

# A multi- analytical approach for the characterization of seventeenth century decorative wall paintings in two Norwegian stave churches: a case study at Eidsborg and Heddal, Norway

Ashley Amanda Freeman <sup>1\*</sup>, Lavinia de Ferri <sup>2</sup>, Joy Mazurek <sup>3</sup>, Fabrizio Andriulo <sup>2</sup> and Chiara Bertolin <sup>1\*</sup>

<sup>1</sup> Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, Richard Birkelands vei 2B, Gløshaugen, 7491 Trondheim, Norway

<sup>2</sup> Department of Collection Management-Museum of Cultural History, University of Oslo, Kabelgaten 34, 0580 Oslo, Norway; l.de.ferri@khm.uio.no (L.d.F.); fabrizio.andriulo@khm.uio.no (F.A.)

<sup>3</sup> Getty Conservation Institute, Science Department 1200 Getty Center Drive, Suite 700, Los Angeles, CA 90049, USA; JMazurek@getty.edu

\* Correspondence: ashley.a.freeman@ntnu.no; chiara.bertolin@ntnu.no

## Pigments within the Norwegian artists' palette

**Table S 1:** List of pigments found in distemper wall paintings in Norwegian stave churches. Table S1 is adapted from Table 3 in Olstad [1] which compiles the findings from two studies using IR spectroscopy, SEM, microscopic examination, and/or microchemical analysis [2, 3].

| Colour | Pigment                   | Time period            |
|--------|---------------------------|------------------------|
| White  | Chalk                     | 1600s-1700s            |
| Yellow | Orpiment                  | 1600s-1700s            |
|        | Yellow ochre / iron oxide | 1600s-1700s            |
| Red    | Cinnabar                  | 1600s-1700s            |
|        | Red lead                  | Medieval               |
|        | Red ochre/ iron oxide     | 1600s-1700s            |
| Blue   | Indigo                    | 1600s-1700s            |
|        | Smalt                     | 1600s-1700s            |
| Black  | Charcoal Black            | 1600s-1700s            |
|        | Bone char                 | Medieval & 1600s-1700s |

**Table S 2:** Colour and pigment assumption for the decor in Heddal and Eidsborg, as cited in conservation reports [4-6].

| Colour           | Pigment assumption                           |                          |
|------------------|--|--------------------------|
|                  | Heddal [4, 5]                                | Eidsborg [6]             |
| Beige            |  | Raw umbra and chalk      |
| Black            | Carbon based                                 | Charcoal black           |
| Green            |  | Green earth and chalk    |
| Pale green       |  | Indigo and orpiment      |
| Grey-brown       |  | Raw umbra                |
| Light grey       | Chalk and carbon black                       | Chalk and charcoal black |
| Orange           |  | Orpiment and English red |
| Pale pink / pink | Organic dye (possibly kermes or madder lake) | English red and chalk    |
| Reddish yellow   |  | Orpiment and English red |
| Brownish red     |  | English red              |
| Warm red         |  | Cinnabar                 |
|                  |  | Orpiment and English red |

|                      |                          |                                     |
|----------------------|--------------------------|-------------------------------------|
| Red                  | English red or red ochre |                                     |
| White                | Chalk                    | Chalk                               |
| White- greyish white |                          | Chalk, possibly with charcoal black |
| Yellow               |                          | Orpiment                            |

## Structural and interior changes of Heddal and Eidsborg

**Table S 3:** Brief history of structural and interior changes of Heddal and Eidsborg, described in the conservation reports of Wedvik [4, 5] and Solberg, Norsted, and Spaarschuh [6].

|           | Heddal [4, 5]  | Eidsborg [6]  |
|-----------|--|---|
| 1200-1300 | Constructed in 1200s   | Constructed 1250-1300   |
| 1600s     | In the late 1600s, fixtures were mounted to the walls, galleries were added to the nave, and the medieval décor was overpainted with a glue-based paint.   | The northern wall of the nave was rendered in 1604, whereas the southern wall is dated as 1640/49.  |
| 1800s     | Between 1849 and 1851, the Baroque restorations were removed, and the decorative wall paintings were covered with panels. Concurrently, the structure underwent its first reconstruction.  | Eidsborg was rebuilt twice, once in 1826 and later in 1845. During these reconstructions, the nave was extended, widows were inserted into the nave's southern wall, and the interior décor was covered with panels.  |
| 1900s     | The third and final restoration of the interior was performed between 1930 and 1955, in which the 19th century panelling was removed revealing the 17th century distemper paint and fragmented medieval décor. Once the pictorial layer was exposed, consolidation and extensive retouching were performed. Additionally, in the 1950s, the wooden structure was "restored" to its medieval configuration. | In the 1920s, in an attempt to return the church to its medieval appearance, most of the 19th century alterations were removed. The wall panelling was taken down and the large 19th century windows were replaced with smaller ones. During this reconstruction, the décor on the nave's southern wall suffered and consequently preservation measures were taken. |
| 2000s     | Prior to the 2009 consolidation treatment, dust and debris removal was carried out with a brush, whereas spot cleaning was performed with a damp compress. In addition, thick adhesive layers from the 1950s treatment, were softened with water and mechanically removed from the wall.   | Due to the overall fragility of the décor within Eidsborg (i.e., water sensitivity and loss in cohesive and adhesive properties), neither aqueous cleaning nor dusting was conducted prior to the 2007 consolidation treatment. Although after the consolidant dried, localized debris removal was achievable from the décor's surface.                             |
|           | For both churches, localized consolidation was achieved by applying sturgeon glue to the flaking paint through Japanese tissue paper. Specifically, for Eidsborg it was found that a 2.5 % solution of sturgeon glue was most ideal, whereas in Heddal a 2 % solution was used. Following this treatment, and before drying, excess glue was removed from the Japanese paper by blotting.                  |   |
|           | In 2013 an assessment of these consolidation treatments was performed, and further adhesive or cohesive failure was observed [7]. Consequently, in 2014 NIKU and Riksantikvaren developed a joint project to better understand the overall effects of sturgeon glue. The Sturgeon Glue Project is still ongoing.   |   |

## Sample collection

On 27<sup>th</sup> of September 2018, a sampling campaign was carried out at Heddal and Eidsborg stave church, within the framework of Sustainable Management of heritage Buildings in a Long-term perspective (SyMBoL) Project (Project No. 274749). The sampling concentrated on areas of red pigments within the distemper decorative wall paintings.

**Table S 4:** Sample description and sampling location in nave of Heddal and Eidsborg. Sample naming convention: name of church, sample category (1 – treated with sturgeon glue, 2- untreated, 3- treated with sturgeon glue and in poor condition), letter signifying specific sample. See **Figure S 1** for visual representation of sampling location and specimen collected. See manuscript for map of sampling points (**Figure 3**).

| sample description and sampling location                                |  |                       |  |
|---|--|-----------------------|--|
| <b>H1a: four-layered stratigraphy (red, grey, orange, white)</b>        |  |                       |  |
| Northern wall   | 2nd plank from the north-west post             | 180 cm from the floor | 25 cm from the north-west post                             |
| <b>H1b: four-layered stratigraphy (red, grey, orange, white)</b>        |  |                       |  |
| Northern wall   | 3rd plank from the north-west post             | 166 cm from the floor | 66 cm from the north-west post                             |
| <b>H1c: four-layered stratigraphy (red, grey, orange, white)</b>        |  |                       |  |
| Northern wall   | 3rd plank from the north-west post             | 193 cm from the floor | 84 cm from the north-west post                             |
| <b>H1d: three-layered stratigraphy (red, grey, white)</b>               |  |                       |  |
| Northern wall   | 2nd plank from the door's proper right         | 228 cm from the floor | 75 cm to the right from the door in the middle of the wall |
| <b>H1e: four-layered stratigraphy (red, grey, black, white)</b>         |  |                       |  |
| Northern wall   | 2nd plank from the door's proper right         | 233 cm from the floor | 58 cm from the door to the right.                          |
| <b>H2a: three-layered stratigraphy (red, grey, white)</b>               |  |                       |  |
| Northern wall   | 1 <sup>st</sup> plank from the north-east post | 310 cm from the floor | 22 cm from the post to the right.                          |
| <b>H2b: four-layered stratigraphy (red, grey, black, white)</b>         |  |                       |  |
| Northern wall   | 4th plank from the north-east post             | 332 cm from the floor | 96 cm from the post to the right.                          |
| <b>H2c: four-layered stratigraphy (red and white, grey, red, white)</b> |  |                       |  |
| Northern wall   | 3rd plank from the north-east post             | 341 cm from the floor | 57 cm from the post to the right.                          |
| <b>H2d: four-layered stratigraphy (red, grey, orange, white)</b>        |  |                       |  |
| Northern wall   | 6th plank from the north door                  | 285 cm from the floor | 232 cm from the north portal.                              |
| <b>H2e: four-layered stratigraphy (red, grey, orange, white)</b>        |  |                       |  |
| Northern wall   | 6th plank from the north eastern corner post   | 260 cm from the floor | 202 cm from the north portal                               |

**H3a: five-layered stratigraphy (red and white, grey, black, orange, white)**

|               |                                      |                       |                                 |
|---------------|--------------------------------------|-----------------------|---------------------------------|
| Northern wall | 3rd plank from the post to the left. | 150 cm from the floor | 65 cm from the post to the left |
|---------------|--------------------------------------|-----------------------|---------------------------------|

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**E1a: three-layered stratigraphy (red, black, white)**

|               |                              |                       |                           |
|---------------|------------------------------|-----------------------|---------------------------|
| Southern wall | 8th plank from main entrance | 158 cm from the floor | 10 cm from the windowsill |
|---------------|------------------------------|-----------------------|---------------------------|

**E1b: two-layered stratigraphy (red on white)**

|               |                              |                       |                          |
|---------------|------------------------------|-----------------------|--------------------------|
| Southern wall | 8th plank from main entrance | 192 cm from the floor | 8 cm from the windowsill |
|---------------|------------------------------|-----------------------|--------------------------|

**E1c: three-layered stratigraphy (red, black, white)**

|               |                                     |                       |                                  |
|---------------|-------------------------------------|-----------------------|----------------------------------|
| Southern wall | 4th plank from the post to the left | 164 cm from the floor | 141 cm from the post to the left |
|---------------|-------------------------------------|-----------------------|----------------------------------|

**E1d: two-layered stratigraphy (red on white)**

|               |                                     |                       |                           |
|---------------|-------------------------------------|-----------------------|---------------------------|
| Southern wall | 2nd plank from the post to the left | 181 cm from the floor | 65 cm from the windowsill |
|---------------|-------------------------------------|-----------------------|---------------------------|

**E1e: three-layered stratigraphy (red, black, white)**

|               |                              |                       |                                   |
|---------------|------------------------------|-----------------------|-----------------------------------|
| Southern wall | 3rd plank from main entrance | 153 cm from the floor | 190 cm from the post to the right |
|---------------|------------------------------|-----------------------|-----------------------------------|

**E2a: three-layered stratigraphy (red, black, white)**

|               |                                    |                       |                                 |
|---------------|------------------------------------|-----------------------|---------------------------------|
| Northern wall | 4th plank from the north-west post | 220 cm from the floor | 145 cm from the north-west post |
|---------------|------------------------------------|-----------------------|---------------------------------|

**E2b: three-layered stratigraphy (red, black, white)**

|               |                                    |                       |                                 |
|---------------|------------------------------------|-----------------------|---------------------------------|
| Northern wall | 5th plank from the north-west post | 183 cm from the floor | 181 cm from the north-west post |
|---------------|------------------------------------|-----------------------|---------------------------------|

