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Towards building a Cathodoluminescence (CL) database for pigments: characterization of white pigments

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Abstract

Paintings and painted surfaces are considered to be extremely complex due to their multitude of materials and thus form the basis for particularly intricate Cultural Heritage studies. The combination of Scanning Electron Microscopy (SEM) with Cathodoluminescence (CL) can serve as a powerful tool for the identification of individual pigments. SEM/CL has the potential of identifying both organic and inorganic pigments and can focus on a micrometer or even nanometer scale. The combination with Energy Dispersive Spectrometry (EDS) allows for robust, cross-checked, elemental and mineralogical characterization of pigments. In order to apply SEM/CL in a routine-based way for the identification of pigments, it is necessary to have a robust, open-access database of characteristic CL spectra of pigments. A large project has been undertaken to create such a database, focusing primarily at the pigments, both organic and inorganic, which were most commonly used from antiquity until today. In the present paper, the CL characterization of common white pigments is presented. White pigments were selected, due to their significance and frequency of use, since they were also present on the ground layers or mixed with other pigments in most of the painting layers. More specifically, the CL spectra of samples in pure form of calcite, kaolinite, lead white, zinc oxide, barium sulfate, lithopone and titanium white are presented. In all cases, the CL spectra present characteristic bands, which allow for a secure identification of the pigments. In order to facilitate comparison with other databases, EDS and RAMAN spectra are also presented. Additionally, the effect of weathering on the CL spectra was evaluated, by comparison to naturally and artificially aged samples and to pigments identified on areas of two paintings, of the 19th and 20th c., respectively. Finally, the effect of binding media was also studied, using combination of pigments with four common media: egg yolk, linseed, walnut and poppy oil. Overall, both weathering and binding media appear to cause minor differences in the occurring spectra, without preventing the identification of pigments.

Keywords: Cathodoluminescence, White pigments, Lithopone, Binding media, Artificial ageing

Introduction

Cathodoluminescence (CL) is the optical phenomenon produced by the interaction between high energy electrons from a cathode ray tube and a crystalline solid. CL studies focus on the fluorescence emission, the wavelengths of which are characteristic of the electronic states

of the structure of the material. More specifically, fluorescence wavelengths are representative of the point defects that affect the crystals, such as atom vacancies, chemical impurities etc. [1]. When an electron, excited from the valence to the conduction band, returns to ground state, energy is partly or fully emitted as light [2]. Different defect types distort the structure of the crystal lattice in well-defined ways creating characteristic traps in the band gap [3]. In minerals, these defects result from specific conditions during mineralization (i.e. speed of cooling and temperature, pressure and chemistry of the

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melt, metamorphic events such as dynamic recrystallization, sedimentation processes such as cementation) [4, 5]. Therefore, CL spectra, recording the wavelengths of emitted photons, provide information about the crystallization or genesis of minerals and their mineralization history.

CL is commonly applied in a wide variety of geological material [6, 7]; in recent years an increasing number of applications in archaeological and Cultural Heritage artefacts has also been published. A few examples of the successful application of CL is the analysis of quartz for the classification and provenance analysis of pottery [8–11], natural [12] and man-made glass [13–15], the examination of weathering effects on Greek white marble [16], the analysis of lime carbonates in plaster from Mexico [17], the provenance analysis of Late Neolithic ornaments (beads and bracelets) made of spondylus shells from Hungary [18] and the characterization of lapis lazuli artefacts and pigments [19]. Similar efforts using solid state luminescence protocols were practiced in the past either for the characterization of cultural material, as presented for example by Zacharias et al. [20], or on synthetic materials; a review for the later was written by Yukihiro et al. [21].

The potential of applying SEM/CL for the identification of pigments presents strong interest, since it could successfully tackle some of the analytical problems which can significantly complicate the analysis of paintings and painted materials (e.g. pottery). The characterization of pigments presents multiple difficulties, the most important being: (1) the very small thickness of paint layers, (2) the large number of layers, including paint layers, ground layers, substrate etc., (3) mixing of pigments within the same paint layer, (4) presence of other particles, primarily organic, due to binding media and other ingredients, (5) weathering of pigments, etc. These issues combined with practical considerations during the analytical process (difficulty in extracting microsamples from valuable and/or sensitive paintings, necessity to characterize both organic and inorganic components in micro-level) constitute paintings and painted material as the most complex type of Cultural Heritage materials.

The above mentioned difficulties have led in recent years to a significant increase in—and improvement of—applied techniques, with an emphasis on non destructive and in-situ techniques [22, 23]. Despite the need for sampling, the so far limited applications of SEM/CL in the analysis of paintings have provided with very promising results [15, 24, 25], since the technique can be applied on both organic and inorganic pigments, on a micrometer to nanometer scale. Also, it is expected that similar manufacturing processes will result to similar luminescence properties. The combination with EDS can lead to

a robust, elemental and mineralogical characterization of pigments.

Brief overview of white pigments and binding media

White pigments hold a very significant role in the painter's palette; they are very frequently applied as a ground layer, in many cases combining multiple white pigments together, or used plain or mixed with other pigments to produce several shades of colours. A short summary of the most common historical white pigments is given in the following paragraphs. Additionally, some basic information on the common types of binding media is provided.

Lime white

Lime white, CaCO_3 , is probably the oldest white pigment in the world. It most commonly consists of chalk, a white pigment of limited hiding power, mainly used for painting grounds; under ordinary conditions it is a stable pigment [26]. Chalk is a very pure limestone, formed during the cretaceous period, of fine calcite crystals consisting mainly of fossil remains of the shells and skeletons of microscopic plankton. It can also contain small amounts of other minerals, usually quartz and clay minerals. There are many deposits throughout the earth that are exploited commercially.

Kaolinite

Kaolinite, $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$, is named after the original type locality of Kao-Ling, China and occurs most commonly as compact earthy masses of microscopic crystals or as larger pseudo-hexagonal tabular crystals. Pure forms of the mineral are white, although the presence of impurities (such as iron and magnesium) may colour it grey or yellow. Kaolinite is common worldwide and forms as secondary deposits usually from the decomposition of feldspar group minerals. Alternatively, it can form as the final alteration product after illite and montmorillonite, if sufficient water is present [26].

Kaolinite is well known for its use in the manufacture of porcelain, as well as in the manufacture of paper and paint [26]. Members of the kaolinite sub-group have been identified at rock art sites in various locations throughout the world [27–29].

Lead white

Lead carbonates were extensively used as cosmetics by ancient Egyptians, Greeks, and Romans; this application of lead carbonates continued up to 18th c. AD [30]. Additionally, from the Roman period onwards, lead white has been by far the most important of the white pigments used in Europe. The term can generally be used for any

lead-based white pigment and can even be extended to describe lead chloride oxides, lead phosphates and lead sulfates; it usually refers to lead carbonate hydroxide, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ [31].

