## [Supplementary material]

## The Maya wall paintings from Chajul, Guatemala

Jarosław Źrałka<sup>1,\*</sup>, Katarzyna Radnicka<sup>2</sup>, Monika Banach<sup>3</sup>, Lucas Asicona Ramírez<sup>2</sup>, María Luisa Vázquez de Ágredos-Pascual<sup>4</sup>, Cristina Vidal-Lorenzo<sup>4</sup>, Lars Frühsorge<sup>5</sup> & Juan Luis Velásquez<sup>2</sup>

<sup>1</sup> Institute of Archaeology, Jagiellonian University, Poland

- <sup>2</sup> Proyecto Conservación de los Murales de Chajul (COMUCH), Guatemala
- <sup>3</sup> Institute of Ethnology and Cultural Anthropology, Jagiellonian University, Poland
- <sup>4</sup> Department of Art History, University of Valencia, Spain
- <sup>5</sup> Department of Cultural History and Cultural Studies, University of Hamburg, Germany
- \**Author for correspondence* ( $\square$  *zralka.j@gmail.com*)

# Results of physicochemical analysis of pigments from Chajul House 3

## Materials and methods

Sixteen samples of pigments were taken from the Asicona family house (Chajul), which were subsequently subjected to organoleptic and physicochemical research that will be described in the following paragraph. Table S1 shows the samples that were considered in this study.

Sample No.	Location of the mural painting where the samples were taken
CH-1	The chest of Individual 6
CH-2	The chest of Individual 6
CH-3	The leg of Individual 6
CH-4	The leg of Individual 6
CH-5	The ornament under Individual 6
CH-6	The head of Individual 14

Table S1. Description of the samples discussed in this research.

CH-7	The arm of Individual 12
CH-8	Close to the head of Individual 14
PM-1	The leg of Individual 4
PM-2	The leg of Individual 3
WM-1	Panel 4, grout or bottom
WM-2	Panel 3, flower (up, to the left)
WM-3	Panel 3, flower (up, to the left)
WM-4	Panel 3, vase (to the right)
WM-5	Panel 3, flower (up, to the right)
N	Layer of blue paint covering the adobe bricks of the wall

The present text reports the chemical data obtained during the physico-chemical analysis of samples from the Asicona family house mural painting (Quiché Department, Guatemala) and describes the analytical protocol established for the complete characterisation of these colouring materials. For this purpose, a multi-technique approach was developed based on the combination of Light Microscopy (LM), Scanning Electron Microscopy-X-Ray microanalysis (SEM-EDX), X-ray powder diffraction (XRPD), FTIR spectroscopy and Gas Chromatography-Mass Spectrometry (GC-MS). The equipment used in each case is described below:

*Optical microscopy (LM):* to analyse samples with this technique, they needed to be set in a polyester mounting resin which hardened after around 24 hours and provided a small mount which was then polished until reaching the level of the colour micro-sample set within the resin. This required a Struers Knuth-Rotor 2 and Struers DAP 6 lapper/polisher and the use of decreasing grain size silicon carbide abrasive discs. Once the Chajul samples had been prepared in this manner, they could then be studied by a Leica DMR optical microscope with an incident/transmitted light system and polarisation system in both cases.

*Scanning Electronic Microscopy combined with energy dispersive X-ray (SEM-EDX)*: the resin mounts holding the colour samples for analysis under optical microscopy were also used for analysis by scanning electronic microscopy, although in this case the samples

required a carbon coating. The combination of this microcopy technique with energy dispersive X-ray microanalysis was conclusive in the identification of materials of mineral origin employed in each of the substrates of the mural stratigraphy: the mortar render, the render and the paint film. The scanning electronic microscope employed was JEOL model JSM 6300 with a Link-Oxford-Isis microanalysis system, operating at 10-12 kV voltage between cathode and anode. The ZAF method was employed to correct any inter-elemental effects in the semi-quantitative analysis.

