Rendiconti Lincei. Scienze Fisiche e Naturali (2020) 31:913–917
https://doi.org/10.1007/s12210-020-00960-4

Imaging the antique: unexpected Egyptian blue in Raphael's *Galatea* by non-invasive mapping

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Received: 9 September 2020 / Accepted: 18 September 2020 / Published online: 4 October 2020

Abstract

Unexpected finding of Egyptian blue emerged in Raphael's fresco *Triumph of Galatea* at Villa Farnesina, in Rome. This pigment is the oldest man-made blue, dating back to Egyptians who manufactured it first and whose occurrence was thought to be lost with Romans. Thanks to advanced imaging techniques it has been possible to non-invasively map its distribution throughout the frescoed surface and to obtain a non-invasive imaging stratigraphic analysis indicating whether pure painting layers, mixtures or overlapping occurred. Egyptian blue identification on Raphael's *Galatea* is so far the earliest of sixteenth century, and could be the first step towards its tracking in Renaissance, demonstrating that non-invasive techniques are a mandatory step not only for materials identification but also for understanding art history and its dynamics.

Keywords Raphael · Egyptian blue · Macro X-ray fluorescence (MAXRF) · Red-induced luminescence (RIL) · Non-invasive analyses · Villa farnesina

1 Introduction

In 2020 the fifth centenary of Raphael's death is celebrated throughout the world. On this occasion the Accademia Nazionale dei Lincei, has planned a technical study of the *Triumph of Galatea* (Fig. 1, top row, left), the fresco painted by Raphael inside Villa Farnesina, the Lincei's representative headquarters in Rome. The aim was to characterize the painting technique and materials by means of the most advanced non-invasive imaging techniques, to have a thorough technical knowledge of this artwork in view of the exhibition "Raphael in Villa Farnesina: Galatea and Psyche". Surprisingly, during the investigations, the discovery of a pigment related to the technologies of the Antiquity occurred. This pigment is the oldest man-made blue known as 'Egyptian blue'. It was first manufactured by Egyptians and extensively used in Antiquity from 3000 B.C. until Roman period and since then, apart sporadic occurrences during high Middle Ages, no further traces of it were ever found, replaced by others easier- and ready-to-use blue pigments.[1]

[1] C. Seccaroni, P. Moioli, Pigmenti a base di rame. Fonti storiche e analisi scientifiche. *O.P.D. Restauro*, 216–252, (1995).

This contribution is a peer-reviewed version of a paper presented at the international meeting of the Non Destructive Techniques on Cultural Heritage (NDT-CH 2018) held October 12, 2018 in Buenos Aires (Argentina)S. I :Non-destructive techniques for cultural heritage

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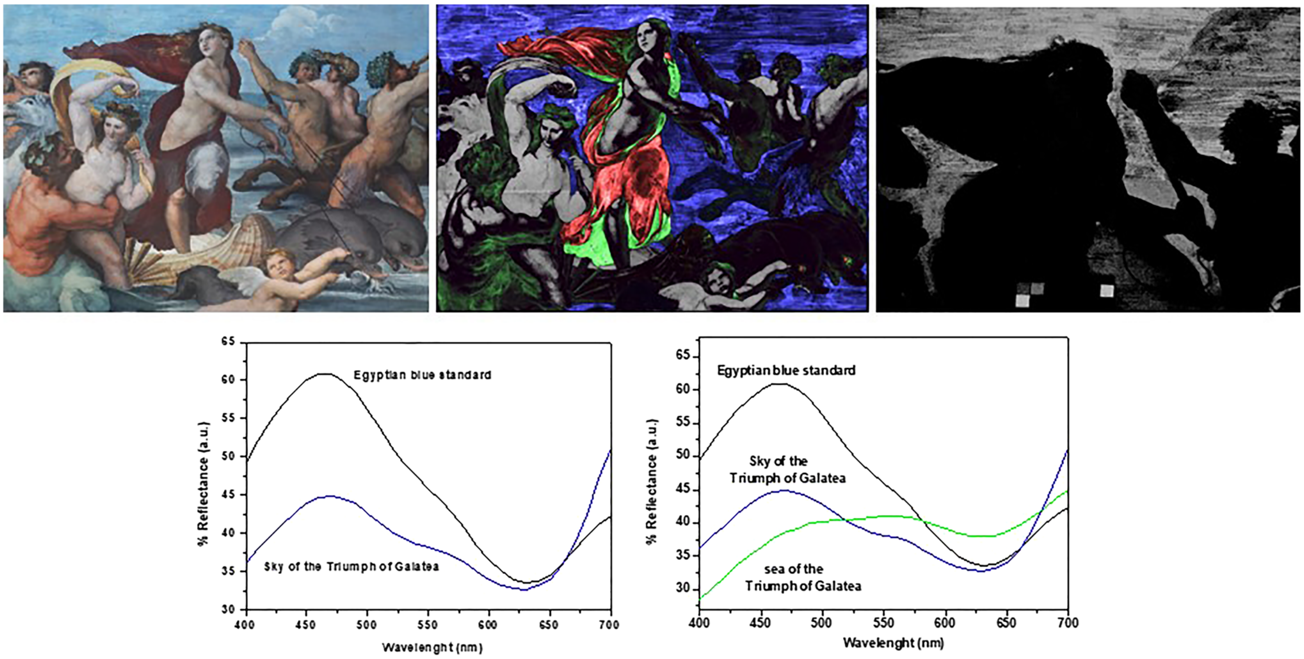

