

# Analysis of prehispanic pigments from “Templo Mayor” of Mexico city

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The application of modern electron microscopy and X-ray diffraction techniques to the study of ancient pigments has proved to be very useful. In the present work we report the study of pigments from Mexica (Aztec) culture which developed in Central Mexico from 1325–1521 AD; we study the blue, ochre, red and black pigments. We found in the most cases the paints were made of a clay substrate that contained metal particles such as Fe, Ti, Mn and Zn, in different phases. This technology was found similar to that of earlier mesoamerican cultures. © 2001 Kluwer Academic Publishers

## 1. Introduction

The application of materials science techniques analysis to prehispanic pigments has produced very interesting results in the study of origin and manufacturing of those materials [1–3]. In particular the use of electron microscopy has become an important tool, because its possibilities of obtaining the structural, chemical and crystallographic characterization on the samples. The combination of SEM, TEM, X-ray diffraction and FTIR with molecular simulation methods using, can be helpful to understand the structure and the physical properties of these materials [4]. The comparison of experimental and simulated analytical data can help to a full characterization of these paints [5].

Localized in the Mexico City downtown, the “Templo Mayor” (main Temple) represents one of the most important prehispanic building of Mexica culture which develops in the Mexico valley during 1325–1521 AD. The Mexica (or Aztecs) build a great civilization and were the ones that faced the Spanish conquest in 1521. Their main city Tenochtitlan was destroyed by the Spanish conquests over its place Mexico city was built. In 1978 the Templo Mayor ruins were discovered. The Mexicas built the temple in the Late Post-classic period. Several mural paintings as shown in Fig. 1 were found, which are important cultural expressions, as the case of the “Recinto de los Guerreros Aguila”. Which was built in several steps with a rich diversity of paint techniques, over different plasters. In “Templo Mayor” site pigments of different colors (Blue, red, yellow, black and white) were found which make a polychromatic palette for the murals, employed over different mount-

ing materials. In some samples, the pigment was applied directly on the mud wall and in other cases on different kind plaster (based on small or coarse aggregates). This is an important point due to the adhesion properties of pigments, which are mainly in function of interaction between plaster and pigment. However it is important to consider the preservation materials used in the murals and the environmental factors that affect their properties, as humidity, pressure, pollution, etc. These factors may cause the structural modifications in pigments and consequent changes in their chemical and physical properties. In the Fig. 2 we shown schematic of the mural, in which it is possible to observe the stratigraphic layer from a mural painting, to help to understand the different kind of interactions that are presents.

In this work we use the electron microscopy, X-ray diffraction, FTIR and molecular simulation techniques



Figure 1 Mural paint of “Templo Mayor”.

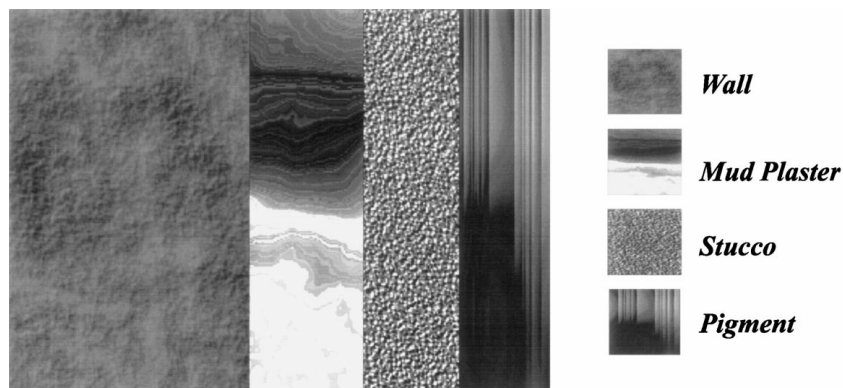


Figure 2 Stratigraphic scheme of mural painting.

for the characterization of pigments found in the “Recinto de los Guerreros Aguila” of “Templo Mayor”.

## 2. Experimental methods

In order to analyze the composition and the structure of the paint materials used by the Mexicas, different pigment were analyzed by techniques of electron microscopy (scanning, and high-resolution transmission) combined with energy dispersion X-ray analysis and FTIR.

