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Maya Blue, an Ancient Guest–Host Pigment: Synthesis and Models

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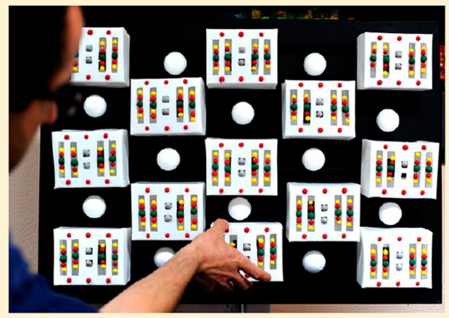
Supporting Information

ABSTRACT: The blue of the ancient Maya civilization, Maya blue (MB), can be an excellent example for the introduction of composite materials at high school or at first-year college levels. In addition to the synthesis of MB, made according to an old recipe, a simple model of beads and LEDs has been developed mimicking this organic–inorganic hybrid (a mixture of the organic dye indigo with a clay: palygorskite). This allows teaching–learning activities where the instructor can (i) explore the rich history of MB (including that of indigo); (ii) perform the synthesis of MB in the lab; (iii) reveal the remarkable stability of MB; and finally (iv) lead the student to understand the interactions between indigo individual molecules and the clay host in MB using an imaginative and simple model.



KEYWORDS: *General Public, First-Year Undergraduate/General, High School/Introductory Chemistry, Interdisciplinary/Multidisciplinary, Laboratory Instruction, Hands-On Learning/Manipulatives, Dyes/Pigments, Nanotechnology, Solid State Chemistry*

Color is an amazing topic to engage students into scientific literacy. The discussion of this topic embraces innumerous possibilities, ranging from artistic to physical and chemical points of view. Maya blue (MB) and its history (including the mythic indigo, responsible for the color of MB) can attract students with a wide spectrum of interests. Consideration of the production, structure, and history behind Maya blue, and in general of other ancient dyes,[1−3] is an excellent starting point for the introduction of composite materials at a high school or first-year college level.

Indigo, known for more than 5000 years, is one of the oldest sources of blue color.[4] First extracted from *Indigofera* (with more than 700 extant species), its synthesis is in the genesis of the modern chemical industry recognized with the 1905 Nobel Prize in Chemistry to Ludwig von Baeyer.[5,6] Maya blue was the blue pigment used by the Maya civilization, still present in mural paintings, sculptures, and other objects in Chichen Itza and Yucatan (Mexico). This organic–inorganic hybrid was historically obtained by mixing indigo from *Indigofera suffruticosa* leaves with clays available in the Yucatan Peninsula.[7−9] The clay most commonly associated with MB is palygorskite, a colorless mineral clay with a layered structure made of two silicate tetrahedral sheets linked by an octahedral metal sheet.[7,10] However, sepiolite or mixtures of the two clays have also been reported to be used. Both palygorskite and sepiolite consist of hydrated magnesium aluminum silicates; the latter has nearly the same physical properties of the former but presents a higher magnesium, aluminum, and iron content and has a slightly larger unit cell size.

The precise structure of MB, particularly in regard to the species involved in this hybrid, together with the type of interactions established between indigo and the clay host, is still a subject of current dispute.[7,8,11] Nonetheless, its rediscovery (in particular the search for a recipe that allows production of the original MB) has promoted the synthesis of new organic–inorganic MB-based hybrid materials making use of fibrous clays and organic pigments.[12−20] Particularly amazing is the stability shown by MB toward acid and alkali attacks, a fact that by itself introduces a new topic in a classroom: stabilization of natural pigments through composite materials, where MB can be considered a precursor of modern nanocomposite materials.[7]

In the current activity the student is first led to synthesize MB, according to what was (presumably, as there are no historical texts available) the recipe[21] used by this ancient civilization. This is then followed by the construction of a model of beads and LEDs where the molecular dimensions of MB and indigo are equated, therefore establishing a multidisciplinary interaction between different fields (material science, chemistry, and mineralogy) and, more specifically, of composite materials and their importance to the stabilization of natural organic pigments.

