

EVIDENCE FOR THE USE OF EGYPTIAN BLUE IN AN 11TH CENTURY MURAL ALTARPIECE BY SEM-EDS, FTIR AND SR XRD (CHURCH OF SANT PERE, TERRASSA, SPAIN)*

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The present study shows the analysis performed on pigment samples taken from Sant Pere (Terrassa, Catalonia, Spain), a remarkable church built in the Romanesque style. On the basis of the results obtained from the analysis, an interesting discussion arises after finding evidence of Egyptian blue in one of the samples, a discovery that was not expected due to the time period of the samples. The pigments were identified by the combined use of FTIR and SEM with an EDS facility. For the blue pigment, since the EDS and FTIR analyses suggested the possible presence of cuprorivaite, micro-XRD experiments using synchrotron radiation were run.

KEYWORDS: PAINTING, EGYPTIAN BLUE, CUPRORIVAITE, CALCIUM OXALATE, FTIR, XRD

RESEARCH AIM

During the process of restoration of an altarpiece in the church of Sant Pere (Terrassa, Catalonia, Spain), several analytical studies were carried out in order to determine the materials with which the altarpiece was painted, as well as their state of conservation and the painting techniques used. The aim of this paper is to show the presence of an unexpected blue pigment (Egyptian blue) in an altarpiece painted in a period in which the use of such pigment was lost. Thus, it is important to underline this occurrence in some areas of the painted surface in a period of time when this material was not used at all in any of the contemporary sites.

The stone altarpiece is one of the few stone pre-Romanesque altarpieces remaining in Catalonia and it was found in its original place in 1856. Thus, the study of the technique used by the painters in such a unique piece was of particular interest. Moreover, the modifications and ancient restorations made on the altarpiece, which took place mainly from the 10th to the 14th centuries, during the construction and modification of the church, could help us to understand the kind of interventions made on that kind of work of art.

Finally, the experimental data are also to be taken into account while restoring the paints, in order to avoid degradation due to incompatibilities between restoration products and original pigments and to assure the most accurate process.

INTRODUCTION

The church of Sant Pere, built in the Romanesque style, is one of the most remarkable monuments of Terrassa (a city 30 km from Barcelona, located in the northeastern region of Catalonia). The church is a part of a monumental ensemble of three Romanesque churches, together with

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Sant Miquel and Santa Maria. The complex is of particular interest not only because of the beauty of the Romanesque complex, but also because it represents different historic-artistic periods in Catalonia, dating back from the Iberian culture to the present time (Ballbè i Boada 1988).

The Romans founded the city of Egara next to an Iberian village called Egosa. The remains of the Roman city are preserved all around the modern city of Terrassa and ceramic remains of the Iberian culture have also been found. A Provincial Council took place in Egara from 614 to the Muslim conquest in AD 718.

The three churches were built next to the Roman city following the Byzantine model of two churches (Sant Pere and Santa Maria) and a baptistery (Sant Miquel). The churches were finished around the end of the 11th century or the beginning of the 12th. Thus, they exhibit a characteristic Romanesque style, although the pre-Romanesque Visigoth buildings are partially preserved in the present structures (Ballbè i Boada 1988). The churches were declared National Monuments in 1931.

Remarkable Romanesque and pre-Romanesque paintings are present in both Santa Maria and Sant Miquel. Sant Pere's transept and apse date back to the 10th–11th centuries and a mosaic on the floor also dates to the 10th century. In that very same location, a late sixth century Roman mosaic placed in front of Santa Maria church was also found, together with several ancient archaeological remains dating back to the Iberian and Roman periods.

The altarpiece in Sant Pere de Terrassa is of particular interest due to the fact that stone altarpieces were not just rare in Catalonia (even though some of them can be found in the western region of Catalonia), but they were practically non-existent during the pre-Romanesque period and are more characteristic of the Gothic. This sole fact makes Sant Pere's altarpiece a unique and singular work of art. The studied altarpiece (2.80 × 3.50 m) consists of a wall closing the apse of the church with a mural painting representing several figures and geometric decoration. It is made of three rows of mural paintings: the two upper lines are made of blind arches (two arches in the top row and four in the middle row), where Jesus, Saint Peter and the evangelists are represented, and an area at the bottom with some unidentified figures (Fig. 1).

