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The rediscovery of Jan Ruyscher and its consequence

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The rediscovery of Jan Ruyscher and its consequence

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Abstract

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

Despite a prestigious career, Ruyscher, who possiblywas 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 tomultispectral 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 panelindicated that the tree was probably cut down in the mid-18th century, whereasspectroscopic analyses pinpointed the 20th century as a timeframe for the application of the pictorial layers. The applied methodologyshed 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, andthe 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.

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

1. Introduction

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

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

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

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

This rather controversial situation canbe solvedwith the help of scientific analyses, which provide objective data to unravel the nature of the object. A preliminary dating of the object was pursued by dendrochronology but following inconclusive results the panel was further dated by ^{14}C analysis.

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

2. Materials and Methods

2.1. Object of study

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

Several samples were collectedfrom the wooden support for radiocarbon datingand from the painting surface tocharacterize the palette (Supplementary Materials 1-2).

2.2. Methods

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

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

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

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

FTIR analyses were performed with an iN^{TM}10MX Nicolet microscope (Thermo Fisher Scientific, Waltham, MA, USA) coupled to a mercury cadmium tellurium (MCT) detector inattenuated total reflection (ATR) mode(conical crystal germanium). The spectral range is from 4000 to 675 cm^{-1}, the spectral resolution 4 cm^{-1} and 64 scans were acquired.

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

3. Results

3.1. Radiocarbon dating of the support

Upon calibration, the measured ^{14}C agescorresponded to the period between the 16thand 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 ^{14}C dates, the sequence of sampled tree rings can be wiggle-matched to the calibration curve IntCal13, hereby overcoming themultiple age possibilitiesfrom 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 17thand the mid-18th centuries.

3.2. Materials characterisation

Preliminary documentation with multispectral imaging determinedanoverall 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 areaswere observed and a peculiar bright yellow fluorescence colour on the trees at the left side wasdetected. On the back of the panel, an inscription, clearlyvisible under UV light, links the object to Jan Ruyscher.

Pictorial layers. In all tested locations,the XRF identification of titanium, barium and zinc suggests ageneral use oftitanium white, barium sulphate and zinc oxide (zinc white) or zinc sulfide (which, inassociation with barium sulfate, is characteristic of lithopone). These white pigments were introducedto the art market fromthe 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 layerscontainingfine 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 onvarious 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.Thepigment responsible for the green hue of

sample no. 2 was not identified.The presence of iron may hint tothe 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 particlesare found, likely to be ochres and possiblycontributing 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 likelyindicative of lead white, wasalso 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 yellowishretouched area on the trees (sample no.3)consists of yellow ochres,likely cadmium yellow (Supplementary Materials 4) and azinc species, probablyzinc white due to the intense and characteristic UV fluorescence. The green layer containsPigment Green 8 (PG8, nitroso green, *Colour Index* 10006). However, it is unclearwhether this fragment represents anarea of original material or a reworkedzone. The thick varnish found on all samplesis 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 ispure 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 ofzinc revealed by the SEM-EDS spectracan be associated to zinc oxideor zinc sulfide. The S peak also detected in the SEM-EDS spectra can relate either tothe 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 pigmentsare 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

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

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

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

While the too young support and pigment anachronisms strongly contradict a Ruyscher attribution, the forger in question put a lot of effort in making the object look authentic: recent inscriptions on the back of the panel, in chalk (*Ruischer*) and in red felt-tip (*Jan Ruyscher*), complement a copper plaque nailed to the frame with the note *Jan Ruischer, 1625 - 1675*. Badging the reverse of an object with inscriptions, stamps and dates to make the object look older than in fact it is, is a trick that forgers commonly use.The intention of deceit is hereby evident inthe re-use of asupport with the aim to create the impression ofan older aspect to the object, which is to be classified as an act of fraud.The re-use of a support is a common *modus operandi* among forgers, to which many,such Beltracchi or Van Meegeren,have confessed. Unfortunately, few studies are published about forgers' palettes, therefore a comparison to a known forger revealed itself laborious. Was this particular forger ofRuyschersimply unlucky with the choice of the substrate? Both forgers Joni and van Megeeren were active in the 1930s, could they have authored the*Paysage de montagne*? An attributionto Joni could be excluded as he was an Italian painter specialised in Middle Ages art(Muir and Khandekar 2006), which does not match with an allegedly 17th century Flemish painting, whereas van Meegerentended to usehistorical pigments and create a convincing craquelure, thus showing a level of sophistication in the elaboration of the fraud(Held 1951). The use of titanium white over the entire painting shows poor art historical knowledge, which strongly contrasts with Beltracchi's style using only a reduced palette of pigmentsthat he knew to be historically correct, and who furthermore mostly painted artfrom the 20th century.The build-up of anachronistic features in all layers of the object present similarities with the Trotter forgery case(Smith et al. 2012), which was marked by the omnipresence of titanium white in the ground layer and many anachronistic colourants such as phtalocyanine green.Radiocarbon analysis of the support and pictorial layer revealedthe forger's scheme in recycling an appropriately aged canvas to convey the illusion of authenticity(Hendriks et al. 2019). Trotter, who specialised in forged American primitives,was active in the late 1990s and as the FBI only located 16 out of the 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 forgerrecycled 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 postulatethat 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 providescritical arguments for the identification of a period of creation of the painting, a possible reconstruction of its history and theclassification 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 layersnumerous material anachronisms indicative of the 19th century were found. However, the most decisive argumentof the painting's date is the presence of titanium white in the ground, indicating that the painting could not have beenexecuted at an earlier datethan 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 anoldsupport, 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 willaid tobetter understand the practice of forgers and potentially avoid the spreading of fakes within the art market.

