

Spectroscopic characterization of a sepiolite-based Maya Blue pigment

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ABSTRACT - Maya Blue, an ancient pigment used by Mayas in Mesoamerica, can be considered an ancestor of modern nano-composites as it forms by grinding and heating the guest indigo molecule with a hosting clay framework (palygorskite or sepiolite). Specific bonds form between the guest dye and the hosting matrix, conferring the pigment an exceptional stability to both acid and alkali attacks. While most works have been focused on the study of the palygorskite/indigo complex, this project is aimed to unveil the structural features of Maya Blue when sepiolite is the hosting framework. A freshly-synthesized sepiolite-based Maya Blue was prepared accordingly to ancient Mayas recipes and investigated with various spectroscopic techniques (Uv-visible, FTIR, Raman). All evidences show that by strongly crushing and heating (190°C in air or 150°C in vacuum) the sepiolite + indigo (2 wt%) composite, the dye aggregates dissociate to monomers favouring diffusion inside the clay tunnels emptied from loosely bound zeolitic H₂O. Once encapsulated indigo partly decomposes to dehydroindigo, its oxidized form, whose flexible molecule can easily diffuse inside the tunnels slightly changing the pigment colour (from deep blue to blue/green). Applied heating, however, does not cause loss of Mg-coordinated OH₂ which forms H-bonds with the indigo reactive groups (C=O and N-H) after encapsulation, thus stabilizing the

composite. Spectroscopic evidences supporting presence of H-bonds are less evident in sepiolite-based rather than in palygorskite-based composites with indigo. In fact while indigo is perfectly juxtaposed in the narrower tunnels of palygorskite (6.4 x 3.7 Å), receiving H-bonds on both sides of the molecule, in the wider tunnels of sepiolite (10.6 x 3.7 Å) its molecule has to get near to one border in order to form a single bond. In a sepiolite-based Maya Blue pigment the global number of possible host/guest interactions is therefore dramatically halved with respect to a palygorskite-based one, inevitably reducing resistance to chemical attacks. Consequently, the extent of Maya Blue renowned stability is directly related to the composition of its main clay constituents.

RIASSUNTO - Il Blu Maya, un antico pigmento utilizzato dai Maya nell'America centrale, può essere considerato un antesignano dei moderni composti d'inclusione, prodotto della macinazione e riscaldamento dell'indaco con un minerale argilloso (palygorskite o sepiolite). Specifici legami si formano tra la molecola ospite e la matrice ospitante, conferendo al pigmento un'eccezionale stabilità chimica nei confronti di attacchi acidi e basici. Dal momento che la maggior parte dei lavori sin qui pubblicati è stata incentrata sullo studio del complesso palygorskite/indaco, il presente progetto è stato finalizzato alla

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descrizione delle caratteristiche strutturali del Blu Maya quando il reticolo ospitante è costituito dalla sepiolite. Un Blu Maya di sola sepiolite è stato sintetizzato basandosi sulle antiche ricette Maya e caratterizzato mediante svariate tecniche spettroscopiche (Uv-visibile, FTIR, Raman). Le risultanze hanno dimostrato che macinando e scaldando (190°C in aria o 150°C in vuoto) una miscela di sepiolite + indaco (al 2% in peso), gli aggregati grossolani di colorante si dissociano in monomeri favorendone la diffusione nei canali dell'argilla, svuotati dell'H₂O zeolitica debolmente legata. L'indaco, una volta incapsulato, in parte si trasforma in deidroindaco, la sua forma ossidata, la cui molecola più flessibile può facilmente diffondere nei canali provocando un lieve viraggio di colore del pigmento (da blu scuro a blu/verdastro). Il riscaldamento applicato, comunque, non provoca la perdita dell'OH₂ coordinata al Mg, che a seguito dell'incapsulamento forma legami-H con i gruppi funzionali dell'indaco (C=O e N-H), stabilizzando il composto. Le evidenze spettroscopiche a carico dell'esistenza di questi legami-H sono meno pronunciate in un Blu Maya di sola sepiolite rispetto ad un analogo composto di palygorskite. Mentre l'indaco, infatti, si incastra perfettamente nei canali più stretti della palygorskite (6.4 x 3.7 Å), ricevendo legami-H su entrambi i lati della molecola, nei più ampi canali della sepiolite (10.6 x 3.7 Å) la sua molecola deve avvicinarsi ad un bordo per formare un singolo legame. In un Blu Maya di sepiolite il numero globale di possibili interazioni tra la molecola ospite e la matrice ospitante è perciò drasticamente dimezzato rispetto ad un analogo pigmento di palygorskite, riducendosi di conseguenza la resistenza agli aggressivi chimici. Pertanto l'effettiva entità della rinomata stabilità del Blu Maya risulta essere direttamente correlabile alla composizione dei suoi principali costituenti argillosi.

KEY WORDS: *Maya Blue*; *sepiolite*; *indigo*; *spectroscopy*; *host/guest interaction*.

INTRODUCTION

Maya Blue is a famous blue pigment used by ancient Mayas in Pre-Columbian America, mainly in the Yucatan peninsula (Mexico), from VI to XVI century A.D. Wonderful artefacts

decorated with Maya Blue such as pottery, statues and mural paintings (Fig. 1) can still be admired nowadays in several Mexican archaeological sites, such as Chichén Itzá, Bonampak, Cacaxtla, El Tajin and others.

Maya Blue is the result of a combination between a microporous clay mineral (palygorskite and/or sepiolite, which ancient Mayas caved from local outcrops) and the indigo dye (extracted from the leaves of the *Indigofera Suffruticosa* plant; Reyes-Valerio, 1993). The pigment forms by strongly crushing the clay with the dye and moderately heating (120-190°C) the resulting blue mixture. Maya Blue immediately attracted the interest of the Scientific Community due to its astounding stability, as the pigment is virtually unaffected by both acids or alkali attacks and immune to light exposition. In order to acquire stability, however, the clay/dye mixture must be adequately heated: an unheated mixture, though similar in aspect to Maya Blue, lacks resistance to chemical agents.

Sepiolite and palygorskite are fibrous, colourless, phyllosilicate clay minerals. In their structure octahedral (O) and tetrahedral (T) sheets alternate along the *x* crystallographic axis: O sheets, however, are broken in ribbons elongated along *z* whereas T sheets, in order to maintain their continuity, show a waving course due to a periodic inversion in the orientation of apical oxygens, which point alternatively up and down bonding to the O strips. Projection of the structure on (001) can be described as chessboard-like disposition of TOT units (Ferraris *et al.*, 2004) (Fig. 2). This arrangement causes micro-tunnels, filled by weakly-bound zeolitic H₂O and exchangeable cations, to cross the framework running along [001]. Tightly-bound structural OH₂, on the other hand, completes the coordination of cations at the edges of O ribbons, protruding in the tunnels. A complicated web of H-bonds links zeolitic H₂O molecules among them and to the Mg-coordinated OH₂. Both zeolitic H₂O and



Fig. 1 - Mural painting from the archaeological site of Bonampak (Mexico); background is painted with Maya Blue pigment (taken from <http://www.regiosfera.com/resuelto-el-misterio-del-azul-maya/>).