■ STRUCTURE OF PALYGORSKITE AND MAYA BLUE

The structure of palygorskite together with the implemented model (with the corresponding match of the beads to the atoms of the clay structure) is presented in Figure 1. The computer model of the structure shows both the structure of palygorskite and the relative molecular dimensions of this to that of indigo. Palygorskite can be constructed from the American Mineralogist Crystal Structure database[22] in this case from the coordinates given by Chiari et al.[23] and with a freeware molecular graphics software (for example the VMD;[24] alternative used programs were Crystal Maker for Windows

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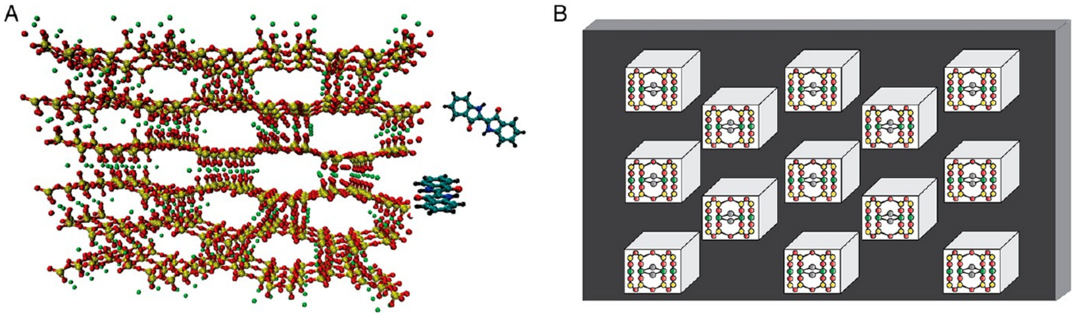

Figure 1. (A) Structure of palygorskite obtained from crystal data and VMD program (without water in the channels). Along with the structure of palygorskite one can find the molecular structure of indigo. The version of indigo is in the same scale as that of the palygorskite. (B) Model made with corrugated plastic. Thirteen palygorskite unit structures are shown. Color labels: green is either Al or Mg; red is O; yellow is Si; and gray is the terminal hydroxide.

version 2.3.2 and MOLDRAW). The structure of indigo was obtained from ChemSpider and then imported to MarvinView[25] and saved in *xyz* coordinates that were further imported to VMD (or Crystal Maker). In the resulting structure (Figure 1), the zeolitic waters are omitted for clarity purposes, but can be easily added with the (VMD) program or with table tennis balls in the bead and LED model. The VMD program facilitates the construction of the overall clay from the basic unit cell together with indigo (with molecular scale dimensions). In this way a clear visualization of the interaction between the host palygorskite and the guest indigo can be displayed (Figure 1).

In both situations (computer model and bead model), the student can visualize the presence of large channels.[26] The student is also led to the observation that the clay channels may accommodate either water (in the case of the clay host with no dye) or indigo (in the case of MB) and that some of the water must be removed (this fact is linked to the recipe by the removal of water from the zeolitic channels at temperature of 190 °C) so that indigo can interact more strongly with the clay's channels. Both models (computer and bead) also allow the visualization that the dye can only penetrate into the clay channels if perpendicular to the canvas or paper plane (vide supra). This is due to the dimensions of the empty channels, defined by a rectangular geometry with length × width of 10.6 × 3.7 Å for sepiolite versus 6.4 × 3.7 Å for palygorskite, and of 4.8 × 12.3 Å for indigo.

Moreover, the exact location of indigo in Maya blue is still a subject of debate; namely, (i) is the dye found inside the cavities or outside the pores, forming a kind of shell, or (ii) is it found in other "molecular" possibilities or environments.[27−29] Moreover, the instructor can further explore the type of interactions of indigo with the clay, which involves hydrogen bonding of the carbonyl indigo groups with the clay silanol units or structural waters; although possible, no strong indigo−structural water bonds, N−H···O, have been detected.[30,31] Indeed, it should be discussed that, even if feebler, these interacting waters are not the zeolitic ones (which are removed in the heating process), but those bonded to the magnesium, aluminum, and silanol units of the clay.

This aspect (zeolitic waters exchange with indigo) can be further explored aiming at a better illustration of the Maya blue structure. In Figure 1 the channel structure of palygorskite forms a checkerboard (or chessboard) pattern. The "empty squares" of the chessboard have water molecules; these are the structural waters that are connected to the aluminum and magnesium of the clay. These aspects are further explored in the Supporting Information (Part IV, Other computational views of Maya blue, and Part V, Using the Beads and LEDs Maya blue model).

■ ACTIVITY

Detailed instructor notes and lesson plan recommendations with schematic drawings are available in the Supporting Information. The total time of the activity is two lessons of 2−3 h each.

