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Concerns over colour durability in the nineteenth-century industrial revolution: insights from John Ruskin's teaching collection

Tea Ghigo^{1*}, Michele Occhipinti², Andrew Beeby³, Kelly Domoney¹ and Daniel Bone¹

Abstract

The numerous new pigments that gradually became available to artists during the nineteenth-century Colour Revolution were received with contrasting attitudes. The initial enthusiasm for new chromatic possibilities was soon nuanced by concerns about the stability and performance of industrial materials. This study focuses on the work of John Ruskin, the famous art critic of Victorian England, whose artistic production was as impressive as his penmanship. Archival research into nineteenth-century literature is combined with material analyses with macro-XRF, XRD and FORS on a group of watercolours by Ruskin preserved at the Ashmolean Museum to determine his attitude towards pigment stability. The results show that he was very concerned with colour durability and chose his materials carefully, using the treatise *Chromatography* by the chemist George Field (first edition 1835) as guidance. The material analyses also provided new insight into the composition of specific pigments, revealing the use of a hitherto unreported cobalt-based blue.

Keywords Pigments, Nineteenth -century, Non-invasive analyses, Britain, Cobalt-based pigment

Introduction

Since the late eighteenth century, scientific and industrial progress had led to significant breakthroughs in colour manufacture that impacted arts and fashion. The beginning of the nineteenth century brought the first wave of new colourants, as dozens of inorganic, industrially manufactured pigments, such as cobalt blue, chrome yellow and chrome green, were developed and introduced on the market [1–5]. Furthermore, a second exponential wave of colourants was commercially introduced following William Perkin's discovery of mauveine in 1856, which ushered in an era of organic coal-tar colourants.

The vivid hues and affordability of these new products resulted in their immediate adoption in arts and crafts and their rapid diffusion across and beyond Europe [6, 7].

The colour revolution that continued developing throughout the nineteenth century was received with contrasting feelings by British artists. The initial excitement around new chromatic possibilities made Joseph Mallord William Turner and the Pre-Raphaelites, among many others, engage rapidly (more or less intentionally) with these new materials [8–12]. By contrast, William Holman Hunt adopted a more cautious approach towards industrial colour manufacture and, from the 1870s onwards, regularly conducted experiments to test pigment durability [13, 14]. During a lecture at the Royal Society of the Arts in 1880, he fiercely voiced his concerns and exposed the lack of stability of the colours marketed, which he attributed to widespread industrial adulteration with cheaper products, including anilines [15–17]. Besides Hunt, the late nineteenth-century

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literature frequently reported warnings about the performance and stability of the new products [3:347–70].

This contribution focuses on John Ruskin, a polymath and one of the foremost commentators of the Victorian Era. Ruskin is globally renowned for his role as a writer, philosopher and art critic. In fact, his outstanding penmanship often reported frustration about colour shifting in artworks, particularly regarding Turner's watercolours [18:13]. Ruskin's activity as an artist, which occupied most of his life, is less known internationally but equally impressive. Perhaps because he earned fame as a professional critic and writer more than an artist, his numerous watercolours have never been investigated from a material point of view. This study aims to fill this void and determine how the nineteenth-century debate on colour stability influenced Ruskin's artistic production by revealing how he chose his painting materials.

Methods

Watercolours

Twenty-five watercolours by John Ruskin were selected for this study, giving preference to those which exhibited the most chromatic variety. They all proceed from Ruskin's Teaching Collection at the Ashmolean Museum, which Ruskin curated after he was appointed a Slade Professor of Art at Oxford in 1871. The collection includes studies and exercises on drawing and colouring used as lecturing materials during Ruskin's art classes. The watercolours from this collection reflect a short period of Ruskin's activity as an artist, as they date mainly to the 1860 and 1870s, with only two earlier exemplars from the 1840s. A complete list of the works studied is available in the Additional file 1: Table S1.

Survey of Ruskin's written works and nineteenth-century technical literature

A systematic and extensive survey of Ruskin's literature and private letters was carried out to retrieve information on the pigments he intended to use and cross-link it with the material analysis results. In addition, several nineteenth-century technical sources providing information on pigment composition were examined.

MA-XRF, Bruker Crono XRF spectrometer

The Bruker Crono XRF spectrometer features a rhodium target tube and a 50 mm² SDD detector with energy resolution < 140 eV for Mn K α with an input count rate of up to 500,000 cps. It allows for a fast collection of elemental maps on up to 600×450 mm areas for elements in the range 13 < Z < 82 (in air). The analytical time in automatic acquisition mode is ca. 25 min for an area of 100×100 mm with a 0.5 mm collimator. The data presented in this article were obtained with a 0.5 mm

collimator operating at 50 keV and 200 μ A and processed using the Bruker ESPRIT Reveal software.

XRD, Bruker Hydra XRF + XRD spectrometer

This instrument features a 30 W micro-focus X-rays generator with Cu anode and parallelising poly-optics, a 50 mm² SDD detector with energy resolution < 140 eV for Mn K α for XRF measurements and a photon counting 2D-detector to perform XRD measurements at angles between 20° and 40° 2-theta in the first run and 40° and 60° 2-theta in the second. For best performance, a 220 μ m collimator and acquisition time of 300 s per run is used, resulting in a 10 min measurement time per spot. The diffraction patterns were characterised by comparison against the Powder Diffraction Files from the ICDD database (<https://www.icdd.com/>).

FORS, University of Durham

A custom-built fibre optic reflectance spectrometer that operates in the range 400–2500 nm and designed specifically for the study of fragile works of art is used to record the FORS spectra [19]. This equipment delivers a light beam of 2.5 mm diameter and a total power of < 0.5 mW to the investigated surface, at a working distance of 3 cm. In the range 400–1000 nm the bandwidth of the system is 3.5 nm, whilst in the SWIR region, 900–2500 nm, the bandwidth is 8 cm⁻¹, corresponding to 2.5 nm at 1750 nm. The spectra were recorded relative to a Spectralon standard and took 1 s per measurement. Assignment of the pigments via reflectance spectra was done by comparison to published reflectance spectra [20, 21] and online databases by the CNR-IFAC (<https://spectradb.ifac.cnr.it/>).

