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Between past and future: Advanced studies of ancient colours to safeguard cultural heritage and new sustainable applications

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ABSTRACT

Heritage materials are highly complex systems of unknown and intrinsically heterogeneous compositions and unmonitored long-term modifications. In this microreview, we describe our interdisciplinary approach, its importance to new treatments tailored to prevent changes to historical colours, and innovative strategies for their identification in artworks. We illustrate our methodology through the study of medieval Islamic manuscripts from the Fondo Ka'ti. These advanced studies have shown the remarkable properties of ancient dyes, their resilience and durability, properties designed by our ancestors through sustainable materials processing. This lost knowledge can be shared with the community empowering them to create new sustainable applications, from unique art pieces to regional value-added products.

1. Ancient colours in cultural heritage

Cultural heritage treasures risk losing to degradation what makes these objects unique—their colour [1–3]. This is particularly critical for organic dyes, which are fundamental colours of the palette found in medieval manuscript illuminations, Fig. 1 [4–10]. Following Pasteur's belief that "we are not able to conserve what we do not know," knowledge of the original materials that comprise our cultural heritage urgently needs to be furthered, ensuring their conservation and transfer to future generations. In recent years, we have shown that fundamental mechanisms are key to understanding the colour changes of anthraquinone reds, indigo blues, and flavonoid yellows [2,11–13]. Through this knowledge, we have also contributed to the development of advanced analytical methods for their *in-situ* characterisation [14–17]. Our systematic investigation of historical reproductions has proved crucial for advancing this research [18–21].

In Section 1 of this microreview, we describe our interdisciplinary approach and its importance to new treatments tailored to prevent changes to historical colours, along with innovative strategies for their identification in artworks. Section 3 illustrates our methodological approach through an original case study; and finally, Section 4 presents future perspectives for creating new, sustainable applications based on the science of use recovered from the past.

1.1. Organic-based colourants in a complex milieu

By the time Mediterranean civilizations were being founded, what we consider the classical palette of natural dyes had already been established, having been preserved for centuries, if not millennia, Fig. 1 [22,23]. This eclectic palette was only challenged by the audacity of chemists, who created new molecules and colours never before seen, from the mid-19th century onwards [23–25].

These natural dyes and their metal-ion complexes have been used for textiles, manuscript illuminations, paintings, and other works of art [1,2,23]. For example, anthraquinones and their hydroxy derivatives have been used as red dyes and pigments since pre-historic times, and we can

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find written accounts of the use of anthraquinone reds and purples as dyes in ancient Egypt [26]; anthraquinone lakes (e.g., madder red) were also very popular with Impressionist painters, including Vincent van Gogh. Pure dyes, such as indigo, were also used as painting materials, for example, in medieval illuminations [1,23].

To preserve these colours from the past, the colour's formulation needs to be identified, and the fundamental mechanisms of degradation must also be understood [2,12,13,27–33]. Over the past decade, great progress has been made in understanding the degradation mechanisms of millenary dyes, such as indigo, an icon of our civilization and material culture. The knowledge acquired about indigo's photophysics and photochemistry in complex matrices has enabled the environments in which it is most at risk to be predicted [2,11,12]. We have also discovered that our ancestors selected specific, durable dyes, such as indigo blues, flavonoid yellows, and anthraquinone reds, because a highly efficient excited-state proton transfer provides a 'self-protective channel' that minimizes photodegradation. De Vries proposed that this mechanism, shared with DNA bases, has been preserved as a *molecular fossil* [34]. This *molecular fossil*, inscribed in ancient colours, is the basis of a resilience that will inspire new and environmentally friendly applications.

Anthraquinone reds and indigo blues may undergo fading in paintings, while they may be incredibly resilient as showcased in millenary Andean textiles or medieval illuminated manuscripts. In order to be lightfast, a molecule must absorb damaging radiation and safely dissipate it before irreversible chemical reactions occur. The excess of absorbed energy may be dissipated through radiative or non-radiative decay pathways. These safe processes for returning to the ground state compete with unsafe electron-transfer reactions that usually are responsible for irreversible photochemistry. Photodegradation studies, using irradiation wavelengths >300 nm, can be used to simulate natural ageing mechanisms, in times much faster than other techniques such as thermal ageing [33]. To achieve this goal, it is necessary to prove that natural and photochemical ageing share the same degradation mechanism. When this is the case, photodegradation quantum yields (Φ_R) are essential to understanding their stability and are an accurate way to quantify the relative stability of these colourants in a complex milieu [33].

As an example, we can highlight our recent studies on flavonoid yellows, where the Φ_R values obtained in solution irradiating at 366 nm provide a scale to accurately measure the stability of flavonoid yellows: Lut-7-*O*-glu > Que-3-*O*-glu > Kaem-3-*O*-glu ≈ luteolin ≫ quercetin ≥ kaempferol. The higher stability of luteolin yellows is explained by the high protective effect offered by excited state proton transfer based on the 5-hydroxyflavone six-membered-ring, which is more stable than that the 3-hydroxyflavone five membered-ring, Fig. 2. Nagaoka et al. also showed that electron transfer to other compounds is enhanced through the OH in position C3 when compared to OH in C5. The combination of these two effects-higher protection due to OH in C5 and higher reactivity by electron injection caused by OH in C3-makes quercetin and kaempferol the most unstable structures. When the OH in C3 is protected by a monosaccharide, electron transfer and oxidation are avoided, and the molecules attain a stability comparable to luteolin.

1.2. *Anthraquinone reds, indigo blues and flavonoid yellows: a science of use*

Time resilience is intrinsic to these dyes. However, their remarkable durability in millenary objects, such as Andean textiles, is the result of the silent changes introduced in the colorant formulations, a science of use we inherited in the form of unique artworks [2,4,35–37]. It is this "science of use" that has made these colours durable and endowed them with the highest possible performance, which we aim to unravel through reverse engineering to enable the design of new sustainable applications, Fig. 3. Hence, another vital ingredient for understanding colour stability relies on reproducing these ancient colours [29–31], based on a

