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Microanalysis study of archaeological mural samples containing Maya blue pigment☆

M. Sánchez del Río[a,*], P. Martinetto[b], A. Somogyi[a], C. Reyes-Valerio[c], E. Dooryhée[b], N. Peltier[b], L. Alianelli[d], B. Moignard[e], L. Pichon[e], T. Calligaro[e], J.-C. Dran[e]

[a]*ESRF, BP220, F-38043 Grenoble, France*
[b]*Laboratoire de Cristallographie, CNRS, BP166 F-30842 Grenoble, France*
[c]*INAH, Mexico DF, Mexico*
[d]*INFM-OGG c/o ESRF, BP220, F-38043 Grenoble Cedex, France*
[e]*C2RMF, 6 Rue des Pyramides, F-75041 Paris Cedex 01, France*

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Abstract

Elemental analysis by X-ray fluorescence and particle induced X-ray emission is applied to the study of several Mesoamerican mural samples containing blue pigments. The most characteristic blue pigment is Maya blue, a very stable organo-clay complex original from Maya culture and widely used in murals, pottery and sculptures in a vast region of Mesoamerica during the pre-hispanic time (from VIII century) and during the colonization until 1580. The mural samples come from six different archaeological sites (four pre-hispanic and two from XVI century colonial convents). The correlation between the presence of some elements and the pigment colour is discussed. From the comparative study of the elemental concentration, some conclusions are drawn on the nature of the pigments and the technology used.

Keywords: Maya blue; Organo-clay complex; Pigment; Mural painting; PIXE; XRF; Elemental analysis

1. Introduction

Ancient American cultures have developed highly sophisticated painting techniques manifested in beautiful artworks. In particular, mural painting is in the tradition of the Mesoamerican civilization. There are magnificent examples of the pre-hispanic mural art, like the paintings of Bonampak, Cacaxtla and Teotihuacan. During the colonization, churches and convents were primarily decorated with frescos, in opposite to European religious art that preferred altarpieces. In the XX century, well-known Mexican artists like Rivera, Orozco and Siqueiros mastered the fresco technique. The fresco painting requires a particular technological know-how to prepare the walls, substrates, mortar, plaster, binding media and pigments. Not all pigments can be used, because they must bind perfectly with the calcareous materials, otherwise the artwork is destroyed sometime after its creation. Moreover, the pigments must be deposited in wet (*buon fresco*) in a limited time, also requiring high artistic capabilities. In this work, we perform elemental analysis of pigments in Mexican mural samples with the aim of identifying the pigments and obtaining information on the technological and historic aspects.

Among the different aspects that can be studied in the mural paintings, there is a pigment with particular interest: Maya blue [1–3]. It is typical of Maya culture and 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. Maya blue is very different from any other pigment used in other parts of the world. It was rediscovered by Merwin [4] in 1931 when

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* Corresponding author. Tel.: +33 476882513; fax: +33 476882542.
E-mail address: srio@esrf.fr (M. Sánchez del Río).

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studying paintings from Chichén Itza's Temple of Warriors. Perhaps, the most striking property of Maya blue is that it is an almost indestructible pigment: it resists concentrated acids, alkalis and organic solvents. This extreme stability explains why many artworks have survived during centuries under the drastic conditions of temperature and humidity of the tropical forest. Because of its high stability, the pigment was originally believed to be a pure mineral. Then, X-ray diffraction studies showed the presence of palygorskite, a clay mineral of fibrous nature. Shepard [5] suggested that the blue colour was due to the presence of indigo. These ideas strengthened in the 1960s, when palygorskite (and also sepiolite) was combined with synthetic indigo forming complexes with similar characteristics to the pigment found in archaeological samples [2,3]. Then, it was well established that Maya blue is made of two ingredients: indigo and palygorskite. In 1993, Reyes-Valerio [1], based on historic documents, proposed and reproduced a method to fabricate the pigment that is compatible with the pre-hispanic technology. He used the leaves of the *Indigofera suffruticosa* plant, well known in Central America, and *sacalum*, a white earth coming from the Yucatan Peninsula, known by the Mayas, which is mainly composed of palygorskite.