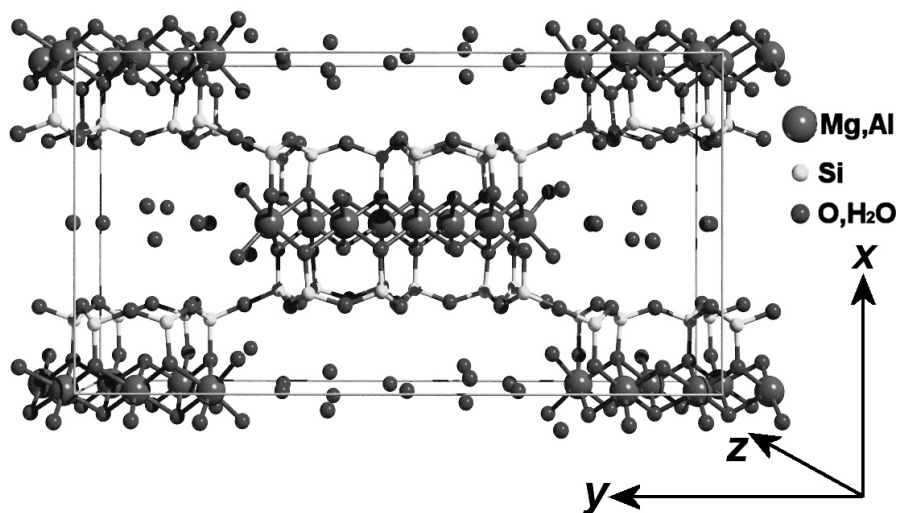


Fig. 2 - The crystal structure of sepiolite projected on (001) (fractional coordinates by Post *et al.*, 2007). Unit cell is outlined with continuous lines.

structural OH₂ can leave the structure by progressively heating the clay, but while the former is lost at moderate temperatures (120-200°C), higher ones are requested for the latter (> 300°C).

Main difference between sepiolite and palygorskite stands in the dimensions of the micro-tunnels, which are larger in the former (10.6 x 3.7 Å) and narrower in the latter (6.4 x 3.7 Å). As a consequence, each TOT ribbon counts eight O sites in sepiolite whereas only five (central one usually empty) appear in palygorskite. While this last can be considered an intermediate di/tri-octahedral phyllosilicate, due to contextual presence of Mg and Al, sepiolite is exclusively tri-octahedral [ideal crystal-chemical

formula: Mg₈Si₁₂O₃₀(OH)₄(OH₂)₄·8H₂O]. Due to their peculiar structural features, both sepiolite and palygorskite were investigated with regard to their ability to exchange cations and absorb small organic molecules in the clay micro-tunnels or on the fibres surface (Akyuz and Akyuz, 2004; Polette-Niewold *et al.*, 2007; Giustetto *et al.*, 2006) and as support for catalysts (Occelli *et al.*, 1992; Suarez *et al.*, 2008; Zheng *et al.*, 2010).

Indigo is a well-known blue dye, both natural and synthetic, whose molecule (Fig. 3) contains a cross-conjugated chromophore composed of a central C=C bond carrying two donor (amine units: N-H) and two acceptor groups (carbonyl units: C=O). Distribution of electric charge in the basic chromophore is strongly influenced by

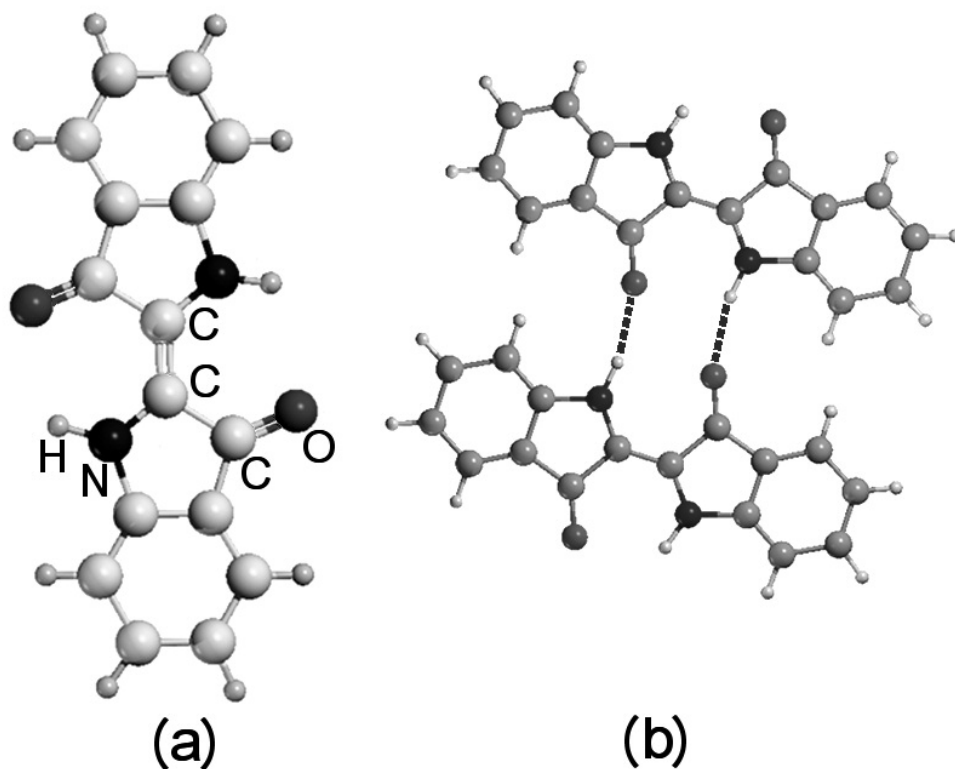


Fig. 3 - The molecule of indigo, with indication of the donor and acceptor groups (a); importance of inter-molecular forces (dashed lines) in dimer formation (b).

inter-molecular forces between reactive groups of separate molecules, responsible for aggregates formation (dimers or crystalline indigo). In spite of the brilliant colour of Maya Blue, the amount of indigo expected to react with the activated clay during the pigment synthesis is rather low, not exceeding 2 wt% (Kleber *et al.*, 1967; Chiari *et al.*, 2003; Giustetto *et al.*, 2005; Giustetto *et al.*, 2006, Chiari *et al.*, 2008).