Objects handling

Most of the watercolours investigated are mounted in conservation mount board measuring 60×45 cm. To minimise their physical stress, they were analysed in their mounts after making sure that the background signal generated by the back mount was not swamping the signal emitted from lighter elements in the watercolours during X-ray-based analyses. During analyses, the watercolours lay on a bespoke Perspex frame about 5 cm high with a set of interchangeable inserts with cut-outs of different sizes, adaptable to the dimensions of the painted area. This set-up supported the watercolour's frame and mount, allowing the painted area to be analysed without elemental interference from the underlying table. The analyses were conducted in an environmentally controlled room without natural light. Relative humidity was set to 45–55%RH using a portable Defensor PH28 humidifier and Albert dehumidifier, thermostat-controlled central heating maintained the temperature

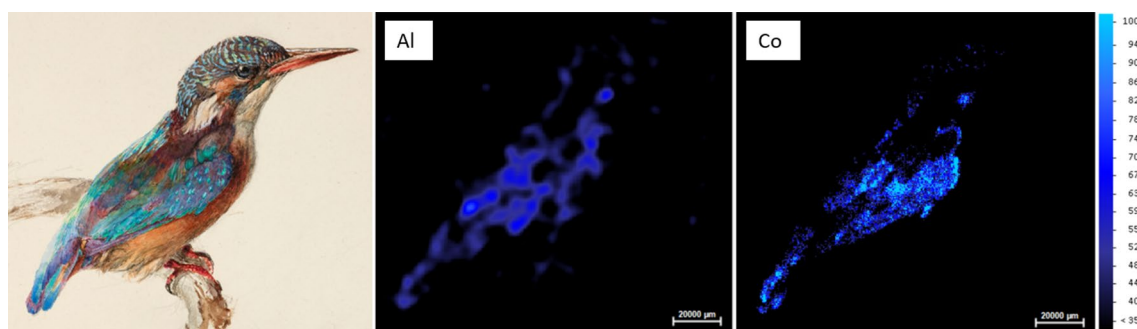


Fig. 1 Left: Study of a Kingfisher (WA.RS.RUD.201). Right: macro-XRF elemental maps of aluminium and cobalt

to 19–21 °C, and light levels were kept at <math>< 50</math> lux to minimise light exposure and interference during FORS analyses.

Results

Literature survey

Ruskin did not often mention painting materials in his works. Only two extensive lists of pigments were found, one given in the *Elements of Drawing* (1857), where he suggested to his readers what colours to use, and the other in a private letter to Dante Gabriel Rossetti from 1855, where he listed the pigments he was using. Furthermore, in his *Elements of Drawing*, Ruskin showed that he was aware that different pigments have various grades of stability and warned his readers that Antwerp and Prussian blue were not very permanent, while indigo was even more fugitive [18:15]. Although these lists date to almost the same year and largely overlap, they are significant for comparison with the material analyses carried out on Ruskin's teaching collection, as they predate the watercolours investigated by 10–20 years. A complete list of pigments mentioned in Ruskin's texts is reported in the Additional file 1: Table S2.

Material analyses

The Additional file 1: Table S3, lists the pigments identified on the watercolours investigated. Zinc white was found on almost all of them. This pigment was used for white highlights as well as mixed with the coloured pigments to obtain lighter tones yet less watery layers of colour, a practice that Ruskin recommends in his *Elements of Drawing* [18:15].

Blues

XRF analyses frequently detected the presence of cobalt in the blue pigments used by Ruskin. nineteenth-century sources report a long list of commercial names for cobalt-based blue pigments, such as Leithner's, Thenard's or Dumont's blues, but rarely provide precise information

on their chemical composition [3]. The most insightful source for this purpose is Thomas Salter's edition of *Chromatography* [22], a treatise originally published in 1835 and re-edited in 1841 by George Field, a chemist who decided to apply his skills to the study and manufacture of pigments and dyes [23, 24]. Salter added to the information Field includes on cobalt-based pigments, and divided these compounds into the stannic blues (containing cobalt and tin), the aluminous blues and the siliceous blues (smalts). He then explained that the aluminous blues could be prepared using either the arsenate, the borate or the phosphate of cobalt.

On most watercolours studied, macro-XRF detected cobalt and aluminium only, with no arsenic, boron or phosphorus. Figure 1 shows the visible image and elemental maps of aluminium and cobalt on *Study of a Kingfisher* (WA.RS.RUD.201). Despite the lower resolution of the aluminium map, it is possible to observe that this element's emission intensity increases in correspondence with the cerulean plumage on the kingfisher's body, which contains cobalt as well.

XRD analyses on a blue area of *Asphodel* (WA.RS.ED.023), similarly containing aluminium and cobalt only, retrieved a diffractogram matching the pattern for cobalt aluminium oxide mixed with zinc white (Fig. 2). Cobalt aluminium oxide is mentioned in the 1924 edition of *The Colour Index* (C.I. n. 1285) under the name Thenard's blue, prepared by precipitating cobalt nitrate with sodium phosphate to obtain cobalt phosphate and then calcinating this product with alumina [25].

In a few cases, cobalt was found together with phosphorus, aluminium and potassium. Figure 3 shows the macro-XRF maps obtained on *Study of Dawn: purple Clouds* (WA.RS.ED.005) for cobalt, phosphorus and potassium (green, blue and red, respectively). All these elements are present in the bright blue pigment used in the bottom area of this watercolour (which appears white on the elemental map). Furthermore, the XRF spectrum of this blue area shows that it also contains aluminium.

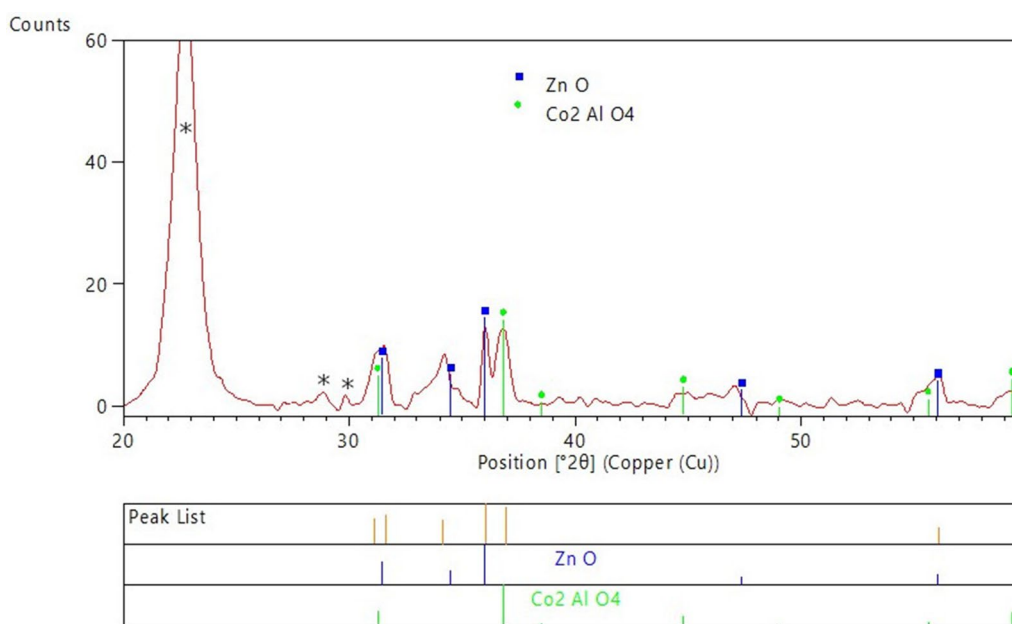


Fig. 2 X-ray diffractogram of a blue area on Asphodel (WA.RS.ED.023). The asterisks indicate peaks from the paper support

XRD analyses retrieved a diffractogram partially matching a mixed phosphate containing potassium, aluminium and cobalt, with formula $KCoAl(PO_4)_2$ and a monoclinic crystalline habit. This composition suggests that cobalt phosphate and alumina were used to manufacture this blue pigment, but the resulting product, containing potassium as well, is not described in nineteenth-century sources, nor does it appear in the 1924 edition of *The Colour Index* [25]. The structure of a similar orthophosphate of potassium cobalt and aluminium with formula $K(CoAl)_2(PO_4)_2$ has been recently elucidated in the literature [26].