**E2c: three-layered stratigraphy (red, black, white)**

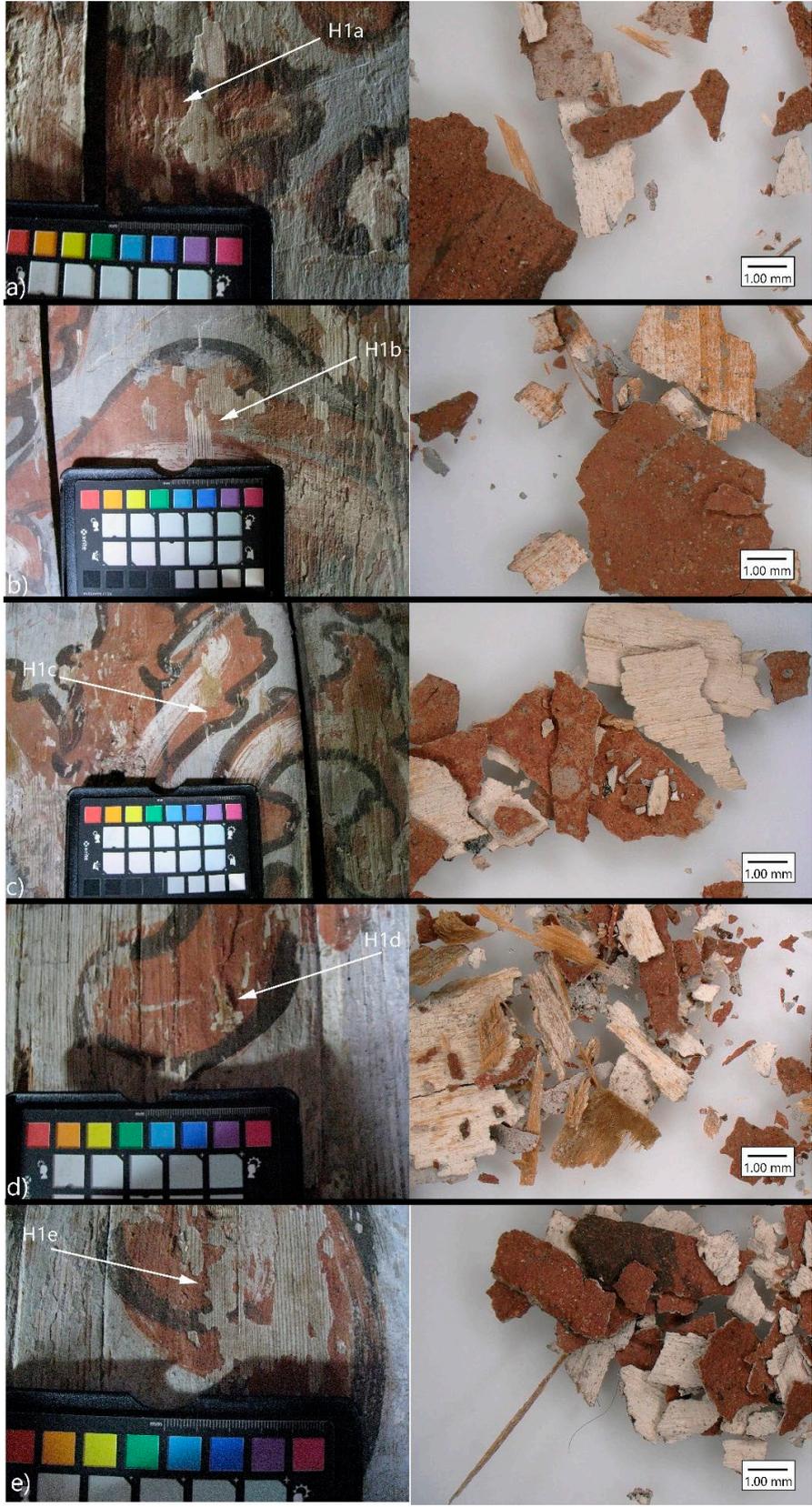
|               |                                    |                       |                                   |
|---------------|------------------------------------|-----------------------|-----------------------------------|
| Northern wall | 5th plank from the north-west post | 183 cm from the floor | 179,5 cm from the north-west post |
|---------------|------------------------------------|-----------------------|-----------------------------------|

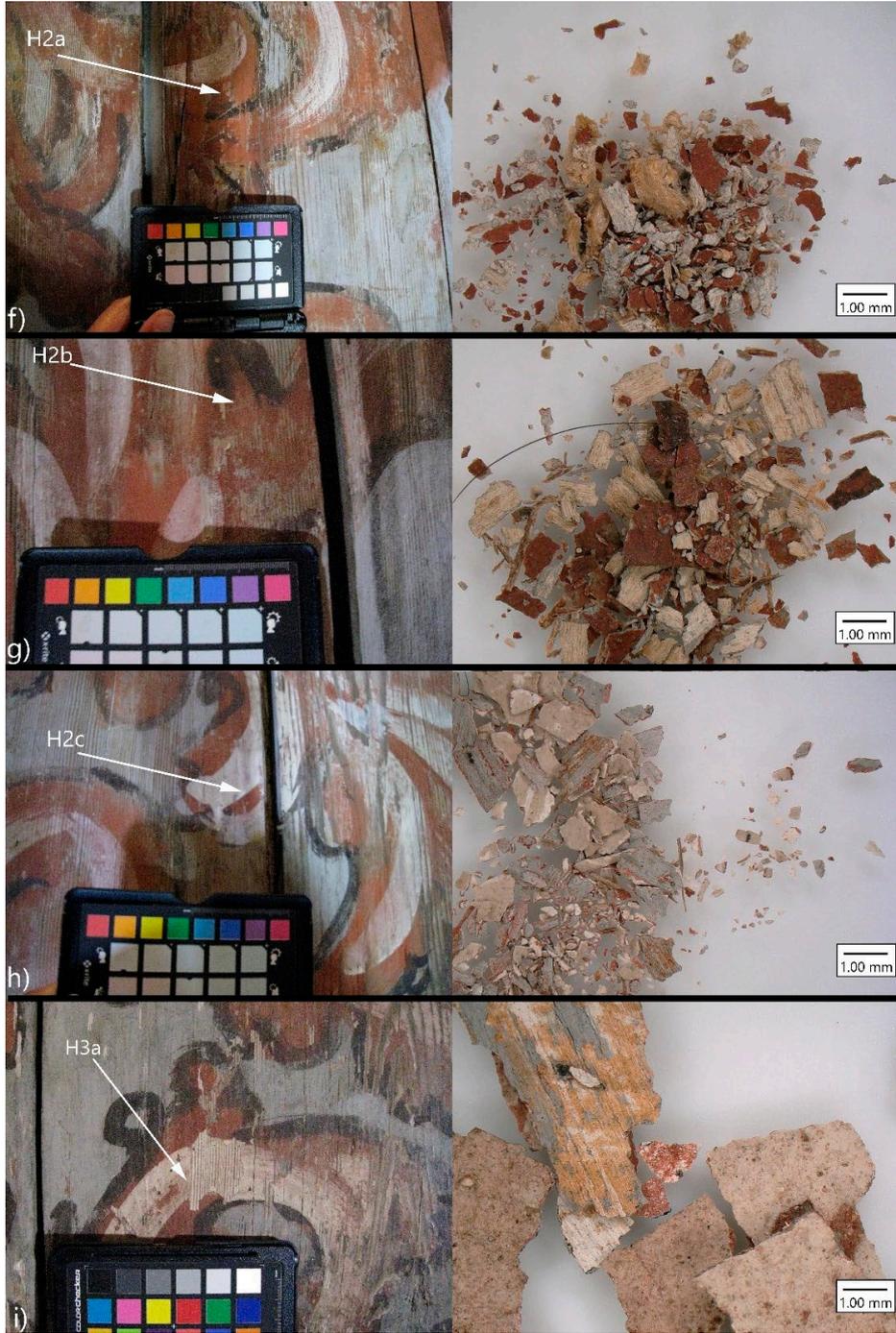
**E2d: three-layered stratigraphy (red, black, white)**

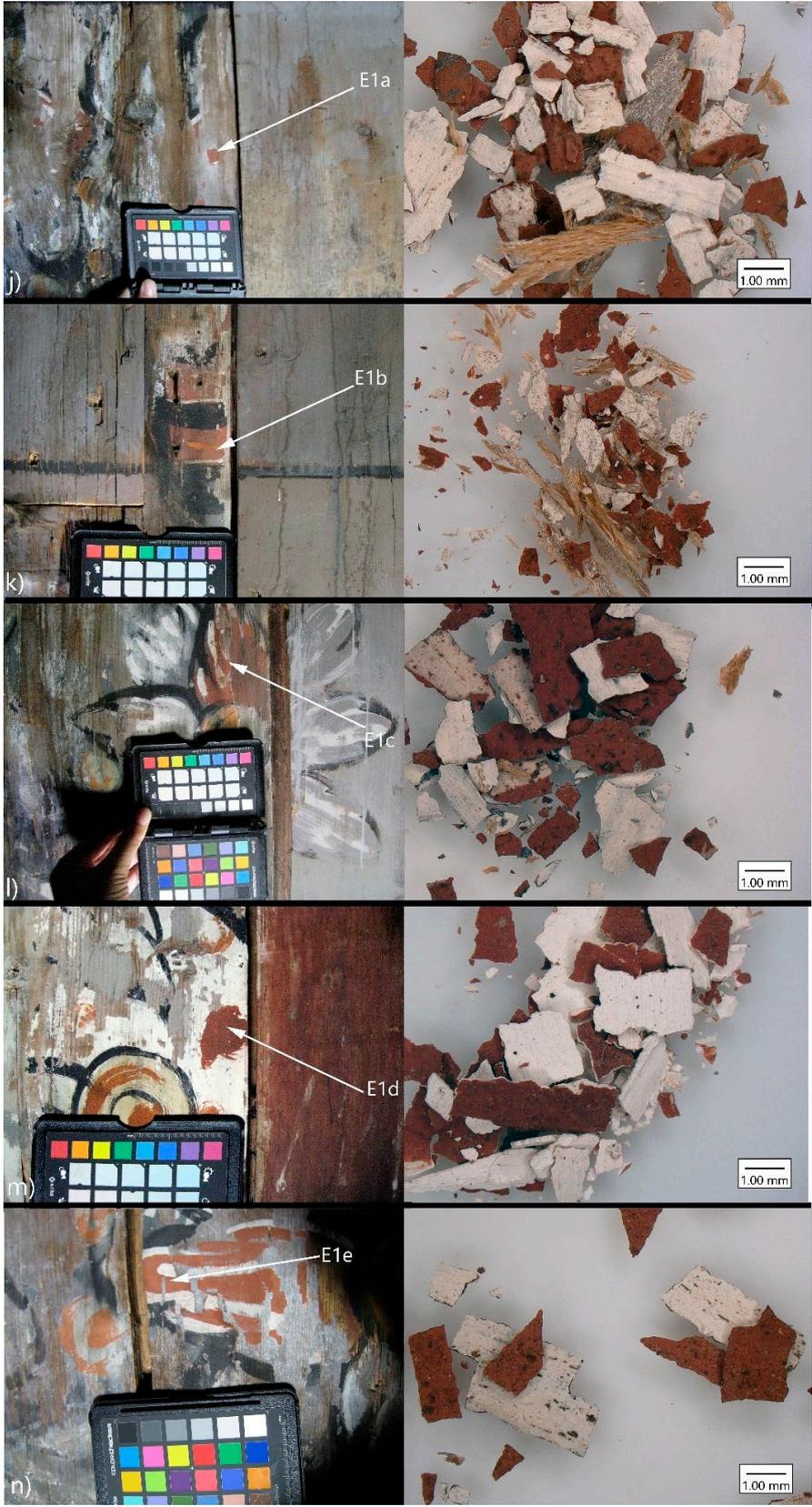
|               |                                    |                       |                                 |
|---------------|------------------------------------|-----------------------|---------------------------------|
| Northern wall | 7th plank from the north-east post | 188 cm from the floor | 235 cm from the north-east post |
|---------------|------------------------------------|-----------------------|---------------------------------|

