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Heritage Science

A multi-analytical study of historical coated plaster surfaces: the examination of a nineteenth-century V&A cast of a tombstone

--Manuscript Draft--

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Abstract:	A multi-analytical study was designed to characterise historical coated plaster surfaces. The method was applied to investigate the surface coatings of the nineteenth-century plaster cast of the tombstone of the Presbyter Bruno that belongs to the Victoria and Albert Museum collection. At first, selected samples of the object were examined with Visible Light Reflectance and Ultra-Violet Fluorescence Optical Microscopy (VLR- and UVf-OM respectively) and Scanning Electron Microscopy (SEM) demonstrating a consistent stratigraphy featuring a bulk, an interface and an uppermost layer. The latter layer appeared to consist of an aged coating and dirt. Overpainted and repaired areas of the object generated samples that had additional layers on top of the aforementioned stratigraphy. A layer that seemed to be an additional surface varnish or a coating that had not been absorbed to the bulk has been observed in a couple of samples. Elemental characterization was carried out with energy dispersive x-ray spectroscopy (EDS) and further analyses were performed with x-ray diffraction (XRD) and Fourier-transform infrared (FT-IR) spectroscopy with focal plane array (FPA) imaging which confirmed that the bulk of the object is made of gypsum plaster containing mostly silicate and carbonate inclusions. Gas Chromatography/mass spectrometry (GC/MS) and pyrolysis-GC/MS with extraction methods based on n-propanol followed by pentafluoropropionic anhydride (PFPA), tetramethylammonium hydroxide (TMAH) and 3-trifluoromethylphenyltrimethylammonium hydroxide (m-TFPTAH) were performed to detect organic media. The results suggest that the organic medium used for the surface coating is a diterpenic resin that contained silicon, aluminium and traces of other inorganic elements. The organic medium of overpainted areas was based on alkyd resins and the in-paints were characterised as a blend of silicon and barium at varied concentrations. This multi-analytical approach can generate a better understanding of manufacturing, component materials and conservation issues of coated plaster objects.
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Response to Reviewers:	Comments from the Editors and Reviewers Editorial Comments Please download the attachment which contains comments from reviewer #2 and corrections. My original reading of the article was that it is of only local interest and reports a very local conservation study. Heritage Science is an international journal and we only publish papers that have an international interest, outside the close circle of the authors. Otherwise, there are many local or more specialist magazines where such studies can be reported. However, reading your introduction it does seem that the work has a more generic interest in the study of plaster casts that workers outside your local environment may appreciate. This wider interest should be reflected in the title and abstract as this would draw in international readers who often judge whether to spend time reading a paper in detail by bibliometric searches primarily of titles, abstracts and keywords. Dear editor, Thank you for the reviews and your advice. Indeed, our intention through this research on the representative case study is to draw international interest. We anticipate this will be an appealing paper for the following reasons: - the interest in plaster replicas has grown in the last 20 years but there are very few material studies published so far (Risdonne et al., 2021). There is a real necessity of published material on the topic; - plaster casting in the nineteenth century was a very popular business and the methods for making casts were standardised, despite the huge quantity of additives and coating materials (Payne, 2020; Risdonne et al., 2021); - in few cases historic plaster casts were analysed before conservation and the results were published or analysis was undertaken but the results remained unpublished (Isella et al., 2017; Wolbers & Little, 2007); - this paper represents a relatively virgin field of study in terms of availability of references, including mock-ups references and case studies (Graepler & Ruppel, 2019); - today there are more than 260 collections of casts in the world ranging from small collections to large ones consisting of thousands of objects (the V&A collection holds about 4000 objects) (Graepler & Ruppel, 2019; Hubbard, 2015; Risdonne et al., 2021); - in the nineteenth century, the V&A cast collection has inspired many organisations across the world to build collections to resemble the one at the V&A (Disalvo, 2012; Gianasso, 2014; Risdonne et al., 2021); - plaster cast and moulds selling have been documented between museums across countries so much so that we are not sure how far the moulds have travelled (Disalvo, 2012; Frederiksen & Marchand, 2010). The V&A have traded casts with other Museums in the UK and internationally, purchased casts with workshops and private collectors (Baker, 1982; Graepler & Ruppel, 2019). For these reasons, presented in the introduction of the paper and extensively discussed elsewhere (Risdonne et al., 2021), we anticipate this will be an appealing paper and will inspire further research on the subject. We have modified the title, the abstract and the keywords to better explain our study and make it appealing to a broader international audience. In particular, the title is changed to: A multi-analytical study of historical coated plaster surfaces: the examination of a nineteenth-century V&A cast of a tombstone The revised Abstract starts with this sentence: “A multi-analytical study was designed to characterise historical coated plaster surfaces.” The revised Abstract finishes with this sentence: “This multi-analytical approach can generate a better understanding of manufacturing, component materials and conservation issues of coated plaster objects.” The keywords were also revised, as follows: Coated Plaster Casts Organic Coatings Multi-analytical examination Optical Microscopy Scanning Electron Microscopy (SEM) Fourier-transform Infrared Spectroscopy (FT-IR) X-Ray Diffraction (XRD)

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Energy Dispersive X-ray Spectroscopy (EDS)
Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS)
Please find below our detailed responses to the reviewers and attached the revised manuscript and Figures in line with the reviewers' recommendations.
Kind regards,
The Authors

Technical Comments from the Editorial Office:
Funding and Acknowledgement:
Kindly include separate 'funding ' and 'acknowledgement' statements under the declaration section. I notice that you have included the funding information in the 'Acknowledgements' section. Kindly change the name of the section to 'Funding'. Please note that the 'Funding' section is different from the 'Acknowledgements' section (where individuals who contributed to the article but are not eligible for authorship are acknowledged).

We have divided the two sections according to your recommendations.

Reviewer #1:
The publication "Multi-analytical examination of the surface layers of the V&A cast of the tombstone of the Presbyter Bruno" is an example of a case study. The manuscript concerns the plaster casts. The authors focused on a multianalytical approach using various techniques such as XRD, FTIR, SEM-EDS or GC / MS. The combination of information from many techniques gives complete information about the tested object. It should be noted that the analyses were conducted thoroughly. The presented research stages can serve as a model for this type of analysis. Therefore, I recommend this manuscript for publication.

We thank Reviewer #1 for the review and the feedback. We are delighted to receive such a positive response. We indeed hope that the methodology of this case study will be inspirational in future studies on historical plaster casts.

Reviewer #2:
The multi-analytical approach to the examination of the cast in this case study is well constructed. The author's research and analyses are very useful as they provide a direct link from the written record regarding plaster casting techniques and the techniques which were used to create these specific casts. This article will be useful for others in heritage studies or with similar collections to be able to compare or contrast their own collections. Furthermore, this will help conservators to understand the coatings and binders.
The article should be published with minor revisions.

We thank Reviewer #2 for reviewing our work. We have made amendments according to the recommendations and we hope we cleared any doubts raised in the comments. We also apologise for the overall poor quality of the images, which were fully readable in their original format. There could have been an issue with the compression processes in the pdf conversion and we should have noticed in the proofs. We have increased the resolution by 5x-15x so that the publishable version will be at the standards of the journal.
We also want to highlight that instead of providing supplementary material alongside this paper we cited our full dataset of findings that were deposited in the online repository Figshare. The dataset is therefore fully searchable and citeable as:
Risdonne, Valentina; Theodorakopoulos, Charis (2021): Database of Results. V&A cast of the tombstone of the Presbyter Bruno (REPRO.1873-380). Northumbria University. Dataset. https://doi.org/10.25398/rd.northumbria.13469925
The dataset had been referenced at the end of the paper (also in the proof manuscript) in section 'Availability of data and materials' and, prompted by Reviewer #2, we added 'Dataset of analysis' as the last section of the experimental to highlight this before discussing our findings.
Page 9, Line 29 of the MS Word file (manuscript):
'Dataset of analysis
A comprehensive dataset for the analysis of this object was deposited in Northumbria University's Figshare repository [23]. A full database of results in a spreadsheet format and with plots and figures was compiled. The description of the samples and images of

the sampling site location can also be found in the dataset.'
The dataset, therefore, is fully accessible and is supplementary material for our paper.

Further responses to Reviewer #2 comments:
Page 7-10, Experimental: I would suggest table 1 and table 2 to be included as supplementary data rather than in the manuscript, as they do not strictly add any additional information.
As suggested and given that the supplementary data of this work is fully available in the dataset (https://doi.org/10.25398/rd.northumbria.13469925), including the sampling sites and the GC/MS data, we have decided to remove tables 1 and 2.
Page 9, line 29: I think it is a typo. What is the range of the FTIR spectrometer?
Apologies for the oversight. We have added this to the 'Experimental'. Page 8, Line 16 of the Word manuscript:
'The FT-IR spectrometer range is 350-4000 cm-1 in the ATR mode and 650-4000 cm-1 in the DR mode.'
Page 10, line 8: possible typo, oil s, should be oils?
Indeed, that was a typo and we edited it.
Page 11, line 24-56. Are there any EDX data to support the FTIR results?
The FT-IR analysis of the cross-sections are all supported by EDS, but this was not possible for the dust sample. The SEM-EDS equipment at NU cannot analyse powdery material, due to the vacuum conditions required in the gigantic chamber. We have given a broad interpretation of the dust component by using references in FT-IR databases, as well as previous studies on dust (detailed in the references). The focus of this study was not the interpretation of the dust, which was nonetheless preliminarily undertaken. As the issue of dust is really important for cast collections, we hope that further studies will follow on this topic.
Page 12. In the "plaster bulk" paragraph, the authors refer to FTIR data that are not presented in the paper or as supplementary data, but only include Figures of EDX analysis, which are also summarised in table 5. It would be more useful to include the FTIR data in some form as they represent a substantial part of the whole paragraph to support their analysis. The lack of those spectra makes it difficult to evaluate the results. For instance, in line 31, they indicate the presence of kaolin because of the IR vibrations centred at 950-1100 cm-1. Were the characteristic peaks of kaolin at approx. 3690 and 3620 cm-1 identified as well?
As suggested by Reviewer #2, we have added two additional examples of FT-IR spectra acquired, alongside the references for gypsum and casting resin, in Figure 10. Further information should be seeked in the dataset (more than a hundred spectra are available, https://doi.org/10.25398/rd.northumbria.13469925). The characterisation of the organic compounds was based on GC/MS and the inorganic part was detected by EDS and XRD. FT-IR interpretation was mainly complementary to GC/MS due to the broadness of the peaks obtained in the DR mode of the FT-IR. As reported across the results section (for example in page 13, line 26 in the Word manuscript), a range of materials was deducted by the EDS and GC/MS results and compared to the FT-IR spectra. Also due to the large number of different types of materials in the samples (clays, carbonates, sulfates and organic materials), the FT-IR peaks overlap with each other and it was not possible to interpret compositions by just using FT-IR. Therefore, we skimmed the possible components based on historical sources and the EDS, XRD and GC/MS results and confirmed with FT-IR. Kaolin is given in the results as an example, as it would match well the EDS and FT-IR contribution. The kaolin contribution at approx. 3690 and 3620 cm-1 is plausible, but cannot be individually seen as close to the plaster and carbonates contributions in the same area. The choice of the DR FT-IR, in this case, was due to the small size of the samples taken from the museum objects, which were, therefore, cast in resin to be also studied with other techniques.
Page 12, line 19-21. The author suggests that the Al detected could be a result of sample preparation. Do they observe comparable counts of Al on all the samples analysed?
To some extent in the average EDS spectra calculated from the EDS mapping, although variations are observed due to the different porosity, as well as the different absorption of the casting resin from the bulk. The presence of Al in the EDS mapping can be seen in the same regions where pores were observed in the OM and BSE images (please refer to the full range of EDS mapping images in the dataset, https://doi.org/10.25398/rd.northumbria.13469925). Therefore, it can be hypothesised that the Al-based polishing solution was trapped in the pores of the cross-section, as