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Declaration of interest

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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 1

Click here to access/download;Figure;Figure 1.tif

Figure 2

Click here to access/download;Figure;Figure 2.tif

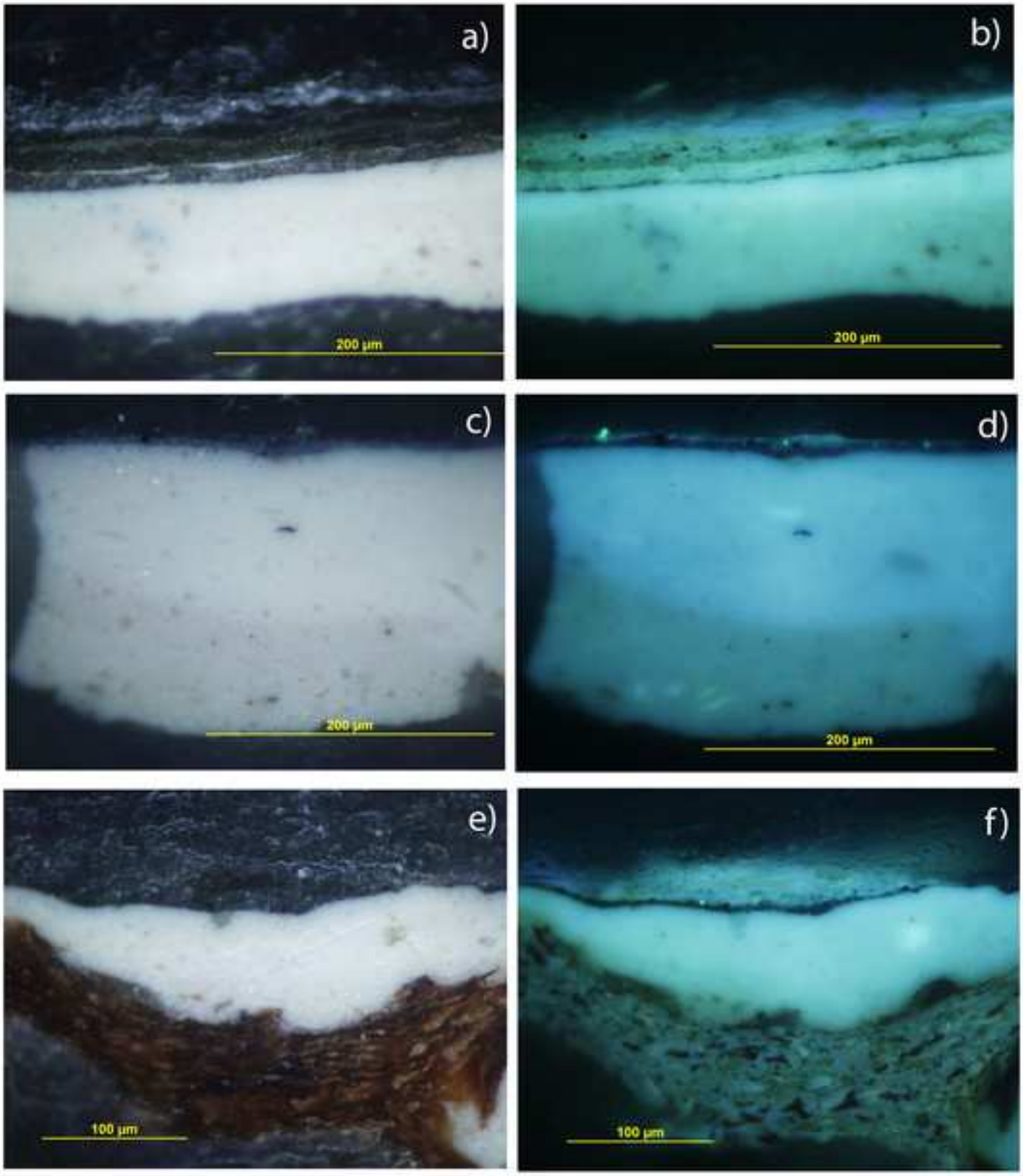

Figure 3

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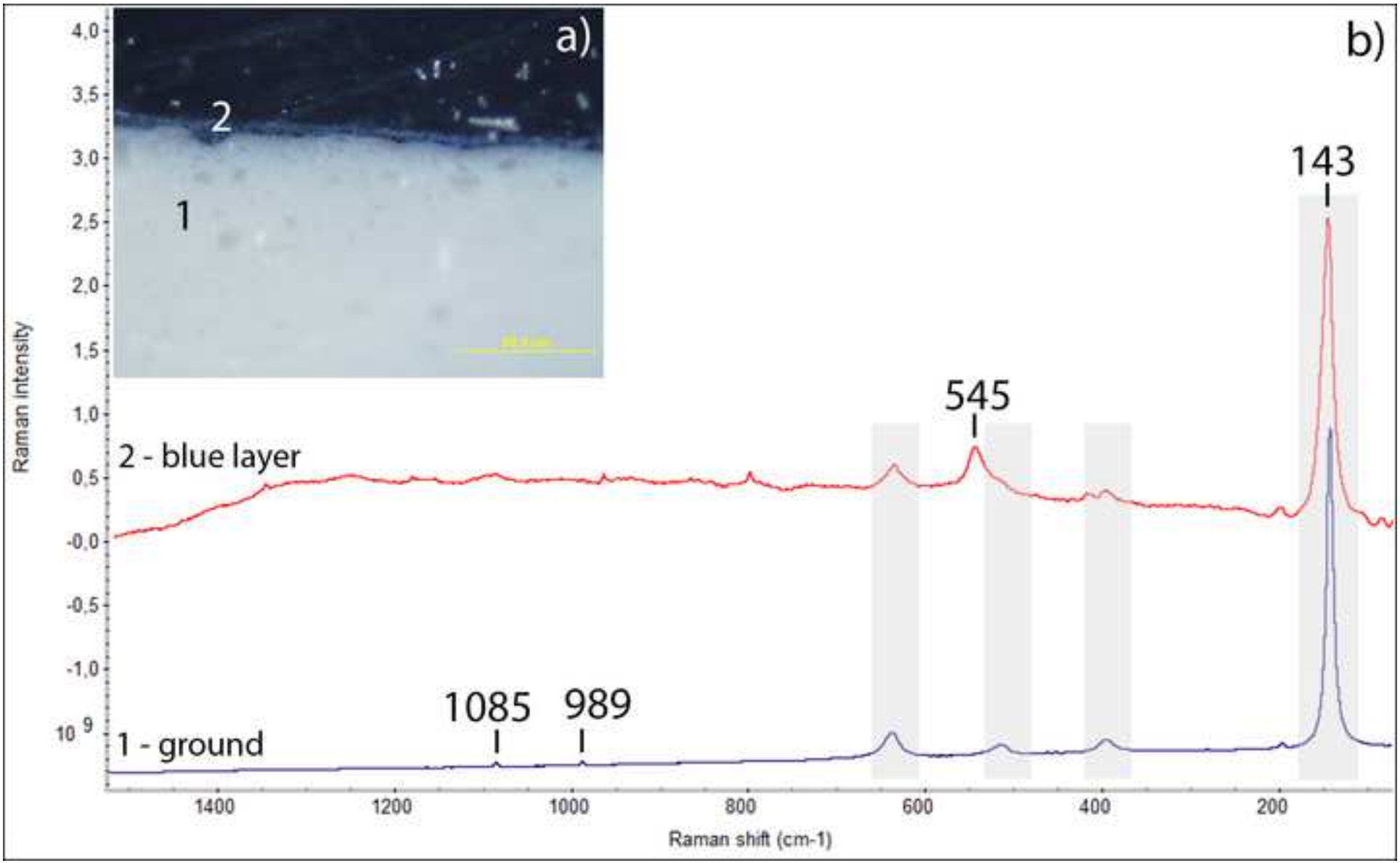

