Egyptian Blue Pigment in East Mediterranean Wall Paintings - a study of the lifetime of its optical infrared emission

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Abstract

This study presents advances in the application of laser-based methods to image and measure the luminescence lifetime of historical wall paintings containing Egyptian blue. Samples from Tel Kabri, a major Aegean site dated to 18th C. BCE, from the Roman city of Caesarea Maritima, from the 4-5th C. Byzantine tomb in Lohamei Haghetaot and from a 6th C. Byzantine church of Shivta, have been studied using time-resolved photoluminescence spectroscopy and imaging. Taking into account the high-sensitivity of the emission lifetime to the micro-environment surrounding the emitting species, here we show for the first time that the optical emission from historical samples containing Egyptian blue particles exhibits meaningful lifetime variations. Indeed, the wall paintings from Tel Kabri, Lohamei Haghetaot and Shivta present the shortest emission lifetime, close to 115-120 μs. However, samples from Caesarea Maritima wall paintings exhibit a different optical emission which dumps more slowly with an average lifetime of 130 μs. Egyptian blue pigment particles, synthetized with modern methods, are associated with the longest emission lifetime of 147 μs. This study suggests that there is a possible link between the lifetime of the pigment's emission and its synthesis method.

KEYWORDS

Conservation science, Egyptian Blue, Luminescence, lifetime, pigment

1 | INTRODUCTION

This work is focused on the analysis of the luminescence properties of Egyptian blue pigment in Eastern Mediterranean wall paintings from the Aegean site of Tel Kabri, the Roman site of Cesarea Maritima and the Byzantine sites of Lohamei Haghetaot and Shivta.
Recent research has demonstrated how Egyptian blue gives rise to very strong and unique luminescence in the infrared,[1,2,3,4,5] and many examples of new discoveries of Egyptian blue in paintings have been published, often in cases where the presence of the blue paint is invisible to the naked eye, ranging from Middle-Bronze Age Aegean wall paintings,[6] Greek art,[7] early Roman wall paintings,[8] Roman vases,[9] to Early Christian wall paintings[10].

Due to the strength of the infrared luminescence of the pigment, luminescence is perhaps the most straightforward method for detecting the pigment analytically.[1,2,3] Studies of the lifetime of synthetic cuprorivaite report that the long-lived emission - centred at 910 nm - has a lifetime on the order of 107 μs and a quantum yield of 10 %.[1] Other lifetime measurements by Borisov et al.[5] suggest that the emission lifetime seems to be sensitive to pigment crystal size and synthesis methods: the luminescence lifetime of modern synthetised Egyptian blue was 159 μs and, after sintering and after grinding, it showed a net decrease to 126 μs. In situ analysis of a Late Period Cartonage using a time-resolved photoluminescence imaging system yielded lifetimes of approximately 120 μs.[11]

Egyptian Blue is one of the oldest synthetic pigments, which consists of Calcium Copper Silicate ($CaCuSi_4O_{10}$ or $CaOCuO(SiO_2)_4$). It was commonly used throughout most of the ancient world as a pigment in various artefacts such as paintings, wall paintings, tombs, mummies, coffins and in ceramic glazing.[12] Egyptian Blue became widespread in Egypt around 2600 BCE, although its first known use was earlier, possibly on 2900 BCE.[13] Recent studies of wall paintings from the 18th C. BCE finds of Tel Kabri, Israel, show that Egyptian blue was used continuously in the Eastern Mediterranean area.[6] The continuity of the use of that pigment in the early Byzantine period was recently studied in the Byzantine site of Shivta – Israel.[14] Egyptian blue was very commonly used during the Roman period, but later it occurred sporadically including in the Middle-Ages and beyond.[14,15,16,7,17, 18,19,20]

The aim of this work is to present laser-based time-resolved photoluminescence imaging for the detection of long-lived emissions from Egyptian blue in wall painting samples, and for the assessment of lifetime properties which could be related to production and grinding of the pigment. In the past, time-resolved photoluminescence imaging and spectroscopy has been effectively applied to the study of many painting materials including

pigments and organic materials,[24???] with recent applications on Egyptian Blue,[1] and artefacts painted with the ancient blue pigment.[11]

Commento [u1]: 21 or 24???

