Received: 11 May 2017 | Revised: 11 July 2017 | Accepted: 30 August 2017
DOI: 10.1002/col.22181

RESEARCH ARTICLE

WILEY

Identification of vivianite, an unusual blue pigment, in a sixteenth century painting and its implications

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Abstract
Vivianite, a blue pigment employed in the past practically only in Northern and Central Europe, but with very limited use, was identified in an early sixteenth century painting, stylistically with Flemish features, from a church in Portugal. The identification of this iron phosphate mineral was made by SEM-EDS based on the atomic ratio between phosphorus and iron in layers of blue paint (area analysis) and in particles of these same layers (spot analysis). This painting, about which there is no document to prove its authorship, becomes the first case, known in detail, of a sixteenth century painting containing vivianite. Moreover, this find and the presence of a chalk ground, also identified, strongly support the hypothesis of being a Flemish painting.

KEYWORDS
authorship, painting, provenance, SEM-EDS, vivianite

1 | INTRODUCTION

The work of art on which this study focuses is a triptych of the early sixteenth century, currently housed in the baptistery of the church of Saint John the Baptist, in Tomar, Portugal, a building classified as a National Monument. Known as the *Triptych of the Life of Christ*, it consists of a central wooden panel, 258 cm high and 199 cm wide, and two outer wings panels, also made of wood, painted on both sides (Figure 1).

There are no documents that relate to the commission and painting of the triptych. Only based in the stylistic characteristics, a Flemish origin for it has been accepted since 1888, when it was first proposed by the art historian Karl Justi.[1] This hypothesis has been accepted by most of the art historians until today, in spite of some divergences relating to the true authorship of the paintings. Some of them refer only its Flemish origin in general,[2] while others consider this triptych a work attributable to Quinten Massys (c. 1466–1530), one of the most important painters of Antwerp;[3] however, some other specialists attribute these paintings to Eduard, the Portuguese, a Massys disciple and follower, who is known to have been active in Massys' workshop from 1504;[1,4] lastly, another art historian considers that the author of the triptych is an unidentified master very influenced by Massys' style.[5]

The triptych was object of a conservation and restoration intervention[6] and, within this framework, a technical study was carried out using a multi-analytical approach. During the analysis of the central panel, pigments frequently used in paintings of the sixteenth century were identified, as expected, but, among the blue pigments, in addition to the usual azurite or its synthetic equivalent (a basic copper carbonate), an unusual blue pigment, vivianite (an iron phosphate), was detected.

Vivianite is a pale blue iron phosphate mineral, which occurs naturally as a secondary mineral, both in oxidized mines and in lacustrine sediments or peat deposits, in several parts of the world.[7–9] In Europe, the sedimentary deposits found in Germany, Flanders and, specially, The Netherlands were of particular historical importance.[10] The geochemical processes involved in its formation have been reviewed by Rothe et al.[9] and its structural and thermodynamic properties by Capitelli et al. and by Ogorodova et al.[11,12]

With the formula $Fe_3(PO_4)_2{\cdot}8H_2O$, vivianite is colourless and translucent in its pristine state, but after mined, upon exposure to light and air, it turns to green, then to blue and, finally, to a very dark bluish-black. This colour change

FIGURE 1 Central panel of the polyptych, representing the *Baptism of Christ*

results from the partial oxidation of ferrous iron into ferric iron and the shift in the balance between them.[7,9,13]

In art technical sources, unquestionable references to vivianite, usually under the name of blue ochre or native Prussian blue, seem to exist only from after the end of the eighteenth century,[14] although several sources of the seventeenth and early eighteenth centuries probably refer to the pigment.[10]

Vivianite identification has been made in geological samples through various techniques, including X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) and infrared, Raman and Mössbauer spectroscopies,[9] but in works of art it has been made mainly by SEM-EDS, polarized light microscopy and XRD.[15] Through these techniques, however, it was identified in a very limited number of cases. In a review made ten years ago, its use was registered only in ten cases in mural painting (on stone or mortar), seventeen cases in easel painting on wood or canvas (although some cases involve more than one painting) and twelve cases in other wooden works (such as sculptures and furniture).[7] The mural paintings are mainly medieval works from Germany and Austria and the easel paintings, besides a medieval German painting, are from Austria and the Low Countries and are dated from the seventeenth and eighteenth centuries. The new cases which have since then been known, do not change this background. In the last published survey, about 70 works with vivianite are mentioned, dating from 1050 to 1780, deriving, in almost all cases, from Germany, Austria, and The Netherlands.[15] It seems that no published case of use in sixteenth century easel paintings is known, with the exception of a brief reference, without details, to "two unpublished sixteenth century examples, identified by EDX analysis": the painting "Christ and the Virgin", from the National Gallery, London, with the inventory number NG 295, probably dated from 1500–1550 and catalogued as "after Quinten Massys", and a Paolo

