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Alfeld, Matthias; Mösl, Kristina; Reiche, Ina

DOI
10.1002/xrs.3195

Publication date
2020

Document Version
Final published version

Published in
X-Ray Spectrometry

Citation (APA)
Alfeld, M., Mösl, K., & Reiche, I. (2020). Sunset and moonshine: Variable blue and yellow pigments used by Caspar David Friedrich in different creative periods revealed by in situ XRF imaging. *X-Ray Spectrometry*, *50 (2021)*(4), 341-350. https://doi.org/10.1002/xrs.3195

Received: 28 January 2020 | Revised: 17 June 2020 | Accepted: 29 July 2020

DOI: 10.1002/xrs.3195

SPECIAL ISSUE ARTICLE

X-RAY SPECTROMETRY WILEY

Sunset and moonshine: Variable blue and yellow pigments used by Caspar David Friedrich in different creative periods revealed by in situ XRF imaging

Matthias Alfeld[1] | **Kristina Mösl**[2] | **Ina Reiche**[3,4]

[1]Department of Materials Science and Engineering, Delft University of Technology, Delft, The Netherlands

[2]Alte Nationalgalerie, Staatliche Museen zu Berlin-Stiftung Preußischer Kulturbesitz, Berlin, Germany

[3]Rathgen-Forschungslabor, Staatliche Museen zu Berlin-Stiftung Preußischer Kulturbesitz, Berlin, Germany

[4]PSL University, ENSCP, IRCP UMR 8247 CNRS/Centre de recherche et de restauration des musées de France, Paris, France

Correspondence
Matthias Alfeld, Department of Materials Science and Engineering, Delft University of Technology, Mekelweg 2, 2628 CD, Delft, The Netherlands.
Email: m.alfeld@tudelft.nl

Funding information
Alte Nationalgalerie, Staatliche Museen zu Berlin-Stiftung Preußischer Kulturbesitz; Rathgen Forschungslabor, Staatliche Museen zu Berlin-Stiftung Preußischer Kulturbesitz

Caspar David Friedrich (1774–1840), one of the most famous German 19th c. painters, created paintings throughout his artistic life using different paint palettes, including many new pigments from the turn from the 18th to the 19th century. In that regard especially blue and yellow pigments are the focus of this non-invasive chemical study using X-ray fluorescence imaging, as these are a landscape painter's major colours. Four paintings from the collection of the Alte Nationalgalerie, Staatliche Museen zu Berlin-Stiftung Preußischer Kulturbesitz, spanning over two important decades of Friedrich's artistic career, were investigated in situ to determine the chemical composition of the blue pigments used in the sky and the yellow hues used in the sunsets and moonlight. The results indicate the use of iron based yellow pigments as well as smalt based blue pigments in Friedrich's early works, while chromium-based yellow pigments and cobalt blue are used in later paintings. The finding of cadmium sulphide in a painting dated in 1817, probably as a historical retouching, is interesting and requires further research. This in situ non-invasive imaging study, although limited to one analytical technique, shows Friedrich's introduction of new synthetic pigments into his paint palette, which varies over the time. These results are important to better understand the painting technique of Caspar David Friedrich and his contemporaries.

1 | INTRODUCTION

While visually engaging, paintings are also valuable for their material nature. The choice of pigments reflects the artistic, economic and technological circumstances of a painting's creation, namely the training of artists, their preferences, the price, as well as the availability and the perceived value of pigments. Knowledge of the pigments present in a work of art can thus shed a great deal of light on the circumstances under which the work was painted. The material character of a painting is also important for conservation purposes and has motivated the development of a multitude of instruments for the investigation of historical paintings.[1,2] A mayor development of the last years was a trend from the analysis carried out on carefully selected points to imaging techniques. This allows for the acquisition of more representative data, as any point measurement might be influenced by the presence of a sub-surface layer not visible to the naked eye or other random local variations in paint composition.

However, given that analysis of even a few points with even the simplest techniques require a high level of effort, it is not surprising that only a small fraction of the paintings in museums have been investigated.

The Alte Nationalgalerie (ANG), which is part of the Staatliche Museen zu Berlin-Stiftung Preußischer Kulturbesitz (SMB-SPK), is the custodian of the world's largest collection of paintings by Caspar David Friedrich (1774–1840) who was one of Germany's most important 19th-century landscape painters. In spite of his importance only few studies on his painting technique have been published so far.[3–6]

The first half of the 19th century-Friedrich's creative period-was characterised by a changing paint palette, from traditional to modern pigments.[7,8] Of particular interest are the changes in yellow and blue hues, a landscape painter's major colours. Historical yellow pigments such as Naples yellow were driven out of the market by chrome yellow, which was industrially produced from about 1810 onwards (pp. 188–189, 213 in Reference 9; p. 56 in Reference 10; p.105 in Reference 11). In the course of the 18th and early 19th century traditional blue pigments, like azurite, natural ultramarine and smalt, were gradually superseded by Prussian blue, cobalt blue and synthetic ultramarine.[12–15]