X-ray powder diffraction (XRPD) was carried out on randomly oriented samples after grinding the powder samples in an agate mortar. A Bruker D8 Advance system, operating in  $\theta:\theta$  mode was used; generator setting 40 kV, 40 mA, Cu anode (Cu-K $\alpha$  = 1.5418 Å), Ni filter, 2 $\theta$  range 5-80°, step size 0.01°, scan speed 0.5° min<sup>-1</sup>. Qualitative phase determination was carried out using the software QualX2.0 (Altomare *et al.* 2015) and the correlated COD database (Gražulis *et al.* 2009). Quantitative Phase Analysis (QPA) was carried out using the software Quanto (Altomare *et al.* 2001).

Attenuated Total Reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR): The analysis of the Chajul samples by this spectroscopic technique was made using Vertex 70 equipment operating with attenuated total reflection and using a coated FR-DTGS detector for temperature stabilisation. This technique enables the joint detection of mineral and organic colouring materials.

*Gas chromatography-mass spectrometry* (GC-MS): a technique specializing in the characterization of organic substances. The gas chromatograph used in the characterization of the samples was an Agilent 6890N (Agilent Technologies, Palo Alto, CA, USA). The chromatograph is docked with an HP 5973 mass detector. The column used was an HP-5MS-5% phenyl and 95% polydimethylsiloxane). The oven temperature program was 60-220 ° C, with an increase of 1 °C/min; the temperature was maintained at 220 °C for 3 min. The injector temperature was at 250 °C. The injection volume was 1  $\mu$  L (95:5), with an inlet pressure of 7.96 psi. The carrier gas was He. The interface temperature was 280 °C. For the mass detector, the ionization temperature was set at 230 °C. The GC-MS database (NIST Library version 2002) was used for the possible identification of the organic components.

#### **Results and discussion**

The studies carried out in the laboratories of the Scientific Park of the University of Valencia indicate that the materials and techniques applied in the preparation of the murals in the

Asicona family house continued almost unchanged since the pre-Columbian times. Physicochemical analysis of Chajul samples led to the identification of a colour palette typical for pre-Columbian Maya mural paintings, at least in the Maya Lowlands: white lime (CaCO<sub>3</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>), ocher and red earth (of possible local origin), and the so-called 'Maya blue' (sample N) present (Table S2 and Figures S1 & S2). These pigments were typically employed during the pre-Columbian times and the tradition of their use begins during the Middle Preclassic period (first millennium BC) in the Maya area.

Sample	Compounds identified	Pigment
CH-1	Iron (Fe), aluminum (Al), silica (Si), potassium (K), and titanium (Ti)	Red earth/Fe-based pigment
CH-2	Iron (Fe), aluminum (Al), silica (Si), potassium (K), and magnesium (Mg)	Red earth/Fe-based pigment
CH-3	Iron (Fe), aluminum (Al), silica (Si), and calcite (Ca)	Red earth/Fe-based pigment
CH-4	Calcium (Ca), phosphorus (P) Iron (Fe), aluminum (Al), silica (Si), potassium (K), and other minor compounds	Calcium apatite + Red earth/Fe-based pigment
CH-5	Iron (Fe), aluminum (Al), silica (Si), potassium (K), and phosphorous (P)	Red earth/Fe-based pigment
CH-6	Iron (Fe)	Hematite Fe <sub>2</sub> O <sub>3</sub>
CH-7	Iron (Fe), aluminum (Al), silica (Si), and calcite (Ca)	Red earth/Fe-based pigment
CH-8	Calcium (Ca), phosphorus (P)	Calcium apatite +
	Iron (Fe), aluminum (Al), silica (Si) and magnesium (Mg)	

Table S2. Pigments identified by physicochemical analysis.

		Red earth/Fe-based
		pigment
PM-1	Iron (Fe), aluminum (Al), silica (Si), potassium (K), and magnesium	Red earth/Fe-based
	(Mg),	pigment
	titanium (Ti), chlorine (Cl). As minor compound we found chromate	
	(Cr)	
PM-2	Iron (Fe), aluminum (Al), silica (Si), potassium (K), and magnesium	Red earth/Fe-based
	(Mg), and	pigment
	titanium (Ti). As minor compound we found chromate (Cr)	
WM-1	Iron (Fe), aluminum (Al), silica (Si), and titanium (Ti) –the Ti in	Red earth/Fe-based
	very low quantity-	pigment
WM-2	Iron (Fe), aluminum (Al), silica (Si), and titanium (Ti)	Ilmenite (FeTiO <sub>3</sub> ).
WM-3	Calcium carbonate (CaCO3)	Calcite
		+
	Iron (Fe), aluminum (Al), silica (Si)	Red earth/Fe-based
		pigment
WM-4	Iron (Fe), aluminum (Al), silica (Si), potassium (K), and magnesium	Red earth/Fe-based
	(Mg)	pigment
WM-5	Iron (Fe), aluminum (Al), silica (Si), potassium (K), and titanium	Red earth/Fe-based
	(Ti)	pigment
N	Indigo + aluminosilicate (paligorskita-type clay)	Maya blue pigment