Lead carbonate hydroxide is chemically equivalent to the naturally occurring hydrocerussite, which is extremely rare and therefore rarely used as a pigment source. During the Roman period, Vitruvius in the 1st c. BC and Pliny in the 1st c. AD describe the synthesis of this mineral, called “cerussa” at the time, by steeping lead in vinegar [26]. The processes used by the Romans are the basis of the medieval to 17th c. technologies for lead white manufacture. A thorough description of the most common production methods of lead white until the early 20th c. is given by Eastaugh et al. [26].

The pigment is permanent, relatively stable in all media (but particularly when used in oil). On the contrary, it was rarely used in fresco, where lime white was substituted. It was commonly adulterated with other white pigments, particularly chalk, baryte and kaolinite. The use of lead white has been widely reviewed [indicative publications: 32, 33].

The concern over lead poisoning increased during the Industrial Revolution. Although lead white continued to be marketed, alone and combined with other pigments, its presence sharply decreased in the first half of the 20th c., from nearly 100% to less than 10% by 1945 and it was widely abandoned in the period after World War II [34].

Zinc oxide

In the second half of the 18th c. an effort began to find viable substitutes for lead white, in response to the increasing awareness of the health hazards entailed in its manufacture and use [32]. The search was oriented in particular towards investigating zinc oxide (ZnO) for this purpose. Although known since antiquity as a by-product of brass production and for its medicinal properties, this substance was seemingly never used as a pigment [33, 35]. The development and refinement of methods for producing a non-poisonous white pigment from zinc metals or ore, and the improvement of the material itself, led to the production of a pigment, which was first commercialised by Winsor & Newton in 1834 under the name Chinese White and marketed as an artists’ pigment in a watercolour medium. Shortly thereafter it was improved for use in oil, when Leclaire succeeded in improving its drying and covering properties, inferior until then to the also still less costly lead white. By 1859, zinc oxide white, which had a further advantage over lead-based pigments because it did not blacken in the presence of hydrogen sulfide, was being produced on an industrial scale in Europe and the United States.

Barium-based pigments

Besides zinc oxide white and kaolin, which was still being used primarily for grounds and as an additive and filler, several barium-based materials (such as barium sulfate, BaSO_4) were also proposed as artists’ pigments, either in the form of natural ground barytes, or the more pure synthetically produced pigments such as blanc fixe [36]. The reduced hiding power of these substances, however, tended to restrict their use in the paint industry as extenders for lead, zinc, and later, titanium compounds, or as a base for lakes. These pigments were introduced commercially in the early 19th c.; after 1950, although they were still available both in their natural and synthetic forms, they sharply declined in production for artistic purposes.

Another white material developed in this period was the composite pigment lithopone ($\text{BaSO}_4 \cdot \text{ZnS}$), which was obtained by precipitating zinc sulfide with barium sulfate. It was first produced according to patents granted in France around 1850 [35]. Initially, the most common lithopone pigments were produced using equivalent solutions of barium sulfide and zinc sulfate, which ended up producing a mixture of approximately 29.5 percent zinc sulfide and 70.5 percent barium sulfate. However, purer and higher strength varieties have since been manufactured, with varying ratios of the two ingredients; two grades of lithopone, known as gold and bronze seal, contain between 40 and 50 percent zinc sulfide, resulting in a pigment with much more hiding power and tinctorial strength [37].

Despite the cheapness of its manufacturing processes and good properties as pigment, lithopone had the tendency to darken when exposed to sunlight. In the late 1920s, a small amount of cobalt, varying from 0.02 to 0.5% of the zinc content, was added prior to the calcination process to prevent discoloration. Nevertheless, the usage of lithopone as an artists’ pigment was difficult to establish and it was primarily used as a cheap extender for other white pigments, like ZnO [38].

Titanium white

The elementary metal titanium, never found unbound from other elements in nature, was first discovered in England in 1791 by William Gregor in the iron titanium oxide ilmenite, and by M.H. Klaproth also in rutile ores in Germany in 1795, who confirmed it is a new element and gave it its name. Before that, the use of titaniferous minerals for the production of pigments is not attested, though in Mayapan site (Yucatan Peninsula, Mexico) a small amount of nanocrystalline TiO_2 particles (in rutile form) has been consistently detected using phase mapping in red pigment samples [39]. During the 19th c.

several attempts were carried out to produce coloured pigments from natural ground titaniferous minerals, including titanium dioxide, with limited success. Most of these attempts focused on the most common crystallographic form of TiO_2 , rutile; of the other two forms, anatase and brookite, the former was used rarely and the latter does not seem to have ever been used directly as a pigment [40].

The first successful attempts to manufacture superior quality synthetic products took place practically simultaneously in Europe and the US in the early 20th c. The first commercially successful composite pigments of anatase were obtained in the 1920s, through precipitation of anatase titanium dioxide onto a barium sulfate base. Despite the fact that the rutile form was much less rare and was known to possess better hiding power and weathering properties than anatase, difficulties in its refinement continued to privilege the latter. Only in 1937 were successful methods for producing synthetic rutile developed, with the pigment becoming widely available in the market in the second half of the 20th c. [26].

The initially high cost of titanium dioxide whites shortly diminished, as various drawbacks typical of the early manufacturing methods were overcome. Combined with the high quality of the produced pigment, titanium white almost completely supplanted the other white pigments by the middle of the 20th c. [40].

Binding media

A binding medium is the film-forming component of paint. A pigment should not dissolve in the binding medium nor be affected by it. However, it is well established that different binding media can strongly affect the paint, especially after ageing. Additionally, binding media, which are usually organic substances, can significantly hinder the identification of pigments, by altering their signals as determined by various analytical techniques.

Before the Middle Ages, artists used pigments in beeswax (encaustic) melted and manipulated with hot rods. Since the early Middle Ages, paintings on wood panels have traditionally been produced in egg tempera. Egg yolk is a semi-opaque medium: it can be used translucent or nearly opaque.

During the Renaissance, egg tempera was gradually supplanted in popularity by oil paint on canvas. In oil painting, the most popular oil for binding pigment, thinning paint and varnishing finished paintings is linseed oil. The linseed oil comes from the flax seed, a common fiber crop. Linseed oil tends to dry yellow and can change the hue of the colour [41].

Safflower, walnut and poppy seed oils are sometimes used in formulating lighter colors like white because they “yellow” less on drying than linseed oil. They have the drawback of drying more slowly and may not provide the strongest paint film [41]. Poppy seed oil, for example, takes 5–7 days to dry, compared to 3–5 days for linseed oil.

Methods

Research aim

The main aim of the present work is the formation of a robust database of characteristic CL spectra of pigments, focusing primarily on those which were most commonly used from antiquity until today. This will allow for a more extensive application of SEM/CL in the examination of paintings and painted materials. White pigments have been selected as the first case study, due to their significance and frequency of use, since white pigments were also applied on the ground layers or mixed with other pigments in most of the painting layers.