A recent XRF investigation conducted at the State Research Institute for Restoration in Moscow on an original Winsor & Newton “Artists’ Permanent Water Colours” chart, dating to after 1932, showed that the pigment labelled “Smalt” had this same elemental composition, containing cobalt, potassium, phosphorus and aluminium¹. We know from his letters that Ruskin purchased Winsor & Newton watercolours for at least part of his life [18:36]. Therefore, it is likely that the complex cobalt-based pigment found in his watercolours corresponded to the “Smalt” sold by Winsor & Newton, which interestingly did not contain any silicon.

Together with cobalt-based blues, this study revealed the sporadic use of Prussian blue, identified with FORS in blue areas rich in iron and potassium, and indigo detected with FORS.

Greens

The macro-XRF spatial distribution of copper and arsenic frequently revealed the co-presence of both elements in green areas on the watercolours investigated, indicating the regular use of emerald green. Figure 4 shows the case of *Afternoon in Spring at Neuchâtel* (WA.RS.ED.298.a). The elemental map shows that copper and arsenic (blue and red, respectively, resulting in a purple colour together) are present in the area of the sea close to the shore (which appears blue-greenish because emerald green is mixed with Prussian blue) and, in a lesser amount, in the green field on the left side. The presence of emerald green on this watercolour was confirmed by XRD, which retrieved the pattern of copper acetate arsenate.

Furthermore, macro-XRF highlighted, in a few cases, the use of chromium-based greens. Two main chromium-based greens were available on the nineteenth-century market: chromium oxide and chromium oxide hydrated, the latter marketed as viridian. XRD allows one to distinguish these two pigments since the former produces a characteristic diffraction pattern, while the latter is inherently poorly crystalline and does not produce a diffraction pattern [27]. Figure 5 shows the X-ray diffractogram obtained on a chromium-rich green area of *Study*

¹ Unpublished results presented at the MA-XRF scanning in Conservation, Art and Archaeology conference, Delft 2022. Alina Krotova and Daria Filatova, “Investigation of three 20th -century Winsor & Newton colour charts by micro-XRF”.

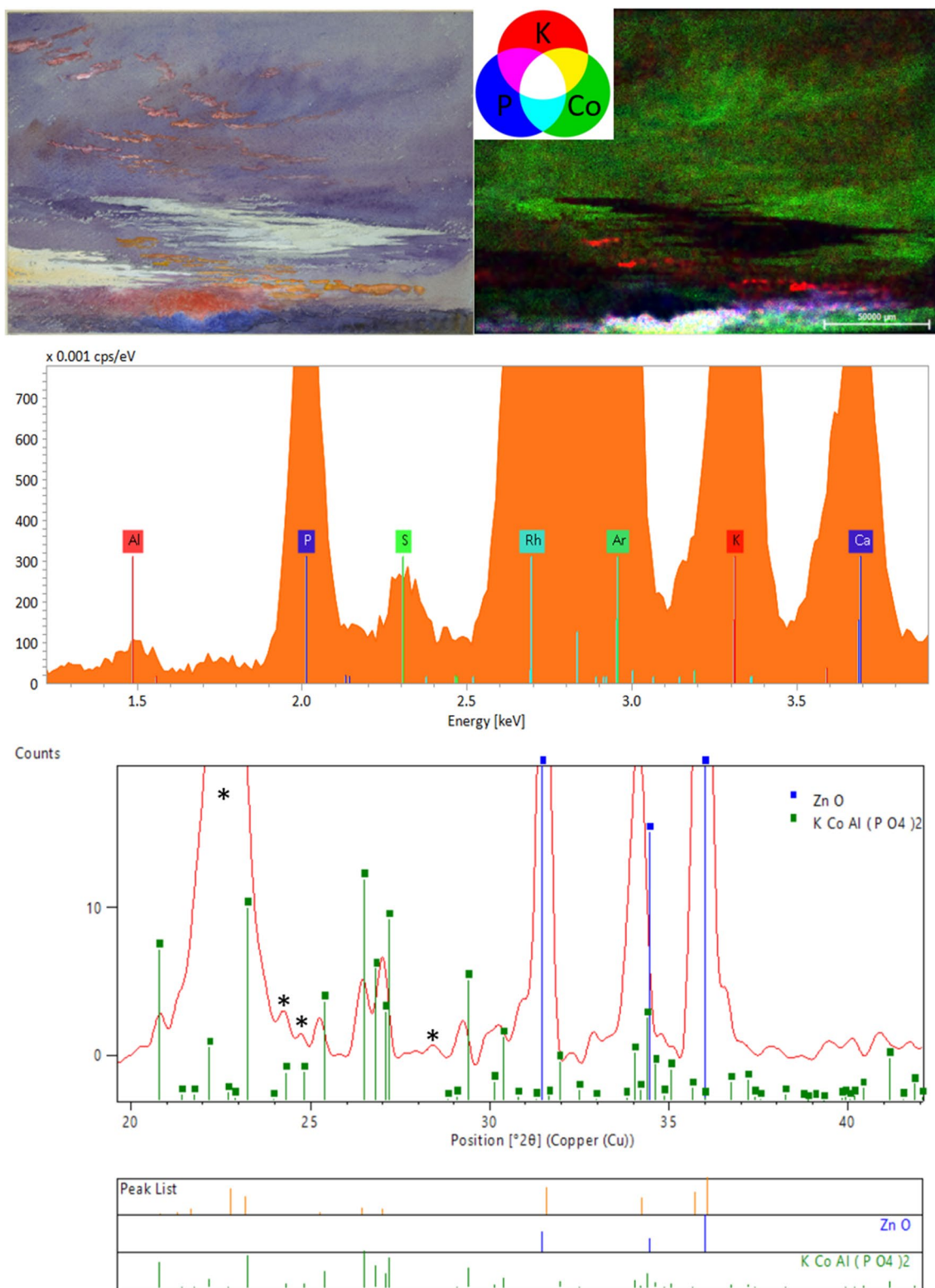


Fig. 3 Top left: Study of Dawn: purple Clouds (WA.RS.ED.005). Top right: macro-XRF maps of cobalt (green), phosphorus (blue), and potassium (red). Middle: XRF spectrum of the bright blue area. Bottom: XRD diffractogram of the bright blue area, the asterisks indicate peaks from the paper support