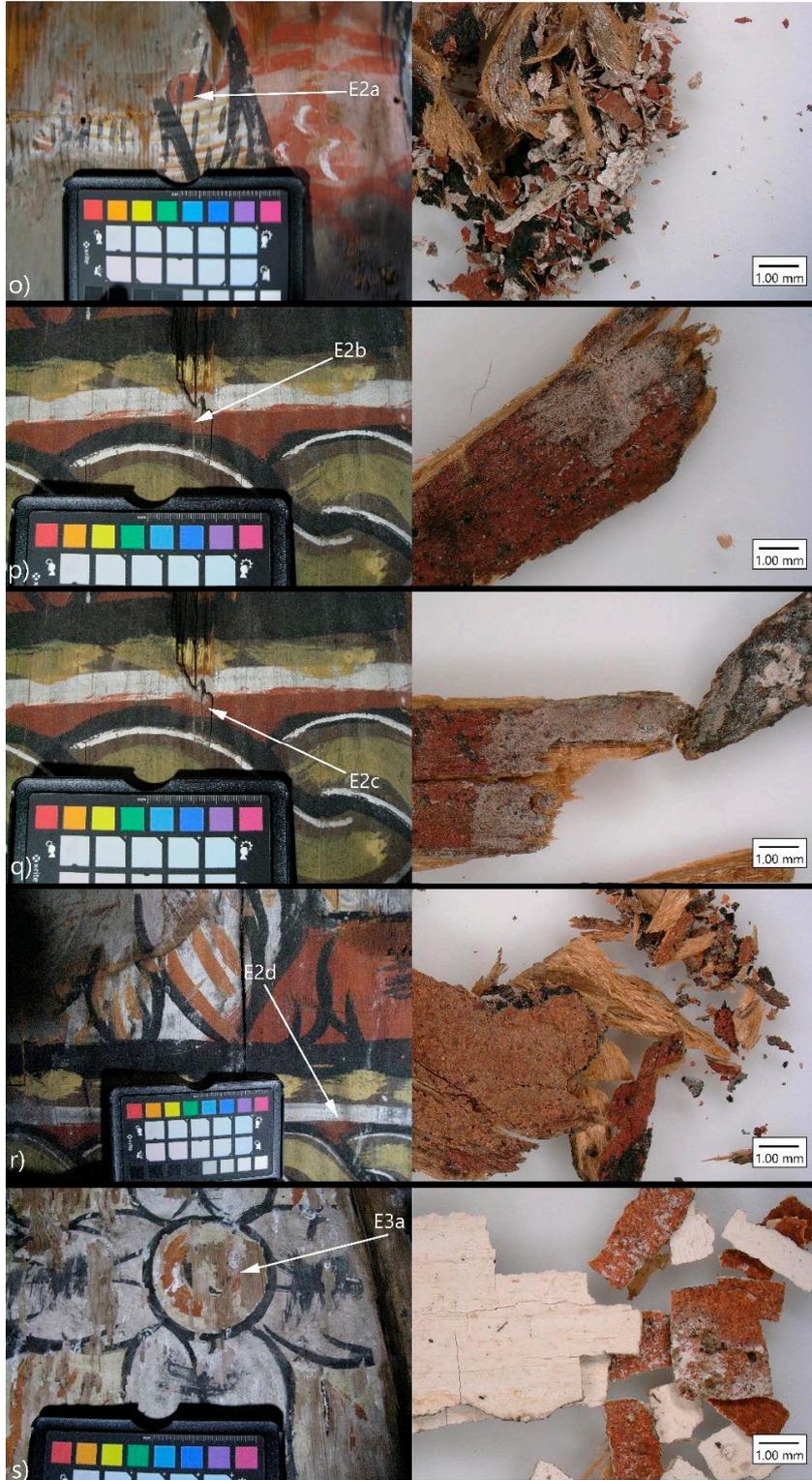
**E3a: two-layered stratigraphy (red on white)**

|               |                                    |                       |                                |
|---------------|------------------------------------|-----------------------|--------------------------------|
| Southern wall | 1st plank from the south-west post | 270 cm from the floor | 27 cm from the south-west post |
|---------------|------------------------------------|-----------------------|--------------------------------|









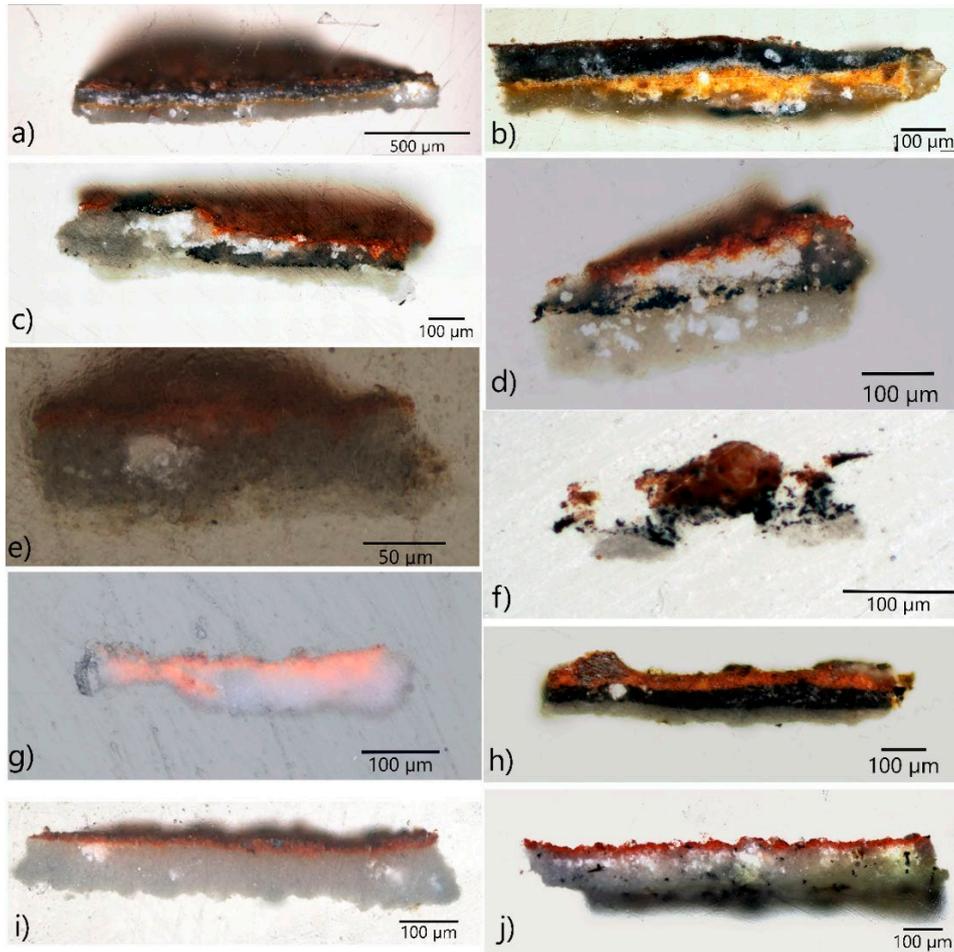
**Figure S 1:** Image of sample location within Eidsborg and Heddal and microscopic image of collected specimen. (Left image): Arrow identifying sample location prior to sampling, (Right image): microscope image of collected sample (100x). Refer to **Table S 4** for numerical location of sampling and description.

### **Chemical Composition of intermediate layers**

All Heddal samples contained a grey pigmented layer, which similarly to the white ground layer, mainly consists of a Ca-based material (**Figure S 5**). In [5, 6], the light grey/whitish-grey layer found for both churches is assumed to be a mixture of chalk and carbon black. Although, it is not possible to identify carbon black by means of SEM-EDS. Two of these Heddal samples (H1a and H1b) also contained an orange layer (**Figure S 2**) which displayed similar EDS results compared to that of the red layer. These results suggest that, like the red pigmented layer, the orange layer is also an ochre pigment. Although the orange layer probably contains goethite (FeOOH) as dominant colouring phase, which is in agreement with previous findings of 1600s -1700s distemper paints from other stave churches [1].

Three of the examined cross-sectional samples contained a black layer (E1a, E1c, and H1e). The EDS results obtained for this layer showed the occurrence of Ca, Si, and Al, as the most common constituents. The most prevalent difference between the black layers within these two churches is the weight percentage of these elements. The results for Eidsborg are rich in Ca (>89 wt. %) and contain relevantly low amounts (1-3 wt. %) of Si and Al, whereas these three components are considered as a major component (>10 wt. %) for the Heddal specimen (H1e). Additionally, H1e contained minor amounts of P (3 wt. %). Although only one sample from Heddal contained a black layer (H1e), the combined presence of Ca and P in this sample is suggestive of a bone black pigment. However, the FT-IR spectrum acquired from H1e did not permit a definitive confirmation of calcium phosphate (presumably in form of hydroxyapatite) as hypothesized from EDS data: its main band could contribute to the shoulder observed at  $\sim 1114\text{ cm}^{-1}$ , even if the total amount of such phase is (if present) probably too low to be actively responsible for any of the identified features. Although, previous examination of other Norwegian 1600s-1700s polychrome wall paintings has identified the black layer as charcoal black or bone char [1] (**Table S 1**), which is in agreement of the pigment assumptions of Heddal[4] and Eidsborg [6] (compiled in **Table S 2**).

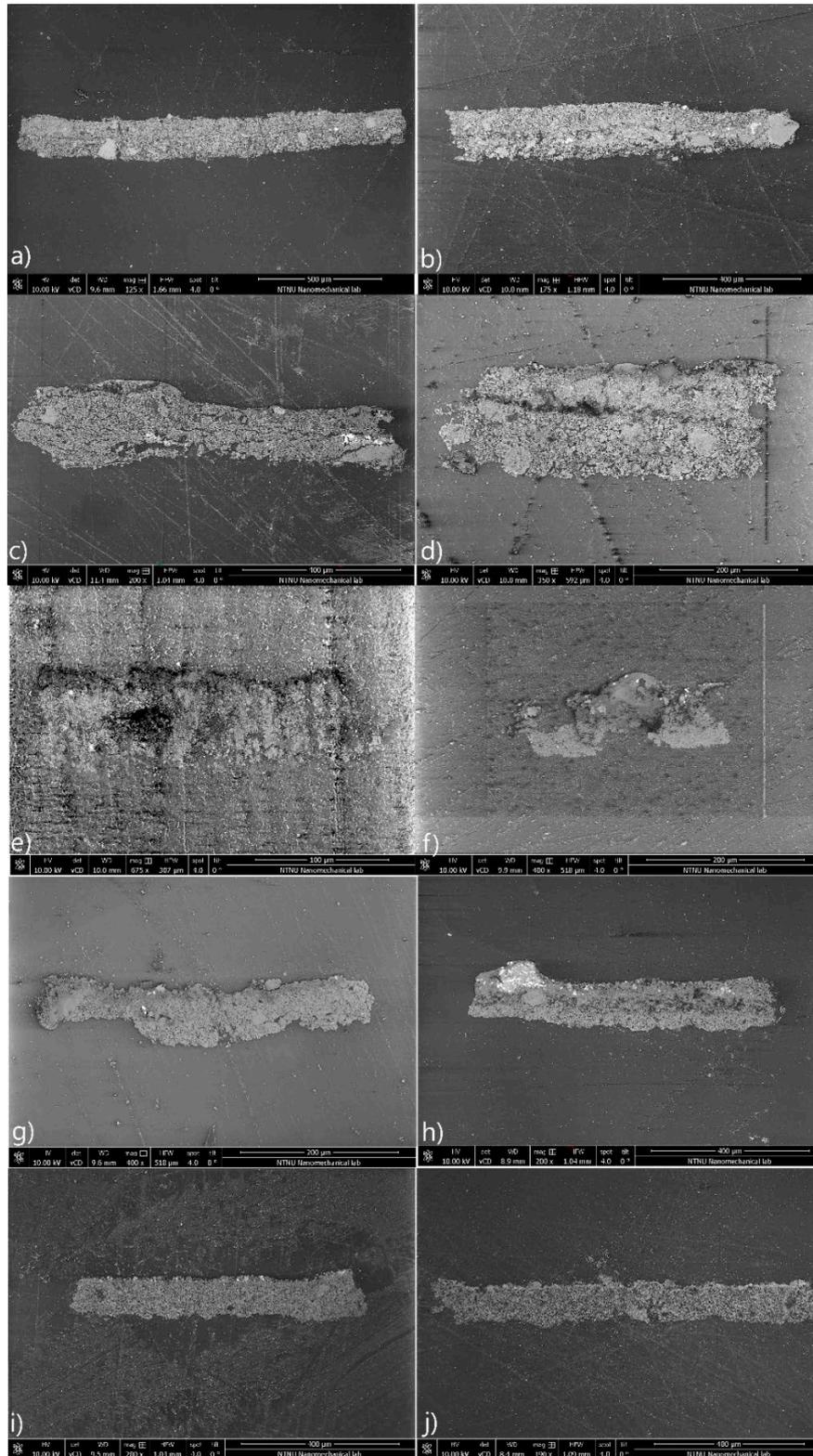
### Microscopic analysis: optical microscopy and scanning electron microscopy



**Figure S 2:** Microscopy images of cross-sectional samples from Heddal and Eidsborg: a) H1a, b) H1b, c) H1d, d) H1e, e) H2a, f) E1a, g) E1b, h) E1c, i) E1d, and j) E2a. Cross-sectional samples were prepared by embedding distemper paint fragments in Technovit® 2000 LC (Heraeus Kulzer, Germany)

**Table S 5:** Summary of cross-sectional sample's stratigraphy through microscopy analysis, where ND means not detected. See **Figure S 1** for corresponding microscopic image of samples.

| Thickness of layer (μm) | H1a      | H1b     | H1d     | H1e     | H2a     | E1a | E1b   | E1c     | E1d      | E2a     |
|-------------------------|----------|---------|---------|---------|---------|-----|-------|---------|----------|---------|
| Red                     | 27 - 33  | 10 - 14 | 15 - 20 | 17 - 28 | 7 - 13  | ND  | 19-35 | 53-78   | 18-28    | 15 - 25 |
| Grey                    | 39 - 79  | 33 - 79 | 38 -144 | 43 - 74 | 34 - 49 |     |       |         |          |         |
| Orange                  | 14 - 20  | 26 - 61 |         |         |         |     |       |         |          |         |
| Black                   |          |         |         | 12 - 27 |         | ND  |       | 40 -54  |          |         |
| White                   | 93 - 127 | 49 - 65 | 37 - 61 | 82 - 85 | 13 - 24 | ND  | 45-87 | 21 - 46 | 87 - 103 | 80 - 90 |



**Figure S 3:** SEM-BSE images of cross-sectional from Heddal and Eidsborg: a) H1a, b) H1b, c) H1d, d) H1e, e) H2a, f) E1a, g) E1b, h) E1c, i) E1d, and j) E2a. See **Figure S 2** for microscopic image of cross-sectional samples.