	indicated in page 11, line 6 (Word file) in the reviewed manuscript. In other regions, the presence of Al overlaps with Si and K or Mg in the EDS mapping, as well as with clearly shaped mineral inclusions in the BSE images, as also clarified in page 11, line 9 (Word file) in the reviewed manuscript. In this case, the Al component is likely part of a clay mineral, as indicated in page 11, line 10 (Word file) in the reviewed manuscript. Page 13, A question for the authors if it is possible that the pine resin was absorbed into the surface of the plaster through the casting process, through a coating on the piece mould? The yellowish-greyish appearance of the cast indicates that the cast has been coated. By looking at the cross-sections the penetration of the coating into the plaster bulk is visible as an even interface layer. This is reflected in the manuscript across the 'Results and discussion' section and can be seen in Figure 9. It appears implausible that a coating applied to seal the mould, once dry, would have been evenly absorbed by the liquid poured plaster. This would have been more likely if the coating on the mould was wet, applied immediately before the pouring process (maybe as a separating agent). I did not found mention of the use of such resins as separating agent in the literature (Risdonne et al., 2021). Regardless, we added the following sentence to include the option suggested by Reviewer #2. Page 12, Line 31 of the Word manuscript: 'It is also possible that the organic material derived from accidental contamination in the studio of the plasterer or it might have even been transferred from the mould during the casting process.' Page 14, line 25-29: the authors describe the presence of polyester resin. Is this from the sample preparation? Should this refer to Figure 11 too? Indeed, the polyester resin is the casting resin as described in the experimental section (Page 7, Line 13) and discussed across the results section. The FT-IR reference for the casting resin can be seen in Figure 11 (now Figure 10, moved to be used as a reference in page 14 as recommended by Reviewer #2). Page 14, line 35. Are the authors referring to layer 2 in Figure 12? The layers are not highlighted in Figure 10. As described in the experimental and throughout the results section, the numbers of the layers for each sample are described in Table 1 (which was Table 5 in the original manuscript but moved to be used as a reference in page 14 as recommended by Reviewer #2). It was not possible to graphically show the layering of all the samples in the paper, but the full description and graphic division of the layers can be seen in the dataset, https://doi.org/10.25398/rd.northumbria.13469925. In addition, we added the reference to Table 1 each time layers are mentioned in the results section (pages 10, 11, 13, 15 of the Word manuscript). Page 14. The authors are describing the FTIR spectrum in Figure 10, but the quality of the spectrum makes it difficult to evaluate the results. Is there a better IR data that could be used instead? We have improved the quality of the spectrum in Figure 10 (now Figure 11). All the FT-IR spectra for this study are shown in the dataset: https://doi.org/10.25398/rd.northumbria.13469925. The authors should also consider including the chromatograms discussed for the analysis of the Coating (page 14-15) as figures or supplementary data. 10 chromatograms related to the results of analysis of the coating discussed in the results section can be found in the dataset: https://doi.org/10.25398/rd.northumbria.13469925. Also, we added the following sentence to clarify this: 'The full record of GC/MS results is provided in the dataset [24].' (Page 12, Line 28 and Page 14, Line 12 of the Word manuscript) Page 15, line 49. Is this Figure 12? The authors identify alkyd paint for the presence of dimethyl phthalate only. In which quantity is it found? were other products observed that could confirm the identification? The chromatogram is not shown. The chromatogram and the peaks areas integrations can be seen in the dataset: https://doi.org/10.25398/rd.northumbria.13469925. We suggest that the 'quantity' (relative abundance) of the dimethyl phthalate (as well as the relative abundances of the other markers) should not be considered diagnostic in these samples. This was for example discussed for the A/P and P/S ratios in Page 12, Lines 14-21 of the Word manuscript, as due to the small quantity of the organic component if compared to the inorganic portion. Moreover, the relative abundances are not considered reliable in degraded samples, as in most of the cultural heritage material (Colombini & Modugno, 2009).

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Dimethyl phthalate indicates the presence of alkyds. Alternatively, it may mean that plasticisers such as dioctyl phthalate may have contaminated the paint or also the presence of polyvinyl adhesives and BEVA®371 and cellolyn. The use of alkyd paint is documented in the V&A Cast Courts for conservation retouching purposes and there are no records for the use of polyvinyl adhesives and BEVA®371 and cellolyn. Moreover, the presence of dimethyl phthalate was only detected in the samples taken from areas of repair showing repaints. Therefore, we have suggested the most plausible option, which is the presence of alkyds. The use of dimethyl phthalate as a marker for alkyd resin is advocated in (Colombini & Modugno, 2009; Duce et al., 2014; Horie, 2010; Singer & McGuigan, 2007; Wei et al., 2013). For clarity, we have added (in Page 14, from line 29 of the Word manuscript):
'Phthalic compounds can indicate the presence of a range of different twentieth-century materials. In art conservation they can be found, for example, in alkyd paints, polyvinyl adhesives and BEVA®371 and cellolyn [61]. Given that the phthalates were detected in the sample showing an additional refill and retouching layer and that V&A conservators have confirmed that polyvinyl adhesives, BEVA®371 and cellolyn are not documented as used in the Cast Courts, it is postulated that the dimethyl phthalate is due to the presence of alkyd paints.'
Due to the limited space, we have decided to prioritise the discussion of the original coating, showing only an OM micrograph (Figure 12) of an area of repair where the dimethyl phthalate marker was detected (and the chromatograms and full analysis can be seen in the dataset, https://doi.org/10.25398/rd.northumbria.13469925).
Figures should be generally improved to make labels more readable (example Figure 5) and EDX maps with a better contrast. In Figure 6, I would suggest the authors to highlight the XRD peaks rather than include Table 3.
We have increased the resolution of the images to compensate for the effects of compression. Labelling font has also been increased. We could not label the XRD peaks in this instance due to a large number of peaks and their vicinity, which would make them unreadable when printed on an A4 page, therefore the necessity of Table 3 in the originally submitted manuscript (Table 2 in the revised version). Extended images and labelled XRD diffractograms can be seen in the dataset.
In Figure 8, the authors should show a close-up of the pine resin markers as they are difficult to read. They could perhaps improve visualisation by cutting the chromatogram just to the area of interest for the analysis, as they state that peaks in the range of 4.18 – 16.99 are not diagnostic.
We have modified Figure 8 by including a close-up of the 16-30 minutes area.

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Research article

A multi-analytical study of historical coated plaster surfaces: the examination of a nineteenth-century V&A cast of a tombstone

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Abstract

A multi-analytical study was designed to characterise historical coated plaster surfaces. The method was applied to investigate the surface coatings of the nineteenth-century plaster cast of the tombstone of the Presbyter Bruno that belongs to the Victoria and Albert Museum collection. At first, selected samples of the object were examined with Visible Light Reflectance and Ultra-Violet Fluorescence Optical Microscopy (VLR- and UV*f*-OM respectively) and Scanning Electron Microscopy (SEM) demonstrating a consistent stratigraphy featuring a bulk, an interface and an uppermost layer. The latter layer appeared to consist of an aged coating and dirt. Overpainted and repaired areas of the object generated samples that had additional layers on top of the aforementioned stratigraphy. A layer that seemed to be an additional surface varnish or a coating that had not been absorbed to the bulk has been observed in a couple of samples. Elemental characterization was carried out with energy dispersive x-ray spectroscopy (EDS) and further analyses were performed with x-ray diffraction (XRD) and Fourier-transform infrared (FT-IR) spectroscopy with focal plane array (FPA) imaging which confirmed that the bulk of the object is

made of gypsum plaster containing mostly silicate and carbonate inclusions. Gas chromatography/mass spectrometry (GC/MS) and pyrolysis-GC/MS with extraction methods based on n-propanol followed by pentafluoropropionic anhydride (PFPA), tetramethylammonium hydroxide (TMAH) and 3-trifluoromethylphenyltrimethylammonium hydroxide (m-TFPTAH) were performed to detect organic media. The results suggest that the organic medium used for the surface coating is a diterpenic resin that contained silicon, aluminium and traces of other inorganic elements. The organic medium of overpainted areas was based on alkyd resins and the in-paints were characterised as a blend of silicon and barium at varied concentrations. This multi-analytical approach can generate a better understanding of manufacturing, component materials and conservation issues of coated plaster objects.

Keywords

Coated Plaster Casts

Organic Coatings

Multi-analytical examination

Optical Microscopy

Scanning Electron Microscopy (SEM)

Fourier-transform Infrared Spectroscopy (FT-IR)

X-Ray Diffraction (XRD)

Energy Dispersive X-ray Spectroscopy (EDS)

Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS)

Introduction

This work represents a pilot case study designed to establish a wider campaign of sampling and scientific analyses of the surface layers of the casts produced in the nineteenth century, in the framework of a collaborative doctoral partnership of Northumbria University with the V&A Museum (AH/R00322X/1) [1]. Part of the project focused on the characterisation and the ageing characteristics of the original coatings of historical plaster casts [2]. In the nineteenth century, the plaster cast replicas of famous artworks were used extensively in schools and museums [3]–[5]. The aim was to educate and inspire those who studied or appreciated art. They were also fashionable among the more affluent people who decorated their homes with plaster ornaments and copies of well-known sculptures [6]–[9].

The object of this study is a nineteenth-century plaster cast of the Tombstone of Presbyter Bruno, part of the Victoria and Albert Museum (V&A) collection (museum accession number REPRO.1873-380[1], Figure 1) and displayed in the Cast Courts (Gallery 46A). The 'Copy of the Tombstone of Presbyter Bruno' is a plaster replica of an original tombstone from the Cathedral of Hildesheim (Germany), by Friedrich Heinrich Nicolaus Küsthardt the elder (Göttingen 1830 – Hildesheim 1900) [10], [11].

The original tombstone is dated 1194 and is still located in Hildesheim Cathedral. In 1873, the Museum acquired several plaster casts of key sculptural decorations in Hildesheim Cathedral, all produced by Küsthardt, among them, the tombstone, purchased directly from Küsthardt in 1873 for £6.

Küsthardt's plaster copy of the tomb slab, 218.5 cm high by 77.0 cm wide, is currently displayed between a mix of casts of different origin, as well as a variety of early Christian monuments and other reproductions from Hildesheim Cathedral. The cast is mounted on a wooden display frame, and on its reverse, is another German reproduction depicting an upper left portion of a wooden doorway from the Church of St Maria im Kapitol, in Cologne (the original was carved c. 1065 by an unknown carver) [12].

Neither cast appears in any of the early photographs of the V&A galleries. Yet later pictures of Küsthardt's cast on its own, held in the V&A curatorial department, reveal that it was formerly mounted upright on a different backing, with metal brackets supporting its base (Figure 2). The brackets were later removed which explains the current losses to the plaster under the relief. The photographs also reveal a series of exposed metal screws at the front to attach the plaster to its wooden or metal supporting frame (Figure 2). Many of the casts in the collection have been fixed to their supports with similar metal screws. Often the screw-heads have been filled and retouched to conceal them, which is the case with Küsthardt's piece. The positions of fixings are easy to recognise, as the filler is often slightly proud and, in many instances, split around the edges. This is due to the corroding metal or shrinkage of the filler. Also, the overpaint is often of a slightly different colour, either because of ageing, or the retouching was aimed to be noticed, in case the objects needed deinstalling.

A close examination shows that the cast is made of three sections, which sit directly on top of one another, with pieces of wood wedged between them. Interestingly, the original sandstone slab,

[1] The Museum nos. can be used to find the objects in the V&A Website - Search the Collections (2020).

which is mounted on the south wall of the choir at Hildesheim cathedral, is carved from a single block of stone, although it has additional stone sections added at the top and on its base, which have not been replicated in the V&A copy. Also, by comparing archival images of the original slab, some of the losses to the original stone surface do not show on the cast, as can be observed. It may be that some of the surface details on the original stone were lost after the cast was made, or some of the details on the cast were later reworked.

The top section of the cast has various vertical and horizontal lines under the arch surrounding the Christ's head. The lines have been sanded down, suggesting the cast could have been made using a piece mould technique. Piece moulds tend to leave raised seamlines on casts and, they were often disguised by sanding them down [2].

The outer edges of the cast have been covered with painted plywood sheeting, to conceal their unevenness (Figure 3). Interestingly, the edges of the original stone slab are finely finished. Many casts in the V&A collection were not meant to be viewed all around. They are often unfinished at their sides and the top and were later covered with either fabric, card, wood, or metal to disguise the exposed areas and to protect them from dust.