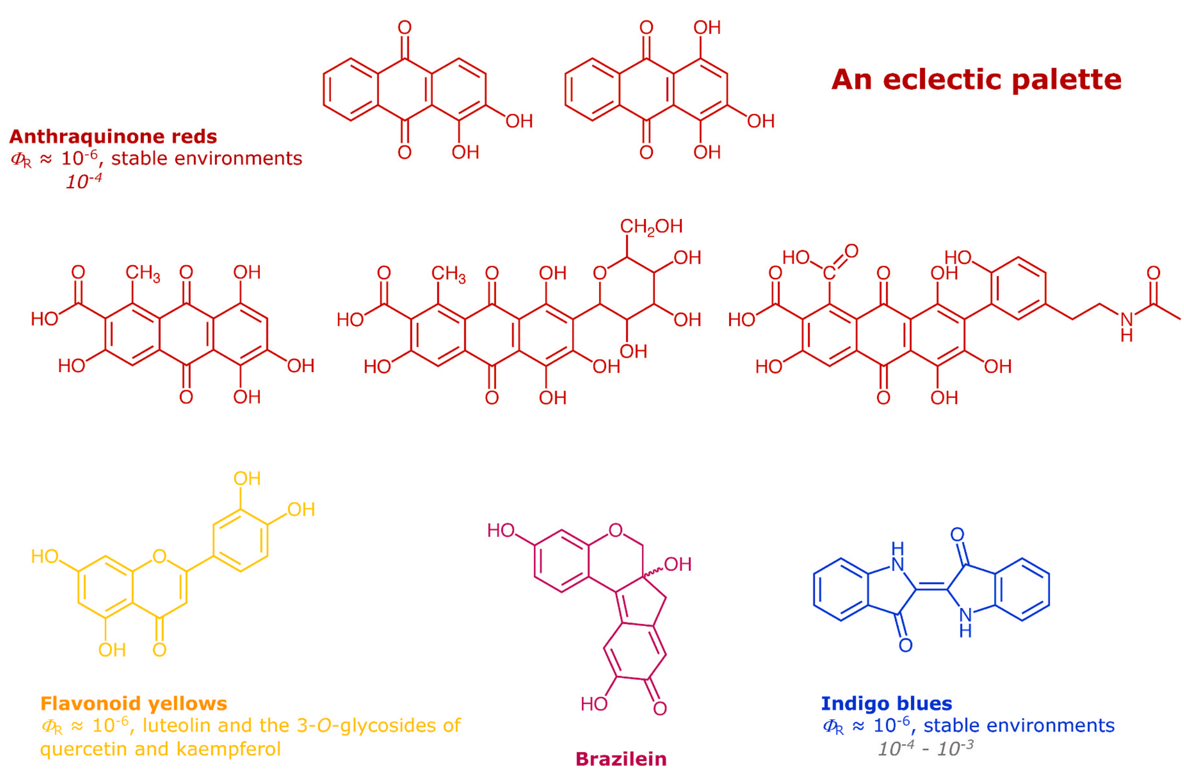

Fig. 1. Natural dyes used in the past for textiles, manuscript illuminations, paintings and other works of art. An eclectic palette that our ancestors selected because a highly efficient excited-state proton transfer provides a 'self-protective channel' that minimizes photodegradation, as shown by their photodegradation quantum yields (Φ_R). For more details please see text. By row, from left to right; 1st *row*: alizarin and purpurin; *2nd row*: kermesic acid, carminic acid, lac dye; *3rd row*: luteolin, brazilein, indigo = indigotin.

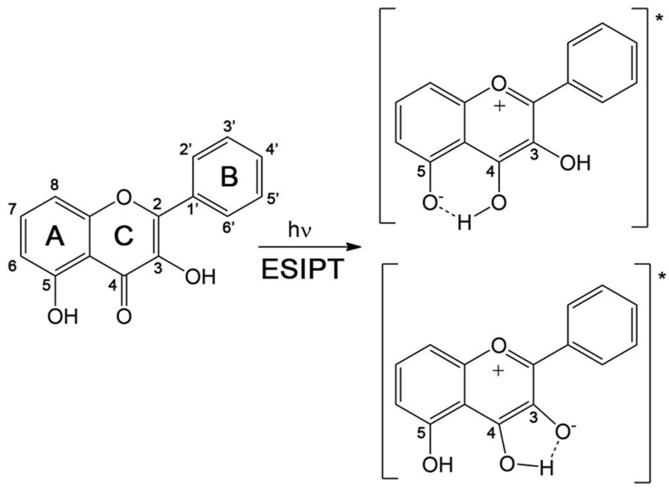

Fig. 2. The drastic change in the p*K*a of the carbonyl and hydroxyl group in C3 and C5, in the excited state, promotes an ultrafast excited proton transfer, which acts as a photoprotective mechanism for these yellow dyes. The 5-hydroxyflavone proton transfer in the excited state involves an intramolecular hydrogen bond six member-ring which is stronger than that in 3-hydroxyflavone possessing a five member-ring, allowing for a more efficient ESIPT.

detailed characterization of these intrinsically heterogeneous systems [2,38–40]. This know-how was lost at the turn of the 20th century with the rise of industrially produced synthetic dyes.

To prepare medieval pigments and paints, we researched several medieval technical sources, in particular, a manuscript entitled *The Book on How to Make All the Colour Paints for Illuminating Books*, which, hereafter, shall be referred to as *The Book of All Colours*. This *Book of All Colours* describes the manufacture of colours used 'to illuminate, paint, and write'. The original text dates to the 13th century or earlier, and it survived in a 15th-century copy (written in Portuguese, in Hebraic characters) [21,41,42]. The original manuscript, Ms. Parma 1959, folios 1r-20r, is kept at the Biblioteca Palatina, in Parma (Italy).

During the first stage of research, we focused on the chemical rationalisation of the processes described in the medieval text, gathering in-depth knowledge on the reaction mechanisms, which was essential to design experiments with which we could study the role played by each ingredient. The ingredients were either the primary reactants or acted as catalysers or modulators. In reconstructing pigments, we made use of chemical 'shortcuts', provided they did not compromise the historical accuracy of our study. This methodology enables reference materials with as much historical accuracy as possible, validated by its "closeness to the true value", the historic material or artwork under study (as will be exemplified). Ultimately, these studies will allow the original appearance and condition of the artworks to be assessed, while advancing knowledge toward their conservation.

1.3. Why a multi-analytical approach for the characterisation of paint formulation in manuscript illuminations

1.3.1. Analysing both the original materials and the reconstructions

Advanced methods of analysis are used to identify all the components present in a medieval paint (the paint formulation), including colourants, binders, varnishes, and other additives, as exemplified below, Fig. 4. These components are essential for a medieval paint's applicability and durability.