Apart from the technical availability of new materials on the market it is also important to take a look at Friedrich's contemporaries and their practise of pigment use. A close friend of Friedrich in Dresden in the 1820s, the influential physician and self-taught landscape painter Carl Gustav Carus (1789–1869), used chrome yellow, cobalt blue and synthetic ultramarine, the latter as early as it was released on the market.[16] Johan Christian Clausen Dahl (1788–1857), another important landscape painter in Dresden and life-long companion of Friedrich, is known for his choice of traditional yellow and blue pigments, switching to chrome yellow and synthetic ultramarine not before the 1830s and 1840s respectively.[17]

Results of the few published and unpublished studies on Friedrich's pigments[3–6,18] as well as an ongoing PhD research project[19] suggest the late 1810s and the 1820s to be crucial periods in Friedrich's oil painting practise with remarkable shifts in the artist's use of pigments. It seems that at the beginning of his career in oil painting Friedrich preferred yellow earth pigments and Naples yellow and almost exclusively the traditional blue pigment Smalt [3,5,6 reports no. 3408 and 3410 in Reference 18], whereas in his later works he preferred chrome yellow and cobalt blue [4, reports no. 3409 and 3410 in Reference 18].

Considering the results of prior studies, it is expected that Friedrich changed his paint palette during his creative periods according to the availability of the new pigments on the market and was inspired by the practise of his professional contemporaries. This paper's main objective is to verify this hypothesis by the XRF based identification of yellow and blue pigments used by Friedrich in the two decades after he began working with oil painting, in 1807.

2 | MATERIAL

Four paintings from the collection of the Alte Nationalgalerie in Berlin have been selected for studying the variable pigment palettes used in different creative periods of Friedrich. The paintings are shown in Figure 1, their dimensions and inventory numbers are given in Table 1. These paintings are: (1) Zwei Männer am Meer/Two Men by the Sea (1817), (2) Mann und Frau in Betrachtung des Mondes/Man and Woman Contemplating the Moon (1818/1824), (3) Waldinneres bei Mondschein/Deep in the Forest by Moonlight (1823/1830) and (4) Riesengebirge (German name for the Krkonoše mountains in Czech republic) (1830/1835). It should be noted that with the exception of Two Men by the Sea, none of the paintings is precisely dated.

The choice of the studied paintings was guided by the knowledge of the estimated creation periods. So that the study covered the aforementioned decades of the late 1810s and 1820s, which is the presumed period of a possible shift in Friedrich's choice of pigments from smalt to cobalt blue and from Naples yellow to chrome yellow.

3 | EXPERIMENTAL

This investigation of the elemental composition and distribution of the blue and yellow pigments in the paintings was performed by XRF imaging. For the acquisition of XRF maps an XGLab ELIO mobile XRF scanner was used. The instrument, described in detail elsewhere,[20] consists of a measurement head with a Rh anode X-ray tube and a 25 mm^2 energy dispersive SD-detector and two cameras for observing the object. The measurement head is mounted on a motorised stage of 10×10 cm^2 travel range mounted on a flexible tripod. Due to its tripod it is one of the most flexible commercial instruments for on-site XRF imaging.

All data was acquired in a single day at Alte Nationalgalerie in Berlin in March 2019 when the museum was closed to the public. During the investigation the X-ray tube was operated at 4 W (40 kV and 100 μA). The scanning was done with a dwell time of 1 s per pixel and step sizes of approx. 0.5 mm horizontally 1.0 mm vertically. The Table 1 summarises the information about the dimension of the scanned areas in the four selected paintings.

The choice of step sizes allowed for a reduction of the total acquisition time. By stretching the images in post-processing a higher apparent lateral resolution was

FIGURE 1 Investigated paintings: (a) (1) Two Men by the Sea, Inv. No. A II 884, (b) (2) Man and Woman Contemplating the Moon, Inv. No. A II 887, (c) (3) Deep in the Forest by Moonlight, Inv. No. NG 12/92 and (d) (4) Riesengebirge, Inv. No. AI 1079. Kilger, Nationalgalerie, Staatliche Museen zu Berlin-Stiftung Preußischer Kulturbesitz. Numbered rectangles on the images indicate the investigated areas numbered as a function of the painting, respectively: (a) map1_1-3, (b) map2_1-3, (c) map3_1-2 and (d) map4_1-2 [Colour figure can be viewed at wileyonlinelibrary.com]

obtained. The data was fitted, making use of the open source software packages PyMCA[21] and Datamuncher.[22] If multiple pictorial elements/colour zones were present in a scan, local colour zones were manually selected and their average spectra extracted in the PyMCA ROI imaging tool. Spectra that were selected in this manner are labelled with an "*" and the areas they were selected from are indicated in the elemental distribution images.