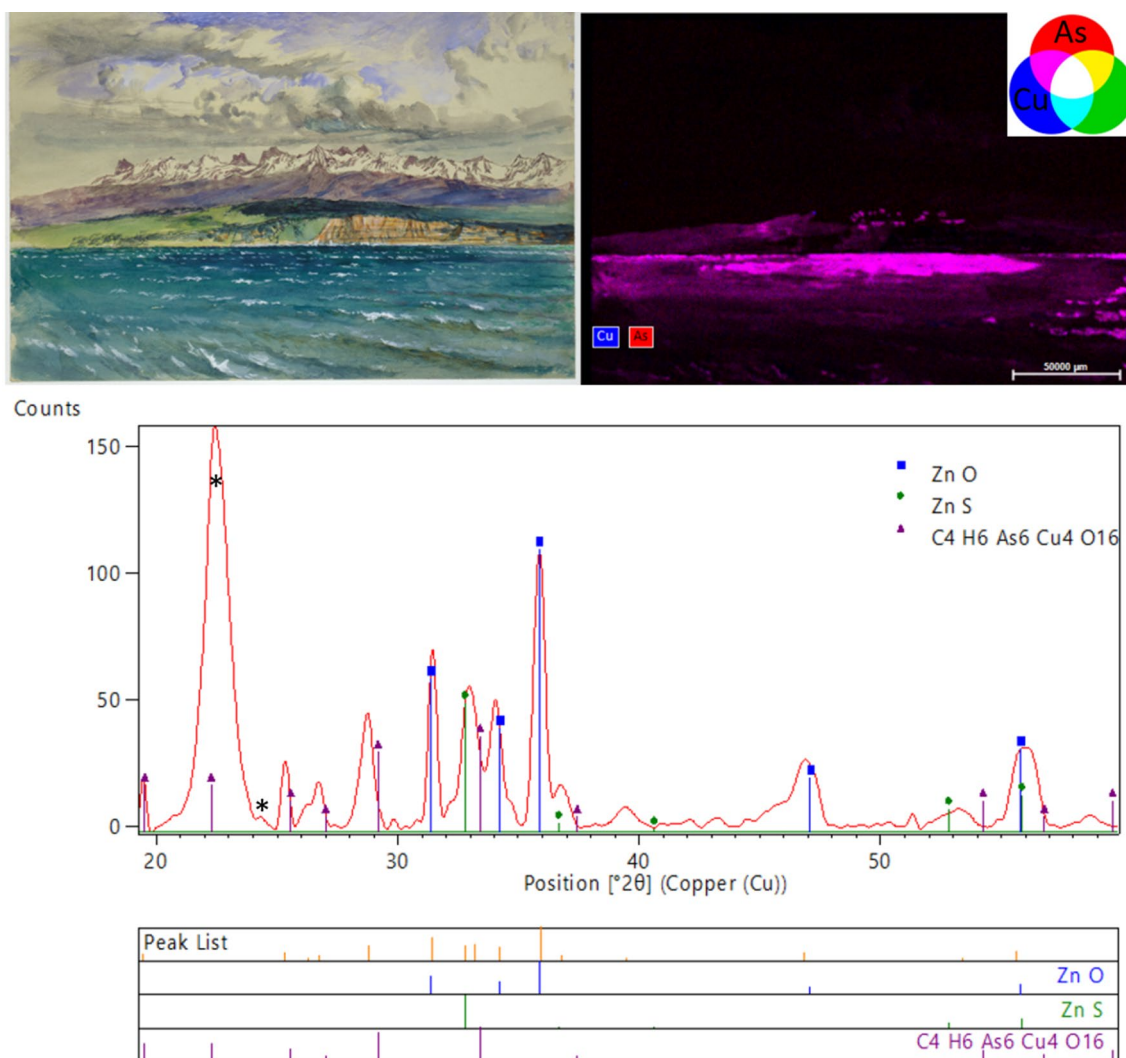


Fig. 4 Top left: Afternoon in Spring at Neuchâtel (WA.RS.ED.298.a). Top right: macro-XRF maps of copper (blue) and arsenic (red). Bottom: XRD diffractogram of a greenish area, the asterisks indicate peaks from the paper support

of a Chinese Enamel (WA.RS.ED.202). Together with zinc oxide and sulfide (both of which were often found in commercial preparations of zinc white [5]), the diffractogram shows the pattern of chromium oxide.

Yellows

Macro-XRF analyses often revealed the co-presence of barium and chromium in yellow areas, indicating the use of lemon yellow. In these regions, XRD sometimes confirmed the presence of barium chromate. Figure 6 shows the elemental maps for chromium and barium (red and yellow, respectively) acquired on a pale yellow area of *Study of Clouds, Norwood* (WA.RS.ED.289bis.b) together with a diffractogram obtained on the pale yellow wash, which matches the reference pattern of barium chromate.

Cadmium yellow was also used regularly and was identified based on the elemental distribution of cadmium and sulphur. Figure 7 shows the spatial distribution of these two elements obtained on the *Shield of Geoffrey Plantagenet* (WA.RS.RUD.008). While sulphur is ubiquitous across the area investigated, its intensity of emission increases in the pink and yellow areas of the shield. The presence of cadmium in the yellow region is shown in the elemental map, and both elements are observed in the XRF spectrum obtained on a portion of the ordinary. Natural yellow ochre (identified based on the co-occurrence of iron, silicon and in some cases potassium) was sometimes found as an alternative to lemon yellow (barium chromate) and cadmium yellow, while, in a few cases, the absence of an XRF fingerprint, or the presence