The stratigraphic morphology of some fragments have been identified by using SEM with secondary and back scattering electron signals, finding characteristic material evidences of each strata; the elemental chemical composition was determined by means of Energy Dispersion Spectroscopy (EDS) and its mineral composition using standard X-ray diffraction with the powder method. The structural characterization was analyzed by HREM. SEM PHILLIPS and TEM JEOL-4000FX were used for the microscopy analysis. A diffractometer SIEMENS D-5000 for the X-ray diffraction analysis was used. The crystal structure was obtained from electron diffraction patterns and High resolution images.

The models proposed for the pigments and their corresponding HREM, crystalline habit and X-Ray diffractograms were simulated by Cerius<sup>2</sup> software from Molecular Simulation Inc. [2].

## 3. Results

We started by studying the mounting material from the support materials. It was found that the material was a mixture of Calcite ( $\text{CaCO}_3$ ) with Anorthite sodic ordered ((Ca, Na)(Si, Al)<sub>4</sub> O<sub>8</sub>) and Albite ( $\text{NaAlSi}_3\text{O}_8$ ), which is classified, in the paglioclase mineral group (usually used for the primary slice before any pigment application). These materials were removed from the sample in order to analyze the pigment materials.

By using the EDS analysis in the SEM we found in the different color pigment, the elemental composition shown in Table I. The red is composed mainly by oxygen and iron but with a significant quantity of Al and Si; while Ochre has a bigger proportion of Si and Al together to O and the Fe percentage is smaller; even more for the Blue and Black pigments the Fe proportion is even smaller while the Si and Al quantities are larger. It is really significant the contribution of Mg in the case

TABLE I Elemental composition, % atomic (EDAX)

ELEMENT	Red M035	Ochre M035	BlueM039	Black
C	0.908	0.621	0.716	0.893
O	65.382	77.894	64.927	80.077
Na	-	0.280	-	0.411
Mg	-	0.479	5.906	0.644
Al	4.305	4.363	2.111	3.881
Si	5.978	9.867	21.89	11.009
P	0.181	-	-	-
S	0.372	-	0.781	-
K	0.872	0.441	0.227	0.453
Ca	1.099	1.261	0.956	1.231
Ba	0.852	-	-	-
Ti	-	0.271	-	0.131
Mn	-	-	-	0.287
Fe	20.049	4.524	2.714	0.983
Zn	-	-	-	-

TABLE II Mineralogical composition (XRD)

SAMPLE	PRESENT MINERALS
Red M035	Anorthite sodian, Montmorillonite, Hematite
Ochre M035	Calcite, Albite, Quartz, Goethite, Hematite
Blue M039	Albite, Anorthoclase, Palygorskite
Black	XXXXXXXXXXXX
Clay M004	Anortite
Mud plaster M040	Albite, Illite
Soil from a burial	Albite, Anorthite sodian

of Blue color in which their percentage is even larger than Al.

XRD was used to characterize the crystal structures in each pigment. The result of this analysis is shown in Table II. Where is observed the mineral composition of Red, Ochre, Blue and some components from the support materials such as clays and soil found mixed with the pigments. The main identified mineral crystals on the pigments are hematite for red, goethite, and calcite for ochre and palygorskite for blue. Based on this crystallographic characterization the structure models for the main mineral were build and are shown in Fig. 3.

The details of each pigment are as follows:

a) *Red*: The red pigment contained basically Hematite on mud plaster. In this case from EDS analysis we can observe that the quantity of Fe is major that in others pigments, around 20%, the rest elements as Si,

