials in which the oxidation of indigo to dehydroindigo occurs, exhibit a significant peak splitting of those samples heated at 130–180 °C. Fig. 8 shows that this peak splitting, attributable to the co-existence of different topological redox isomers in the indigo-palygorskite association, is entirely absent for both indigo and specimens prepared by crushing indigo with montmorillonite, a laminar

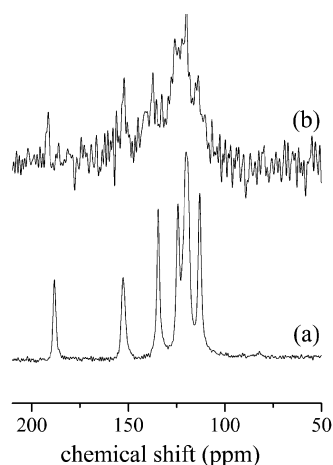
clay in which the indigo-silicate association is restricted to 'external' adsorption of dye molecules onto the clay. This response remains unchanged for indigo-palygorskite specimens treated at temperatures between 130 and 150 °C for 24 h. As previously noted, the heating process for the indigo-palygorskite specimens determines the appearance of voltammetric peak splitting.

All these results, consistent with those obtained with Vis/UV spectroscopy and solid-state multinuclear magnetic resonance ( $^1\text{H}$ - $^{13}\text{C}$  CP MAS,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ), described in detail elsewhere,<sup>51</sup> clearly suggest that the 'uniqueness' paradigm related to the indigo-palygorskite association should be revised, as suggested, in particular, by  $^1\text{H}$ - $^{13}\text{C}$  CP MAS NMR data. Fig. 9 shows the  $^{13}\text{C}$  CP MAS NMR spectra of indigo dye, pure and incorporated into the palygorskite clay. Main resonances of indigo molecule are observed in both spectra (the signal/noise ratio in spectrum (b) is very low because of the small amount of indigo). The resonances attributed to the carbon of the carbonyl group (188 ppm), as well as the signals between 135 and 120 ppm are modified as



**Fig. 8** Deconvolution of square-wave voltammograms for: (a) indigo, (b) indigo-montmorillonite after thermal treatment at 130 °C during 24 h, (c) indigo-palygorskite, (d) indigo-palygorskite after thermal treatment at 130 °C during 24 h. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.





**Fig. 9**  $^{13}\text{C}$  CP MAS NMR spectra of indigo dye (a) and indigo dye hosted into palygorskite clay (b). Due to the very small content of indigo in the Maya Blue sample, 60 000 scans were collected for the latter spectrum.

the dye is incorporated in the clay. These signals are assigned to the carbon between the carbonyl and amine (124 ppm) and carbons of the benzene ring (113, 134, 120 ppm). The significant differences of these signals, concerning position, width and intensity, suggest changes in the chemical environment of these carbons if dye is hosted into clay. Particularly, it seems that the relaxation process changes if the dye is incorporated in the inorganic matrix. This result confirms several host–guest interactions in the Maya Blue complex. A multinuclear solid-state NMR study has been performed and results will be discussed in detail elsewhere.<sup>51</sup> All these data suggest that the ‘uniqueness’ paradigm should probably be replaced by a more complex view of this system where different dyes and different topological isomers are distributed in the palygorskite framework, thus defining a polyfunctional hybrid material.

#### 4. Conclusions

Examination of available electrochemical, microscopic and spectroscopic data on genuine MB samples and synthetic MB-type specimens prepared from indigo and palygorskite, sepiolite and other clays, suggest that the implicit ‘uniqueness’ paradigm should be revised. MB then appears as a complex, nanostructured hybrid organic–inorganic material, where dehydroindigo, and probably other minority dyes accompanying indigo, are all guest molecules which are distributed in different sites in the host palygorskite framework.

Further, it is conceivable that different types of interactions (hydrogen bonding with carbonyl and/or amine groups, direct bonding with metal ions, etc.) are present in the MB structure. As the physico-chemical properties of the topological isomers may be significantly different, the properties of the material could be modulated by varying the proportion of the different isomers, which, in turn results from the application of different synthetic strategies, particularly thermal treatments. In that sense, MB could be viewed as a polyfunctional hybrid material to a certain extent, a view which can appear potentially interesting in terms of the development of new polyfunctional hybrid materials.

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