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The Rediscovery of Jan Ruyscher and Its Consequence

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Flavia Fiorillo, Laura Hendriks, Irka Hajdas, Mariangela Vandini, Eric Huysecom (2022). The Rediscovery of Jan Ruyscher and Its Consequence. JOURNAL OF THE AMERICAN INSTITUTE FOR CONSERVATION, 61(1), 55-63 [10.1080/01971360.2020.1822702].

Availability:

This version is available at: <https://hdl.handle.net/11585/859714> since: 2024-01-08

Published:

DOI: <http://doi.org/10.1080/01971360.2020.1822702>

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(Article begins on next page)

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Fiorillo, F., Hendriks, L., Hajdas, I., Vandini, M. & Huysecom, E. The Rediscovery of Jan Ruyscher and Its Consequence. *Journal of the American Institute for Conservation* 61, 55–63 (2022).

The final published version is available online at:

<https://doi.org/10.1080/01971360.2020.1822702>

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Journal of the American Institute for Conservation

The rediscovery of Jan Ruyscher and its consequence

--Manuscript Draft--

Manuscript Number:	JAC378R2
Full Title:	The rediscovery of Jan Ruyscher and its consequence
Article Type:	Short Communication
Keywords:	panel painting; radiocarbon dating; pigment analysis; Jan Ruyscher; forgery
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Corresponding Author's Institution:	Universita di Bologna
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Order of Authors Secondary Information:	
Abstract:	In 2014 a painting attributed to the 17 th century Dutch artist Jan Ruyscher appeared on the art market. Despite a prestigious career, Ruyscher, who possibly was a pupil of Rembrandt and Hercules Seghers, vanished from art history after his death and was only rediscovered in the 1930s. In this research paper, the combination of multiple analytic techniques ranging from radiocarbon dating of the support material to multispectral imaging and spectroscopic analyses (XRF, SEM-EDS, FTIR and Raman) of the pictorial layer offers a comprehensive analysis of the object. Radiocarbon analyses of the wooden panel indicated that the tree was probably cut down in the mid-18 th century, whereas spectroscopic analyses pinpointed the 20 th century as a timeframe for the application of the pictorial layers. The applied methodology shed new light on the story of the object itself. The painting was created at the earliest in the 1930s possibly as a consequence of the rediscovery of Ruyscher, and the deliberate use of an aged panel supports an intent to deceit and hence classifies the object as a forgery. The painting under study was furthermore compared with artworks of renowned forgers in an attempt to identify the forger in disguise.
Additional Information:	
Question	Response
Author Comments:	
Response to Reviewers:	Ref.: JAC378R1 The rediscovery of Jan Ruyscher and its consequence Journal of the American Institute for Conservation Comments from the Editors and Reviewers: Reviewer #1

1 **The rediscovery of Jan Ruyscher and its consequence**

2

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12

13 **Abstract**

14 In 2014 a painting attributed to the 17th century Dutch artist Jan Ruyscher appeared on the art
15 market.

16 Despite a prestigious career, Ruyscher, who possibly was a pupil of Rembrandt and Hercules
17 Seghers, vanished from art history after his death and was only rediscovered in the 1930s. In this
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26 the object as a forgery. The painting under study was furthermore compared with artworks of
27 renowned forgers in an attempt to identify the forger in disguise.

28

29 **Keywords:** panel painting, radiocarbon dating, pigment analysis, Jan Ruyscher, forgery

31 1. Introduction

32 The painter Jan Ruyscher is one of several “Little Dutch Masters” of the 17th century who today are
 33 very poorly known, and whose paintings may be counted on one hand. His career, however, was
 34 relatively long and somewhat prestigious. Born in the Netherlands around 1625, most likely in
 35 Franeker in the region of Friesland, Jan Ruyscher was active in Amsterdam from 1645. Several
 36 authors believe that he may have been a pupil or possible followers of Rembrandt (Welcker 1932a;
 37 Bol 1969; “Jan Ruyscher”; Sumowski 1983), and he was probably the sole disciple of
 38 Hercule Seghers (Welcker 1932a). The date of his death is unknown, but must have been at latest
 39 1675 (Welcker 1932a). Despite this rich and diverse career, only some rare engravings, a few
 40 unsigned paintings attributed to him and two signed paintings constitute his legacy.

41 The painting *Paysage de montagne*, said to have come from an important Swiss collection, was put
 42 on public sale on the 20th of December 2012 in Cannes (Cannes auction, auctioneers: Nicolas
 43 Debussy and Carine Aymard, lot no. 26), with a certificate of authenticity from the Parisian expert
 44 René Millet testifying to its status as a work of Jan Ruyscher.

45 Two years after the auction, a restoration of the object was undertaken but as the oxidised varnish
 46 was partially removed the use of non-17th century pigments was postulated (private
 47 communication).

48 In 2017, the painting was handed over to an expert from the Lempertz auction house in Cologne,
 49 who suggested that it was in fact a modern copy (private communication).

50 This rather controversial situation can be solved with the help of scientific analyses, which provide
 51 objective data to unravel the nature of the object. A preliminary dating of the object was pursued by
 52 dendrochronology but following inconclusive results the panel was further dated by ¹⁴C analysis.

53 Complementary characterisation of the materials was carried out with a wide range of techniques -
 54 non-invasive analyses (VIS photography, UV fluorescence, X-ray fluorescence spectroscopy (XRF))
 55 and micro-invasive analyses on cross-sections, such as scanning electron microscopy coupled with
 56 energy dispersive spectroscopy (SEM-EDS), Fourier transform infrared microscopy (FTIR) and
 57 Raman microscopy. The combination of the radiocarbon results and materials characterisation, in
 58 comparison with Ruyscher's lifetime, objectively defined the nature of the artwork. At the same
 59 time, a better understanding of why a painting allegedly made by a minor artist of the 17th century
 60 showed up in the art market of the 20th century was sought.

62 2. Materials and Methods

63 2.1. Object of study

64 The tableau depicts a broad valley at the heart of an encompassing mountain landscape (Figure 1).
65 A signature may be distinguished at the bottom left, partially erased except for the letters “*Rau*”.
66 The support for this painting is a bevelled panel of wood measuring 17 x 20.7 cm. The style and its
67 framing resembles an engraving by Jan Ruyscher held at the Rijksmuseum since 1816 (Inv, No. RP-
68 P-OB-12.875). This engraving was thought to have only one edition until 1998, when the Bassenge
69 auction house put up a second for sale (Galerie Gerda Bassenge auctions - Berlin, 27-11-1998, No.
70 5403).

71 Several samples were collected from the wooden support for radiocarbon dating and from the
72 painting surface to characterize the palette (Supplementary Materials 1-2).

73

74 2.2. Methods

75 The radiocarbon measurements were conducted on the MICADAS ¹⁴C dedicated system (Synal,
76 Stocker, and Suter 2007). The radiocarbon ages obtained were calibrated to real calendar ages using
77 the Oxcal v4.3.2 software (Ramsey 2009) with the IntCal13 atmospheric calibration curve (Reimer
78 et al. 2013).

79 Visible photography was performed with a Nikon D800 (36 Mp), two Mada Tec ultraviolet sources
80 (365 nm) were used for UV photography. XRF was performed with an energy dispersive
81 spectrometer (EDS) EIS-XRS38 (Electronic Industry Support (E.I.S.), Italy) with a tungsten
82 filament, a circular spot of 3 mm diameter, 30 kV, 0.2 mA and for 300 seconds (live time).

83 Cross-sections' documentation was carried out on a BX51M microscope (Olympus, Tokyo, Japan).
84 A 100W halogen projection lamp was used for visible light, while the UV source is an Ushio
85 Electric USH102D lamp.

86 Back-scattered electron images (BSE) and EDS spectra were collected on a low-vacuum FEI-
87 Quanta Inspect S (FEI, Hillsboro, OR, USA), equipped with a Philips New XL-30 microprobe. EDS
88 analyses were carried out at 30 kV, a W filament current of 100 μA, for 100 seconds.

