In-Situ Identification of Palygorskite in Maya Blue Samples Using X-Ray Powder Diffraction

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In spite of the abundance of colors found in the murals and other objects that correspond to the Classic Mayan period (600-900 A.D.), a peculiar hue captured the interest of researchers. The most well known researcher was Merwin who first identified the pigment in 1931.[1] In 1946 Gettens named the hue Maya blue, or Azul Maya, when it was believed to be found only in Mayan regions.[2] However, the pigment is encountered not only on wall paintings and pottery from ancient Mayan sites, but in many other places in Central America as well. Therefore, there are open questions as to whether there was ancient technology transfer by the Mayans to other cultures or if the other cultures discovered this technology on their own.

Reconstruction of the method that pre-Hispanic artists used to create exceptional paints has been a challenge. The pigment is not a copper mineral and has no relation to natural ultramarine, ground Lapis Lazuli or Lazurite as originally thought. The Azul Maya pigment is composed of a natural clay (Palygorskite) and a natural dye (indigo) and has unprecedented stability when exposed to acid, alkalis, solvents, and bio-corrosion.

This report presents the research conducted at the University of Texas El Paso (UTEP) and at the Instituto Nacional de Investigaciones Nucleares (ININ) that has been dedicated to the reconstruction of techniques used by Meso-american painters in the manufacture of the Maya Blue pigment. The work started as a result of the UTEP PI's (RRC) involvement with the Materials Research Society "Materials Science in Art and Archeology Group" which evolved into a collaboration with ININ and has been funded by the General Electric Faculty for the Future program.

In order to determine the nature of the pigment, it was necessary to apply synchrotron x-ray diffraction techniques to fragments of actual ancient Meso-american murals that exhibit the presence of the Maya Blue. The technique of choice for these studies is powder diffraction which relies on the fact that solid materials give distinctive diffraction patterns which can be used for "finger printing" of their crystalline phases. Powder diffraction has been used in the laboratory for the last 50 years for routine materials analysis. Bringing this well established technique to a synchrotron results in an ultra-high resolution instrument which allows unprecedented precision in the determination of crystal structures and thus the separation of mixed phase materials with very similar crystal structures. Beam line 2-1 at the Stanford Synchrotron Radiation Laboratory has been dedicated to powder diffraction and takes full advantage of the synchrotron source resulting in a very high resolution instrument capable of resolving lattice parameter differences as small as 0.03% at Zn K-edge (9659 eV).

The samples used in this work were provided by the Instituto Nacional de Antropologia e Historia. This study and others have indicated that the Indigo, which is accountable for the color of the pigment, locks into the channels in the Palygorskite clay creating the characteristic color and stability. In particular, high resolution transmission electrom microscopy (HRTEM) studies have suggested that pure samples of palygorskite are nearly impossible to obtain unless the channels are stabilized by the partial insertion of indigo, as found in Maya Blue. Synchrotron data of Maya blue is helping to validate the assertion that indigo is inserted into the clay structure because the small lattice parameter differences can be studied in detail. Additionally, for the first time, palygorskite has been identified from original mural fragments; the other studies were performed using material removed from the materials and ground into powders. This is particularly important because conventional x-ray instrument studies did not provide the resolution necessary to see specific impurities in the palygorskite phase which will eventually allow us to the elucidate the origin of the starting material used by Mayans and further understand the technology transfer.

The analyzed sample, Azul 117, is from Morgadal Grande, Mexico having dimensions of 5x3x3 mm and weighing approximately 1mg. We can see in Figure 1 and 2 optical micrographs of the mural fragment investigated. Figure 1 is a cross-sectional view showing two layers, a thick white layer, and a fine layer (approximately 50 μm thick) of blue green pigment of Maya Blue. In figure 2, a perpendicular view exhibits the classical Maya Blue seen by an observer of the murals. The sample was mounted on a sample holder using vacuum grease, analyzed and characterized at the x-ray powder diffraction (XRPD) station (Beam Line 2-1) at the Stanford Synchrotron Radiation Laboratory (SSRL). The wavelength used was 1.239Å (10Kev).