The original design was modified some time after being finished (probably around the 14th century when the Gothic paintings were made) and new figures and decoration were drawn on top of the ancient ones. Nevertheless, both designs can still be observed nowadays. Later on, several repaints, reparations and redraws were done without being documented during the different modifications of the church. Although the altarpiece has been preserved in its original position, it was covered for years and it was only found during a restoration process in the church in 1856.

The state of conservation of the piece looks partially deteriorated mainly because the space between the wall and the apse had been filled with different materials. Owing to that, salts had reached the painted surface, causing the decay and detachment of the paint layers. Moreover, the colours and design of the altarpiece are difficult to appreciate because of the application of an organic material on the surface during the process of restoration that took place after it was found (20th century). This layer is partially detached and the accumulation of dust on the surface is notorious.

The colour palette used in this piece is limited. White, black, red and several ochres are the colours and pigments that are the most used. Blue has been applied in different background figures in the three rows of the altarpiece. Probably, a sky of stars was the background for some of the pieces. Additionally, very small blue spots can be appreciated, surrounding the aureole of some figures.

The common colours at that time were limited to green earths, black from vegetal coal or burned bone, and a wide variety of ochres, reddish and brown, supplied by more or less local



Figure 1 (A) The design of the altarpiece in Sant Pere, Terrassa. (B) A detail of one the pictures on the altarpiece, in which blue, red and ochre colours are present.

clays (Merrifield 2004). Blue pigments, which were normally expensive, were replaced in the Pyrenean area by a local pigment (aerinite) associated with small outcrops of volcanic rocks, which gives a pale blue, far from the intense and exciting blue produced by azurite or lapis lazuli pigments (Casas *et al.* 1992).

The use of Egyptian blue has never been documented in this region, nor for stone pre-Romanesque altarpieces of any kind. Thus, the interest in the characterization of the altarpiece as a singular work of art and the evidence for the use of Egyptian blue as a pigment in the 10th century or in ancient restorations makes the results of the analyses of particular interest.

EXPERIMENTAL

Sampling and techniques

To characterize the materials used in this altarpiece, small samples (less than 2 mm²) representative of each colour in the altarpiece were collected in coordination with the restorers, with the aim of determining the painting materials (pigments, filler and binder) as well as the painting technique and their state of conservation. Samples were taken with a surgical scalpel and placed on a concave slide. They include some plaster substratum and coloured layers. Table 1 summarizes the samples analysed and the sampling points are also indicated.

Table 1 Samples collected, description and origin area in the stone altarpiece

Sample	Description	Colour	Altarpiece sampling area
SPT 1	Mortar	–	Left area of the bottom row
SPT 2	Pigment sample	Black	Left area of the bottom row
SPT 3	Pigment sample	Red	Middle row, second arch from the left
SPT 4	Pigment sample	Blue	Middle row, third arch from the left
SPT 5	Pigment sample (overlapping)	Black–red	Middle row, first arch from the left
SPT 6	Pigment sample	Ochre	Middle row, fourth arch from the left
SPT 7	Pigment sample	White	Middle row, third arch from the left

Optical microscopy

Samples were preliminarily observed using a low-magnification microscope (a stereo-microscope) in order to examine the number and sequence of the painting layers, including the support, and their superficial state of preservation. Part of each sample was embedded in polyester resin, using methyl ethyl ketone peroxide as hardener, cut with a low-deformation diamond saw and polished to allow the study of the cross-section under a reflecting dark-field optical microscope. A Carl Zeiss 60374 analytical microscope equipped with a camera was used for visible light microscopy of the cross-sections.