4 | RESULTS

The in situ XRF imaging results of the four analysed paintings are summarised in Table 2. The paintings and the results are presented in the order of their creative period. The analysed zones of different colour were found to be relatively homogeneous in terms of XRF signals. This was expected based on visual inspection, but only the representative mapping results allowed confirming this. Therefore, average spectra can be used to determine the characteristic elements of the pigments in the paint layers. The average spectra of different areas are shown for the individual paintings in the Figures 2, 4 and 7. The spectra feature a number of elemental lines typical for the chemical composition of historical paintings but there is also some evidence of artefacts from the instrument. The following elements originate likely from the paint layers, they are mentioned in the order of importance: Lead (Pb) is present in lead white (lead carbonate). Calcium (Ca) is present in chalk or gypsum, typically added to paint as an extender or present in the ground. If these components were used in the ground layer Ca would in general not be detected due to the X-ray absorption in the overlaying paint layers, but the more energetic X-ray radiation of strontium (Sr), which is often a minor component in Ca components, would be detected. Iron (Fe) is present in all spectra, most likely because the yellow and brown earth pigments are used throughout the paintings. Minor amounts of titanium (Ti) and barium (Ba) are detected in all investigated areas with a homogeneous distribution, not correlated to any pictorial features. As the abundance of Ti is below the limit of detection for the individual pixel its signal cannot be clearly attributed to a source. Ti can be found in low concentrations in earth pigments, but it might also be present in trace form in the painting's renewed varnish. Also

TABLE 1 Dimensions and mapping details of the four investigated paintings by Caspar David Friedrich

Painting	Number of scans	Scan number, scan dimension and step size (h x v)
(1) Zwei Männer am Meer/Two Men by the Sea (1817), 51.0 × 66.0 cm^2, A II 884	3	map1_1: 19.5 × 19.0 mm^2, 0.5 × 1.0 mm^2 map1_2: 19.5 × 19.0 mm^2, 0.5 × 1.0 mm^2 map1_3: 25.0 × 24.0 mm^2, 0.5 × 1.0 mm^2
(2) Mann und Frau in Betrachtung des Mondes/ Man and Woman Contemplating the Moon (1818/1824), 34,0 × 44,0 cm^2, A II 887 (BSJ 404)	3	map2_1: 19.5 × 19.0 mm^2, 0.5 × 1.0 mm^2 map2_2: 24.0 × 29.0 mm^2, 1.0 × 1.0 mm^2 map2_3: 19.0 × 19.5 mm^2, 1.0 × 0.5 mm^2
(3) Waldinneres bei Mondschein/Deep in the Forest by Moonlight (1823/1830), 70.5 × 49.0 cm^2, NG 12/92	2	map3_1: 19.5 × 19.0 mm^2, 0.5 × 1.0 mm^2 map3_2: 14.5 × 21.75 mm^2, 0.5 × 0.75 mm^2
(4) Riesengebirge (1830/1835), 72.0 × 102.0 cm^2, A I 1079	2	map4_1: 29.5 × 29.0 mm^2, 0.5 × 1.0 mm^2 map4_2: 19.5 × 19.0 mm^2, 0.5 × 1.0 mm^2

TABLE 2 Investigated paintings (oil on canvas) by Casper David Friedrich in the order of their assumed creation period with German and English name, dimensions and inventory number

	Blue		Yellow/orange	
Painting	Elements detected	Pigment inferred	Elements detected	Pigments inferred
(1) Zwei Männer am Meer/Two Men by the Sea (1817), 51.0 × 66.0 cm^2, A II 884	Map1_1–2: Co, As, Ni, K, Si	Smalt	Map1_3: Cr, Pb Cd Fe	Lead chromate Cadmium yellow (Sulphide) Yellow earth
(2) Mann und Frau in Betrachtung des Mondes/Man and Woman Contemplating the Moon (1818/1824), 34,0 × 44,0 cm^2, A II 887 (BSJ 404)	Map2_1: Cape: K, Fe Map2_2: Sky: Co, Ni	Prussian blue Cobalt blue	Cr, Pb	Lead chromate
(3)Waldinneres bei Mondschein /Deep in the Forest by Moonlight (1823/30), 70.5 × 49.0 cm^2, NG 12/92	Map3_1: Co, Ni	Cobalt blue	–	
(4) Riesengebirge (1830/1835), 72.0 × 102.0 cm^2, A I 1079	Map4_1: Co, Ni	Cobalt blue	Map4_1–2: Fe	Yellow and red earth

Note: Further, elements found in blue and yellow/orange areas are shown and the deducted pigment.

a blind contribution from the instrument cannot be completely excluded. The signal intensity of Ba varies between paintings. It is highest for Deep in the Forest by Moonlight, the only data set in that Ba-K lines were also observed (not shown). This is in the same data set that the strongest Sr signals are also recorded in, which may suggest that the ground layers for this painting were prepared in a different way. We will follow up on this in future research.

Elements present in the spectra but linked to the experimental conditions are Argon (Ar) which is present in the surrounding atmosphere (a blind contribution) and Rhodium (Rh) whose lines are part of the primary radiation used for this XRF set-up and coherently scattered by the painting.

Further relevant results for blue and yellow areas are described in the following paragraphs for each of the investigated paintings.