Veronese's painting.[16] Besides, as for other types of works of the sixteenth century, vivianite was only detected in a mural painting and two sculptures.[17,18]

In English mural paintings from the medieval period, it seems to have been used only where the mineral was found locally and, at least in some cases, for its own colour and not as a substitute for other more expensive blue pigments.[19]

Vivianite is generally stable in its blue form, but some cases in which the pigment had altered to a yellowish-coloured or to a grey material have been reported, either in mural[19] or in easel painting.[13] The problem was confirmed in synthesized samples.[20] It has already been hypothesized that conservation treatments contribute to this change in paintings.[19]

In this context of the use of vivianite in painting, the results obtained for the *Triptych of the Life of Christ*, presented here, seem to be important because they extend the very few number of known cases of the sixteenth century works where this pigment was employed and provide new data for the discussion of the history of art issues posed by the triptych.

2 | EXPERIMENTAL

The central painting of the triptych, where the *Baptism of Christ* is represented, was examined following the usual methodology in these circumstances, through macroscopic and microscopic observations using a magnifying glass and optical probe, ultraviolet fluorescence photography, infrared reflectography and radiography. With this analytical resources it was possible to distinguish between original paint and later restorations.[6]

In areas where the access of a portable X-ray spectrometry (XRF) equipment was possible, such as in the lower part of the painting, elemental spectra were obtained in different motifs and colours with a view to the identification of pigments. This noninvasive method of analysis was performed with a spectrometer composed of an X-ray tube with a Ag anode and a multichannel system Amptek XR-100CR, operated at 30 kV and 25 μA during 180 s.

The colour characterization was carried out with a Konica Minolta CM-700d colorimeter, having been obtained reflectance spectra, between 400 and 700 nm, in different points of the surface after removal of the varnish.

For the characterization of the stratigraphy of the chromatic layer, microscopic cross-section samples were collected in several places of the painting. In the present study only the results obtained for two samples are presented: the samples collected from an area of the blue of the water (sample PC6) and from a cloud in the sky (sample PC22), both from original paint areas. The samples were mounted in an acrylic resin and, after polishing, the cross-sections were analyzed by optical microscopy (Olympus CH30 microscope) and scanning electron microscopy (Hitachi 3700N microscope) coupled with X-ray energy dispersive spectrometry (Bruker Xflash 5010 spectrometer) (SEM-EDS). The SEM-EDS equipment was operated in the variable pressure mode (40 Pa) at 20 kV and the samples were analyzed directly, without metallization. Elementary semi-quantification was performed using the software Quantax through the PB-ZAF method.

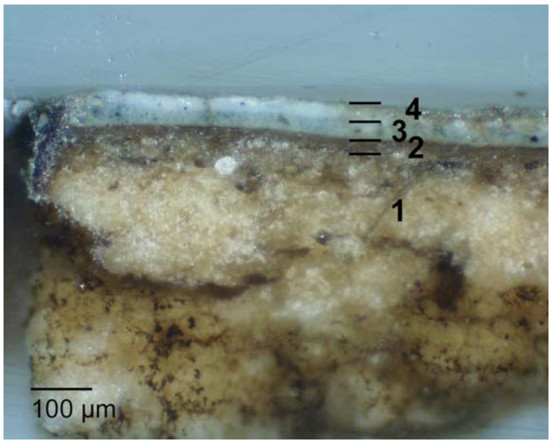

FIGURE 2 Cross sections of the Sample PC22, collected from the sky, observed through optical microscopy: (1) ground layer; (2) size layer; (3) light blue stratum; (4) whitish stratum