According to the most quoted hypothesis, in the synthesis of Maya Blue indigo is adsorbed within the micro-tunnels as a result of the heating, which causes loosely bound zeolitic H₂O to leave the clay thus favoring dye diffusion. In addition, specific host/guest interactions are likely to form between the clay and indigo, thus stabilizing the dye inside the clay structure and conferring the pigment its renowned stability. Maya Blue has therefore to be considered a forerunner of modern nanocomposite materials as encapsulation within the pores guarantees shielding from external environment, while formation of host/guest interactions assures permanence *in situ* of the chromophore. The real nature of such bonds, however, is still disputed, whether H-bonds between structural OH₂ and indigo reactive groups (Chiari *et al.*, 2003; Fois *et al.*, 2003; Reinen *et al.*, 2004; Giustetto *et al.*, 2005; Giustetto *et al.*, 2006) or direct metal-oxygen bonds between octahedral cations at the edges of O strips and the dye carbonyl group (Polette-Niewold *et al.*, 2007; Manciu *et al.*, 2008; Tilocca and Fois, 2009).

Several analytical methods have been used so far to investigate the structural features of Maya Blue and the sorption of indigo in the hosting clay framework. Most studies, however, focused on the interaction between indigo and palygorskite. Basing on such premises and following-up the in deep structural studies performed on the palygorskite-based pigment, this work is aimed to investigate the dye environment and the nature of the chemical

bonds when sepiolite is the hosting framework. This in order to check whether and how presence of wider tunnels may influence both the nature and/or the strength of the host/guest interactions, affecting the composite stability. As in palygorskite, the guest indigo molecule is supposed to enter the wider sepiolite nano-tunnels due to consistent H₂O loss during heating (Hubbard *et al.*, 2003; Ovarlez *et al.*, 2006; Domenech *et al.*, 2009; Giulieri *et al.*, 2009). Presence of larger tunnels (10.6 x 3.7 Å) should facilitate diffusion.

Experimental conditions adopted in the current study were modeled, as far as possible, on the ancient Mayas procedures, in order to re-create a composite analogue to original Maya Blue starting from pure precursors. It is generally reputed that moderate temperatures were reached during the pigment preparation, as heating between 100 and 200°C allow formation of a stable compound (Sanchez del Rio *et al.*, 2009). It cannot be excluded, however, that more severe thermal treatments (> 300°C) may affect the nature and strength of the host/guest interactions, implying formation of similar although alternative sepiolite + indigo adducts, characterized by peculiar structural features (Giulieri *et al.*, 2009).

MATERIALS AND EXPERIMENTAL

The perspective of studying archaeological Maya Blue specimens, although appealing, was immediately discarded as such samples always include traces of the below substratum (i.e. plaster or mortar), lacking the requested quality standards. Besides, authentic Maya Blue usually contains a mixture of palygorskite or sepiolite, although other clays (i.e. illite and montmorillonite) may be present too. For all these reasons, the current study was performed on freshly-synthesized sepiolite + indigo (2 wt%) composites, a procedure already adopted in past works (Chiari *et al.*, 2003; Hubbard *et al.*, 2003; Giustetto *et al.*, 2006).

Natural sepiolite and synthetic indigo were provided by Sigma-Aldrich (cod. nos. 70253 and 56980 respectively).

In order to prepare freshly-synthesized sepiolite-based Maya Blue specimens, the well-established procedure codified in literature for the laboratory preparation of Maya Blue was adopted (Van Olphen, 1966; Sanchez Del Rio *et al.*, 2006; Polette-Niewold *et al.*, 2007). Such procedure mainly consists of three phases: i) mixing and dry grinding sepiolite with synthetic indigo (2 wt.%); ii) heating up to 190°C for 22 hours; iii) purification of the powders through Soxhlet extraction in CHCl₃, in order to remove the exceeding dye unfixed to the hosting matrix. A different procedure was adopted for samples analyzed by means of IR techniques, for which sepiolite was previously activated (heating in vacuum at 120°C, removing most zeolitic H₂O), ground under glove-box in Ar atmosphere with 2 wt% indigo and further heated in vacuum at 150°C (dehydration effects analogous to heating in air at 190°C).

UV-visible spectra in transmittance mode were collected using a Varian Cary 300 Bio spectrophotometer in the 800-200 nm range on an indigo CHCl₃ solution. UV-visible-NIR spectra in diffuse reflectance mode were collected using a Varian Cary 5000 spectrophotometer in the 2500-200 nm range, on samples previously diluted with BaSO₄ (1:3/1:20).

Infrared (IR) absorption spectra were collected, under controlled atmosphere, on a FTIR Bruker IFS 66 spectrometer, with a resolution of 2 cm⁻¹ and collecting 64 scans for each spectrum. All samples, in the form of thin films supported on Si plates, were outgassed under vacuum at 150° C for 1.5 hours in order to eliminate zeolitic H₂O.

Raman spectra were collected on a Renishaw micro-Raman system 1000 on powder samples, excited with a He-Cd green laser beam operating at 532 nm in the range 1100-1800 cm⁻¹, addressed with an optical microscope. The

scattered signal was collected on a CCD detector located at 180° with respect to the incident beam.

RESULTS AND DISCUSSION

UV-Vis spectroscopy

UV-visible spectra were collected both on pure indigo and on the sepiolite + indigo (2 wt%) adduct in all different stages of the synthesis procedure (Fig. 4).

The absorption spectrum of indigo in a CHCl₃ solution (curve a) shows a well-defined maximum at 603 nm, related to the $\pi \Rightarrow \pi^*$ transition. The deep minimum between 500 and 370 nm is responsible for the deep blue-colour of the solution and consistent with the presence of a double cross-conjugated system formed by both donor and acceptor groups (Klessinger and Lüttke, 1963).

The isolated indigo molecule (gaseous) is known to have its lower energy band at 540 nm. Variations in the location of absorption maxima are related to the particular chemical environment of the dye molecule, either in solution and in the solid-state (Reichardt, 2003). Perturbations due to interactions cause sensible shifts towards lower energies, whose magnitude is related to both their strength and number. As such, position of the absorption band in the indigo CHCl₃ solution (603 nm) is related to the fairly weak connections - if any - between the dye molecules and a non-polar solvent.

The diffuse reflectance spectrum of solid-state indigo dispersed in an inert matrix (BaSO₄; curve 1) shows a significant shift of the absorption maximum towards higher wavelengths, reaching 660 nm (weak shoulder at 554 nm). Such shift implies dye molecules in solid-state are strongly linked one another by means of inter-molecular hydrogen bonds, responsible for aggregate formation (dimers and/or crystalline indigo) and absorption of lower energy light. Analogous effect exerted by polar solvents (such as ethanol

and acetone) appears to be weaker (Reinen *et al.*, 2003).