Scanning electron microscopy

The same polished sample was carbon coated for study under the scanning electron microscope (SEM) with a coupled energy-dispersive X-ray spectroscopy (EDS) facility. SEM images were taken using a JEOL (Tokyo, Japan) JSM-840 (secondary and backscattered electron detection) with a LINK AN 10000 micro-analyser. The acceleration voltage used was 20 keV.

Infrared spectroscopy

The remaining fragments of each sample were analysed by Fourier transform infrared spectroscopy (FTIR), using a diamond cell that allows the beam to be focused on a particular grain according to its colour and appearance when observed with visible light microscopy. The equipment used was an infrared spectrometer Bomem MB-120, equipped with a SpecHra-Tech 'IR-Plan' advanced analytical microscope. The spectral range recorded was 4000–720 cm^{-1} when working with the microscope and 4000–350 cm^{-1} when working with the anvil cell. The spectra were collected in transmission mode with a resolution of 4 cm^{-1} , using a DTGS detector. The different layers were separated mechanically by using a dissecting knife and tungsten needles (made by the authors) under a stereo-microscope.

X-ray powder diffraction and SR XRD

For the characterization of the crystalline phases (in the mortar and preparation layer where there was a sufficient amount of sample), a Siemens D-500 X-ray diffractometer (scintillation counter, graphite secondary monochromator, Cu $K\alpha$ radiation, 20 kV, 40 mA) was used.

The blue sample was analysed by micro-XRD at station 9.6 of the Synchrotron Radiation Source at Daresbury Laboratory (UK). A wavelength of 0.08664 nm was used and the slit width was 200 μm . The patterns were acquired in transmission geometry by a CCD collecting plate at 150 mm and fitted with the ESRF FIT2D package (Hammersley *et al.* 1996). The sample was prepared as an attempt to select only blue grains from the blue spots and place them in a silica capillary tube (although it was impossible to avoid some preparation layer grains amongst the blue ones).

RESULTS

Mortar and preparation layer

The XRD pattern of the mortar under the preparation layer (sample SPT 1) indicated that the main constituents were calcite (CaCO_3) and quartz (SiO_2), but small amounts of dolomite [$(\text{CaMg})(\text{CO}_3)$] and clays (illite, kaolinite) were also present. These results are consistent with a lime mortar used as a substrate, which is constituted by lime (which becomes calcite after hardening) and small grains of quartz and dolomite, with some contamination by clays.

The XRD patterns of the preparation layer from pigment samples (SPT 2 to SPT 7) showed the same composition as the mortar and, in addition, traces of calcium sodium phosphate ($\text{NaCa}(\text{PO}_4)$). This phosphate could be related to a decay by-product associated with some organic additive, frequently applied to these layers.

In some of the samples, the presence of biological colonization was detected (Garcia-Vallès *et al.* 1998), mainly consisting of fungi that developed hyphae, which penetrated through the paint and the preparation layer (Fig. 2).

The presence of magnesium sulphate (epsomite, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) has been reported in areas of the altarpiece where painting no longer exists, and its origin has been related to the lixiviation of the mortars and other materials filling the space between the altarpiece and the apse, which was heavily affected by humidity and water infiltrations. The crystallization of epsomite is one of the main problems that has affected the conservation of the mural painting in the past.

Pigment layer results

The pigments and other phases identified, as well as the analytical techniques used and the SEM–EDS results, are shown in Table 2 for the different colours represented in the samples taken.

White, black, red and ochre samples

Analytical investigations carried out on the painting layers of samples SPT 2, 3, 5, 6 and 7 (Fig. 3 (A)) by both EDS and FTIR determined a limited variety of pigments, mostly based on clay minerals with different amounts of iron oxides (red and ochre samples), calcite (white samples) and charcoal black (Ionescu *et al.* 2004).

Optical microscope observation on cross-sections allow the identification of a couple of layers (a pigment layer on a white preparation layer) for all of the samples except SPT 5, where two pigment layers were identified (black on top and red on the preparation layer) due to overlapping of the drawing.