Figure S1. ATR/FTIR spectra of Maya blue sample from mural paintings of Asicona family house (Chajul) (a) before and (b) after treatment with diluted hydrochloric acid (HCl) for removing CaCO<sub>3</sub>. Maya overlapped bands in the 1600-1750- cm-1 region correspond to the carbonyl frequency of indigo (theoretical 1629cm-1), dehydroindigo (theoretical 1736cm-1), 38 and zeolitic water.



Figure S2. EDX spectrum of the palygorskite type clay identified in sample N, which should have been used as an inert matrix of the indigo characterized in the same sample by ATR-FTIR. Note the presence of aluminium, silica and magnesium as major components, which is characteristic of magnesium alumniniosilicates, a group to which paligorskite belongs, among other clays.

The Maya blue pigment was identified directly on the layer covering the adobe bricks of the wall (Figures S1 and S2). The greyish hue of this pigment may have two causes: (a) conservation problems or (b) a decline in traditional knowledge concerning the preparation of this pigment. Figure S1 shows the ATR-FTIR spectra of sample N (a) before and (b) after being treated with hydrochloric acid (HCl) to remove calcium carbonate (CaCO<sub>3</sub>). Both spectra show the overlapped bands in the 1600-1750- cm-1 region that correspond to the carbonyl frequency of indigo (theoretical 1629 cm-1), dehydroindigo (theoretical 1736 cm-1) (Doménech et al. 2008), and zeolitic water (Sanz et al. 2012). In addition, the EDX spectrum (Figure S2) shows a clay composed of aluminum, silica, magnesium and iron, which corresponds to palygorskite or sepiolite magnesium aluminosilicates, among others, such as montmorillonite. The indigo identified in sample N, therefore, could have been precipitated into a palygorskite, faithfully following the formula of traditional Maya blue. In this sense, it should be remembered that Maya blue can be considered as a hybrid organic-inorganic material resulting from the attachment of indigo, a blue dye extracted from *Indigofera* suffruticosa and other species, as well as local clay, palygorskite. Natural indigo is formed by indigotin (3H-indol-3-one, 2-(1,3-dihydro-3-oxo-2H-indol-2-ylidene)-1,2-dihydro), a quasiplanar molecule of approximate dimensions  $4.8 \times 12$  Å.6. The inorganic component of Maya blue, palygorskite, is a fibrous phyllosilicate with an ideal composition of (Mg,-Al)<sub>4</sub>Si<sub>8</sub>(O,OH,H<sub>2</sub>O)<sub>24</sub>,nH<sub>2</sub>O.

The ancient Maya prepared this pigment by crushing dry indigo with palygorskite, with subsequent (or parallel) heating at temperatures below 250°C. Alternatively, a 'wet' procedure can be used by macerating indigo leaves in a suspension of palygorskite, then perhaps followed by sancochado, batido and heating of the clay now impregnated by the indigo dye (Reyes-Valerio 1993; Vandenabeele et al. 2005; Sánchez del Río et al. 2008). In this context, Kleber et al. (1967), Van Olphen (1967), Cabrera Garrido (1969), Littmann (1982), Torres (1988), Reyes-Valerio (1993), Vandenabeele et al. (2005) and Sánchez del Río et al. (2006a, 2006b, 2008) have suggested different preparation procedures of Maya blue which, roughly, imply different modifications of the above 'dry' and 'wet' procedures this work has been reviewed briefly by Sánchez del Río et al. (2006a). More recently, Arnold et al. (2008) have reported that burning incense was one way in which the ancient Maya made Maya blue in the context of ritual ceremonies (Doménech et al. 2007a-c). In accordance with these studies, the colour technology of the Maya blue was complex. The artist should be aware of important aspects such as the time and temperature to which the colour should be baked (dry procedure). At more than 250 ° C, for example, the rings of the indigo break and the preparation of the pigment fails. The result is a more greyish colour and very similar to the one we have in the Asicona family house. That is why it is so important to document this blue-grey pigment in the aforementioned colonial house. We believe that its hue stems from the fact that (1) the pre-Hispanic Maya blue was still in use but (2) the technology that guaranteed optimal preparation was already in decline, as a result of its progressive substitution with other blue colours of mineral origin. While the iron colours identified in the Asicona family house had also been widely used in the Old World (in other words: its use in colonial times did not denote a pre-Hispanic origin), the presence of Maya blue conferred Maya socio-cultural identity to the architecture and artwork where it was employed. This must have been progressively avoided by the new Spanish power, because the new times required new "stamps" of identity.