89 FTIR analyses were performed with an iNTM10MX Nicolet microscope (Thermo Fisher Scientific,
90 Waltham, MA, USA) coupled to a mercury cadmium tellurium (MCT) detector in attenuated total
91 reflection (ATR) mode (conical crystal germanium). The spectral range is from 4000 to 675 cm⁻¹,
92 the spectral resolution 4 cm⁻¹ and 64 scans were acquired.

93 Raman spectra were collected with a Senterra Microscope (Bruker, Karlsruhe, Germany). Analyses
94 were carried out with a 785 nm laser with a power up to 10 mW, in the 50-2600 cm⁻¹ spectral region
95 and with a resolution of 3-5 cm⁻¹.

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3. Results

3.1. Radiocarbon dating of the support

Upon calibration, the measured ¹⁴C ages corresponded to the period between the 16th and beginning of the 20th centuries -that hinders further precision due to the particular shape of the calibration curve. However, given the age difference between the ¹⁴C dates, the sequence of sampled tree rings can be wiggle-matched to the calibration curve IntCal13, hereby overcoming the multiple age possibilities from single dating. The wiggle matching model implemented within the Oxcal software looks for the optimal solution (Monte-Carlo simulation and chi-square test) within the probability distribution of the whole curve, where the yearly ring distance between the analysed samples is used as a boundary condition (Bronk Ramsey, van der Plicht, and Weninger 2001). In the present case, the outer tree ring was determined to date to 1661-1664, and the youngest to 1730-1753 (2σ, 95% confidence interval). These results imply that the tree was growing between the end of the 17th and the mid-18th centuries.

3.2. Materials characterisation

Preliminary documentation with multispectral imaging determined an overall good state of conservation of the painting, showing a flat surface without major paint losses (Figure 1). UV fluorescence highlighted the presence of a final thick layer of varnish covering the whole surface; several restored areas were observed and a peculiar bright yellow fluorescence colour on the trees at the left side was detected. On the back of the panel, an inscription, clearly visible under UV light, links the object to Jan Ruyscher.

Pictorial layers. In all tested locations, the XRF identification of titanium, barium and zinc suggests a general use of titanium white, barium sulphate and zinc oxide (zinc white) or zinc sulfide (which, in association with barium sulfate, is characteristic of lithopone). These white pigments were introduced to the art market from the 18th century onwards, and a further investigation in cross-section was necessary to assess whether they were used in the original layers or belonged to restoration materials. The stratigraphy of the samples consisted of a double white ground and few, thin pictorial layers containing fine particles (<10 μm), covered by a thick varnish (Figure 2). The results on the cross-sections are summarised in **Error! Reference source not found.** Ultramarine was the predominant pigment identified on various shades of blue (Figure 3), and it is likely to be artificial due to the rounded-shape of the crystals (Eastaugh, Walsh, and Chaplin 2004; Plesters 1993). In the blue sky (location marked as 1 in Figure 1a and Supplementary Materials 3) cobalt was also found by XRF, hinting to the use of cobalt blue. The pigment responsible for the green hue of

sample no. 2 was not identified. The presence of iron may hint to the use of green earth (XRF spots nos. 4 and 5); however, the stratigraphy consisted of a dark green matrix in which only fine orange and yellow particles are found, likely to be ochres and possibly contributing to the Fe peak in XRF. The brown colour of the landscape (sample no. 4) is due to a carbon-based black pigment and ochres. Titanium white (anatase), calcium carbonate, barium sulfate, zinc white/lithopone were found to be omnipresent, mixed in all layers, indicative of a deliberate addition during the paint mixing to achieve the desired hue or simply present as extenders of other pigments. Lead, most likely indicative of lead white, was also found by XRF to be omnipresent. A lipid binder was detected and weak peaks associated to zinc carboxylates were found in several of the cross-sections, indicating the beginning of the degradation process between the binder and the zinc pigment (Hermans et al. 2015).

Restoration materials. The yellowish retouched area on the trees (sample no. 3) consists of yellow ochres, likely cadmium yellow (Supplementary Materials 4) and a zinc species, probably zinc white due to the intense and characteristic UV fluorescence. The green layer contains Pigment Green 8 (PG8, nitroso green, *Colour Index* 10006). However, it is unclear whether this fragment represents an area of original material or a reworked zone. The thick varnish found on all samples is identified as Laropal A81 resin (Supplementary Material 5).

The **ground** on all samples consists of two layers: the lower one is off-white while the upper one is pure white (Figure 2). Both showed a similar composition: titanium white (anatase) mixed with barium sulfate and calcium carbonate (Figure 3). The latter is characterised by FTIR as calcite mixed with aragonite (Supplementary Material 6). The presence of zinc revealed by the SEM-EDS spectra can be associated to zinc oxide or zinc sulfide. The S peak also detected in the SEM-EDS spectra can relate either to the sulfide form but can also be linked to barium sulfate, preventing the possible identification of zinc sulfide. Moreover, as Zn compounds are poor Raman scatterers no bands were detected, and the characteristic infrared absorptions of the two pigments are out of the 4000-750 cm^{-1} IR region used in this study. The two ground layers were applied at the same time as there is no discontinuity between them, the difference in colour may be explained by a different concentration of binder.

4. Discussion

The investigation of the support revealed the first signs of inconsistency with the attribution. The ^{14}C results indicate that the organic material used as support was still living/growing at the time of Ruyscher's death. Radiocarbon ages that post-date the activity period of the attributed artist lay the

163 basisfor the indication of a fraud. In the alleged painting by Ferdinand Léger case, where concerns
164 had been raised regarding a fake, similar results were observed(Caforio et al. 2014).

165 The second piece of evidence isprovidedby the study of the artwork's stratigraphy, whichdoes not
166 match the technique used in the 17thcentury. No other study was published on Ruyscher's
167 technique, thus preventing any comparative approach. However, a comparison to works by
168 Rembrandt, of which Ruyscher was allegedly a pupil, was pursued. The identified white ground
169 topped with meagre layers enclosing fine pigment particles strongly diverge from Rembrandt's
170 many layers with coarse particles over a yellowish ground (Wieseman 2010; Groen
171 2005).Moreover, the construction of the object can be discussed thanks to the cross-sections(Figure
172 2): while a complex layered structure is emblematic of a painting that is built up in stages, a single
173 layer of colour is very seldom observed in a copy. Based on the comparison of materials present in
174 an artwork with information on the earliest date of their discovery or production, the earliest
175 possible date of realisation of a painting, the *terminus post quem*, can be established. Although very
176 effective, few works are reported in literatureas owners seldom want to publicly advertise their loss.
177 Among a few known cases, anachronistic pigments were found on a purported Chagall
178 nude(Chaplin and Clark 2016) similarly to alleged Russian avant-garde artworks(Saverwyns 2010;
179 Chaplin, Clark, and Singer 2014) as well as forged works of the abstract expressionist Jackson
180 Pollock(Khandekar et al. 2010). Nonetheless, despite the amount of gathered data in some cases an
181 accurate dating of the artwork is still often impossible in the absence of a decisive material
182 anachronism. The example of Wolfgang Beltracchi, an infamous forger of the 21th century,
183 perfectly illustrates how forgers are aware of the science limitation and adapt to their time.
184 Beltracchi managed to avoid any pigment anachronisms over 30 years of practice with a home-
185 made palette bearing only pigments which were historically consistent with purported signed date
186 of the works. In the case under study, although the pictorial layers contain traditional pigments,
187 such as lead white and ochres, we also find pigments commercialised in the 19th century, such as
188 artificial ultramarine blue, possibly cobalt blue and zinc compounds.In contrast to the
189 aforementioned anachronistic cases, where the sore point was made out in the pictorial layer, the
190 present case displays its mostdecisive indication of fraud in the ground layerin the presence of
191 titanium white in the form of anatase. Developed in 1919,the pigmentmade a slow entrance on the
192 marketand become gradually accepted as white pigment throughout the 1930s(Laver
193 1997).Titanium white is a well-known 20th century red flag whose identification has exposed many
194 forgeries. Among others, its identification revealed Beltracchi'snumerous forgeries, being employed
195 as additive but not declared by the paint vendor in the tube paint's compositions(Hufnagel and
196 Chappell 2016).A timeline combining all the results underlines the discrepancies between the ages

197 of the support and introduction dates of pictorial materials with Ruyscher's lifetime (Figure 4). The
198 materials characterisation points to the painting's creation in the 20th century, in particular from
199 1930s onwards, due to the presence of titanium white. This period coincides with a rediscovery of
200 Jan Ruyscher's works, as a private collector, Albertus Welcker, published a monograph dedicated to
201 the artist (Welcker 1932b). His study was reedited in five parts between 1932 and 1936, appearing
202 over 4 issues of the review *Oud Holland*. One can also speculate whether its creation occurred at the
203 end of the 20th century, inspired by the selling in 1998 of a copy of a Ruyscher's engraving
204 conserved at the Rijksmuseum of Amsterdam (see section 2.1).