Figure 4

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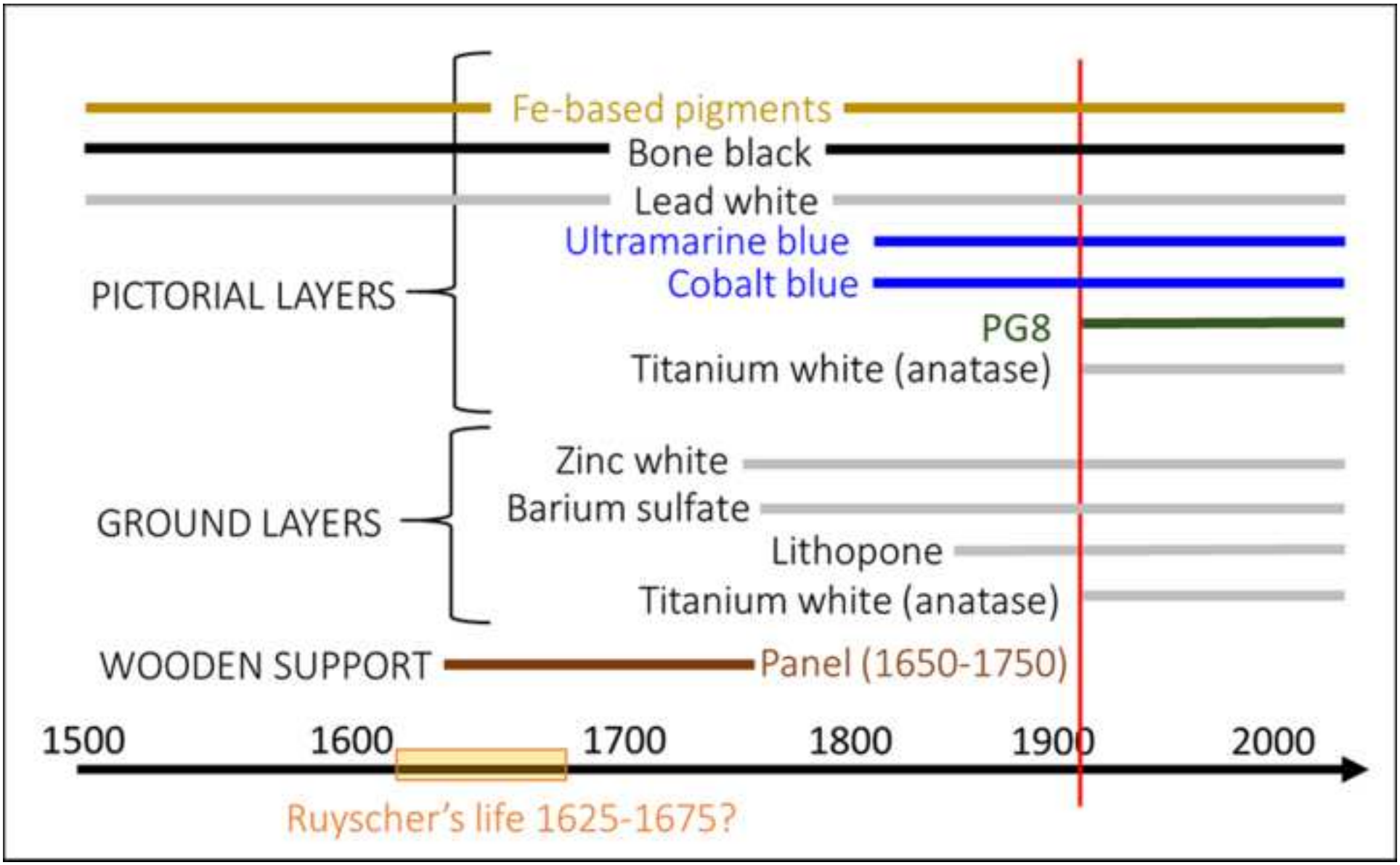

Table 1

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 19th century; b) mid-18th 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 ^{14}C age and uncertainty and the corresponding calibrated time interval.
Figure S-1. Wiggle-matched calibration of the ^{14}C 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

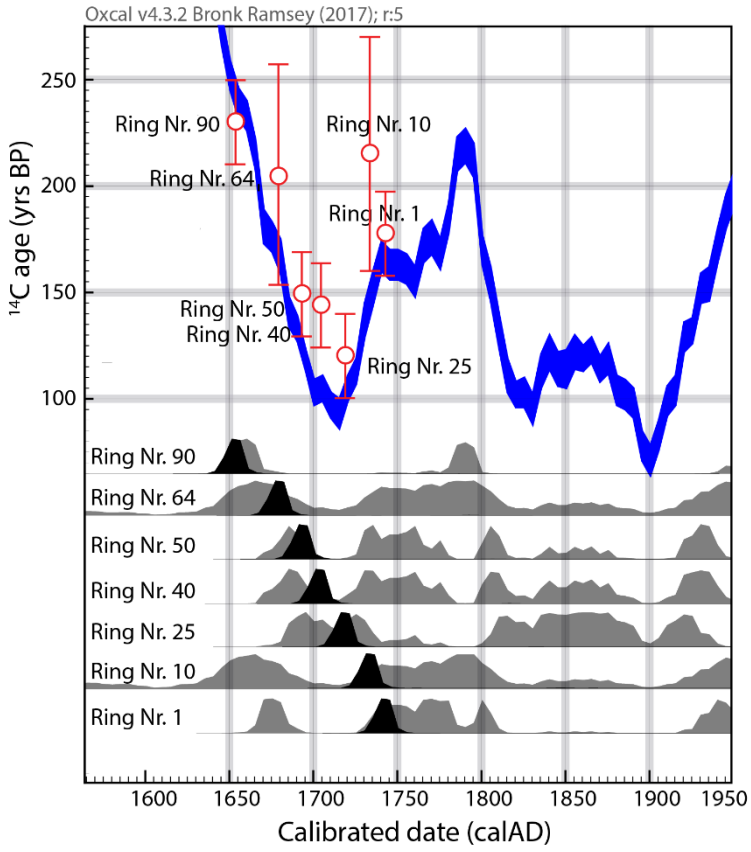

Figure S-1. Wiggle-matched calibration of the ^{14}C ages obtained from the wooden panel. The top part of the figure shows the ^{14}C measurement (red circles, error bars indicate 1σ) plotted against the calibration curve IntCal13 (blue). By knowing the number of rings (i.e. years) between each sample, the measured data, expressed in years before present (yrs BP), can be adjusted to the curve and converted to calendar years on the x-abscise. 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