A similar outcome occurs when indigo is solvated in the host matrices of microporous clay minerals. A mixed and ground sepiolite + indigo (2 wt%) composite (curve 2) shows an absorption maximum at 648 nm, related to the same $\pi \rightarrow \pi^*$ transitions, slightly shifted (-12 nm) with respect to pristine indigo. Presence of such shift implies the dye molecules do not form aggregates when solvated on sepiolite, but rather specific interactions with the hosting matrix, whose nature and strength are different from

inter-molecular bonds occurring among indigo molecules. It is remarkable how such interactions tend to form already during grinding (curve 2) and progressively stabilize after heating and Soxhlet extraction (curves 3 and 4), as confirmed by the further slight shift of the absorption maximum.

Careful examination of the mixed and ground composite spectrum (curve 2) suggests presence of an additional broad shoulder at 603 nm, a position typical of the quasi-isolated indigo molecule, which is consistent with results obtained on analogous palygorskite-based

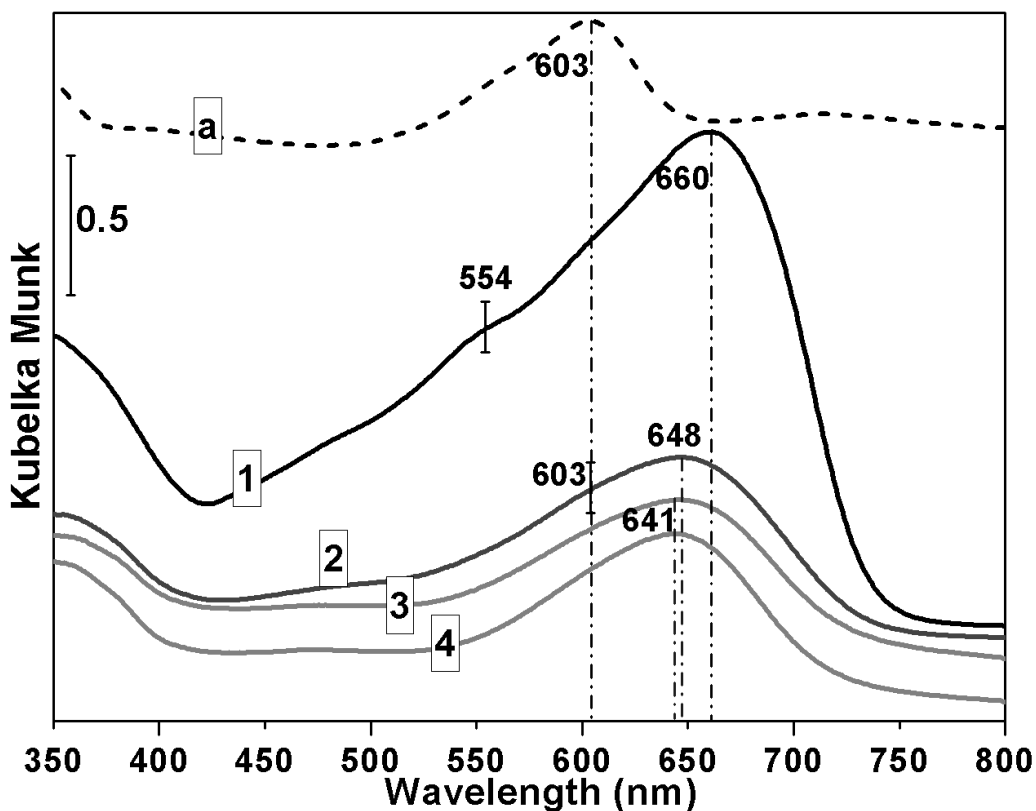


Fig. 4 - UV-visible absorption spectrum of indigo in CHCl_3 solution (a) and diffuse reflectance spectra of solid-state indigo (1) and sepiolite + indigo (2 wt%) composite after crushing (2), heating (3) and Soxhlet extraction in CHCl_3 (4). Spectra were shifted on Y axis for sake of clarity.

composites by Reinen *et al.* (2003). Presence of such shoulder might be explained as bigger indigo particles, when strongly crushed to the hosting matrix, tend to dissociate in smaller units causing progressive disappearance of intermolecular bonds and formation of indigo monomers which, as such, might easily diffuse inside the sepiolite tunnels. Subsequent heating (curve 3) and Soxhlet extraction in CHCl_3 (curve 4) cause progressive disappearance of such shoulder, as indigo monomers link to the clay matrix due to formation and stabilization of host/guest interactions.

The progressive decrease of absorption in the 550–600 nm region in subsequent stages of the synthesis procedure causes the colour of the resulting composite to vary from deep to greenish-blue.

FTIR spectroscopy

FT-IR spectra were collected both on isolate precursors (sepiolite; indigo) and on the sepiolite + indigo (2 wt%) adduct while heating the powders in vacuum at 150°C , in order to observe variations of the IR-active vibrational modes in the exact moment of the pigment synthesis.

In the hydroxyl stretching region ($2800\text{--}3800\text{ cm}^{-1}$) of the IR spectrum of sepiolite evacuated at 150°C (Fig. 5, curve 1) two separate doublets can be observed at high wavenumbers. The first one (3738 and 3726 cm^{-1}) is related to superficial silanols whereas the second (3691 and 3680 cm^{-1}) to hydroxyls in the octahedral sheet (Mg-OH). These last appear to be moderately perturbed, presumably as the result of a limited loss of coordinated OH_2 , causing partial transformation to sepiolite di-hydrated (Hayashi *et al.*, 1969; Giulieri *et al.*, 2009). Most relevant features, however, are two broad maxima located at 3600 and 3531 cm^{-1} . Such bands can be observed only after heating, as at room temperature (not shown here) they are overlapped by the broad signals related to physisorbed and zeolitic H_2O , and can

be related to the anti-symmetric and symmetric stretching frequencies of the tightly-bound coordinated OH_2 (Cannings, 1968; Frost *et al.*, 2001). Most coordinated OH_2 is therefore still tightly bound to the sepiolite framework at the adopted heating experimental condition (150°C in vacuum).