205 While the too young support and pigment anachronisms strongly contradict a Ruyscher attribution,
206 the forger in question put a lot of effort in making the object look authentic: recent inscriptions on
207 the back of the panel, in chalk (*Ruischer*) and in red felt-tip (*Jan Ruyscher*), complement a copper
208 plaque nailed to the frame with the note *Jan Ruischer, 1625 - 1675*. Badging the reverse of an
209 object with inscriptions, stamps and dates to make the object look older than in fact it is, is a trick
210 that forgers commonly use. The intention of deceit is hereby evident in the re-use of a support with
211 the aim to create the impression of an older aspect to the object, which is to be classified as an act of
212 fraud. The re-use of a support is a common *modus operandi* among forgers, to which many, such
213 Beltracchi or Van Meegeren, have confessed. Unfortunately, few studies are published about
214 forgers' palettes, therefore a comparison to a known forger revealed itself laborious. Was this
215 particular forger of Ruyscher simply unlucky with the choice of the substrate? Both forgers Joni and
216 van Meegeren were active in the 1930s, could they have authored the *Paysage de montagne*? An
217 attribution to Joni could be excluded as he was an Italian painter specialised in Middle Ages
218 art (Muir and Khandekar 2006), which does not match with an allegedly 17th century Flemish
219 painting, whereas van Meegeren tended to use historical pigments and create a convincing
220 craquelure, thus showing a level of sophistication in the elaboration of the fraud (Held 1951). The
221 use of titanium white over the entire painting shows poor art historical knowledge, which strongly
222 contrasts with Beltracchi's style using only a reduced palette of pigments that he knew to be
223 historically correct, and who furthermore mostly painted art from the 20th century. The build-up of
224 anachronistic features in all layers of the object present similarities with the Trotter forgery
225 case (Smith et al. 2012), which was marked by the omnipresence of titanium white in the ground
226 layer and many anachronistic colourants such as phthalocyanine green. Radiocarbon analysis of the
227 support and pictorial layer revealed the forger's scheme in recycling an appropriately aged canvas to
228 convey the illusion of authenticity (Hendriks et al. 2019). Trotter, who specialised in forged
229 American primitives, was active in the late 1990s and as the FBI only located 16 out of the
230 announced 55 fraudulent objects, this possibility cannot be excluded, although the object in

question surfaced on the European market and not in the US. While an answer as to when could be more or less appraised, the answer to who remains uncertain. Our forger recycled an older panel but was in the end betrayed by the age of it, he lacked the in-depth knowledge of Van Meegeren or Beltracchi and was as sloppy as Trotter, making numerous pigment anachronisms. This relatively low level of hierarchisation among the known different forgers allows to postulate that our forger was less skilled and his work is most likely to be spotted on as fraud.

5. Conclusion

The methodological approach applied in this study provides critical arguments for the identification of a period of creation of the painting, a possible reconstruction of its history and the classification as a forgery. The investigation of the different layers of the object revealed many anachronistic features with Ruyscher's time of activity (1625-1675). Starting from the support, the wooden panel was radiocarbon dated to the mid-18th century. Within the pictorial layers numerous material anachronisms indicative of the 19th century were found. However, the most decisive argument of the painting's date is the presence of titanium white in the ground, indicating that the painting could not have been executed at an earlier date than the 1930s. This coincides with a time when Ruyscher's artworks were rediscovered and became noteworthy. Even if the signature on the back could be a genuine misattribution, scientific results show inconsistencies with the purported date of attribution and a possible intention of deceit by the re-use of an old support, therefore the object is classified as a forgery. In the attempt of reconstruction an object's history, the question to when is the easiest to answer based on scientific evidence, while the authorship is much more complex, in particular when seeking to identify a forger. While renowned artists are constantly being studied, hereby always increasing our knowledge regarding their technique, little is known about forgers. Thus, owing to a lack of published data that prevented a direct comparison, this study wants to underline the importance of a more comprehensive study on forgeries of the 20th century, which will aid to better understand the practice of forgers and potentially avoid the spreading of fakes within the art market.

Acknowledgements

We would particularly like to thank Suzanne Stocker for her perspicacity and for pointing out the possibility of a forgery. We acknowledge Lukas Wacker for running the ¹⁴C measurements on the MICADAS and Salvatore Andrea Apicella for his help with the multispectral imaging. We also thank Mr. Félix Walder, from the Underwater Archaeology and Dendrochronology laboratory of the city of Zurich for the previous dendrochronological analyses. A special thanks to Alexander

265 Walmsley for his help in translating this article. Finally, we also thank Dr Susann Krüger, Curator
266 at the Staatliche Kunstsammlungen Dresden for providing us with all the information concerning
267 Jan Ruyscher's drawing in their possession.

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270 **Declaration of interest**

271 **Funding:** This work was partially supported by the ETH grant ETH-21 15-1.

272 **Disclosure statement:** the authors declare that they have no competing interests.

273

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Figures captions

Figure 1. a) Visible light photography of the painting, the spots measured by XRF are indicated as red circles and sampling areas as blue squares; b) UV fluorescence image, highlighting restored areas. A curious yellow fluorescence is visible in the upper left corner near the trees.

Figure 2. Images of the cross-sections under visible (left) and UV light (right): a-b) sample no. 2; c-d) sample no. 3; e-f) sample no. 4. The double white ground was applied directly on the wooden panel, which was overlayed with thin paint layers.

Figure 3. a) Cross-section of sample no. 1; b) Raman spectra on the blue and ground layers: the presence of titanium white is detected (peaks highlighted by the grey bands), as well as barium sulfate (989 cm^{-1}), calcium carbonate (1085 cm^{-1}), ultramarine blue (545 cm^{-1}).

Figure 4. Timeline of the overall results: the identified materials with their earlier date of commercialisation and the dating found for the panel are inconsistent with Ruyscher's lifetime. The red line indicates the theoretical *terminus post quem*.