On the other hand, the chemical-analytical results indicate that there is another technological aspect of the paintings that is associated with the pre-Hispanic mural paintings of the Maya Lowlands: the composition and stratigraphy of the underlying plaster. The colour of the mural was spread in two calcareous layers. The lower mortar is much thicker and more irregular than the upper plaster. The main component of both levels/layers is calcium carbonate (CaCO<sub>3</sub>) of local origin. It is interesting that this material in some panels is combined with aragonite, which means: calcium carbonate (CaCO<sub>3</sub>) obtained by grinding shells. This could indicate the survival in the Maya area of a pictorial tradition that was very

widespread during the Postclassic, especially in coastal regions and cities (Magaloni 1996; Vázquez de Ágredos 2010). Its presence in the Asicona family house could indicate the use of two sources for obtaining different lime: (1) mineral of local origin and (2) water formations with the presence of shells, such as rivers.

In conclusion, from a technical point of view, the mural painting preserved in the Colonial Asicona family house represents the survival of the pictorial tradition of the Maya Lowlands. The underlying stucco and the colours used in this work of art have the same origin and composition as those of pre-Hispanic times. The materials used are probably of local origin and could have been prepared by the Maya who lived in Colonial times under the power of the Conquistadors. While the iconography shows clear differences with the pre-Columbian Maya and reflects the new power group and its ideals, the technique still manifests a socio-cultural Maya pre-Hispanic identity.

### **Optical microscopy (LM)**

The optical microscopy (LM) shows an earthy and opaque texture very characteristic of the Fe-based compounds in all the samples (Figure S3). The different shades can be due to two factors: (1) The use of iron minerals of different local origin and composition or (2) the application of thermal procedures to modify the chromatic nuances of these same minerals. On the other hand, this same technique shows specific degradation pathologies, especially the migration of calcium carbonate and salts to the pictorial surface as a result of high humidity.



N – layer of blue paint covering mud bricks (below the painting) CH-1- The chest of Individual 6.



CH-2- The chest of Individual 6.



**CH-4-** The leg of Individual 6.



**CH-6-**The head of Individual 14.



CH-8- Area close to the head of Individual 14. PM-1 The leg of Individual 4.



**CH-3-** The leg of Individual 6.



CH-5- The ornament under Individual 6.



**CH-7-** The arm of Individual 12.





**PM-2-** The leg of Individual 3.







WM-2- Panel 3, flower (up, to the left). WM-3- Panel 3, flower (up, to the left).





WM-4- Panel 3, vase (to the right). WM-5- Panel 3, flower (up, to the right). Figure S3. Photographs featuring all samples being subject of Optical Microscopy (LM) analysis.

## X-ray powder diffraction (XRPD)

The physicochemical analyses by X-ray powder diffraction (XRPD) on the render yielded an unequivocal result: calcium carbonate in a pure – or almost pure – state (Figures S4–S6). In other words: the mortar and the plaster of this painting were made with microcrystalline matrices of carbonated lime and the addition of a load that was also calcareous (equivalent to the *sascab* of the ancient Maya). The small quantity of magnesium does not qualify the lime of the Spectrum 2 (Figure S5) as dolomite. The small amount of aragonite in Spectrum 3 (Figure S6) could indicate (a) its intentional mixture with mineral origin lime or (b) lime extraction from a quarry close water sources.