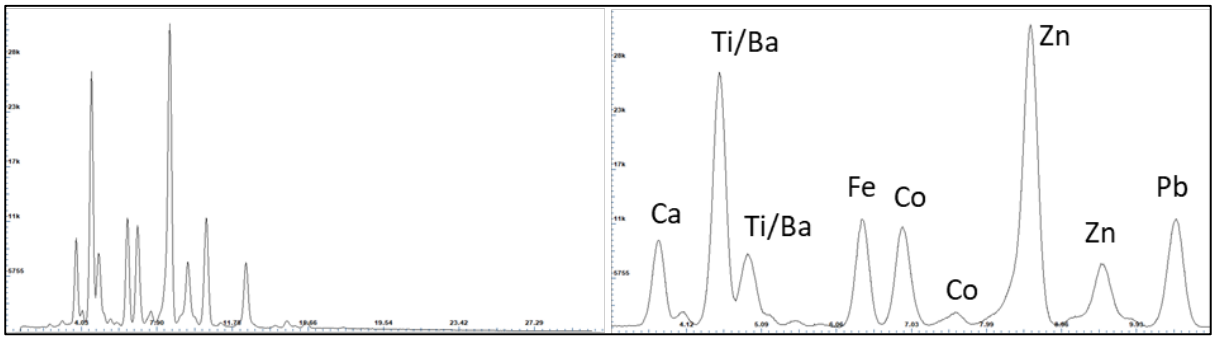

Figure S-2. a) XRF spectrum collected on spot no.1 (Figure 1a), corresponding to the blue sky; b) magnification of the range 3-10 kV, the presence of cobalt is detected (Kα 6.92 and Kβ 7.60). Cobalt blue is then suggested.

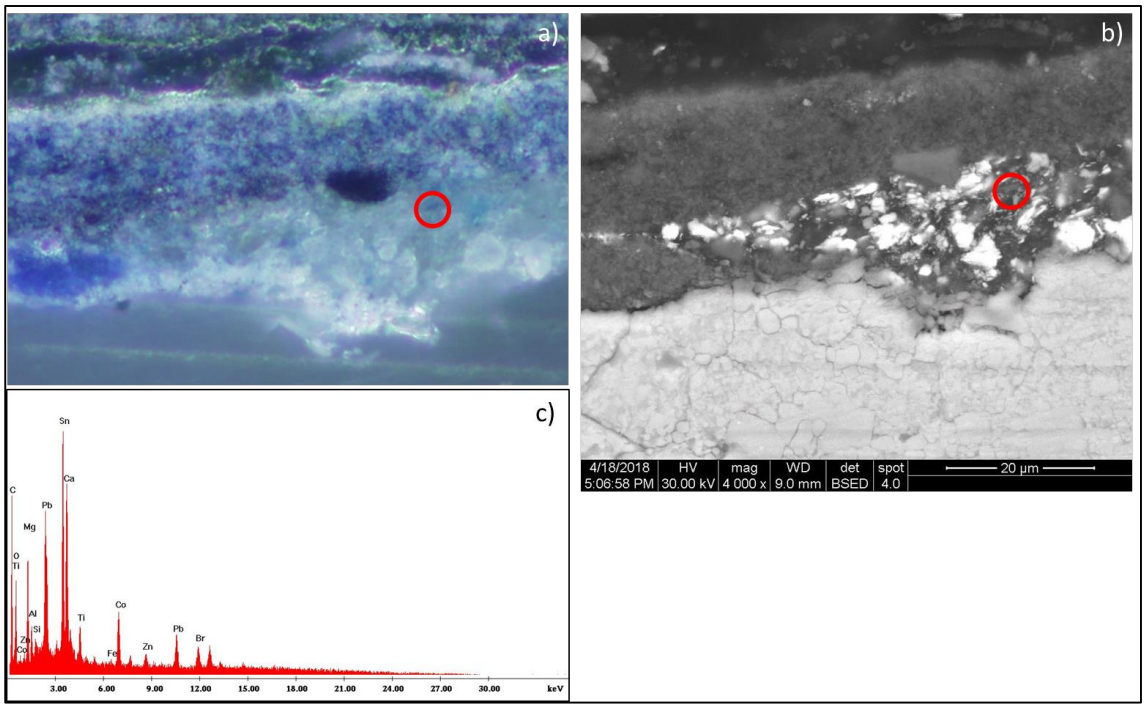

Figure S-3. Analysis on a light blue layer of sample no. 3 (retouched area): a) image of the cross-section, the red circle indicates the spot analysed, corresponding to a bluish particle; b) SEM-BSE image, the particle analysed appears grey; c) SEM spectrum: Sn and Co are identified, among other elements. 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