A close examination of the underside reveals that there is a small section of metal visible at the back of the cast, on the left side. It could be what remains of the old bracket after it was cut back, or it could be part of a larger metal support. Metal and wooden supports are commonly found on the backs of the plaster casts. Using a metal detector, it was revealed that the top and middle parts of the cast have less metal backing support than the lower part of the cast.

Küsthardt's cast has been restored on several occasions since it came to the museum some 148 years ago. Unfortunately, there are no records of any of the previous restorations, but a close examination reveals that numerous localised areas on the surface have been repaired with a filler and touched up using different paints and colours at different times. It was fairly common before the 1970s, for the restorers, not to document their treatments. However, many casts in the collection have names and dates pencilled on discreet areas on the object's surface. This information helps to pin down when objects were restored and by whom. Casts also might have traces of old materials on their surfaces: residue of soap or residue of casting materials such as gelatine, or items at their backs including, packages of soap, pigments, cloths, sponges, tools, newspapers, letters, food packaging etc. Unfortunately, due to the framing of the cast, it is difficult to observe the back of Küsthardt's cast.

Although there are no signatures or dates on Küsthardt's cast visible at the front, apart from museum numbers near the base and at the top, and Küsthardt's company label can be found on the top right corner on the lower section. It reads: 'Bildhauer, FR Küsthardt, Hildesheim' in embossed lettering (Figure 3).

There are also many tool-marks and possibly fingerprints where the plaster surface has been worked on. Several raised areas, particularly on the lower sections, are also covered in pencil marks. These were probably left by various artists and students who sketched and drew the object in the galleries ever since they were built. Similar pencil marks on the plaster surfaces have been observed by the authors in art schools' collections, as for example the one in the Hatton Gallery in Newcastle upon Tyne.

Research on plaster cast objects often remains unpublished at large within the records of collection holding organisations and individual case studies fail to represent the breadth and complexity of the materials that can be found in the eclectic cast collections due to case specificity [13]–[16], whereas often useful insight on the properties of materials can be found in studies on building decorative materials [17], such as plasterworks [18] and mortars [19]. Megens *et al.* [20], on the other hand, have demonstrated that systematic elemental analysis is required to uncover the provenance and composition of plaster used to replicate art and decorative objects: traces analysis, size and distribution of porosity and mineral shape and growth can be characteristic of a particular group of artefacts. Gypsum plaster (calcium sulfate, $CaSO_4 \cdot 0.5H_20$) has consistently been found as the main component of the bulk of the nineteenth-century plaster casts [2]. However, organic (such as resins and gums) and inorganic compounds (such as clay, sand, lime), as well as larger structural elements (such as fabrics, wooden or metal batons or even bones) were combined and added during the plaster production, as used to improve mechanical properties, such as hardness and water resistance or to control setting time and the casting procedure [2], [20]. The complexity of the organic and inorganic blended compositions in the plaster artefacts suggests that a multi-analytical approach would be more appropriate. For example, Field emission gun–scanning electron microscopy (FEG-SEM), XRD and Particle induced X-ray emission (PIXE) allowed the examination of Renaissance stucco related materials, which indicated that the composition of the mineral phases influences its sustainability and sensitivity to moisture sorption processes [21].

The full characterization of the materials of the cast will also provide fundamental information for the deterioration processes and guide conservation decisions. Typical damage observed is related to environmental conditions or unsuitable protection and handling. Plaster objects may become

heavily soiled and covered with dirt and dust layers. Exposure to high relative humidity levels causes the migration of deposits into the plaster's porous structure. Due to alternating swelling/shrinking cycles in time and the fragility of plaster materials, objects often lose their texture, crack or break into fragments [22].

This study aims to characterise the materials used to produce the surface layers of the plaster casts, either to provide the plaster with certain properties and to achieve the desired appearance. While VLR- and UV*f*-OM allowed the identification of the stratigraphy, SEM-EDS and XRD were used to monitor the inorganic composition and FT-IR and (py)-GC/MS to characterise the organic components. Trace analysis to investigate the provenance of the object were not carried in this study, being beyond the scope. The study of the object served as a pilot study for the determination of an analytical strategy for the examination of the surfaces of plaster casts that will eventually allow a better understanding of the workshops' practices in place in the nineteenth century and define more specifically targeted conservation methods. Archival information was available in the Registry of Reproductions of the V&A Museum (1873), in the museum Collection Management System (CMS) and the V&A archive currently at Blythe House, London.

Experimental

Sampling

A total of thirteen samples from selected areas were taken, according to British Standard BS EN 16085:2012 (ISBN 978 0 580 70588 5). Before the sampling, a careful survey was performed to prevent any risk and to minimize the quantity of sample collected, which was never larger than 1.0 mm across, and maintain the integrity of the object. The sampling procedure was fully documented [23]. The sampling areas were determined by many factors, such as accessibility and significance, but also avoiding foreground areas. The samples were taken from areas of pre-existing loss and undercuts or marginal areas. The utmost attention was given to ensure that the samples were collected limiting any contamination. Before being stored in the vials, the samples were numbered with the museum accession number and the progressive sampling number, which is used throughout the study to identify the samples, as follows: *MUSEUM ACCESSION OBJECT NUMBER_PROGRESSIVE SAMPLE NUMBER.*

Technical Photography

Regular visible photographs were taken with a Panasonic DCM-FZ38 camera under the gallery's normal illumination (i.e. diffuse lighting, skylight window natural light and mixed artificial

illumination). Colour and dimension references were ensured through the Past Horizons® Credit Card Photography Scale. The images were processed with Adobe Photoshop® CC 19 and white-balanced through the Past Horizons® Credit Card Photography Scale. The objects were also rendered in Autodesk® AutoCAD® 2019 for mapping purposes (Figure 4).

Stereomicroscopy

A StereoZoom® LEICA S6D stereomicroscope was used to observe the samples, to understand the shape of the samples, the position of the layer in the stratigraphy and to define the processing of the sample. The Leica S6D Stereomicroscope has a 10x eyepiece and the objective magnification range from 0.63x to 4.00x. When possible, samples were split into two parts: one fragment was embedded in polyester resin to allow the observation of the stratigraphy and the analysis of the layers and the other was put aside for destructive analyses.

Samples for cross-sectional analysis

The samples were embedded in Alec Tiranti™ Ltd clear casting resin, which required 48 hours to cure and harden. Alec Tiranti™ Ltd clear casting resin consists of styrene and methyl methacrylate / polyester resin (Product Code: 405-210) and liquid hardener (BUTANOX M-50 methyl ethyl ketone peroxide, solution in dimethyl phthalate - Product Code: 405-810) in the proportion 4 mL : 1 drop.

Visible Light Reflectance (VLR) and Ultraviolet Fluorescence (UVF) Optical Microscopy (OM)

Optical microscopy was performed with an Olympus BX51 Metallurgical Microscope equipped with four objectives (magnification of x5, x20, x50 and x100), and an x10 eyepiece. 50 µL of white spirit were added on the surface of the cross-section to improve the saturation under the microscope. The microscope is equipped with a 6-cube filter turret which allows operating the system in reflected visible light (brightfield and darkfield mode) and reflected UV light (365 nm) using a 100 W mercury burner.

X-Ray Diffraction (XRD)

The XRD analyses were performed with a Rigaku SmartLab SE equipped with a HyPix-400, a semiconductor hybrid pixel array detector and a Cu source. The analyses were performed in Brag-Brentano geometry mode, with 40 kV tube voltage and 50 mA tube current. The diffractograms were processed with SmartLab II software. The data was compared to the data available in the RUFF™ database [24] and the Crystallography Open Database (COD) Database [25].

Scanning Electron Microscope (SEM) - Energy Dispersive X-Ray Spectroscopy (EDS)

The SEM-EDS analyses were performed with a field emission TESCAN MIRA 3 with gigantic chamber. The SEM is equipped with a back-scatter detector (BSE) and back-scatter in-beam detector (In-

beam BSE). For the EDS analytical part, it has an Oxford Instruments setup: Software: AztecEnergy, X-ray detector X-Max 150 mm^2 and X-ray detector X-Max Extreme, low energy detector for thin films, high resolution and low voltage. The samples were analysed by SEM-EDS Low Vacuum Mode (10-15 Pa). EDS Mapping and data processing were performed with Aztec Oxford software. A fragment of sample 2 was mounted on appropriate support, adhered with silver paint and coated with a layer of platinum (5 nm thick). This sample preparation is required when high vacuum SEM-EDS (1.5x10-2 Pa) is performed. This mode allows a higher magnification with a better definition.

Fourier-Transform Infrared Spectroscopy (FT-IR) with Focal Plane Array (FPA) imaging.

A Perkin Elmer Frontier FT-IR spectrometer (350 cm^{-1} at a best resolution of 0.4 cm^{-1}) was used, equipped with a UATR Diamond/ZnSe ATR accessory and combined with a Spectrum Spotlight 400 FT-IR microscope equipped with a 16×1 pixel linear mercury cadmium telluride (MCT) array detector standard with InGaAs array option for optimised NIR imaging. Spectral images from sample areas are possible at pixel resolutions of 6.25, 25, or 50 µm. The Perkin Elmer ATR imaging accessory consists of a germanium crystal for ATR imaging. These run with Perkin Elmer Spectrum 10™ software and with SpectrumIMAGE™ software. Baseline and Kubelka-Munk corrections were applied to the raw data acquired in diffuse reflectance (DR). The FT-IR spectrometer range is 350-4000 cm^{-1} in the ATR mode and 650-4000 cm^{-1} in the DR mode.

Gas Chromatography/Mass Spectrometry (GC/MS) and pyrolysis - Gas Chromatography/Mass Spectrometry (py – GC/MS)

The instrument used for GC/MS is a Thermo Focus Gas Chromatographer with DSQ II single quadrupole mass spec. The column is an Agilent DB5-MS UI column (ID: 0.25 mm, length: 30 m, df: 0.25 µm, Agilent, Santa Clara, CA, USA), fitted with a Pyrola 2000 Platinum filament pyrolyser (PyroLab, Sweden). The helium carrier gas flow rate was 1.5 ml/min with a split flow of 41 mL/min and a split ratio of 27. The temperature of the detector was set at 280 °C and the inlet injector temperature to the GC was kept at 250 °C. The pyrolysis chamber was heated to 175 °C, and pyrolysis was carried out at 600 °C for 2 s. Samples derivatization was necessary for GC/MS [26]–[30] and carried with *n*-propanol followed by pentafluoropropionic anhydride (PFPA) [31], to derivatise protein component of proteinaceous paints and adhesives, while yielding the propyl esters of fatty acids derived from lipids and diterpenoid acids derived from natural resins and thus allows the choice of a single method for the analysis of artists media which contain either oils or proteins or mixtures of both proteins and oils or even resins. 1 mg of pulverised sample was hydrolysed in 150 µL of Hydrochloric acid (HCl) and the excess Oxygen was removed. The solution

was heated at 90°C for 3 days and placed in a vacuum desiccator for 24 hours to remove the acid. After 180 µL of propan-1-ol : acetyl chloride (3:1) were added, the solution was heated at 110 °C for 45 minutes, then at 50°C for 30 min. The reagent excess was then removed via nitrogen. The residue was dissolved in 50 µL 0.2% pyridine and 150 µL of dichloromethane (DCM) and 150 µL perfluoropropionic anhydride (PFPA) were added before heating at 110°C for 15 minutes [31]. The sample was then injected into the column with the aid of a micro-syringe and the MS thermal Programme (3) was set as follows: Seg1 start 13.00 Scan events MS, Heated zones Ion Source 250 °C, Detector Gain 1.21·105 (Multiplier Voltage 1025 V). Oven: Initial temp 60 °C hold 2 minutes Ramp 1 6.0 °C/min (rate), 250 °C, hold 0 min. Ramp 2 25 °C/min, 300 °C, 20 min hold. Mode: split. A pulverised sample of the order of 0.5 mg was either directly derivatised in an aliquot of 1 µl of 25 wt% in methanol tetramethylammonium hydroxide (TMAH) and placed on the Pt filament, or methylated with 3-trifluoromethylphenyltrimethylammonium hydroxide (5 wt% in Methanol) CAS number 68254-41-1, $C_{10}H_{14}F_3NO$ m-TFPTAH (commercially known as MethPrep II). Methylation has been widely used for the analysis of artists' media where it is useful for the analysis of both seed oils and natural resins which contain diterpenoid acids or triterpenoid acids such as moronic acid from mastic [29], [31]–[33]. MethPrep II methylation was achieved either (1) by adding to the sample 1-3 drops of MethPrep II, depending on sample size, and heating at 60°C for 24 hours or (2) by adding 30 µl of MethPrep II each 0.3 mg of sample and heating at 60°C for 24 hours. The MS Thermal programme (1), (2) or (3) were set for the analysis, as described hereafter. Thermal Programme (1). Seg1 start 2.40 Scan events MS, Heated zones Ion Source 250 °C, Detector Gain 1.21·105 (Multiplier Voltage 1025 V). Oven: Initial temp 40 °C hold 4 minutes Ramp 1 10.0 °C/min (rate), until 250 °C, hold 15 min. Mode: splitless. Thermal Programme (2). Seg1 start 2.40 Scan events MS, Heated zones Ion Source 250 °C, Detector Gain 1.21·105 (Multiplier Voltage 1025 V). Oven: Initial temp 40 °C hold 4 minutes Ramp 1 10.0 °C/min (rate), 250 °C, hold 45 min. The acquisition was carried out in a Total Ion Count mode, where all ions in the range 40–800 m/z were monitored. The Xcalibur™ 2.2 and PyroLab™ software were used to control the instruments. The former was then supported by the library browser supported NIST MS Version 2.0 [34] which facilitated data processing.