Seven of the most common white pigments (calcite, kaolinite, lead white, zinc oxide, barium sulfate, lithopone and titanium white) were analysed in pure form, using SEM/CL. In order to facilitate comparison with other databases, EDS and RAMAN analyses were also carried out. Additionally, parameters such as the ageing of pigments and the effect of binding media were also studied, by the analysis of especially prepared samples. Finally, the spectra of pigments in pure powder form were compared to similar pigments identified on the surface of two paintings (from the 19th and 20th c., respectively).

Samples

It is common for manufacturers of contemporary paints and dry materials to omit mentioning some of the components, such as technological additives for imparting certain properties to paints or inert fillers to reduce the cost of dry pigments and paints [24]. Since the purpose of this study is to create a database of the CL signal of pigments, samples in pure form were selected for analysis. More specifically, lead carbonate (PbCO_3), zinc oxide (ZnO) and barium sulfate (BaSO_4) commercial samples (Sigma Aldrich) were analysed in powder form. Lithopone was also a commercial sample (“Artists pigments Premium Kunstler-pigments”, lithopone no. 108), made in Germany by H. Schmincke & Co. The calcite (CaCO_3) was a pure spar sample; both the calcite and the kaolinite samples came from the Geology scientific collection of the National Museum of Natural Sciences-CSIC, Madrid, Spain.

The titanium dioxide pigment corresponds to the rutile crystallographic form; the sample has undergone natural ageing of more than 15 years. Additionally, 4

reference samples, produced in 2001, consist of a mixture of Ti white with 4 of the most common types of binding media, namely: egg yolk, walnut oil, linseed oil and poppy seed oil. For the preparation of the egg tempera samples, the egg yolk was separated from the egg white, and then removed from its skin. For one part of egg yolk, one part of vinegar and two parts of water were added. The mixture was stirred very well and mixed with the medium. All samples were left at room temperature for two days to dry before undergoing the accelerating ageing process proposed by Meilunas et al. [42] (oxidative type of ageing): samples were heated in air at 120 °C for 24 h and then cooled again to 25 °C. For the heating process a Gallenhamp—Hotbox Oven of size 2, with stainless steel lining and fan for even heat distribution was used.

Finally, three microsamples of two paintings, representing cross-sections with multiple colour layers each, were also analysed. Two samples come from a 19th c. painting entitled “Game” (oil on canvas, with inv. No P838) by an unknown artist and one sample comes from a 20th c. painting entitled “Hydra” (oil on cloth, with inv. no K595) by Economou Michael [43]. They both belong to the collection of the National Gallery – Alexandros Soutzos Museum in Greece. The microsamples were detached by the conservators of the National Gallery before the conservation process of the paintings and were embedded in resin and polished.

Methods

The micromorphology, topography and distribution of the components in the samples were determined using a FEI INSPECT Scanning Electron Microscope (ESEM) of the Museo Nacional Ciencias Naturales (Madrid, Spain). The ESEM microscope in low vacuum mode can work with hydrated samples to be studied in their original state using the large field detector (LFD), since it is close to the sample in order to avoid electron losses, and the Back Scattering Electron Detector (BSED).

The SEM resolution at low-vacuum was at 4.0 nm at 30 kV (BSED). Energy Dispersive Spectrometry (EDS) of the samples was carried out with an energy dispersive X-ray spectrometer by Oxford Instruments, using INCA software for the quantification of the data. In EDS analysis an accelerating voltage of 20 kV was used. Precalibration tests of SEM/EDS chemical measurements were previously performed on internal standards to improve the ZAF correction procedure (Z: atomic number; A: Absorption effect; F: Fluorescence effect).

The SEM setting previously described has MONOCL3 Gatan (CL) detectors, making it possible to work in panchromatic and monochromatic mode with a PA-3 photomultiplier attached to the ESEM. The photomultiplier tube covers a spectral range of 250–850 nm and is more

sensitive in the blue parts of the spectrum. A retractable parabolic diamond mirror and a photomultiplier tube were used to collect and amplify the CL signal. No filters were applied to standardize the sensitivity of the photomultiplier tube. The samples were positioned at 16.23 mm beneath the bottom of the CL mirror. The excitation for CL measurements was provided at 30 kV electron beam. The settings of the analyses were as follows: dwell time: 1.5 s, range: 600 nm, step size: 1.5 nm. Depending on the sample (homogeneity of material, preparation method) CL analyses were carried out either on bulk surfaces or individual inclusions. All CL spectra presented below were the outcomes of single analyses but are considered representative of multiple analyses carried out on different areas of each sample.

The samples were analysed by Raman microscopy of the Museo Nacional Ciencias Naturales –CSIC (Madrid, Spain). The micro-Raman spectroscopy analysis was performed by both single spectra using Thermo-Fischer DXR Raman Microscope (West Palm Beach, FL 33407, USA) which has a point-and shoot Raman capability of one micron spatial resolution with an Olympus BX-RLA2 Microscope and CCD (1024 × 256 pixels) detector, motorized xy stage, auto-focus and microscope objectives Olympus UIS2 series (West Palm Beach, FL 33407, USA) all controlled through OMNIC 8.3 software. The light at 780 nm of a frequency doubled Nd:YVO4 DPSS solid laser (maximum power 14mW) was used for excitation. The sample was inspected with the 20 × objective to select areas. The spectra were obtained with using the 20 × and 50 × objectives of the confocal 25 µm slit and grating of 900 lines/mm. These conditions and excitations at 780 nm give an average spectral resolution of 2–4 cm⁻¹ in the wavenumber range of 200–3200 cm⁻¹. The sample spot size was approximately 1–2 µm, in accordance with the objective used. An integration time of 10 s × 4 accumulations was enough to get acceptable results. The calibration and align spectrograph were checked using pure polythene.

Results

Characteristic CL spectra

Of the above mentioned 7 common white pigments, kaolinite, calcite and zinc oxide have been studied in the past using SEM/CL [44–48]. The detailed analysis of these 7 samples suggests that they all present CL spectra with characteristic bands, as shown in the following figures. Based on the CL panchromatic images, an evaluation can be made on the strength of the signal, as brighter areas suggest a stronger CL signal. Based on this observation, information can be drawn on the homogeneity of the material. More importantly, a pigment showing strong signal will be easier identified in a real case study, i.e.

when present in small quantities, mixed with other elements and aged. In order to facilitate comparison with other pigment databases, EDS and Raman spectra of each pigment analysed are also presented in the Supplementary Material.

The calcium carbonate sample analysed (in pure calcite form, as shown by its Raman spectrum shown in Additional file 1: Table S1) presents a clear CL spectrum, with a strong band at 416 nm, a band at 460 nm and a wide band at 765 nm. Two shoulders are also noted at 334 and 386 nm (Fig. 1). The common defects of geological calcitic material have been discussed in detail in literature [46, 47].

Kaolinite also presents a clear CL spectrum, with a strong wide band at approximately 365 nm; and two smaller bands at 678 and 754 nm. Two shoulders are also noted at 334 and 386 nm (Fig. 2). A detailed description of the main defect centers of kaolinite is given by Götze et al. [44]. The sample analysed consisted of grains with diverse chemical and CL signal, as expected; the main bands of the spectrum, however, are consistently present, allowing for the identification of the pigment.