4.1 | Painting 1: Two Men by the Sea (1817)

The two spectra of blue areas (Map1_1 &_2 in Figure 2) belonging to Two Men by the Sea (Inv. No. A II 884) contain, in addition to the aforementioned elements, silicon

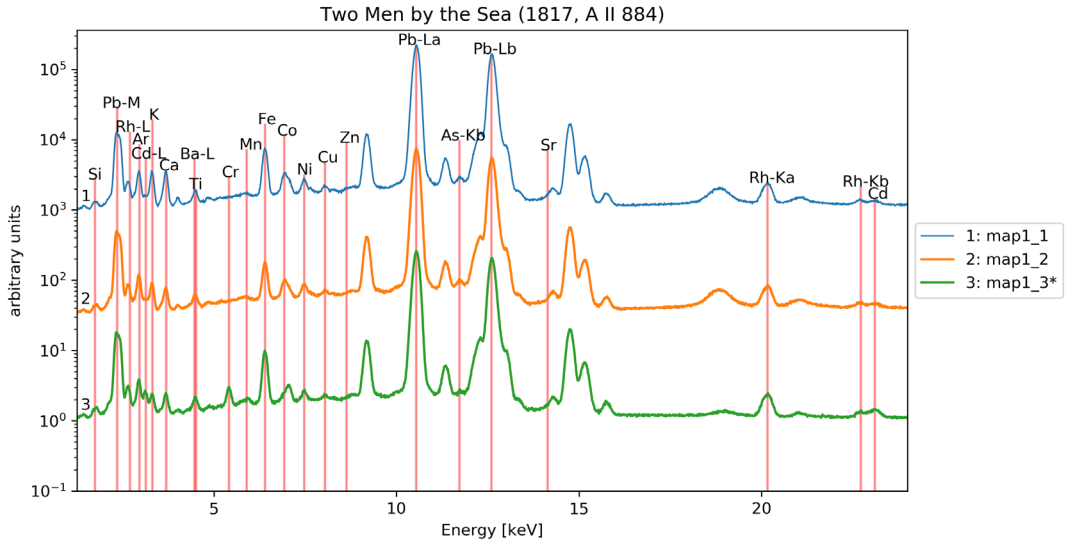

FIGURE 2 Average spectra of Two Men by the Sea (Inv. No. A II 884, 1817). Legend is in same order as the spectra. The area of the average spectrum of map1_3* was manually selected [Colour figure can be viewed at wileyonlinelibrary.com]

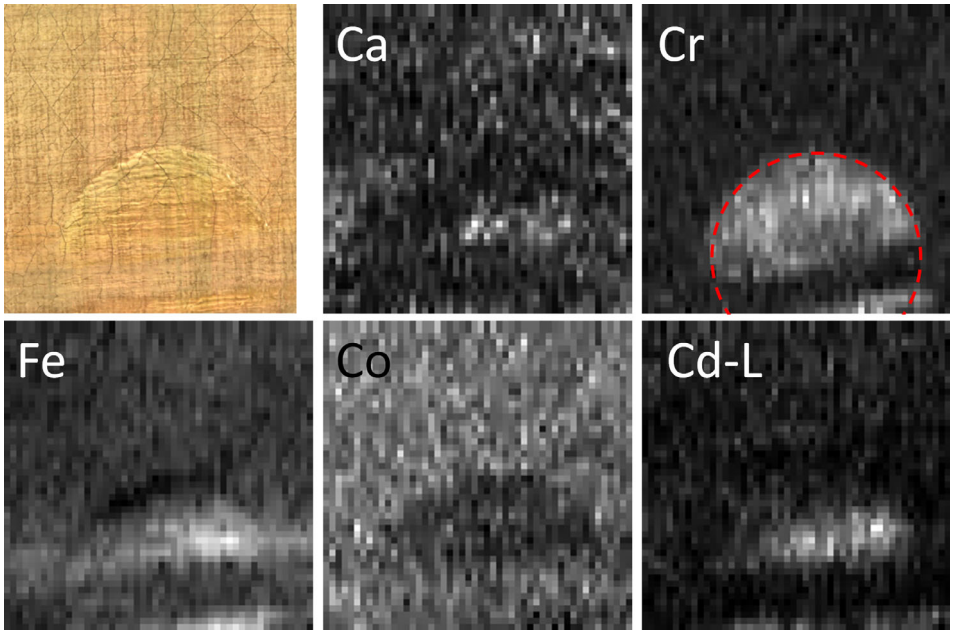

FIGURE 3 Optical image and elemental distribution maps (Ca, Cr, Fe, Co and Cd-L, 25 × 24 mm^2) of the studied area map1_3 of the paintings Two Men by the Sea Inv. No. AII 884. The dashed line indicates the area in that the average spectrum map1_3* was extracted [Colour figure can be viewed at wileyonlinelibrary.com]

(Si), potassium (K), cobalt (Co), nickel (Ni) and arsenic (As). These are all elements typically associated with smalt, a ground, K-rich glass with trace amounts of Co as colouring agent to make it blue. Bismuth (Bi), another typical, minor component of smalt, could not be identified with certainty due to the spectral overlap of its lines with those of Pb.