The chemical origin of Maya blue stability has initiated a scientific debate revived at present, with theories suggesting that the indigo seals the channels in the palygorskite clay [2,6] or penetrate into the channels [3,7,8]. From the archaeological and anthropological point of view, it is unknown how the Maya Blue originated and spread to many cultures in Mesoamerica. Many other questions have not been answered yet, as the dating of the artworks, origin of the used clays (mined or collected in nature), and the reasons why it disappeared in the late XVI century.

In this work, we present trace element measurements on archaeological mural samples containing the Maya blue pigment. The mural samples come from six different archaeological sites (four pre-hispanic and two from XVI century colonial convents). The goal of these studies on archaeological samples is to obtain information of the components of the pigments and substrates, and relate this information with archaeological questions (origin of the clays, painting techniques, colours, etc.).

2. Experimental results and discussion

Archaelogical samples from six different sites were provided by one of the authors (C. Reyes-Valerio). They were obtained with the courtesy of the Mexican Instituto Nacional de Antropología e Historia (INAH). In particular, we are indebted to Dr. Alejandro Martínez Muriel for the samples from Cacaxtla and Tamuin.

Five samples studied come from Mexican pre-hispanic archaeological sites: two from Cacaxtla (Tlaxcala, ca. X–XIII?) [sample codes: CA1 and CA2] and the others from Tamuín (San Luis Potosí, Huastec culture, ca. XI, XII) [TAM], El Tajín (Veracruz, Totonaca culture, ca. XI–XII) [TAJ] and Tajín Chico (Veracruz, ca. XI–XII) [TAC]. Two other colonial samples come from Mexican Franciscan convents: Cuauhtinchan (Puebla, 1550–1570?) [CUA] and Jiutepec (Morelos, 1540–1570?) [JIU]. Several samples are shown in Fig. 1.

The spot- and scanning μ-X-ray fluorescence measurements were performed at the ID 22 undulator beamline of the ESRF in single bunch mode. The beam was monochromatized to 15 keV using a double crystal Si [111]

Fig. 1. Picture of three samples: left: Tamuin (TAM), center: Cacaxtla (CA2), right: Jiutepec (JIU). On the edge of TAM, it can be clearly observed an underlying red layer.

monochromator, and focused by a Kirkpatrick-Baez mirror system into a micrometric spot (about 1.2 μm vertically and 3 μm horizontally). The sample was mounted on a sample stage containing two translation and a rotation motor stages and was monitored using an optical microscope. The X-ray fluorescence spectra were collected by a Si(Li) (Gresham) solid-state detector of 140 eV/Mn-K_α energy resolution.

PIXE experiments were conducted at the AGLAE (Accélérateur Grand Louvre d'Analyse Elementaire) [9] located beneath the Musée du Louvre in Paris. The PIXE facility is based on a 6SDH-2.2 MeV tandem Pelletron from National Electrostatics. A submillimeter beam was used and the sample was usually scanned in order to average over a 0.5×0.5 mm^2 zone. Objects were set on a 3-D sample holder monitored by a video camera that ensured a correct position of the beam normal to the mural sample surface. Two Si(Li) detectors oriented at 45° to the proton beam recorded the X-ray spectra, being dedicated respectively, to the low energy X-rays (0.3–10 keV) from low-Z major elements of the matrix, and the high energy X-rays (5–40 keV) emitted by trace elements.

3. Results of XRF experiment

Microfluorescence experiments were performed at the ESRF ID22 beamline on two samples, TAM and CA2. All