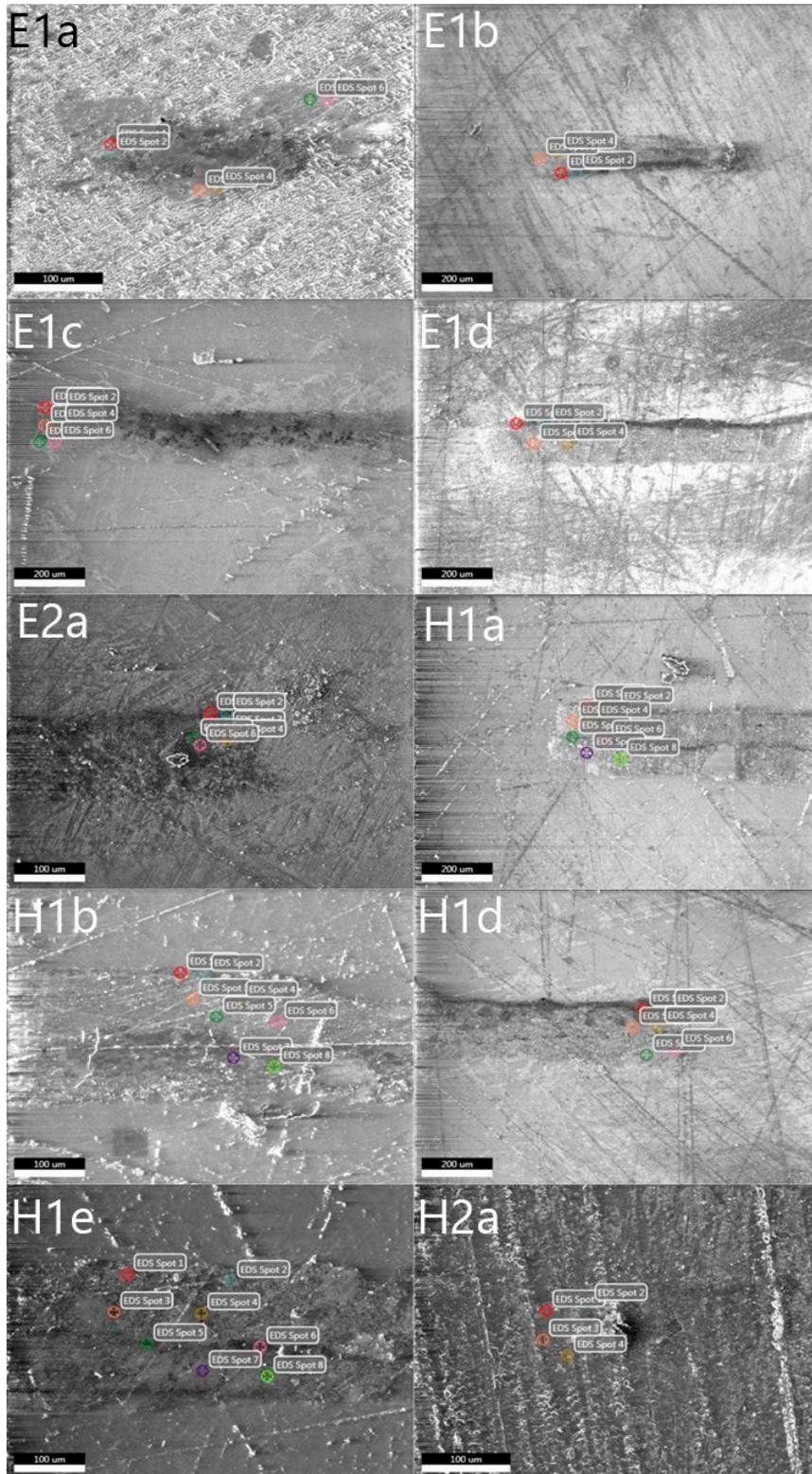
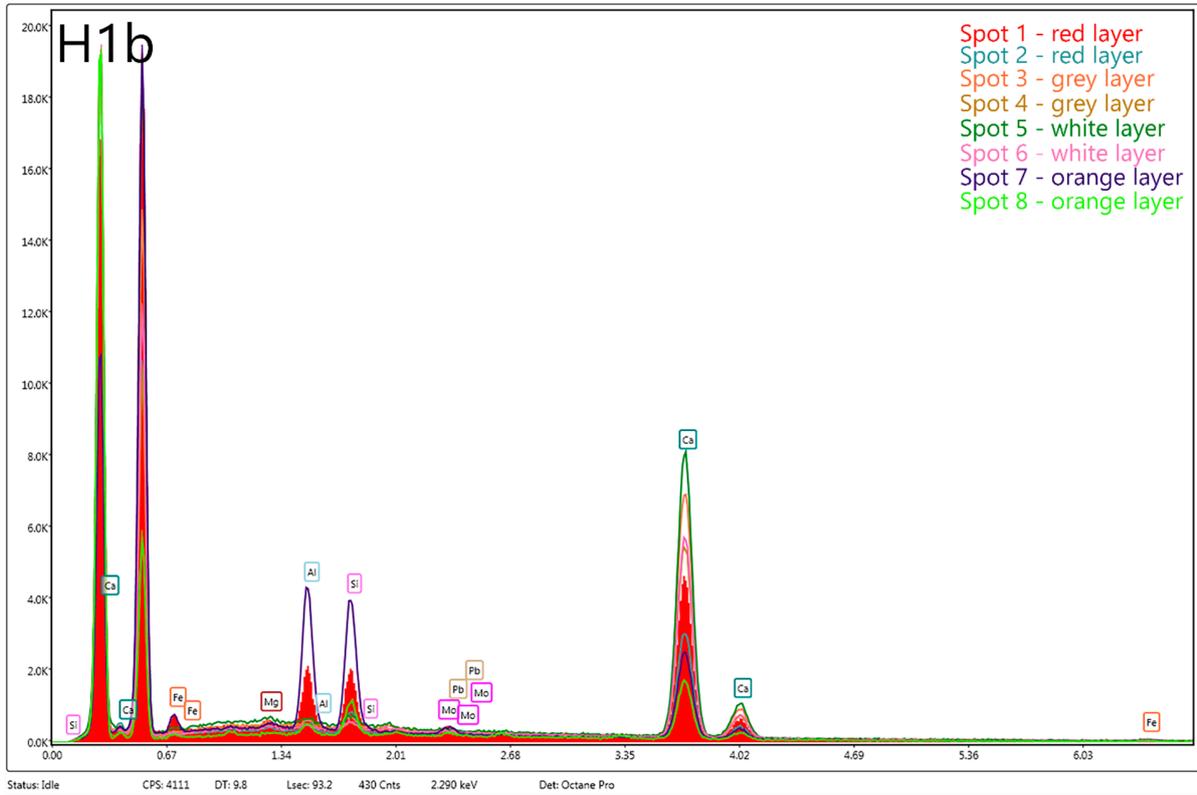
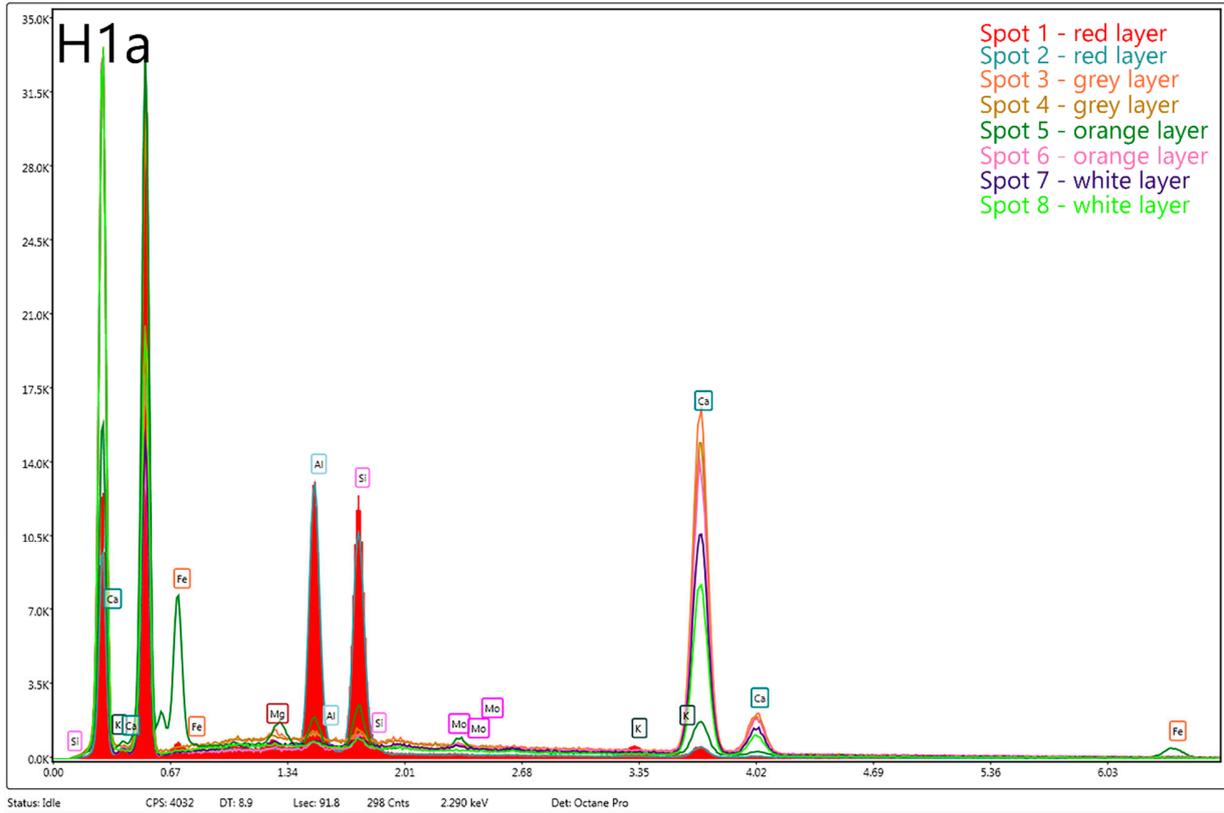
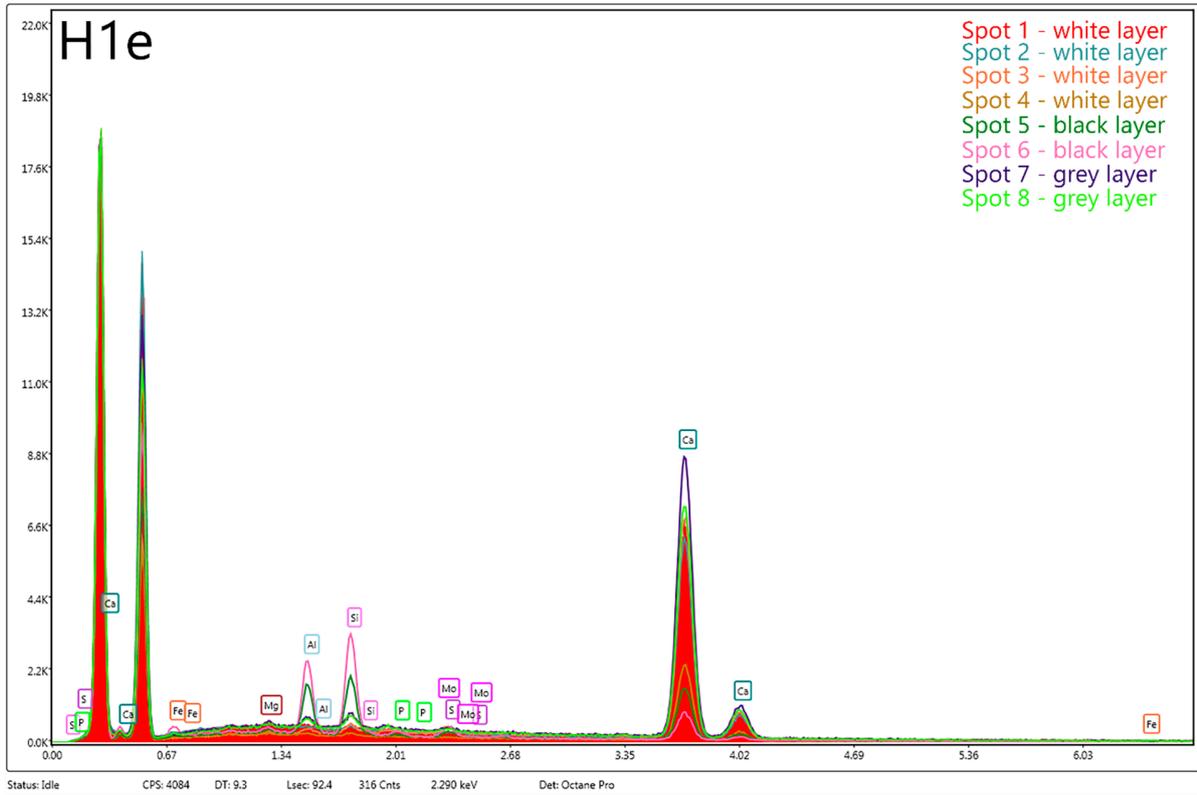
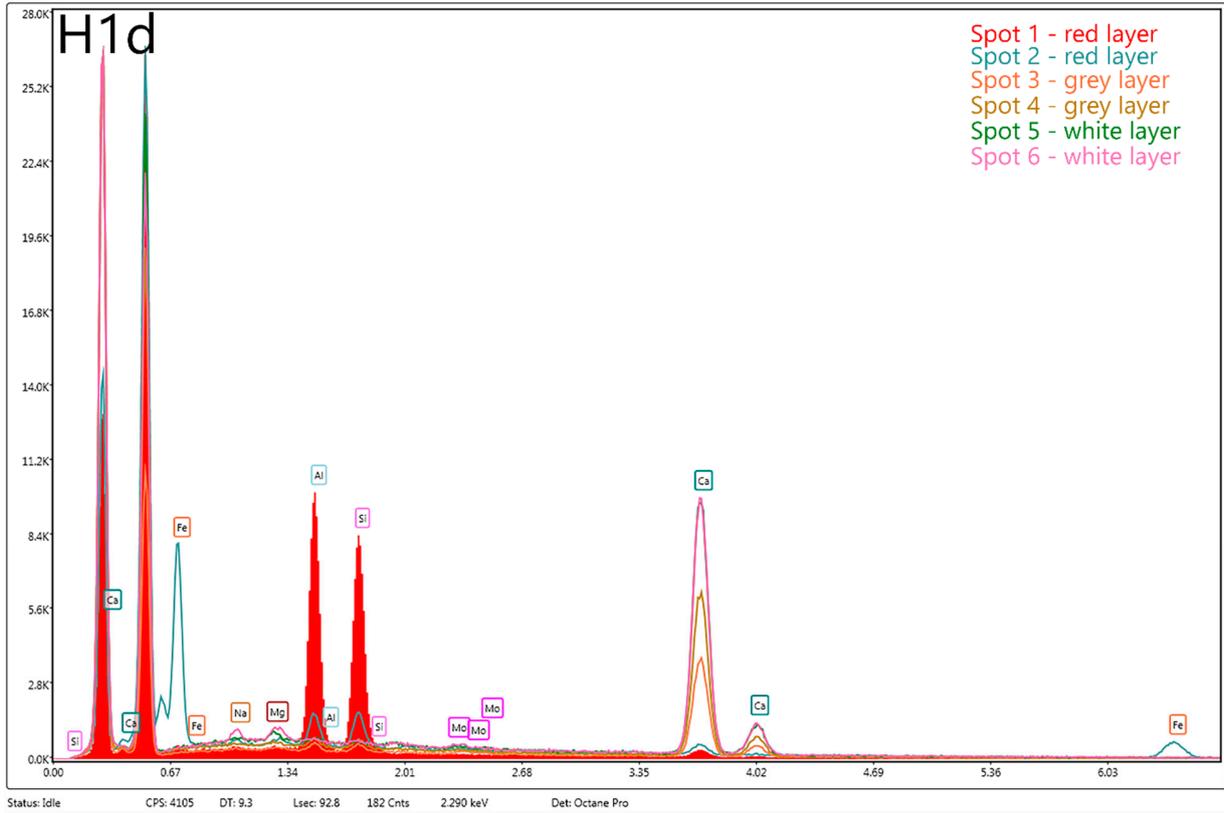
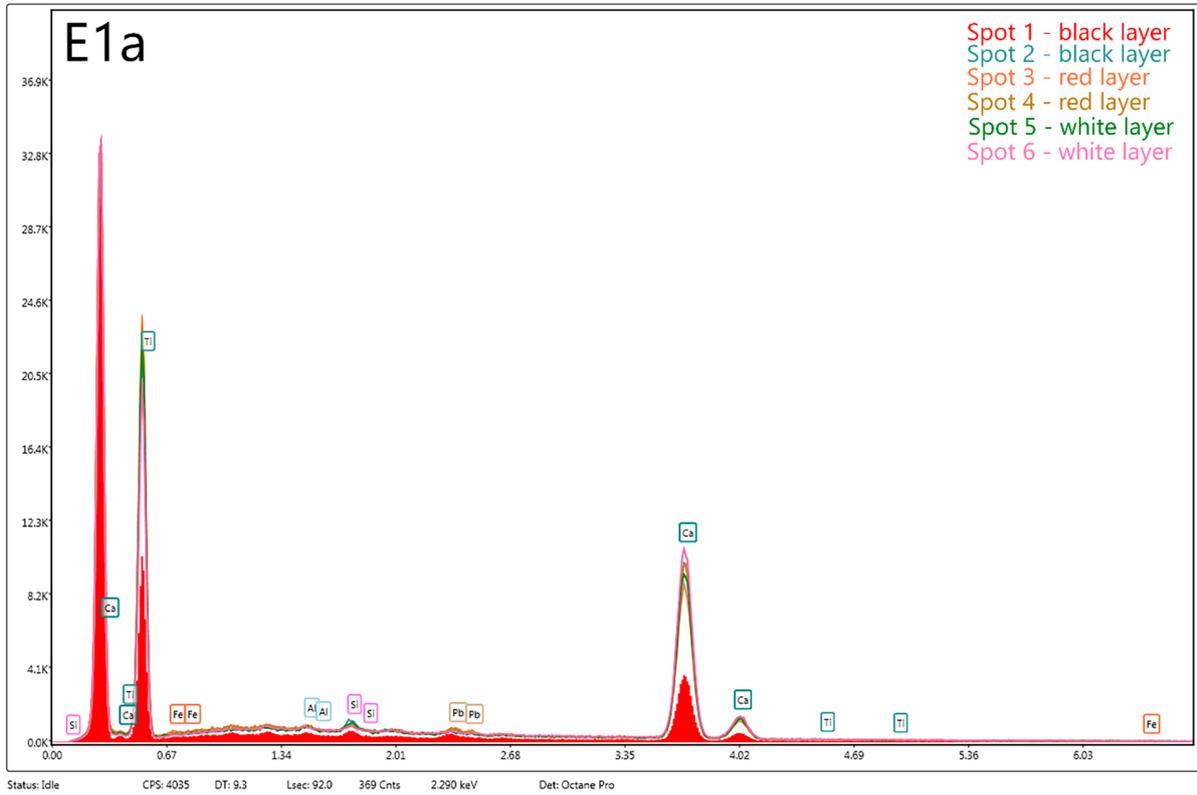
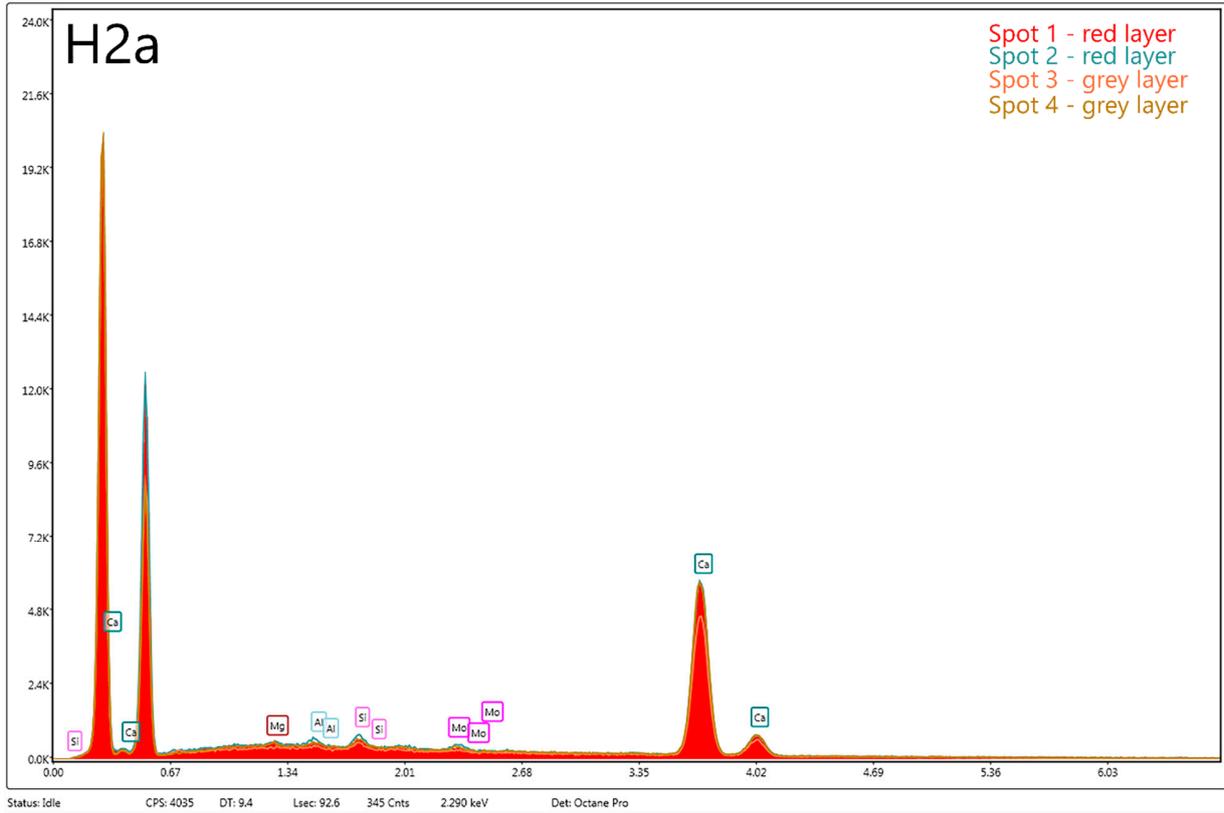
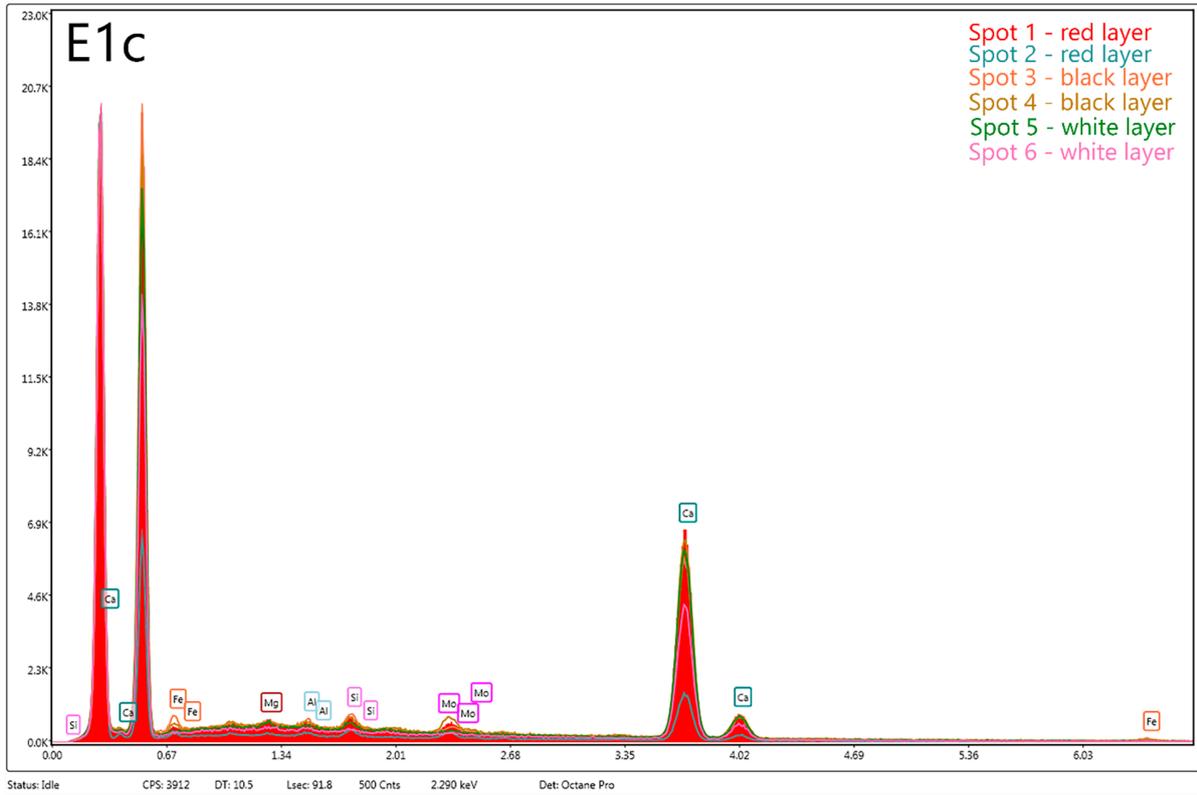
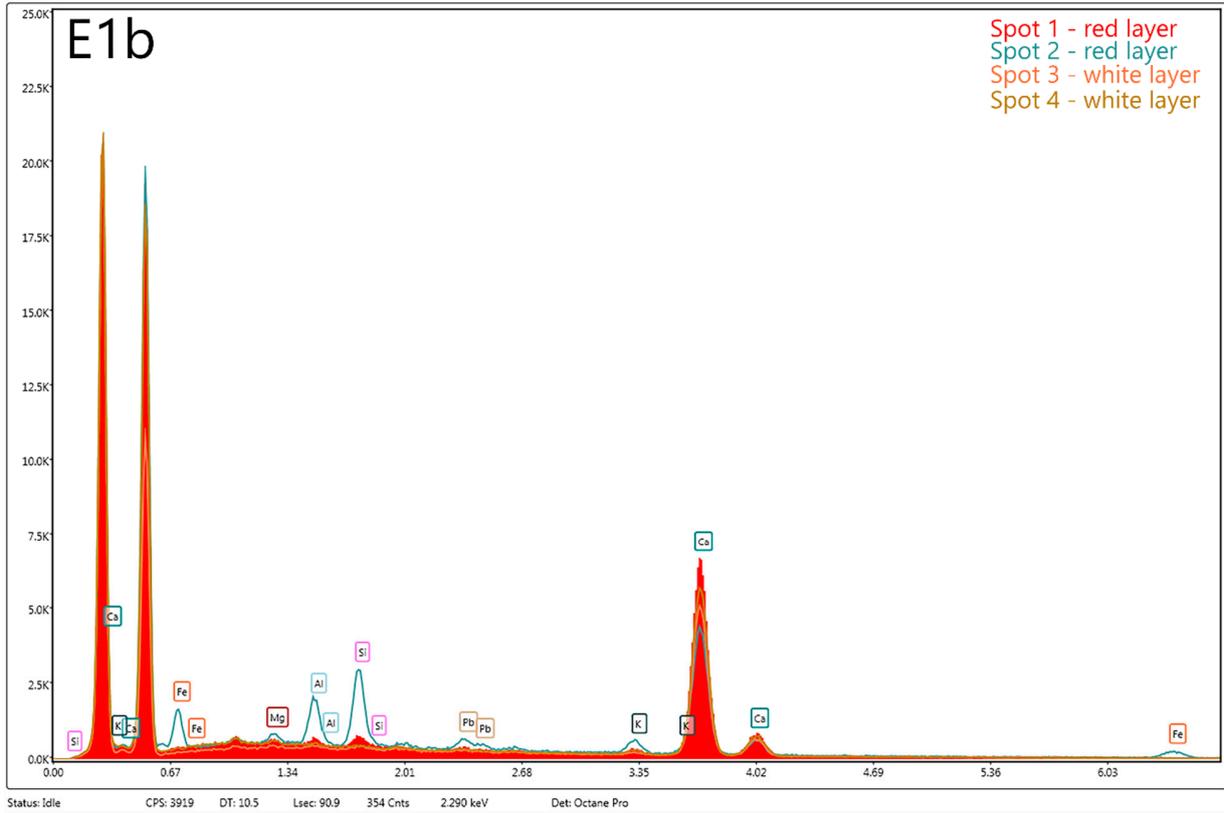