Here, we report the study of different samples from wall paintings with time-resolved photoluminescence (TRPL) imaging, complemented by analysis of samples using optical microscopy and scanning electron microscopy coupled with energy dispersive x-ray spectroscopy (SEM-EDX).

2 | NOTES ON THE PRODUCTION OF EGYPTIAN BLUE AND THE PARTICLE SIZE

The ancient production of Egyptian blue must have been in the hands of very competent specialists and large workshops for its production have been identified in Amana and elsewhere.[25,26,13] Egyptian blue synthesis requires the firing of a mixture of a copper salt, calcium carbonate and quartz usually with a small amount of a sodium flux to temperatures between 850-1050.[25,7,26] Frit cakes of the pigment from the 2nd Millenea BCE from Egypt have been studied by Hatton et al. [13] and these cakes would be ground to produce the pigment with large particle sizes reported to be as large as 150 μm. Variations in the sources of materials used for the production of Egyptian blue have been documented, with copper coming from copper salts, ores or bronze, and different fluxes could be used. It is noteworthy that bronze melts at approximately 950°C. Nonetheless, there is evidence that pigments were prepared in very similar way at different geographic locations in the Aegean and eastern Mediterranean sites during the Bronze Age period.[27]

The synthesis processes of Egyptian blue production have received much attention: Bianchetti et al.[28] demonstrated Egyptian blue production using different sources of natural raw Egyptian materials in different experimental conditions. Kakoulli[7] prepared eight different formulas to produce Egyptian blue, using temperatures between 830° and 1100° C. Different ground particles were produced, varying in size between 125-250 μm. Two experimental methods have recently been reported for the production of the pigment described by Johnson-McDaniel et al.[29,30]: The melt-flux method requires lower temperature (875 °C), and produced smaller-sized particles in the laboratory (5-15 μm crystallites by SEM), while solid state synthesis yielded larger particle sizes (15-50 μm) but requires higher synthesis temperatures (1020 °C), thus above the melting point of bronze. In archaeological studies, Grifa et al.[26] demonstrated that high temperatures were achieved in synthesis using crucibles from Cuma, thus exceeding the thermal stability of cuprorivaite crystals (950–1050°C), thus within the range for both synthesis routes.

Studies of the particle size of ancient Egyptian blue show great variation between eras and sites: Brysbaert[27] examined Egyptian Blue grain size from 15 different Bronze Age Aegean sites, showing a great average size variation between 13 and 130 µm. Linn et al. (2017) examined Egyptian blue particles from Middle Bronze Age Aegean wall paintings of Tel Kabri, showing that their size varies between 30-100 µm. Comparisons of the particle size of Egyptian Blue from Aegean Bronze Age period to Roman period, show a significant reduction in the particle size in later period, suggesting a process of finer grinding of the pigment as part of its manufacturing: for example the particle size of Egyptian Blue from the Roman period from Caesarea Maritima were measured approximately to 10-30 µm.[8] More recent Egyptian Blue particle from Shivta has particles size of the same magnitude as of Caesarea, between 20–40 µm.[10]

3 | SAMPLING AND METHODS

A reference sample from Kremer Pigments (Germany) of Egyptian blue was purchased and analysed for comparison with historic samples. The pigment was finely ground using a mortar and pestle and ground samples were analysed together with the coarser blue as supplied.

A variable number of samples from wall paintings fragments from Tel Kabri, Caesarea Maritima, Shivta and Lohamei Haghetaot were studied as part of this work.

Tel Kabri is located in the Western Galilee area of Israel and is among the very few East Mediterranean sites that revealed examples of Aegean-style paintings. The paintings found in Tel Kabri are probably the oldest representation in that region dated to the late 18 C. BCE,[21] and fragments have been studied in detail elsewhere.[6] Caesarea is located on the eastern Mediterranean coast. A settlement existed there for at least 1500 years, from the Persian period until the end of the Crusader period when the city was demolished. Samples in this study are from wall paintings dated to both the Early and Late Rome periods.[8] The early Christian tomb in Lohamei Hagetaot in the Western Galilee area has been dated to the 4-5th C. and contains wall paintings that were using Egyptian blue (R. Linn – unpublished data). The 6th C. early Christian wall paintings from the southern church of Shivta in the Negev Desert contain Egyptian blue as recently reported. [10]

3.1 | MICROSCOPY

Optical Microscopy was employed to examine the surfaces of samples and suitably prepared cross-sections. A Leica DMRX Polarized Light Microscope was used for the optical

analysis of samples. Cross-sections were prepared from the samples and mounted in polyester resin in styrene with Butanox M50 hardener. The cross sections were examined in incident light for the analysis of the stratigraphy of the paint layers.

Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM-EDX) was carried out using a Zeiss Sigma HD scanning electron microscope with Oxford Instruments AZtec integrated EDS, X-Max 80, used for high magnification imaging of the pigment particles and elemental analysis of Egyptian Blue.

3.2 | TIME-RESOLVED PHOTOLUMINESCENCE (TRPL)

The emission decay kinetic from samples was analysed with TRPL imaging.
The TRPL imaging unit[21] is based on a nanosecond laser excitation source combined with a time-gated intensified camera (C9546-03, Hamamatsu Photonics, Hamamatsu City, Japan), capable of capturing transient phenomena for emission lifetime measurement.

The laser beam (λ= 532 nm, Pulse energy = 60 μJ, Pulse duration = 1.0 ns), emitted by a Q-switching laser source (FTSS 355-50 Crylas GmbH, Berlin, Germany), is magnified with suitable optics in order to illuminate a circular area of about 5 cm in diameter to uniformly illuminate the wall painting surface. Gated images of the optical emission from sample surfaces are detected with the aid of the gated intensified camera, equipped with a proper lens camera and employing a gate width of 500 μs. The overall spatial resolution of the device, which is essentially limited by the image intensifier, is close to 50 μm.

The TRPL imaging measurement is based on the detection of a sequence of PL gated images at delays ranging from 0 to 900 μs with respect to laser pulses. Following data acquisition, it is possible to reconstruct the emission decay kinetic in each point of the analysed surfaces and to calculate the luminescence lifetime in each pixel by fitting the intensity decay using a monoexponential fit.

Analysis of the emission spectrum from samples was additionally carried out using laser-induced photoluminescence spectrometry. Laser excitation at 532 nm is provided by the same laser source of the TRPL imaging device, while optical emission is detected using a steady-state spectrometer (TM-CCD C10083CA-2100, Hamamatsu Photonics) with sensitivity in the range 320–1100 nm and a spectral bandwith of 6 nm. Through fibre optics, both the laser and the spectrometer are connected to a remote optical probe, working in the 45–0 configuration that allows excitation and analysis of a spot size of 1 mm in diameter on sample surface.

5 | THE MICROSCOPIC CHARACTERISTICS OF THE PIGMENT

Generally large particles of Egyptian Blue which are often up to 100 μm in length are found in many of the samples from Tel Kabri as seen in images of cross-sections and from the surface of blue areas in macro images in Figure 1. The pigment particles are of varying hue, ranging from dark to pale blue, some particles have sharp edges typical of the glassy pigment. Remarkably, the pigment is also found as an under-layer in areas where red paint has been applied over the surface.

Egyptian blue from Caesarea Maritima (Figure 2) is generally much more finely ground and particles as small as 10 μm are common, with many particles exhibiting the typical bright blue characteristic of the pigment. Unlike the earlier wall paintings from Tel Kabri, here the pigment is present only on the top layer of the painting.

The presence of Egyptian blue in samples from Shivta (Figure 3) and Lohamei HaGetaot was ascertained only through in-situ infrared imaging, and can be seen only following careful examination of cross-sections, which contain faintly blue particles of 25-40 μm length.

Figure 1

Figure 2

Figure 3

6 | ELEMENTAL ANALYSIS

In all cases the composition of the particles is similar to that reported by others with concentrations of Cu, Ca and Si reported in Table 1. The high concentrations of Si similar to those reported in blue frit samples [13]. Traces of Sn and As were detected in samples from Tel Kabri and powdered samples from Caesarea Maritima, which suggests that bronze filings could have been used in the production of the pigment, as has been reported by studies of frit and in Egyptian Blue.[13, 23, 24] Samples from Shivta do not contain detectable Sn or As which may be evidence that a copper salt was used there during synthesis.