Figure S4. Spectrum 1: render of calcium carbonate (CaCO<sub>3</sub>).



*Figure S5. Spectrum 2: render of calcium carbonate (CaCO<sub>3</sub>) and magnesium (Mg) in a low quantity.* 



*Figure S6. Spectrum 3: render of calcium carbonate (CaCO3) and aragonite (CaCO3) in a low quantity.* 

Scanning Electronic Microscopy combined with energy dispersive X-ray (SEM-EDX)



Figure S7. Sample CH-1 (the chest of Individual 6). The spectrum shows red earth (Fe) accompanied with aluminium (Al), silica (Si), potassium (K), and titanium (Ti) in a very low quantity. All these components were able to be incorporated into the iron during the geological formation process.



Figure S8. Sample CH-2 (the chest of Individual 6). This spectrum comes from another sample obtained in the same character and place. It confirms that the pigment is red earth mainly composed of iron and aluminiosilicate (Si, Al). There is a low proportion of magnesium associated with aluminium (Al) and silica (Si).



Figure S9. Sample CH-3 (the leg of Individual 6). The spectrum shows red earth (Fe) accompanied with aluminium (Al) and silica (Si). The calcium carbonate comes from the underlying plaster.



Figure S10. Sample CH-4 (the leg of Individual 6). The large amount of calcium (Ca) and phosphorus (P) suggests that this pigment was made with a calcium apatite and iron (Fe). Interestingly that the two sources to obtain calcium apatite are: fluorapatite ( $Ca_5(PO_4)_3F$ ) and hydroxyapatite ( $Ca_5(PO_4)_3OH$ ). The absence of fluor in our spectrum indicates that our sample features the second type: hydroxyapatite, which is mainly obtained from animal and human bones.



Figure S11. Sample CH-5 (the ornament under Individual 6). The spectrum shows red earth with the presence of aluminium (Al) silica (Si), and potassium (K). Small amounts of phosphorus and calcite can also be seen. The latter material comes from the underlying plaster. The phosphorus is explained because this component may be present in soils in which these red lands are formed.



*Figure S12. Sample CH-6 (the head of Individual 14). The spectrum shows a pure hematite (Fe<sub>2</sub>O<sub>3</sub>). The identified lime comes from the underlying plaster.* 



Figure S13. Sample CH-7 (the arm of Individual 12). The spectrum shows red earth with the presence of aluminium (Al) and silica (Si). The identified lime comes from the underlying plaster.



Figure S14. Sample CH-8 (area close to the head of Individual 14). The combination of phosphorus and calcite in large quantities lead us again to suggest the presence of calcium apatite [hydroxyapatite ( $Ca_5(PO_4)_3OH$ )] combined with red earth. This latter colouring material composed by iron aluminium, and silica is the most common in all of our samples. It was probably source locally and was known in pre-Hispanic and colonial times.



Figure S15. Sample PM-1 (the leg of Individual 4). The spectrum again shows an Fe-based pigment with aluminium (Al) and silica (Si) that has been identified in other samples of the same mural painting. However, in sample PM-1, this Fe-based red is linked to other components, such as potassium (K), titanium (Ti), or chlorine (Cl), which he had to add during his geological formation. This means that this pigment in this sample was used raw

(not purified after being remove from the quarry), and this is interesting because in other samples the opposite is true. Chromium is a posterior material (its synthesis and use as pigment does not occur until the nineteenth century by Vauquelin). Its presence here might indicate interventions (restorations?) in our current era or between the nineteenth and twentieth centuries. In the following sample (Figure S16) we have this same pattern.



Figure S16. Sample PM-2 (the leg of Individual 3).



Figure S17. Sample WM-1 (Panel 4, mortar). The spectrum shows a very pure Fe-based compound with silica (Si) and aluminium (Al). A low quantity of titanium (Ti) has been identified, and its presence could explain the orange hue of this sample.



