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Fe *K*-edge XANES of Maya blue pigment

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Abstract

The utilization of techniques used in Materials Science for the characterization of artefacts of interest for cultural heritage is getting more and more attention nowadays. One of the products of the ancient Maya chemistry is the "Maya blue" pigment, made with natural indigo and palygorskite. This pigment is different from any other pigment used in other parts of the world. It is durable and acid-resistant, and still keeps many secrets to scientists even though it has been studied for more than 50 years.

Although the pigment is basically made of palygorskite $Si_8(Mg_2Al_2)O_{20}(OH)_2(OH_2)_4.4H_2O$ and an organic colourant (indigo: $C_{16}H_{10}N_2O_2$), a number of other compounds have been found in previous studies on archaeological samples, like other clays and minerals, iron nanoparticles, iron oxides, impurities of transition metals (Cr, Mn, Ti, V), etc. We measured at the ESRF ID26 beamline the Fe *K*-edge XANES spectra of the blue pigment in ancient samples. They are compared to XANES spectra of Maya blue samples synthesized under controlled conditions, and iron oxides usually employed as pigments (hematite and goethite). Our results show that the iron found in ancient Maya blue pigment is related to the Fe exchanged in the palygorskite clay. We did not find iron in metallic form or goethite in archaeological Maya blue.

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1. Introduction

X-ray Absorption Spectroscopies (XAS) are well suited to treat some problems of interest for the Cultural Heritage Science and Archaeological

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research. EXAFS (Extended X-ray Absorption Fine Structure) is able to extract structural information (interatomic distances, number and type of backscatterers) around a given selected atom (the photoabsorber). XANES (X-ray Absorption Near-Edge Spectroscopy) gives both structural information (distances and bond angles) and electronic information (vacant orbitals, electronic configuration and site symmetry of the photo-absorbing atom). For example, XANES was used to analyse the valence state of Fe and Mn in roman glasses in relation with the production methods [1], for studying the local order around Cu and Ag ions in renaissance pottery [2], for analysing the Fe valence in the hydration layer of obsidian [3], or for studying firing techniques in pottery [4].

Maya blue is a pigment original from Maya culture. It was widely used in murals, pottery and sculptures in a wide region of Mesoamerica in the pre-Hispanic time (from VIII century) and during the colonization until 1580. It is a pigment very different from any other blue pigment used in other parts of the world. It was well established in the sixties [5,6] that Maya blue is made with two ingredients: blue indigo dye, which was obtained in Central America from the leaves of the *Indigofera suffruticosa* plant (commonly called *añil*), and palygorskite, a clay mineral of fibrous nature very common in the Yucatan peninsula. Maya blue still keeps many secrets to scientists and archaeologists, even though it has been studied for more than 50 years. Perhaps the most striking property is that it is extremely resistant to chemicals (acids, alkalis and solvents) and bio-degradation, which has permitted the survival of many artworks during centuries under the drastic temperature and humidity conditions of the tropical forest. Although several theories have been formulated, the origin of this stability is still not clear.

Iron is not a main component of Maya blue: it is neither present in indigo ($C_{16}H_{10}N_2O_2$) nor in the theoretical formula of palygorskite $Si_8O_{20}Al_2Mg_2(OH)_2(H_2O)_4.4(H_2O)$. However, the existence of Fe nanoparticles has been reported in archaeological Maya blue, which may be originated from the *añil* plant, and which may be the cause of the great resistance of the pigment [7]. Another paper [8] presents a XAS (XANES and EXAFS) study at the Fe *K*-edge of two archaeological samples containing Maya blue from the Maya zone (Chichén Itzá and Tulum). The authors analysed the experimental XANES data and found that the XANES is compatible with that of goethite. Their EXAFS results seem to be compatible with the main presence of goethite.

In this paper, we present new measurements of Fe *K*-edge XANES on archaeological samples from Cacaxtla (Tlaxcala, Mexico) and compare the spectra with several references: Maya blue prepared in the laboratory, goethite, hematite, and metallic iron. The analysis of our experimental data indicates that the Fe in Maya blue is due to the substitutional iron always present in natural palygorskite.

2. Experimental

Fe *K*-edge XANES spectra were recorded at room temperature at the ESRF undulator beamline ID26 [9] operating in four bunch mode, with an approximated photon flux of 10^{11} photons/s/0.1%bw. A fixed-exit Si (2 2 0) double-crystal monochromator was used, providing an energy resolution of about 0.4 eV at the Fe *K*-edge. For all spectra, a metallic Fe reference foil was used to provide an energy calibration for the monochromator. We used two silicon mirrors for the rejection of the harmonics coming from the incident X-ray beam. XANES data were recorded in quick-scan mode by simultaneously scanning the monochromator angle and the undulator gap with a typical energy step of 0.25 eV and counting 20 ms per point. Each scan took 30 s. The spectra were acquired in fluorescence mode, using a Si photo-diode, and I_0 was recorded by another Si photo-diode from the fluorescence signal of a titanium foil. The samples were positioned at 45° with respect to the beam. For all experimental spectra, we subtracted a linear pre-edge background and then we normalized the edge-jump to one.

We measured two archaeological samples from Cacaxtla (Tlaxcala, Mexico) mural paints. They contain several colours (red, black and two hues of Maya blue). They have been previously