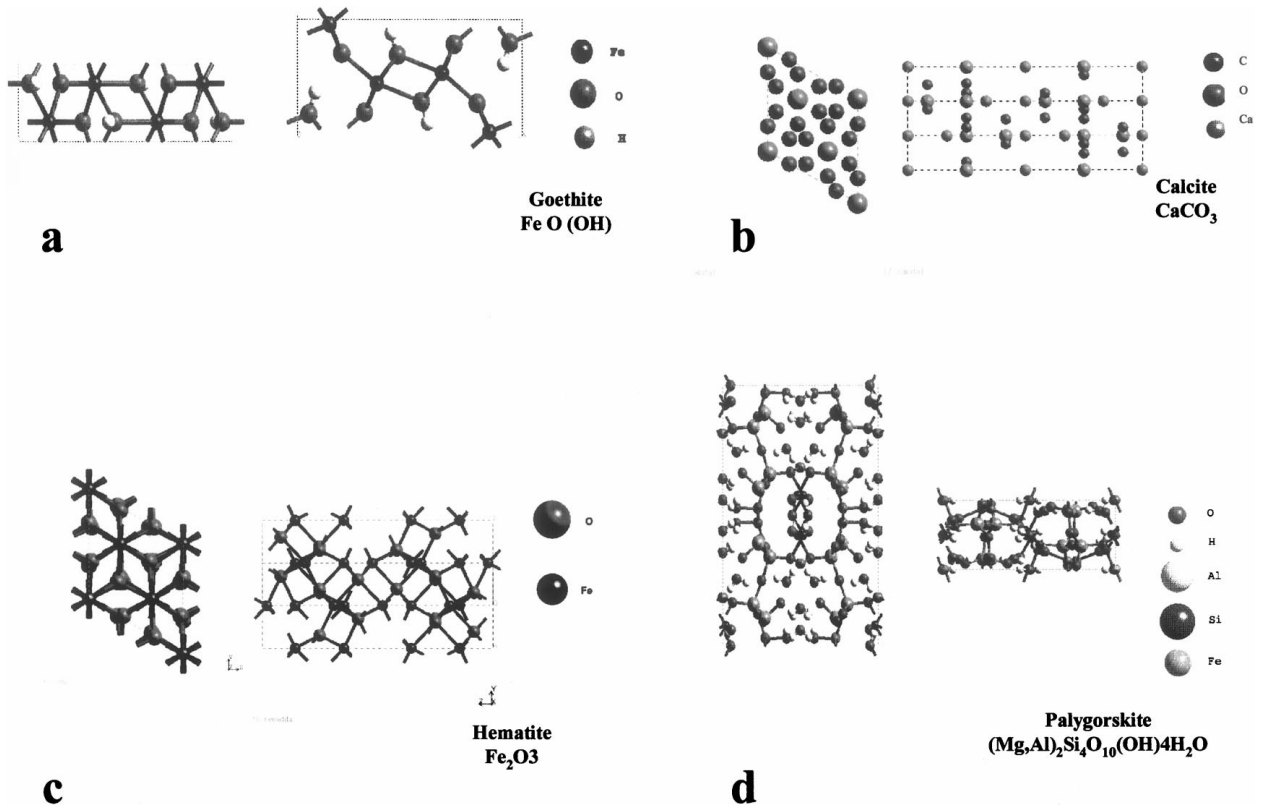


Figure 3 Unit cell view in two different orientations for each mineral found in pigments for the Aztec culture.