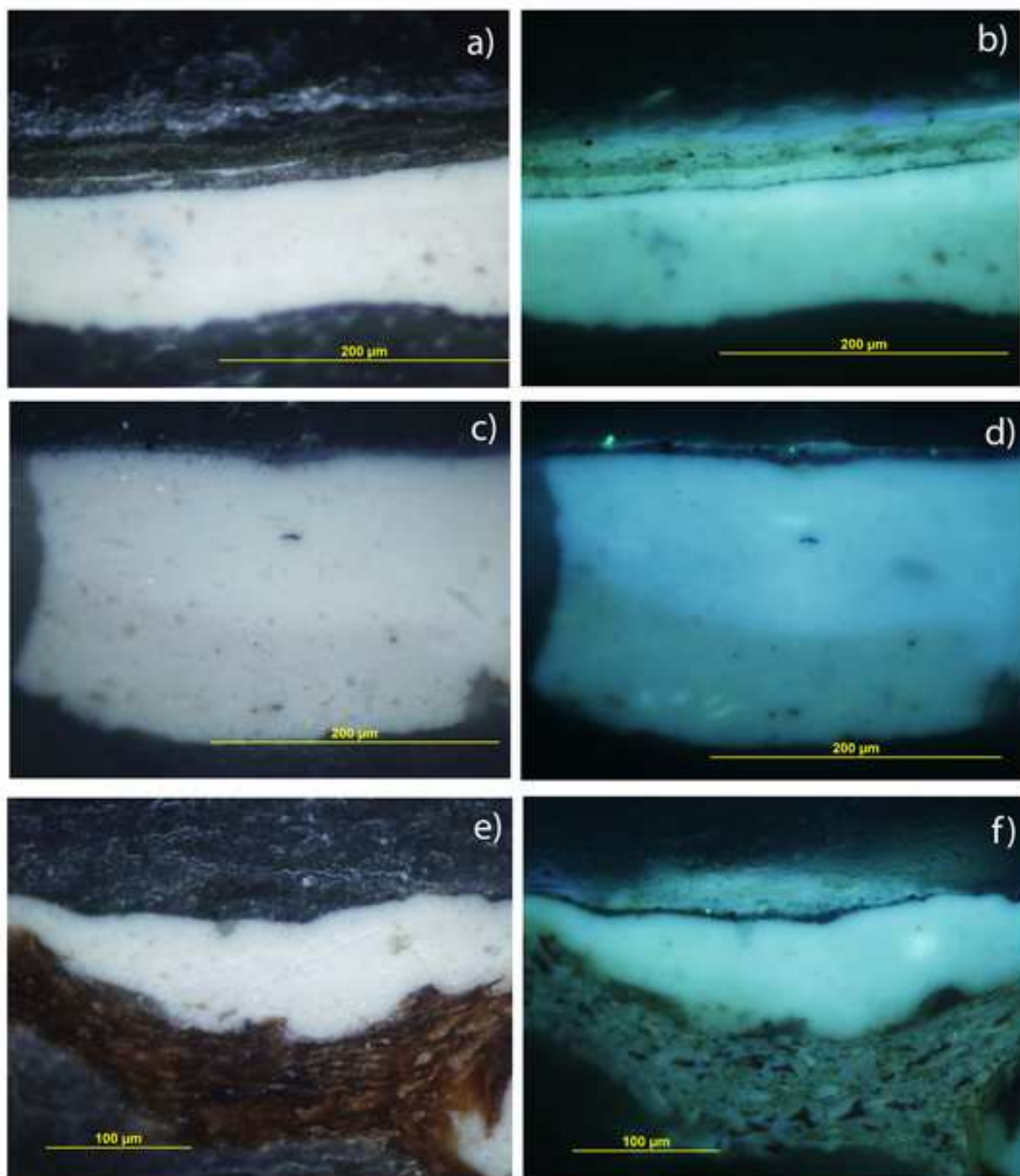
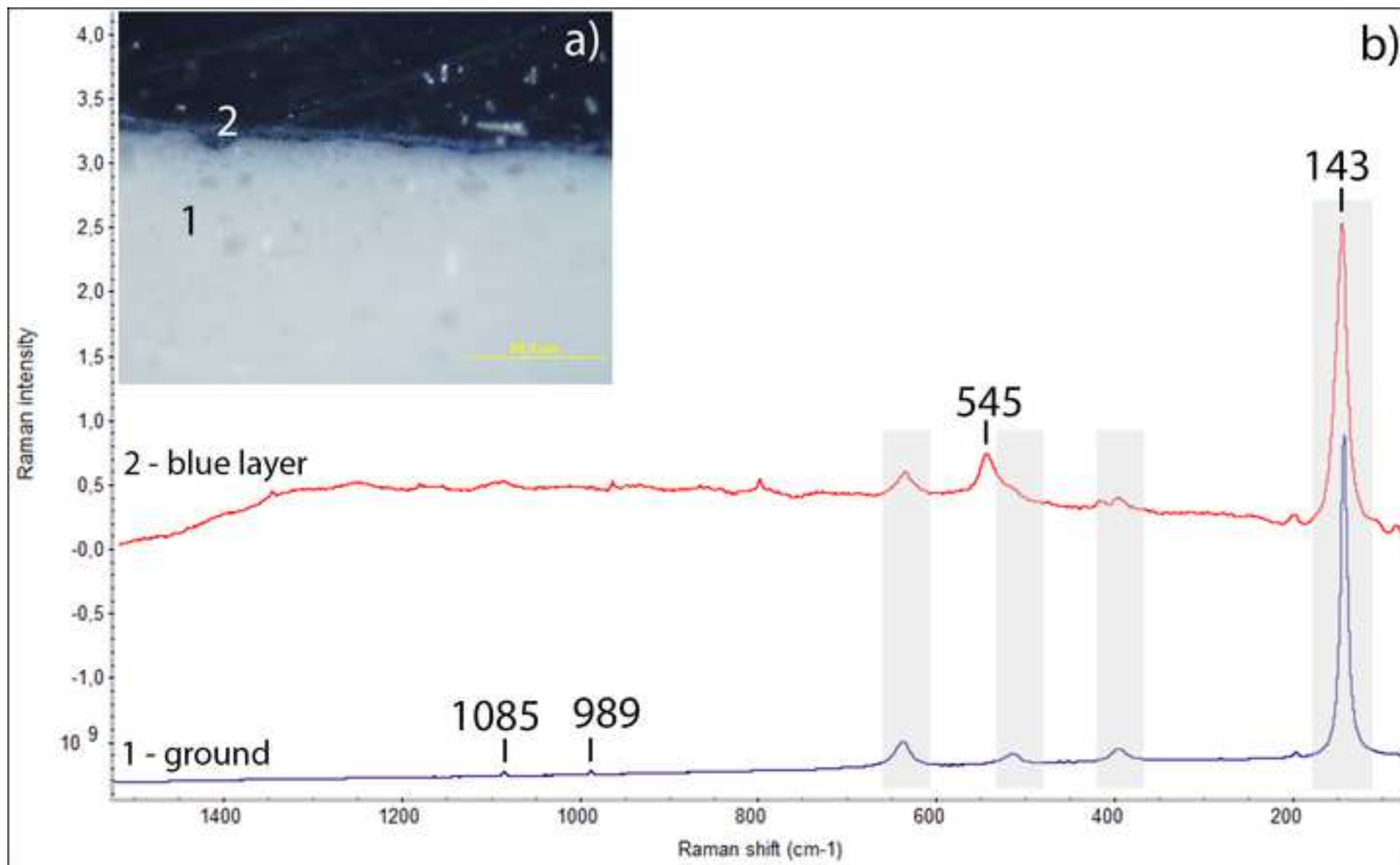