In Figure 3, the elemental distributions of Ca, Cr, Fe, Co and Cd-L together with the optical image of Map1_3 are shown representing the orange-yellow sunset of Two Men by the Sea. The sunset was created using iron (Fe), chromium (Cr) and cadmium-(Cd) containing pigments (see local average spectrum in Figure 2). Note that the Cd-K_α line overlaps with the Pb-L pile-up peak in the spectrum and thus seems to be present also in the other spectra as well. Fitting the average spectra by PyMCA confirms the presence of Cd, as the contributions of the pile-up and the Cd-K line can be separated. This is further confirmed by the presence of the Cd-L line. It is not possible to correlate the Cr and Pb intensities, as the Pb signal is constant throughout the area, probably resulting from a subsurface or ground layer.

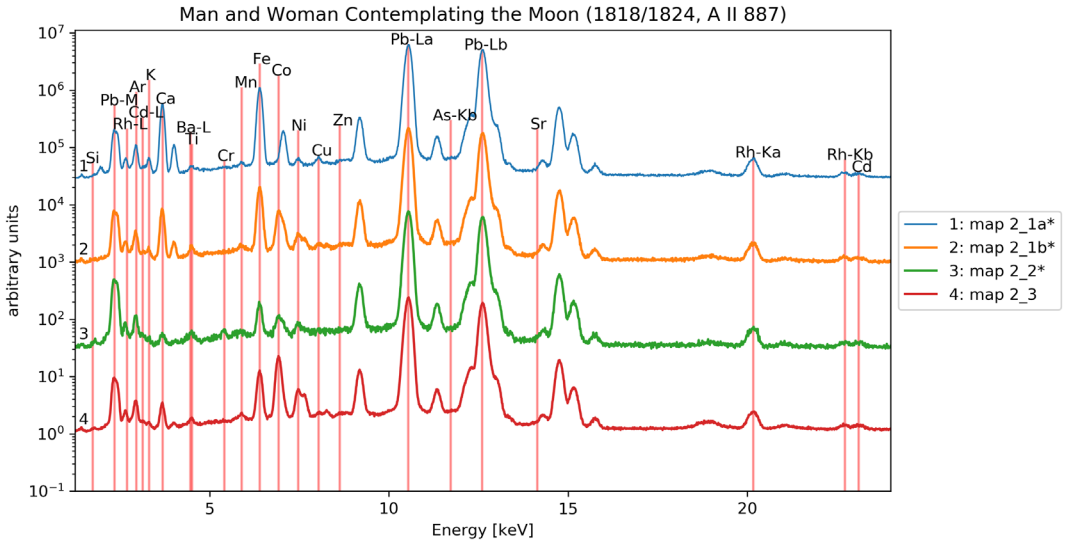

FIGURE 4 Average spectra of Man and Woman Contemplating the Moon (1818/1824). The area of the average spectra of map2_1a*, map2_1b* and map2_2* was manually selected [Colour figure can be viewed at wileyonlinelibrary.com]

However, considering the yellow colour it is likely that yellow lead chromate was used ($PbCrO_4$), as Cr oxides are in general of green colour and no other element was detected that commonly serves as a counterion to chromates in pigments. A common, commercial name for the pigment based on lead chromate is chrome yellow. The yellow Cd pigment is likely to be a mixture of cadmium yellow (Cadmium Sulphide, CdS) and the Fe-containing yellow earth.

4.2 | Painting 2: Man and woman contemplating the moon (1818/1824)

Four average spectra of the painting Man and Woman Contemplating the Moon (Inv. No. A II 887) are shown in Figure 4. The two top spectra belong to area map2_1, whose elemental distribution images are also shown in Figure 5. The third and fourth spectra are corresponding to area map2_2 and the average spectrum of the sky in area map2_3. When comparing these spectra it is obvious that two different blue pigments were used. In the purple sky Co and Ni but no As, Si or K are found, while in the spectrum of the man's cape strong K and Fe signals can be detected. We conclude from this that the sky was painted employing Co blue ($CoAl_2O_4$). Given the dark blue tone and the presence of K and Fe, we believe the pigment used for the cape was Prussian Blue ($K^{I}Fe^{III}[Fe^{II}(CN)_6]$). The edge of the moon in Man and Woman Contemplating the Moon also contains Cr (Figure 6 and the third spectrum in Figure 4). Here we also infer the use of yellow lead chromate.

4.3 | Painting 3: Deep in the Forest by moonlight (1823/1830)

The two spectra of the blue areas of the painting Deep in the Forest by Moonlight (Inv. No. NG12/92) indicate the usage of Co blue (see Figure 7). The visible peak near the Si line in the spectra is actually due to a Pb-M line that is difficult to distinct from the background in the other spectra. Both spectra feature weak Zinc (Zn) signals due to past conservation treatments using a Zn based pigment, most probably Zinc White (ZnO), which became available only late in the 19th century. These areas are also visible under UV illumination. In the elemental distribution images, not shown, it could be seen that the paint of the trees was applied on the already painted sky, as one would expect in a systematic painting approach by Friedrich.