Fig. 1 Top row The *Triumph of Galatea*. Left: visible light image; centre: MA-XRF image with the main elements indicated in different colors, Cu (blue), Fe (green), Hg (red), Ca (grey); right: RIL image showing in the white areas the luminescence and distribution of Egyptian blue (a panel with Egyptian blue painted at different dilutions is included in the lower part of the image, as luminescence standard for comparison). Bottom row, from left: visible reflectance spectra recorded on the sky (blue line) compared with Egyptian blue standard (black line) and comparison among the sky (blue line), sea (green line) and the standard Egyptian blue standard (black line) (color figure online)

2 Materials and methods

2.1 Visible reflectance

The visible reflectance measurements have been carried out by a portable spectrometer CM-700d produced by Konika Minolta. The spectrometer is equipped with an UV radiation filter Xenon lamp and a silicon photodiodes array detector. The analysis range is 400–700 nm with a slit of 10 nm.

2.2 Near infrared emission luminescence

Punctual luminescence measurements were collected by a portable prototype. As the excitation light source, a portable laser with emission centered at 637 nm was used and focused into a probe system. The signal emitted from the surface was collected by a high-sensitivity Avantes CCD spectrometer (200–1100 nm) through a fused silica fiber optic cable. Cut-on filters were used in front of the detector to eliminate the second-order excitation light. The spectral resolution is about 20 nm using a 600-µm fiber optic diameter. This fiber allows a surface area of 2 mm^2 to be analyzed. A model based on the Kubelka–Munk theory of diffuse reflectance was applied to take into account of the fluorescence self-absorption and re-emission in solid state.

2.3 Macro X-ray fluorescence (MA-XRF) scanning

MAXRF scanning measurements have been performed with the commercial CRONO device (XGlab-Bruker). The spectrometer is equipped with a 50 mm^2 Silicon Drift Detector (SDD) with energy resolution down to 130 eV at Mn-Ka line and fast digital readout electronics able to process up to 1 Mcounts per seconds (output count rate) and single pixel/spectrum dwell time down to 10 ms. The exciting source is a high efficiency 50 kV X-ray tube with Rh anode coupled with three automatically software-selectable collimators between 0.5 mm and 2 mm and a set of 5 X-ray filters. The XRF head is mounted on motorized stages XYZ that allow up to 60×45 cm^2 (XY) scanning area with speed up to 4.2 cm/s and 7.5 cm focusing axis (*Z*). The measurements have been performed at 1 cm distance, without any direct contact between the paintings and the instrument using the alignment system integrated in CRONO, made by a couple of lasers (axial and focal) and a micro-camera, able to observe a 2×2 cm^2 area at 10X magnification. The scanner has been mounted on the available instrument trolley that enabled an accurate tilting of the motorized frame to align the scanner parallel to the painted wall and allowed a height coarse regulation of the measured area from 120 cm up to 220 cm from the floor.

Due to time constrains and necessity to acquire small details with good spatial resolution to discriminate small details on the wall painting a fast and high-resolution scanning acquisition mode has allowed to scan an area of 237 × 195 mm^2 in about 40 min with the 0.5 mm collimator aperture and a pixel size of 0.5 × 0.5 mm^2. The maps have been performed with horizontal motor speed of 42 mm/s with on-the-fly acquisition time of 10 ms for each spectrum. The X-ray tube source was configured at maximum power settings with a voltage of 50 kV and current of 200 μA.