7 | TIME-RESOLVED PHOTOLUMINESCENCE IMAGING ANALYSIS

All samples show the typical and narrow emission spectrum of cuprorivaite, with a maximum

emission at 910 nm, with no detectable variations in the emission among samples, as shown in Figure 4.

Figure 4

Instead, clear differences in the emission lifetime are observed between samples. Indeed, Egyptian Blue powder from Kremer pigment, synthetized with a modern process, exhibited the longest lifetime value (146 μs) which does not change following grinding of the pigment, the emission lifetime of historical samples is noticeably reduced with a maximum relative variation of -20% detected in the blue paint from Tel Kabri and Shivta, which exhibit a lifetime between around 115-118 μs. The calculated lifetime values for each sample are presented in Table 2.

It is noted that within each sample, detectable variations of the estimated lifetime are observed in imaging measurements. As a descriptive example (shown in Fig. 5), in a sample from Cesarea Maritima site we detect a lifetime with a relative variation of 5% (1 ∫) in the different points that were measured. A comparison between different samples from sites highlights in Figure 5 the variation in the lifetime of Egyptian blue.

Figure 5

The emission lifetime detected in historical samples is noticeably reduced with respect to the synthetic pigment produced with the modern synthesis process. Taking into account the high sensitivity of emission lifetime to the micro-environment of the emitting species,[31] we can correlate the detected difference between historical samples and the modern reference with the presence of impurities or charged crystal defects that modify the micro-environment of CuO_4^{6-} ions in the cuprorivaite mineral. In particular, the lifetime decrease detected in the historical samples suggests that the emission decay kinetic is affected by a higher level of non-radiative de-excitation paths. Indeed, it is possible that this change is induced by mechanical stress during grinding, an essential step in the production of Egyptian blue pigment from frit. Nonetheless, on the basis of the present research, no clear correlation between particle size and lifetime can be made, and more data is needed regarding the composition, the crystal structure and the crystal defects of the blue pigments, which could inform the interpretation of lifetime differences.

8 | CONCLUSIONS

The luminescence of the pigment Egyptian blue from four sites in the Eastern Mediterranean over two Millennia ranging from late 18th C. BCE to the 6th C. CE has been measured. While the emission spectra are constant, the luminescence lifetime among samples studied varies significantly, with no apparent correlation between particle size, location or age. In addition, variation within the same wall painting sample suggests that grinding may affect the luminescence decay. The synthesis process used for the production of Egyptian blue, both in terms of the impurities introduced and the temperatures employed could also have a substantial influence on the micro-environment of the chromophore CuO_4^{6-} and thus on the luminescence properties of the pigment. Future studies should aim to gather more data on luminescence properties of Egyptian blue in situ, with complete characterisation of samples with complementary techniques. It will be of interest to carry out future analytical research on a wider selection of Egyptian blue historical samples to assess the role of trace elements and structural defects on the photoluminescence decay properties of this precious pigment employed in a time spanning three millennia.

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Figure Captions:

Figure 1: Image of a cross-section of wall paintings from Tel Kabri showing the white ground, covered by a light red layer, large particle of Egyptian blue and a thick red layer, and fine black particles on the surface of the samples (left). Macro image of the surface of a sample from Tel Kabri, which contains typical Egyptian blue shiny blue particles of hues, varying from dark to pale blue, (right) (Photo: R. Linn)

Figure 2: Image of the surface of a wall painting sample from Caesarea Maritima, in which sharp-edged particles are seen distributed in white matrix (left). Particles of Egyptian blue vary in size and many are small, ~10 μm in length (right) (Photo: R. Linn)

Figure 3: Image of a cross-section from Shivta, showing particles of Egyptian (Photo: R. Linn)

Figure 4: Emission spectra recorded from different samples of wall paintings share a maximum at 910 nm

Figure 5: Lifetime maps of the reference Egyptian blue pigment and six historical samples painted with Egyptian blue from different sites (see Table 2 for mean lifetime value and related standard deviation in each sample)