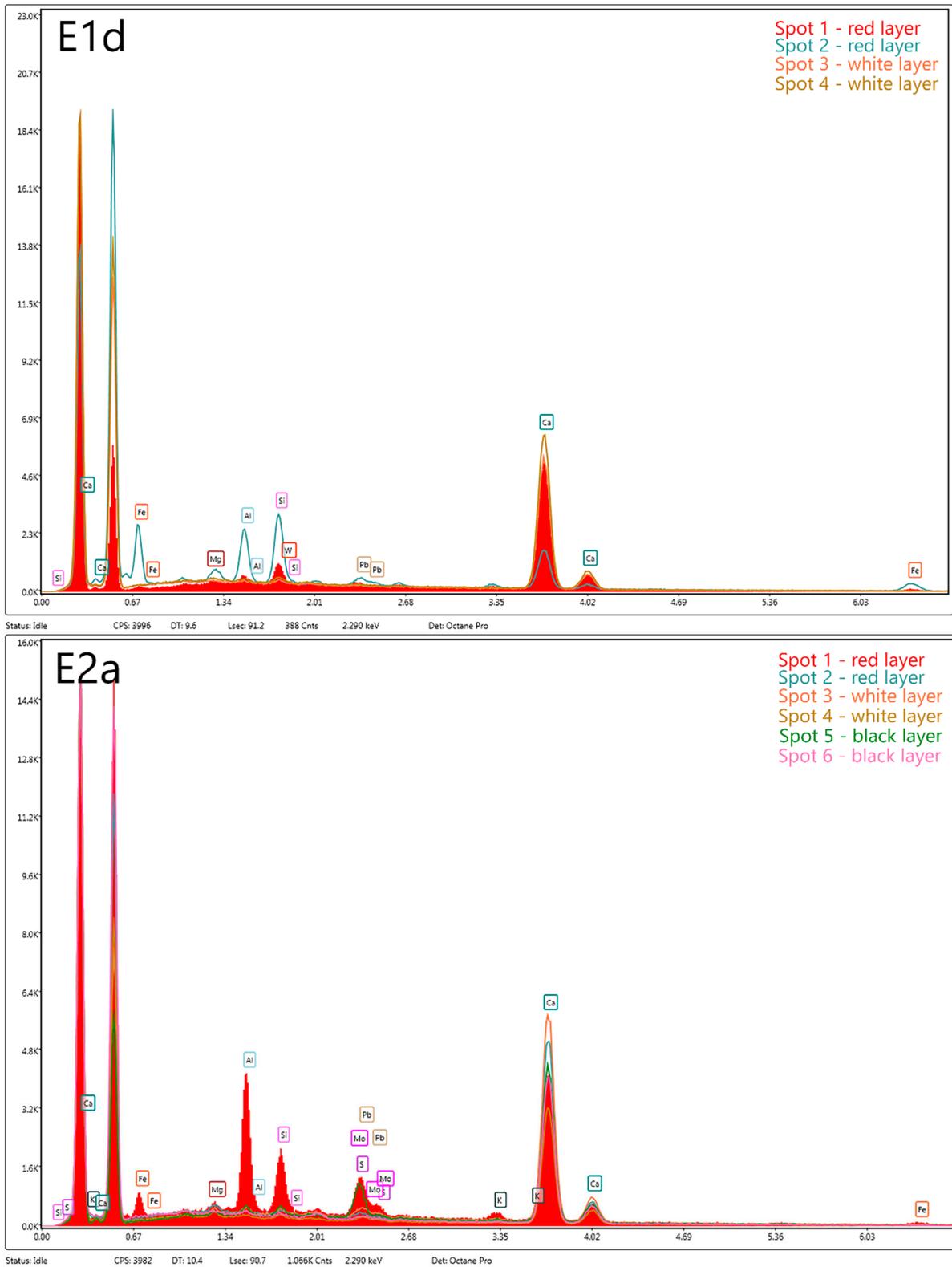
Figure S 4: Spot analysis images of cross-sectional samples