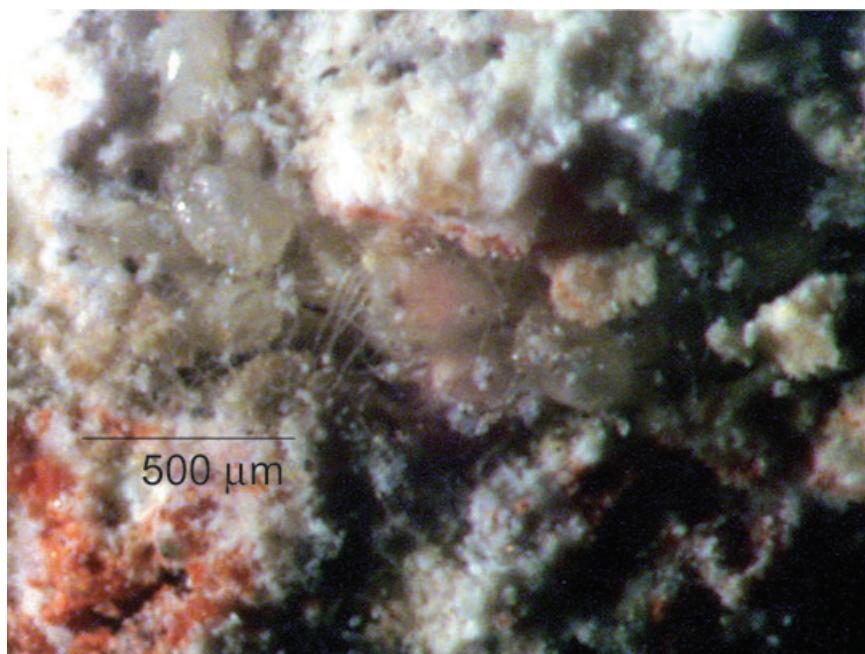


Figure 2 The presence of biological colonization in the red sample preparation layer.

Table 2 Summary of the colours, identified pigments, techniques used and main results obtained

Colour	Elemental composition	Identified pigment	Other phases identified	Analytical technique
Red	Si, Ca, Al, Mg, Fe, P	Red earth Fe_2O_3 + clay	$\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	SEM, EDS, FTIR
Yellow/ochre	Si, Ca, Al, Fe, Mg (Ti, S, K)	Yellow ochre $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ + clay	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	SEM, EDS, FTIR
White	Ca, Si, Mg, S	Lime (CaCO_3)	$\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	SEM, EDS, FTIR
Black	Ca, Si, Al, K, Mg	Coal black		SEM, EDS, FTIR
Blue	Si, Ca, Cu, K, S, Fe, Al	Egyptian blue ($\text{CaCuSi}_4\text{O}_{10}$)	$\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	SEM, EDS, FTIR, SR XRD

The absorption bands found in the FTIR spectra of the different colours correspond to the silicate signal (1033 and 910 cm^{-1}) due to the earth pigments (clays) (Bikiaris *et al.* 1999) and peaks assigned to their crystallization water (3694 and 3617 cm^{-1}) (Van der Weerd *et al.* 2004). Kaolinite seems to be present in most of the samples as a filler (1117, 1033, 1010 and 915 cm^{-1}) (De Benedetto *et al.* 2002).

The FTIR spectra also suggest the presence of organic matter, highlighted by the absorption at 1727 cm^{-1} , indicating the presence of a C=O bond of esters, and absorptions at 3025, 2954 and 2923 cm^{-1} , corresponding to the stretching vibration of hydrocarbon chains (Doménech Carbó

