Maya Blue: A Fresh Look at an Old Controversy

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It is extraordinary how two interpretations of the same evidence can lead to radically different conclusions. Beginning in 1962 an intellectual dispute arose over the composition of the pigment known as "Maya Blue" which caused and is still causing a great deal of confusion. The main argument is whether indigo can be detected in Maya Blue and, if present, was it the only colorant used to make the pigment.

"Maya Blue" is the name given to a pigment of extraordinary durability and richness of color which appears to have been widely used on murals, ceramics, and manuscripts in pre-Columbian America. The first examples date from the Maya Classic Period, and there is evidence to suggest that it continued to be used into the twentieth century (Gettens 1962:563; Torres 1988:126).

The composition and method of manufacture of Maya Blue has confounded and confused scholars and scientists for more than sixty years. The bright blue color endures weathering and harsh burial conditions. In the laboratory it resists solvent extraction and even boiling in concentrated nitric acid. Today, however, no historic or ethnographic data survive concerning this pigment or its manufacture.

In 1962 R. J. Gettens published an article describing the properties of Maya Blue and the failed attempts to identify fully the components of the pigment. He reported that the main constituent was identified in the 1950s by Elizabeth West Fitzhugh as the rare clay mineral attapulgite, known in Europe as palygorskite. In its natural state, however, attapulgite is usually white in color, and one analysis after another failed to identify an additive which could be responsible for the blue color.

Gettens also recorded the analysis of a sample of blue pigment labeled Azul de Tekax which had been collected by A. Everett Austin in the 1920s at Chichén Itzá. Fitzhugh's analysis of this sample led Gettens to conclude that this clay-based pigment had been reinforced with an organic dye, perhaps indigo. The pigment's resistance to degradation, however, suggested to Gettens (1962:563) that the colorant in Maya Blue was either a synthetic product or a mineral additive hitherto unidentified. In the same year (1962) Anna Shepard published her own convictions that Maya Blue could be a clay-organic complex, although she had formulated this opinion several years before (Shepard 1958:453). She reports that early attempts to extract or identify any organic component in archaeological samples had failed, but as samples became available she sent them to be analyzed by various analytical organic chemists. In referring to these analyses, however, she invariably reported that there was insufficient evidence to suggest an organic additive (Shepard and Gottlieb 1962).

In 1966, H. Van Olphen succeeded in preparing a blue pigment by mixing indigo and attapulgite and applying heat for an extended period of time. This pigment exhibited all of the properties of Maya Blue, including its resistance to solvents and acids. Since then, it was assumed by many researchers that indigo was the colorant used in the manufacture of Maya Blue.

Shepard, however, showed guarded enthusiasm. Her article with Pollock (1971) is seemingly the most complete work by any author on the subject. It covers virtually every aspect surrounding the riddle of Maya Blue—a history of early investigations including her own, a discussion of Van Olphen's findings, ethnographic and historic data concerning sources of clays and indigo-bearing plants, methods of dye preparation, speculations on the importance of Maya Blue in trade and culture, and analyses (both qualitative and quantitative) of clay samples including data from X-ray diffraction. Upon review of these gathered data, Shepard (Shepard and Pollock 1971:90) concluded that "consequently, identification of the colorant of Maya Blue is still a problem."

Anyone conducting a literature search today would be likely to trust this report on Maya Blue written by one of the most thorough and methodical researchers in the field of ceramic technology and ethnohistory. Several texts on the subject of Maya pottery decoration cite Shepard and Gottlieb (1962) as a main reference (e.g., Rice 1985) for information about this unusual pigment.

Littmann (1980:93) echoed her reservations most clearly when he wrote, "Yet in no case has the presence of indigo in Maya Blue been confirmed by any acceptable technical procedures." Apparently this point of view was later disputed,[1] because Littmann (1982:404) later wrote "...several reviewers of my earlier article indicated that they continue to believe that indigo was the source of the blue color, though they presented no data to confirm their opinions." Nonetheless, Littmann (1980) discusses several works not mentioned by Shepard and Pollock. Among these are two scientific studies from the late 1960s, one written in French (Kleber et al. 1967), the other in Spanish (Cabrera Garrido 1969). Both were published in technical conservation publications, and both appear to be discredited by Littmann's criticisms.

Since Littmann had discounted these studies, and Shepard does not include them in her 1971 update, many scholars were led to believe that scientists had failed to identify the blue component of Maya Blue. The truth is that Kleber et al. (1967) and Cabrera Garrido (1969) demonstrated **without doubt** the presence of indigo in samples of Maya Blue taken from archaeological objects.