4.4 | Painting 4: Riesengebirge (1830/1835)

The two spectra of the blue areas of the painting Riesengebirge (Inv. No. A I 1079) have similar spectral XRF features as the painting Deep in the Forest by Moonlight and thus also indicate the presence of Co blue (Figure 8). The spectrum from area Map4_1 in Riesengebirge is recorded in the still bluish mountain and not in the reddish sky (Figure 9). The yellow sky around the sunset in Riesengebirge contains no Co, but an enhanced Fe signal with respect to the usual Fe signal detected in the painting, which let us to conclude that

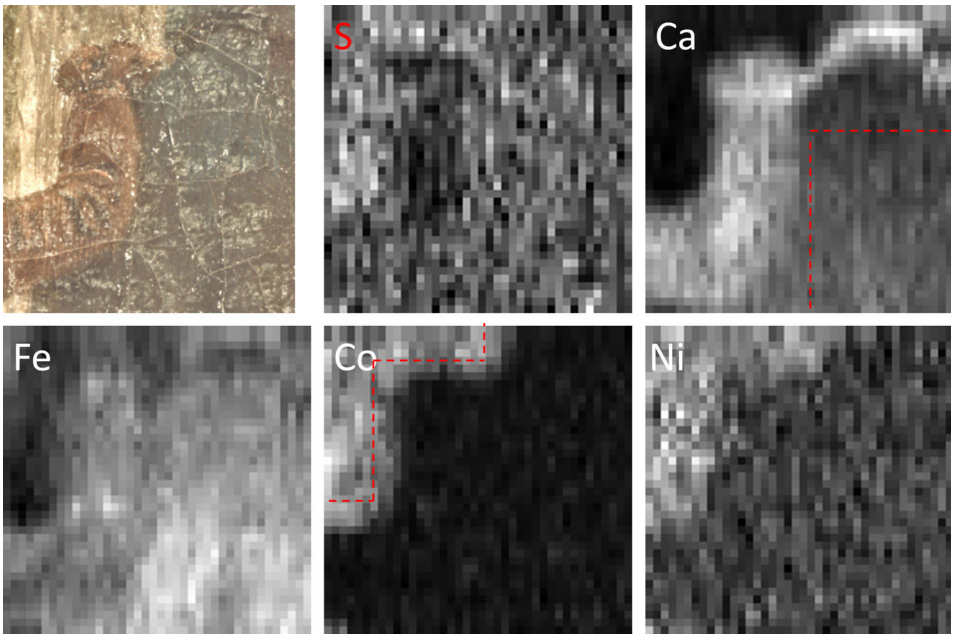

FIGURE 5 Optical image and different elemental distribution maps (S, Ca, Fe, Co and Ni, 20 × 20 mm^2) of the studied area map2_1 of the sky around the figures of the painting Man and Woman Contemplating the Moon Inv. No. AII 887, illustrating the use of two blue pigments. The colour balance of the camera recording the image is slightly off. The dashed line in the Co distribution image indicates the area in that the average spectrum map2_1b* was extracted, the lines in the Fe distribution image the area of spectrum map2_1a*, respectively [Colour figure can be viewed at wileyonlinelibrary.com]

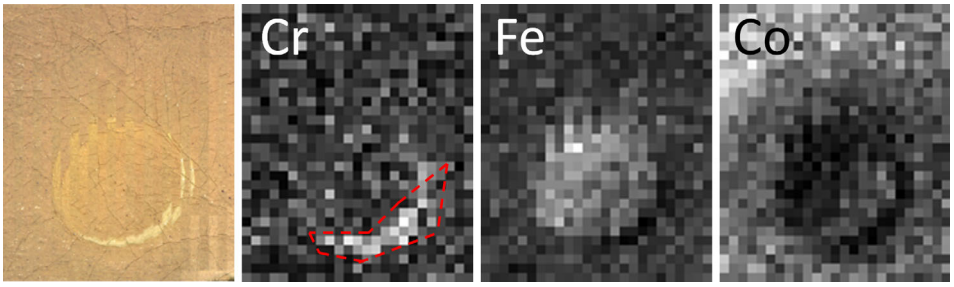

FIGURE 6 Optical image and elemental distribution maps (Cr, Fe and Co 25 × 30 mm^2) of map2_2 of Man and Woman Contemplating the Moon AII887. Due to mechanical problems the optical image of the ELIO instrument is slightly distorted. The dashed line in the Cr distribution image indicates the area in that the average spectrum map2_2* was extracted [Colour figure can be viewed at wileyonlinelibrary.com]