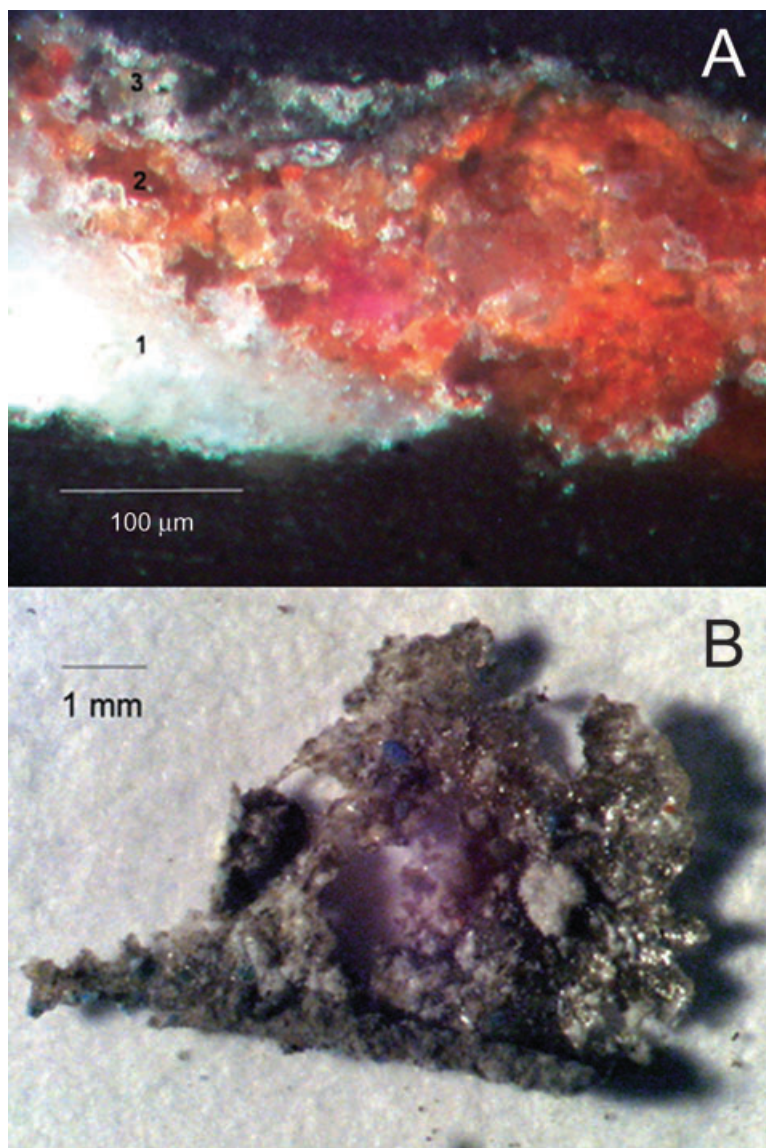


Figure 3 (A) An optical microscopic image of a polished cross-section of the red sample, showing the three layers of the red sample: (1) the preparation layer; (2) the red layer, or pigment layer; and (3) the top or coating layer. (B) The surface of the sample, where the top-coating layer can be clearly distinguished.

et al. 1996). Nevertheless, those absorption bands are not sufficient for the reliable identification of an organic binding medium.

Most of the painted surfaces appear to be coated with a protective layer (Fig. 3 (B)) which, in many cases, caused part of the paint to detach, due to the retraction associated with its hardening. By comparison with the standards, the FTIR spectra peaks indicated the presence of a synthetic resin, probably an acrylic (Derrick *et al.* 1999; Learner 2004).

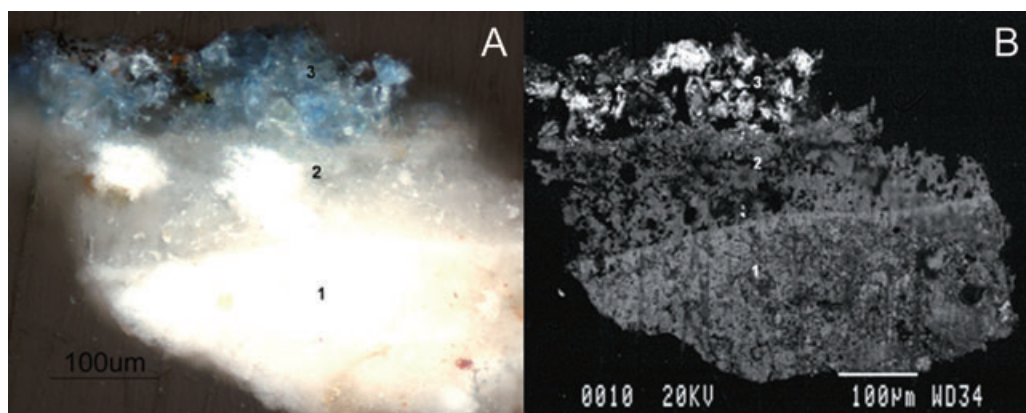


Figure 4 (A) Optical microscopic images of the blue sample cross-section. (B) A backscattered SEM image of a polished section of the blue sample. Three layers can be easily distinguished in both images.