**Figure S 5:** EDS spectrum of historic paint samples from Heddal and Eidsborg

**Table S 6:** Summary of common ESEM-EDS results of samples from Eidsborg and Heddal. Concentrations higher than 10 weight per cent (wt. %) are considered major, whereas minor concentrations are between 1 - 10 wt.%. Values lower than 1 are not listed. See following tables for wt.% values.

| Colour | SEM-EDS           |                          | Sample location                        |
|--------|-------------------|--------------------------|--|
|        | Major constitutes | Minor constitutes        |  |
| Red    | Fe, Ca, Al, Si    | Mg, S, K                 | H1a, H1d                               |
|        | Fe, Ca, Al        | Si, Mg, S, K             | E2a                                    |
|        | Fe, Ca            | Al, Si, Mg, S, K         | E1c, H1b, H2a <sup>1</sup>             |
|        | Fe, Ca            | Al, Si, Mg, S, K, Pb     | E1a <sup>1</sup> , E1b                 |
|        | Fe, Ca, Al, Si    | Mg, S, K, Pb             | E1d                                    |
| Grey   | Ca                | Al, Si, Mg,              | H1a, H1b, H1d, H1e, H2a                |
| Orange | Fe, Ca, Al, Si    | Fe, Ca, Pb, Mg,          | H1b                                    |
|        | Fe, Ca,           | Fe, Ca, Al, Si*, Pb, Mg, | H1a                                    |
| Black  | Ca, Al, Si        | Fe, Pb, P, Mg,           | H1e                                    |
|        | Ca                | Al, Si, Fe, Pb, P, Mg,   | E1a, E1c, E2a                          |
| White  | Ca                | Al, Si, Mg               | H1a, H1b, H1e, H2a, E1a, E1b, E1c, E1d |
|        | Ca                | Al, Si, Mg, Na           | H1d                                    |
|        | Ca                | Al, Si, Mg, Pb           | E2a                                    |

<sup>1</sup>Fe was not found using EDS spot analysis, but was confirmed with XRD

Concentrations higher than 10 wt.% can be considered major, whereas minor concentrations are between 1 - 10 wt.%, and concentrations lower than 1 are not listed.