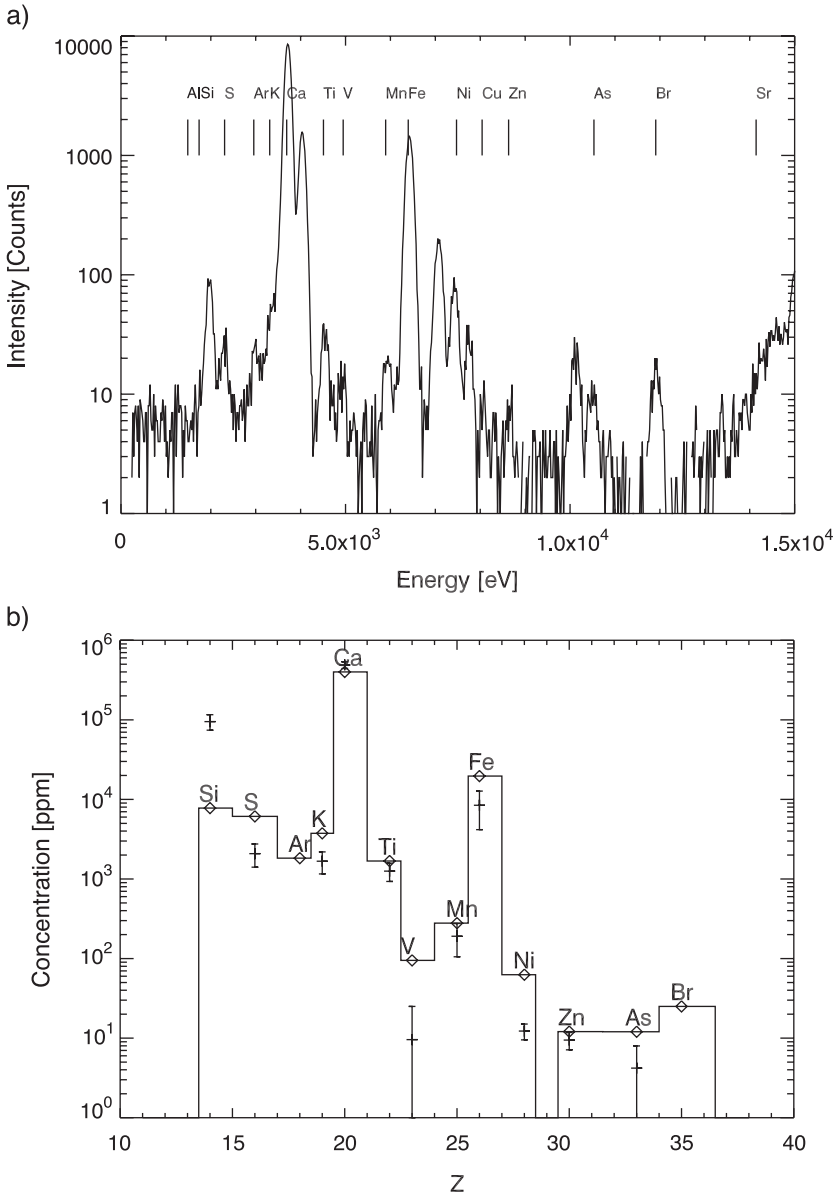

Fig. 2. (a) XRF spectra of the Maya blue pigment from the sample from Tamiun, recorded at ESRF/ID22. (b) Elemental concentration inferred from the XRF spectrum (diamonds) compared with PIXE data on the same sample (crosses and error bars of one standard deviation, calculated from the measurements on six different positions on the sample).

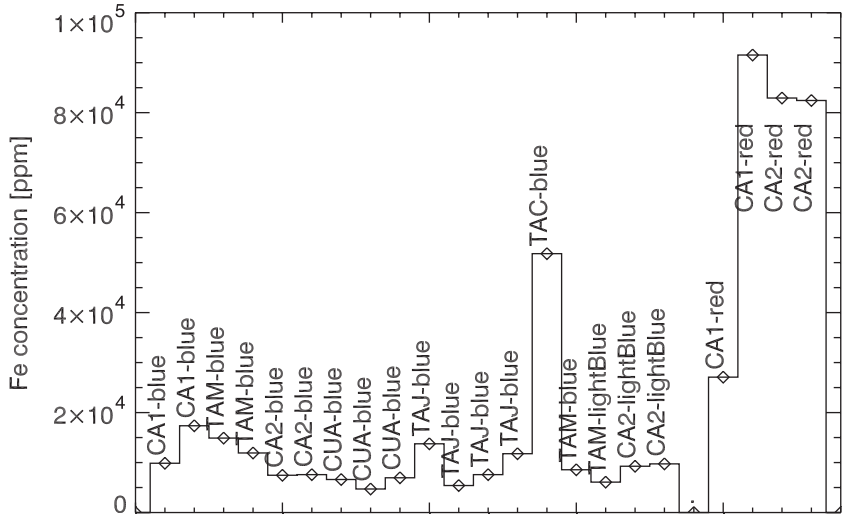

Fig. 3. Concentration of Fe in blue and red pigments from the samples studied, showing the dominant concentration of Fe in red.