Dataset of analysis

A comprehensive dataset for the analysis of this object was deposited in Northumbria University's Figshare repository [23]. A full database of results in a spreadsheet format and with plots and

figures was compiled. The description of the samples and images of the sampling site location can also be found in the dataset.

Results and discussion

The analyses were chosen to ensure the understanding of the coating materials, which was the scope of the research. However, a sample of incoherent dirt and dust was taken from the base of the tombstone (sample 1) and a sample of plaster bulk was taken from a deep crack (sample 2) to confirm the expected composition of the substrate. Samples 3 to 12 were taken so to be representative of the stratigraphy of the object from the surface to 0.5-1.0 mm towards the core of the object.

Dust

Dust deposited on the tombstone was sampled (Sample 1) and analysed to have a better understanding of the contaminants present in Gallery 46A, and eventually be able to discriminate which elements found on the surface can be attributed to the environmental dust in the galleries. Under the microscope, the sample seems to be mostly made of fibres of various colours (red, green, blue, Figure 5). FT-IR analysis highlighted that the dust is made mostly of sulfates (such as gypsum and other varieties) with the asymmetric bending modes of SO_4 at 435, 600 and 667 cm^{-1}, the SO_4 symmetric and asymmetric stretching at about 1005 and 1105 cm^{-1} and the v_2 H_20 of the sulfates at about 1620 and 1680 cm^{-1} [35], [36]; carbonates (such as calcite) suggested by the peaks at 875 and 1425 cm^{-1} corresponding to out-of-plane bending and asymmetrical stretching vibration peaks of O–C–O [35], [37], respectively; silicates and other metal oxides generated several peaks in the fingerprint area [35], [38]–[41] and unidentified organic material(s) are suggested by the peaks in the 1200-1300 cm^{-1} area (v CN), the peaks at 1360 cm^{-1} (v CN aromatic amine), 1580 cm^{-1} (δ NH of amine I), 1714 cm^{-1} (v CO of esters) and the CH vibrational mode at 2852 and 2917 cm^{-1} [42], [43], possibly deriving from the fibres and other residues of human interaction (skin, oils and as such) [39], [42], [44] (Figure 5). Overall, the sulfates and carbonates can be due to the building works, but the fibres and organic contribution derive from the visitor interactions.

Plaster Bulk

The substrate (layer 0 in samples 3 to 13, as described in Table 1) largely consists of gypsum plaster (calcium sulfate, $CaSO_4 \cdot 0.5H_20$), confirmed by EDS spectra and mapping (see for example sample 3 in Figure 6). XRD analysis on all the samples also confirmed that the mineral gypsum is the main component in the sample, as shown for example in the diffractogram of sample 3 (Figure 6) and

indicated by the characteristic diffraction peaks in Table 2 and consistent with the gypsum references available in published databases [24], [25]. FT-IR spectra also showed the presence of gypsum plaster with the peaks at about 1005 and 1105 cm^{-1} (SO_4 symmetric and asymmetric stretching) and 1600 and 1680 cm^{-1} (v_2 H_20 of the sulfates), and also the sulfate overtones centred on 2220 cm^{-1} area, due to the combination of bending and vibration modes of H_2O ($v_1 + v_3$ and $2v_3$) related to the presence of gypsum [35], [36], [45], [46]. Aluminium (Al) was detected by EDS in all the layers of all the samples analysed and, as in the samples analysed as cross-sections, Al can be also due to the use of an Alumina suspension (Agar Scientific Micro-polish Alumina 0.3µm – B8226) to obtain the final polish. Al is likely present, together with potassium (K) and silicon (Si) as part of silicate inclusions (visible in the EDS mapping and spectra, Figure 7), which constitute clay minerals [47] and are reported to be present as a natural contaminant of mineral gypsum [2], [48]. FT-IR spectra suggest vibrations in the 950-1100 cm^{-1} region, characteristic of clay minerals (Si-O containing minerals, such as kaolin, $Al_2Si_2O_5(OH)_4$) [40], [47]. FT-IR peaks at 1440 and 1770 cm^{-1} (v CO_3) and overtone centred at 2400 cm^{-1} suggest the presence of calcite (calcium carbonate, $CaCO_3$), as suggested in other studies [26], [40], [43]–[45]. Minor variations of the position of the FT-IR peaks related to the inorganic components can be observed for several reasons, one of which is the local substitution of elements such as Magnesium (Mg) and lead (Pb) in the gypsum and other minerals' structure [35], [40], [44], [45], [47]. Mg was also detected in all the samples by EDS and it is possibly an exchangeable element of the sulfate variety $MgSO_4$ (more or less hydrated, chalcanthite $CuSO_4 \cdot 5H_2O$, kieserite $MgSO_4 \cdot H_2O$, starkeyite $MgSO_4 \cdot 4H_2O$, hexahydrite $MgSO_4 \cdot 6H_2O$, epsomite $MgSO_4 \cdot 7H_2O$ and meridianite $MgSO_4 \cdot 11H_2O$). Small quantities of sulfate varieties such as barite ($BaSO_4$), celestite ($SrSO_4$), anglesite ($PbSO_4$) and the Mg varieties mentioned above can be naturally present in the gypsum quarries or form after the rehydration of the gypsum plaster that occurs after the addition of water to the calcined powdered gypsum plaster [2], [47], [48]. These secondary mineral phases are commonly found in minerals [47] and, for example, suggested by trace studies on *stucco* objects [21]. This composition of the plaster was consistently found in layer 0 of samples 3 to 8 and 10 to 13 (Table 1). Sample 5 shows additional small inclusions of titanium (Ti) in the plaster bulk and sample 9 shows inclusions made of silicon (Si), aluminium (Al), iron (Fe) strontium (Sr) throughout the stratigraphy (Figure 7). EDS mapping and XRD analysis confirmed that despite inclusions of calcium carbonate are present in the bulk, the object is largely made of gypsum plaster (made from gypsum) rather than lime plaster (made from calcite), which is instead often used for outdoor architectural details [4], [6], and was also found in the analysis of other casts

[35]. Sample 2 was taken from the inner plaster bulk (about 5 cm from the surface), exposed on a deep crack of the tombstone, to understand whether the organic coating visible on the surface was also used as an additive in the plaster mixture, as suggested as possible by the historical literature [2], [48]–[50]. No organic materials were detected in sample 2 by FT-IR. Py-TMAH-GC/MS analysis indicated the presence of abietane skeleton diterpenoids due to the occurrence of the peaks at m/z 315, 299, 285, 253 and 239 (Figure 8 and Table 3) [29], [51]: 7-Oxodehydroabietic acid, methyl ester at retention time, RT, 25.47 min and methyl dehydroabietate at 25.57 min in the chromatogram. The fragments at m/z 314 and 253 suggest the presence of a compound formed by oxidation of pine resin biomarkers, as suggested in several case studies [29], [51]. The peak at m/z 314 is related to the molecular ion of this degradation marker and the fragment at m/z 253 results from the loss of a methyl group followed by that of neutral formic acid [29]. The base peak at m/z 239 is reported as characteristic of the fragmentation of dehydroabietic acid [29]. This acid is the main degradation marker formed by the aromatisation of abietadienic acids, which are the major constituents of raw pine resins. Fatty Acids (FA) were also detected at 17.50 min (dimethyl azelate), 21.68 min (methyl palmitate) and 23.60 min (methyl stearate) (Table 3), as consistent with the relevant literature [27], [29]. The ratios azelate/palmitate (A/P = 0.7) and palmitate/stearate (P/S = 2.2) suggested that the resin has been mixed with an oil, or the FA are either from other sources of lipids or naturally present in the resin [28], [29], [51]. It was suggested in other studies [52], [53] that the intensity of the FA peaks can change, as affected by matrix effects due to the presence of inorganic pigments. This would change the P/S ratio and therefore invalidate the correlation which allows the determination of the type of lipid. Due to the lack of previous studies on the effects of the predominance of the inorganic portion over the organic component on the areas of the FA peaks in the chromatogram, further research on this topic is required. Due to the complexity of the mixture, as often happen in the case of cultural heritage materials, separation methods are required prior the mass analysis so that several components arrive in the ion source one at a time [29]. For this reason, other peaks that can be assigned to small fragments of amine and lipids between 4.18 min and 16.99 min in the chromatograms have not been considered diagnostic in this sample (Figure 8). The full record of GC/MS results is provided in the dataset [23]. The inconsistency of the FT-IR and py-TMAH-GC/MS results in sample 2 may suggest that a very small quantity of resin was added in the plaster [2], [48] or that such small amount had penetrated deep in the plaster from the surface. It is also possible that the organic material derived from accidental contamination

in the studio of the plasterer or it might have even been transferred from the mould during the casting process.

An interface layer, that appears yellow under visible light reflectance and possibly consists of a portion of the lower layer soaked with the surface coating(s), showing characteristics of both layers, is visible in samples 3 to 6 and 8 to 13 (Figure 9). The tabular crystalline structure typical of gypsum plaster can be seen in the substrate layer and the interface layer in the BSE image [21], [47], [54]. In samples 10 and 11 the casting resin homogeneously penetrated the stratigraphy and in samples 3, 4, 5, 6, 8, 12 and 13 layer 1 appears 'denser' than layer 0 (Table 1), suggesting that the coating layer had penetrated the plaster, filling the pores and impeding the casting resin occupying the voids and possibly preserving the mineral structure of the gypsum plaster (Figure 9). This was visible in the BSE image as well as through the EDS mapping (casting polyester resin and catalyst are mainly made of organic compounds C, H and O). The presence of the casting resin (polyester resin) was also detected in all the layers by FT-IR spectra (δ OH phenol at about 1312 cm^{-1} and δ CH aromatic at about 1760 cm^{-1}, as can be seen in the reference in Figure 10).

Coating

Samples 3 to 5 and 8 to 13 show a coating layer, that appears dark under visible light reflectance (layer 2 in these samples as described in Table 1), and it likely consists of a pigmented organic medium and dirt. EDS mapping and spectra show that this dark layer contains calcium sulfate but consists mostly of Si and Al (Figure 11). Traces of other elements can be seen and the composition varies from sample to sample (Table 1), suggesting that the trace elements in the surface layers derive from both the plaster substrate and the dirt deposited onto the surface. The presence of the polyester casting resin (Figure 10) and gypsum plaster ($CaSO_4 \cdot 0.5H_20$, characteristic peaks as described above) was detected in all the layers by FT-IR, including the surface. The presence of an organic medium is indicated in all the FT-IR spectra and the position of the peaks suggest that is likely a wax or resin (CH bending and stretching); however, the crowded appearance of the spectra and the broadness of the peaks impede the unique assignment of such contributions. The several peaks that can be identified in the area over 3000 cm^{-1} cannot be considered uniquely diagnostic, as OH and NH stretches occur in this region and once again due to the complexity of the mixture, the water present in the crystals and the pores of the plaster, as well as in the organic components will add up in this area. Calcium oxalate might be also present in layer 2, but it was not possible to uniquely assign its peaks, as usually close to the vibrations characteristic of calcium sulfate, as also suggested in other studies [46]. Py-TMAH-GC/MS of samples 3, 4, 5, 8, 9 shows the markers

characteristic of a diterpenic resin (similarly to sample 2, Figure 8), such a rosin or pine resin, possibly mixed with a non-drying oil or another source of lipids, similar to what is suggested in relevant literature [27]–[29].