**Table S 7:** EDS results of red layer

| Red Layer   |      |          |          |          |          |          |          |          |          |          |          |
|-------------|------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| sample name | spot | Al       | Si       | Ca       | Fe       | Pb       | K        | Mg       | Mo       | W        | S        |
|             |      | Weight % |
| E1a         | 3    | 1.81     | 1.72     | 91.48    |          | 4.58     |          |          |          |          |          |
| E1a         | 4    |          |          | 96.17    |          | 3.83     |          |          |          |          |          |
| E1b         | 1    |          | 1.23     | 98.19    |          |          |          |          |          |          |          |
| E1b         | 2    | 5.47     | 9.33     | 63.77    | 10.83    | 4.79     | 4.64     | 1.18     |          |          |          |
| E1c         | 1    | 1.44     | 1.90     | 90.55    |          |          |          | 1.49     | 3.90     |          |          |
| E1c         | 2    | 2.58     | 3.99     | 79.12    | 3.96     |          |          | 1.58     | 8.76     |          |          |
| E1d         | 1    |          | 2.51     | 95.29    |          |          |          |          |          | 1.46     |          |
| E1d         | 2    | 12.60    | 16.77    | 41.93    | 15.89    | 9.52     |          | 3.28     |          |          |          |
| E2a         | 1    | 13.77    | 5.85     | 67.45    | 1.15     |          | 2.90     |          |          |          | 8.23     |
| E2a         | 2    |          |          | 97.08    |          |          |          |          | 1.56     |          |          |
| H1a         | 1    | 37.52    | 45.88    | 7.31     | 1.92     |          | 5.50     | 1.87     |          |          |          |
| H1a         | 2    | 43.69    | 47.86    | 8.45     |          |          |          |          |          |          |          |
| H1b         | 1    | 7.13     | 7.34     | 76.26    | 4.13     |          |          | 1.48     | 3.66     |          |          |
| H1b         | 2    | 3.28     | 4.82     | 85.82    |          |          |          |          | 6.07     |          |          |
| H1d         | 1    | 43.15    | 47.60    | 6.32     | 1.26     |          |          | 1.66     |          |          |          |
| H1d         | 2    | 7.96     | 8.44     | 10.05    | 73.55    |          |          |          |          |          |          |
| H2a         | 1    | 1.55     | 2.06     | 92.71    |          |          |          | 1.41     | 92.71    |          |          |
| H2a         | 2    | 1.61     | 2.11     | 92.07    |          |          |          | 1.01     | 3.19     |          |          |

**Table S 8:** EDS results of black layer and black particles

| Black Layer |      |    |    |    |    |    |   |    |    |    |   |
|-------------|------|----|----|----|----|----|---|----|----|----|---|
| sample name | spot | Al | Si | Ca | Fe | Pb | P | Ti | Mg | Mo | S |

|                        |   | Weight % |
|------------------------|---|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| <b>E1a</b>             | 1 | 2.51     | 3.04     | 94.16    |          |          |          |          |          |          |
| <b>E1a</b>             | 2 |          | 1.36     | 96.46    |          | 1.84     |          |          |          |          |
| <b>E1c</b>             | 3 | 1.81     | 2.55     | 87.05    | 4.43     |          |          | 1.43     | 2.73     |          |
| <b>E1c</b>             | 4 | 1.36     | 1.94     | 89.53    | 1.58     |          |          |          | 5.59     |          |
| <b>H1e</b>             | 5 | 13.43    | 16.48    | 62.49    |          |          |          | 1.84     | 5.76     |          |
| <b>H1e</b>             | 6 | 20.00    | 29.97    | 33.00    | 4.46     |          | 3.45     | 2.96     |          | 6.17     |
| <i>Black Particles</i> |   |          |          |          |          |          |          |          |          |          |
| <b>E2a</b>             | 5 | 2.11     | 2.08     | 79.13    |          | 6.22     |          | 1.41     | 9.05     |          |
| <b>E2a</b>             | 6 | 1.55     | 1.18     | 93.75    |          |          |          | 1.38     | 2.14     |          |

**Table S 9:** EDS results of grey layer

| <b>Grey Layer</b> |      |          |          |          |          |          |
|-------------------|------|----------|----------|----------|----------|----------|
| sample name       | spot | Al       | Si       | Ca       | Mg       | Mo       |
|                   |      | Weight % |
| <b>H1a</b>        | 3    |          |          | 99.04    |          |          |
| <b>H1a</b>        | 4    |          |          | 98.84    |          |          |
| <b>H1b</b>        | 3    | 1.21     | 1.60     | 97.19    |          |          |
| <b>H1b</b>        | 4    |          |          | 98.95    |          |          |
| <b>H1d</b>        | 3    | 1.02     | 1.32     | 97.66    |          |          |
| <b>H1d</b>        | 4    |          |          | 98.52    |          |          |
| <b>H1e</b>        | 7    |          | 0.98     | 98.59    |          |          |
| <b>H1e</b>        | 8    | 1.21     | 1.78     | 94.49    |          | 1.93     |
| <b>H2a</b>        | 3    |          | 1.20     | 98.53    |          |          |
| <b>H2a</b>        | 4    | 1.07     | 1.68     | 93.95    |          | 2.48     |

**Table S 10:** EDS results of orange layer

| <b>Orange Layer</b> |      |    |    |    |    |    |    |    |
|---------------------|------|----|----|----|----|----|----|----|
| sample name         | spot | Al | Si | Ca | Fe | Pb | Mg | Mo |

|            |   | Weight % |
|------------|---|----------|----------|----------|----------|----------|----------|----------|
| <b>H1a</b> | 5 | 5.98     | 8.43     | 27.02    | 44.27    |          | 6.17     | 8.12     |
| <b>H1a</b> | 6 |          | 1.46     | 97.80    |          |          |          |          |
| <b>H1b</b> | 7 | 19.33    | 19.06    | 52.80    | 2.52     |          | 1.65     | 4.63     |
| <b>H1b</b> | 8 | 2.76     | 10.96    | 81.97    |          | 4.30     |          |          |

**Table S 11:** EDS results of white layer

| White Layer |      |          |          |          |          |          |          |          |
|-------------|------|----------|----------|----------|----------|----------|----------|----------|
| sample name | spot | Na       | Al       | Si       | Ca       | Pb       | Mg       | Mo       |
|             |      | Weight % |
| <b>E1a</b>  | 5    |          |          | 1.22     | 98.44    |          |          |          |
| <b>E1a</b>  | 6    |          |          | 1.18     | 97.94    |          |          |          |
| <b>E1b</b>  | 3    |          |          | 1.26     | 98.74    |          |          |          |
| <b>E1b</b>  | 4    |          |          | 1.03     | 98.97    |          |          |          |
| <b>E1c</b>  | 5    |          |          |          | 98.56    |          |          |          |
| <b>E1c</b>  | 6    |          | 1.62     | 1.51     | 96.87    |          |          |          |
| <b>E1d</b>  | 3    |          | 1.32     | 1.39     | 96.15    |          | 1.14     |          |
| <b>E1d</b>  | 4    |          | 1.17     | 1.50     | 96.14    |          | 1.19     |          |
| <b>E2a</b>  | 3    |          | 1.78     | 1.67     | 89.26    | 2.82     | 1.49     | 2.98     |
| <b>E2a</b>  | 4    |          | 1.71     | 1.46     | 91.22    | 3.81     | 1.80     |          |
| <b>H1a</b>  | 7    |          |          | 1.10     | 98.31    |          |          |          |
| <b>H1a</b>  | 8    |          | 1.29     | 1.81     | 96.89    |          |          |          |
| <b>H1b</b>  | 5    |          | 1.40     | 1.66     | 95.65    |          | 1.29     |          |
| <b>H1b</b>  | 6    |          |          | 1.06     | 98.70    |          |          |          |
| <b>H1d</b>  | 5    |          |          |          | 98.98    |          |          |          |
| <b>H1d</b>  | 6    | 1.85     | 1.19     | 1.00     | 91.69    |          | 2.18     | 2.08     |
| <b>H1e</b>  | 1    |          |          |          | 99.09    |          |          |          |
| <b>H1e</b>  | 2    |          |          |          | 99.12    |          |          |          |
| <b>H1e</b>  | 3    |          | 1.07     | 1.72     | 92.59    |          |          | 4.62     |
| <b>H1e</b>  | 4    |          |          |          | 98.65    |          |          |          |

## Fourier-Transform Infrared Spectroscopy

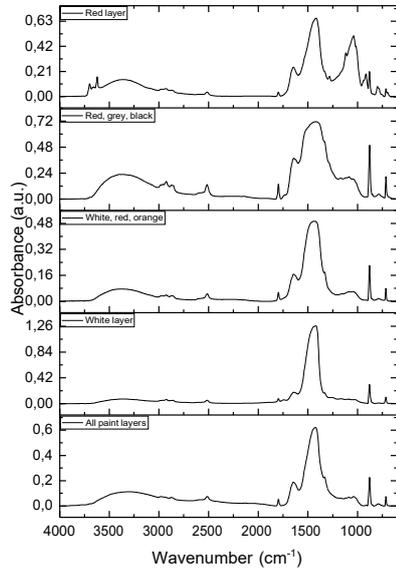
**Table S 12:** Spectral interpretation of historic paint samples, with assignment of the main absorption bands according to in literature.  $\nu$  = stretching;  $\nu_s$  = symmetric stretching;  $\nu_a$  = asymmetric stretching;  $\delta$  = bending;  $\delta_s$  = symmetric bending;  $\delta_a$  = asymmetric bend

| Compound assignment   | Vibrational wavenumber (cm <sup>-1</sup> )         | Vibrational mode  | Ref. no  |
|---|--|---|----------|
| Ca sulphates  | 672  | $\nu_4(\text{SO}_4)^{2-} \delta_a$  | [8]      |
|   | 1619   | $\delta$ H-O-H  |          |
| Calcite (CaCO <sub>3</sub> )  | 711 - 2878   | $(\text{CO}_3)^{2-}$  | [9-11]   |
|   | -2921-2929   | attributed to $2\nu_3$ in dolomite (MgCaCO <sub>3</sub> ) or to organic material ( $\nu\text{CH}_2$ ) | [10, 12] |
| Dolomite  | 1446 sh  | $\nu_3(\text{CO}_3)^{2-}$   | [10]     |
| Quartz  | -696   | $\delta_a\text{O-Si-O}$   | [13]     |
|   | 779 -1153  | $\nu_s\text{Si-O}$  |          |
|   | 11056sh-1159 sh; 1057-1166                         | $\nu_s\text{Si-O}$  |          |
| Clay mineral (Kaolin/montmorillonites/degraded clays/ amorphous silica) | 755  | OH translation  | [14]     |
|   | -788   | amorphous silica ( $\nu_s\text{Si-O}$ )   |          |
|   | -850   | $\delta$ OH in Al-Mg(OH)  |          |
|   | -914   | $\delta$ OH inner hydroxyl groups / $\delta$ Al-O-H (linked to $2\text{Al}^{3+}$ )                    |          |
|   | -941   | $\delta$ Al-O-H   |          |
|   | 1010 sh, 1006-1116                                 | $\nu\text{Si-O}$  |          |
|   | -1642, 1162, -1640                                 | $\delta$ H-O-H  | [15-19]  |
|   | 1642   | $\text{C=O} + \text{C=C vibrations (aromatic ketones)} / \delta$ H-O-H                                |          |
|   | -3621  | $\nu$ OH (inner oxydrils, between the tetrahedral and octahedral sheets)                              |          |
|   | -3657  | $\nu$ OH out of plane (octahedral surface of layers)  |          |
| -3696   | $\nu_s$ OH in-phase (octahedral surface of layers) |   |          |
| General clay minerals   | 780  | amorphous silica ( $\nu_s\text{Si-O}$ )   |          |
|   | -850   | $\delta$ OH in Al-Mg(OH)  | [15-17]  |
|   | 1038sh, ~1114                                      | $\nu\text{Si-O}$  |          |