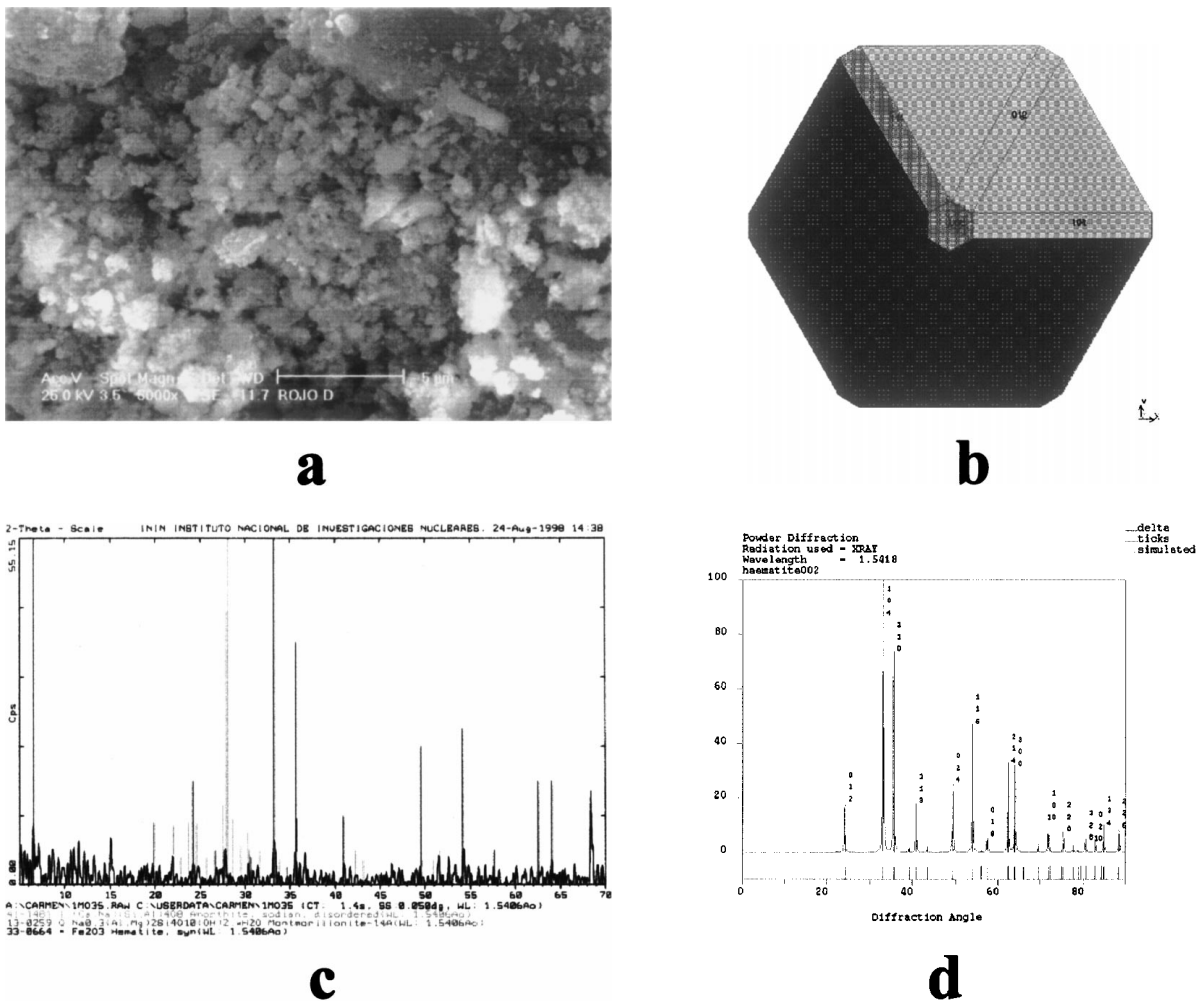
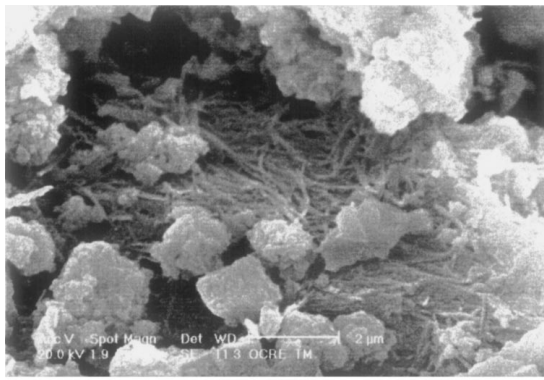
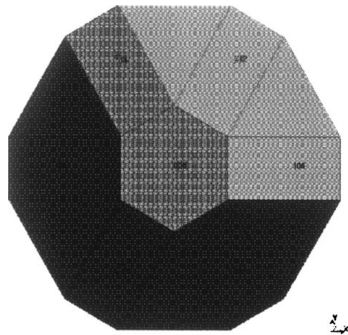