The first article to appear in print was published by Kleber et al. (1967). These Belgium-based scientists were working in the shadow of Van Olphen's success. Proceeding on the assumption that indigo might be the colorant in the clay-based pigment, they analyzed seven archaeological samples from a variety of geographic and cultural areas and analytically compared them to samples of blue pigment prepared in the laboratory from attapulgite and indigo. A brief description of some of their results follows:

—Microscopic analysis was compatible with the observations of other investigators, showing only the basic optical properties of the pigment.

—Spectrophotometric data of a blue pigment prepared from indigo and attapulgite by the vat-dying technique (Van Olphen 1966:645) showed close similarities with that obtained for archaeological samples.

—X-ray diffraction, which had been used many times before to identify the component attapulgite, was tested as a detection technique. The diagrams show that although lines attributable to indigo could be found in a synthetic sample containing 11 percent indigo, these lines do not appear in a sample containing 3.5 percent indigo. Attenuation trials showed that percentages of indigo below 5 percent could not be detected by x-ray diffraction.

—Diffraction patterns were analyzed for the archaeological samples and lines attributable to indigo were found in several samples, but this determination is too near the 5 percent limit of detection to be considered a reliable method for identification.

—Electron microscopy and electron diffraction were also tried. Both confirmed the presence of attapulgite in all samples analyzed, but indigo could not be identified.

—The authors proceeded with infrared absorption spectroscopy, an analytical technique in which light energy from the infrared spectrum is used to excite the molecular bonds between atoms. Certain bonds are known to absorb light at characteristic frequencies, thereby making this technique very useful for identifying organic molecules. According to Kleber et al. (1967:47), the light frequencies at which indigo absorbs, as well as the molecular bonds responsible for these absorptions, have been established by Luttke and Klessinger. The infrared absorption spectra for pure indigo, pure attapulgite, a mixture of indigo and attapulgite, and, finally, an authentic sample of Maya Blue, are presented by Kleber et al. (1967:49). Analysis of the spectrum obtained from the Maya Blue sample reveals the four diagnostic peaks of indigo in a region where attapulgite does not absorb.

—A detail of the spectral analysis of two other samples is most convincing (fig. 1). The dotted line represents absorptions of an archaeological sample. The solid line represents those of pigment prepared synthetically by heating to 190 degrees Centigrade, followed by extraction of the excess indigo with chloroform (final concentration of indigo calculated to be 1.5 percent). Both curves clearly show four absorptions attributable to indigo.

—Kleber et al. (1967) also include their speculations on the mechanism of the indigo/attapulgite complex. A definite shift in the electrophoretic mobility of attapulgite after being treated with indigo led them to conclude that the colorant acts as a cationic additive on the dispersed electronegative colloidal clay. The exact mechanism which produces the phenomenal stability of indigo, however, was not determined by the authors.

The work by Kleber et al. (1967) was well researched and well executed and there seems to be no basis for the criticisms expressed by Littmann (1980:92).

Two years after Kleber et al. (1967) completed their work, an additional study of Maya Blue was published by Cabrera Garrido (1969) which further reinforced the evidence for indigo and included additional valuable experiments. This work was published in Madrid and, like its Belgian counterpart, does not seem to have been widely available.

Perhaps these two important scientific evaluations from the late 1960s were simply overlooked by Shepard and Pollock (1971), but why analytical data prior to 1967 reportedly yielded no positive evidence is unclear. Shepard's "Updated record" mentions that in 1962 samples of Maya Blue found at Zaachila, Guatemala, had been sent to Professor Max Saltzman (then of the Analine Division of Allied Chemical Corporation) for identification of the colorant. Curiously, Shepard reports no results from Saltzman's analyses.

Saltzman, who is a renowned specialist in the field of dye research and has been analyzing dyes in museum textiles since the 1950s, was contacted by the senior author in May 1989 concerning his efforts. He reported that indeed he and technician Jack Christiansen had performed solution spectrophotometry on a number of samples of Maya Blue. He stated that he had found indigo in all the samples sent to him by Shepard back in the early 1960s, and that the evidence was as clear as any he had seen.