Py-TMAH-GC/MS of samples 8 and 9 shows peaks that were assigned, as based on previous studies [29], [55], to a betullin-like triterpene marker (at t= 30.08-33.49 min, Table 3), suggesting that, as rarely are diterpene and triterpene molecules are rarely found together in a plant resin, a birch, dammar or mastic is additionally present in the stratigraphy. The full fragmentation patterns of the markers characteristic of dammar and mastic were not detected, but this can be due to the natural degradation of the molecules or to the derivatization processes applied to the already degraded organic material, as suggested in [29], [56], [57] The small quantity of the organic material, when compared to the inorganic portion, also contributed to the small relative abundance of the di- and tri-terpene molecules in the chromatogram. The full record of GC/MS results is provided in the dataset [23].

The contributions of the organic material as shown in the FT-IR spectra of all the layers indicates that either the material was added to the wet gypsum plaster wet mixture or that the coating has also penetrated in the bulk. The latter seems also possible as the average depth of the samples is about 0.5 mm. The characterization of unknown organic materials in aged samples has been recognised as the most challenging application of GC/MS techniques [29]. Moreover, in sample 8 an additional layer (layer 3) fluoresces white under UV illumination, suggesting that these could be an additional layer or that layer 2 has not been absorbed evenly, as seen in the other samples. The same was also observed in samples 11, 12 and 13.

Areas of retouching

Sample 4 is characterised by the same stratigraphy described above but presents an additional layer (layer 3), purple under visible illumination (Figure 12). EDS mapping suggested that this layer is mostly made of iron (Fe), silicon (Si) and titanium (Ti). Py-TMAH-GC/MS of this sample highlighted that a drying oil modified alkyd paint is the medium in this layer, suggesting that they were applied after the 1920s [30], [58], [59]. Dimethyl phthalate was detected at t= 16.25 min in the chromatogram (Table 3) and was considered a marker for aged alkyd paints mixtures, as it is reported to be forming in these paints upon ageing [30], [31]. Phthalic compounds can indicate the presence of a range of different twentieth-century materials. In art conservation they can be found, for example, in alkyd paints, polyvinyl adhesives and BEVA®371 and cellolyn [60]. Given that the phthalates were detected in the sample showing an additional refill and retouching layer and that

V&A conservators have confirmed that polyvinyl adhesives, BEVA®371 and cellolyn are not documented as used in the Cast Courts[2], it is postulated that the dimethyl phthalate is due to the presence of alkyd paints. Samples 6 and 7 broadly present the same stratigraphy of the other samples, however, the coating layer is made of K, Fe, Si and Al and traces of Na, Pb and Cl in sample 6 and Fe and Ba and traces of Mg, K and Cl in sample 7. In samples 8, 11, 12 and 13 an additional surface layer (layer 3 in these samples) fluoresces milky-white under UV illumination. No differences can be seen in the FT-IR spectra of these samples nor the GC/MS chromatograms, suggesting that either layer 3 is an additional layer of varnish made of the same material of the medium of layer 2 (diterpene resin) or layer 3 is an unabsorbed portion of the medium of layer 2 visible on the surface.

Manufacturing as suggested by the stratigraphy

In summary, the stratigraphy of the samples is quite consistent, featuring a 'substrate' layer, an 'interface' layer and a coating 'dark' layer, likely a combination of aged coating and dust. On top of these, some samples feature additional layers, having been overpainted or having been sampled from an area of repair. The bulk of the object is made of gypsum plaster, which contains several types of inclusions (including silicates and carbonates). By looking at the results, it is possible to hypothesise that in the surface layer, containing silicon and aluminium, but also traces of other elements, the medium is a diterpenic resin. Areas of repairs consist of overpaints made of alkyd paint, suggesting that they were applied after the 1920s [30], [58], [59], and inpaints containing silicon or barium. Areas showing an additional varnish layer might have locally highlighted or the additional layer might be due to a local difference in the surface absorbance or to an accidental spillage (as for example in sample 12, see Figure 3). A summary of the results can be seen in Table 1 and has also been compiled in a comprehensive dataset [23].

Conclusions

A multi-analytical approach allowed the characterization of the surface coatings of the object. A 'substrate' layer made of gypsum plaster, an 'interface' layer and a coating 'dark' layer, likely a combination of aged diterpenic resin coating and dust were identified. Overpaint made of alkyd paint and areas of repair were also highlighted. Due to the immense variety of recipes for the

[2] Personal communication with the V&A Conservation team (January 2021)

manufacturing of the nineteenth-century plaster casts, the stratigraphy of a plaster cast might result in a complex combination of organic media and inorganic features, even more complex when modern treatments have been applied for the care of the cast. As a multi-analytical approach in studies on similar materials has been proven effective, the combination of techniques for the characterization of inorganic and organic components is fundamental in plaster artefacts. This study demonstrated that the suggested methodology for the characterisation of the coatings of historical plaster casts can provide information on nineteenth-century manufacturing. This case study suggests an analytical protocol that combines diverse methods to characterise the manufacturing of such artefacts. The investigation is ongoing and additional elements are still needed to have a comprehensive understanding of the cast manufacture and history, but the results discussed and summarised here demonstrate that despite the many analytical challenges of studying the complex composition of the cast, a thorough and comparative study can unveil the secrets of this nineteenth-century art. Further investigation is required to study the deterioration of those compounds on the sub-molecular level.

Abbreviations

BSE: Back Scattered Electron; EDS: Energy Dispersive Spectrometry; FT-IR: Fourier-Transform Infra-Red; FPA: Focal Plane Array; GCMS: Gas Chromatography-Mass Spectrometry; OM: Optical Microscopy; PL: Proper Left; PR: Proper Right; py: pyrolysis; SEM: Scanning Electron Microscopy; TMAH: tetramethylammonium hydroxide; UVF: Ultraviolet Fluorescence; VLR: Visible Light Reflectance; XRD: X-ray Diffraction.

Availability of data and materials

All data generated during this study are discussed in this published article and are fully available at the Figshare permanent data link: https://doi.org/10.25398/rd.northumbria.13469925

Authors' contributions

Analyses were performed at the Northumbria University laboratories by VR under the supervision of CT. The project was initiated by CT and CH, who supervised the work in the Galleries. JP provided technical observations on the object.

Competing interests

The authors declare that they have no competing interests.

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Figures captions

Figure 1. Plaster cast of the tombstone of Presbyter Bruno (V&A accession number: REPRO.1873-380), ca. 1873. © Victoria and Albert Museum, London / as specified by the rights holder.

Figure 2. An early photograph of the cast shows that metal brackets were used to hold it upright (orange arrows). In this early image the screws that secure it in position are still visible (yellow arrows).

Figure 3. The cast still retains the stamp of the workshop of Friedrich Küsthardt (A). A closer look at the object revealed the plywood sheeting used to conceal the cast's edges unevenness (B). An accidental spillage was highlighted under UV illumination from the area where sample 12 was taken (C).

Figure 4. The outline of the Tombstone drawn in AutoCAD with marked sampling sites (red), pencil marks (pink) and the areas showing retouching (purple) and tool marks (blue).

Figure 5. Sample 1. Fibres of different colours are visible in the micrographs taken with Spotlight 400 FT-IR microscope (A). ATR-FT-IR analysis of the dust, baseline and Kubelka-Munk correction applied (B).

Figure 6. EDS mapping and spectra (A) showed that sample 3 is made of calcium (Ca), sulfur (S) and oxygen (O) (calcium sulfate). Carbon (C) is present as detected from different sources (environment, casting polyester resin and organic media). XRD diffractogram (B) shows the characteristic peaks of gypsum, as also confirmed by comparison with the RUFF database [24] and COD Database [25].

Figure 7. Clay minerals (Al-Si silicates) are present in the stratigraphy of all the samples. EDS mapping and spectra (A and B) of sample 9 show the inclusions made of Aluminium (Al) and Silicon (Si), but also iron (Fe) and strontium (Sr). In other samples magnesium (Mg), titanium (Ti) and potassium (K) are present in the silicate inclusions.

Figure 8. py-TMAH-GC/MS chromatogram of sample 2 in the full retention time range, 0-40 min (A) and a narrower range, 16-30 min (B). The peaks up to 16.99 min are due to smaller lipid and amine fragments which are not diagnostic in this sample. The identification of pine resin was possible upon determination of the following markers: dimethyl azelate **1**, methyl palmitate **2**, methyl stearate **3**, 7-oxo-dehydroabietic acid methyl ester **4** and methyl dehydroabietate **5**. The mass spectra of compounds **4** (C) and **5** (D) are also shown.

Figure 9. High vacuum SEM-EDS ($1.5x10^{-2}$ Pa) of sample 2 allowed a higher magnification; BSE image (C) shows the tabular structure of the gypsum plaster. SEM-EDS Low Vacuum Mode (10-15 Pa) of the samples cast in resin allowed to acquire the BSE image of the full stratigraphy. In sample 12 the *tabular* structure can be observed in layers 0 and 1 and layer 1 appears denser in the BSE image (B) and has a yellow tone under VLR OM (A). In sample 10 the BSE image (D) shows that the casting resin was absorbed evenly in the pores.

Figure 10. FT-IR spectra acquired in ATR mode (gypsum plaster reference) (A), and in DR of polyester casting resin reference (B) and from layer 2 of sample 6 (orange line in C) and sample 9 (blue line in C).

Figure 11. Sample 11: the surface layer appears dark under VLR OM (A) and the interface layer is yellow under VLR OM. No characteristic fluorescence was observed in the UV-*f* OM (B). EDS mapping shows that the surface layer is mostly made of Si and Al. FT-IR analysis (C) shows a broad band that suggests the presence of gypsum, casting resin and an organic medium.

Figure 12. Sample 4's VLR OM (A) and BSE images (B) and EDS mapping. The sample was taken from an area of overpaint. Al= aluminium, Si= silicon, Ti= titanium, Fe= iron.

Tables

Table 1. Summary of findings in the samples' layers.