Figure 3



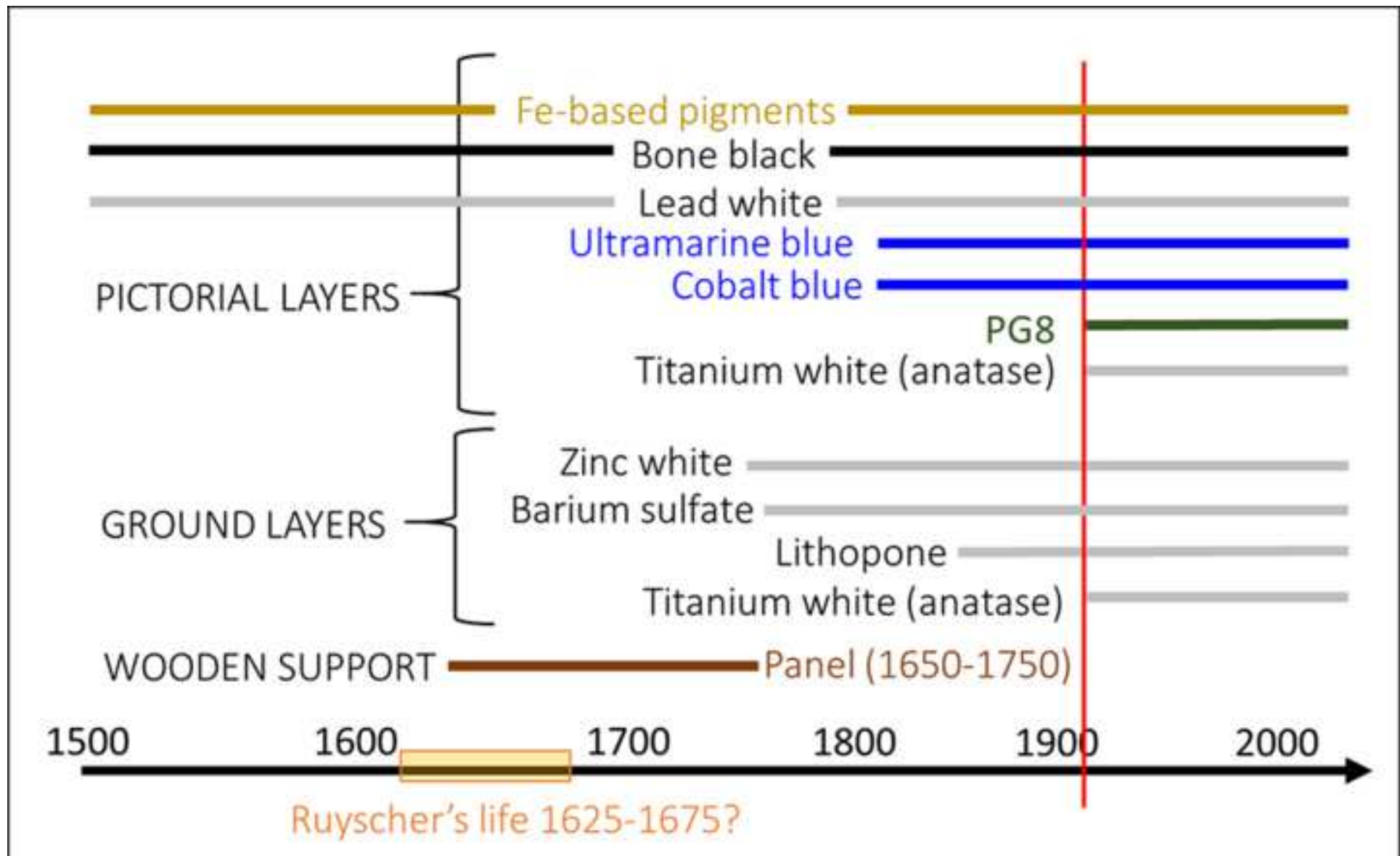


Table 1

Table 1. The results of SEM-EDS (small amount in brackets), FTIR (cm⁻¹) and Raman microscopy (cm⁻¹) on the colours analysed on the painting.

	Colour, sample	Method	Laboratory data	Interpretation
Pictorial layers	Blue (samples 1-4)	SEM-EDS	Na, Al, Si, S, K, Fe, Ti, Ca, Zn, (Pb)	ultramarine blue ^{a)} , earth pigments, titanium white, lead white, zinc compounds ^{b)}
		FTIR	2925, 2850, 1730	drying oil
			1650, 1450, 1410, 875, 855	calcite, aragonite
			1535, 1398	zinc carboxylates
			~1000	silicates/ultramarine blue ^{a)}
		Raman	1085	calcite
			140, 390, 515, 635	titanium white (anatase)
	545		ultramarine blue ^{a)}	
	Green (samples 2)	SEM-EDS	Ca, P, Ti, Fe, Zn	earth pigments/ possible green earth, titanium white, bone black, zinc white ^{b)}
		FTIR	1650, 1470, 1450, 1410, 876, 852	calcite, aragonite
			1175, 1105, 1067	barium sulfate ^{c)}
		Raman	143	titanium white (anatase)
	Brown (sample 4)	SEM-EDS	Mg, Si, Al, P, Ca, Ti, Fe, Zn, (Pb)	earth pigments, bone black, zinc white ^{b)} , lead white
FTIR		-		
Raman		1330, 1600	carbon-based black	
Restoration materials	Yellow (sample 3)	SEM-EDS	Al, (Si), S, Cd, Ca, Ti, Ba, Fe, Zn	titanium white, cadmium yellow ^{d)} , barium sulfate ^{c)} , yellow ochres, calcium compound, zinc white ^{b)}
		FTIR	143	titanium white (anatase)
	Green (sample 3)	SEM-EDS	C, Al, Si, S, Ca, Ti, Ba, (Zn)	titanium white, barium sulfate ^{c)} , zinc compound ^{b)} , calcium compound, silicates, possible organic colourant
		FTIR	-	
		Raman	1075, 1146, 1298, 1504, 1585	Pigment Green 8
	Varnish (all samples)	FTIR	2917, 2846, 1730	drying oil
			1650, 1485, 1085, 1060, 841, 757	Laropal A81
Ground	White ground (common to all samples)	SEM-EDS	S, Ca, Ba, Ti, Zn	calcium compound, barium sulfate, titanium white, zinc compound ^{b)}
		FTIR	2920, 2850, 1730	drying oil
			1650, 1470, 1450 1410, 872, 855	calcite, aragonite
			1180, 1107, 983	barium sulfate ^{c)}
		Raman	143, 395, 510, 640	titanium white (anatase)
			1085	calcite
989	barium sulfate ^{c)}			
Pigments commercialisation (Eastaugh, Walsh, and Chaplin 2004): a) first half of the 19 th century; b) mid-18 th century as the first attempts to use zinc oxide, marketed in 1834 but only successfully produced in France in 1845 and in other countries after 1850, while lithopone became commercialised in 1874; c) 1782; d) in the 1840s.				

Supplementary Materials

The rediscovery of Jan Ruyscher and its consequence

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Supplementary Material 1. Samples preparation

Treatment and preparation of samples collected for radiocarbon analysis and materials characterisation.

Supplementary Material 2. Radiocarbon data

Table S-1. Radiocarbon results including ETH code, respective ring number, measured ¹⁴C age and uncertainty and the corresponding calibrated time interval.

Figure S-1. Wiggles-matched calibration of the ¹⁴C ages obtained from the wooden panel.

Supplementary Material 3. Pictorial layers: cobalt compounds

Figure S-2. XRF spectrum collected on spot no.1, corresponding to the blue sky.

Figure S-3. Analysis on a particle on sample no. 3, suggesting the presence of cerulean blue.

Supplementary Material 4. Pictorial layers: cadmium yellow

Figure S-4. Cross-section of sample no. 3, corresponding to a retouched area.

Figure S-5. SEM-EDS analysis on the final green layer: cadmium was identified.

Figure S-6. A second area analysed on the green layer.

Supplementary Material 5. Varnish investigation.

Figure S-7. FTIR analyses on the ground and the varnish.

Supplementary Material 6. Ground layer.

Figure S-8. Cross-section of sample no. 3 and SEM and FTIR analyses.

Supplementary Material 1. Samples preparation

Radiocarbon samples

The preparation procedure involved first a soxhlet cleaning treatment with chloroform, hexane, acetone and ethanol (Bruhn et al. 2001) before the standard acid-base-acid (ABA) protocol was applied (Hajdas et al. 2004; Hajdas 2008). The cleaned material was converted to graphite using the fully automated graphitization unit AGE (Wacker, Němec, and Bourquin 2010).

Pictorial samples

The four cross-sections were obtained by embedding the samples in KBr pellets (the sample is placed on top of a KBr pellet obtained with 300 mg of KBr pressed at 2 tons for 30 seconds, the powder of 300 mg of KBr is added over the sample and it is pressed at 3 tons for 120 seconds). Afterwards, the pellet is embedded in polyester resin. The sample is then dry polished with Struers Silicon Carbide Paper (120, 500, 800, 1000) and Micromesh Carbide Paper (4000, 8000, 12000), decreasing the grit size until reaching the polished cross-section (Prati et al. 2012).

Supplementary Material 2. Radiocarbon data

Table S-2. Radiocarbon results including ETH code, respective ring number, measured ^{14}C age and uncertainty and the corresponding calibrated time interval.