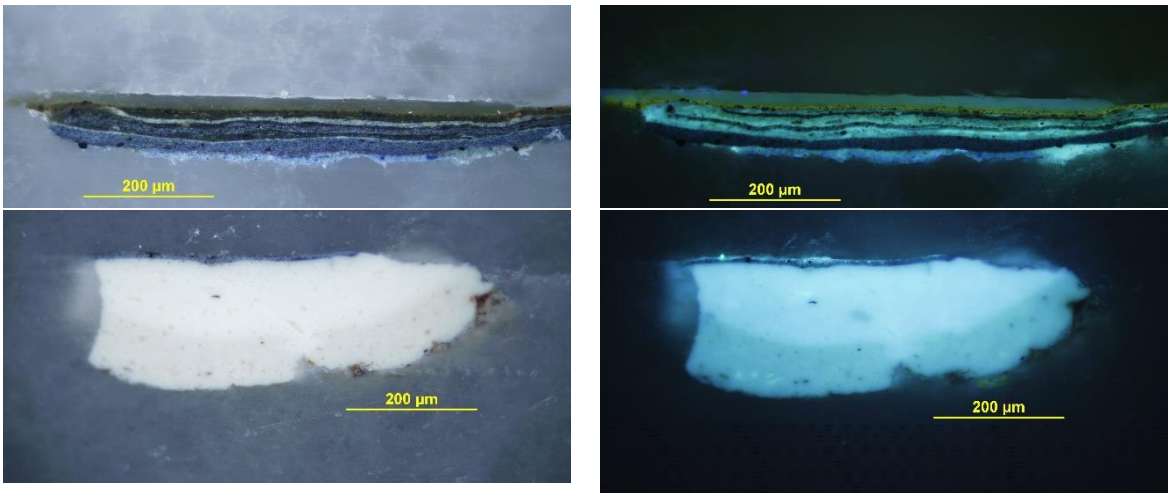

Figure S-4. The sample no. 3, collected on the retouched area at the left side of the painting, broke in two pieces, possibly due to the many retouched layers not adhered to the original blue pictorial one. Both fragments were embedded and studied in cross-sections. The bottom part shows the double ground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

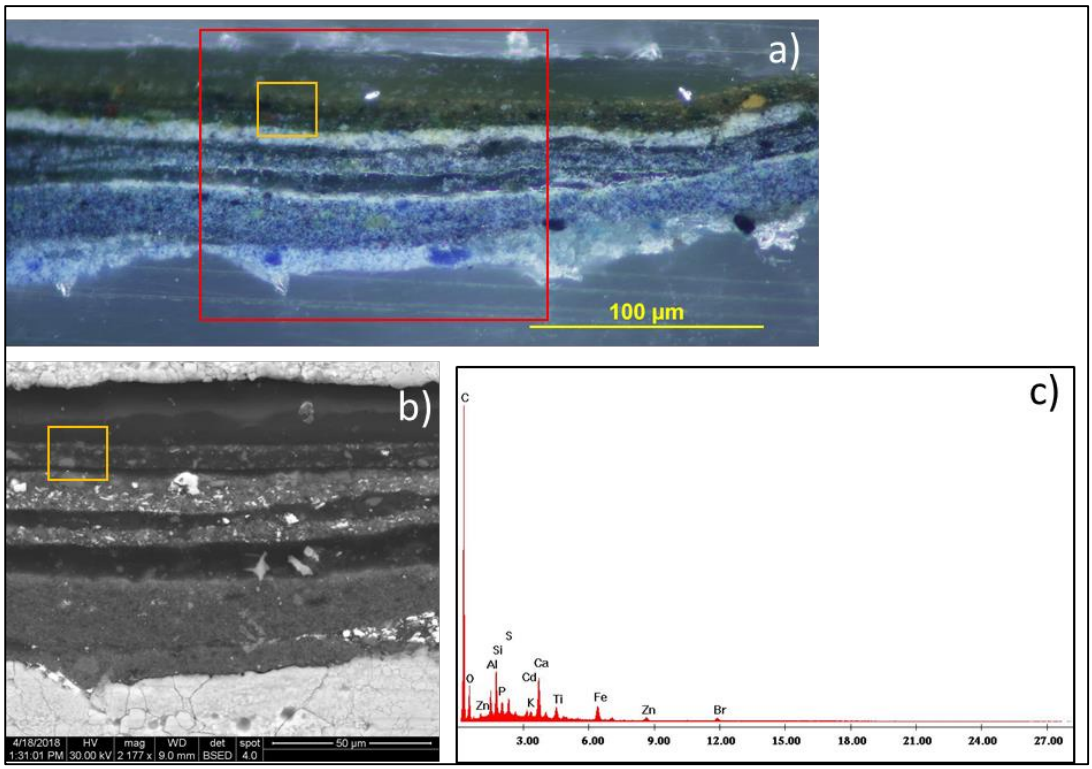

Figure S-5. a) Cross-section of sample no. 3; b) SEM-BSE image of the area indicated by the red square in a); on both a) and b) the yellow square indicates the area of analysis; c) SEM-EDS spectrum: cadmium was identified.