As mentioned before, the lead carbonate selected for analysis was in the form of PbCO_3 . The pigment produced low CL signal, suggesting that its identification will be difficult if present in small quantities. The spectrum, however, shows a characteristic band at 474 and a smaller band at 436 nm (Fig. 3).

The titanium dioxide sample analysed (in the form of rutile, as shown by its Raman spectrum shown in Additional file 1: Table S1) produced low CL signal, as can also be seen from the low intensity of the panchromatic image (inset image of Fig. 4). Therefore, the identification of the pigment, if present in small quantities, will be more difficult than the other white pigments examined. This has also been noted by Kadikova et al. [24]. However, the spectrum shows two characteristic sharp bands at 434 and 472 nm, as well as a wider band at 800 nm (Fig. 4). It should be highlighted that though the analysed sample had undergone natural ageing of minimum 15 years, the resulting spectra are identical to those presented by Kadikova et al. [24], which corresponded to a titanium white pigment of the “Schmincke” paint set.

The zinc oxide sample produced a CL spectrum with a strong sharp band at 390 nm (Fig. 5); the wider band at 776 nm is the second order of the diffraction grating, associated with the design of the instrument. A small wide band at approximately 495 nm is also noted. A detailed description of the emission centers and defects of ZnO is given by Ton-That and Phillips [48]. It should be highlighted that zinc oxide produced very strong signal, suggesting that it would be possible to identify even very small quantities of the pigment.

The barium sulfate pigment analysed produced a CL spectrum with a characteristic wide band at approximately 556 nm (Fig. 6, top); a small wide band at 390 nm is also noted.¹ The lithopone sample also produced a characteristic spectrum with multiple bands: a strong band at 364, smaller bands at 468, 572, 702 and 764 nm and a shoulder at 428 nm (Fig. 6, bottom).

The clear distinction of the CL spectrum of lithopone compared to the spectra of barium sulfate and zinc oxide is very significant. The identification of lithopone is not straightforward with elemental analysis techniques, such as X-ray fluorescence or SEM/EDS, since the produced data does not permit the distinction between lithopone from mixtures of barium sulfate and zinc sulfide or zinc oxide present as unprecipitated compounds [38]. Even with spectroscopic techniques, such as Raman, it is very difficult to identify the pigments used, when a combination of any of these three pigments is used (e.g. in a mixture of lithopone with ZnO , the characteristic bands of ZnO coincide with the typical spectrum of pure lithopone).

Monochromatic images

Taking monochromatic images for specific wavelengths of emission, it is possible to identify the distribution of a pigment, even if multiple pigments with a similar elemental composition are present on the same area. For example, on one area of the micro sample of the painting “Game”, a complicated elemental analysis occurred by SEM/EDS, suggesting the simultaneous presence of Zn, Ba, S, Ca, Pb, all of which could be related to the presence of white pigments (Fig. 7, top). The high amount of zinc can either be attributed to a pigment of ZnO or to lithopone, as mentioned before. The EDS mapping of Zn, shown in Fig. 7 (bottom left), does not provide any further information. However, the monochromatic image at 390 nm (the main band of ZnO , which does not appear on the lithopone spectra, as shown in Figs. 5 and 6), clearly shows strong emissions at this wavelength (Fig. 7, bottom right). It is possible therefore to attribute zinc to the pigment ZnO , instead of lithopone.

Effect of ageing

Ageing of pigments can significantly alter both their colour and their chemical fingerprint, making their identification more complex. In order to evaluate the

¹ The CL spectrum presented in Fig. 6 (top) is indicative of the pure form of the barium sulfate pigment. It should be mentioned that on a previous publication by Palamara et al. [15], a composite area of analysis, consisting of Ba, S, Pb and Si, was presented, showing a more complex CL signal. Based on the new evidence, only the band at approximately 560 nm corresponds to BaSO_4 , whereas the bands at 432 and 474 nm correspond to PbCO_3 and the band at 315 nm is still under investigation, though possibly connected to Si.

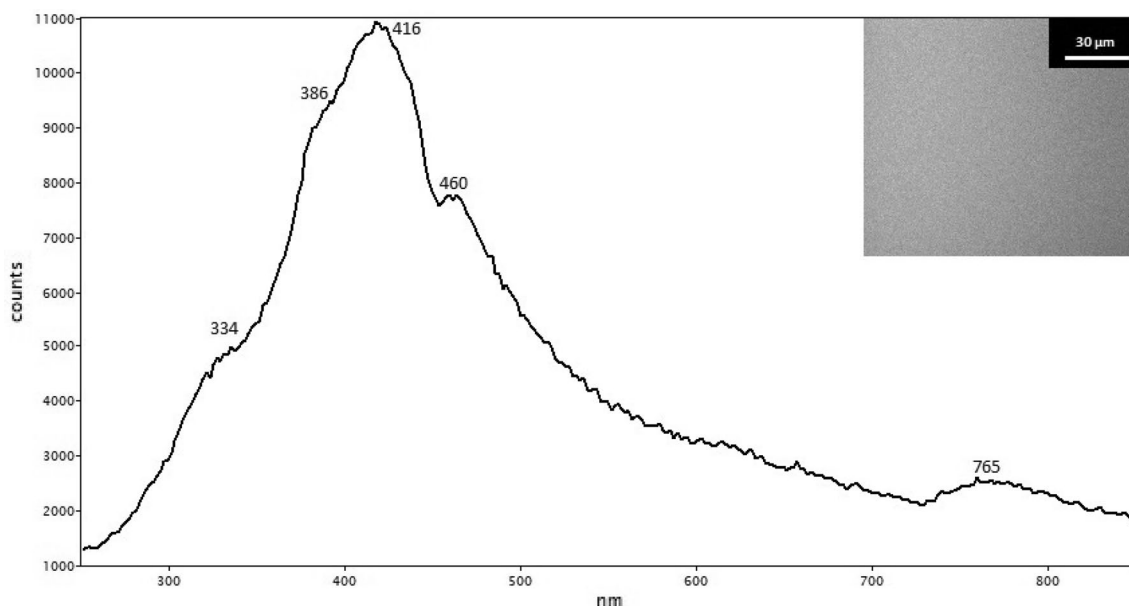


Fig.1 CL spectrum of CaCO_3 in the form of calcite (inset image: panchromatic image of the sample, showing a very homogeneous material with strong signal)