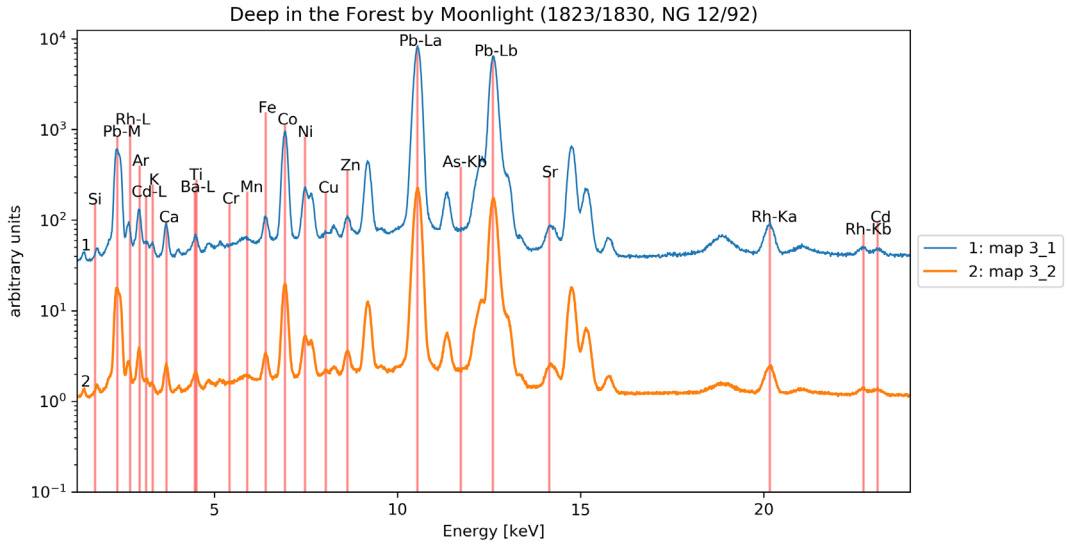

FIGURE 7 Average spectra of Deep in the Forest by Moonlight (1823/1830) [Colour figure can be viewed at wileyonlinelibrary.com]

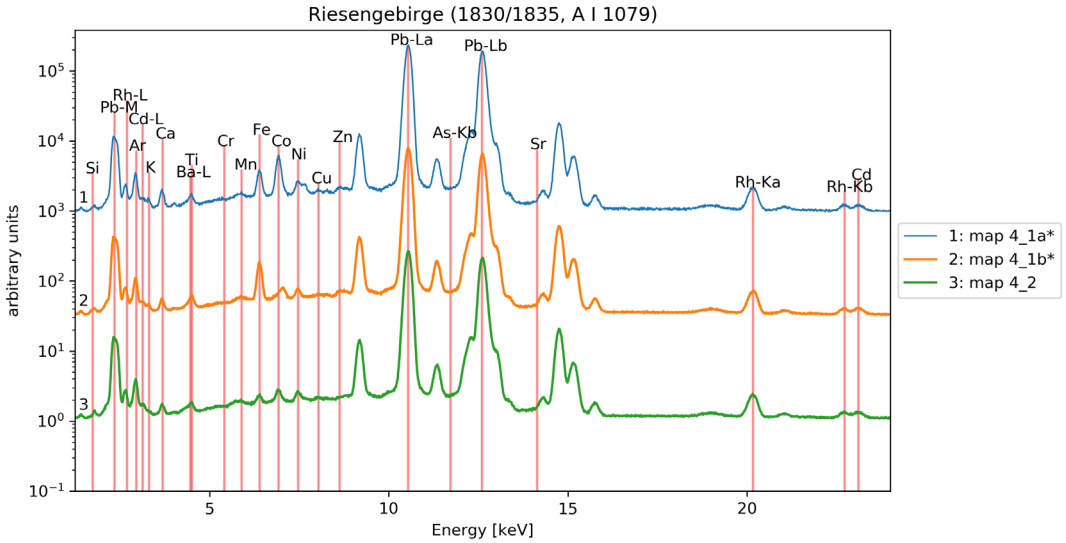

FIGURE 8 Average spectra of Riesengebirge (1830/1835). The area of the average spectra of map4_1a* and map4_1b* was manually selected [Colour figure can be viewed at wileyonlinelibrary.com]

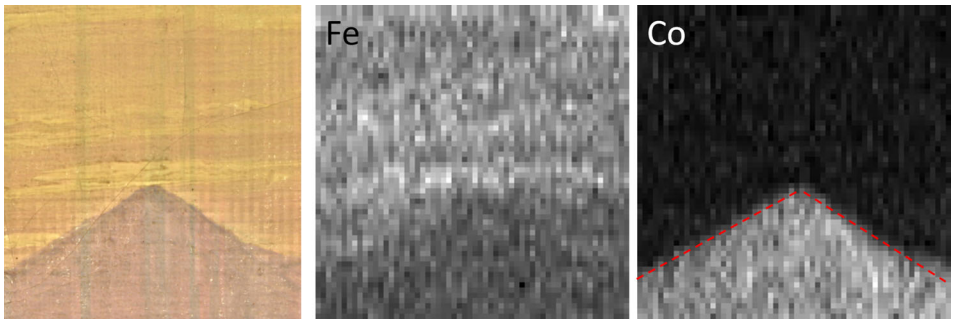

FIGURE 9 Optical image and Fe and Co elemental distribution maps (30 × 30 mm^2) of the studied area map4_1 of the top of the mountain in the painting Riesengebirge, Inv. No. AI 1079. The average spectra of two areas were taken: map4_1* below the dashed line, map4_2* above it [Colour figure can be viewed at wileyonlinelibrary.com]

here yellow and red earth pigments were used to achieve the desired tone. The main colouring components in these pigments, next to minor mineral phases, are the yellow Goethite (α-FeOOH) and red Haematite (Fe_2O_3).

