New clues in the search to rediscover the mysterious Maya Blue formula

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The recipe and process for preparing Maya Blue, a highly-resistant pigment used for centuries in Mesoamerica, were lost. We know that the ingredients are a plant dye, indigo, and a type of clay known as palygorskite, but scientists do not know how they were 'cooked' and combined together. Now, a team of chemists from the University of Valencia and the Polythecnic University of Valencia (Spain) have come up with a new hypothesis about how it was prepared.

Palace walls, sculptures, codices and pieces of pottery produced by the ancient Maya incorporate the enigmatic Maya Blue. This pigment, which was also used by other Mesoamerican cultures, is characterised by its intense blue colour but, above all, by the fact that it is highly resistant to chemical and biological deterioration. Indeed, it was used centuries ago and when it is analysed now it appears virtually unchangeable.

There is no document that verifies how this paint was prepared and so it remains a mystery. Archaeologists and scientists have sought to uncover the mystery in recent years but it seems that researchers cannot come to an agreement.

The dominant theory proposes that there is a single type of Maya Blue that was also prepared in a unique way and that a specific type of bond binds the two components: one organic component, indigo -the dye used for denim that is obtained from the Indigofera suffruticosa plant in Mesoamerica- and another inorganic component, palygorskite, a type of clay characterised by its crystal structure full of internal channels.

But the work of a team from the University of Valencia (UV) and the Polytechnic University of Valencia (UPV) seem to contradict this 'monoist' version. "We detected a second pigment in the samples, dehydroindigo, which must have formed through oxidation of the indigo when it underwent exposure to the heat that is required to prepare Maya Blue," stated Antonio Doménech, a UV researcher.

"Indigo is blue and dehydroindigo is yellow," the expert explained, "therefore the presence of both pigments in variable proportions would justify the more or less greenish tone of Maya Blue. It is possible that the Maya knew how to obtain the desired hue by varying the preparation temperature, for example heating the mixture for more or less time or adding more of less wood to the fire."

Another of the unsolved questions is how the dye molecules are distributed in palygorskite's crystal network. According to some scientists, the indigo adheres to the exterior of the clay structure with the 'brick' shape although it could also form a sort of 'cover' on the entrance to the channels.

However, other researchers believe that the indigo penetrates into the channels. This is the theory supported by the team from Valencia that has just published a study in the *Microporous and Mesoporous Materials* journal on the reactions that could be behind the formation of the blue pigment.

Two-stage process

The results reveal that two stages occur when both components are heated to temperatures between 120 and 180 ºC. In the first and fastest of the two stages water evaporates from the palygorskite and the indigo bonds to the clay, although a part oxidises and forms dehydroindigo.

In the second stage it would appear that the dye disperses through the channels in the clay. "The process is similar to what happens when we pour a drop of ink into a glass of water," Doménech said, drawing a comparison, although he acknowledges that "this is a hypothesis" at present.

The researcher's team, like other groups in other parts of the world, is also investigating the secret of the unknown chemical bonds that bind the organic to the inorganic component. These bonds are the reason behind Maya Blue's resistance.

In addition to palaces and buildings of the Maya nobility, this pigment is traditionally associated with ritual ceremonies conducted by priests, and may even have been used during human sacrifices. Containers holding traces of the pigment found at the bottom of some natural and man-made wells on the Yucatán peninsula point to this ceremonial use.

Studies such as the one published by US anthropologists in 2008 on a bowl found in the Sacred Cenote of Chichén Itzá led some media outlets to state that the mystery of Maya Blue had been solved. "The bowl contained Maya Blue mixed with copal incense so the simplified conclusion was that it was only prepared by warming incense," stated Doménech.

The researcher believes that the composition and function of Maya Blue could have varied down through the centuries: "Although quite a few samples would be required, it could be possible to establish the evolution in its properties and preparation throughout the Maya culture from approximately 150 B.C. to 800 A.D., in such a way that we could establish a chronology based on analysing the pigment. This provides a far more 'flexible' view of this culture, breaking with that traditional monolithic view of inflexible ritualism."

Small greenish balls in La Blanca

In support of this view, the team also recently found other pigments that are different from Maya Blue but follow the same pattern of a plant dye combined with clay. They found small greenish balls with this material in the ancient Maya city of La Blanca, modern day Guatemala, and it is assumed they were used to plaster and decorate the walls of palatial buildings.

"These materials were certainly not within the reach of the common people but they signal a more 'everyday' use of the pigments that would not have had to be restricted to ritual or ceremonial activities," Doménech pointed out and said by way of conclusion: "Maya Blue can be considered a polyfunctional material as it can combine different organic components with an inorganic carrier, which, in addition, can be distributed and react differently, thereby producing functions that are also different."

This video is in Spanish:

More information: Domenech, A. et al. Application of solid-state electrochemistry techniques to polyfunctional organic-inorganic hybrid materials: The Maya Blue problem, *Microporous and Mesoporous Materials* 166 (15): 123-130, 2013.

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