The diffraction pattern of the Azul 117, figure 3, indicates the presence of Palygorskite and Calcite. The simulated diffraction pattern (from the CERIUS2 program) of Calcite is overlaid on the experimental data as seen in Figure 3. Extraction of the Calcite reflection pattern leaves the Palygorskite peaks as the main component of the pigment. Figure 4 is an expansion of the early part of the diffraction pattern that clearly shows the difference in character of the Palygorskite peaks with respect to the Calcite. This is the first time that Palygorskite has been directly identified from an actual mural fragment. The quality of the data is such that we will be able to completely extract the Palygorskite pattern and refine the lattice parameters. Previous structural determination of the Palygorskite structure was obtained on very poor quality diffraction data obtained using conventional sources and small samples. Currently obtained synchrotron diffraction data are of very high quality allowing extraction of the Palygorskite diffraction peaks from the major impurity (Dolomite) and perform a structural refinement. Preliminary results indicate that the structure is significantly different from the reported structure. Obtaining a refined structure will then permit us to more closely define the Indigo/Palygorskite interaction. This identification will enable us to further understand the materials and techniques used by the ancient Maya artists.

In should also be noted that Maya Blue is a metal-free pigment of very high quality. Therefore, an understanding of the formation of Maya Blue may lead to a new class of metal free and thus environmentally benign paints.

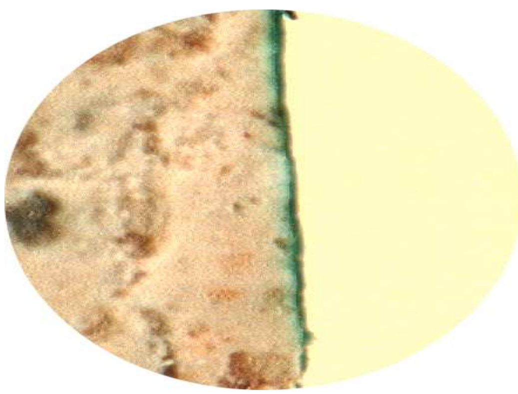

Figure 1. A cross-sectional view showing two layers, a thick white layer, and a fine layer (Approximately 50 mμ) of blue green pigment.

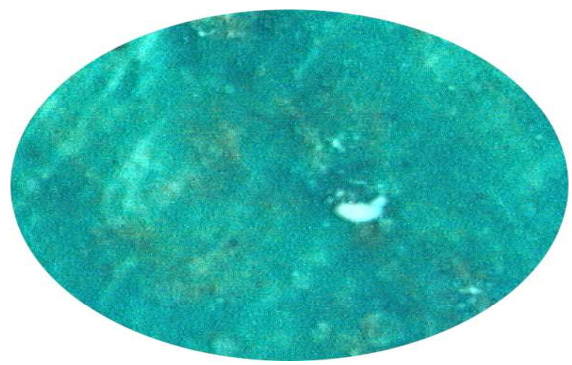

Figure 2. A perpendicular view of classical classical Maya Blue seen by an observer of the murals.