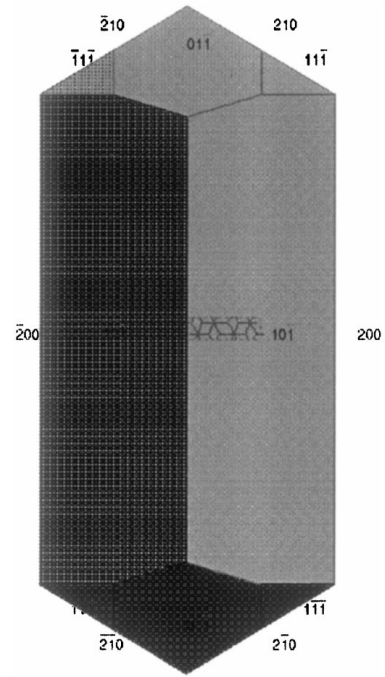
Figure 4 Results obtained for the red pigment which is composed by hematite ( $\text{Fe}_2\text{O}_3$ ). a) SEM secondary electron image showing the crystals. b) The expected habit for the hematite crystals. c) Experimental X-ray diffraction pattern of the red pigment. d) calculated X-ray diffraction pattern for hematite showing agreement with the one referred in c).



**a**

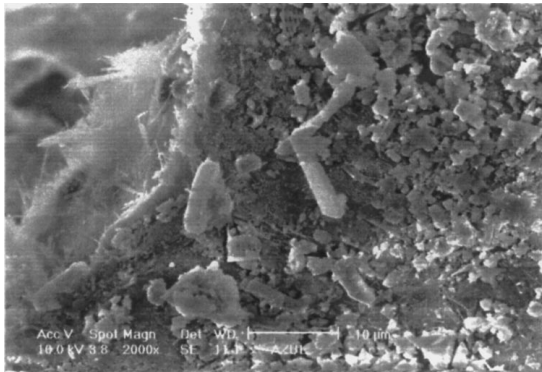


**b**

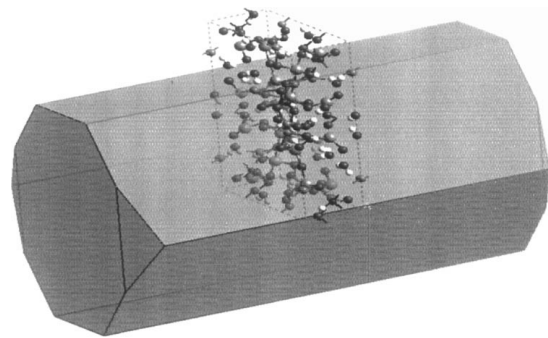


**c**

Figure 5 a) SEM secondary electron image showing the ochre color. Fibers and large crystals are observed that correspond to calcite and goethite mineral respectively. b) The expected crystal habit of calcite and c) the expected crystal habit of goethite.



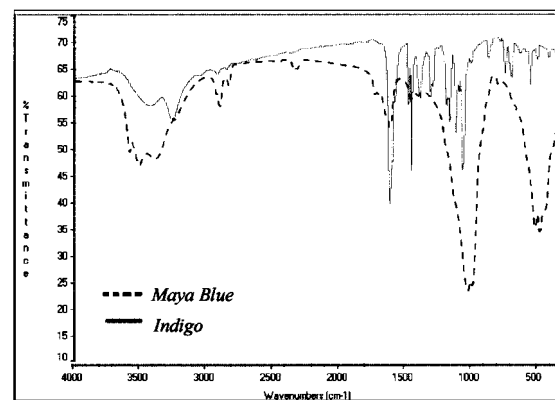
**a**



**b**



**c**



**d**

Figure 6 a) SEM secondary electron image showing the palygorskite crystals. b) The expected crystal habit of palygorskite. c) High-resolution images of the fibers from blue color. d) Maya blue FTIR spectrum.

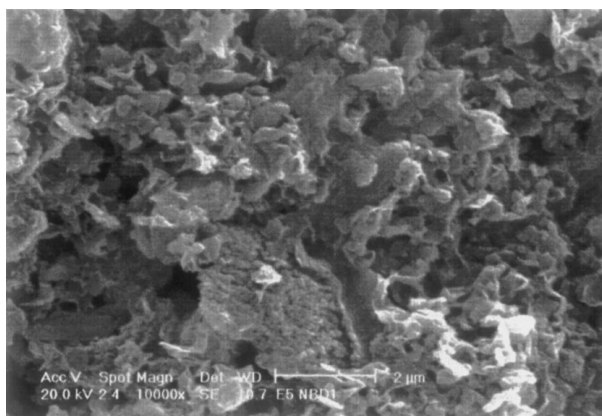
Al, S, K, Ca, Ba and C correspond to minor fractions of Feldspars and Carbonates. This can be observed, in the SEM micrograph (Fig. 4a), as aggregates with round shape that correspond with the crystal habit calculated (Fig. 4b). The corresponding experimental and theoretical diffraction patterns (Fig. 4c and d) corroborate the existence and predominance of Hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in the red pigment.