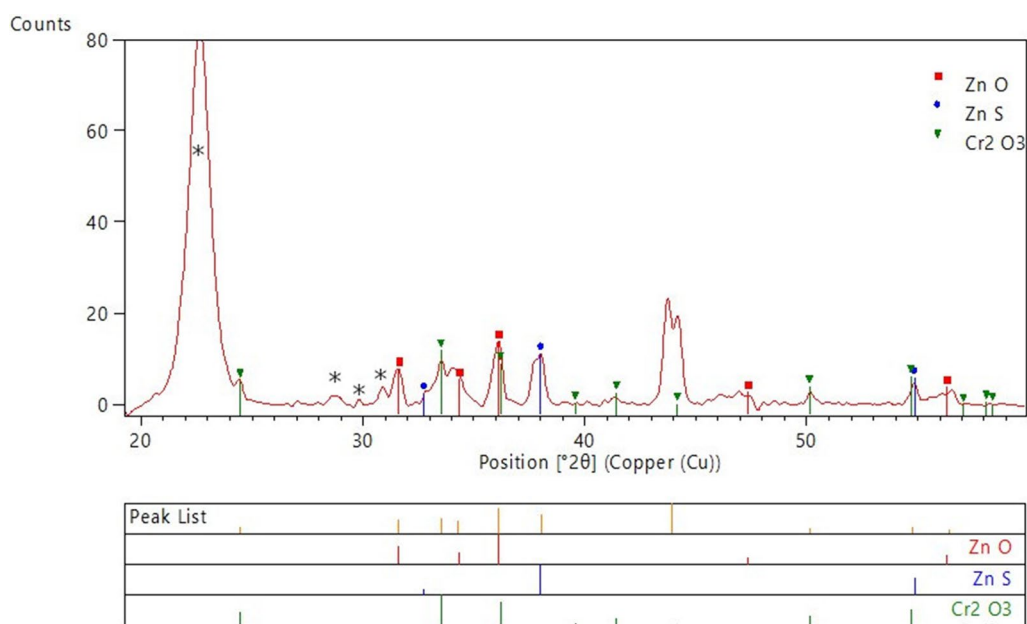


Fig. 5 X-ray diffractogram of a green area on Study of a Chinese Enamel (WA.RS.ED.202). The asterisks indicate peaks from the paper support

of aluminium and sulphur in yellow regions hinted at organic colourants.

Reds

Red tones were frequently obtained using vermilion or ochre. Red, orange and brown ochres were often found to contain silicon, and in a few instances also potassium and titanium, thus suggesting the use of natural earths.

Furthermore, elements such as aluminium, sulphur, potassium and calcium were frequently found in iron-free red areas, hinting at the use of red and pink lakes. FORS analyses sometimes cast further light on the nature of red and pink lakes, revealing the use of different colours prepared from madder. Figure 8 shows *Drawing of a red parrot* (WA.RS.ED.161), together with a reflectance spectrum obtained on the plumage below the parrot's eye. Two absorption maxima are observed at 512 and 547 nm

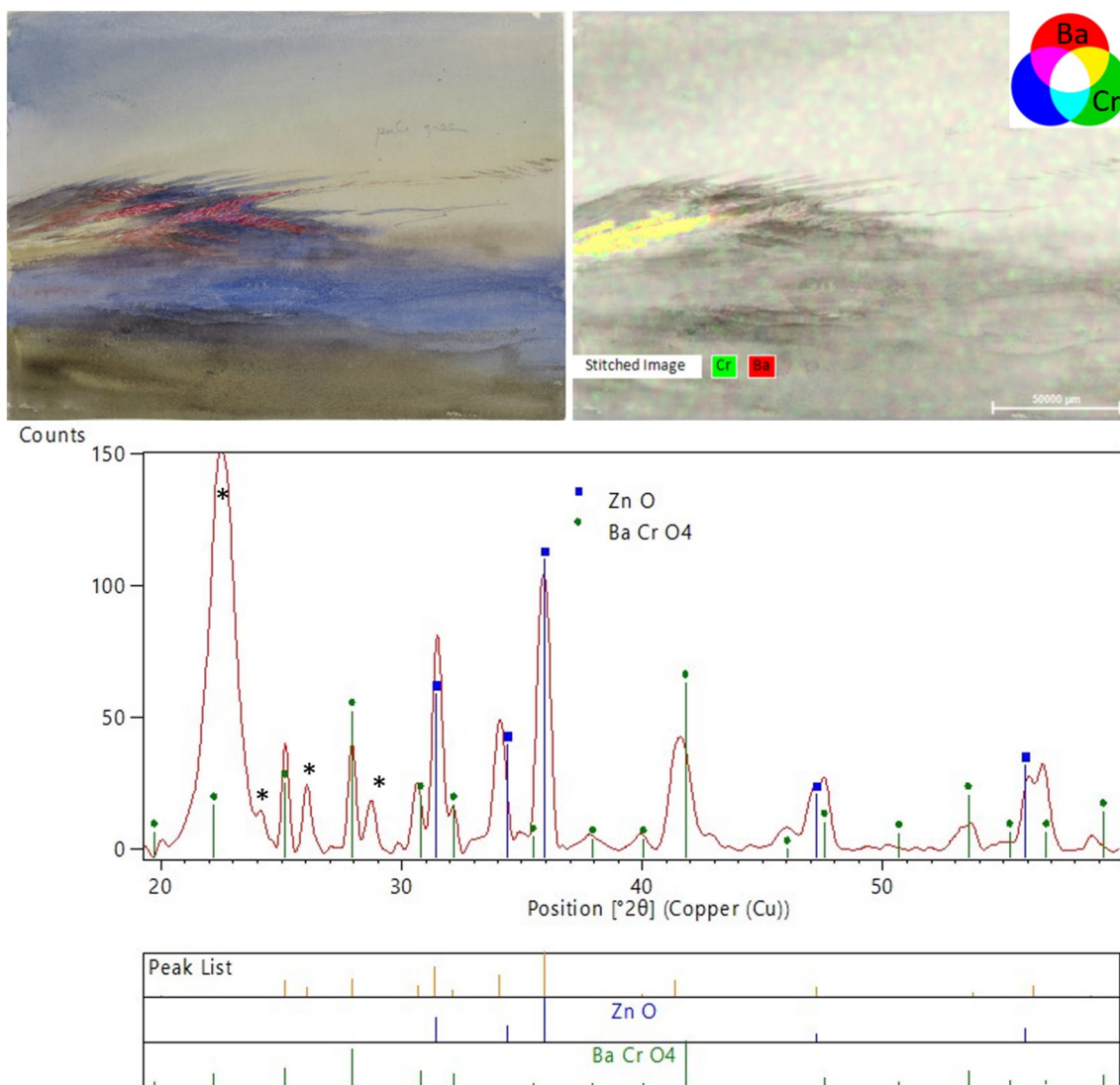


Fig. 6 Top left: Study of Clouds, Norwood (WA.RS.ED.289bis.b). Top right: macro-XRF maps of chromium (green) and barium (red) overlapping a stitched image of the watercolour. Bottom: XRD diffractogram of the pale yellow wash, the asterisks indicate peaks from the paper support

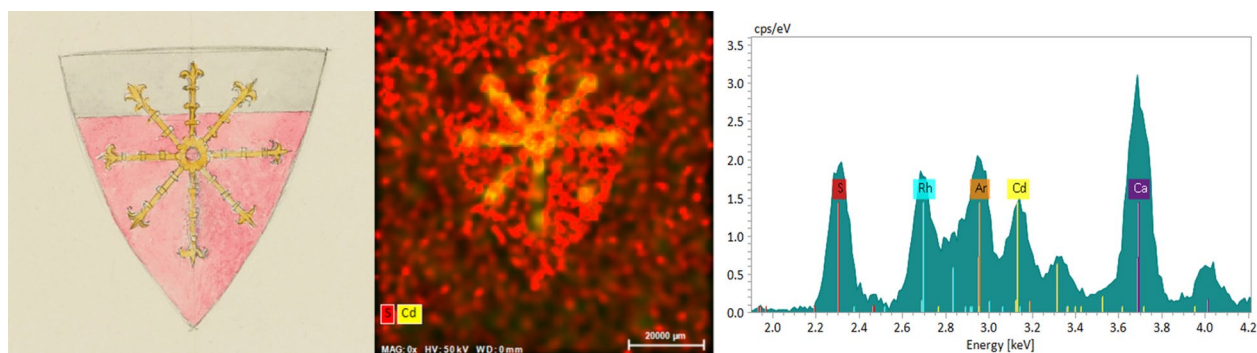


Fig. 7 Left: The Shield of Geoffrey Plantagenet (WA.RS.RUD.008). Middle: macro-XRF map of sulphur (red) and cadmium (yellow). Right: XRF spectrum obtained on the yellow area