In paint reproductions, we are able to use every analytical technique necessary for in-depth characterisation, including a study of dyes by high-resolution mass spectrometry (HRMS/MS), coupled with an HPLC or Ultra Performance Liquid Chromatography systems, HPLC-HRMS/MS, or UHPLC-HRMS/MS [13,19]. This is not possible on original medieval paints, because it is very difficult to obtain a micro-sample from an illumination with enough material to be extracted for it. So, for dye identification, we combine high spatial resolution (microRaman) and the highest sensitivity (microfluorimetry). UV-VIS spectra in absorbance or reflectance are also very useful to a preliminary dye analysis. To discover more about lake pigment formulations, we need to include Fourier transform infrared microspectroscopy (microFTIR).

1.3.2. A medieval paint characterization: infrared spectra hand in hand with microspectrofluorimetry

Heritage materials are highly complex systems of unknown and intrinsically heterogeneous compositions and unmonitored long-term modifications. A medieval colour based on a brazilwood lake pigment can be revealed by combining the information of its infrared spectra with the molecular fluorescence spectra [43] Fig. 5. The former enables one to quantify the binders and additives, along with its conservation condition [38,44–48]. Microspectrofluorimetry enables the acquisition of emission and excitation spectra in the same micro spot (*in situ* without any contact with the sample or work of art being analysed), which is decisive when using molecular fluorescence for dye identification. It offers high sensitivity and selectivity, combined with good spatial resolution and fast data acquisition [14,49–51]. The importance of sensitivity is evident when it is known that dyes used in the past fade over time or may have been applied as a very thin layer, or mixed with an inorganic pigment or extender, being present in very low concentrations. The correct excitation spectrum may be identical in shape to the

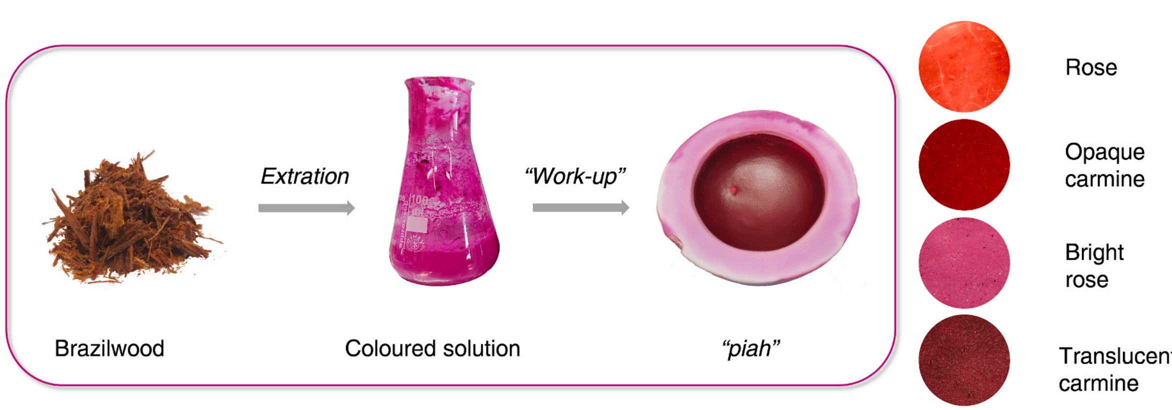

Fig. 3. Producing a medieval brazilwood lake pigment. In the four recipes for producing rose colours from brazilwood in *The book of all colours*, brazilein, the main chromophore in brazilwood, is extracted in an acid or basic medium, which determines the hue of the pigment produced. Alum is added together with additives (lead white, chalk, gypsum) which influence the opacity of the pigment. Filtration of the colored solution over a chalk or gypsum stone (piah feitah de gis o de pedra kri) improves filtration and introduces chalk or gypsum into the final formulation when the dried pigment is scraped from the stone.

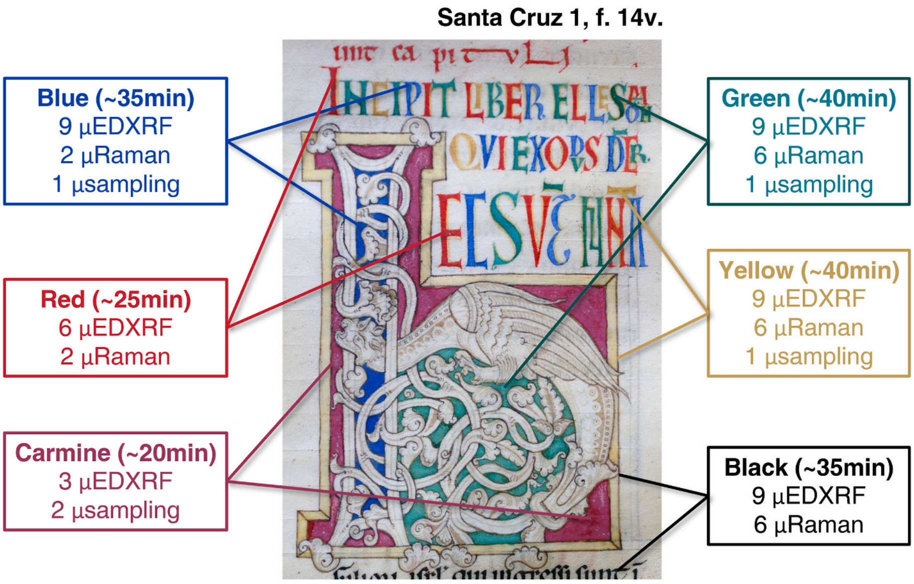

Fig. 4. The pink colour used in this Romanesque initial was made admixing vermilion with lac dye in a proteinaceous binding medium. The acquisition of the data necessary for a complete characterization of the formulation took 3h [38]. Vermilion was identified through Raman microscopy by its characteristic bands at 252 cm^{-1} and 282 cm^{-1}. Infrared spectroscopy clearly shows the proteinaceous binder fingerprint. Microspectrofluorimetry and surface-enhanced Raman spectroscopy identified lac dye by comparison with references. Santa Cruz 20 manuscript, 12th c., in the collection of Biblioteca Pública Municipal do Porto.