SAMPLE	TYPE	NOTES	no. of LAYERS	LAYERS	PLASTER	INTERFACE	COATING	OVERPAINT

1	dust	fibres and mixture of organic and inorganic material	-	-	-	-	-	-
2	plaster from the inner bulk		-	-	calcium sulfate, calcium carbonate, clay minerals, Al, Mg, Si, diterpenic resin	-	-	-
3	cross-section		3	2. Dark layer 1. Yellowish and undefined layer 0. Plaster bulk	calcium sulfate, calcium carbonate, clay minerals, Mg, diterpenic resin	Intermediate of plaster and dark layer	Mostly Si and Al; Fe, Ti and traces of Na, Cl and K, diterpenic resin	-
4	cross-section	edge area of sampling	4	3. Purple layer 2. Dark layer 1. Yellowish and undefined layer 0. Plaster bulk	calcium sulfate, calcium carbonate, clay minerals, Mg, diterpenic resin	Intermediate of plaster and dark layer	Mostly Si and Al, traces of K, Ba, Zn, Cl and P, diterpenic resin	Fe, Si and Ti, traces of K, Ba, Zn, Cl and P, drying oil modified alkyd paint
5	cross-section		3	2. Dark layer 1. Yellowish and undefined layer 0. Plaster bulk	calcium sulfate, calcium carbonate, clay minerals, Mg, Ti, diterpenic resin	Intermediate of plaster and dark layer	Mostly Si and Al, traces of Mg, Ti, Na, Fe and K, diterpenic resin	-
6	cross-section	area of repair	3	2. Dark layer 1. Yellowish and undefined layer 0. Plaster bulk	calcium sulfate, calcium carbonate, clay minerals, Mg, Ti, traces of K and Fe, organic medium	Intermediate of plaster and dark layer	Mostly K, Fe, Si and Al, traces of Na, Pb and Cl, organic medium	-
7	cross-section	area of repair	2	1. Yellowish and undefined layer with large orange and black particles 0. Plaster bulk	calcium sulfate, calcium carbonate, clay minerals, organic medium	-	Mostly Fe and Ba, traces of Mg, K and Cl, organic medium	-
8	cross-section	fluorescent varnish	4	3. Varnish 2. Dark layer 1. Yellowish and undefined layer 0. Plaster bulk	calcium sulfate, calcium carbonate, clay minerals, Mg, Cl, diterpenic resin, possibly additional triterpenic resin or birch	Intermediate of plaster and dark layer	Mostly Si and Al, traces of K, Fe and Na, diterpenic resin, possibly additional triterpenic resin or birch	-
9	cross-section		3	2. Dark layer 1. Yellowish and undefined layer 0. Plaster bulk	calcium sulfate, calcium carbonate, clay minerals, Mg, Al, Sr and Fe, diterpenic resin, possibly additional triterpenic resin or birch	Intermediate of plaster and dark layer	Mostly Si, Al, Mg, Sr and Fe, traces of K and Ti, diterpenic resin, possibly additional triterpenic resin or birch	-

10	cross-section		3	2. Dark layer 1. Yellowish and undefined layer 0. Plaster bulk	calcium sulfate, calcium carbonate, clay minerals, Mg, organic medium	Intermediate of plaster and dark layer	Mostly Si and Al, traces of K and Cl, organic medium	-
11	cross-section		4	3. Varnish 2. Dark layer 1. Yellowish and undefined layer 0. Plaster bulk	calcium sulfate, calcium carbonate, clay minerals, Mg, organic medium	Intermediate of plaster and dark layer	Mostly Si and Al, traces of Fe and Mg, organic medium	-
12	cross-section	fluorescent varnish	4	3. Varnish 2. Dark layer 1. Yellowish and undefined layer 0. Plaster bulk	calcium sulfate, calcium carbonate, clay minerals, Mg	Intermediate of plaster and dark layer	Mostly Si and Al, traces of P, Cl and Fe, organic medium	-
13	cross-section	fluorescent varnish	4	3. Varnish 2. Dark layer 1. Yellowish and undefined layer 0. Plaster bulk	calcium sulfate, calcium carbonate, clay minerals, Mg, diterpenic resin	Intermediate of plaster and dark layer	Mostly Si and Al, traces of Fe, Mg, Cl, Ti and Na, diterpenic resin	-

Table 2. XRD peaks observed in the diffractograms of samples 2 and 3 and found in the RUFF database gypsum references R060509 and R040029.

XRD peaks, 2θ [°]			
Sample 2	**Sample 3**	**R060509**	**R040029**
11.6304	11.67299	11.6688	11.6553
20.6882	20.74514	20.7682	20.7582
23.3816	23.37026	28.1588	28.1498
26.8718			
29.121	29.10739	29.1507	29.1396
31.0975	31.12382		
	32.09465		
33.4643	33.34622		
	34.53655		34.6194
	35.94149		35.9997
	36.65667	36.0027	36.65
	37.3434	37.4189	37.4124
40.5746	40.63457		
43.4695	43.38031		42.2079
	44.16252		44.2309
45.8294	45.51888	45.5453	45.5268
	46.495		46.4606
47.8711	47.85724	47.8955	47.8848

	48.35782	48.4221	48.3983
	48.72981		
	50.32856		
	50.73068		
	51.34237		
	54.41229		54.4676
	55.14868	55.2183	55.191
	55.81309		55.8618
56.6775	56.7291		
58.2058	58.19157		60.3599
	64.75298		
	65.8196		
67.0222	66.7291		66.7077
68.9538	68.66935		
	70.65909		
71.4685	71.22731		
	74.11747		
	76.56741		
	77.39589		
	79.61351		

Table 3. Most relevant py-TMAH-GC/MS mass spectrum fragmentation peaks for the materials characterization across the samples.

RT (min)	m/z	Assignment
16.25	55, 69, 74, 83, 87, 111, 129(100), 138, 171, 188	dimethyl phthalate
17.50	74(100), 87, 97, 111, 143, 152, 178, 185	dimethyl azelate
21.68	74(100), 87, 101, 129, 145, 185, 227, 270	methyl palmitate
23.60	74(100), 87, 129, 143, 199, 255, 298	methyl stearate
25.47	187, 207, 253(100), 313, 328	7-Oxodehydroabietic acid, methyl ester
25.57	141, 155, 197, 239(100), 253, 314	methyl dehydroabietate
30.08	79(100), 121, 138, 160, 189, 205, 442	betullin

Figure 1

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Figure 2

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Figure 3

Click here to access/download;Figure;Figure 3.tif

Figure 4

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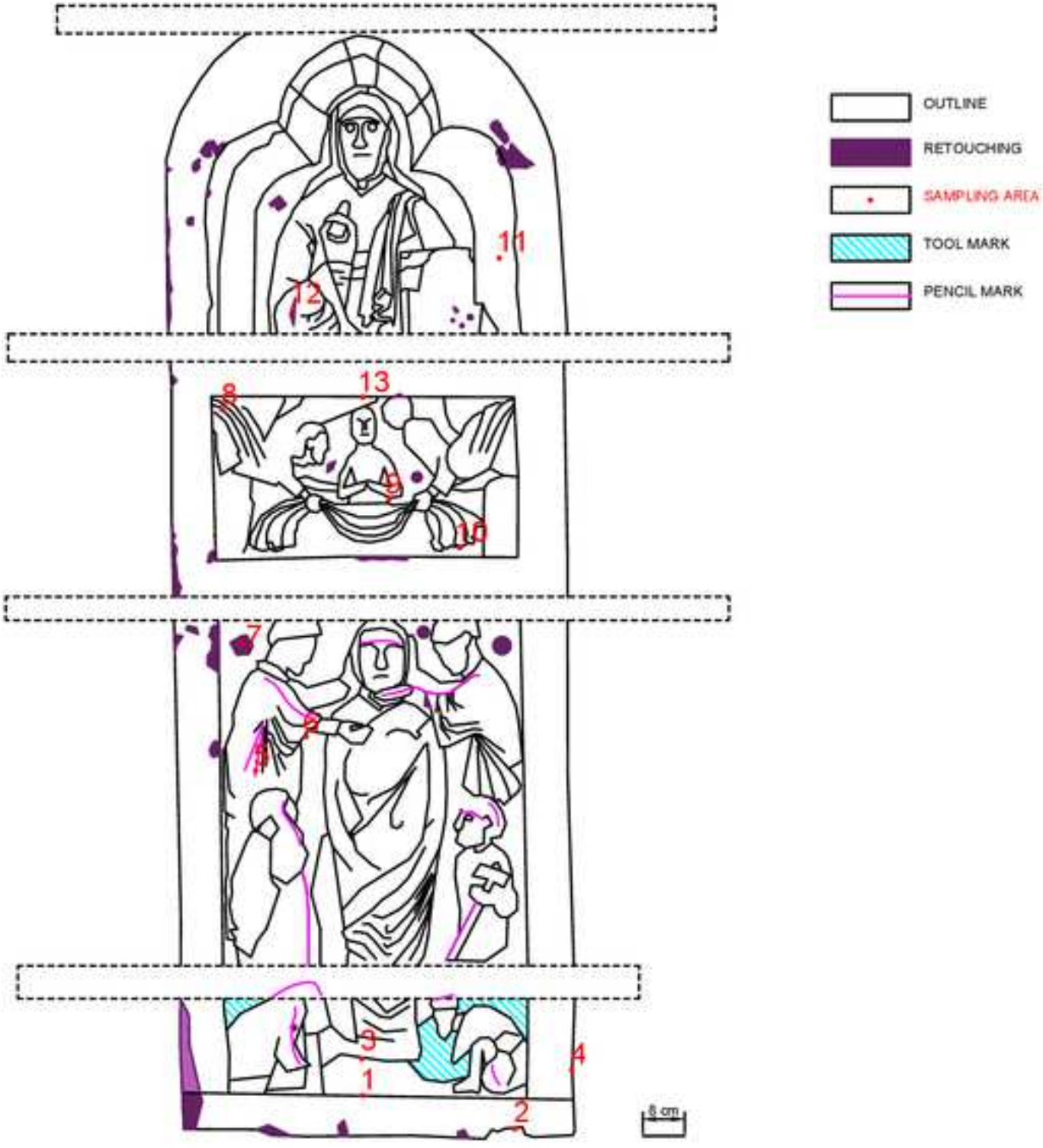

Figure 5

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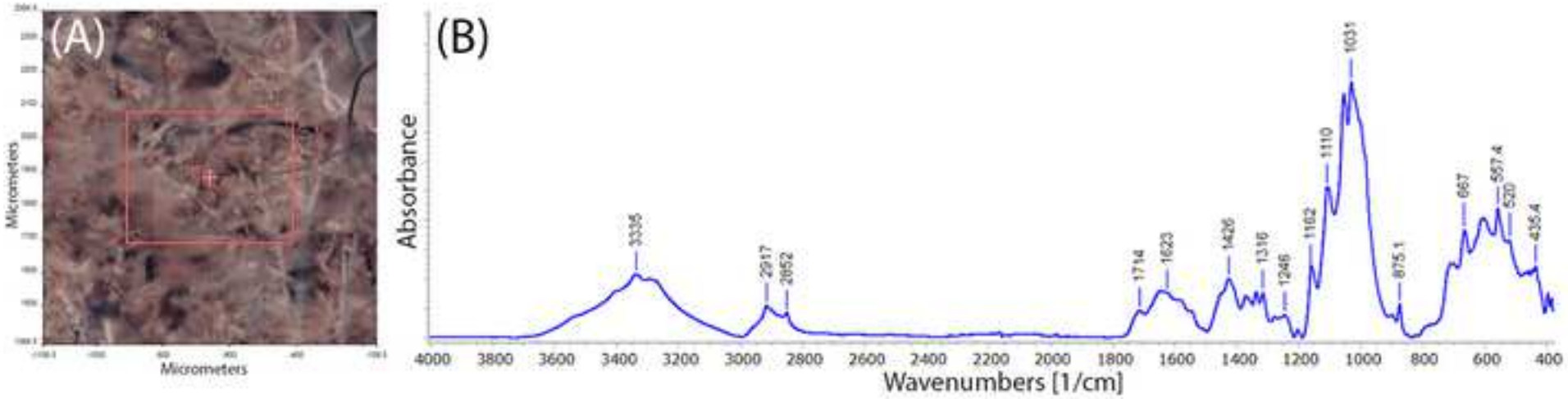