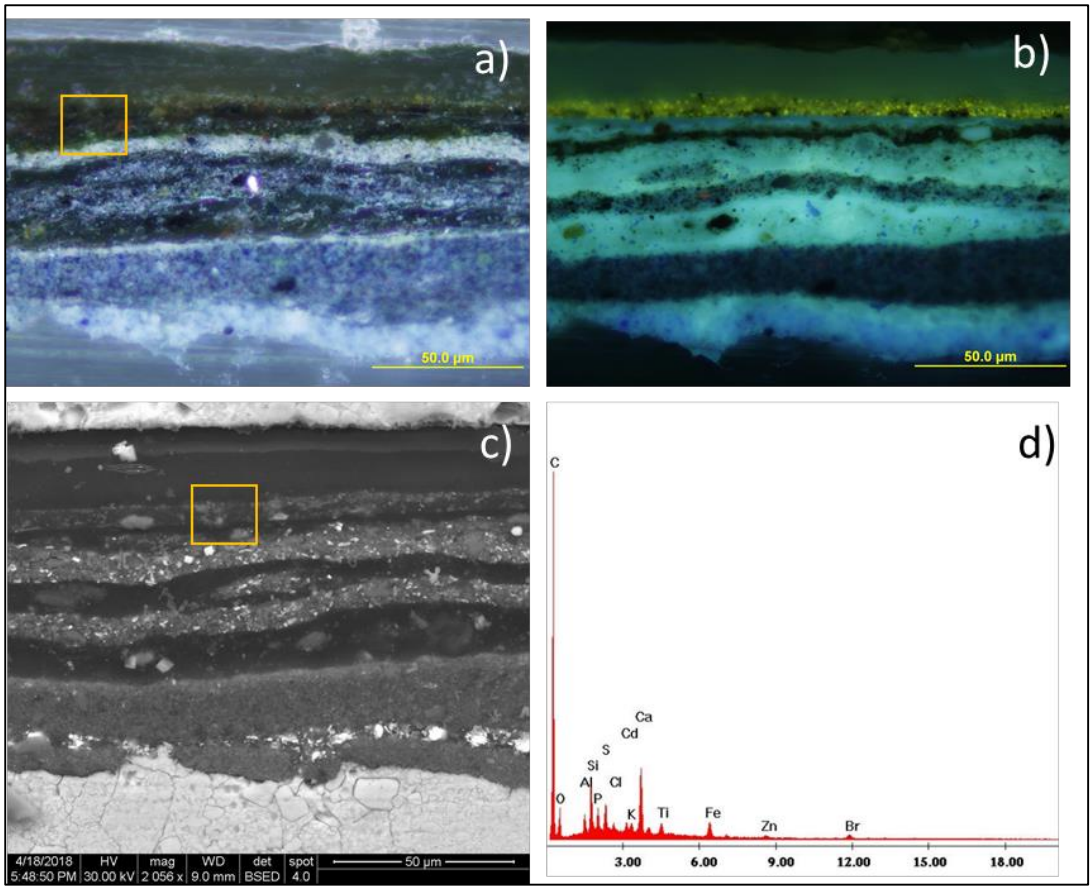

Figure S-6. SEM-EDS analysis on a second area of sample no. 3.

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 21th century (de la Rie et al. 2000; Leonard et al. 2000).

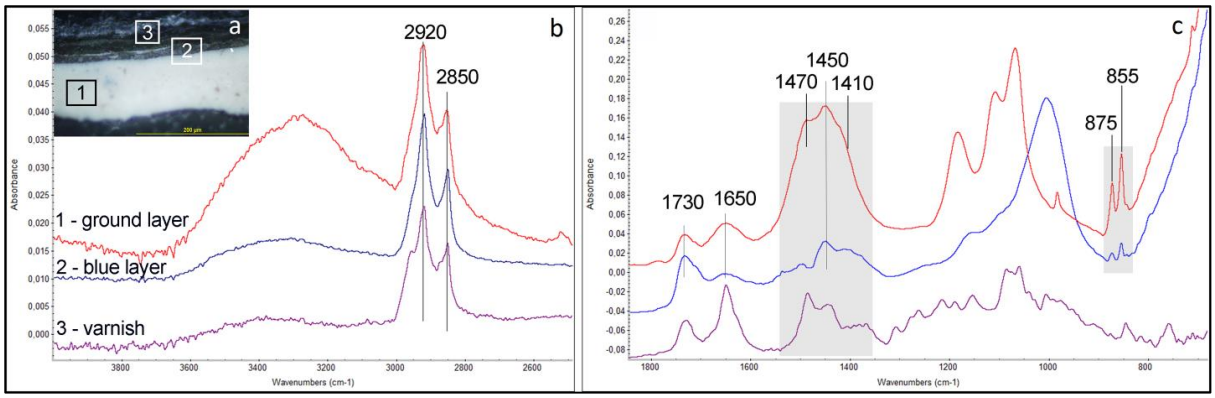

Figure S-7. a) Cross-section of sample no. 2, the areas analysed are indicated by squares: 1) for the white ground, 2) blue pictorial layer and 3) varnish; b- c) FTIR spectra indicating the omnipresence of calcite (1650, 1410, 875 cm^{-1}) and aragonite (875, 1450, 1470 cm^{-1}) through the paint layers. 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.