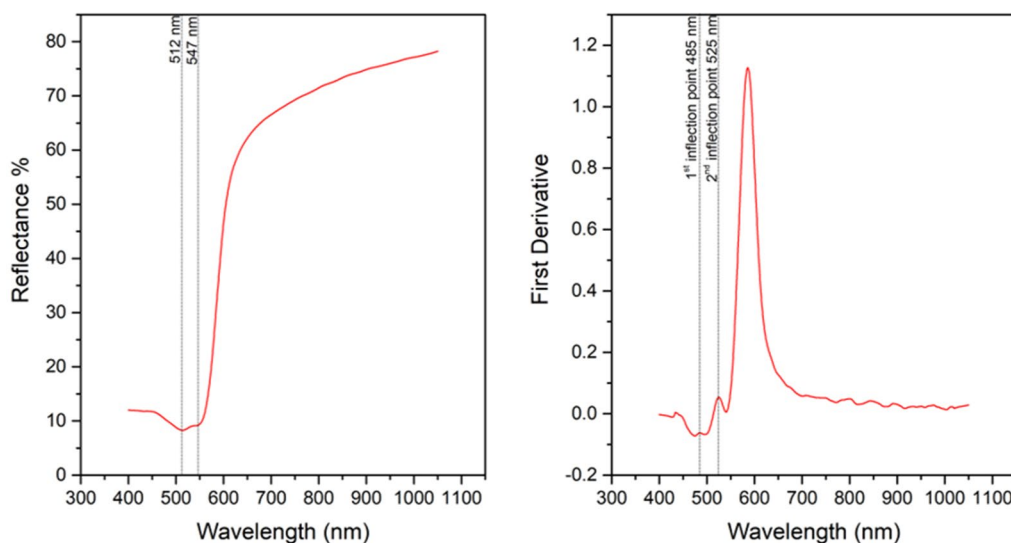
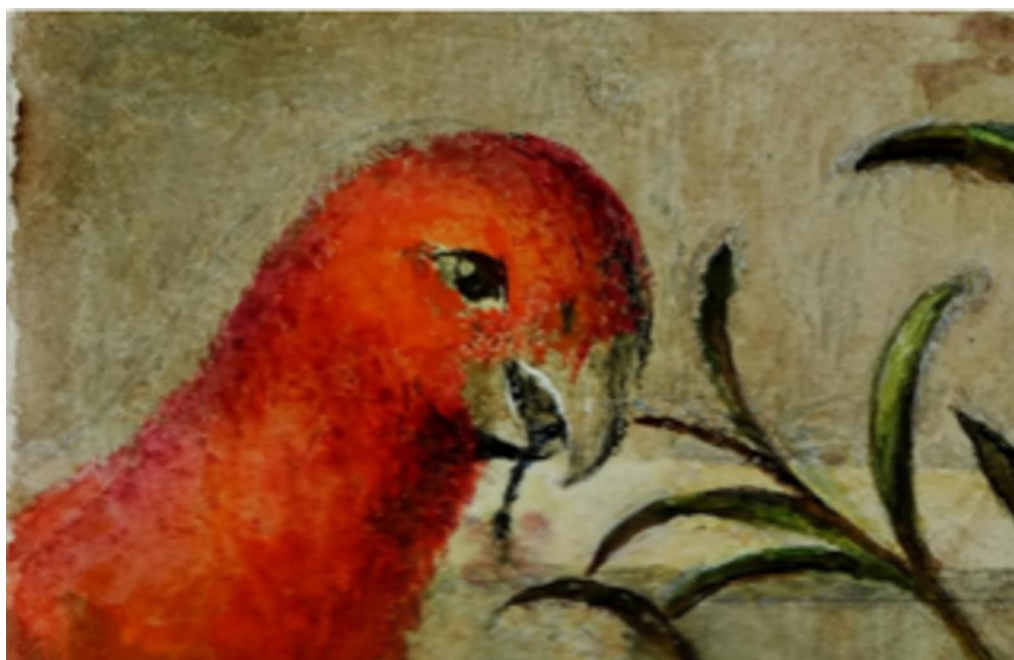


Fig. 8 Top: Drawing of a red parrot (WA.RS.ED.161). Bottom: Reflectance spectrum (left) and first derivative transformation (right) of a red area below the parrot’s eye

purple is rich in chlorine, as shown in the elemental map in Fig. 10. Since the work dates to 1867, a decade after the discovery of mauveine, the presence of chlorine might hint at the use of anilines, which were frequently produced as hydrochloride salts [25:172–5].

Discussion

The comparison of Additional file 1: Tables S2 and S3 shows that, despite the gap in time, the list of pigments collated from Ruskin’s texts mostly coincides with the pigments identified on the watercolours, showing that Ruskin sourced his colours carefully and consistently.

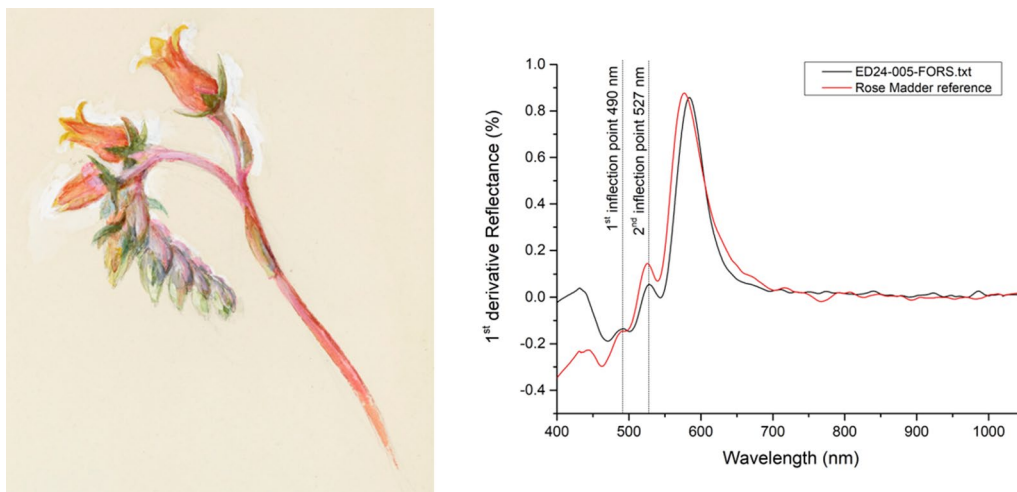


Fig. 9 Left: Houseleek (WA.RS.ED.024). Right: reflectance spectrum of a pink area with reference reflectance spectrum of pink madder