recorded spectra show high concentration of Ca and Fe. A typical spectrum recorded by pointing the beam to the blue pigment in TAM sample is shown in Fig. 2a. A semi-quantitative analysis was done in the following way: (i) the XRF spectra were fitted using the AXIL [10] code to obtain the net peak areas corresponding to the characteristic X-ray lines of the different elements; (ii) we supposed an infinitely thick $CaCO_3$ matrix (thick target formula in p. 43 of Ref. [11]); and (iii) we calculated the concentrations of the measured elements from their peak area intensities taking into account their fluorescence yields and the absorption of their characteristic X-ray lines in air and within the 8-μm Be detector window. The relative concentrations were obtained by normalizing with the supposed Ca amount in the matrix (40%). The secondary and higher order effects were neglected during the calculation. This procedure gives the concentration results in Fig. 2b, which are compared with the more precise PIXE quantification (see later).

The presence of Ca is explained by the fact that it is a *fresco* painting. The plaster is created with lime (CaO) that becomes slaked lime ($Ca(OH)_2$) when mixed with water. The pigments are applied to this substrate in wet and, during the drying process, part of the slaked like flows to the surface and reacts with CO_2 from air, forming a crystalline layer of $CaCO_3$ that makes fresco paintings very resistant to climatic conditions (waterproof) thus conserved for a long time.

The presence of Fe can be explained from several origins: (i) Fe oxides, in particular hematite (α-Fe_2O_3), are used as red pigments in the murals, and it could also be present as residuals or by mixing pigments in other colours, like in blue; (ii) Fe is very frequently found in minerals used to prepare the substrate ($Ca(OH)_2$ mixed with sand, clays and other minerals); (iii) Fe is always present in palygorskite (the main component of Maya blue) as cation substitutions; and (iv) it has been suggested that Fe impurities in Maya

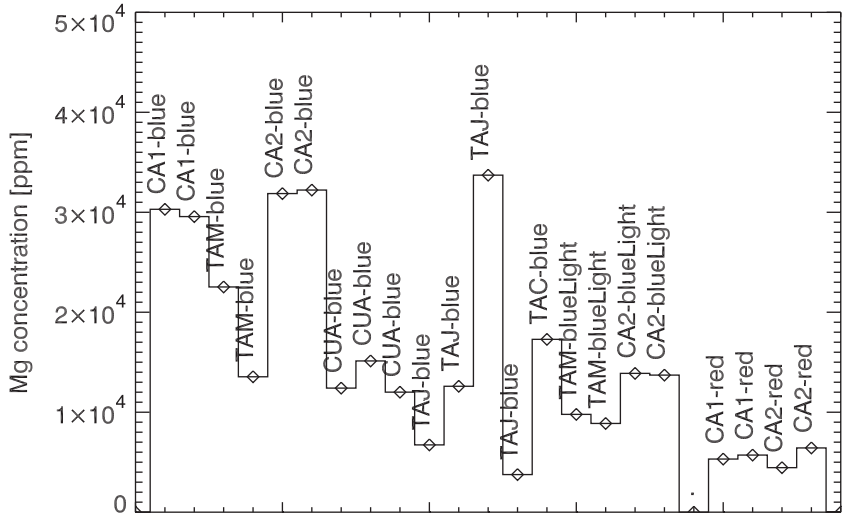

Fig. 4. Concentration of Mg in blue and red pigments from the samples studied, showing the dominant concentration of Mg in blue.

