The Secret of the Maya Blue: A problem of diffusion in a microporous solid

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The adsorbed ^{129}Xenon detected by NMR is an excellent probe to determine microporous solid properties difficult to detect by classical physico-chemical techniques [1,2]. Indeed the very large and extremely polarisable electron cloud of xenon makes this atom particularly sensitive to its immediate environment. Small variations in the physical interactions with the latter cause marked perturbations of the electron cloud which are transmitted directly to the xenon nucleus and greatly affect the NMR spectrum. The corresponding chemical shift depends on the dimensions and structure of the free space, on the chemical composition of the pore walls and on the ease of diffusion of the atoms in the crystallites. This technique has been mainly used to solve the secret of the Maya Blue (MB) synthesis which is also a problem of diffusion in micropores [3].

The famous pre-Columbian Maya Blue pigment (2600 years b.c.) has been the subject of much research aimed at explaining the extreme stability of this hybrid organic/inorganic pigment present in mural paintings in Mayan Temples in the Yucatan, in many ceramic objects, in the large monolith, *Tlaltecuhtli,* representing the Aztec Earth god, etc.

In the MB pigment, the host is palygorskite clay (with tunnels having a 3.7 x 6.4 Å cross-section for the hydrated form), and the guest is the indigo molecule ($C_6H_{10}N_2O_2$). Depending on the various authors, the indigo lies in grooves at the surface of the clay fibers, inside the tunnels where it replaces the zeolitic water, or stays at the tunnel entrances. For this reason this research is focused on the mechanism of MB preparation and the final location of the indigo.

The dye was added to clay in three ways: i) the traditional Mayan technique, where palygorskite is mixed with an aqueous extract of leaves of the añil plant; ii) the synthetic method where the clay is mixed with synthetic indigo, either finely ground and heated to 180 °C or dissolved in DMSO, since it is not soluble in water. The treatment in an Accelerated Weathering Tester to simulate ageing corresponds to 10 years in real time.

NMR spectra of ^{29}Si, ^{27}Al, ^{13}C and mainly adsorbed xenon ^{129}Xe show that, after ageing, only the sample prepared by the traditional technique contains indigo inside the palygorskite tunnels. With samples prepared from synthetic indigo, an interaction between indigo and the external surface of the clay is favoured.

Acid treatment of samples after ageing provides evidence for the chemical resistance of pigments prepared by the traditional technique as compared to the synthetic samples. This result agrees with the distribution of dye in the samples, as elucidated by NMR.

The indigo dye from añil leaves is water-insoluble; therefore, it must be deposited on the wall of the vessel and on the external surface of the clay without diffusion into the pores, according to the results on the synthetic samples. NMR spectra prove that indoxyl, a smaller precursor of indigo from añil leaves, is adsorbed on the clay surface and diffuse more easily into the pores, where it is ultimately oxidized by atmospheric oxygen, UV and hot climate, to provide indigo.

These results have resolved the mystery regarding the preparation of MB and its final state.

References

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