Moreover, the phases detected to be associated with the painting but which do not correspond to the pigment or the filler, such as calcium oxalate (weddellite, $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), could be considered as oxidative decay by-products of the binder (Cariati *et al.* 2000; Rampazzi *et al.* 2004), although their origin has not yet been clarified (Doménech Carbó *et al.* 1996). However, according to the biological hypothesis of their origin (Garcia-Vallès *et al.* 1998), calcium oxalates could be precipitated from oxalic acid secreted by the bio-colonization that was detected (mentioned above). The occasional presence of magnesium sulphate (epsomite, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) has also been reported for some samples by FTIR.

The problem of the blue

Blue was the only colour that was not part of the common pigments (Casas *et al.* 1992; Merrifield 2004), which is the reason why special attention was paid to its study. Furthermore, the ancient documentation related to the pigments used in this period suggested that blue colours could be obtained from a limited number of possible raw materials, namely azurite, lapis lazuli and the so-called aerinite (mostly used in the Pyrenees). However, the analyses carried out on the blue samples did not fit with any of those pigments.

A cross-section of the blue painted layers is shown in Figure 4, where it can be seen that the blue layer (Layer 3) was applied over an intermediate layer (Layer 2) which is on the support (Layer 1). Layer 1 corresponds to the preparation layer described below. The EDS analyses (Table 3) of Layers 1 and 2 indicate the presence of Ca, Si, Mg and S elements that correspond to a lime applied before painting.

The FTIR spectrum of Layer 2 suggests the use of a wax, due to the characteristic CH_2 bands shown: 2915 cm^{-1} (with a shoulder at 2950 cm^{-1}) and 2850 cm^{-1} (Derrick *et al.* 1999). The use of a wax as an intermediate layer is specific to the blue sample (SPT 4), as it has not been found in any of the other samples from the altarpiece (Fig. 3 (A)). The spectrum of Layer 1 contains strong carbonate absorptions due to the presence of calcium carbonate and a strong calcium oxalate signal.

Identification of the binding media is also not straightforward. The combination of peaks visible suggests the presence of the same binding media as in the other samples. Those peaks are

Table 3 Description of the three layers in the embedded cross-section of the sample SPT 4 in Figure 4

Layer	Colour	Elements	Identification
3	Blue	Si, Cu, Ca (K, S, Fe, Al)	Colour layer
2	Grey	Ca, Si, Mg (S)	Wax
1	White	Ca (Mg)	Preparation layer

not intense due to the high pigment concentration and are partially overlapped by carbonate and silicate bands.

The main elements in the blue areas (Layer 3) are Si, Ca and Cu, together with other minor elements such as Al, S, K and Fe (Table 2). According to the bibliography (Mazzocchin *et al.* 2004a), the simultaneous identification of the three main elements (Cu, Ca and Si) should have been sufficient to indicate the presence of Egyptian blue (EB), which is a calcium copper silicate obtained by heating together (at 850°C) a calcium compound (limestone), a copper compound (minerals or bronze fragments), silica and flux (usually plant ash). Nevertheless, since this is not a common painting material in this period, the decision was made to carry out other complementary analyses.

The FTIR spectra of the same layer (Layer 3) indicated the presence of bands in the characteristic region of silicates (1025–1080 cm⁻¹) (Mirti *et al.* 1995) and the prominent bands of weddellite (calcium oxalate dihydrate: CaC₂O₄·2H₂O) at 1640, 1322 and 790 cm⁻¹ (Maravelaki-Kalaitzaki 2005). Kaolinite was deemed to be present owing to the existence of the corresponding peaks mentioned above.