ETH code	Ring Nr.	^{14}C Age [yrs BP]	Calibrated time range interval	
88451	90	230 ± 23	1641	1665
88450	64	204 ± 57	1667	1691
88644	50	148 ± 16	1681	1705
88449	40	144 ± 23	1691	1715
88643	25	121 ± 22	1706	1730
88448	10	215 ± 58	1721	1745
88447	1	177 ± 21	1730	1754

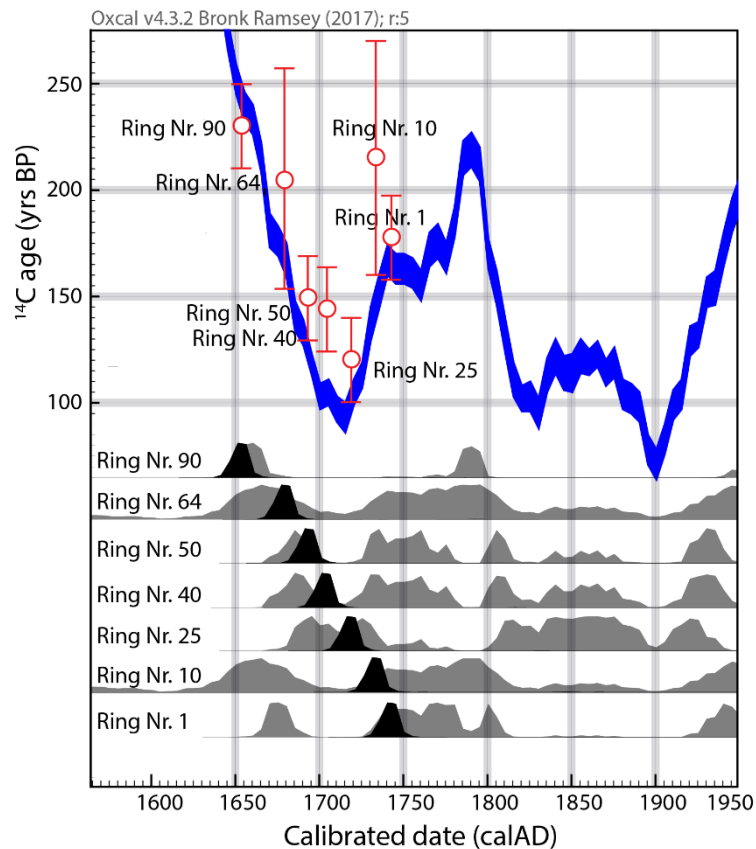


Figure S-1. Wiggle-matched calibration of the ^{14}C ages obtained from the wooden panel. The top part of the figure shows the ^{14}C measurement (red circles, error bars indicate 1σ) plotted against the calibration curve IntCal13 (blue). By knowing the number of rings (i.e. years) between each sample, the measured data, expressed in years before present (yrs BP), can be adjusted to the curve and converted to calendar years on the x-abcise. The lower part of the figure represents the probability distribution of a single date calibration (grey histograms), each point is individually calibrated and results in a large time window covering the mid-17th to 20th century. By wiggle-matching the data, i.e. incorporating the year difference between the samples as boundary condition, a much better fit is gained as displayed by the final black histograms.

Supplementary Material 3. Pictorial layers: cobalt compounds

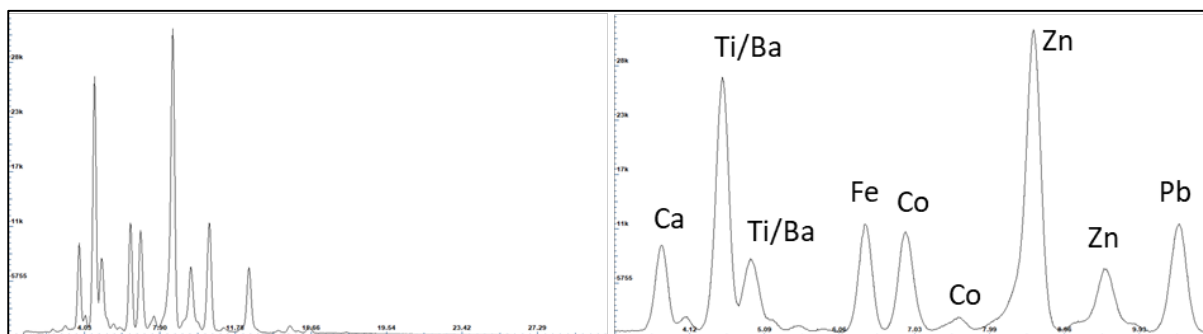


Figure S-2. a) XRF spectrum collected on spot no.1 (Figure 1a), corresponding to the blue sky; b) magnification of the range 3-10 keV, the presence of cobalt is detected (K α 6.92 and K β 7.60). Cobalt blue is then suggested.

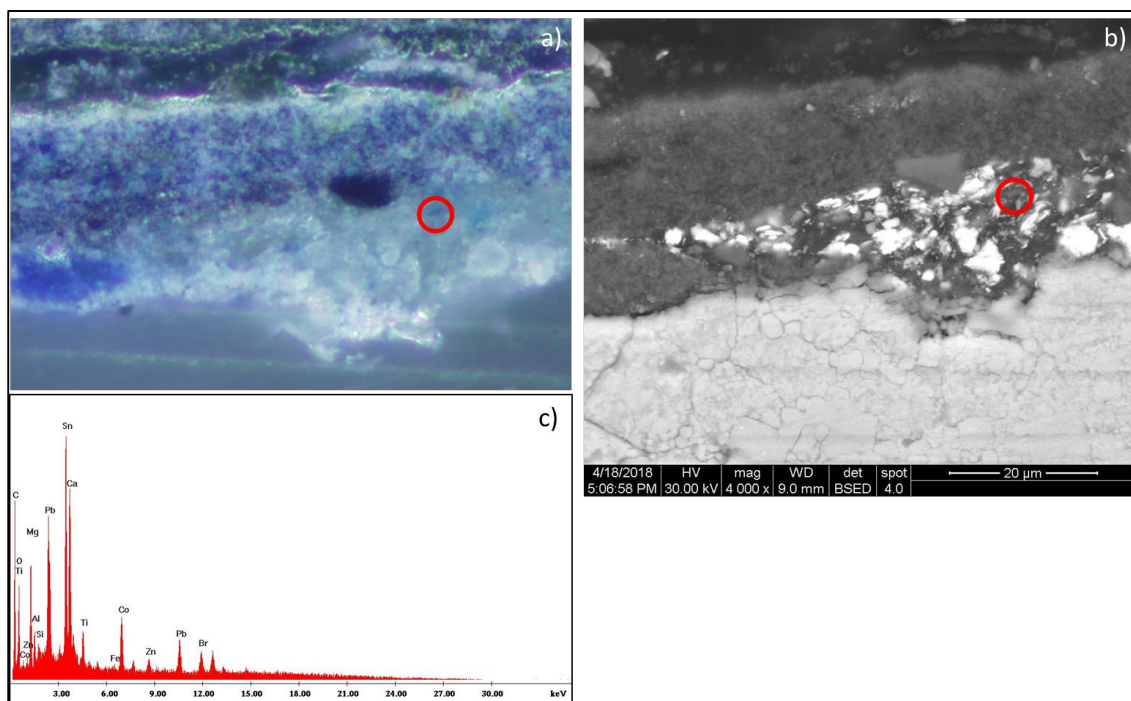


Figure S-3. Analysis on a light blue layer of sample no. 3 (retouched area): a) image of the cross-section, the red circle indicates the spot analysed, corresponding to a bluish particle; b) SEM-BSE image, the particle analysed appears grey; c) SEM spectrum: Sn and Co are identified, among other elements. This is the only layer where these two elements are found together, thus suggesting the presence of cerulean blue. However, only two particles contain Co and Sn are found, therefore they are probably an impurity and not considered to be representative.