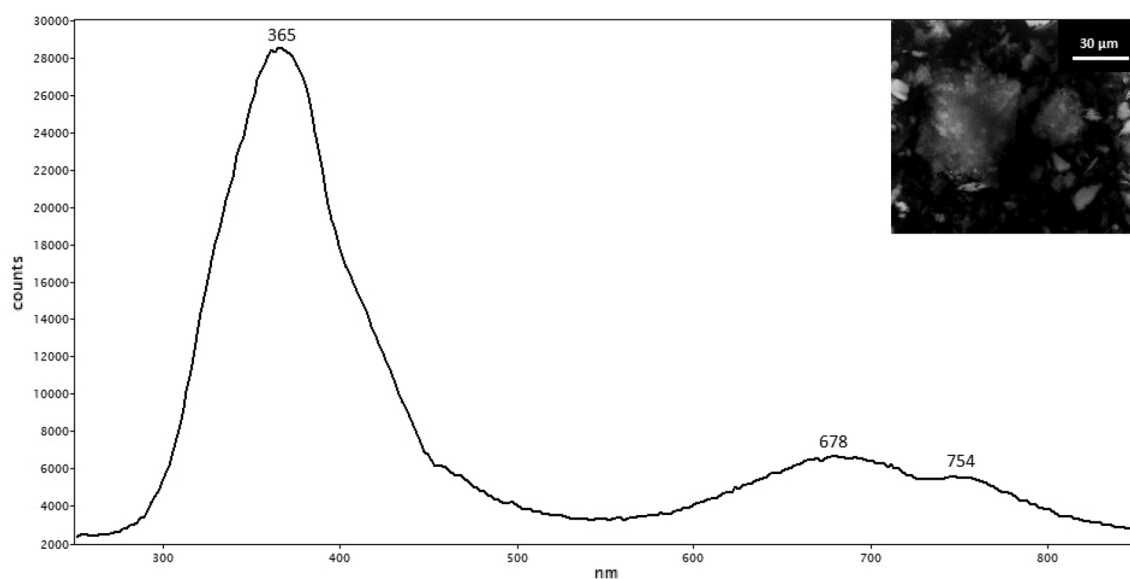


Fig.2 CL spectrum of kaolinite (inset image: panchromatic image of the sample, showing significantly varied strength of signal among grains)

effects of ageing to the CL signal, a comparison was carried out between some of the pure white pigments with naturally aged samples in pure form and with undissolved particles identified on the two 19th and 20th c. paintings (“Hydra” and “Game”).

As mentioned above, the naturally aged (minimum 15 years) sample of Ti white presented an identical

spectrum compared to modern pigments presented by Kadikova et al. [24] (Fig. 4). Additionally, comparison of modern lead white and ZnO pigments with undissolved particles of the same pigments from the two 19th and 20th c. paintings suggest very limited effect on the CL spectrum. More specifically, the undissolved lead white particles present identical spectrum with the modern

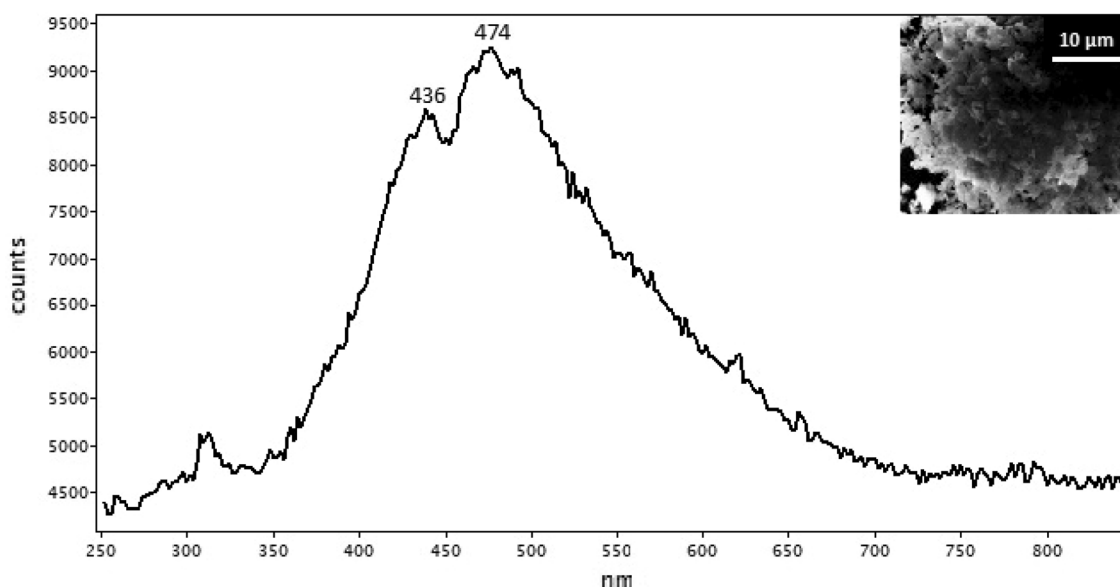


Fig.3 CL spectrum of PbCO_3 (inset image: panchromatic image of the sample, showing areas of stronger signal)

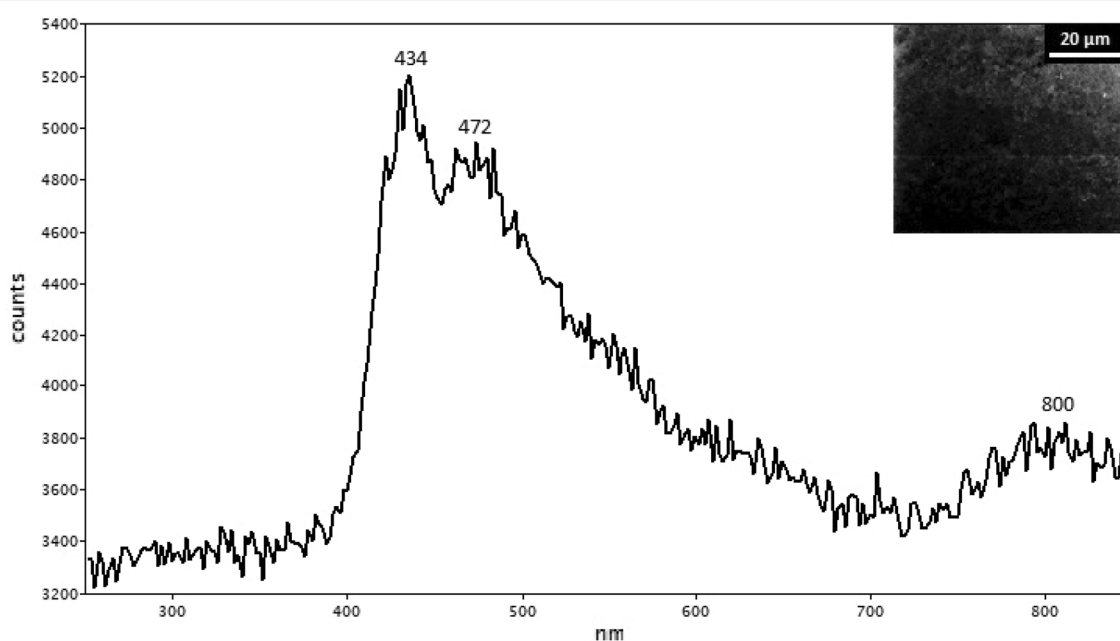


Fig.4 CL spectrum of TiO_2 (in rutile crystallographic form, naturally aged for a minimum of 15 years) (inset image: panchromatic image of the sample, showing generally low signal, with only a few brighter areas)

pure pigments, even though they may not correspond to the same crystallographic forms of lead carbonates (Fig. 8).