The original test results that Saltzman sent to Shepard have not been found, but solution spectrophotometry has been shown to identify reliably organic dyes (Saltzman

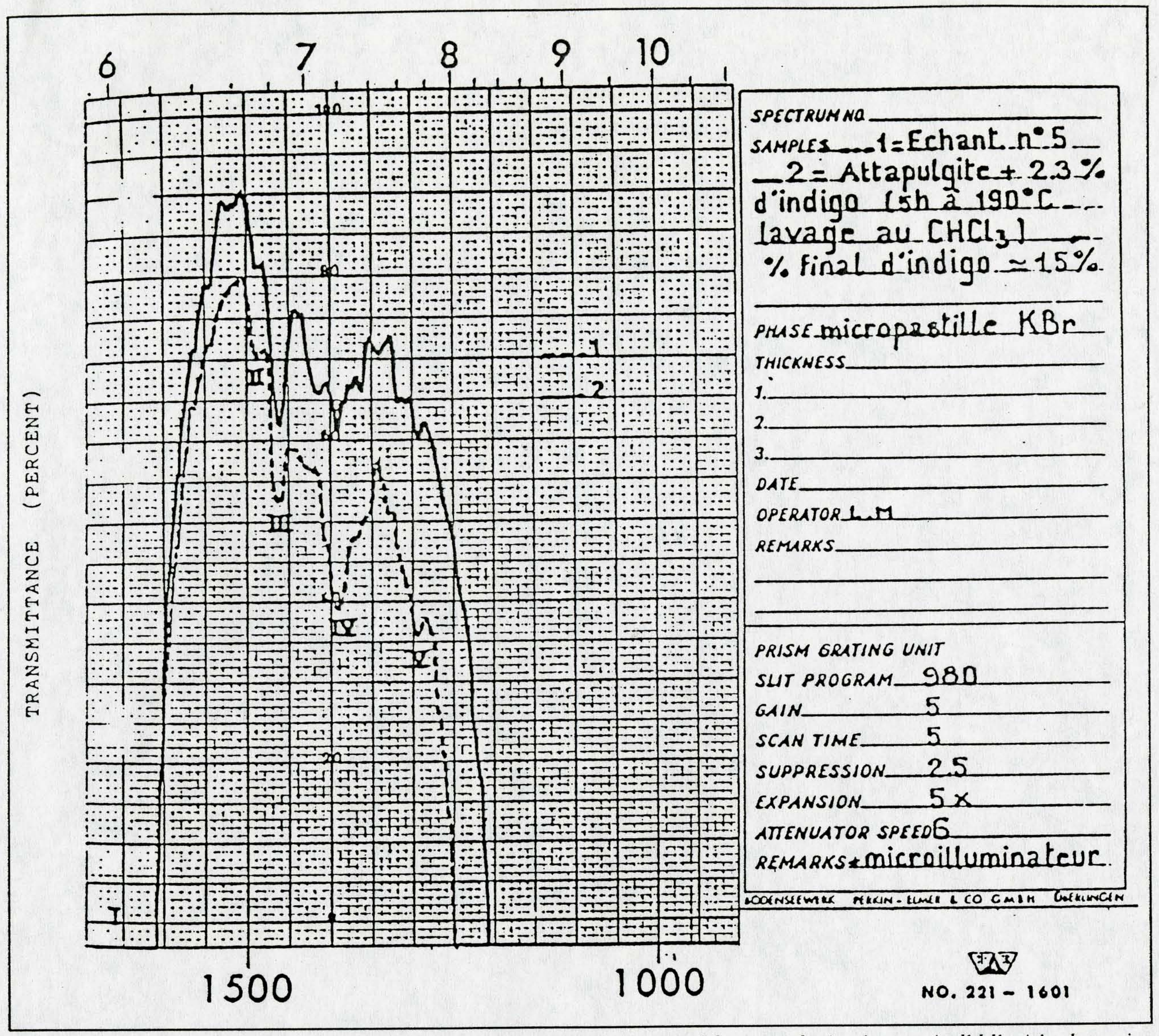

Fig. 1 Infrared absorption spectra for an ancient pignent (broken line) and for a synthetic pigment (solid line) in the region 1600–1400cm - 1. From Kleber, Masschelien-Kleiner, and Thissen 1967.

1986:31). Typical solution spectra published in Saltzman (1986:30) demonstrate how indigo can be easily distinguished from dibromoindigo (a purple dye extracted from mollusks) and can even be identified in a mixture of dyes.

Shepard, however, remained unconvinced and insisted that indigo alone could not be responsible for the remarkable stability observed in ancient samples of Maya Blue. Although Saltzman had successfully extracted indigo from the samples, the sample remained blue. This led Shepard to suspect that the non-extractable blue was the real colorant and indigo was perhaps only a reinforcing additive.

As a result, Shepard apparently refused to report Saltzman's findings until she was absolutely certain that there was no other organic or inorganic component that could be responsible for the blue color. This conservative approach is normally admirable, but in retrospect, her caution merely perpetuated the confusion. Shepard consulted a colleague, Robert L. Feller (a Senior Fellow at the Mellon Institute) concerning her reservations. He became concerned that, valid or not, the analytical results obtained by Saltzman might be lost if she did not publish them. In what turned out to be an incredibly prophetic letter dated September 1964, Feller warned her that if she did not publish these findings, the Maya Blue question would remain unsettled for "the next several years until someone in Europe publishes their own brilliant discovery of indigo" (used with permission).