*b) Ochre:* For the case of the ochre pigment mount on the stucco, we found that this pigment contains around 4.5% of Fe and a major quantity of oxygen that the red pigment. Na, Mg, Ca and K can be associated with Feldspars such as Albite and Anorthite; Mg and Ca can be associated with Carbonates such as Dolomite and Calcite. We identified two kinds of minerals forming fibers and aggregates on the SEM micrograph (Fig. 5a). These morphologies correspond to the calculated habits for Calcite CaCO<sub>3</sub> and Goethite Fe O (OH) as shown in Fig. 5b and c). The corresponding X-ray diffraction patterns confirm the presence of these minerals by mapping the elements and with the SEM-EDS was possible to identify the fibers as Goethite and the aggregates as Calcite. Even when there are evidences of other structures the main contribution comes of these two compounds.

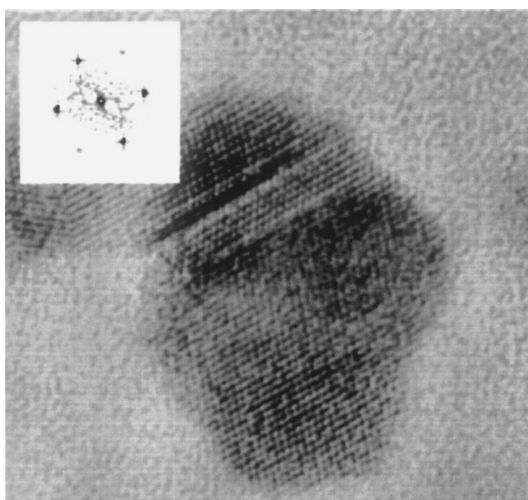
*c) Blue:* In the case of the blue pigment upon mud plaster, we can identify the major proportion in atomic percent of Mg (5.9%) and of Si (21.89%), these elements form the main part of chemical composition from Palygorskite clay, SEM images show two types of minerals in the shapes of square crystals and fibers (Fig. 6a). We identify these two minerals using X-ray diffraction as Calcite and Palygorskite respectively. High-resolution images of the blue color show the structure of the Palygorskite fibers growing morphology how is shown in Fig. 6b. The composition of this color is similar to composition to the Maya blue (Fig. 6c) which has been widely studied on the literature [1].

This pigment was analyzed by FTIR and we found that the main bands identified in synthetic indigo patterns are very close to the maya blue ones (Fig. 6d). In the sample of maya blue for a wavenumber of 1026.9 cm<sup>-1</sup> shows a tetrahedral substitution and in the case of the synthetic indigo for a wavenumber of 1072.49 cm<sup>-1</sup> shows a constraining of the C-N stretching bond; there are others bands which are quite similar as such as the ones shown in Table III.

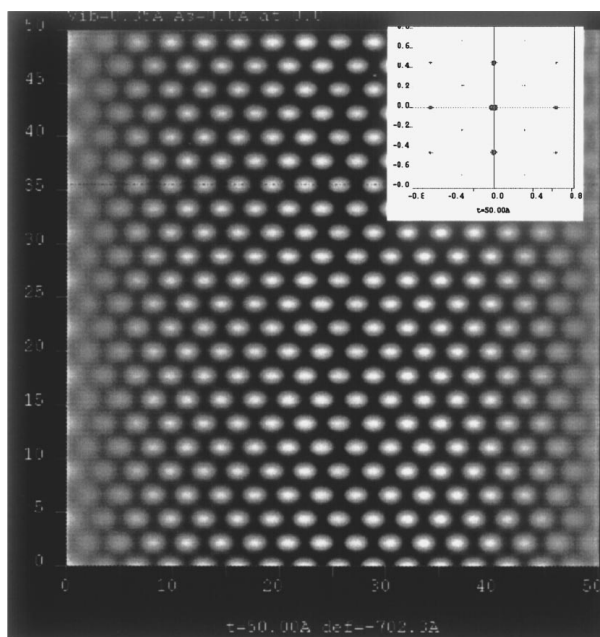
According to the literature, in layer clays can be introduced organic molecules with polar character (such as water, indigo, etc.). So we suppose that is possible to



**a**



**c**



**b**

Figure 7 a) SEM secondary electron image of the black pigment. b) Crystal habit expected for MnO<sub>2</sub> crystals. c) High resolution TEM image of the MnO<sub>2</sub> crystal.

