Maya Blue: archaeological puzzle and source of inspiration for nano-structured pigments

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Abstract

The turquoise blue pigment Maya Blue (MB) was widely used in Mesoamerica up to *ca.* 1500, on pottery, textiles and frescos (figure1). Its brightness and durability are remarkable, specially considered in the light of its deceptively simple present day synthesis, by heating together powdered indigo and palygorskite clay[1]. Palygorskite occurs as nano-fibres, typically some tens of nm in width and up to a few µm long. The crystal structure defines rectangular *ca.* 0.7x1.2 nm interior channels and surface grooves. It is generally agreed that indigo acquires chemical and physical stability by entering these channels and grooves.

Yet despite some years of study with the experimental and theoretical tools of modern analytical materials science[2-5], the detailed structure of MB, and its relation to its astounding chemical and physical stability, remain subjects of debate. While study of archaeological samples and laboratory synthesized MB have shed much light on the problem, better understanding can come from contrasting and comparing MB with analogous, archaeo-inspired materials, both successful and unsuccessful, based on the same principles of fitting an organic dye into an inorganic host matrix with well defined nano-cavities.

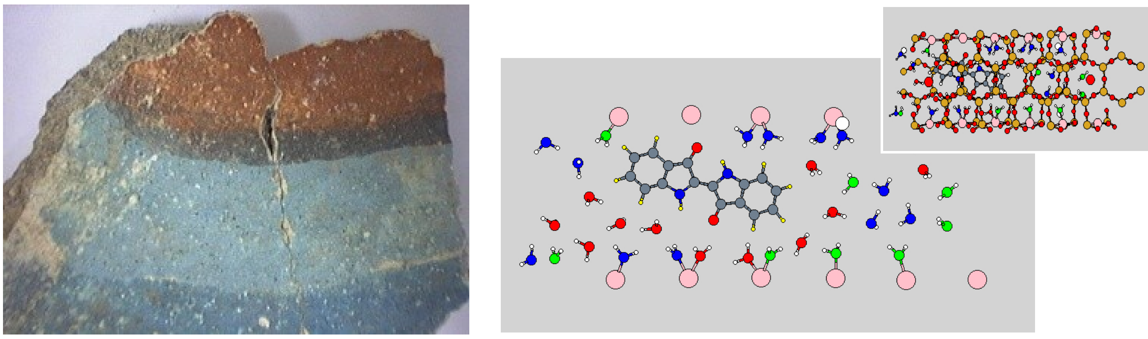
Here, we apply this novel approach to MB[6] and zeolite-based analogues[7-9], employing a variety of techniques, including *in situ* XRD, thermo-gravimetric analysis, optical spectroscopy, confocal microscopy and molecular modelling, to propose an updated view of the structure and dynamics of this fascinating material. The results indeed point to indigo being sequestered in the channels of palygorskite, but call into question current understanding of the reasons for the stability of the material. Our experimental conclusion, that stability derives more from steric screening of the dye in the channels than from chemical complexation, is supported by the molecular simulations. This screening is exhibited in the association of indigo with silicalite, forming a pigment analogous to MB, figure 2, resistant to photodegradation and oxidation by nitric acid.

References

[1] H. Van Olphen, *Science*, **154** (1966) 645-6.
[2] G. Chiari, R. Giustetto, J. Druzik, E. Doehne, G. Ricchiardi, *Appl. Phys. A*, **90** (2008) 3-7.
[3] B. Hubbard, W. Kuang, A. Moser, G. A. Facey, C. Detellier, *Clays and Clay Minerals*, **51** (2003) 318-26.
[4] E. Fois, E. Gamba, A. Tilocca, *Microporous Mesoporous Mater.* **57** (2003) 263-72.

[5] A. Tilocca, E. Fois, *J. Phys. Chem C*, **113** (2009) 8683-87.
[6] C. Dejoie, *PhD Thesis,* Université J. Fourier de Grenoble, 2009.
[7] C. Dejoie, P. Martinetto, E. Dooryhée, P. Strobel, S. Blanc, P. Bordat, R. Brown, F. Porcher, M. Sanchez del Rio, and M. Anne, *ACS Applied Materials & Interfaces*, **2** (2010) 2308–16.
[8] C. Dejoie, P. Martinetto, E. Dooryhée, E. van Elselande, S. Blanc, P. Bordat, R. Brown, F. Porcher, M. Anne, *Applied Spectroscopy*, **64** (2010) 1131–38.
[9] P. Bordat *et al* , in preparation for *J. Phys Chem C* (2013).
[10]R. J. Gettens, *Am. Antiquity* **7** (1926) 557-64.

Figures



(a) **(b)**

Figure 1: (a) Fresco fragment from Cacaxtla, coloured with Maya Blue; (b) : molecular dynamics simulation of indigo in a palygorskite channel (inset), host cut away except Mg (pink) to show water and indigo.

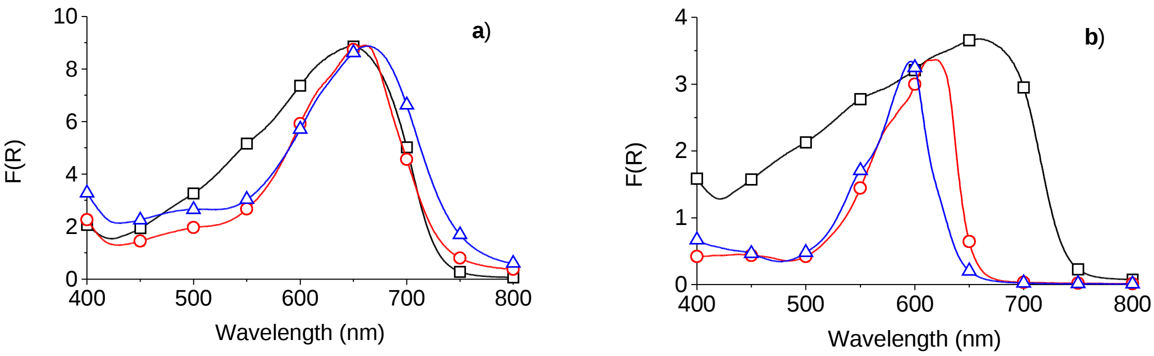


Figure 2: Normalised Kubelka-Munk transforms, F(R), of the UV-visible diffuse reflectance of indigo-nano-porous guest-host systems (2%wt. Indigo): *(a)* reconstituted MB; *(b)* indigo-silicalite. Symbols: □ unheated mixtures; ○ heated hybrids; Δ heated hybrids after the nitric acid test. Persistence of the blue colour in presence of nitric acid (the Gettens test[10]) is a hallmark of Maya Blue.