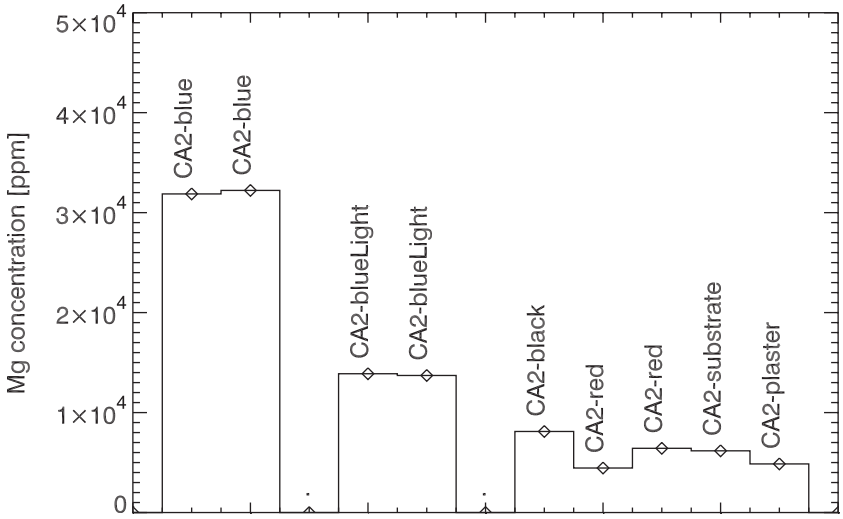

Fig. 5. Concentration of Mg in several positions on the CA2 sample. From the Mg concentration, it can be observed that the concentration in blue is more than twice that in light blue.

blue pigment coming from the *Indigofera* leaves are fundamental for the stabilization of the pigment [12]; however, this hypothesis has been discarded by several authors [6,7]. We certainly cannot distinguish Fe from these diverse origins, but we certainly found more Fe in the red pigment. Moreover, Fe is found in the substrate and also in samples of raw palygorskite clay. We performed line scans showing a large variation of major element concentrations. It evidenced the granular structure of the sample surface. It can be observed by visual inspection or optical microscopy that in these samples the blue seems to be painted on top of a red layer, and this is a reason why the concentration of Fe can rise in some areas, corresponding to red grains or parts where the overlapping blue layer is deteriorated. In addition, the black colour (charcoal) in the Cacaxtla sample is found on top of a blue layer (itself on top of red).

4. Results of PIXE experiment

PIXE spectra on the different pigments in the samples from the six archaeological sites plus some references

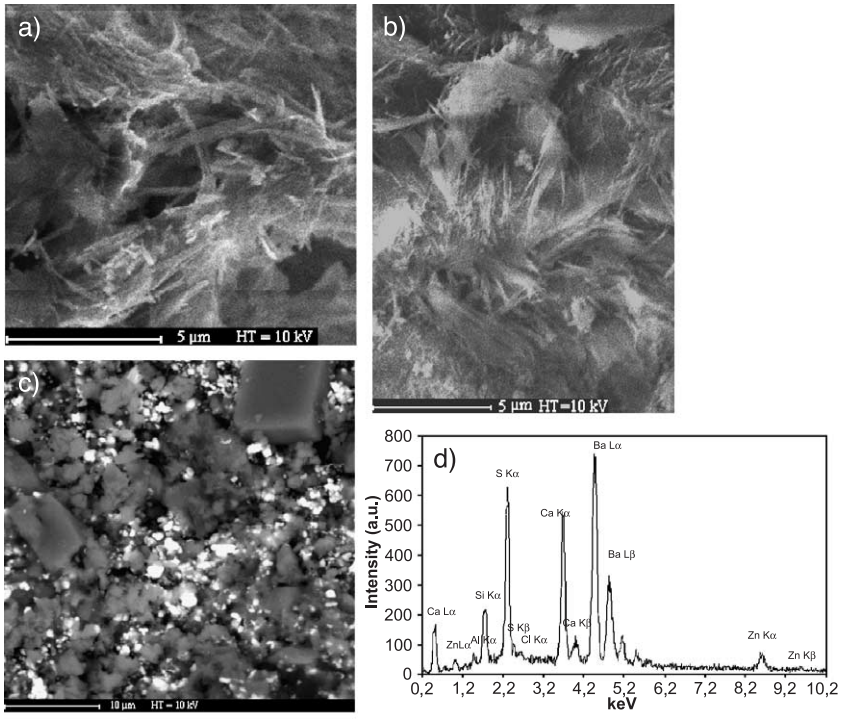

Fig. 6. SEM images of: (a) synthetic Maya blue, (b) palygorskite clay, (c) pigment from Jiutepec sample. The latter image, recorded in backscattering mode, shows large crystals of calcite and bright grains containing heavy elements. (d) SEM-EDX analysis of a bright grain, showing a high content of Ba and Zn.