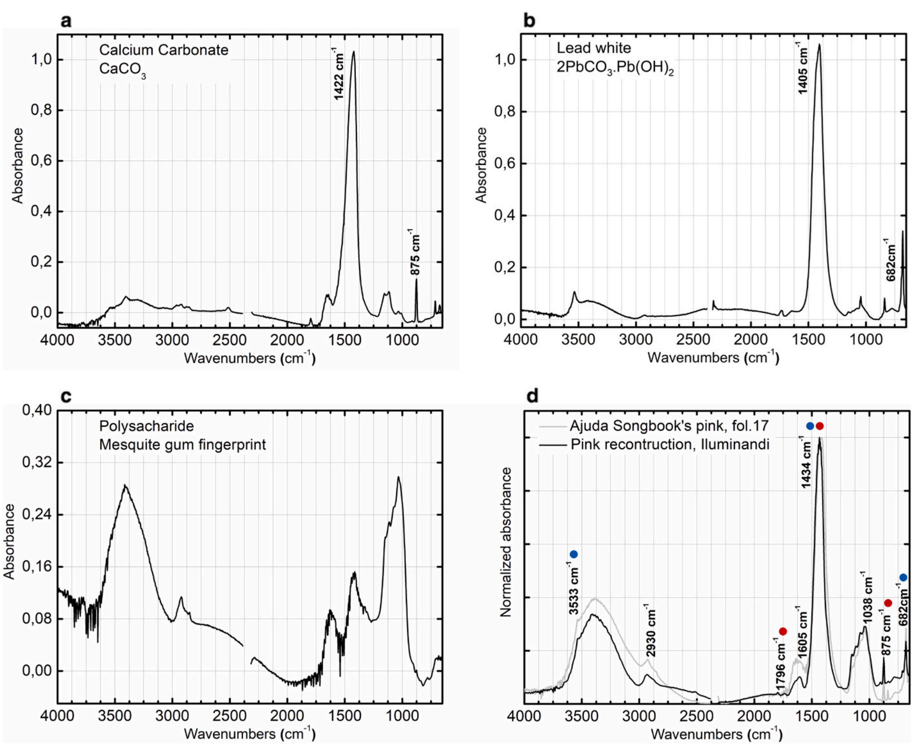

Fig. 5. The paint formulation disclosed by infrared spectroscopy. The spectra of **a)** calcium carbonate (filler), **b)** lead white (pigment) and **c)** a polysaccharide (binding medium) were acquired in books of hours. They allow to better understand the complexity of the full formulation reproduced following a medieval recipe and compared with **d)** the light pinks found in Ajuda Songbook; components in formulation are marked as it follows lead white (•), calcium carbonate (•) and binder (grey line). For more details please see text.

absorption spectrum and an emission spectrum reflects the probability of transition from electronic states and associated vibrational levels [43]. For this reason, a well-resolved emission spectrum can be characteristic of a compound. However, historical dyes usually exhibit broad bands due to their environment and state of conservation. Thus, these broad bands make it difficult to acquire a unique fingerprint that allows unequivocal identification of the molecule, as in Raman spectra [51–53]. On the other hand, these molecular spectra carry essential information on the specificities of the recipe, which can be determined by using a database of historically accurate reproductions and chemometrics [39,40,54–57], Fig. 6.

Fig. 5 depicts the infrared spectrum of a characteristic pink colour from the Ajuda Songbook [58]. This colour is based on brasilein, the main dye extracted from brazilwood scrapings [55]. This colour is also one of the important ones used in books of hours [56,57], which we were able to reproduce following the recipes in *The book of all colours*. The specificities of the brazilwood recipes were proved by applying statistical methods (principal component analysis and hierarchical cluster analysis) to emission and excitation spectra in UV–Visible, revealing molecular fluorescence signatures in colours based on brazilwood lake pigments [40]. However, the paints found in the Ajuda Songbook are based on a different dye formulation. As such, we were able to reproduce the paint formulation very well using infrared spectroscopy, identifying its main ingredients: calcium carbonate as filler; lead white as the pigment that produces light pink; and the binder as a polysaccharide with a fingerprint similar to mesquite gum. On the other hand, the final

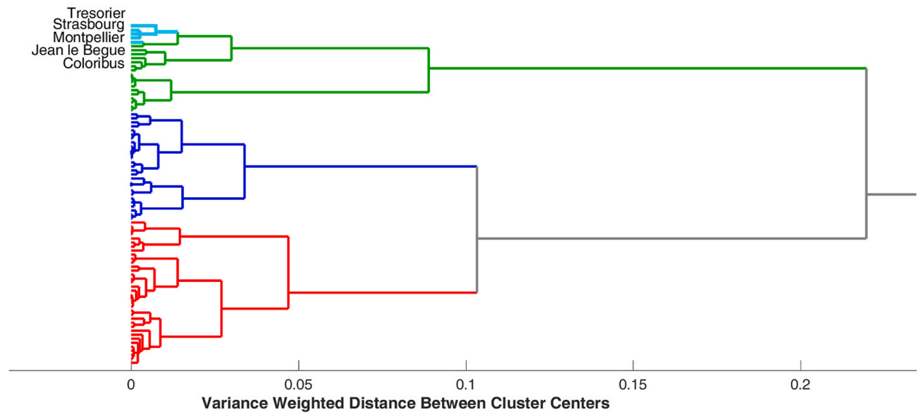

Fig. 6. Brazilwood pinks in Ajuda Songbook are different from those found in books of hours. Thus, new recipes were tested (light blue). Principal component analysis applied to excitation and emission spectra of all the historical samples of brazilwood based paints: Ajuda Songbook (green), books of hours (blue) and books of hours (red), show that in these new formulations the chromophore colour is close but not yet there.

recipe for the chromophore colour is close but not yet there, as shown by chemometrics applied to the molecular fluorescence spectra, Fig. 6. This knowledge allows us to know more about the conservation condition of the colour and to predict what the original colour could have been, as will be discussed below.

1.4. Colour degradation in manuscript illuminations

The Middle Ages gave rise to our modern science and technology and bequeathed to us an inheritance of beautiful works of art, like medieval codices, which we want to last forever. To preserve manuscript illuminations for future generations, we must combine both human and natural sciences methodologies. This holistic approach provides an in-depth examination of the creative processes, material composition of medieval illuminations, techniques used, and deterioration processes.

Organic dyes were central in medieval manuscript illuminations and this holistic approach is helping to predict original colours and to understand why certain colours have remained in excellent condition, preserving both adherence and luminosity, while others have changed over the centuries. Throughout our research, we observed numerous examples of colour materials degradation. The primary findings from our studies on books of hours (14th-15th c.) and on three important medieval Portuguese Romanesque manuscript collection's illuminations (12th-13th c.) show that the most frequently observed deterioration pathologies fall into two categories [1].

i) Changes in colour owing to chemical transformation, as found in read lead and lead white, which have darkened dramatically [46, 47], Fig. 7. The same holds for silver-based colours, profusely applied in the books of hours [56]. In both cases, we found black sulfide-based compounds as final products, such as PbS and Ag_2S [46–48].
ii) Loss of cohesion and adhesion of the pictorial layer to the support, exemplified by bottle-green and lapis lazuli blue [38], Fig. 7. The presence of low quantities of binding media in the paint formulation might explain the lack of adhesion sometimes observed on lapis lazuli and lead white paints. Bottle-green degradation is not related to a low amount of binder. When analysing the presence of calcium oxalate in all the infrared spectra collected for medieval colours in the three important Portuguese Romanesque manuscript collections

Fig. 7. The degradation of bottle-green paints leads to the loss of the green colour due to loss of cohesion and adhesion of the pictorial layer to the support (12th c. Portuguese manuscripts in the collection of Biblioteca Pública Municipal do Porto). The darkening of lead-based pigments is exemplified with lead white used in a light pink in Ajuda Songbook (Biblioteca da Ajuda) 58. The darkened areas may correspond to galena (PbS).