The false colour XRF elemental maps have been processed using both a fast region of interested (ROI) imaging tool performed in real time during the measurements in the instrument control software and spectra peaks deconvolution algorithms available off-line in the Esprit software platform from Bruker. Thus, the background contribution has been removed and a fitting for each set of lines (K, L) have been performed for the relevant elements. Different saturation factors and colour scales have been applied to highlight correlation with the visual image and elements distribution.

2.4 Visible imaging and red induced luminescence (RIL)

Radiation source Custom-made interchangeable and tunable LED light source system composed of two identical units of red LEDs (emission peak at 630 nm), green LEDs (emission peak at 517 nm) and blue LEDs (emission peak at 465 nm) which can be individually used as a chromatic source or simultaneously applied as a white light source. A manual switch allows us to select the specific excitation source by ensuring its spectral purity thus avoiding any wavelength mixing. The system also allows the power (white LEDs, irradiance (Irr) from 224 to 2330 lx; blue LEDs, irradiance from 110 to 1175 lx; green LEDs, irradiance from 87 to 918 lx; red LEDs = from 75 to 760 lx) and the wavelength of the excitation light to be selected. Each radiation source is 30 × 14 cm, and mounted 360 LEDs thus ensuring, at a distance of about 50 cm from the analyzed surface, a homogenous illumination in a 1 m2 area. The homogeneity of the illumination on the analyzed panels and works of art was checked by moving a radiometer along and very close to the whole irradiated surface.

Recording system Range 380–1100 nm. Digital images were collected by means of a camera body Mamiyaleaf IXR with a 80 mm lens, equipped with a digital back Leaf Credo 60 megapixel WS (Wide Spectrum) which allows luminescence signals from 380 to 1100 nm to be collected.

Reference standard Spectralon® non-luminescent gray scale target (99%, 50%, 25%, 12% reflectance in the UV–VIS–NIR range), manufactured by Labsphere, has been used.

3 Results and discussion

Non-invasive measurements throughout the surface of the *Triumph of Galatea*, involved both punctual and imaging techniques focused on the elemental as well as molecular characterization of the materials employed. A map of the elements distribution was obtained by means of macro-X-ray fluorescence (MA-XRF) scanning, showing copper (Cu), iron (Fe) and mercury (Hg) as the main pigment components of the fresco surface, together with calcium (Ca) (Fig. 1, top row, centre). The wide distribution of Cu which emerged did not suffice to recognize the pigment/s responsible for this, since there are many Cu-based pigments showing blue hues[1]. Simultaneous measurements of visible reflectance in punctual mode were then collected in the sky and the sea to fast individuate and distinguish which pigment/s did correspond to such elemental map. The spectrum of Egyptian blue appeared (Fig. 1, bottom row), thus qualifying this result as the most astonishing discovery ever imagined concerning an artist so thoroughly researched that no particular novelties about his palette was expected.

Egyptian blue is mainly composed by a calcium copper silicate, the cuprorivaite ($CaCuSi_4O_{10}$).[2] Since this pigment is characterized by luminescence properties,[3] its distribution was firstly confirmed on selected areas by detecting its emission at 910 nm. Furthermore some years ago, it was demonstrated the possibility to visualize the emission of Egyptian blue over a surface by imaging technique[4]; a recently updated and improved imaging set-up described as Red-Induced Luminescence (RIL)[5] was used to visualize the distribution of Egyptian blue onto the *Triumph of Galatea* detecting its use in the sky, the sea and even in the eyes of *Galatea* (Fig. 1, top row, right).

It should be also noted that the use of this pigment for *Galatea* is even more startling if compared with the blue used by Sebastiano del Piombo who in the *Polyphemus*, next to *Galatea*, employed lapis lazuli[6] from Afghanistan as resulted

[2] A. Pabst, *Structures of some tetragonal sheet silicates*. Acta Cryst. **12**, 733–739 (1959).

[3] G. Accorsi, G. Verri, M. Bolognesi, N. Armaroli, C. Clementi, C.Miliani, A. Romani, *The exceptional near-infrared luminescence properties of cuprorivaite (Egyptian blue),* Chem. Commun*.,* **23**, 3392–3394, 2009.

[4] G.Verri, D. Saunders, J. Ambers, T. Sweek, *Digital mapping of Egyptian blue: Conservation implications,* Studies in Conservation, **55**(sup2), 220–224, 2010.