In the case of ZnO , the CL spectrum of the modern pigment presents the exact same shape, although the bands are shifted to the right (Fig. 9). The ZnO has a broad green-yellow emission that is usually related to

crystalline defects [26]. When ZnO is not pure, crystalline defects can change, causing slight modifications on the spectrum; therefore, the differences noted above could be attributed to the higher presence of crystalline defects on the pigments analyzed on the painting sample or to other defects linked to the more complex chemical micro-environment of a painting.

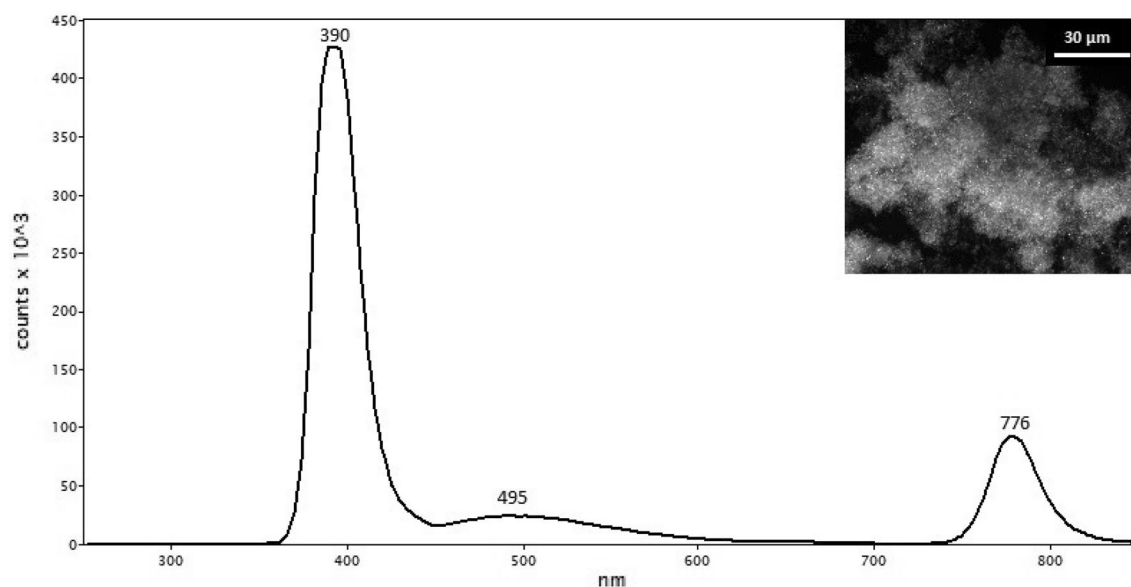


Fig.5 CL spectrum of ZnO (inset image: panchromatic image of the showing very bright areas emitting strong signal)

Effect of binding media—the case study of TiO₂

In order to evaluate the effect of the presence of binding media on the CL signal of a pigment, an experiment was carried out analysing four titanium white samples, each mixed with a different binding medium (egg yolk, linseed, walnut and poppy seed oil) and then thermally aged, following the protocol described before. Each sample was analysed using the same analytical protocol described before, including EDS, CL and Raman analysis.

EDS spectra of the four samples show a strong Ti band and bands of Al and Si, which vary in size, which were also present in the EDS spectrum of the clear TiO₂ pigment (Additional file 1: Table S2). Additionally, a C band is present in all spectra, attributed to the binding media; in the case of egg yolk sample, a small P band is also noted, which can also be attributed to the organic components of the binding medium. The Raman spectra present strong similarities, regardless of the binding medium, with only minor differences in the smaller bands and/or the relative intensity of the two main bands (Additional file 1: Table S2).

The CL spectra produced present a low signal to noise ratio, however some preliminary observations can be made. The 4 resulting spectra show only small differences compared to the pure pigment: the relative intensity of the two main bands is shifted and the lower band at 800 nm has significantly lowered in intensity or is completely absent (Fig. 10). However, the pigment can still be identified, regardless of the binding medium and the artificial ageing. It should be highlighted that the potential of carrying out a simultaneous EDS and CL analysis on the

exact same area of the sample, can be particularly helpful in cases of complex or weathered material like the one presented here.

The results of this case study, though preliminary, suggest that the identification of a pigment with CL would still be possible, even when mixed with binding media. Further analyses are currently under way, in order to better understand the effect of binding media and to evaluate the possibility of identifying different binding media using SEM/CL.

Conclusions

Preliminary results on the study of pigments have so far shown that the combination of Electron Microscopy with Cathodoluminescence can serve as a powerful new tool for the study of paintings and painted materials. Overall, the coupled application of CL analysis with the traditional technique of SEM/EDS presents great advantages. Additional to the elemental analysis, CL offers the possibility of investigating aspects of the electronic states and defects of the structure, therefore allowing a more detailed determination of the analyzed material. The potential of parallel elemental and luminescence mapping on the same areas, and with the high resolution provided by SEM, can lead to a very quick and thorough examination of a sample. Moreover, CL signal can be emitted by both inorganic and organic material.

However, the creation of a CL database for organic and inorganic pigments is necessary in order to use the technique for the study of paintings. The results shown in the