However, it has been reported that absorption bands change their intensity and position within a range of wavelengths depending on the recipe (Riederer 1997; Mazzocchin *et al.* 2004b) and the presence of accidental products of the synthesis, such as quartz, trydimite or amorphous glass (Bruni *et al.* 1999). Bands at 1230, 1008 and 595, 521 and 484 cm⁻¹ are peculiar to EB (Mirti *et al.* 1995). Only one of the spectra recorded showed those bands with sufficient clarity (Fig. 5).

In order to determine accurately the nature of the blue pigment and its composition, small grains of the sample were prepared for irradiation with synchrotron radiation to acquire X-ray diffraction patterns (Fig. 6), which indicated that the phases forming the sample are quartz (SiO₂), cuprorivaite (CaCuSi₄O₁₀) and some organic material degradation products, such as weddellite (CaC₂O₄·2H₂O), magnesium phosphate hydrate and newberyite (MgHPO₄(H₂O)₃). Gypsum (CaSO₄·2H₂O) and cuprite (Cu₂O) were also present as minor phases.

The presence of cuprorivaite confirms the use of Egyptian blue as a pigment. It has been reported (Riederer 1997) that quartz and other silica phases, such as cristobalite, are always present in Egyptian blue in high concentrations. As cuprite was found, that would mean not only that the raw mixture contained an excess of copper (Mirti *et al.* 1995), but also that the pigment was synthesized under reducing conditions (Pagès-Camagna and Colinart 2003).

The phosphates probably come from grains of Layers 1 and 2, introduced in the capillary used to perform SR XRD when selecting blue grains, as traces of phosphates had been also reported in the XRD pattern of the preparation layer.

DISCUSSION

The palette of colours used is limited to quite common pigments, namely those associated with earth (clays with different amounts of iron oxides and hydroxides), charcoal black and lime. The

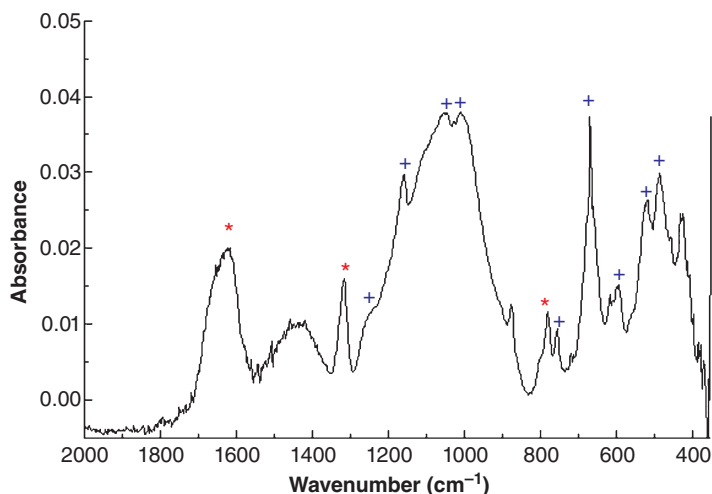


Figure 5 An FTIR spectrum of the blue layer, as a diamond cell transmission spectrum. The plus signs (+) indicate absorption bands of Egyptian blue, at 1230, 1160, 1051, 1008, 800, 755, 667, 595, 521 and 484 cm^{-1} . The asterisks (*) indicate absorption bands of weddellite, at 1640, 1322 and 790 cm^{-1} .