Supplementary Material 4. Pictorial layers: cadmium yellow

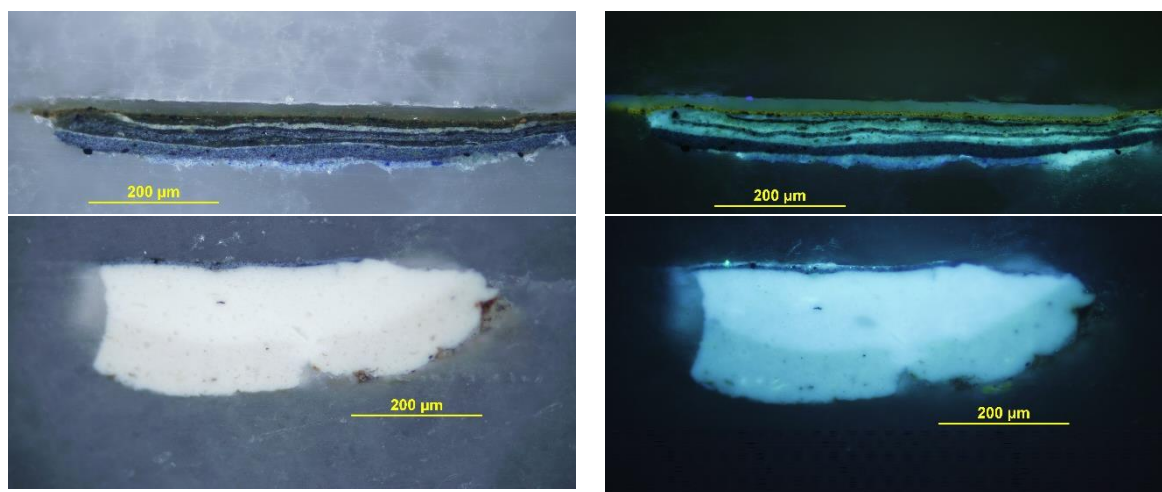


Figure S-4. The sample no. 3, collected on the retouched area at the left side of the painting, broke in two pieces, possibly due to the many retouched layers not adhered to the original blue pictorial one. Both fragments were embedded and studied in cross-sections. The bottom part shows the double ground and a single blue pictorial layer, whereas the upper part contains many thin layers of various composition.

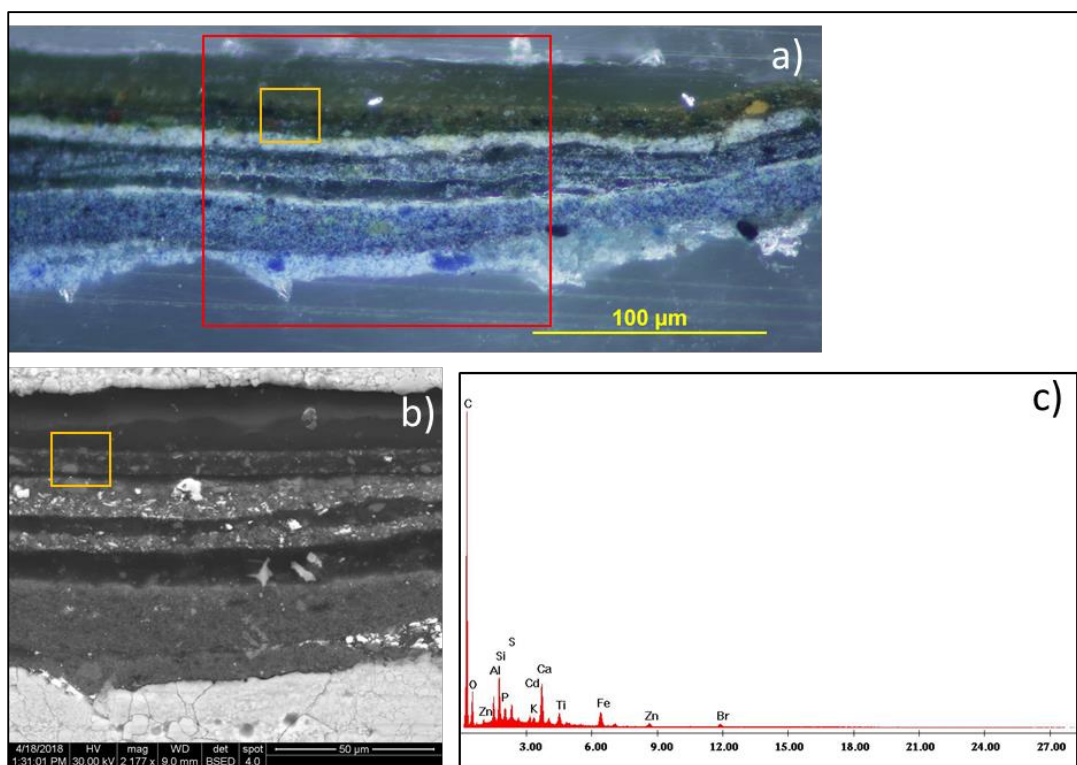


Figure S-5. a) Cross-section of sample no. 3; b) SEM-BSE image of the area indicated by the red square in a); on both a) and b) the yellow square indicates the area of analysis; c) SEM-EDS spectrum: cadmium was identified.

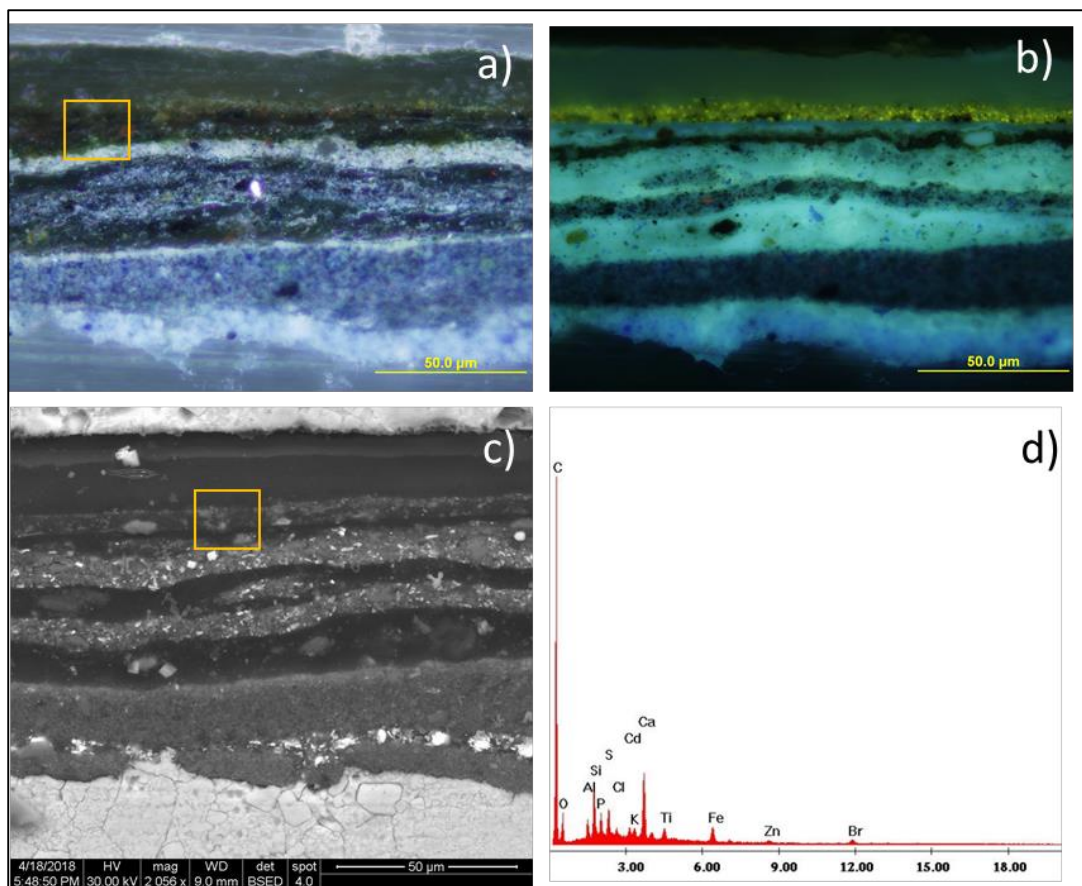


Figure S-6. SEM-EDS analysis on a second area of sample no. 3.