3 | RESULTS AND DISCUSSION

The sample collected from the sky (sample PC22), shows, from bottom to top, the ground layer (a preparatory layer applied to the wood support in order to prepare it for painting), a thin layer of size (an organic material used to seal the absorbent ground), and a colour layer composed of two strata: a light blue and a whitish, corresponding to the sky and to the cloud, respectively (Figure 2). According to the SEM-EDS elemental results, the ground is mainly composed of calcium and carbon compounds without sulphate ions, that is, calcium carbonate. In other samples of the same panel, remains of foraminifera are observed in this layer (Figure 3), leading to the conclusion that calcium carbonate is present in the form of chalk, as expected in a sixteenth century painting made in accordance to the Northern European tradition. Above the ground layer, the surface whitish stratum mainly consists of carbon and lead compounds, that is, lead white as expected in a painting from before the nineteenth century, which is also a major component of the blue stratum. However, this also shows iron and phosphorus as major elements (Table 1), which cannot be related to any common pigment used at that time that could be responsible for the blue colour. In general, iron could be an indicator of Prussian blue, but this synthetic

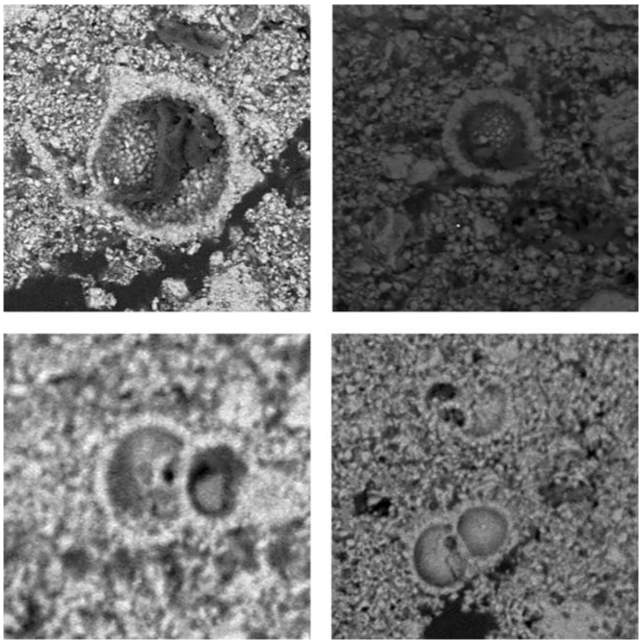

FIGURE 3 Examples of remains of foraminifera found in the ground layer of several samples taken from the central panel

pigment was not available before the eighteenth century and nothing suggests that the sample was collected in a repainted area. Besides, the hypothesis of being Prussian blue does not explain the very high concentration of phosphorus, an element that, in small concentration, is usually related to an animal black pigment, which is not observable in this sample.

Similarly, the sample collected from the blue of the water (sample PC6) shows, over the ground and the size layers, a dark blue stratum with even higher concentration of iron and

TABLE 1 Elemental atomic concentrations (expressed in percentage) obtained by SEM-EDS for samples PC6 and PC22 through area (A19 and A88) and point analysis (P8, P9, and P23), and corresponding ratio between phosphorus and iron concentrations

	Sample PC6			Sample PC22	
Element	**A19**	**P8**	**P9**	**A88**	**P23**
Na	–	–	–	–	4.05
Al	4.88	–	–	2.94	–
Si	8.70	–	–	3.14	–
P	20.76	37.79	37.20	15.89	36.91
K	2.23	–	0.74	1.05	0.56
Ca	11.84	8.11	6.54	15.84	6.33
Fe	30.09	50.35	52.79	20.76	48.11
Pb	21.51	3.76	2.73	40.36	4.03
Total	100.00	100.00	100.00	100.00	100.00
P:Fe	0.69	0.75	0.70	0.77	0.77

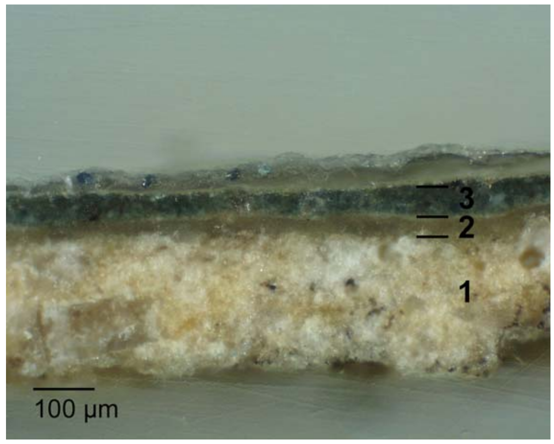

FIGURE 4 Cross sections of the sample PC6, collected from the water, observed through optical microscopy: (1) ground layer; (2) size layer; (3) dark blue stratum

phosphorus (Figure 4; Table 1). The SEM-EDS maps obtained for the two samples show that the distribution of iron and phosphorus is coincident in both blue strata (Figure 5).