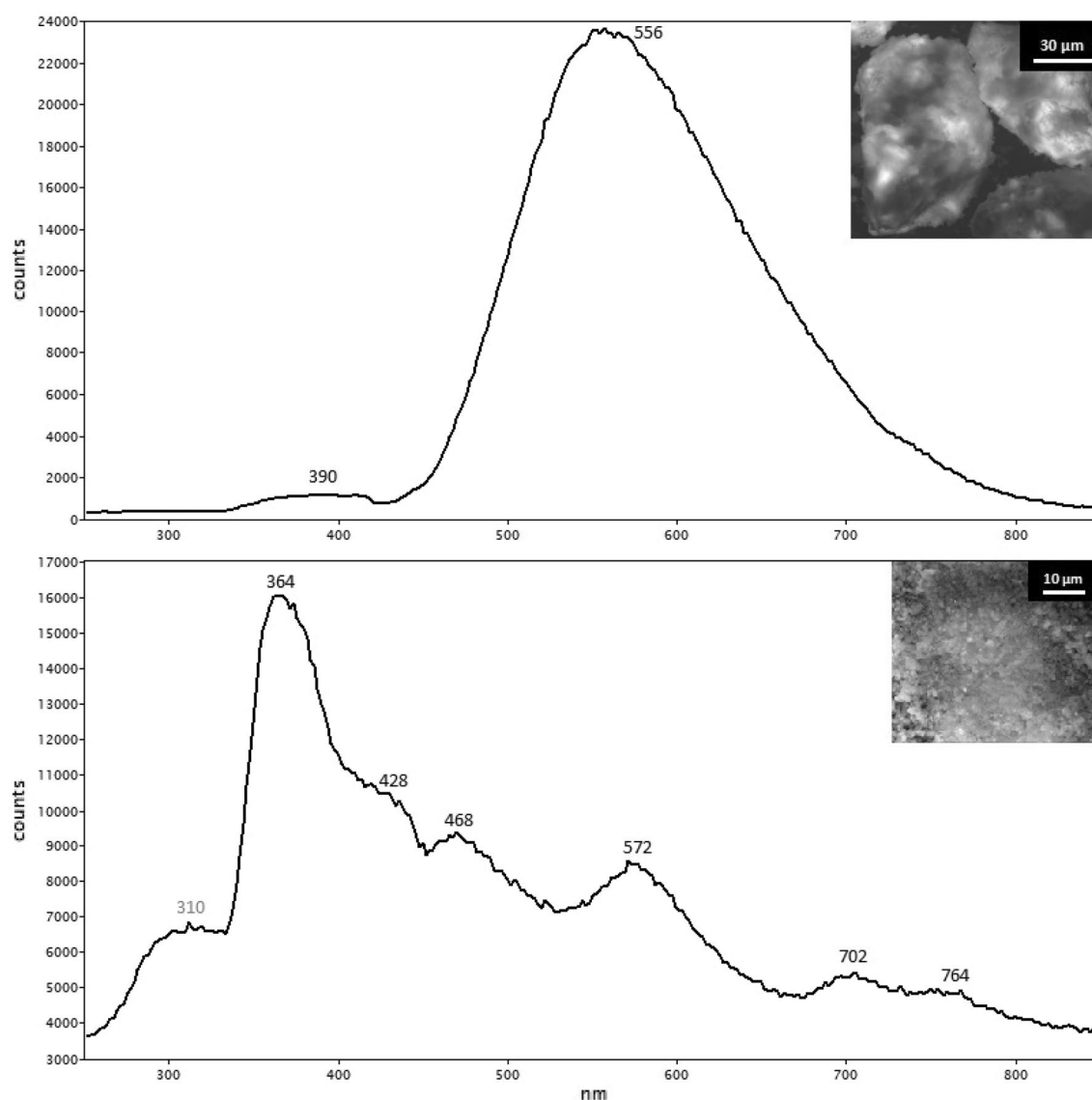


Fig. 6 CL spectra of BaSO_4 (top) and lithopone (bottom) (Inset images: panchromatic images of the samples showing in both cases a strong signal)

present paper of seven of the most common historical white pigments (calcite, kaolinite, lead white, zinc oxide, barium sulfate, lithopone and titanium white) indicate that CL can be successfully applied for their identification. Perhaps the most interesting outcome is the clear distinction of the CL spectrum of lithopone compared to the spectra of barium sulfate and zinc oxide. The identification of lithopone is problematic with most commonly applied techniques, since the produced data usually does not permit the distinction between lithopone from mixtures of barium sulfate and zinc sulfide

or the identification of individual pigments when a more complicate mixture of pigments is applied.

It is important to highlight that in the preliminary experiments undertaken so far, the identification of pigments was possible not only in pure form, but also when mixed with binding media, or when analysing individual grains on a painting layer of a painting. Moreover, aged pigments (naturally or artificially) showed small differences in their CL spectra, further supporting the robustness of the technique. The analysis of more pigments and dyes is currently under way, focusing on the analysis of both inorganic and organic substances, aiming to create

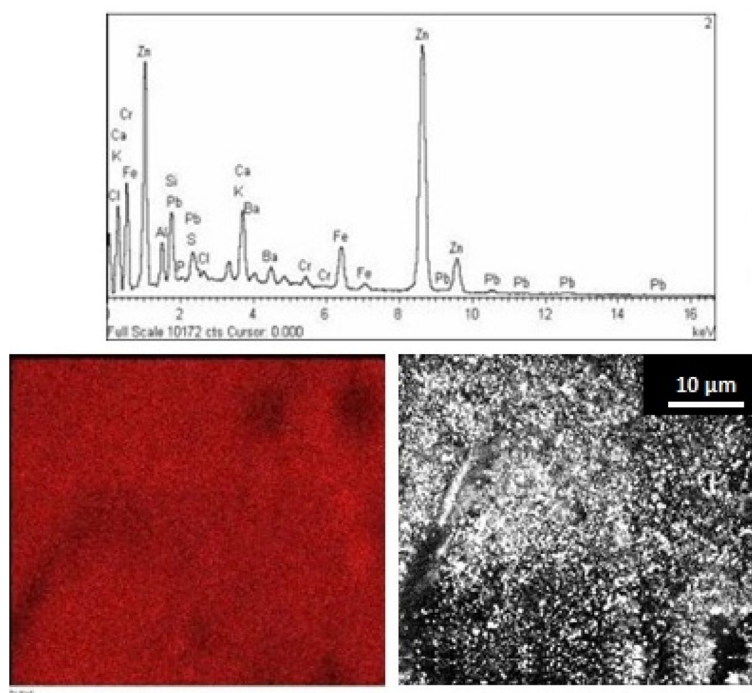


Fig.7 Top: EDS spectrum and Zn mapping of an area of the painting “Hydra”; Bottom: Zn mapping of the same area (left); monochromatic image of the same area for a wavelength emission at 390 nm (right)

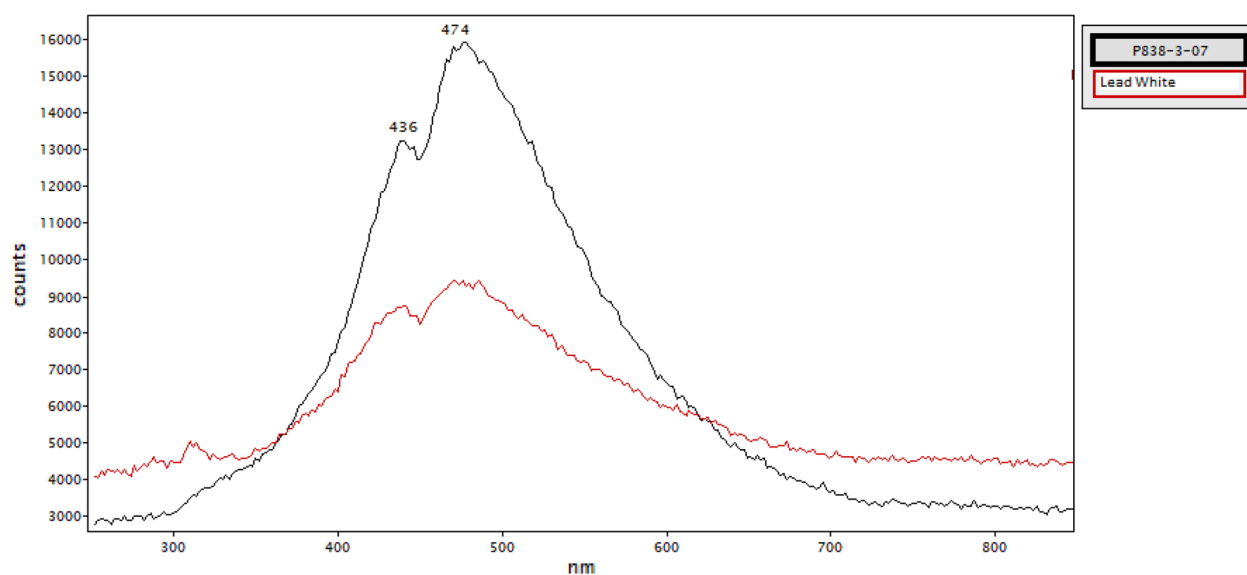


Fig.8 Representative CL spectrum of an undissolved particle of lead white found in an area of a microsample of the painting “Game”. The red line corresponds to the CL spectrum of pure lead white

a detailed, open-access database with the elemental and spectroscopic information of the most significant historical pigments.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-021-00575-4>.