Figure S18. Sample WM-2 (Panel 3, flower; up, to the left). The large amount of titanium (Ti) attached to the iron (Fe) suggests that it is ilmenite (FeTiO<sub>3</sub>). This material was known in Mesoamerica since Preclassic times. The Olmec used it for the preparation of mirrors (like

the hematite). Its other major use in pre-Hispanic times was as an orange pigment. The mural painting of the Maya Lowlands contains numerous examples, as chemical analyses have demonstrated (Vázquez de Ágredos 2010).



Figure S19. Sample WM-3 (Panel 3, flower; up, to the left). The EDX spectrum shows an Febased compound with aluminium (Al) and silicon (Si) that is characteristic in the colour palette used in this mural painting from Chajul. The high proportion of calcite could indicate an intentional mixture (Fe + Ca) to obtain a clearer tonality in the original pigment.



Figure S20. Sample WM-4 (Panel 3, vase; to the right). The EDX spectrum indicates a red earth pigment. It is surprising that in this case the iron is not associated with the aluminium (Al) and the silicon (Si), but to these two components and a third one: magnesium. Therefore, this pigment is different from the previous ones (Fe, Al, Si). Their local source of origin would be another.



Figure S21. Sample WM-5 (Panel 3, flower; up, to the right). The EDX Spectrum shows a Febased pigment associated with kaolin (Al, Si). There are small amounts of potassium (K) and titanium (Ti) linked to this red earth. Both are frequent in this mural painting from Chajul, as the analysis of the preceding samples shows.

In conclusion, we can say that the analyses by SEM-EDX and FTIR (next section) show 5 varieties of pigments used in the mural painting of Chajul:

1. A type of red earth where an Fe-based pigment is linked to silica (Si) and aluminium (Al).

2. A type of red earth where an Fe-based pigment is linked to silica (Si), magnesium (Mg) and aluminium (Al).

3. A pigment based on the mixture of red earth with a white lime (CaCO<sub>3</sub>).

4. A Pigment prepared with calcium apatite -hydroxyapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH) -mixed with red earth.

5. Ilmenite (FeTiO<sub>2</sub>) and other varieties of red earth with a certain proportion of titanium (Ti)

6. Hematite Fe<sub>2</sub>O<sub>3</sub>

7. Maya blue (indigo + magnesium aluminiosilicate, paligorskite type)

All the red earths used must have come from local sources. Possibly the hematite and the ilmenite also came from local quarries, but it must be considered that these materials are not so abundant and may have arrived through short or medium distance trade. Any of these materials could have been used to obtain a wide range of warm shades, with a simple heating in specialized ovens for it. For its part, the Maya blue and the calcium apatite show colours that were much harder to prepare. In both cases, the knowledge for the manufacture and use of these colours came from pre-Hispanic period with almost total certainty. FTIR analyses (see below, Figures S22–S29) were only applied to the eight samples from the first series (CH-1 to CH-8) in order to confirm the majority presence of red earths in these colours and its diversity. The results confirmed this fact without detecting organic components associated with the colours studied. This suggested that the pictorial technique of this mural painting from Chajul was fresco. In this last sense, the study by Gas Chromatography-Mass Spectrometry (GC-MS) did not identify any organic binder associated with the pictorial film either. It is possible, therefore, that this painting was made with the fresco technique, which was widely used in Europe in the Baroque period (seventeenth and eighteenth centuries). However, further studies are needed to completely rule out the presence of organic binder in the mural studied, and in consequence to accept the presence of a fresco as the pictorial technique employed. By the moment, and with the analytical data that we have, this mural painting is shown as an artistic manifestation halfway between the technical knowledge of pre-Hispanic painting (colouring materials) and the one that came to these territories from the Old World (pictorial technical).

# FTIR analyses



MUESTRA	Wavenumber cn	n-1	1			
	CALCITA	Minerales silíceos	Oxidos de			
		HALLOYSITA/	HALLOYSITA/ FELDESPATOS CUARZO			
		KAOLINITA				
CH-1	1390, 870, 710	1150, 1082, 1029,			527	
		914				

Figure S22. FTIR analysis of sample CH-1.



MUESTRA	Wavenumber cn	iber cm-1				
	CALCITA	Minerales silíceos	Minerales silíceos			
		HALLOYSITA/	HALLOYSITA/ FELDESPATOS CUARZO			
		KAOLINITA				
CH-2	1403, 871, 713	3710, 3651, 3627,		790	526	
		1647, 1159, 1121,				
		1085, 1025, 1008,				
		909, 790, 680				

Figure S23. FTIR analysis of sample CH-2.