Addition of indigo to sepiolite (Fig. 5, curve 2) modifies selected vibrational modes related to the hosting framework. In addition, indigo bands are easily identifiable in the composite spectra in spite of its low amount (2 wt%). Doublet related to superficial silanols (3738 and 3726 cm^{-1}) is not altered by indigo addition, implying interaction with the dye does not occur on the fibres surface. Severe intensity decrease of the 3691 cm^{-1} maximum, on the other hand, suggests fixation of indigo increases the stability of the hosting structure, preventing folding due to OH_2 loss (Giulieri *et al.*, 2009). As already seen for pure sepiolite, also in the pigment the applied heating causes structural OH_2 $\nu(\text{OH})$ maxima to appear in the very same positions (3600 and 3531 cm^{-1}), implying presence of indigo does not favour but prevent loss of OH_2 . Additionally, a new broad feature appears at 3408 cm^{-1} , which was not visible in the spectrum of sepiolite. Most feasible explanation is that such feature accounts for perturbation of a certain amount of structural OH_2 , possibly involved in H-bond formation. As zeolitic H_2O is known to have abandoned the clay structure due to applied heating, it is likely that such bonds may be formed with the guest indigo molecule, aptly diffused inside the tunnels. The scarce dye quantity (2 wt%) implies not all structural OH_2 can form H-bonds with indigo, thus explaining persistence of the 3600 and 3531 cm^{-1} maxima related to unperturbed hydroxyls.

The only band directly related to presence of indigo in this region is a broad maximum appearing at 3212 cm^{-1} , related to the dye $\nu(\text{N-H})$. Such band is significantly red-shifted with respect to the one appearing in pristine indigo

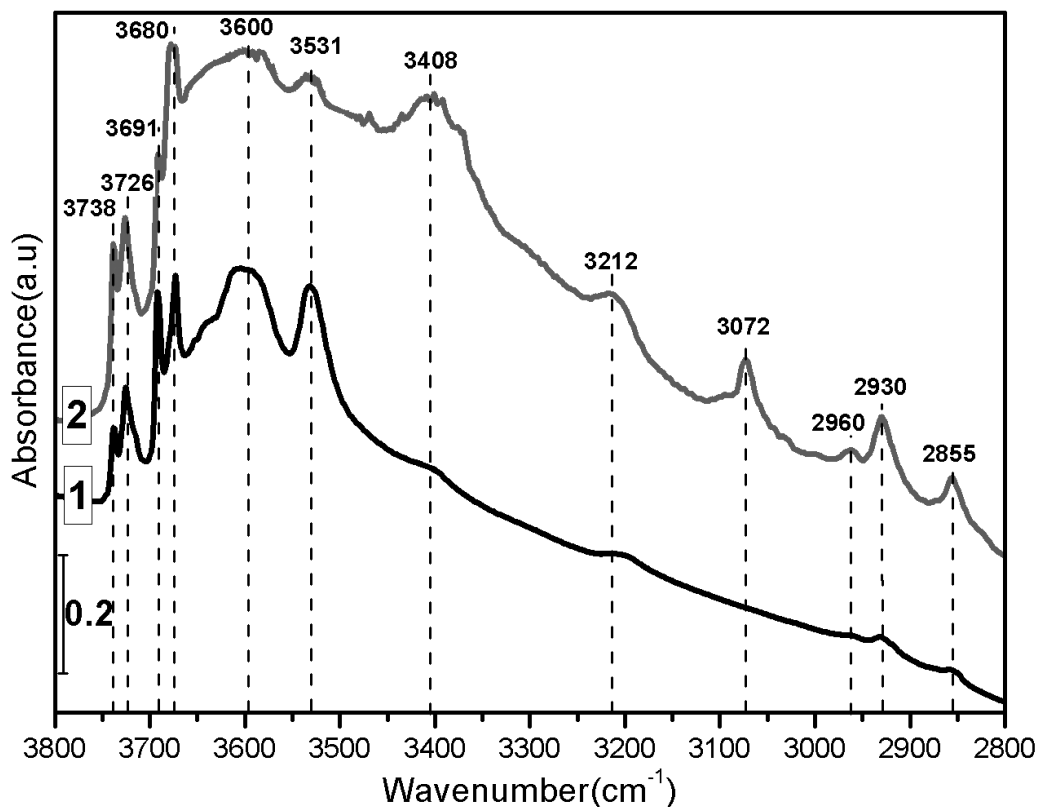


Fig. 5 - IR spectra in the hydroxyl stretching region ($2800\text{--}3800\text{ cm}^{-1}$) of pristine sepiolite (1) and sepiolite + indigo (2 wt%) adduct (2) outgassed in vacuum at 150°C . Spectra were shifted on Y axis for sake of clarity.

(3270 cm^{-1}), suggesting the amine group is somehow involved in formation of host/guest interactions with the inorganic matrix.

In the hydroxyl bending region ($1150\text{--}1800\text{ cm}^{-1}$; Fig. 6) a major broad feature appears at 1615 cm^{-1} in the spectrum of pristine sepiolite evacuated at 150°C (curve 1). Emergence of such band is due to loss at previous temperatures steps of loosely bound H_2O and has to be related to structural OH_2 $\delta(\text{OH})$ (Hayashi *et al.*, 1969; Frost *et al.*, 2001). Once again, addition of indigo to sepiolite and heating at the same level causes an analogous band to appear (curve 2): careful examination, however, reveals non-symmetry of

such feature if compared to the one typical of pure sepiolite, as at least two weak but definite shoulders appear at higher wavenumbers (1623 and 1640 cm^{-1} respectively). Presence of such shoulders is therefore an indirect evidence of the dye addition, being related with all due probability to perturbations affecting a fraction of OH_2 molecules. Again, magnitude of observed shifts suggests possible formation of H-bonds between OH_2 and the guest indigo molecule.

The main IR-active vibrational modes of pure indigo (Fig. 6, curve a) appear in the $1000\text{--}1650\text{ cm}^{-1}$ interval, in a region relatively free from clay related maxima. As stated above, in solid-state