The relationship between iron and phosphorus suggested by their distribution maps is particularly reinforced by the point analysis of blue particles present in the two samples (Table 1). Firstly, these three particles, in terms of elements, are mainly composed of iron and phosphorus, being calcium and lead minor components. Secondly, in these particles, the atomic ratio between phosphorus and iron is near constant. These values are also similar to the ratio values found in the whole strata.

The blue pigments used in ancient paintings, the high concentrations of iron and phosphorus and, also, their association suggest that the blue pigment employed in these samples is vivianite. Moreover, the atomic ratio between phosphorus and iron in the samples (0.73 in average of five

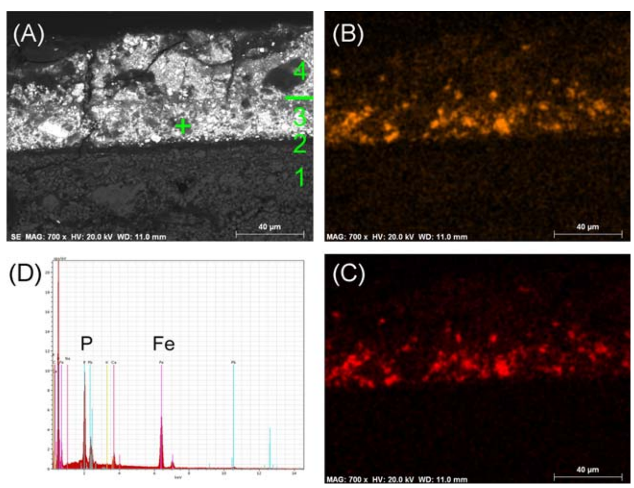

FIGURE 5 SEM-EDS data for sample PC22: (a) backscattering image; (b) P distribution map; (c) Fe distribution map; (d) EDS spectrum obtained in the particle marked with "+" in a). The numbers correspond to the layers indicated in Figure 2

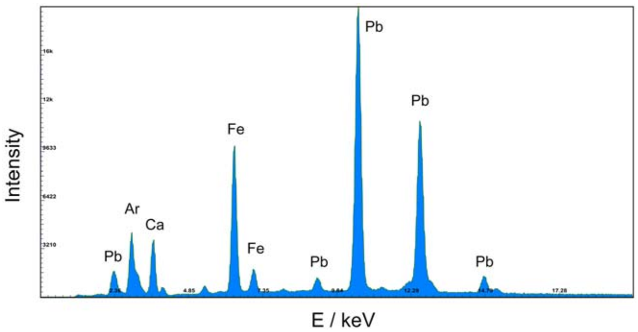

FIGURE 6 XRF spectrum obtained in the blue area of the river

analyses) compares well to the stoichiometric ratio of vivianite (0.67) and to the results obtained by electron microprobe for samples of vivianite (values between 0.67 and 0.83 with an average of 0.74).[11,21,22]

The presence of lead in the spectra of the three particles analyzed by SEM-EDS is easily explained by the lead white of the layer matrix. The calcium that also appears in the three spectra, as well as the potassium and sodium which are also detectable, are elements that may be related to the source of the vivianite itself.[15]

Due to the size of the samples and to the difficulties of accessing the painting with noninvasive equipment, it was not possible to perform any structural analysis (X-ray diffraction or FTIR spectroscopy), which would have confirmed beyond doubt the presence of vivianite, but we think that the above data are sufficient to consider that vivianite was used in this painting.

The presence of iron compounds as main constituents of the chromatic layer in the blue area of the river was confirmed by XRF analyses (Figure 6), suggesting that vivianite was generally used in this area and not just at the point where the sample PC6 was collected. (Phosphorus detection is not possible with the equipment used under the conditions employed.) The elevated position of the zone where the sky was painted did not allow similar measurements in this motif. In other original blue areas of the paintings (not just in the central panel), high concentrations of copper were detected through XRF analyses, suggesting that azurite (or its synthetic equivalent) was employed there.