MUESTRA	Wavenumber cn	1				
	CALCITA	Minerales silíceos	Minerales silíceos			
		HALLOYSITA/	HALLOYSITA/ FELDESPATOS CUARZO			
		KAOLINITA				
CH-3	1395, 870, 711	3708, 3626, 1649,		786		
		1155, 1087, 1028,				
		1012, 786, 679				

Figure S24. FTIR analysis of sample CH-3.



MUESTRA	Wavenumber cn	n-1	1			
	CALCITA	Minerales silíceos	Minerales silíceos			
		HALLOYSITA/	HALLOYSITA/ FELDESPATOS CUARZO			
		KAOLINITA				
CH-4	1408, 872, 711	3708, 3686, 3626,		798, 780	517	
		1146, 1093, 1026,				
		1013, 798, 780				

Figure S25. FTIR analysis of sample CH-4.



MUESTRA	Wavenumber cn	n-1				
	CALCITA	Minerales silíceos	Minerales silíceos			
		HALLOYSITA/	HALLOYSITA/ FELDESPATOS CUARZO			
		KAOLINITA				
CH-5	1395, 871, 711	Minerales arcillosos:		789		
		3708, 3646, 1644,				
		1164, 1084, 1034,				
		1019, 789, 671				

Figure S26. FTIR analysis of sample CH-5.



MUESTRA	Wavenumber cn	cm-1				
	CALCITA	Minerales silíceos	Minerales silíceos			
		HALLOYSITA/	HALLOYSITA/ FELDESPATOS CUARZO			
		KAOLINITA				
СН-6	1417, 873	3732, 3687, 3626,		784	535	
		1633, 999907, 784,				
		682, 669				

Figure S27. FTIR analysis of sample CH-6.



MUESTRA	Wavenumber cn	n-1	l			
	CALCITA	Minerales silíceos	Minerales silíceos			
		HALLOYSITA/	HALLOYSITA/ FELDESPATOS CUARZO			
		KAOLINITA				
CH-7	1403, 871, 713	3710, 3651, 3627,		790	526	
		1647, 1159, 1121,				
		1085, 1025, 1008,				
		909, 790, 680				

Figure S28. FTIR analysis of sample CH-7.



MUESTRA	Wavenumber cn	n-1					
	CALCITA	Minerales silíceos	Minerales silíceos				
		HALLOYSITA/	FELDESPATOS	CUARZO	Hierro		
		KAOLINITA					
CH-8	1408, 872, 711	3708, 3686, 3626,		798, 780	517		
		1146, 1093, 1026,					
		1013, 798, 780					

Figure S29. FTIR analysis of sample CH-8.

## References

ALTOMARE, A., M.C. BURLA, C. GIACOVAZZO, A. GUAGLIARDI, A. MOLITERNI, G. POLIDORI & R. RIZZI. 2001. *Quanto*: A Rietveld program for quantitative phase analysis for polycrystalline mixtures. *Journal of Applied Crystallography* 34: 392–97.

https://doi.org/10.1107/S0021889801002904

Altomare, A., N. Corriero, C. Cuocci, A. Falcicchio, A. Moliterni & R. Rizzi. 2015.

QualX2.0: a qualitative phase analysis software using the freely database POW\_COD.

Journal of Applied Crystallography 48: 598–603.

https://doi.org/10.1107/S1600576715002319

ARNOLD, D. E., J.R. BRANDEN, P.R. WILLIAMS, G.M. FEINMAN & J.P. BROWN. 2008. The first direct evidence for the production of Maya Blue: rediscovery of a technology. *Antiquity* 82: 152–64. https://doi.org/10.1017/S0003598X00096514

CABRERA GARRIDO, J.M. 1969. El 'Azul Maya': sobre el colorante orgánico y la técnica de