(12th-13th c.), we concluded that it is frequently present in bottle-green colour but rare in others. More importantly, in bottle-green paints, a high amount of calcium oxalate strongly correlates with the collapse of amide I and II bands (C=O and O=C–N stretching at 1653 and 1550 cm-1, respectively) in a single, broad band, and to the loss of cohesion of the bottle-green. Therefore, we posit that the copper pigment is promoting protein degradation through a radical mechanism that led to extensive chain scission and cross-linking, where calcium oxalate is one of the final products [1, 38]. This hypothesis is in line with the findings of Nati Salvadó and her colleagues, who have proposed that the presence of calcium oxalate, as weddellite (dihydrate form) and/or whewellite (monohydrate) in Cataluña medieval paints, may be ascribed to binding media degradation [45].

Over the past ten years, breakthroughs supported by advanced analytical techniques have fostered a flourishing field of research, and the study of the materials and techniques used to produce medieval illuminations is reaching maturity. Yet, we have crucial gaps in our knowledge that hinder the development of informed conservation strategies, e.g., on binding medium and lake pigments. Binding media and parchment support are key to the permanence of colours, but their degradation, at the molecular level, has yet to be assessed. This is a pivotal issue to be addressed in the next few years. It is also important to note that a description of interventions for conserving these colours is rare [1].

Table 1
Colorants and binding media identified in the Islamic manuscripts of *Fondo Ka'ti*, as well as a preliminary assessment of their conservation condition, ranging from very bad (*) to good (***). For more information on the paint formulation, see Appendix A.

Titles as in [61]	***Koran***		***Theology treatise***	***Prophet biography***	***Manuscript 19***	***Al-Sarishi poems***
New titles by Nuria de Castilla (NC)	***Koran***		***Prayer book***	***Kitāb al-Shifā'***	***Prayer book***	
Dating by Ismael Diadé	1198 CE		14^{th} c. CE	1468 CE	1485 CE	1468 CE
						
Support	Parchment	Paper	Paper	Paper	Paper	Paper
Inks conservation	*	*	***	***	***	***
Support conservation	**	*	*	*	*	*
[1]Blue / Purple	Lapis lazuli	Azurite	Orcein purple	Azurite	Azurite	Azurite
Organic red	Lac dye red	Lac dye red	Organic red	Lac dye red	Lac dye red	Lac dye red
Yellow	Pararealgar	Pararealgar	-	-	Vermilion + Orpiment	Pararealgar + organic based yellow
Gold	Gold leaf	Gold leaf	Gold leaf	Gold leaf and gold ink	-	Gold ink (powder)
Inorganic red	-	Vermilion	-	Vermilion	Vermilion	Vermilion
Green	Proteinaceous copper green	-	-	-	-	-
Inks used as contour	carbon based ink					
Binding media	proteinaceous and polysaccharide		polysaccharide	proteinaceous and polysaccharide	proteinaceous	polysaccharide

1.5. Tracing the rich diversity of a precious heritage legated by medieval Arabic culture

During the 12th and 13th centuries, the influence of Arabic science and technology was significant on the Iberian peninsula. As a result, the restoration of Islamic manuscripts, which may have been produced in al-Andalus, created an opportunity to study the material and techniques used in the illuminations, for comparison with European-made medieval colours (Flemish and French, for books of hours, 14th-15th c.; Portuguese, for monastic production, 12th-13th c.). The five manuscripts studied come from the *Fondo Ka'ti*, which include a *Koran* (1198), a *theological treatise* (14th c.), a *book of poems from Al-Sarishi* (15th c.), a *biography of the Prophet* (1468), and *manuscript 19* (1485) [59], Table 1 (note the new names proposed by Nuria de Castilla). They were produced either in Andalusian territory or within the Arab diaspora, possibly the latter. Until 2012, the manuscripts were stored in Timbuktu libraries [5–9] and are now preserved at the Timbuktu Andalusian Library (*Biblioteca Andalusi de Tombuctu*, Fondo Ka'ti), and its president, Ismael Diadié Haïdara, dated them [60]. In our first publication, we focused on the organic reds, proving unequivocally that lac dye was used in Islamic manuscripts for the first time and highlighting the richness and diversity of the paint formulations used, Fig. 1 [61]. Microspectrofluorimetry was used to pin-point the recipe used to prepare the colorant and infrared spectroscopy to identify the binding media formulation and its conservation condition, as well as any other additives, if present. Microspectrofluorimetry demonstrated that the dark reds found in the *Koran* and *Mss 19* compared very well to the recipe 'to make red ruby from lukk' from the Ibn Bādīs text (11th c.); while the brighter reds applied in *Al-Sarishi poems* and the *Prophet biography* compared well with a recipe from the Paduan manuscript (16th c.). MicroFTIR completed the characterisation of the paint formulation, identifying the proteinaceous nature of the binding media. It also showed the presence of oxalate compounds, possibly resulting from binding media degradation, a mark of these books' recent and dramatic history. Finally, these red dyes were successfully compared to lac dye colours previously characterised in Portuguese manuscript illuminations from the 12th-13th c. (monastic production from the monastery of Lorvão). In addition, very good spectral comparisons with references, with both emission and excitation fluorescence spectra, enabled us to conclude that the chromophore is well preserved. On the other hand, infrared data indicate that the binding media show signs of severe degradation. The presence of lac dye in these manuscripts affirms historical sources and the use of lac dye in the Arab world [62].