Fig. 10 Top: Growing Shoot of Mock Privet (WA.RS.ED.267). Bottom: macro-XRF maps of chlorine overlapping a stitched image of the watercolour

Resorting to the desired painting materials must have been a nontrivial task at that time, considering that industrial colours were frequently adulterated, their components substituted and sold with deceitful labels, or tagged with names that barely described their material composition. Previous research showed that emerald green was substituted with chromium oxide or double salt of cyanure of iron and cobalt, vermilion was often adulterated with chrome yellow, cadmium yellow with orpiment and chrome yellow, while a fictitious blue black (obtained originally from the calcination of vine leaves) was made by mixing lamp black and blue pigments [15–17]. Although we must acknowledge that some of the pigments identified might have been adulterated with organic colourants that remained undetected during our investigation, the fact that the lists of pigments found in Ruskin's literature consist mainly of inorganic pigments and largely overlaps with material analyses suggests he managed to resort most times to what he intended to use.

Ruskin's palette was quite broad and included several pigments that had recently been introduced on the market and were still relatively new to the artistic world. For guidance and information on pigments, in his *Elements of Drawing*, he advises his readers to refer to Field's *Chromatography* [18:15, 23]. In this treatise, George Field discussed the properties of different pigments and classified them based on their stability to light, damp and pollutants. Interestingly, the majority of pigments used by Ruskin are said to be stable to the action of light, and over half are tagged as the most stable pigments (see the Additional file 1: Table S2, where Field's classification for each of the pigments mentioned by Ruskin is reported). Not only did Ruskin choose durable pigments, but it seems he was aware that, while damp and pollutants could be reduced by adopting environmental control strategies in his Drawing School, the painting materials he used in the watercolours of his teaching collection had to endure a certain amount of light exposure if they were to be used during lectures.

The frequency of use of different pigments in the watercolours investigated corroborates the idea that Ruskin aimed at creating durable artworks. Yellow areas were mostly painted using lemon yellow (barium chromate) and cadmium yellow, more stable than organic yellow colourants (such as gamboge and yellow lake that Ruskin says form part of his palette) that were spotted only a few times.

Blues were mostly identified as cobalt-based pigments rather than Prussian blue, Antwerp blue or indigo, whose lack of durability was well known to Ruskin, as previously discussed. Field stated that well-prepared cobalt blue resisted the action of strong light,

was superior in beauty to all other blue pigments, and worked better in watercolour than ultramarine [23:204].

It might be argued that the frequent use of organic-based red lakes (found in over half of the work investigated) indicates that Ruskin was not much concerned with the stability of his painting materials, considering the notorious lack of permanence of these pigments compared to iron oxides. In a few cases, FORS offered further insight into the composition of these pigments, suggesting the use of madder lakes (Figs. 8 and 9). Interestingly, red, pink and brown madder lakes were much praised by Field, who described them as permanent and among the most valuable pigments for the palette of modern artists, stressing they were indispensable in those works where the pink and crimson colours of nature had to be imitated [23:179–81].

Greens were hardly ever painted by mixing blue and yellow and mainly consisted of emerald green, a very popular pigment in Victorian England because of its unique shade. Although not as durable as chromium-based greens or green earths (identified on Ruskin's watercolours only sporadically), this pigment had a much more vivid hue and was nonetheless lightfast, according to Field.

Ruskin's extensive use of zinc white might seem in disagreement with the argument presented above, considering that it is now seen by conservators as a pigment that might promote colour change or degradation of the support in works on paper. However, Ruskin's faith in the durability of this pigment and its suitability for watercolour painting derived once again from Field's treatise. The chemist maintained that zinc white is valuable and durable in both oil and water, unlike lead white that, when used in water, is "changeable even to blackness" [23:127–31].

However expert Ruskin might have become in procuring durable pigments, he likely fell prey to commercial deceit at times. Most of his dark brown and black pigments were found to be either ochres, umbers or colourants with no XRF fingerprint and compatible with sepia or carbon blacks, regarded by Field as very stable materials. Nevertheless, in a few instances, dark brown tones were found to be rich in copper. Copper browns are occasionally mentioned in nineteenth-century literature, describing them as somewhat unstable compounds [3]. Similarly, Ruskin would have likely avoided using early coal-tar dyes in his works, given their reputation for being fugitive. Yet, the purple colourant rich in chlorine found in *Growing Shoot of Mock Privet* (Fig. 10) perhaps proves that he did not always succeed.

Conclusion

This study used a combination of archival research and material analyses to explore John Ruskin's position, as an artist and teacher, regarding the nineteenth-century debate around pigment stability.

We observed that the pigments identified in a group of watercolours dating mainly to the 1860-70s largely overlap with the pigments Ruskin claimed to be using in his texts from 1855 to 7. Such consistency suggests Ruskin sourced his painting materials with great care and successfully purchased intended materials despite industrial pigments being often marketed with labels that barely described their composition. Therefore, aware of commercial adulteration, he often found ways around it, despite not being as committed to exposing it as it was his pupil William Holman Hunt.

Comparing Ruskin's pigments with the information provided in the encyclopaedic treatise *Chromatography* by the chemist George Field shows he mainly used pigments described as stable, especially to light. Ruskin's care in sourcing his materials shows that, in his practice as an artist, he addressed the concerns on the effect of light on watercolours that the artistic community would see systematically investigated only at the end of the century when the Committee of Council on Education for both Houses of Parliament asked Dr Russell and Captain Abney to undertake a systematic study to elucidate the effect of light on different watercolour pigments [33, 34].

From a technological point of view, this work cast light onto the composition of nineteenth-century pigments. Notably, it provided new insight into cobalt-based pigments, identifying a blue compound containing cobalt, aluminium, phosphorus and potassium, which is not recorded in nineteenth-century literature or in the first edition of *The Colour Index* (1924). A recent investigation of a twentieth-century Winsor & Newton colour chart showed that a cobalt-based pigment with a similar elemental composition was sold as "Smalt". Therefore, this investigation stresses the importance of complementing the study of technical manuals on pigments with the analysis of original nineteenth and twentieth-century colour charts to elucidate the composition of painting materials used in post-industrial heritage collections.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-023-01010-6>.

Additional file 1: Table S1. Date, accession number and title of the watercolours analysed in this study. **Table S2.** List of pigments found in Ruskin's texts with classification of their stability as it appears in George Field's *Chromatography*. **Table S3.** Summary of pigments identified on the watercolours investigated with indication of the analytical method.