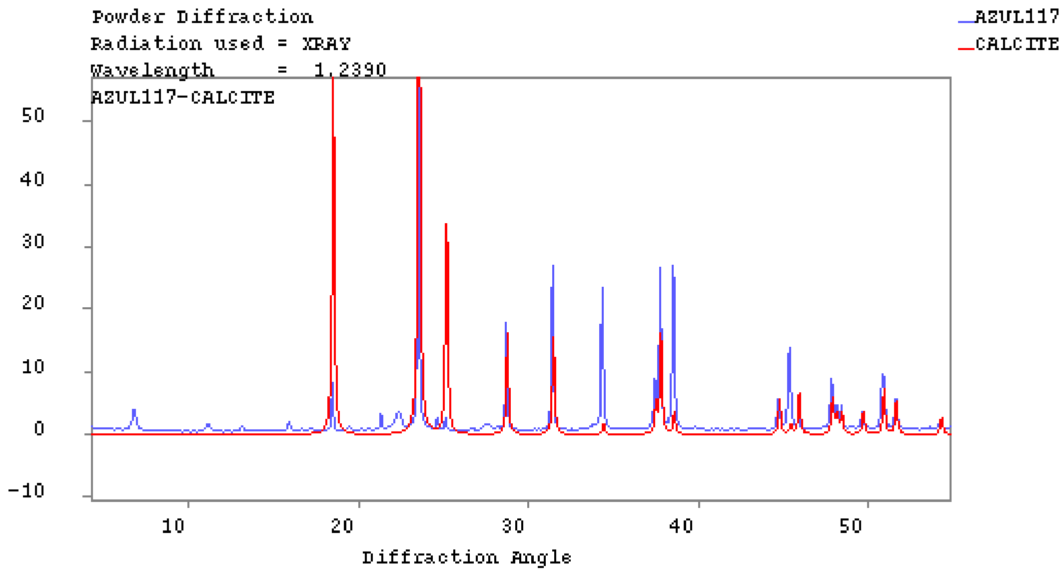

Figure 3. The diffraction pattern of the Azul 117 and simulated diffraction pattern (CERIUS2) of Calcite overlaid on the experimental data.

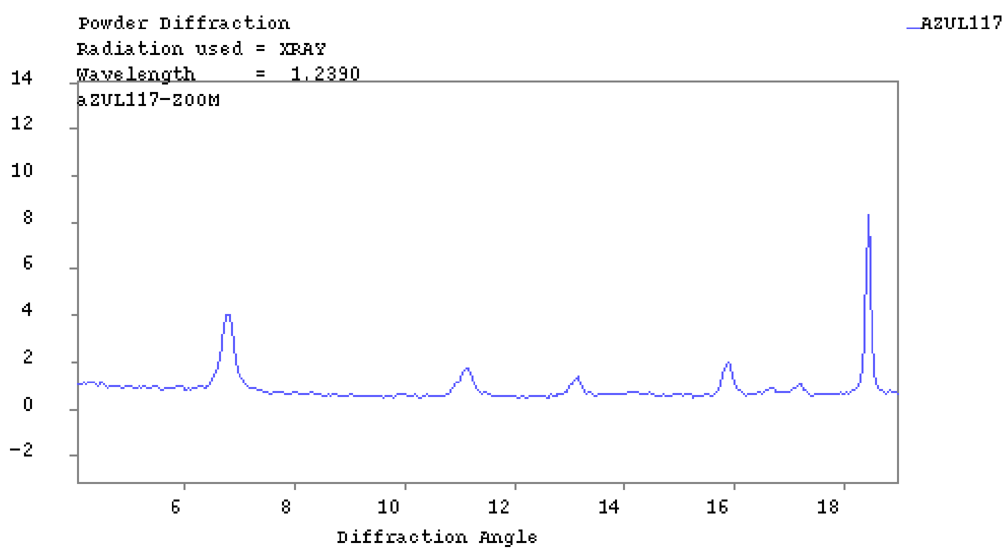

Figure 4. An expansion of the early part of the diffraction pattern that clearly shows the difference in character of the Palygorskite peaks with respect to the Calcite.

R. Chianelli students, L. Polette, C. Gutierrez Wing and N. Ugarte (University of Texas), working on a powder diffraction experiment on BL2-1.

References

1. Gettens, R. *J. Amer. Antiquity*, 27, 557, 1962.
2. Merwin, H. E. Chemical Analysis of Pigments; Merwin, H. E., Ed.; Carnegie Institution of Washington: Washington D.C., 1931; 406, p. 356.