*fabricación del pigmento* (Informes y Trabajos del Instituto de Conservación y Restauración de Obras de Arte, Arqueología y Etnología, vol. 8). Unpublished manuscript, Mexico City. DOMÉNECH, A., M.T. DOMÉNECH-CARBÓ & M.L. VÁZQUEZ DE AGREDOS PASCUAL. 2007a. Indigo/dehydroindigo/ palygorskite complex in Maya Blue: an electrochemical approach. *Journal of Physical Chemistry C* 111: 4585–95. https://doi.org/10.1021/jp067369g
2007b. Chemometric study of Maya Blue from the voltammetry of microparticles approach. *Analytical Chemistry* 79: 2812–21. https://doi.org/10.1021/ac0623686
2007c. Electrochemical monitoring of indigo preparation using Maya's ancient procedures. *Journal of Solid State Electrochemistry* 11: 1135–46. https://doi.org/10.1007/s10008-007-0296-2

DOMÉNECH, A., M.T. DOMÉNECH-CARBÓ, M. SÁNCHEZ DEL RÍO & M.L. VÁZQUEZ DE AGREDOS PASCUAL. 2008. Comparative study of different indigo-clay Maya Blue-like systems using the voltammetry of microparticles approach. *Journal of Solid State Electrochemistry* 13: 869–78. https://doi.org/10.1007/s10008-008-0616-1

KLEBER, R., L. MASSCHELEIN-KLEINER & J. THISSEN. 1967. Study and identification of Maya Blue. *Studies in Conservation* 12: 41–56. https://doi.org/10.1179/sic.1967.006

LITTMANN, E.R. 1982. Maya Blue further perspectives and the possible use of indigo as the colorant. *American Antiquity* 47: 404–408. https://doi.org/10.2307/279911

MAGALONI KERPEL, D. 1996. *Materiales y técnicas de la pintura Maya*. Mexico City: Facultad de Filosofía y Letras, UNAM.

REYES-VALERIO, C. 1993. *De Bonampak al Templo Mayor: el azul Maya en Mesoamérica*. Mexico City: Siglo XXI.

SÁNCHEZ DEL RÍO, M., P. MARTINETTO, C. SOLÍS & C. REYES-VALERIO. 2006a. PIXE analysis on Maya Blue in Prehispanic and colonial mural paintings. *Nuclear Instruments and Methods in Physics Research B* 249: 628–32. https://doi.org/10.1016/j.nimb.2006.03.069 – 2006b. Synthesis and acid resistance of Maya Blue pigment. *Archaeometry* 48: 115–30. https://doi.org/10.1111/j.1475-4754.2006.00246.x

SÁNCHEZ DEL RÍO, M., A. GUTIÉRREZ-LEÓN, G.R. CASTRO, J. RUBIO-ZUAZO, C. SOLÍS, R. SÁNCHEZ-HERNÁNDEZ, J. ROBLESCAMACHO & J. ROJAS-GAYTÁN. 2008. Synchroton powder diffraction of Aztec blue pigments. *Applied Physics A* 90: 55–60.

https://doi.org/10.1007/s00339-007-4264-6

SANZ, E., A. ARTEAGA, M.A. GARCÍA, M.A. CÁMARA & C. DIETZ. 2012. Chromatographic analysis of indigo from Maya Blue by LC–DAD–QTOF. *Journal of Archaeological Science* 39: 3516–23. https://doi.org/10.1016/j.jas.2012.06.019

TORRES, L.M. 1988. Maya Blue: how the Mayas could have made the pigment, in E.V. Sayre (ed.) *Materials issues in art and archaeology* (Symposium Proceedings 123): 123–28.
Pittsburgh (PA): Materials Research Society. https://doi.org/10.1557/PROC-123-123
VAN OLPHEN, H. 1967. Maya Blue: a clay mineral-organic pigment? *Science* 154: 465–67.
https://doi.org/10.1126/science.154.3749.645
VANDENABEELE, P., S. BODÉ, A. ALONSO & L. MOENS. 2005. Raman spectroscopic analysis of the Maya wall paintings in Ek'Balam, Mexico. *Spectrochimica Acta Part A* 61: 2349–56.
https://doi.org/10.1016/j.saa.2005.02.034
VÁZQUEZ DE ÁGREDOS PASCUAL, M.L. 2010. *La pintura mural maya. Materiales y técnicas artísticas*. Mexico City: CEPHCIS-UNAM.