[5] A. Daveri, M. Vagnini, F. Nucera, M. Azzarelli, A. Romani, C. Clementi, *Visible-induced luminescence imaging: A user-friendly method based on a system of interchangeable and tunable LED light sources*, Microchemical Journal, **125**, 130–141, 2016.

[6] C. Miliani, A. Daveri, B. Brunetti, A. Sgamellotti, CO_2 *entrapment in natural ultramarine blue*, Chemical Physics Letters, 466(s 4–6), (2008), pp. 148–151.

by previous non-invasive analyses,[7] a pigment which although costly, would nevertheless have been much easier to procure compared with the Egyptian blue which had to be produced ex novo with procedures and dosage that needed to be worked out.

A joint inspection of MA-XRF and RIL maps permitted to go even further by achieving a stratigraphy per images of the fresco understanding whether pure painting layer, mixtures or overlapping of different pigment layers occur, due to the different penetration extent of these two techniques, being XRF more pervasive than RIL, which reveals only surficial Egyptian blue both pure and in mixture. In doing so, several peculiarities about the choice of materials as well as the fresco execution technique were disclosed. For example, considering the triton near *Galatea* on the right side of the fresco, it is evident from the XRF Cu-map (Fig. 2, top right) how the brush strokes of the sky went by a long shot beneath his head, while RIL image shows that the Egyptian blue in background (Fig. 2, bottom right), used for the sky, was covered by another, more precise, layer of paint to outline the shape of the head which from MA-XRF resulted to be Fe-containing (Fig. 2, bottom left).

Galatea's gaze deserves also few words for the Egyptian blue used to make the eyes *azurage* like the ancients did as a consolidate practice[4]: the RIL image clearly shows the Egyptian blue emission all over the cornea and a comparison with MA-XRF map of Fe let to know the complementary use of Fe-based pigments to outline the periocular area (Fig. 3, right).

The sea is entirely painted with Cu-based pigments as emerged from XRF map (Fig. 4, top right), however, it is not made purely by Egyptian blue as revealed by the visible reflectance spectra (Fig. 1, bottom row). Indeed, RIL image of the sea shows an attenuated luminescence with respect to that of the sky, indicating that Egyptian blue was mixed with another Cu-based pigment. Another peculiarity in *Galatea's* palette is the use of cinnabar, revealed by XRF map of Hg and whose use in frescoes was strongly discouraged since Antiquity,[8] because it turns into metacinnabar with a bluish-grey hue. However it represents one of the typical pigments of the ancients' palette. Comparing the distribution of Fe and Hg with the visible image (Fig. 4, bottom left and right), it can be noted that most of the Pompeian red of *Galatea*'s drapery is made by Fe-based red pigments with a final glaze of cinnabar painted over. The unique area in which cinnabar is used *a fresco* is the one currently turned to grey as clearly showed by both XRF maps of Fe and Hg.

4 Conclusions

The resurgence of Egyptian blue many centuries after its production and use, was really astonishing because it is not a natural pigment and its practice requires the knowledge of the necessary

[7] M. Vagnini, C. Anselmi, A. Sgamellotti, unpublished results.

[8] Marcus Vitruvius Pollio, *De Architectura,* VII, 8–9, 336–341, 1990.

Fig. 2 Detail of triton's head. Top left: visible light image; top right: MA-XRF-map of Cu (Cu is indicated in white); bottom right: RIL image showing Egyptian blue distribution in white; bottom left: MA-XRF-map of Fe (Fe is indicated in white)

technologies to manufacture it. Furthermore, its widespread presence in large areas of this fresco seems to exclude an occasional use of materials remains from archaeological contexts which was also a well-established practice at that time to recreate the ancients' palette.

The use of Egyptian blue shows instead the precise intention of Raphael to paint a mythological subject—as that of Galatea nymph— using the materials of the Antique, in particular those of the ancient Roman painting, which were to be seen at the time in the remains of paintings, in the excavations as well as in the written testimonies of Pliny and Vitruvius with which Raphael was strongly engaged during his Roman stay. In particular Vitruvius wrote about this pigment, that he called *caeruleum*, in his treatise *De Architectura* including therein the recipe for its manufacture.[9] Few other cases of Egyptian blue occurrence in sixteenth century are documented but they are all later than *Galatea*[10,11] [12]making thus

[9] Marcus Vitruvius Pollio, *De Architectura,* VII, 11, 344–345, 1990.