Although analyses point to indigo as the colorant in Maya Blue, there remain a number of unanswered questions. For instance, Shepard's original objections (1971:90) still apply—it is unknown how an organic pigment usually sensitive to solvents and nitric acid can obtain such durability. The work by Van Olphen and others show that heat treatment of the clay-organic mixture causes indigo to become resistant to attack by solvents and acids while the color and overall molecular structure are preserved. Subsequent investigations into the mechanisms involved have thus far been inconclusive (Torres 1974), and this particular part of the mystery remains unsolved.

Nevertheless, pigment synthesis experiments, such as that of Kleber et al. (1967), clearly show how easily a stable, acid-resistant and solvent-resistant blue is prepared using only pure attapulgite, indigo, and heat. This information, coupled with positive identifications of indigo in pigment samples from which the soluble indigo has already been extracted (Kleber et al. 1967), should lead to the logical conclusion that indigo is the colorant in Maya Blue.

This does not mean that the Maya were incapable of preparing stable, blue pigments from other raw materials. Several archaeological samples have been found to contain sepiolite as the main ingredient, a mineral very closely related to attapulgite. It is therefore possible that the Maya were able also to substitute other organic compounds for indigo, perhaps in order to obtain a range of blue colors. The data show, however, that indigo has been the only organic colorant identified to date in archaeological samples.

Conclusions

This paper began as a simple literature search on the subject of Maya pottery decoration. It unfolded as an incredibly complex story surrounding the early attempts of scientists and ethnohistorians to identify the components of the pigment known as Maya Blue. We present here a greatly simplified version of a story that continues to unfold.

Although the majority of analytical evidence points to indigo as the colorant, researchers have not agreed on the validity or interpretation of the data. During the past two decades, this has led to obfuscation, misinterpretation, and inadvertent suppression of valuable information. It is hoped that we have eliminated some of the confusion by this focussed investigation of all sources, most notably, the work by Kleber et al. (1967).

Acknowledgments

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Notes

Additional bibliographic sources for this paper include Bohor (1975), Bradley (1940), Haden et al. (1967), Isphording and Wilson (1974), Morris et al. (1931), Moser (1964), Peirce (1964), and Ruppert et al (1955).

An English translation of the article by Kleber et al. (1967) is available from Linda S. Roundhill, 16906 28th Dr. SE, Bothell, WA 98012.

1. Further inquiry was necessary to determine Edwin R. Littmann's role in the dispute over the composition of Maya Blue, and Dean Arnold graciously supplied documentation for the following account.

Littmann became convinced that Maya Blue was actually composed of a naturally blue montmorillonite clay, despite the evidence pointing to an indigo/attapulgite complex. Littmann prepared an article explaining his theory, which was based upon x-ray diffraction studies. Professor Dean Arnold of Wheaton College was asked to review this article for *American Antiquity* because of his expertise in the ethnominerology of the Yucatán (Arnold 1967; Arnold and Bohor 1975, 1977). For a number of very good reasons, Arnold suggested that Littmann's article should not be published. This opinion was corroborated by Arnold's colleague, Dr. Bruce F. Bohor, a geologist with the U. S. Department of the Interior Geological Survey. One of Arnold's criticisms was that Littmann appeared to be unaware of the extensive work performed ten years earlier linking indigo and attapulgite to Maya Blue. More important, however, Arnold noted that there were "great problems with this paper of a substantive and technical nature," not the least of which was that Littmann's interpretation of the data was flawed due to his apparent lack of expertise in x-ray diffraction analysis.

As a result of the objections by Arnold (and presumably by others), Littmann's original article was not published. Littmann persevered in his endeavor and obtained copies of the articles he had missed from Arnold (Kleber et al. 1967; Cabrera Garrido 1969; and Torres 1974). Littmann remained steadfast in his opinions, however, even after a number of communications with Arnold.

Curiously, Littmann's article appeared three years later in *American Antiquity* under a different title and included severe criticism of all the studies which supported the theory of an indigo-attapulgite complex (Littmann 1980). Dean Arnold was not asked to review this second article.

The "several reviewers" who continued to insist that indigo was the colorant in Maya Blue (Littmann 1980:404) have not yet been identified. It is clear, however, that Littmann had received enough criticism to cause him to at least acknowledge that the indigo-attapulgite complex was a valid theory, for he included his own indigo-attapulgite experiments in his 1982 article. It does not appear, however, that Littmann (1982:407) ever relinquished belief in his own theory of a blue montmorillonite.