A: macro-XRF; B: XRD; C: FORS. The shaded columns report pigments that appear in Ruskin's literature.

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Author contributions

TG: conceptualisation, methodology (archival research and material analyses), investigation (lead), formal analysis (lead), visualisation, project administration, funding acquisition (lead), writing—original draft. MO: investigation (support - XRD), formal analysis (support - XRD). AB: investigation (support - FORS). KD and DB: methodology (objects handling), funding acquisition, writing—review & editing (objects handling). All authors agreed to the final version of the manuscript.

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Declarations

Competing interests

The authors declare no competing interests.

Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

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References

1. Gettens RJ, Stout GL. *Painting materials*. New York: Dover Publications; 1966. p. 342.
2. Harley RD. *Artists' pigments c.1600–1835: a study in English documentary sources*. London: Butterworth & Co; 1970.
3. Carlyle L. *The artist's assistant oil painting instruction manuals and handbooks in Britain, 1800–1900, with reference to selected eighteenth-century sources*. London: Archetype Publications; 2001.
4. Zollinger H. *Color chemistry: syntheses, properties, and applications of organic dyes and pigments*. Hoboken: John Wiley & Sons; 2003.
5. Eastaugh N, Walsh V, Chaplin T, Siddall R. *Pigment compendium: a dictionary of historical pigments*. Amsterdam: Elsevier; 2008.
6. Garfield S. *Mauve: how one man invented a color that changed the world*. New York: WW Norton & Company; 2002.
7. Cesaratto A, Luo Y-B, Smith HD, Leona M. A timeline for the introduction of synthetic dyestuffs in Japan during the late Edo and Meiji periods. *Herit Sci*. 2018;6(1):22.
8. Townsend JH. The materials of J.M.W. Turner: pigments. *Stud Conserv*. 1993;38(4):231–54.
9. Townsend JH. *Painting techniques and materials of Turner and other British artists 1775–1875*. In: Wallert A, Hermens E, Peek M, editors. *Historical painting techniques, materials, and studio practice*. Getty Conservation Institute: Los Angeles; 1995. p. 176–85.
10. Townsend JH. The materials used by british oil painters throughout the nineteenth century. *Stud Conserv*. 2002;47(sup1):46–55.

11. Carlyle L. In: Contemporary painting materials. In: pre-raphaelite painting techniques, 1848-56. London: Tate; 2004.
12. Townsend J, Poulin J, Painting. Materials and methods. In: Lochnan KJ, Jacobi C, editors. Holman Hunt and the pre-raphaelite vision. Toronto: Art Galley of Toronto; 2008.
13. Katz MR, William Holman Hunt and the "Pre-Raphaelite Technique." In: Wallert A, Hermens E, Peek M, editors. Historical painting techniques, materials, and studio practice: preprints of a symposium. Getty Conservation Institute: Los Angeles; 1995. p. 158–64.
14. Katz MR. Holman Hunt on himself: textual evidence in aid of technical analysis. In: Hermens E, editor. Looking through paintings. Baarns, London: Uitgeverij de Prom and Archetype; 1998. p. 415–44.
15. Hunt WH. The present system of obtaining materials in use by artist painters, as compared with that of the old masters. *J Soc Arts*. 1880;28(1431):485–99.
16. Carlyle L. Authenticity and adulteration: what materials were 19th century artists really using? *The conservator*. 1993;17(1):56–60.
17. Townsend JH, Carlyle L, Khandekar N, Woodcock S. Later nineteenth century pigments: evidence for additions and substitutions. *The Conservator*. 1995;19(1):65–78.
18. Ruskin J. The complete works of John Ruskin in 39 volumes. In: Cook ET, Wedderburn A, editors. The Library Edition. Crows Nest: George Allen and Unwin; 1903.
19. Beeby A, Garner L, Howell D, Nicholson CE. There's more to reflectance spectroscopy than lux. *J Inst Conserv*. 2018;41(2):142–53.
20. Fonseca B, Schmidt Patterson C, Ganio M, MacLennan D, Trentelman K. Seeing red: towards an improved protocol for the identification of madder-and cochineal-based pigments by fiber optics reflectance spectroscopy (FORS). *Herit Sci*. 2019;7(1):92.
21. Biron C, Mounier A, Le Bourdon G, Servant L, Chapoulie R, Daniel F. A blue can conceal another! Noninvasive multispectroscopic analyses of mixtures of indigo and prussian blue. *Color Res Appl*. 2020;45(2):262–74.
22. Salter T. Field's chromatography; or, treatise on colours and pigments as used by artists. London: Winsor and Newton; 1869.
23. Field G. Chromatography; or, a treatise on colours and pigments, and of their powers in painting. New edition improved. London: Tilt and Bogue; 1841.
24. Shires LM. "On Color Theory, 1835: George Field's Chromatography". BRANCH: Britain, Representation and Nineteenth-Century History. https://branchcollective.org/?ps_articles=linda-m-shires-on-color-theory-1835-george-fields-chromatography. Accessed 6 Feb 2023.
25. Rowe FM, editor. The colour index. 1st ed. Research Triangle Park: The American Association of Textile Chemists and Colorists; 1924.
26. Chen X-A, Zhao L, Li Y, Guo F, Chen B-M. Potassium cobalt aluminium mixed phosphate, K (Coll, Al) 2 (PO4) 2. *Acta Crystallogr C*. 1997;53(12):1754–6.
27. Hiley CI, Hansford G, Eastaugh N. High-resolution non-invasive X-ray diffraction analysis of artists' paints. *J Cult Herit*. 2022;53:1–13.
28. Langdon-Jones EE, Pope SJ. The coordination chemistry of substituted anthraquinones: developments and applications. *Coord Chem Rev*. 2014;269:32–53.
29. Fabian J, Hartmann H. Light absorption of organic colorants: theoretical treatment and empirical rules. Volume 12. Berlin: Springer Science & Business Media; 2013.
30. Bisulca C, Picollo M, Bacci M, Kunzelman D. UV-Vis-NIR reflectance spectroscopy of red lakes in paintings. In: 9th international conference on NDT of Art, Jerusalem, Israel. Citeseer; 2008. p. 25–30.
31. Reta MR, Cartana R, Anunziata JD, Silber JJ. Solvatochromism of anthraquinone and symmetrical dihydroxy derivatives. Local interactions. *Spectrochim Acta Part Mol Spectrosc*. 1993;49(7):903–12.
32. Swenson JR, Hoffmann R. The interaction of nonbonding orbitals in carbonyls. *Helv Chim Acta*. 1970;53(8):2331–8.
33. Russell WJ, de Abney W. W. Action of light on watercolours. Report to the Science and Art Department of the Committee of Council on Education. London: HMSO London; 1888.
34. Brommelle NS. The Russell and Abney report on the action of light on water colours. *Stud Conserv*. 1964;9(4):140–52.

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