Supplementary Material 5. Varnish

The thick varnish applied as a final layer on the samples is identified as Laropal A81 resin (Getty Conservation Institute 2007) (Figure S-7), which is a low molecular weight urea-aldehyde resin, developed by BASF (Badische Anilin- und Soda Fabrik) in the 1990s, as substitute for ketone resins, such as Laropal K80, due to their tendency for auto-oxidation (de la Rie and Shedrinsky 1989; de la Rie and McGlinchey 1990). Laropal A81 can be used as a varnish (Arslanoglu and Learner 2001) or as a binding medium for retouched paint areas, due to its stability as well as optical and working properties. Its commercialisation began at the beginning of the 21st century (de la Rie et al. 2000; Leonard et al. 2000).

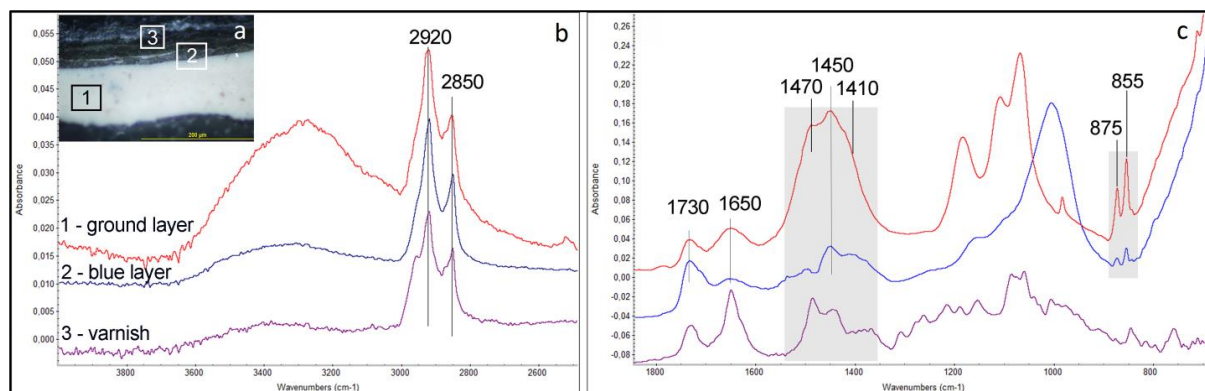


Figure S-7. a) Cross-section of sample no. 2, the areas analysed are indicated by squares: 1) for the white ground, 2) blue pictorial layer and 3) varnish; b- c) FTIR spectra indicating the omnipresence of calcite (1650, 1410, 875 cm⁻¹) and aragonite (875, 1450, 1470 cm⁻¹) through the paint layers. 2920, 2850, 1730 cm⁻¹ are related to the lipid binder, the peaks in the range 1200-900 in the ground are linked to barium sulfate and the band at around 1010 cm⁻¹ in layer 2 is associated to ultramarine. The varnish is identified as Laropal A81.

Supplementary Material 6. Ground layer

The double ground shows a lower off-white layer and an upper pure white one (Figure S-8). SEM images do not show any discontinuity between the two layers, indicating that they were painted at the same time. SEM-BSE spectra are also similar on the areas analysed. Under UV light, a difference can be seen. This may be due to a higher concentration of lipid binder in the lower layer, which shows a yellow UV fluorescence, although the FTIR spectra are also similar.

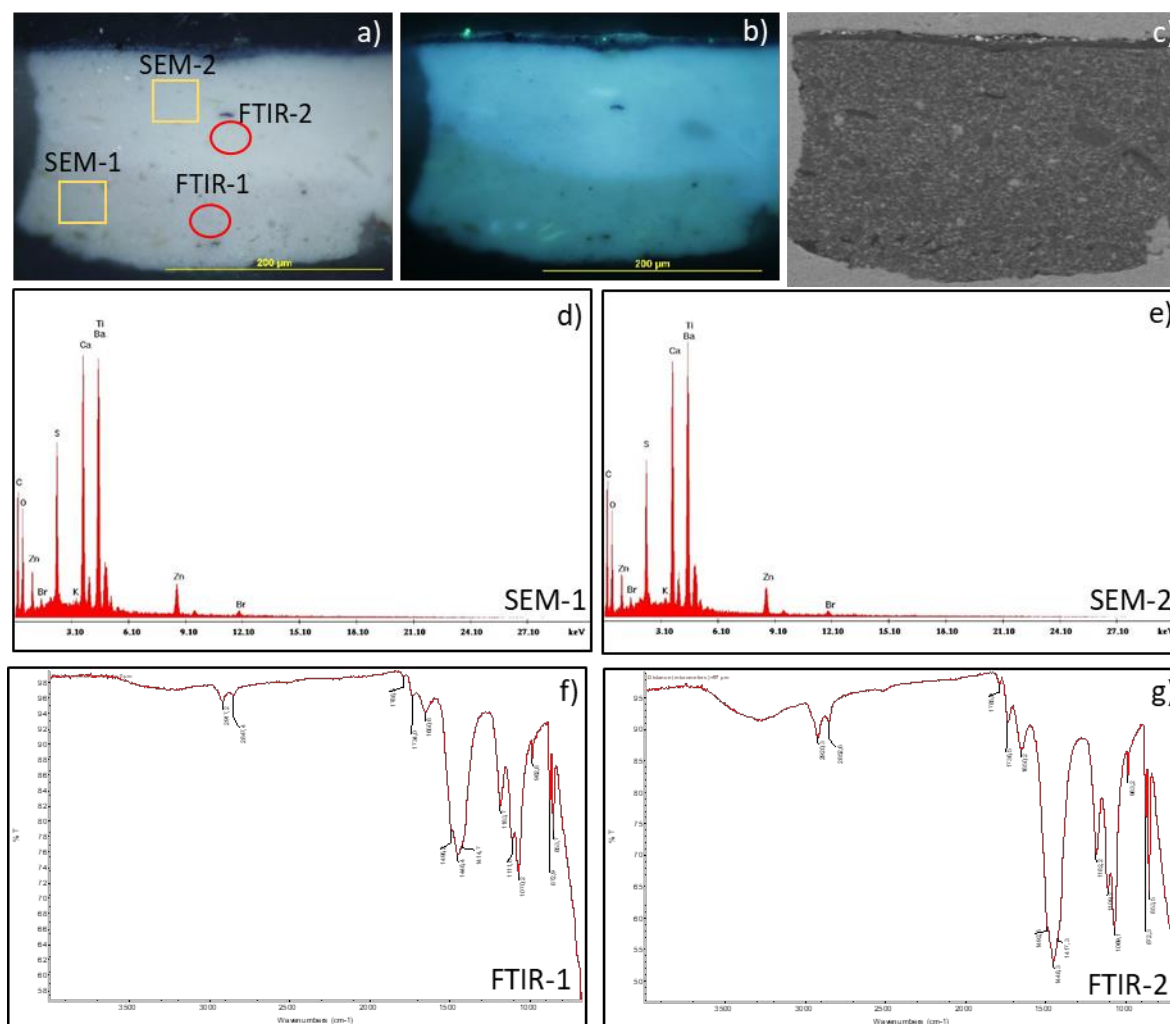


Figure S-8. a) Cross-section of sample no. 3 (original part), areas of SEM and FTIR analyses are indicated with yellow squares and red circles, respectively; b) cross-section under UV light; c) SEM-BSE image; c-d) SEM-BSE spectra collected on the areas indicated in a; f-g) FTIR-ATR spectra.

Moreover, calcium carbonate is characterised by FTIR as calcite ($\sim 1410, 872 \text{ cm}^{-1}$) (Figure S-7), mixed with another type of carbonate with a predominant band at 1450 and a second one at 855 cm^{-1} , found in aragonite polymorph calcium carbonate (Shafiu Kamba et al. 2013; Mohd Abd Ghafar et al. 2017; Islam et al. 2012), the absorption at 1470 is also related to aragonite (Andersen et al. 1991) and the one at 1650 cm^{-1} can be associated to the C=O stretching vibration of carbonates (Ismail et al. 2016).

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