Synthesis of Maya Blue

MB was easily and effectively produced in the laboratory using simple and accessible materials and equipment. The synthesis of MB was based on the procedure proposed elsewhere.[21] The experimental synthetic procedure leading to MB consisted in the mixture of 2 g of clay (palygorskite or sepiolite) with 0.04 g of indigo in 50 mL of water, which led to a 2% mixture (w/w) of indigo/clay. The mixture was then stirred for ≈1 h, vacuum-filtered, and further heated for 5 h at 190 °C. The obtained solid was rinsed with ~50 mL of distilled water and ~25 mL of acetone until no trace of dye (the presence of the dye was followed by the absorption spectra) was found in the washing solvent. Indigo is insoluble in water and (modestly) soluble in acetone. Acetone was used to dissolve and remove the dye molecules that are not bonded to the clay, whereas water was additionally used to assist this procedure and to remove acetone that cannot be left, even if residual, for the acid attack (the mixture acetone:nitric acid can be explosive). The water wash was continued until the litmus paper was neutral and was disposed of before washing with acetone. The mixture was again vacuum-filtered. The final step consisted of the acid attack (with concentrated nitric acid), followed by rinsing again with distilled water and acetone until no traces of indigo were found in the washing solvent(s). The obtained pigment was then left to dry at room temperature. This procedure is schematically presented in the Supporting Information (Synthesis of MB Scheme). It is also worth noting that, in the original recipe used by the Mayans, the acid attack was not performed, so it is likely that "free" indigo may also be present in the pigment used by this civilization.[32] The obtained MB solid together with the (initial) palygorskite clay is shown in Figure 2.

LEDs and Beads Model Construction Details

To create the structural units of palygorskite and sepiolite, four colors of modeling clay were needed to make the beads (Staedtler FIMO modeling material was used and baked according to the instructions of the manufacturer). Green was chosen to represent the aluminum and magnesium metal atoms in palygorskite and sepiolite, red for the oxygen atoms, yellow

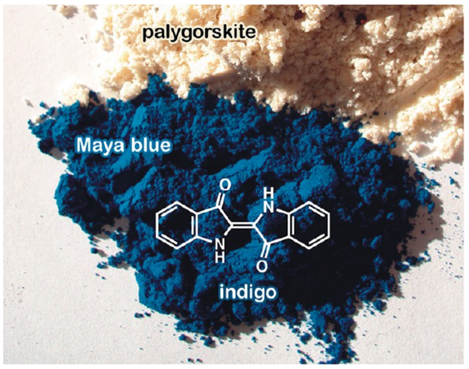

Figure 2. The synthesized MB together with the palygorskite clay. The structure of indigo is also shown.

for the silicon atoms, and gray for the terminal hydroxides. For each palygorskite unit structure, 8 yellow, 4 green, 2 gray, and 14 red beads were used; for sepiolite, 12 yellow, 6 green, 4 gray, and 22 red beads were used. Note that it was necessary to make holes in the beads prior to baking. To do this, wires were used and removed before baking (Figure 3).

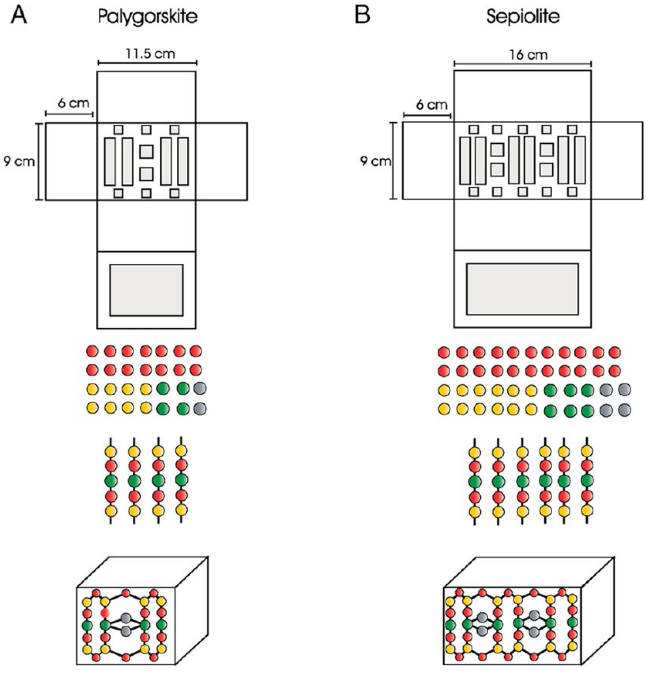

Figure 3. Construction of the (A) palygorskite and (B) sepiolite units. Color labels: green is either Al or Mg; red is O; yellow is Si; and gray is the terminal hydroxide.