(palygorskite, synthetic indigo, modern Maya blue prepared by one of us [1]) were recorded at the AGLAE accelerator. Elemental concentration analysis was done using the GUPIX code [13] and calibration was done using the BE-N standard. The analysis is automated using a graphical user interface developed at AGLAE that runs GUPIX. GUPIX makes a fit for each spectrum, combines the results of the low energy and high energy detectors and writes all the results to a spreadsheet page very convenient for making graphical comparisons using histograms.

A Fe analysis was done in order to identify its presence in the red pigment and in the other sample areas. It can be observed in Fig. 3 that Fe concentration is high in the red zones and it is usually below 2% in the blue ones (with one exception TAC-b).

The presence of Fe in the blue areas could originate from three reasons: (i) mixture of the blue pigment with red pigment (or different layers of paint, as discussed before), (ii) the presence of Fe in the plaster or in the substrate and (iii) the Fe impurities in Maya blue. Therefore, it is not possible to assign unambiguously the presence of Fe to any of these possibilities.

Magnesium is more present (2–4%) in the blue rather than in the red (Fig. 4), plaster and substrate (usually below 1%). Mg is a main component in palygorskite, the theoretical formula of which is: $[Si_8Mg_5O_{20}(OH)_2](H_2O)_4 \cdot 4H_2O$. Thus, a high concentration of Mg in the samples is assigned to Maya blue. In particular, in the case of the Cacaxtla CA2 sample, it is also found that the Mg concentration in the blue pigments is significantly more important than in the red zones or in the substrate and plaster; therefore, Mg can be assigned to blue. Moreover, this sample contains two different hues of blue (Fig. 1) and an interesting conclusion related to the pigment preparation technique can be extracted. It is remarkable that the concentration of Mg is lower (less than 50%) in the light blue than in the dark blue (Fig. 5). This means that the Maya blue pigment was probably mixed with other Mg-free compounds to make it clearer, or may be to use a thicker (or several) pigment layer. We can certainly discard the hypothesis that different Maya blues were prepared with the same clay using different concentration of indigo, which would give similar Mg concentration. The pigment layer, although thin, is quite opaque; therefore, thicker layers of the same pigment would not give, in principle, a so important hue variation as it is observed in the sample. If Maya blue was mixed with other compounds to make it clearer, these compounds should be Ca-based (Ca carbonate or oxide) because the two blues do not present differences in other trace elements.

Other elements like Na, K, Al, S, Ti, Ni, Mn and Sr are found in the pigments, but we could not identify a particular role or observe any particular difference from one sample to another.

5. An unknown blue pigment from Jiutepec convent

One of the mural samples, from the Franciscan convent Jiutepec (JIU), exhibits elemental concentrations very different from all the others. A visual inspection of this sample (Fig. 1) shows that it is much more deteriorated than the other samples, and the blue pigment layer tends to separate from a reddish substrate. The high concentration of the elements S, Ba and Zn is determinant to assess the originality of this blue pigment. This blue is not Maya blue and further investigation was started in order to try to identify the type of pigment that it contains.

We have examined with a scanning electron microscope (SEM) a microsample of the pigment layer detached from the mural sample JIU, and compared it with a synthetic sample of Maya blue prepared by Reyes-Valerio (sample #24 described in Ref. [1]) and with palygorskite (Fig. 6a) clay. These pictures clearly show a fibrous structure in the