TABLE III Characteristics wavenumbers from some bonds

Blue M039	Synthetic indigo
1638.6 cm <sup>-1</sup> zeolitic water	1626.35 cm <sup>-1</sup> N-H flexion
3430.12 cm <sup>-1</sup> zeolitic water	3269.4–3431.4 cm <sup>-1</sup> N-H stretching
474.9 cm <sup>-1</sup> octahedric substitution	XXXXXXXX

find indigo molecules into the channels of Palygorskite and these molecules could take the place of water molecules at determinate conditions. We can not identify molecules of indigo in the FTIR spectra, may be due to the low number of bonds N-H in the sample; the relation of indigo in the samples must be of 0.4% approximately.

*d) Black:* For this pigment we identified an elemental composition with manganese (0.287%) and the quantity of oxygen (80%) very common in the support materials is significant. In this case we have just one small sample, which was impossible to us to obtain XRD information, so then we used the HREM in conjunction with the EDS to identify the main component of this pigment. Results indicate that the material is made of clusters of MnO<sub>2</sub> mineral. The MnO<sub>2</sub> crystals tend to have crystalline habits as indicated in Fig. 7a–c. A HREM of this kind of crystals is shown in Fig. 7c. Relation *a/b* and the angle from the FFT was calculated using a program developed in the group [9] from the experimental HREM image, this analysis confirms that the structure of the manganese oxide is FCC. For verification purposes, the model and its HREM and diffraction pattern were calculated (Fig. 7b) and it shows a [111] orientation as the observed in the experimental evidences (Fig. 7c).

#### 4. Discussion and conclusions

The pigments were characterized with help of SEM, XRD, FTIR and HREM techniques, in function of the sample requirement. Furthermore using theoretical methods we corroborate the experimental results and we reproduced their crystal habits and XRD diagrams for the cases of Red, Ochre and Blue; in the case of the black pigment we used HREM and electron diffraction because not enough quantity of sample was available. Combination of theoretical and experimental analysis provide several advantages and the most important can be considered its easy way to determine and decide when we have evidences of several components which can not be easily identified in a sample.

Even that the studied pigments from “Templo Mayor” (late-post classic period during 1325–1521 AC/ Red Temple) were made by the Aztec culture, they are based on the same minerals by used other cultures, such the Mayas (late classic period during 250–

900 AC/Room 2 of Bonampak) [5, 6] or the Olmecas-Xicalancas of Cacaxtla (Epiclassic period during 750–950 AC/South wall “A” section) [7] in central Mexico.

It is not strange that in all samples were found calcite and quartz, due to that these are associated to the nature of the most of minerals identified from XRD analysis. It is imperative to identify the internal structure of these materials, because their properties depend of the atomic array, the elements composition and the kind of bond; the HREM is powerful tool that we help distinguish the distinct crystalline phases present in the samples, for example: the Palygorskite exist in monoclinic and orthorhombic forms. The HREM has demonstrated its advantages to distinct between different crystal phases when they are present in small samples as the used in this kind of studies; for FTIR analysis, is an excellent technique for obtaining information about occupancy into octahedric sites and bonds of crystalline water. If a cation is substituted by some different atomic radii element, we can observe displacement in the band frequency, for example: Fe atoms produce band with smaller frequency than Mg atoms when we refer to octahedric sites occupancy. These analysis provides a solid base for studies more specific and development of restoration techniques.

It is clear from our results that the Mexica culture used a technology previously developed by other cultures such as the Maya, this may imply a commercial or cultural relationship between the different culture who lived in this region and the mesoamerica area.

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