The basic structures of the units consist of white corrugated plastic boxes with 11.5 × 6 × 9 cm for palygorskite and 16 × 6 × 9 cm for sepiolite; these dimensions were chosen to represent the proportions of real molecular dimensions (1 Å ≈ 2 cm). These boxes were further trimmed in the back to accommodate the LEDs and in the front to accommodate the beads. After assembly of the holed beads with the wires, the latter were glued to the back of the corrugated plastic boxes, and the remaining beads were glued to the other trimmed spaces accordingly. The bonds to the top (or backbone) oxygens and terminal hydroxides can be drawn using a permanent marker (Figure 3).

The system was then assembled by attaching the palygorskite unit structures (boxes) to a 70 × 50 cm black-painted canvas using hook-and-loop strips and placing the LEDs into their positions in the back of the canvas (Figure 4). To ensure that

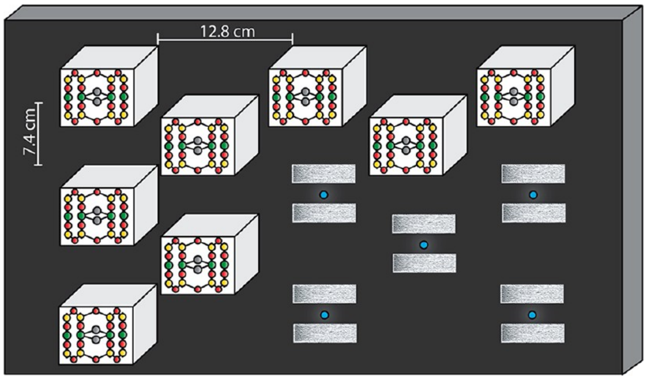

Figure 4. Model for palygorskite displaying the LEDs and hook-and-loop strips to attach the unit boxes.

the structures are placed correctly place markers should be drawn in the canvas. White LED holiday lights covered with transparent blue cellophane were used, which can be switched on when the indigo is inserted into the channels. This option added the representation of the color change upon interaction (incorporation) of the dye within the clay (Figure 5). Also in our model, indigo, which was made of blue pipe cleaners (chenille stems) at a scale of 24.6 × 9.6 cm, was used to illustrate the interaction with the clay when inserting these “dye molecules” into the existing holes after removing the water molecules (table tennis balls). Both indigo and water “molecules” were attached to the canvas with the help of hook-and-loop strips. The fact that indigo molecules can be found both inside the clay channels and in the grooves (the top and lateral “holes”) was is also taken into account by this model.

Illustrating the Differences between Palygorskite and Sepiolite

The differences between the host matrixes can be illustrated by replacing the palygorskite unit boxes with the constructed sepiolite unit structures. The unit (plastic) boxes of palygorskite were easily removed from the canvas and replaced by those of sepiolite (Figure 6). The size (dimensions) of the cavity was larger (21.2 × 7.4 cm) than that of palygorskite, thus showing that the interaction of this clay with indigo was different, therefore allowing equilibrium with the external environment, which further accounted for the lower stability of this hybrid toward acid, alkaline, or organic solvent attack. This stability toward acid attack is experimentally described in the Supporting Information (see Part VI).

■ HAZARDS

If the activity is conducted with the necessary precautions, it offers no particular hazards. However, it is important to stress that indigo (CAS #482-89-3) may cause irritation of the skin and mucous membranes. Acetone (CAS #67-64-1) is a highly flammable liquid and is irritating to eyes. Repeated exposure may cause skin dryness or cracking; vapors may cause drowsiness and dizziness. Nitric acid (70%; CAS #7697-37-2) and sulfuric acid (95−98%; CAS #7664-93-9), both used in the acid attack of MB, are highly corrosive reagents and may be