Figure 6

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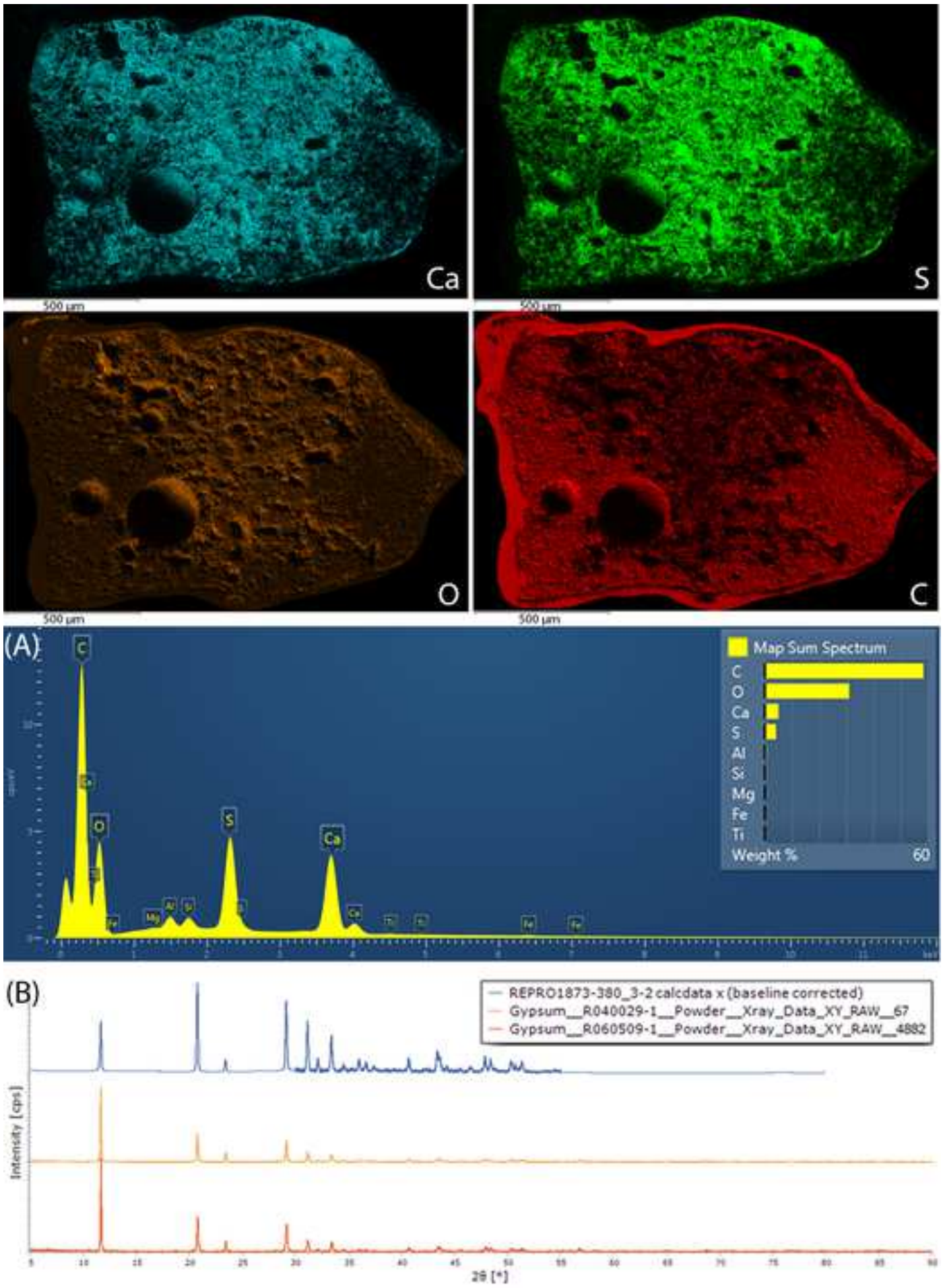

Figure 7

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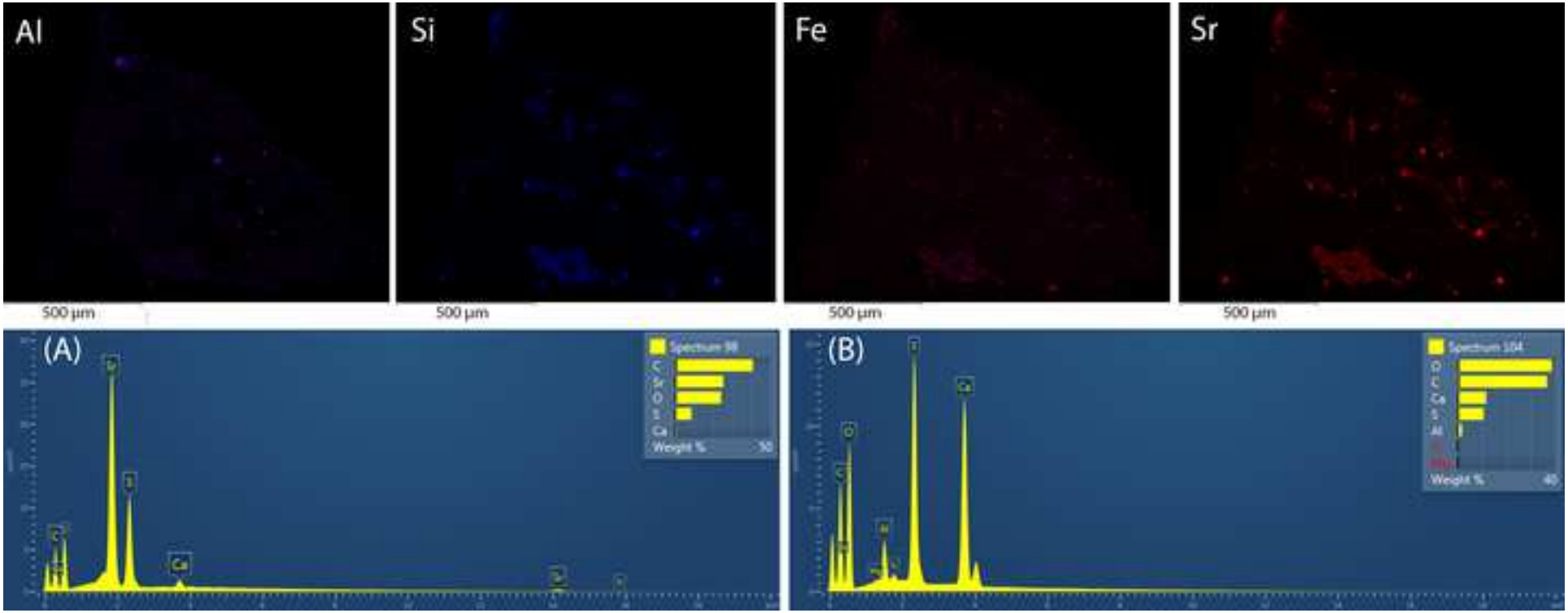

Figure 8

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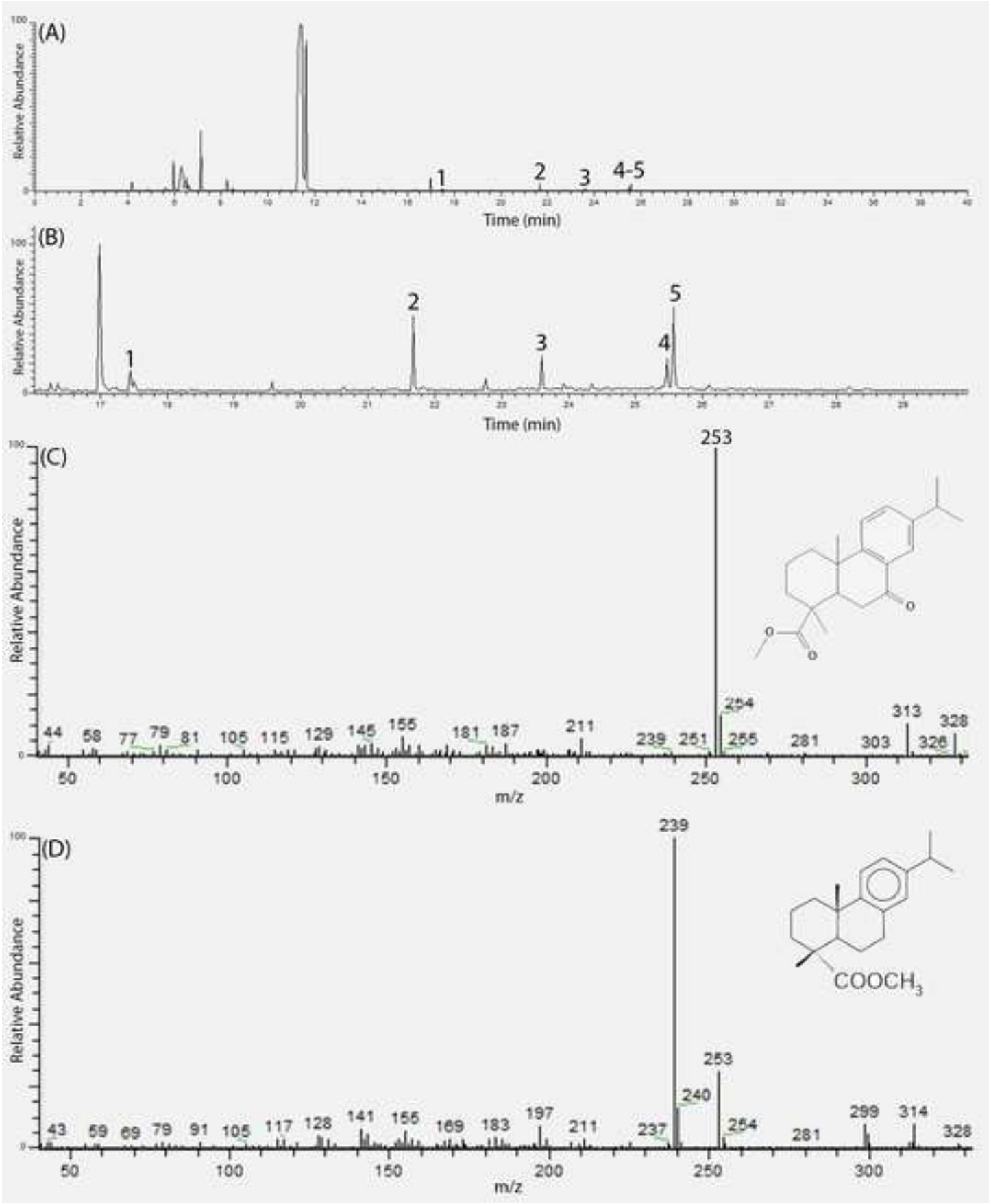

Figure 9

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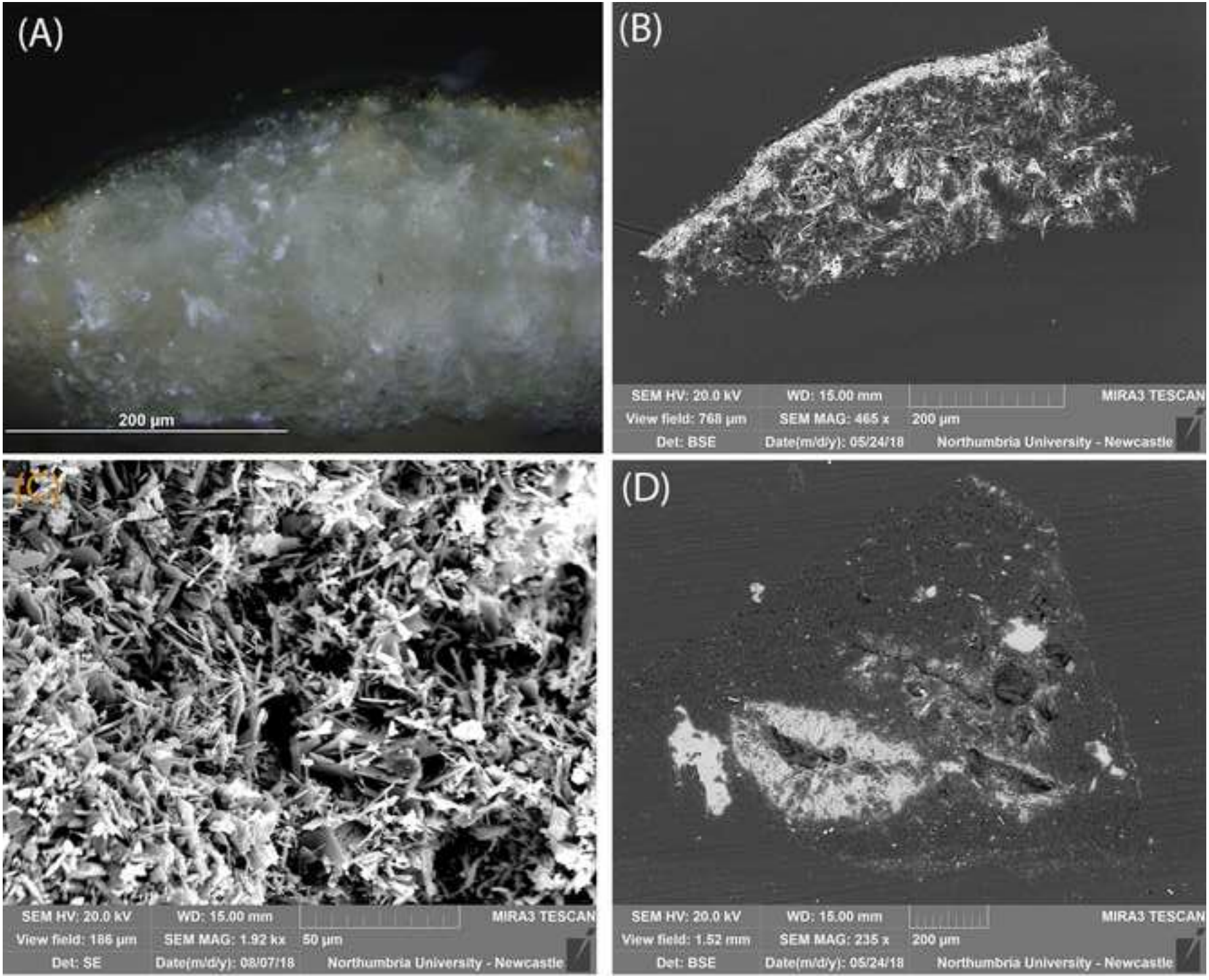