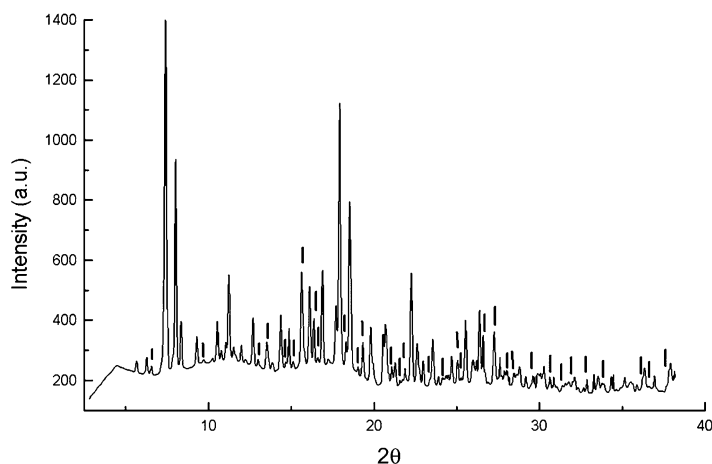


Figure 6 The micro-XRD pattern of the blue sample of Layer 1. Cuprorivaite (JCPDS 12-512) diffraction lines are indicated.

use of common and inexpensive pigments fits with those used in other Romanesque mural paintings in the region. The only colour different from the common Romanesque pigments was the unequivocally identified Egyptian blue in sample SPT 4.

Since the intermediate wax layer between the preparation layer and the pigment is only present in the cross-section of the blue sample SPT 4, and it is a modern product (probably from a restoration), it seems logical to suggest that it corresponds to a product used to fix a partially detached colour layer, and explains why a modern product is found beneath an ancient one. Thus, even if there is no documentary evidence, this confirms that ancient restorations and repairs have affected the piece, confirming what is suggested by the overlapping of figures in the altarpiece design.

Egyptian blue was quite widely used from the third millennium BC to the Roman period. The use of such a pigment after the fall of the Roman empire was rare, but it has been reported (Lazzarini 1982) in some Italian paintings (the church of San Clemente, Rome) and Carolingian wall paintings in Müstair (Switzerland) dated to the ninth century (Riederer 1997), but it has never been identified in the 10th century or later. There are neither written references to the production of Egyptian blue in medieval times (in fact, scholars agree that its manufacture was lost some time in the late Roman period), nor evidence of production of this pigment at the site or in the region.

Therefore, some other hypotheses must be considered: the re-use of an Egyptian blue pigment found nearby during an ancient restoration, the use of a modern pigment in a modern restoration, or the production of Egyptian blue during the Middle Ages. However, Egyptian blue has not been characterized in Catalan paintings of the same period or later. Although the pigment has been characterized in Roman paintings such as the Vila del Munt (Tarragona, Catalonia), no evidence for the production of Egyptian blue in Catalonia during the Middle Ages has been found. Therefore, the use of Egyptian blue during an ancient restoration of the altarpiece (probably in the 12th–14th centuries) seems to be possible only through the re-use of Roman pigment found by the painters, either as powder or as balls (Mirti *et al.* 1995; Tite pers. comm.). It is important to note that the site where the church is located was formerly a Roman settlement. A later restoration process, probably after the finding of the altarpiece in 1856, using modern Egyptian blue seems rather less plausible.

CONCLUSIONS

The use of synchrotron facilities was a necessary tool in order to be completely sure of the nature of the blue pigment as the element composition determined by EDS: the FTIR spectra were indicative but not conclusive (taking into account the manufacturing period of the masterpiece), and the small amount of sample made it impossible to achieve a pattern with a conventional diffractometer. The identification of cuprorivaite in the XRD pattern is conclusive.

Therefore, due to the SR XRD results combined with conventional data (EDS and FTIR results), new data on the historical use of Egyptian blue has been established with a reference to the application of that pigment after the 10th century, later than the findings in San Clemente or Müstair. Moreover, these results add information about the Catalan painters' technique for stone pre-Romanesque altarpieces and about their palette. Also, suggestions about restoration processes such as salt elimination, the removal of superficial organic material and the elimination of the fungi and bacteria that affect the altarpiece can be made taking into account the conservation problems that have been identified.

Finally, the identification of Egyptian blue confirms its use in a period in which this pigment was not at all common, and raises some questions regarding the use and production of this pigment after the ninth century, its possible use as a restoration material and the particular identification of a wax on the preparation layer.

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