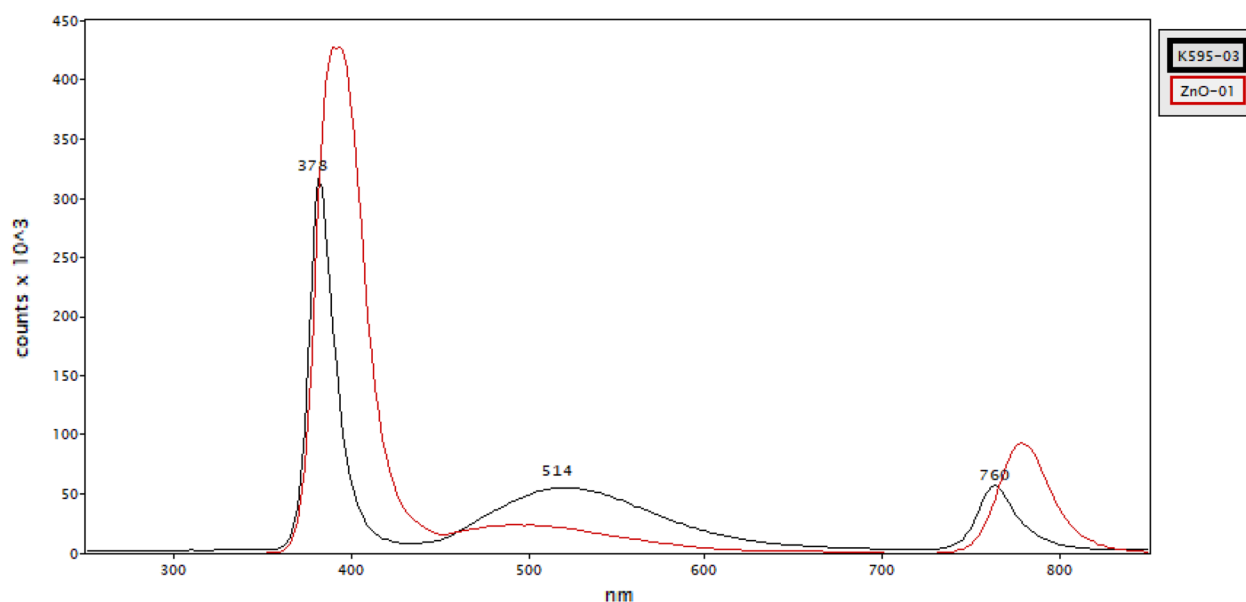


Fig.9 Representative CL spectrum of an undissolved particle of ZnO found in an area of a microsample of the painting “Hydra”. The red line corresponds to the CL spectrum of pure ZnO

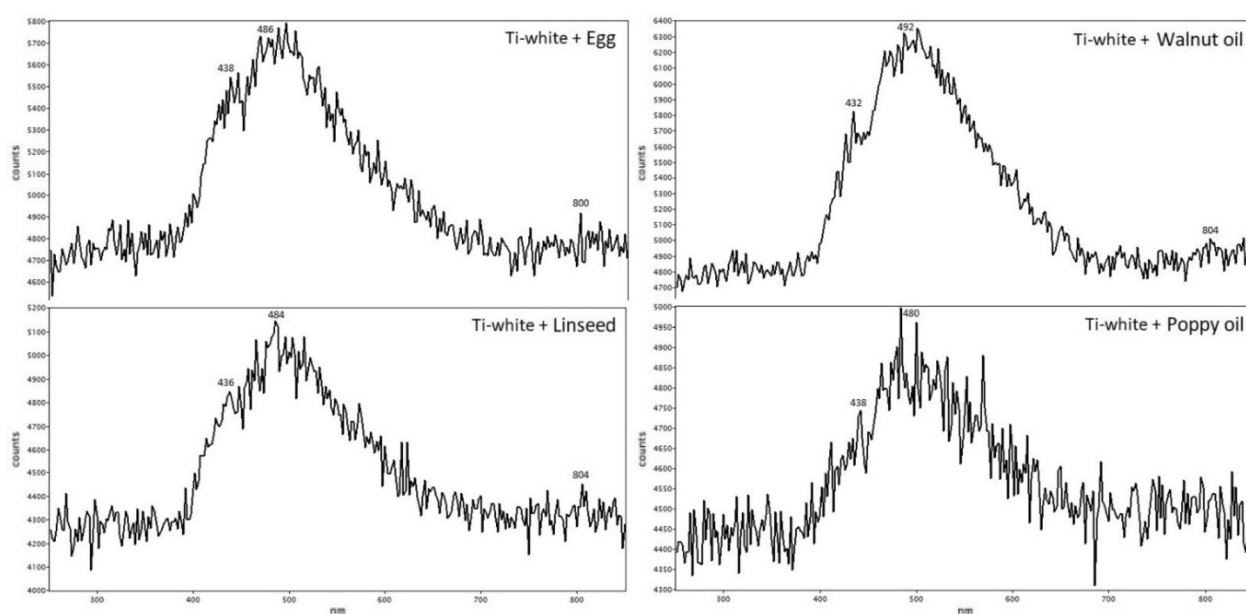


Fig.10 Representative CL spectra of artificially aged titanium white samples mixed with 4 different binding media (egg yolk, linseed, walnut and poppy seed oil)

Additional file 1: Table S1. Backscatter Electron Composition images (BEC), SEM/EDS and Raman spectra of the white pigments in pure form (calcite, white lead, zinc oxide, barium sulfate, lithopone, titanium white).

Table S2. EDS and Raman spectra of the combined samples of titanium white with binding media (egg yolk, linseed, walnut and poppy seed oil, respectively).

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Authors' contributions

EP interpreted the data presented in the paper and was a major contributor in writing the manuscript. PPD assisted in the interpretation of the data and contributed in writing the manuscript. SN assisted in the interpretation of the data

and contributed in writing the manuscript. LTC conducted the CL and Raman analyses. EK provided samples and assisted in the interpretation of the data. AT provided samples and assisted in the interpretation of the data. NZ assisted in the interpretation of the data and contributed in writing the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The most indicative data generated and analysed during this study are included in this published article and its supplementary material. The extended dataset generated during the current study is available from the corresponding author on reasonable request.

Declarations

Competing interests

The authors declare that they have no competing interests.

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