Figure 10

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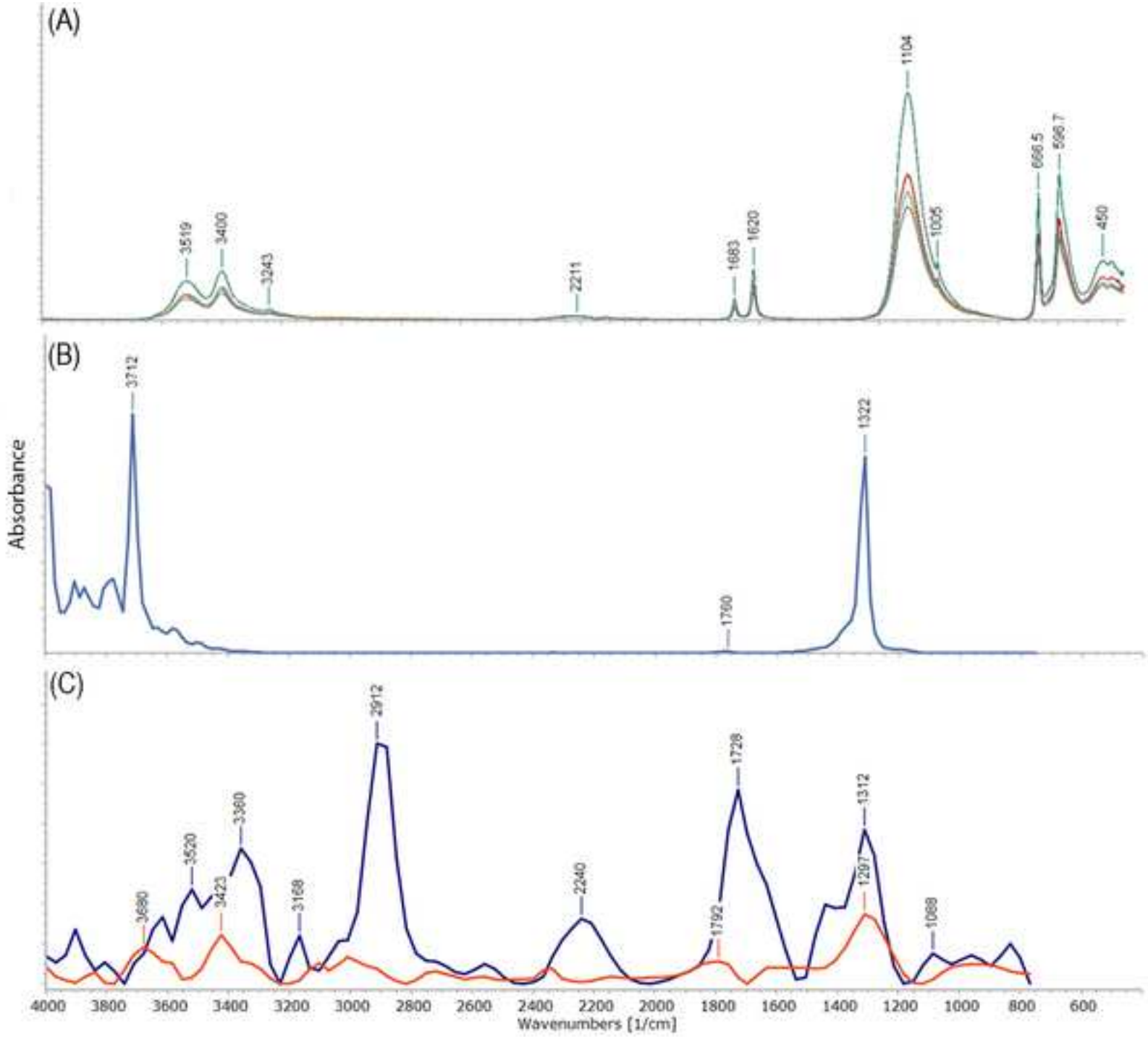

Figure 11

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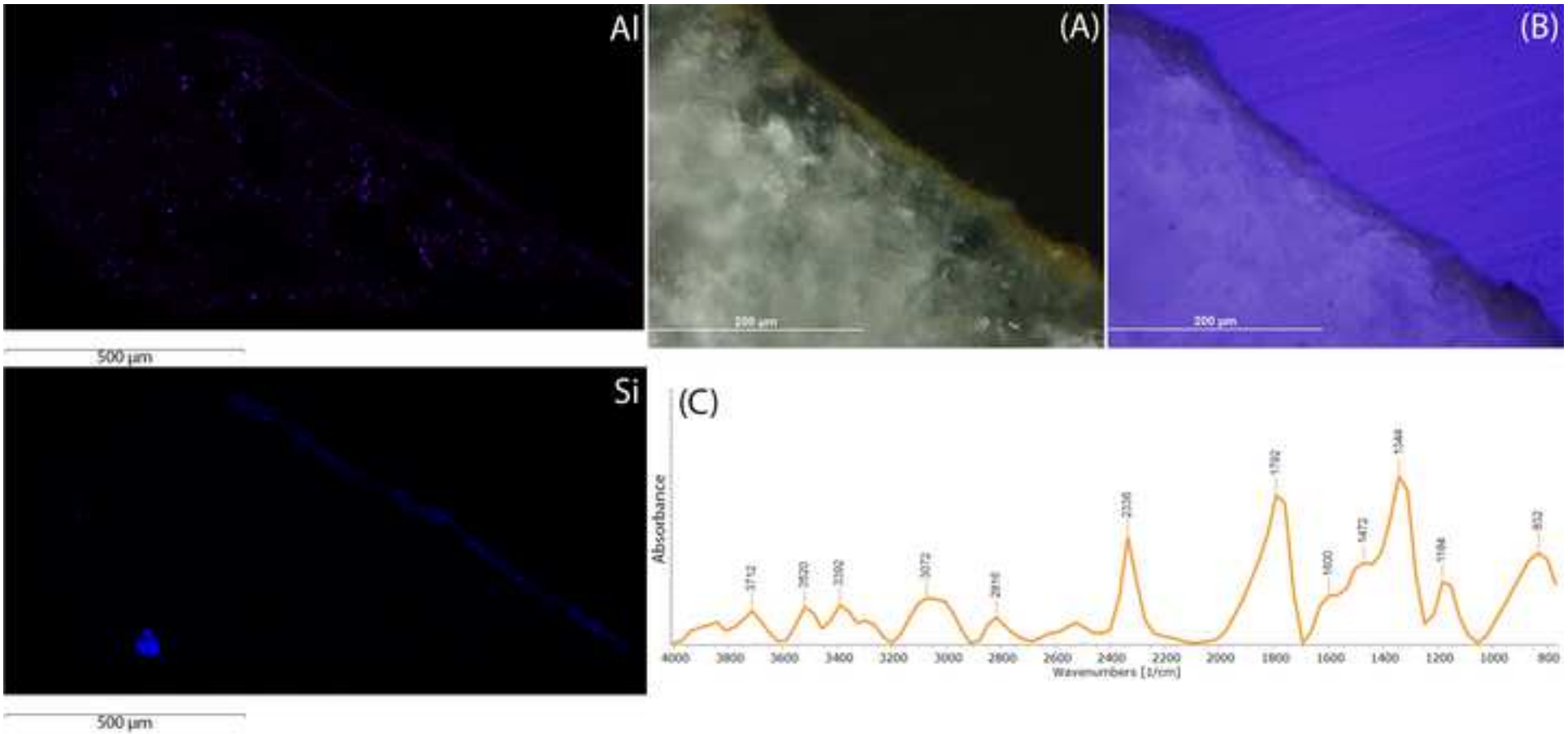

Figure 12

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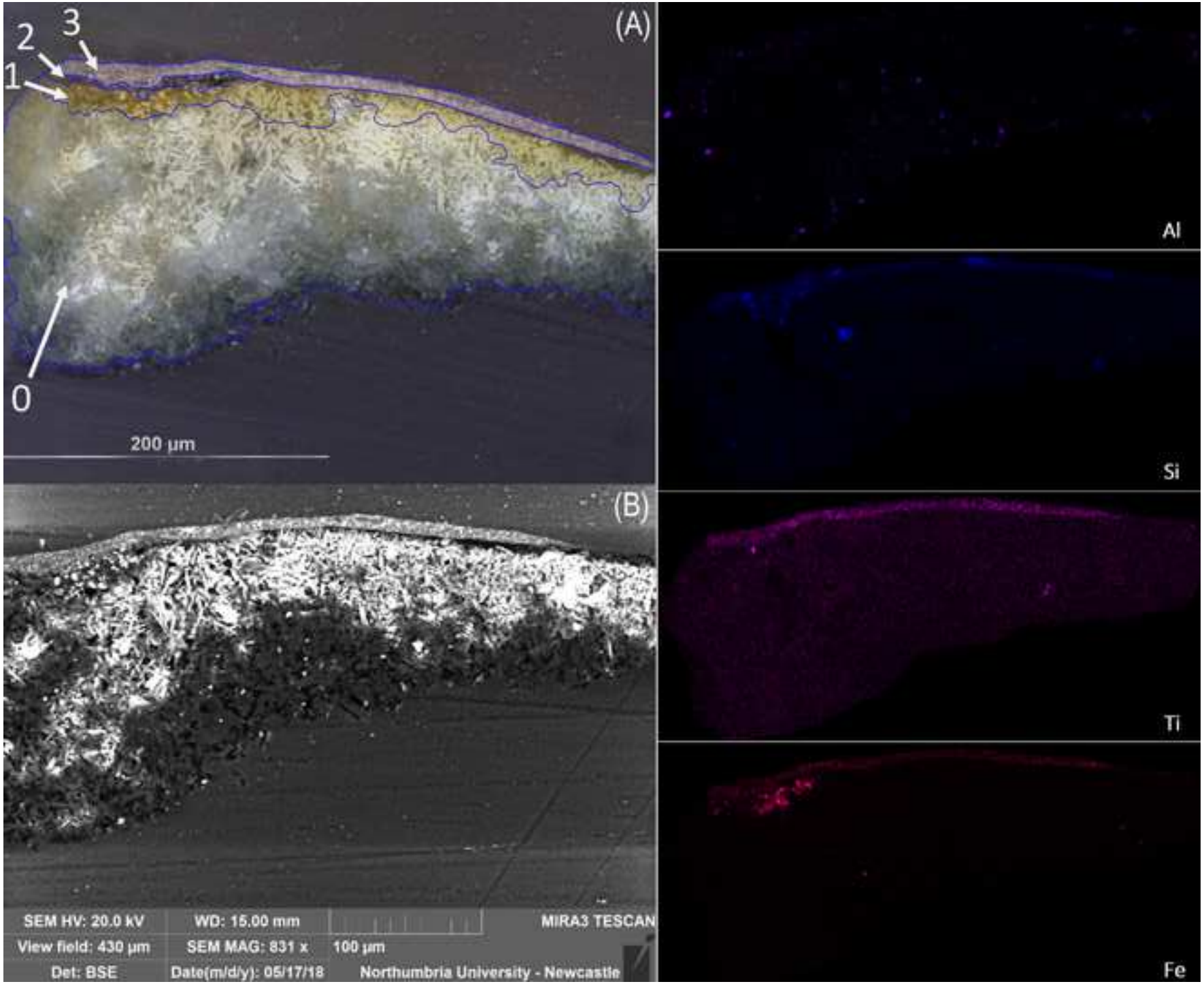

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