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Erratum

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# Errata and comments on "Thermal and Raman-spectroscopic analysis of Maya blue carrying artefacts, especially fragment IV of the Codex Huamantla" [Thermochim. Acta 456 (2007) 56–63]

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#### Abstract

Some errata in the text of the paper "Thermal and Raman-spectroscopic analysis of Maya blue carrying artifacts, especially fragment IV of the Codex Huamantla" [Thermochim. Acta 456 (2007) 56–63] were noticed, and some historical inaccuracies were revealed. A discussion on the methodological approach using Raman spectroscopy to identify Maya blue in the codex is presented here, not questioning, however, the authenticity of the codex.

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### 1. Nature and chronology of Maya blue

Maya blue is a hybrid pigment fabricated by moderately heating a mixture of palygorskite and indigo. Indigo is a dye, soluble in water in its reduced form (leucoindigo). Indigo was known by many ancient civilizations (Egypt, China, Mesoamerica, etc.) and used during several millennia. Indigo was obtained in the past from *Indigofera* plants, known as *añil* in Spanish and *Xiuquilitl* in Nahuatl, the Aztec language (not *Xinquilit* as written in Ref. [1] p. 58). Although Maya blue is some kind of "mineralized" indigo, it is not a dye, thus it does not get attached to fibres. Maya blue is therefore neither "one of the most brilliant dyes" [1] (abstract), nor "natural Maya blue" (p. 58) exists. Consequently, none of the textiles studied in Ref. [1] is supposed to contain Maya blue (as stated on pp. 59–60), but only indigo.

The date of invention of the Maya blue is controversial, as discussed in Ref. [2]. The most probable theory affirms that Maya blue was invented by the Mayas around the VI–VII century. Maya blue is abundant in archaeological finds from the beginning of Late Classic (VI century) in the Usumancinta, Puuc and Peten regions. However, dated artifacts containing Maya blue

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are from VI and VII centuries. Mural paints from Bonampak are dated to A.D. 780–800. The last reported use of Maya blue in Mexico is in colonial mural paints, around 1580. It seems that it was used even later in Cuba, up to the XVIII century [3]. Therefore, it has been used, in the most optimistic case, for slightly more than one millennium, but not for 2000 years, as stated in the abstract [1]. Maya blue was rediscovered in 1931 by Merwin [4], but it was Gettens and Stout [5] who realized that the pigment was new, calling it Maya blue. Therefore Maya blue was not studied in the XIX century, as stated in Ref. [1] p. 58.

#### 2. Language and other errata

An erratum in Spanish: "muy maltrado" (Ref [1] p. 57) should read "muy maltratado". Also, in "terra caliente" and "terra fria" one should write *tierra* instead *terra*. The last error may have persisted from the time of Humboldt. The painter Jopham Moritz Rugendas, who lived in Mexico from 1829 to 1834 titled one of its paints "Jarocho de Terra Caliente", written in the paint backside with his own letters.

The Mayas and Aztecs gained a well-merited position together with the other ancient civilizations, or instead, can be classified as cultures belonging to the Mesoamerican civilization. It is therefore inaccurate to classify Mayas and Aztecs as "Indian tribes" (abstract in Ref. [1]).

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## 3. Palygorskite

Palygorskite can be found in Northern Yucatan, as stated in Ref. [1], in particular in a village called Sacalum (not Saklu'um). Interestingly, this name is a Spanish corruption of the word used by the Mayas for palygorskite, that could be written as Sak lú'um [6].

The chemical formula for ideal palygorskite is  $Al_2Mg_2Si_8O_{20}(OH)_2(OH_2)_4.4(H_2O)$ , where oxygen appears in the structure (O), in the structural hydroxyls (OH), in structural water (OH<sub>2</sub>) and in zeolitic water (H<sub>2</sub>O). The empirical formula depends on the origin of the palygorskite, because all clay minerals present high compositional variability depending on formation conditions. For the Yucatecan palygorskite we have found [7] an average formula  $Mg_{2.21}Al_{1.57}Fe_{0.24}Si_{7.85}Al_{0.15}O_{20}(OH)_2(OH_2)_4.4(H_2O)$ . Note the differences with the values presented in Ref. [1] p. 58, which, by the way, do not correspond to the formula in the reference given.

#### 4. Methodological aspects

The identification of Maya blue in the Huamantla codex was made possible by comparing the Raman spectrum from the codex' blue with Maya blue from an archaeological Maya clay head. The Raman spectrum of Maya blue is similar to that of indigo, because no peaks of palygorskite are present. However, there are additional spectral bands and changes in intensity, as the authors showed in a previous paper [8]. They interpreted these changes as a transformation of the planar indigo molecules when binding to the palygorskite lattice [8]. We believe that this loss of planarity of the indigo molecule is not sufficient to explain the measured intensity of the new peaks [9]. We found that similar spectra can be obtained from indigo mixed with palygorskite without the thermal treatment needed to produce Maya blue, and also from indigo mixed with other clays, in particular sepiolite or montmorillonite. Therefore, the new bands in the Maya blue spectrum, not present in that of indigo, are not exclusive to Maya blue. We thus maintain that Raman spectroscopy is not able to identify Maya blue unambiguously, and that complementary techniques, such us X-ray diffractometry should be used to detect the mineral phase.

The similarity between the Raman spectra of the codex and the Maya head may suggest that both contain Maya blue, but one should be careful about unambiguously ascribing the found bands to this pigment. The blue present in the Mexican codices analyzed until now seems to contain Maya blue, thus there is no reason to argue that the Huamantla codex does not contain Maya blue. Another less probable hypothesis is that the codex was painted with indigo attached to the fibres of the amatl paper and may exhibit a Raman spectrum similar to that of Maya blue. Alternatively, one may think that indigo was mixed with some other clay or mineral, or even with palygorskite without thermal treatment, thus not being identifiable as "Maya blue". When comparing Fig. 6 in Ref. [1] with Fig. 3 in Ref. [9], one sees that the peak at  $1680 \text{ cm}^{-1}$  (or  $1678 \text{ cm}^{-1}$  for the codex) is shifted to higher wavenumbers in the case of indigo plus a non-palygorskite clay, hence supporting the idea of Maya blue. However, the peak at about  $1460 \text{ cm}^{-1}$  is more prominent in the codex than in the Maya head, and looks more like the one we obtained for indigo plus sepiolite or kaolinite. Therefore, it seems reasonable to assign the blue in the Huamantla codex to Maya blue, but the analysis presented is not sufficient for an unambiguous attribution.

The scientific analyses of the Huamantla codex presented in Ref. [1] constitute a valuable contribution to a better understanding of the use of Maya blue in Mesoamerica. The codex, written, as stated, at the end of the XVI century or beginning of the XVII century, is colonial and not pre-Hispanic, since the town of Huamantla was occupied by the Spanish troops in 1534. If we suppose that this codex contains Maya blue, there would be an interesting case for demonstrating the use of Maya blue in colonial times outside colonial convents. Moreover, if the codex is from the XVII century, that would witness one the latest reported uses of Maya blue, perhaps confirming the idea that Maya blue survived in Mexico up to the XX century [2].

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