[10] J. Bredal-Jørgensen, J. Sanyova, V. Rask, M.L. Sargent, R.H. Therkildsen, *Striking presence of Egyptian blue identified in a painting by Giovanni Battista Benvenuto from 1524*, Analytical and Bioanalytical Chemistry, **401** n. 4, 1433–1439, 2011.

[11] M. Spring, R. Billinge, G. Verri, A Note on an Occurrence of Egyptian Blue in Garofalo's *The Holy Family with Saints Elizabeth, Zacharias, John the Baptist (and Francis?),* National Gallery Technical Bulletin, **40**, 74–85, 2019.

[12] G.S. de Vivo, A. van Loon, P. Noble, A. Hirayama, Y. Abe, I. Nakai, D. Bull, *An Unusual Pigment in 16th-century Ferrara: 'Egyptian Blue' in Garofalo's Adoration of the Magi and Ortolano's St Margaret,* in A. Haack Christensen (ed.), Trading paintings and painters' materials 1550–1800, 136–148, London 2019.

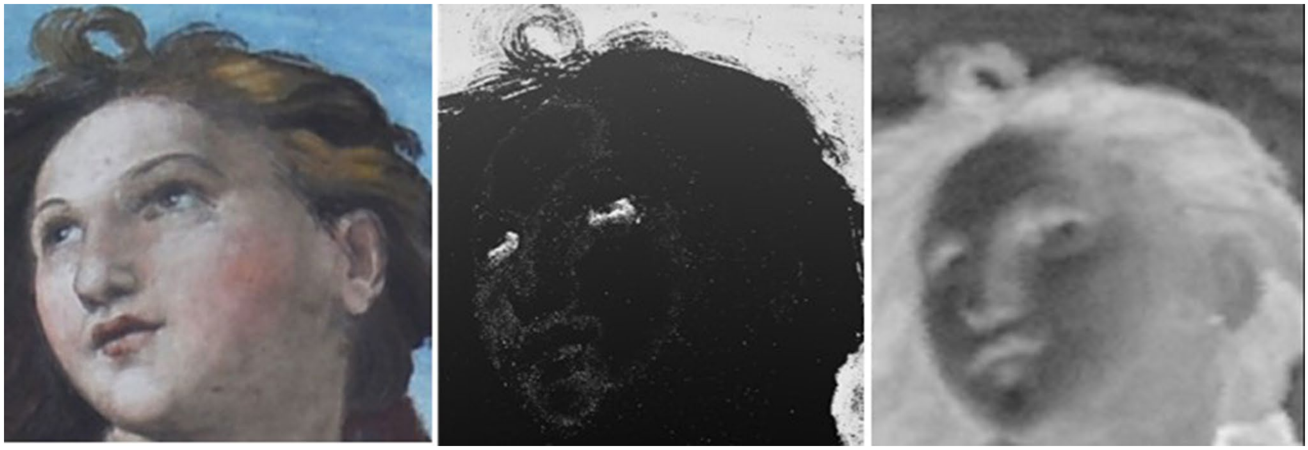

Fig. 3 Detail of *Galatea's* head. Left: visible light image. Center: RIL image showing Egyptian blue distribution in white within the eyes. Right: MA-XRF-map of Fe used for both hair and periocular area (Fe is indicated in white)

Fig. 4 The *Triumph of Galatea*. Top left: visible light image. Top right: MA-XRF-map of Cu (Cu is indicated in white). Bottom left: MA-XRF-map of Fe (Fe is indicated in white). Bottom right: MA-XRF-map of Hg (Hg is indicated in white)

its identification on Raphael's artwork the earliest occurrence on a painting from Renaissance onwards.

Since Raphael's artworks, included wall paintings, have been thoroughly studied in the past without ever finding Egyptian blue, its presence in the *Triumph of Galatea* represents therefore an *unicum* within his production, suggesting an experiment by the Master himself to test and verify the recipes coming from the classical written antique sources that were on top of his interest at that time. The non-invasive approach used in this paper shows the huge potential of imaging techniques for diagnostic purposes which need yet to be, hopefully, further exploited, because of their twofold benefit of being on one side totally non-invasive and on the other to render a complete overview of the investigated object. However, presently, punctual analyses remains still unavoidable and only a skillful integration of imaging and punctual techniques can lead to a great enhance of the diagnostic, comprehension and hermeneutic capability as well.

Acknowledgements Conservator Dr. Virginia Lapenta, and the Staff of Villa Farnesina in Rome, are gratefully acknowledged by the authors.