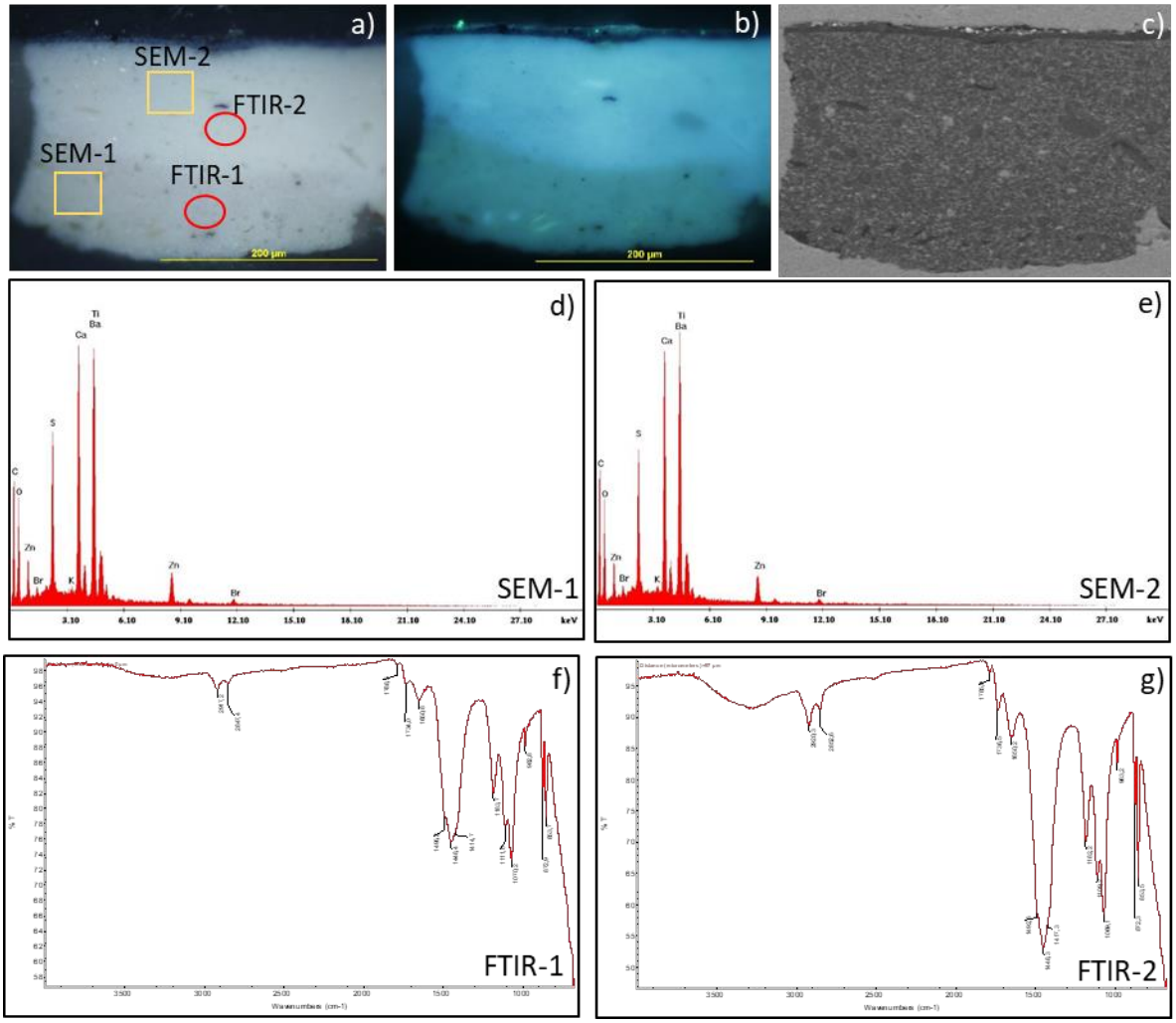

Figure S-8. a) Cross-section of sample no. 3 (original part), areas of SEM and FTIR analyses are indicated with yellow squares and red circles, respectively; b) cross-section under UV light; c) SEM-BSE image; c-d) SEM-BSE spectra collected on the areas indicated in a; f-g) FTIR-ATR spectra.

Moreover, calcium carbonate is characterised by FTIR as calcite (~1410, 872 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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