The full colour palette is discussed below in section 3, focusing mainly on inorganic pigments. Considering the context of how they were made, it is important to compare them first with studies on inorganic pigments on Islamic manuscripts produced in Andalusia (in Spain) and western North Africa (Maghreb). Then, with colours used in artworks from Iran, Iraq and Egypt (Middle Eastern Islam) to discuss differences and to highlight specificities. Technical studies of Islamic manuscripts are limited, and in this microreview, recent publications were selected using the analytical techniques used as criterion. The materials of colour used in medieval Islamic manuscripts produced in the Maghreb were the focus of the French research team lead by Patricia Roger-Puyo and François Déroche [63,64]. Identifications were proposed based on FORS (UV-VIS) and XRF. The main colours are red, green, and blue. Reds are obtained using vermilion and an organic dye (identified by SERS as carminic acid, based on another research team [65]). Lapis lazuli is used for blues and can be associated with azurite and indigo. Greens are copper-based. Yellow and orange colours are not dominant, and whites are rare; the only white based on lead white was detected in one manuscript. Yellows are orpiment-based and orange is obtained by mixing orpiment with vermilion. The perception of whiteness is created using parchment. Two other rare colours, not identified, were purple and a translucent brown. From Middle Eastern Islam, noting a recent publication by Katherine Eremin et al. as well as one by Lucia Burgio et al. [66,67] Besides the pigments described above, lead white enters the palette mainly from the 14th c. on. Orange can be obtained admixing a yellow (orpiment or pararealgar) with vermilion or by using red lead. The nature of the binder was partly addressed; FTIR analysis of a small number of samples indicated polysaccharide binder in all samples, with the occasional presence of proteinaceous material. This type of binding media was also identified in Al-Andalus Arabic manuscripts [68]. From the Republic of Macedonia, five Islamic manuscripts dated from the 16th to 18th centuries were investigated by Raman microscopy and SEM-EDS analyses [69]. Reds were based on vermilion, or a mixture of vermilion and red lead.

During the medieval period, one of the things in common for each colour palette (Western and Middle Eastern Islam) was little variation in the pigments used [63–67]. This was only challenged from the 18th century on by the sporadic use of Prussian blue, emerald green, and lead chromates for orange and yellow [66,67].

2. Experimental

2.1. The manuscripts and overall modus operandi

This project encompasses the study of five manuscripts, specifically a *Koran, Mss 19, Al-Sarishi poems, Prophet biography* and *Theology treatise*. The dating and typology of the manuscripts were defined by the president of the Fondo Ka'ti, Ismael Diadié Haïdara. Details on the manuscripts on Table A1.

The first screening of the manuscripts was carried out by FORS and microEDXRF. For each of the five manuscripts 3 folios were analysed, except for the *Koran* and *Mss 19*, with 4 and 6 folios analysed respectively, and for each colour data was acquired in three areas, in a total of three points per area per folio: *Koran* (fols 1, 30, 47 and 70), *Mss 19* (fols 18, 19, 109, 110, 217 and 218), *Prophet biography* (fols 1, 4 and 107), *Al-Sarishi poems* (fols 1, 4 and 10) and *Theology treatise* (fols 17, 43 and 70). This allowed to select areas to be analysed by microRaman and sampled for microFTIR allowing us to characterize pigments, binders and gain insight into the full paint formulation. One or two areas per colour per manuscript were selected for microsampling, except for the *Al-Sarishi poems* were only vermilion red was sampled, due to the fragile condition of the support. MicroRaman was used *in situ*, with 3 points per colour per folio, or in microsamples. Microspectrofluorimetry was then used for both *in situ* and microsample analysis to identify the colorants present. The criteria for the selection of the folios for analysis was based on ensuring that all the colours present in the manuscripts were part of the selected folios and that they encompassed as much variability as possible.

2.2. Equipment

2.2.1. Micro-sampling

Micro-sampling of the manuscripts was performed with a micro-chisel from Ted Pella microtools under a Leica KL 1500 LCD microscope, (7.1x to 115x objective) and a Leica Digilux digital camera, with external illumination via optical fibers. Micro-samples were taken under a microscope, typically of 20–50 μm in diameter and as such invisible to the naked eye; as we have not yet obtained their weight, even though micro-scales have been used, we can use its detection limit to conclude that they weigh less than 0.1 μg. The micro-samples were used for the infrared analyses and microspectrofluorimetry.

2.2.2. Energy dispersive X-ray fluorescence (microEDXRF)

MicroEDXRF results were obtained using an ArtTAX spectrometer of Intax GmbH, with a low-power molybdenum (Mo) X-Ray tube attaining a microspot with a spatial resolution of circa 70 μm, an X-flash detector refrigerated by the Peltier effect (Sidrift), sustained by a mobile arm (providing a major freedom in choosing the spot of analysis). The accuracy of the incident beam position on the sample is achieved through three beams crossing diodes controlled by an integrated CCD camera; the characteristic X-rays emitted by the sample (at 40°) are detected by a silicon drift electro-thermally cooled detector with a resolution of 160 eV at Mn-Kα. This apparatus allows for a simultaneous multi-element analysis in the element range from Mg (magnesium, atomic number 12) to U (uranium, atomic number 92). The experimental parameters used were: 40 kV of voltage, 300 μA of current, for 120s, under Helium gas flux. Si, Mn, Cu and Pb standards were used as calibration standards in the beginning and at the end of each day of data acquisition.

2.2.3. Fibre optic reflectance spectroscopy

The reflectance spectra were obtained with a reflectance spectrophotometer Ocean Optics, MAYA 2000 Pro, with single beam optical fibres, equipped with a linear silicon CCD detector Hamamatsu, with a spectral range of 200–1060 nm. The light source is a halogen lamp Ocean Optics HL-2000-HP, 20 W output, with a spectral range of 360–2400 nm. The analyses were obtained with 8 ms integration time, 15 scans, and acquired at 45°/45° (light source/acquisition), with a spatial resolution of 2 mm; also, instead of averaging the data from a single point, we followed the manufacturer's advice to use a "Boxcar Width" that averages the data of multiple, adjacent points on the CCD, producing "a smoother plot". A box width of 8 was used to create a smoother plot without losing spectral features. To calibrate the equipment a white reference was used, Spectralon® standard. The spectra were acquired in reflectance mode and presented as apparent absorbance A' = log10 (1/R) for the dyes.

2.2.4. Fourier transform infrared microspectroscopy (microFTIR)

Infrared analyses were performed using a Nicolet Nexus spectrophotometer coupled to a Continuμm microscope (15x objective) with a MCT-A detector cooled by liquid nitrogen. The spectra were collected in transmission mode, in 50 μm areas, resolution setting 4 or 8 cm^{-1} and 128 scans, using a Thermo diamond anvil compression cell. For some infrared spectra the system was purged with nitrogen prior to the data acquisition; for all infrared spectra the CO_2 absorption at circa 2400-2300 cm^{-1} was removed from the acquired spectra (4000- 650 cm^{-1}).To improve result robustness, more than one spectrum was acquired from different sample spots.