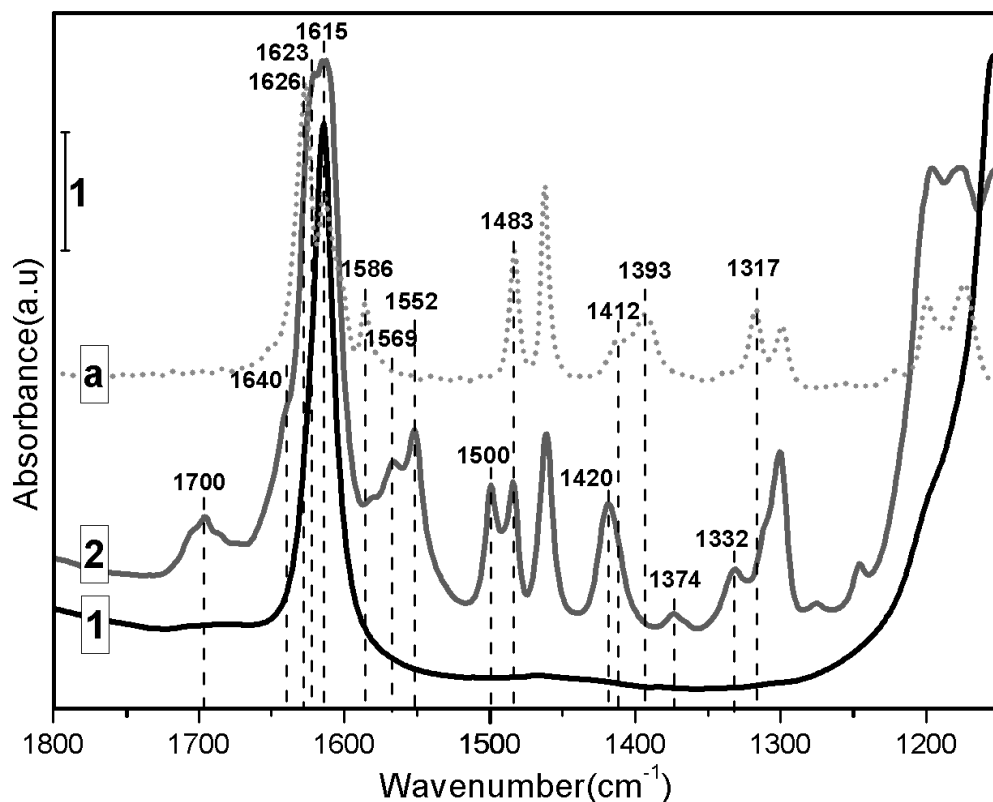


Fig. 6 - IR spectra in the hydroxyl bending region ($1150\text{--}1800\text{ cm}^{-1}$) of pure indigo (a), pristine sepiolite (1) and sepiolite + indigo (2 wt%) adduct (2) outgassed in vacuum at 150°C . Spectra were shifted on Y axis for sake of clarity.

indigo molecules in *trans*-form are bound one another through intra- and inter-molecular bonds, formed by reactive groups (N-H/C=O) within a single molecule or between different molecules respectively (Fig. 3). The anti-symmetric stretch of the C=O group forms a doublet at 1626 and 1614 cm^{-1} , whereas two separate features (shoulder at 1412 and band at 1393 cm^{-1}) are related to in-plane $\delta(\text{N-H})$, the first related to intra-molecular and the second to inter-molecular bonds.

Addition of indigo to the clay causes selected shifts and intensity variations to occur in the vibrational modes attributed to the dye, probable

consequences of host/guest bond formation and strengthening. Unfortunately no consideration can be made about the behavior of the C=O group, as the related features are hidden by the stronger maximum related to OH_2 bending. Luckily no overlapping affects N-H group features, whose band related to inter-molecular bonding (1393 cm^{-1}) disappears in the heated sepiolite + indigo composite (Fig. 6, curve 2). Such evidence is consistent with UV-visible spectroscopy results and confirms that during pigment synthesis dissociation of indigo aggregates occurs, forming isolated monomers which, as such, can easily diffuse inside the host

micro-tunnels. Breaking of inter-molecular bonds, besides, allows indigo reactive groups (N-H/C=O) to interact with the clay framework and establish new bonds. Feature related to intra-molecular bonds (1412 cm^{-1}), alternatively, shows moderate shift towards higher wavenumbers (reaching 1420 cm^{-1}) and intensity increase. Previous experiences (Ovarlez *et al.*, 2006) proved that such interactions are due to split only at temperatures sensibly higher than those applied ($> 300^\circ\text{C}$ in air).

In the pigment spectrum (curve 2), however, several vibrational modes related to the molecule benzene rings $\nu(\text{C-C})$ significantly vary, as per position and/or intensity, with respect to pure indigo (curve a). Such variations can be resumed as follows: i) disappearance of the 1586 cm^{-1} feature; ii) growth of the 1569 and 1552 cm^{-1} bands; iii) splitting of the 1483 cm^{-1} maximum, with appearance of a new band at 1500 cm^{-1} ; iv) shift towards higher wavenumbers of the 1317 cm^{-1} band, which reaches 1332 cm^{-1} . All these variations can tentatively be related to intervened deformations of the molecule due to encapsulation in the hosting matrix. Loss of both planarity and centre-symmetric geometry may be explained by partial transformation of indigo to its oxidized form, dehydroindigo. Presence of dehydroindigo in Maya Blue was reported by several authors (Sanchez del Rio *et al.*, 2009; Domenech *et al.*, 2009) and is reputed to favor the guest diffusion within the tunnels, as the central double bond (C=C) in the chromophore is replaced by a single one, increasing flexibility of the molecule. In addition, presence of dehydroindigo is consistent with a slight color change of the pigment from deep blue to blue-green, as already detected by UV-vis spectroscopy. Weak new maxima at 1700 and 1374 cm^{-1} (curve 2) have also to be related to possible thermal decomposition of indigo and partial transformation to dehydroindigo (Giulieri *et al.*, 2009).

Raman spectroscopy

Raman spectra were collected on pure indigo, on a sepiolite + indigo (2 wt%) ground mixture and on a sepiolite-based Maya Blue pigment after heating and Soxhlet extraction in CHCl_3 (Fig. 7).

No spectrum could be collected on pristine sepiolite due to strong fluorescence effects, as already reported in previous works (McKeown and Post, 2002). Straight comparison between collected and literature data (Witke *et al.*, 2003; Leona *et al.*, 2004; Giustetto *et al.*, 2005; Vandenabeele *et al.*, 2005) shows several analogies, though interpretation is complicated by resonance effects. Intensity of Raman signal is very sensitive to the excitation wavelength and variations sometimes depend from particular experimental conditions rather than different chemical surroundings of the dye molecule.

Assignment of Raman-active vibrational modes of indigo (curve a in Fig. 7) was based on the results of Tatsch and Schrader (1995). All features appearing in the spectra of the sepiolite-based composites with indigo (curves b and c) are related only to the dye molecule, being the clay contribution irrelevant.

Most significant considerations emerge by comparing the pristine indigo (curve a) and sepiolite-based Maya Blue (curve c) spectra. The ground but unheated sepiolite + indigo (2 wt%) mixture (curve b) represents an intermediate but fundamental step, as it is commonly accepted that host/guest interactions start to form even during crushing (Hubbard *et al.*, 2003; Sanchez del Rio *et al.*, 2006).

