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Pre-columbian nanotechnology: reconciling the mysteries of the maya blue pigment*

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Received: 6 October 2006/Accepted: 11 December 2006

Published online: 31 October 2007 • © J. Paul Getty Trust 2007

ABSTRACT The ancient Maya combined skills in organic chemistry and mineralogy to create an important technology – the first permanent organic pigment. The unique color and stability of Maya Blue can be explained by a new model where indigo dye fills the grooves present at the surface of palygorskite clay, forming a hydrogen bonded organic/inorganic complex. Existing theory assumes the dye is dispersed inside the channels of an opaque mineral. Based on data from thermal analysis, synchrotron and neutron diffraction, ESEM and chemical modelling calculations, our new concept of Maya Blue structure resolves this contradiction and suggests some novel possibilities for more durable, environmentally benign pigments.

PACS 61.66-f; 62.23.St; 61.66.Fn; 61.66.Hq

1 Introduction

The composition of Maya Blue has confounded researchers for decades. How could the bright turquoise hue and extreme stability of this hybrid organic/inorganic pigment be explained? How did the Maya combine skills in organic chemistry and mineralogy to create an important technology – the first permanent organic pigment – by binding indigo dye to a clay mineral substrate? Maya blue was first produced by the Mayas about the 8th century AD and extended well into the Spanish colonial era before the technology was lost [1]. Due to its attractive turquoise colour and light fastness, Maya blue was widely used in mural paintings, ceramics, codices [2]. Maya blue is extremely stable: it can resist the attack of concentrated nitric acid, alkali and organic solvents without losing its colour [3]. In the famous wall paintings at Bonampak and Cacaxtla, Maya blue has displayed remarkable durability over hundreds of years of exposure under humid conditions (Fig. 1).


Over the past 50 years, analytical advances have provided the pieces to the puzzle of Maya Blue. X-ray powder

diffraction (XRPD) demonstrated the presence of the clay mineral palygorskite. Later, indigo was identified [4–6] and confirmed with infrared spectroscopy [5, 7, 8, 10]. Maya blue is a complex formed between palygorskite (or sepiolite) clay and indigo dye obtained from the common plant *Indigofera suffruticosa*. However, a simple mixture of palygorskite and indigo is not resistant to chemical attack. Eventually the recipe was rediscovered: the dye/clay mixture requires heating to 100 °C to produce Maya Blue [2, 6, 9].

Although the pieces of the puzzle – indigo and palygorskite clay – had been identified, researchers have struggled since to explain how they fit together to create a material with such remarkable properties. Photoluminescence spectroscopy¹ showed how the experimental spectra of Maya Blue could be obtained by superposing those of the clay and indigo. Molecular modelling calculations on Maya blue were carried out [11–13], demonstrating that no impediment existed for indigo to be inserted in interior channels, which run the whole length of the clay fibres. Transmission electron microscopy (TEM) analysis suggested that nanoscale Fe, Ti and Mn impurities discovered in Maya Blue samples may influence its appearance [14]. Chiari et al. [11] refined the crystal structure of palygorskite and Maya blue using synchrotron radiation XRPD and found that the indigo molecules located in the channels were highly disordered. Neutron diffraction on Maya blue prepared with deuterated indigo [15, 16] positioned without ambiguity indigo inside the clay channels. The six-fold disorder of the indigo molecule postulated in the synchrotron diffraction study was confirmed by the occupancy factor of the deuterium atoms [17].

2 Experimental results

The crystal structure of palygorskite containing indigo as refined by Chiari et al. [11] shows that an indigo molecule occupies three unit cells along the channel (Fig. 2). In order for the indigo molecules to fill the channels, it is first necessary for the zeolitic water to be removed. Once a dye molecule enters the channel, it forms two hydrogen bonds with the clay framework, which have to be simultaneously broken for the molecule to move one step further in. Only

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*This study is dedicated to our mentor and friend Constantino Reyes-Valerio, who, with his expertise, dedication and enthusiasm was able to instill in all of us the desire to study what was one of his life loves: Maya Blue. None of our studies could have been possible without the tremendous contribution of Constantino. We thank him deeply.

¹ D. Ajò, M. Favaro, C. Reyes-Valerio, G. Chiari, R. Giustetto, presented at the ARCHEOMETRY 2000, 32nd Int. Symp. on Archeometry, Mexico City, 2000 (unpublished).



FIGURE 1 Use of Maya blue pigment in the famous wall paintings at Cacaxtla, Mexico

after three steps of this unlikely process can a second dye molecule enter the same channel. Thus, one can infer that indigo fills only the very first part of the channels, on the (001) face (Fig. 2).

XRPD data indicate that indigo's abundance is very limited (between 1 and 2%). In spite of this, the colour imparted to Maya blue is bright, which is difficult to explain if the chromophore-containing molecule is dispersed inside the channels of an opaque mineral [7, 12, 18, 19]. In addition, direct imaging of the Maya blue pigment shows that the micron-scale fibres of palygorskite are actually made-up

of high surface-area bundles of smaller micro-fibres at the 10–100 nm scale (Fig. 3). This indicates a much higher surface to volume ratio than initially expected for palygorskite (fewer interior channels and more exterior grooves).