2.3. Chemometric analysis based on fluorescence spectra in the visible

The data from the case studies was compared with databases for red lake pigments resourcing to a chemometric analysis method [39]. The first database is built up from historically accurate reproductions composed of brazilwood, cochineal, lac dye, and kermes. For the second approach, the database is built up of data from artworks from medieval manuscripts to textiles (11th – 15th c.) where lac dye, cochineal and brazilwood were identified. The chemometric analysis was based on Hierarchical Cluster Analysis (HCA) resourcing to the Ward's algorithm and the Mahalanobis distance. For the first database, the HCA method was fed with scores resulting from a principal component analysis of the dataset. For the second, the HCA algorithm was fed with spectral data (not requiring a previous PCA step). In both cases, excitation and emission spectra in the UV–Visible were pre-processed by applying the 1st derivative (2nd order) followed by the Haar transform. Normalization by area (unit area) is also typically used for the analysis of fluorescence data and was also considered and applied subsequently to the first two methods.

3. Case study

3.1. The colour palette of Islamic manuscripts in Fondo Ka'ti

The colour palette includes some of the highest quality colourants available during the Middle Ages, which were carefully ground and mixed with a polysaccharide and/or proteinaceous matrix, Table 1. The two main pigments are luminous lac dye red and azurite blues, masterfully applied, with the exception of the *Theology treatise*, where an organic purple is applied. In this text we highlight the main aspects related to the colours' materials, with the experimental data for identifying these colorants available in Appendix 1.

The colorants used to "illuminate, paint, and write" are described in Table 1. Lac dye reds were identified unequivocally in all manuscripts, except the *Theology treatise*. Our database of highly characterized references proved invaluable to understanding the complexity and colour diversity of lac dye formulations. For *Al-Sarishi poems* and the *Prophet biography,* we found a complex with aluminium (a lake pigment) that compared very well with one of our historically accurate reconstructions (recipe 113 from the Paduan manuscript, in the Merrifield edition), as well as the dark red used in the *Book of Birds*, Lorvão 5. The dark reds in the *Koran* and *Mss 19* compared well with recipe in the Ibn Bādīs treatise, as well as with a medieval Portuguese red colour applied in *Lectionarium Temporale*, Lorvão 13. In these recipes, no alum was added. These highly characterized materials can be employed to better understand the materials and techniques used to "illuminate, paint, and write" in the Islamic world and to relate them to a period and/or place where they were made.

With the exception of the *Koran*, where lapis lazuli was the blue used in the parchment folia, all blues were obtained from azurite. Of particular note is the sophisticated application of azurite in the *Prophet biography*, in which we encountered three hues of blue, Fig. 8: ***i)*** a brighter tone, where, under the microscope, we did not observe the grain but rather a homogeneous ink applied in the intertwining of vignettes, along with gold; ***ii)*** a blue where the size of the grains is very clear, displaying different colours, including a very intense blue; and ***iii)*** a shade of blue where a yellow or green glaze was placed on top, applied to create shadow and give volume to the letter. In general, we observed colour loss by detachment in azurite paints, which may be related to the grain size (less surface area for binder-pigment contact).

The second important red colour is based on vermilion (HgS), applied in the *Prophet biography, Mss 19*, *Al-Sarishi poems*; and on folio 70 in the *Koran* (paper support), where we also detected the presence of azurite. In all manuscripts, with the exception of *Mss 19*, gold is applied either in leaf or as ink. In the *Koran*, another arsenic-based yellow was identified by microRaman as pararealgar, which is considered a degradation product of realgar. In the *Al-Sarishi poems*, this pigment was found admixed with an (as yet unidentified) organic-based dye. *Mss 19* was the only case where we observed an orange paint, prepared by admixing vermilion with orpiment; a common combination in Islamic manuscripts. It was used in the full-page illuminations of fol.218v and fol.110r, Fig. 9.

The green colour was only found in the *Koran* (parchment folia), having been identified as a proteinaceous copper green, with an infrared spectra similar to the one found in the "bottle-green" of Portuguese monastic illuminations, Fig. 10.

Purple was considered a rare colour by Patricia Roger-Puyo in the studied collections. It is possibly an orcein purple, also known as orchil dye, as it is prepared from several lichen species, such as *Roccella*, *Lasallia*, *Lecanora,* and *Variolaria*, (see Appendix A for a detailed description).

3.2. Comparison with European production for the same period

Compared to the pigments used in medieval European illuminations, two missing pigments are lead white and red lead (also known as minium), which are central pigments in European production, lead white in particular, which is essential for enhancing colours and creating highlights, as well as for producing lighter colours (e.g., admixed with pigments to give light pinks, light blues, etc.). In Roger's research, this pigment was only detected in one manuscript, in a temporal arc from the 9th century to the first quarter of 19th century (Western Islam). In Eremin's comprehensive study (Middle Eastern Islam), lead white enters