Most relevant considerations can be summarized as follows: i) feature related to the symmetric $\nu(\text{C=O})$ gradually red-shifts passing from 1701 (pristine indigo; curve a) to 1695 (ground sepiolite + indigo mixture; curve b) and then to 1690 cm^{-1} (Maya Blue; curve c). The observed red-shift (-11 cm^{-1}) is consistent, though slightly less marked, with the theoretical

value computed by means of *ab-initio* methods for a C=O perturbed by a H-bond (-15 cm^{-1} ; Giustetto *et al.*, 2005). An analogous shift, albeit more evident, was observed for similar palygorskite/indigo adducts (Witke *et al.*, 2003; Leona *et al.*, 2004; Giustetto *et al.*, 2005; Vandenaabeele *et al.*, 2005). Raman spectroscopy exhibits therefore direct evidence about involvement of indigo carbonyl group in formation of host/guest interactions, being such group the effective acceptor of H-bonds donated by the nearest clay structural OH_2 , as shown by FTIR data. ii) maximum at 1365 cm^{-1} , related to $\delta(\text{N-H})$ coupled with $\delta(\text{C-H})$ modes, shows sensible intensity decrease and partial shift

towards higher wavenumbers passing from indigo (curve a) to the ground mixture (curve b) and finally to Maya Blue (curve c), where a new component appears at 1378 cm^{-1} . Such evolution implies the indigo amine unit, as well as the C=O group, is perturbed and involved in formation of mutual clay/dye interactions. An analogous variation was described by Leona *et al.* (2004), though here it is exalted by resonance effects (Giustetto *et al.*, 2005). iii) more or less significant shifts and intensity variations affect selected maxima passing from pure indigo to the sepiolite-based pigment [significant increase and shift towards higher wavenumbers of the 1631 cm^{-1} band of indigo (curve a), related to

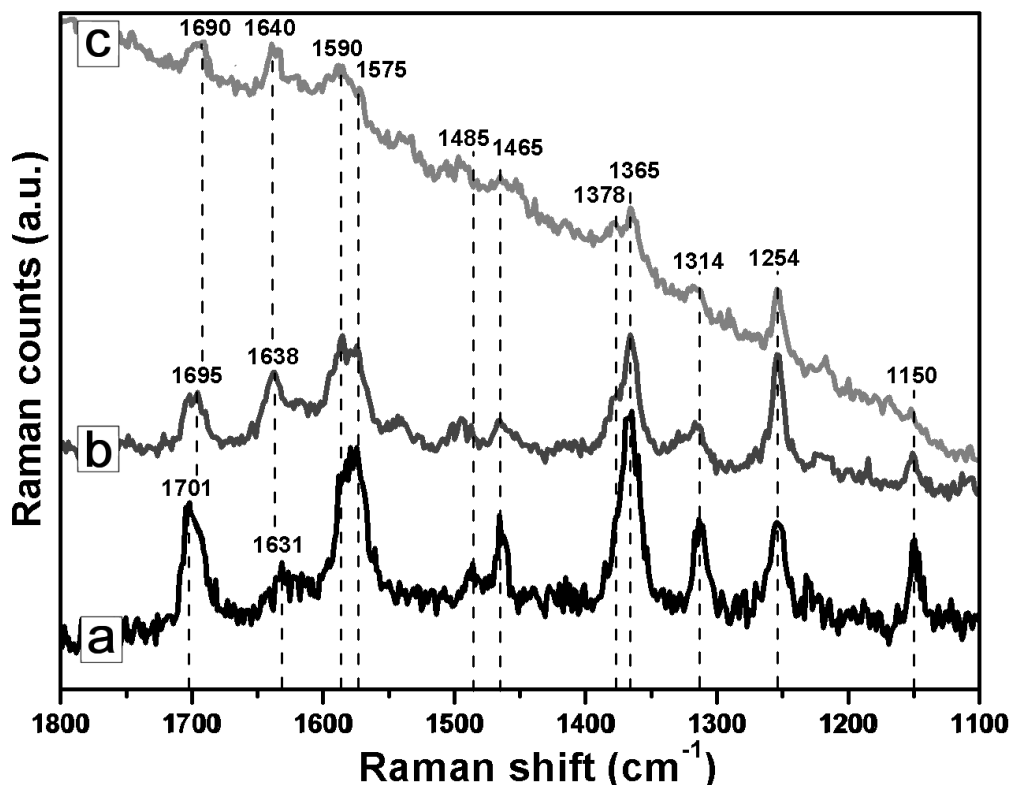


Fig. 7 - Raman spectra of pure indigo (a) and sepiolite + indigo (2 wt%) adduct after crushing (b) and heating/Soxhlet extraction in CHCl_3 (c). Spectra were shifted on Y axis for sake of clarity.

collective $\nu(\text{C-C})$ modes, which reaches 1640 cm^{-1} in Maya Blue (curve c); intensity decrease and shift towards higher wavenumbers of maxima at 1575 and 1365 cm^{-1} (curve a), related to collective $\nu(\text{C-C})$ modes and in-plane $\delta(\text{N-H})$ coupled with C-H respectively, which gradually move to 1590 and 1378 cm^{-1} in the pigment after heating (curve c)]. Such variations are consistent with previous literature data (Witke *et al.*, 2003) and can be explained by intervened activation of Raman-inactive vibration modes of the B_u type, due to loss of planarity of the indigo molecule after adsorption in the hosting sepiolite matrix. Once again, such behavior might be explained by partial transformation of indigo to dehydroindigo, a phenomenon reported by several authors (Giustetto *et al.*, 2006; Domenech *et al.*, 2006; 2007; 2009). iv) at lower frequencies (not shown in Fig. 7), the maximum related to vibrations in the five-member ring shifts towards higher wavenumbers, passing from 549 (pure indigo) to 553 cm^{-1} (sepiolite-based Maya Blue). Such variation, observed also by Vandenabeele *et al.* (2005), is related to combination of charge and symmetry effects (as commented by Coupry *et al.*, 1997, studying dyes spectra fixed on cotton fibers) and again can be justified by activation of Raman-forbidden modes caused by modifications in the planarity of the indigo molecule, due to partial transformation to dehydroindigo.

CONCLUSIONS

A freshly-synthesized sepiolite-based Maya Blue pigment was characterized by means of various spectroscopic techniques (UV-visible, FTIR and Raman), in order to study the adsorption process of indigo inside the clay tunnels and the nature of the host/guest interactions responsible for the pigment stability.

Collected evidences proved that at the adopted experimental conditions (heating at 190°C in air or 150°C in vacuum), analogous to those adopted

by the ancient Mayas while preparing the original pigment, the tightly-bound Mg-coordinated OH_2 does not leave the sepiolite structure, being the related vibrational modes well visible in the IR spectra. Addition of indigo to the clay, besides, perturbs such features suggesting direct involvement of OH_2 in the formation of mutual bonds between the clay and the dye.