5 | DISCUSSION

5.1 | Blue pigments used by Friedrich over his creative periods

The blue pigments in Friedrich's paintings, which were inferred based on the elements detected, from different creative periods are summarised in Table 2. They are in good agreement with their date of introduction according to the Pigment Compedium.[11] Smalt is the oldest blue pigment, which could be identified in the four paintings. Smalt is consistently found in the blue zone of the Two Men by the Sea painting, the oldest of the four studied ones dated in 1817. It is also present in at least in two other early Friedrich paintings: Monk by the Sea (1808–1810) and Abbey in the Oakwood (1809–1810) kept in the ANG.[6] The usage of smalt is a bit surprising, but Friedrich's preference for this old-fashioned blue pigment is well known.[3–6] Prussian blue was developed in the early 18th century in Berlin and slowly superseded smalt in the following decades. Prussian blue was found in the Man and Woman Contemplating the Moon painting dated to 1818/1824.

Cobalt blue was invented as a pigment at the turn of the 18th to the 19th century. It was first used by J. M. W. Turner (1775–1851) in 1806 or 1807, followed by German portrait painter Heinrich Friedrich Füger (1751–1818) who chose cobalt blue for one of his paintings in 1808.[14] Therefore, it is unsurprising to find this pigment in the later Friedrich paintings Deep in the Forest by Moonlight (1823/1830) and "Riesengebirge" (1830/1835). Cobalt blue was found with Prussian blue in the Man and Woman Contemplating the Moon (1818/1824). Notably, no Cu was detected in any investigated area, which excludes usage of a Cu based blue pigment, for example, azurite, in the blue areas.

5.2 | Yellow pigments used by Friedrich over his creative periods

The identified yellow pigments give a more contradictory picture (see Table 2): Yellow earth has been used since pre-history and it is thus reasonable to identify this pigment in Friedrich's paintings. Further, it should be noted that in the investigated areas no Sb, the typical elemental marker of Naples Yellow ($Pb_2Sb_2O_7$), was found. The introduction dates given for lead chromate/chrome yellow vary between 1804 and 1816. In specialised literature a number of commercial production dates are mentioned from 1804 to 1809,[9] about 1818 onwards,[10] between 1804 and 1809 with the commercial market release in England around 1814/16.[11] The earliest findings of chrome yellow in easel painting is in Sir Thomas Lawrence's, Portrait of a Gentleman (before 1810, Bayerische Staatsgemäldesammlung Munich) and ten other paintings of the same decade.[9] This evidence and the sources for chrome yellow, agree with the dating of Friedrich's paintings. The cadmium yellow is likely present in historical retouching material. Notably, it was not detected during previous observations under UV light, as it is covered by thick, yellowed varnish with high fluorescence under UV light. But if Friedrich was an early adoptor of lead chromate, would it be possible that he could access some early cadmium yellow, possibly not made for commercial purposes? This requires additional research into the pigments used in other paintings by Friedrich and into archives, which might provide insight into his efforts in procuring the newest pigments. This is the subject of K. Mösl's ongoing PhD project.[19]

6 | CONCLUSIONS

An investigation of four paintings by Friedrich has shown that he varied the types of blue and yellow pigments he used considerably, seemingly trying new pigments as they became available to him. These results mandate a broader investigation of his pigment use to confirm this conclusion. Our investigation was concentrated on areas of the painting which stood out in an initial visual inspection. To acquire representative information a complete characterisation of more paintings and larger zones is needed. Additionally, it would be helpful to cross the XRF measurements with other complementary, non-invasive methods, such as Reflectance Imaging Spectroscopy or XRD point measurements, which would allow for a more precise determination of the pigments used by Caspar David Friedrich.

The pigments detected on the four paintings illustrate the remarkable shift in the Friedrich's use of materials around 1820. This shift may have been influenced by Johann Christian Clausen Dahl or physician and the self-taught artist Carl Gustav Carus, contemporary painters in Dresden whom Friedrich befriended in 1820. Thus, the results are an important step to a better understanding Friedrich's decision-making and painting technique and contribute to the understanding of mutual influences between painters in early 19th century Germany.

ACKNOWLEDGEMENTS

M. Alfeld thanks the Rathgen Forschungslabor, Staatliche Museen zu Berlin-Stiftung Preußischer Kulturbesitz for supporting his travels and especially S. Tesche for the organisation of the trips in October 2018 and March 2019. The authors thank the team of the Alte Nationalgalerie, Staatliche Museen zu Berlin-Stiftung Preußischer Kulturbesitz for supporting them during the measurements. We thank Jane Sedlak for proof reading the manuscript.

ORCID

Matthias Alfeld https://orcid.org/0000-0001-7974-9564

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How to cite this article: Alfeld M, Mösl K, Reiche I. Sunset and moonshine: Variable blue and yellow pigments used by Caspar David Friedrich in different creative periods revealed by in situ XRF imaging. *X-Ray Spectrom*. 2021;50:341–350. https://doi.org/10.1002/xrs.3195