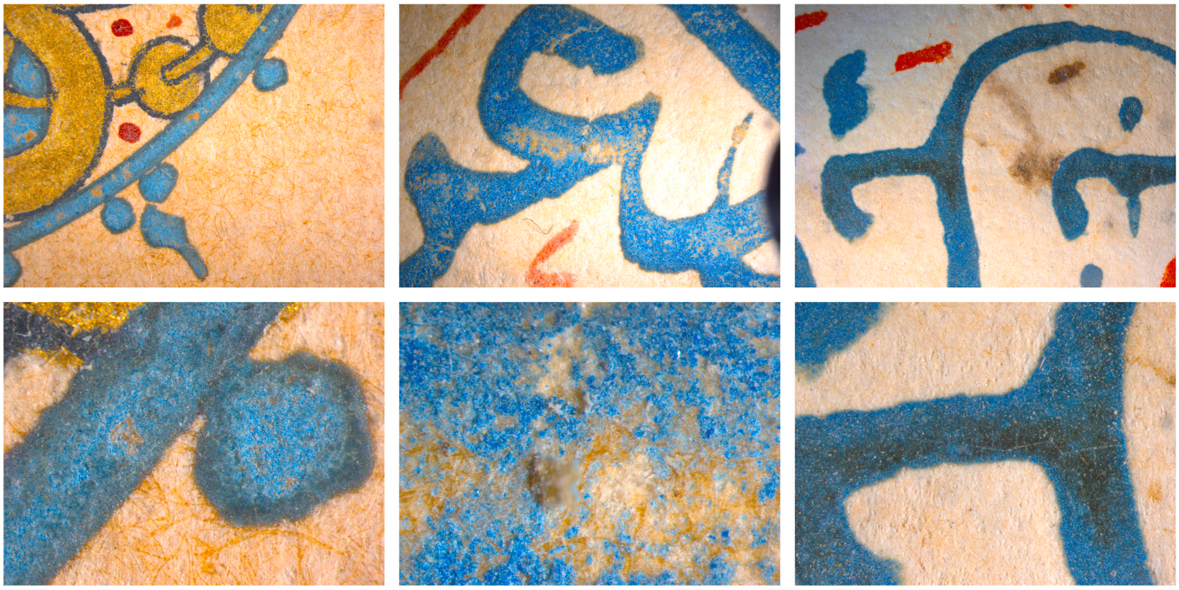

Fig. 8. Macro (up) and micro (down) details of three different shades of blue found in *Prophet biography:* a bright blue, intense blue and a blue were a thin layer of varnish (colored glaze), or another color was applied. As the blue is found extensively detaching from the support it is possible that the bright and intense blue also had a 'glaze', that was lost over time.

Fig. 9. *Mss 19* was the only one where an orange paint was found. It is not based in red lead as common in the European production, but prepared admixing vermilion with orpiment (a common combination in Islamic manuscripts). It was used in the full-page illuminations of fol.110r (*left*) and fol.218v (*right).*

the palette from the 14th century on, with occurrences already in the 13th century. We know that these lead-based pigments tend to darken, particularly if arsenic-based pigments are used in the same manuscript. That is, arsenic-based pigments such as orpiment can act as catalysts for this darkening, transforming them into arsenic sulfides. Is the absence of lead white and red lead related to colour preservation? Or with other aspects in the symbolic sphere?

The absence of the use of green is perplexing. A green-copper proteinate was detected in the oldest part of the *Koran*, it being a very important colour for Islam. To note that in the *Prophet biography* we think that the varnish applied in the azurite blue serves to create a green; a good comparison of this colour with that of malachite green was obtained (through their visible reflectance spectra). Is green absent in these manuscripts? Or, do we have to take into account its state of conservation, a consequence of its dramatic history and diaspora? This may have caused the loss of this yellowish or greenish varnish, which builds the green tone on top of the blue of the azurite. This question will be very interesting to explore in the future.

4. Future perspectives: creating new sustainable applications

"**Paleo-inspiration**, the process of mimicking properties of specific interest (mechanical, optical, structural) observed in ancient and historical systems, is proposed for innovative chemical conception. The inspiration is gained from an advanced study of ancient materials that were often synthesized in soft chemical ways, using low energy resources, and sometimes rudimentary manufacturing equipment" [35].

Over the past decade, our research on the molecules of colour in art has followed the motto described in this quote. Our physical-chemical approach, addressing the structural, electronic, and reactive properties of cultural heritage materials nourished by phenomenological studies, has unravelled the information enclosed in works of art, such as the complex paint systems based on organic dyes [1,2]. These advanced studies have shown the remarkable properties of ancient dyes, their resilience and durability; properties that were designed by our ancestors through sustainable materials processing. This lost knowledge can be shared with local communities to reappropriate these historical materials and create novel applications, as well as empowering them to create regional value-added products.

Historical formulations of natural art materials, such as those organic-based colourants extracted from plants, have grown great interest among contemporary artists as they allow them to engage with and explore the natural world. Reviving and reinterpreting lost methods of craftsmanship opens a world of artistic possibilities that enables the creation of unique and original artworks. This new production of

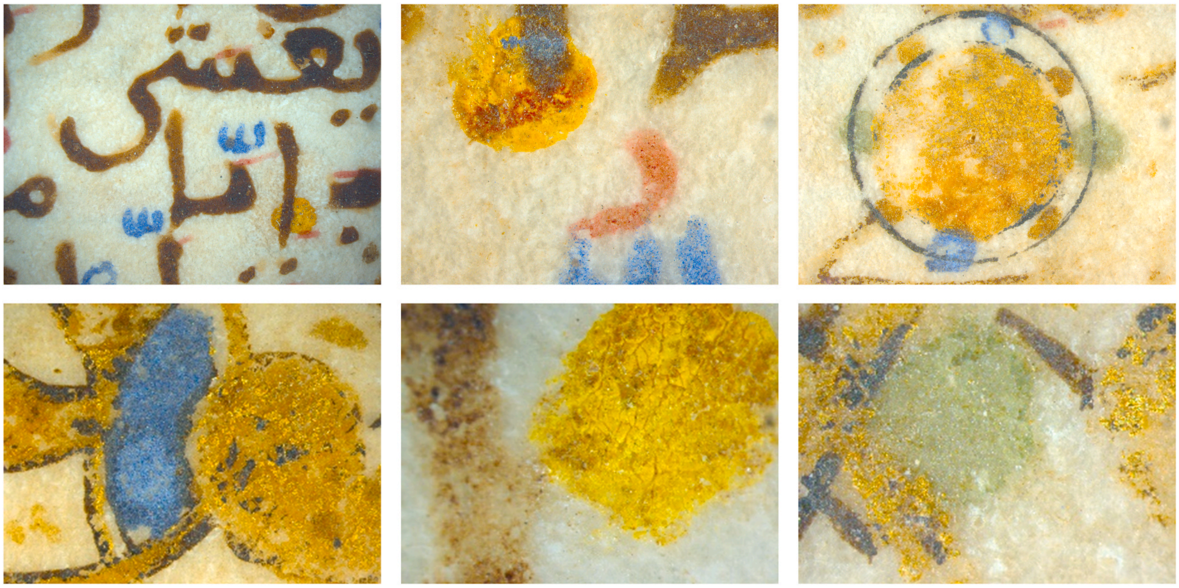

Fig. 10. Macro (up) and micro (down) details of the colours found in the *Koran*. On fol.30r, from left to right: lapis lazuli blue and gold, arsenic based yellow and a green copper proteinate.

sustainable art pieces will have a global impact as it is gaining significant momentum in the art community and market.

Abbreviations

Define abbreviations that are not standard in this field in a footnote to be placed on the first page of the article. Such abbreviations that are unavoidable in the abstract must be defined at their first mention there, as well as in the footnote. Ensure consistency of abbreviations throughout the article.

Author contributions

M.J. Melo coordinated and wrote the first version of the microreview. P. Nabais and R Araújo coordinated the on-site investigations of the Islamic manuscripts with the collaboration of M. Vieira, V. Otero, M. J. Melo, L Martín and M. Sameño. J. Lopes supervised the chemometrics analysis. All authors contributed to the revision and approval of the article's final version.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2022.110815.

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