Fixation on the hosting sepiolite matrix causes indigo aggregates (dimers and crystalline indigo) to dissociate, due to progressive disappearance of inter-molecular bonds favoured by strong crushing and moderate heating of the clay/dye mixture. Dissociation of aggregates implies diffusion inside the clay tunnels of indigo monomers, whose functional groups (C=O ; N-H) become available to react with the clay matrix giving way to formation of host/guest interactions.

Diffusion within sepiolite tunnels is further encouraged by partial thermal decomposition of indigo to its oxidized form - dehydroindigo, evidenced by intervened deformation and loss of planarity of the guest molecule after heating. The more flexible dehydroindigo molecule favours deeper encapsulation inside the sepiolite pores and explains minor colour changes (from deep blue to blue/greenish) observed during the pigment preparation.

All spectroscopic evidences show that the encapsulated indigo molecules are stabilized within the sepiolite tunnels by specific clay/dye interactions, presumed responsible for the composite stability. Such interactions, considering the reactive groups involved and the magnitude of the related vibrational shifts, have been identified as H-bonds formed between the sepiolite structural OH_2 and the indigo acceptor and donor groups (C=O ; N-H). This kind of interaction, albeit usually considered weak, when formed within narrow micropores can be tough to reach and therefore difficult to break. While the C=O groups receive H-bonds from the nearest OH_2 molecules protruding in the tunnels,

it is still doubtful whether the N-H groups may donate analogous bonds to the same OH_2 .

No evidence was found about existence of direct carbonyl/cation ($\text{C}=\text{O}\cdots\text{Mg}$) interactions. It cannot be excluded, however, that such bonds may form if higher temperatures are reached during heating ($> 300^\circ\text{C}$), favoured by loss of coordinated OH_2 .

Presence of H-bonds in a sepiolite-based Maya Blue pigment is consistent with previous studies centered on palygorskite-based analogues (Fois *et al.*, 2003; Reinen *et al.*, 2004; Giustetto *et al.*, 2005; Giustetto *et al.*, 2006; Chiari *et al.*, 2008).

In spite of this, intensities of the related vibrational modes are severely weakened when sepiolite is the hosting framework, as if the global number and/or strength of these interactions could be diminished if compared to a palygorskite-based analogue. In order to justify such evidence, details of indigo encapsulation in the sepiolite framework need to be further discussed.

While in the narrower palygorskite pores ($6.4 \times 3.7 \text{ \AA}$) indigo can be exactly juxtaposed in the middle of each tunnel, receiving H-bonds from coordinated OH_2 on both sides of the molecule, in the larger tunnels of sepiolite ($10.6 \times 3.7 \text{ \AA}$)

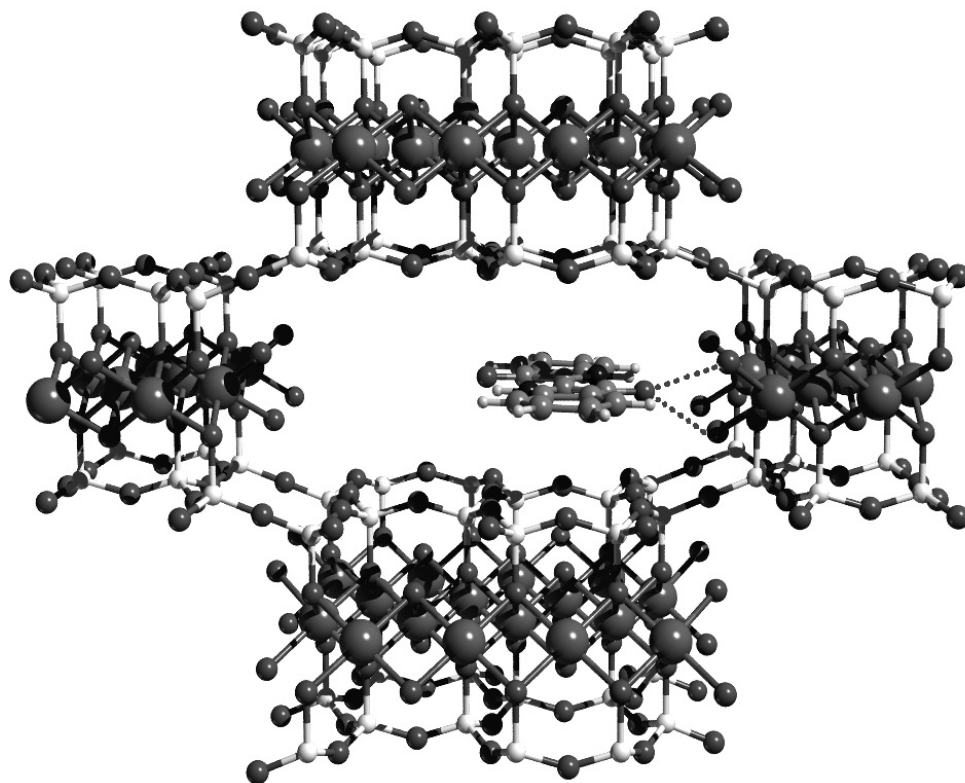


Fig. 8 - Encapsulation of indigo molecule inside a sepiolite tunnel; dashed lines indicate H-bonding between the indigo $\text{C}=\text{O}$ group and the clay OH_2 . Zeolitic H_2O not shown for sake of clarity.

the dye molecule must get close to one tunnel border in order to adequately interact with the clay framework (Fig. 8). Only one side of the indigo molecule, namely the one facing the border of the tunnel, can therefore anchor itself to the clay framework, whereas the opposite side facing the tunnel lumen is bond-free. Such situation cannot be modified by adding another molecule next to the first, as the dye steric impediment is such that two molecules cannot be paired side by side in the same tunnel portion.

The described accommodation for indigo in sepiolite causes the number of host/guest interactions possibly existing in a sepiolite-based Maya Blue to be drastically halved with respect to a palygorskite-based one. This severe reduction in the global number of H-bonds, considered on equivalent indigo amounts (2 wt%), justifies the observed intensity decrease of the spectroscopic features, as a minor fraction of both coordinated OH₂ and dye reactive groups are involved in formation of interactions.

A direct and macroscopic consequence of such situation, coupled with the more enhanced fragility of sepiolite structure compared to palygorskite, is that a palygorskite-based Maya Blue pigment is sensibly more resistant to chemical agents than its sepiolite-based analogue, as performed stability tests seem to corroborate (Sanchez Del Rio *et al.*, 2006). The renowned stability of Maya Blue pigment can therefore be directly related to the composition of its clay constituent: samples mainly formed by palygorskite are more resistant than analogues where sepiolite is the predominant clay.

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