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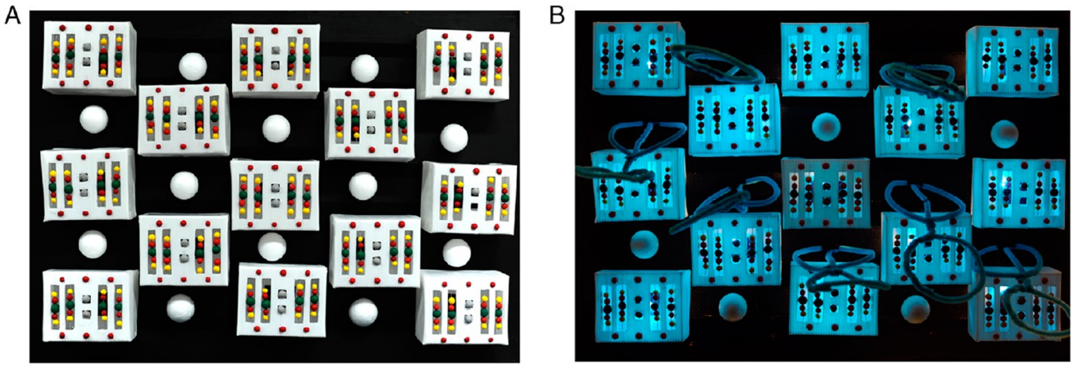

Figure 5. Photos of the model of beads and LEDs for (A) palygorskite with water (represented by table tennis balls) and (B) with indigo (represented by blue pipe cleaners) illuminated with LEDs.

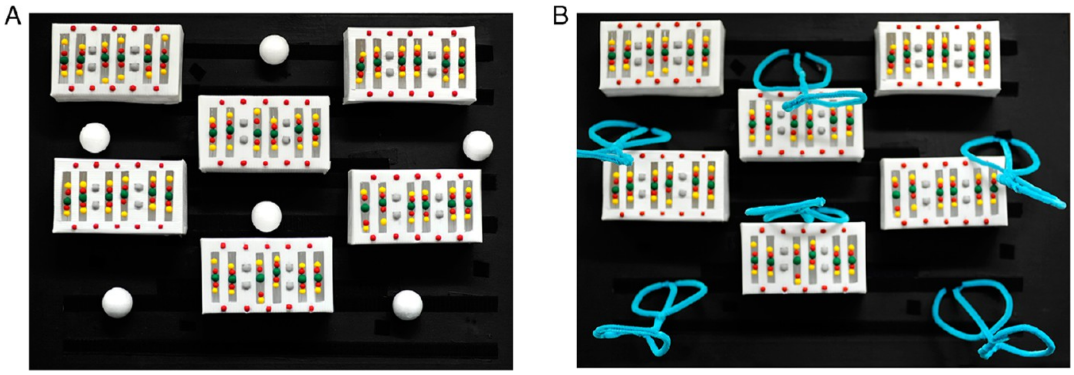

Figure 6. Photos of the model of beads and LEDs for sepiolite with (A) water (represented by table tennis balls) and (B) with indigo (represented by blue pipe cleaners). In this figure, LEDs illuminating the overall structure are not shown.

fatal by ingestion, inhalation, or skin absorption. Their use should be made in a laboratory hood with appropriate gloves.

Palygorskite (CAS #12174-11-7) is a hydrous magnesium aluminum silicate dust, which may irritate eyes and skin; it aggravates pre-existing health conditions, such as asthma; repeated inhalation over extended periods of time may result in lung injury. Sepiolite (CAS #63800-37-3) is a hydrated magnesium aluminum silicate with magnesium partially replaced by aluminum or, to a lesser extent, iron (Fe^{2+}, Fe^{3+}); inhaled dust may contain silica or crystalline quartz (CAS #14808-60-7). With clays, safety glasses or eye protection, in combination with breathing protection and protective gloves, should be used.

■ SUMMARY

The model here presented allows effective pedagogical demonstrations of several important aspects related to organic–inorganic hybrid MB: (i) the history of dyes (with the rich history of indigo); (ii) its production by Maya civilization; (iii) its structure; and (iv) demonstrations of the interactions between indigo molecules and the clay host, applying a self-constructed model of LEDs and beads developed by the student. Another benefit of this model worth mentioning is the utility of discussing MB from an interdisciplinary point of view: artistically (i.e., origin of the colors and dyes) and considering the science of materials and chemistry.

■ ASSOCIATED CONTENT

Supporting Information

Detailed instructor notes and lesson plan recommendations; activity handout. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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