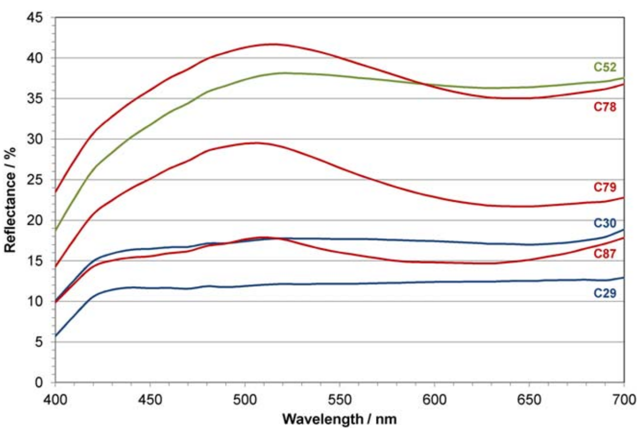

FIGURE 7 Representative reflectance spectra of points in the blue area of the mantle held by the angel (C29 and C30), the river (C52) and the sky (C78, C79, and C87)

The reflectance spectra obtained for original blue areas of the sky and the river are similar and have a maximum slightly above 500 nm, while this maximum is not evident where copper was detected by XRF, being the reflectance practically constant at wavelengths greater than 440 nm (Figure 7). These differences, however, cannot be employed to distinguish areas where each pigment was used, since azurite and vivianite may have significant shade variations (with more or less greenish hue) and, in the cases where the hue is bluer, have similar reflectance spectra with a maximum that can be in the range of about 450 to about 500 nm, depending on the mixtures.[23,24]

This identification of vivianite in a painting from the early sixteenth century is a very interesting result, becoming, as far as we know, the first case dated from that century published with detail.

With regards to the painting in this study, the detection of vivianite is a strong support for the suggestion for its Flemish origins. This probable provenance is also supported by the presence of a chalk ground, which besides being a characteristic of Northern European painting practice, has also been identified in paintings housed in Portugal and made in Flanders or by Flemish origin painters. Contemporary Portuguese painters and, in general, the painters of the South used grounds mainly of gypsum.[25]

In Portuguese collections of art, there are many Flemish paintings, as well as paintings which reveal in their features the Flemish influences, mostly of them produced in the first half of the sixteenth century, partly as a result of the intense political and commercial exchanges that existed between the two countries.[26] Many paintings were imported from Flanders, others were produced in Portugal by artists who travelled from Flanders to carry out painting commission and then returned to their country of origin. Other paintings were made by artists of Flemish origin who moved to Portugal more permanently, where they settled and often worked in collaboration with local Portuguese painters. Therefore, due to this interaction and to the absence of documentary evidence, it is not easy to draw conclusions on authorship of paintings with a Flemish style,[27] and the analytical methods are increasingly important in this cases. The use of a pigment unknown in Portugal, used in Northern Europe and originating from a common mineral in the Low Countries suggests that the triptych was made in Flanders or, at least, by a Flemish painter that expressly moved to Portugal for this commission rather than by a Flemish painter based in Portugal or by a Portuguese painter.

Furthermore, the identification of vivianite, in an unpublished study, in a different painting whose author is in some way related to the Massys workshop ("after Massys") helps to support the hypothesis of this painting originating from Flanders and possibly from an Antwerp based workshop, although the lack of other supporting material makes this proposition relatively limited.

4 | CONCLUSION

The identification of vivianite in the *Triptych of the Life of Christ*, by SEM-EDS, provided a rare case of use of the pigment in the sixteenth century, this being even the first case in easel painting published in detail. Moreover, this identification (reinforced by the ground layer based on chalk) significantly supports the hypothesis that the painting was made in Northern Europe.

ACKNOWLEDGMENTS

To the company Nova Conservação, Lda., for the grant (created to commemorate its 20 years of activity) that support the current study and intervention of conservation and restoration; to Vítor Gaspar, from Instituto Politécnico de Tomar, for the XRF analysis.

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How to cite this article: Cruz AJ, Eires E, Dias L, Desterro T, Rego C. Identification of vivianite, an unusual blue pigment, in a sixteenth century painting and its implications. *Color Res Appl*. 2018;43:177–183. https://doi.org/10.1002/col.22181