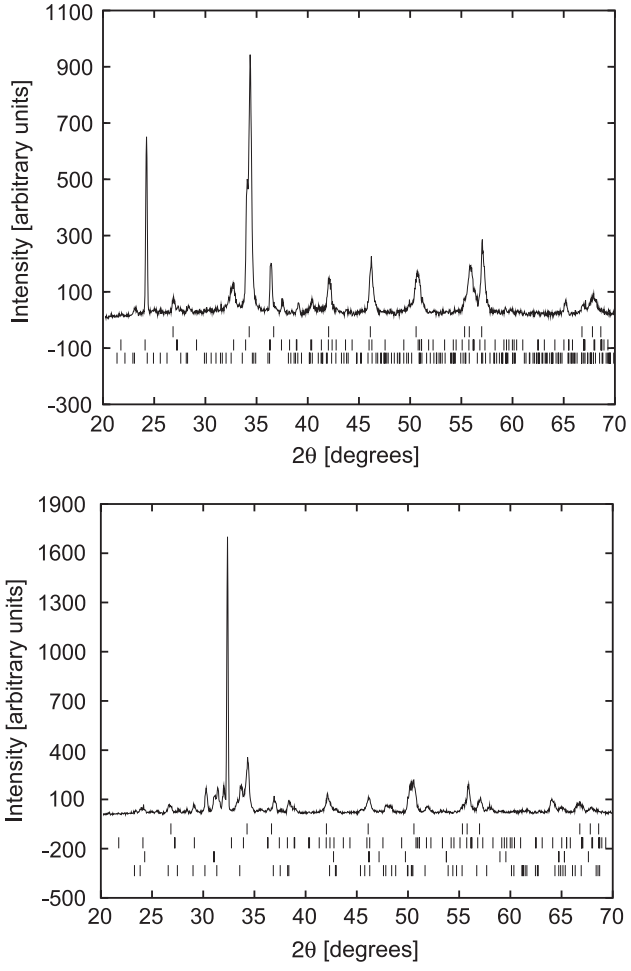

Fig. 7. Top: XRD pattern of the blue pigment from the Cacaxtla sample (CA1). The vertical bars indicate the Bragg positions of the three identified phases: calcite, gypsum and palygorskite (from top to bottom). Bottom: XRD pattern of the blue pigment from Jiutepec. Calcite, gypsum, quartz and barite (from top to bottom) are identified.

raw clay also present in the Maya Blue samples. This structure is not found in JIU, confirming that it is not Maya blue. This is further confirmed by the X-ray spectrum obtained with electron bombardment, which shows a high contribution of Ba, Zn and S (Fig. 6b), in agreement with the PIXE results.

X-ray powder diffraction (XRD) measurements were performed with the aim to obtain the composition of the Jiutepec blue. The Jiutepec sample and a Maya blue sample (CA1) were studied using a diffractometer designed for non-destructive measurements on archaeological samples at the C2RMF laboratory in Paris. The XRD pattern for the Cacaxtla sample is shown in Fig. 7a, where in addition to palygorskite (in Maya blue), calcite ($Ca\ CO_3$) and gypsum ($Ca\ SO_4.2\ H_2O$) are found to be present. It is worth remarking that this spectrum has been recorded directly on the sample using a non-destructive procedure. A non-destructive XRD synchrotron experiment able to identify palygorskite in Maya blue has been already reported [14]. Fig. 7a clearly shows that we were able to identify palygorskite in an archaeological sample containing Maya blue using laboratory X-ray equipment. The XRD pattern of JIU is shown in Fig. 7b. In addition to materials (calcite, gypsum and quartz) commonly found as ingredients of the substrate, barite ($BaSO_4$) is identified. Using the JCPDS database, it was not possible to find a Zn-based compound compatible with the experimental diffraction pattern.

Among the pigments reported in literature [15], only lithopone (a co-precipitated pigment of ZnS and $BaSO_4$) could be consistent with the X-ray fluorescence and diffraction results. But lithopone itself is not a good candidate for two reasons: (i) it is white (perhaps a colorant like indigo could be used to give the blue tonality) and (ii) lithopone is an artificial pigment invented in the XIX century (Gettens and Stout [15] report its invention in 1874), thus it was unknown when the murals were painted (ca. XVI). A restoration using this pigment looks improbable. Further studies are being carried out to try to identify the pigment, by using synchrotron microdiffraction and Raman spectroscopy.

6. Conclusions

Archaeological samples from six Mexican sites were studied by trace element analysis. We found the presence of Fe impurities in all samples. This presence cannot be assigned exclusively to the clay in Maya blue, and must be also related to the red pigment and other minerals used in plaster and substrate. In a sample from Cacaxtla, we found different concentration of Mg in different blue hues. An explanation to this fact is that the artist mixed Maya blue with other Ca-based compounds to make it clearer. We found in several samples two or more layers of paint. The sample from Jiutepec convent (Morelos, Mexico) is the only case in which the blue pigment is not Maya blue. This is an original finding, as the blue pigment from Mexican convents in the same period is Maya blue. Preliminary investigations (SEM and XRD) carried out to identify this pigment suggested a complex rich in Ba and Zn but further investigations are needed to explain the origin of the blue colour.

Acknowledgments

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