Thermal gravimetric analysis was used to study the dehydration of palygorskite and Maya blue. The main thermogravimetric features of palygorskite are caused by water evolution. The important steps are:

1. free pore water and water adsorbed on surfaces evolved below approximately 120 °C;
2. zeolitic (coordinated) water removed over the range of 120–300 °C; and
3. structural water removed at even higher temperatures. These ranges differ somewhat between authors and there is considerable overlap [20, 21].

The weight loss in the first step (free pore water, ending at ~ 120 °C) is much higher for palygorskite than for Maya blue (6.3% and 3.2% respectively). This is compatible with a layer of indigo covering the external surface.

In the second weight loss step, the zeolitic water completely leaves the channels at a temperature which is lower for palygorskite (230 °C) than for Maya blue (280 °C), but the weight loss is nearly the same (4% for palygorskite vs. 4.2% for Maya blue) (Fig. 4).

Chemical modeling calculations [11], showed that the adsorption of indigo on dehydrated palygorskite is exothermic, with adsorption enthalpy of –37 kJ/mol per indigo molecule. In contrast, the adsorption of indigo on hydrated palygorskite is strongly endothermic (152 kJ/mol per molecule), i.e. the

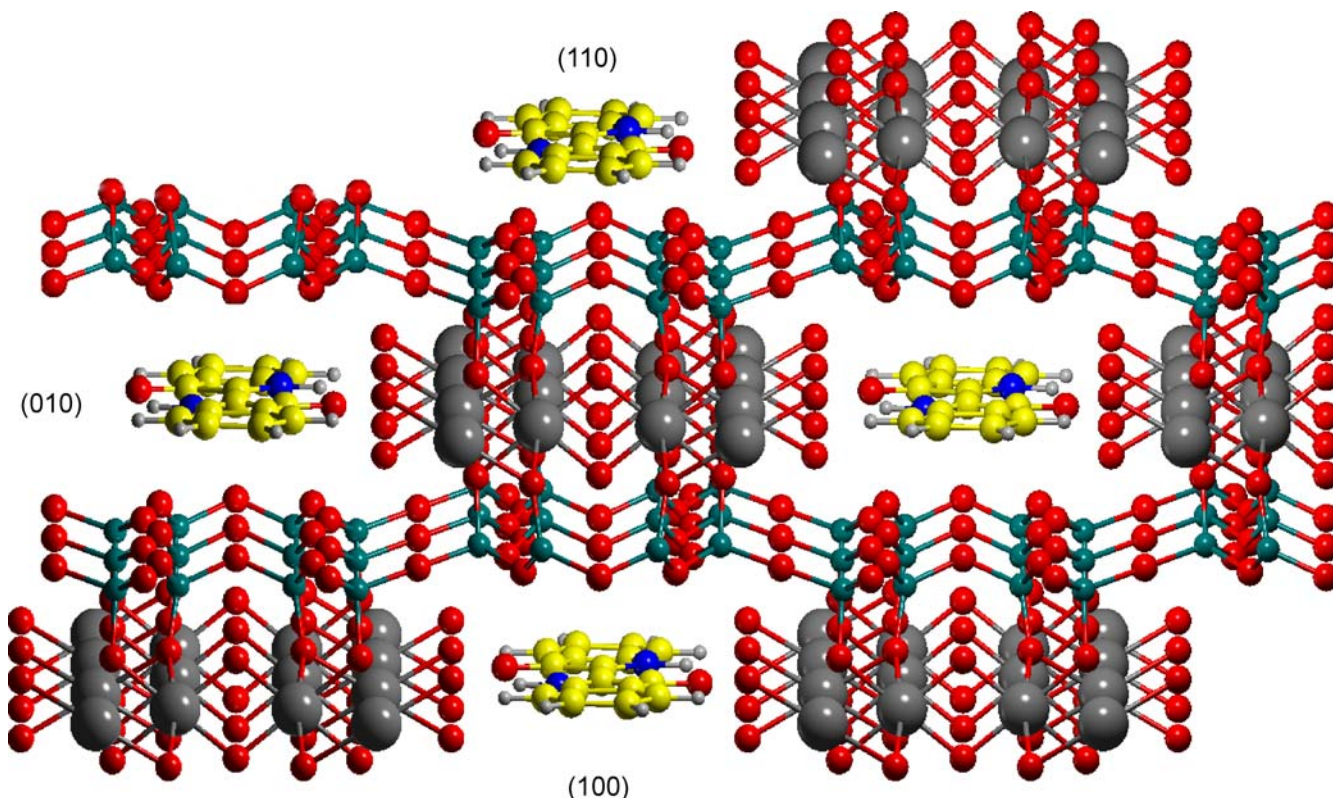


FIGURE 2 Structure of Maya Blue projected on the (001) face of palygorskite. Note indigo (yellow) occupying both channels and grooves (H = White; C = Yellow; N = Blue; O = Red; Si = LightBlue; Mg = Gray)