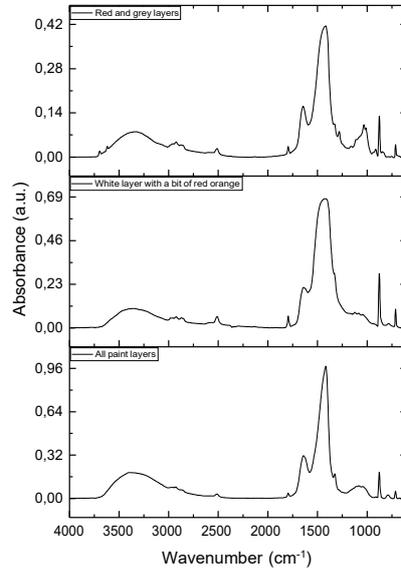
|   |                                  |   |  |
|---|----------------------------------|---|--|
|   | ~1642                            | $\delta$ H-O-H  |  |
|   | 902                              | <i>In-plane</i> $\nu$ C-H   |  |
|   | ~1035                            | $\sim \nu$ C-O *  |  |
|   | ~1056                            | $\nu$ C-O and $\nu$ C-C   |  |
|   | ~1116                            | $\nu_s$ C-O-C   |  |
|   | ~1162                            | $\nu_s$ C-O + $\nu_s$ C-C   |  |
|   | ~1238                            | $\nu$ C-O in Xylene and syringyl ring   |  |
|   | ~1282                            | $\nu$ C-O in guaiacyl ring + OH and $\omega$ CH   |  |
|   | ~1326                            | Syringyl ring breathing with C=O stretching and C1-O vibration in syringyl derivatives of lignin + C-H vibration of cellulose | [20-22]                                |
|   | ~1372-1382                       | $\delta_s$ CH <sub>3</sub> groups and $\delta_a$ CH <sub>3</sub> groups   | *[22] indicates as deformation=bending |
| wood  | 1421                             | $\nu$ aromatic structure  |  |
|   | 1467sh                           | $\delta_a$ CH <sub>3</sub> in methoxyl groups   |  |
|   | 1511sh                           | $\nu$ aromatic structure C=C  |  |
|   | 1619-1644                        | $\delta$ H-O-H  |  |
|   | ~1643                            | C=O + C=C vibrations (aromatic ketones)/ H-O-H bending  |  |
|   | ~1731                            | unconjugated $\nu$ C=O in a carbonyl group  |  |
|   | 1741                             | C=O + C=C vibrations (aromatic ketones)/ H-O-H bending  |  |
|   | ~2851                            | $\nu$ unconjugated C=O related to a carbonyl group  |  |
|   | ~2961                            | $\nu$ C-H   | [22, 23]                               |
|   | ~3388, 3400sh                    | $\nu$ O-H   |  |
| Pine resin (abietic acid/dehydroabietic acid) | 1549                             | COOH overtones  | [24]                                   |
|   | ~2591                            | $\nu$ O-H, overtone/combined bands  |  |
|   | ~1644                            | $\nu$ C=O-N-H + $\delta$ NH <sub>2</sub>  | [19, 25]                               |
|   | ~2873, 2891, 2935, ~2985, 2983sh | $\nu_s$ CH <sub>3</sub>   |  |
| animal protein/ animal glue                   | ~2921, ~2934, ~2985, 3378        | $\nu$ CH <sub>2</sub>   | [19, 25, 26]                           |
|   | 2853                             | $\nu_s$ CH <sub>2</sub>   |  |
|   | 3300                             | $\nu$ NH  | [25, 27, 28]                           |
|   | 3350, 3366                       | $\nu_s$ NH/ $\nu$ CH <sub>2</sub>   | [19, 26]                               |

|                        |  |   |          |
|------------------------|--|---|----------|
|                        | 669  | Unsaturated cycles  |          |
|                        | ~711   | $\gamma$ -(C-H)   |          |
|                        | 721  | Rocking (CH <sub>2</sub> ) /cis C=(C-H) out of plane deformation                                |          |
|                        | 983 sh   | trans-trans conjugated $\omega$ (C-H)   |          |
|                        | ~1158  | $\nu$ (C-O) in triglycerides ester linkage + $\nu_s$ (C-O) of C-CO-O of higher aliphatic esters |          |
|                        | 1234   | $\nu$ (C-O) in triglycerides ester linkage + $\nu_s$ C-CO-O-                                    |          |
|                        | 1372   | Deformation CH in methyl/ $\omega$ (CH <sub>2</sub> )   |          |
|                        | ~1415  | $\nu$ C-O in COOH   |          |
| linseed oil            | 1421, 1708sh                                   | $\nu$ (C-O) in COOH   | [29]     |
|                        | 1623   | (C=C) conjugated  |          |
|                        | ~1642  | Weak cis C=C  |          |
|                        | 1723   | $\nu$ C=O   |          |
|                        | ~1743, 1738sh                                  | $\nu$ (C=O) ketones, ester, acid carbonyl   |          |
|                        | ~2853  | $\nu_s$ (CH)-CH <sub>2</sub>  |          |
|                        | ~2955, 2954sh                                  | $\nu$ (CH)CH <sub>3</sub>   |          |
|                        | ~3004, ~ 3395                                  | $\nu$ (CH)-CHCH=CH unconjugated cis double bonds  |          |
|                        | 3263, ~ 3341, 3430, 3482, 3538, 3480sh, 3540sh | $\nu$ OH  |          |
|                        | 797, 1143, 1452                                | <i>not attributed</i>   |          |
| cured/aged linseed oil | 1172   | $\nu$ -C(O)-OCH <sub>2</sub> -  |          |
|                        | 1417   | $\nu$ C-O in COOH   |          |
|                        | 1642   | Weak cis C=C  | [29]     |
|                        | 2851   | $\nu_s$ (CH) CH <sub>2</sub>  |          |
|                        | 2923   | $\nu_s$ CH <sub>2</sub>   |          |
|                        | 3350   | $\nu_s$ OH  | [29, 30] |

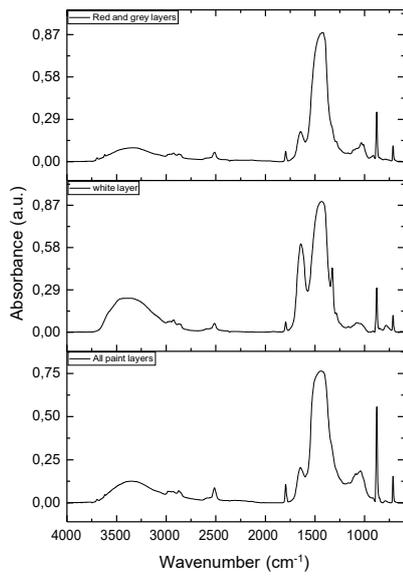
H1a



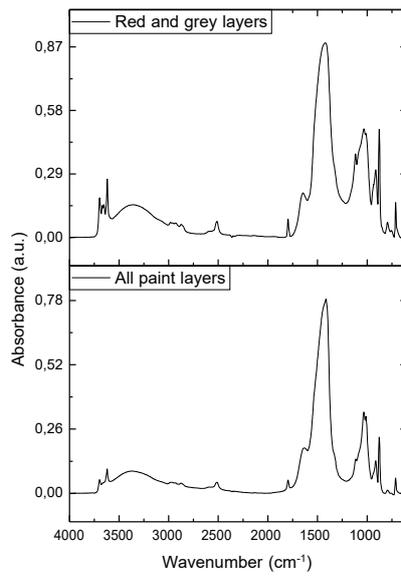
H1b

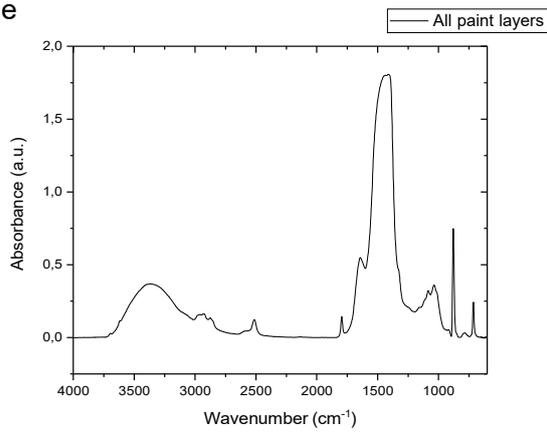
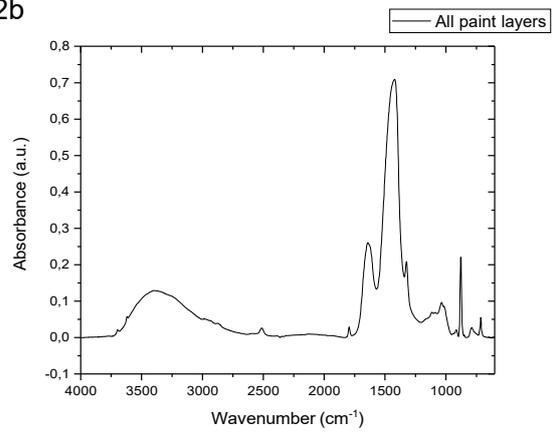
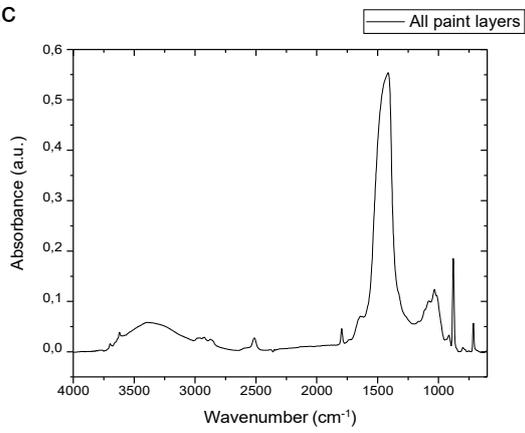
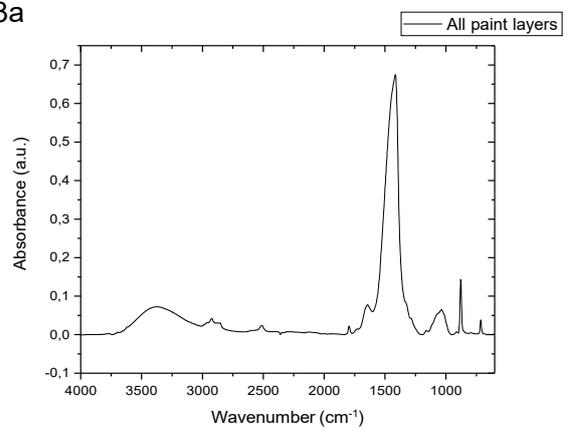
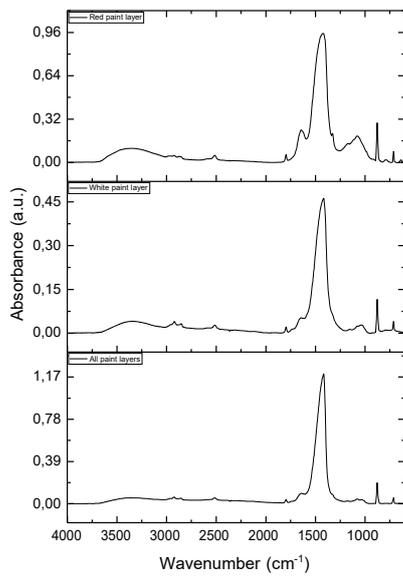
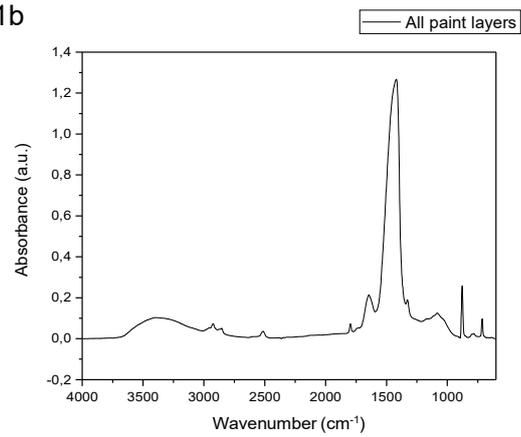


H1c

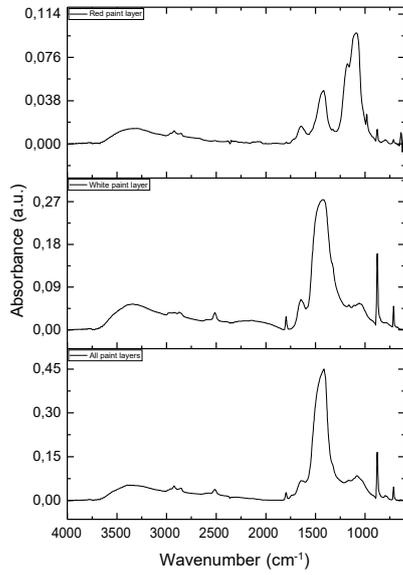


H1d

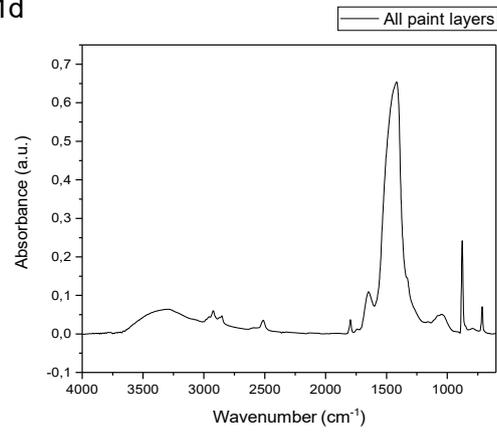


**H1e****H2b****H2c****H3a****E1a****E1b**

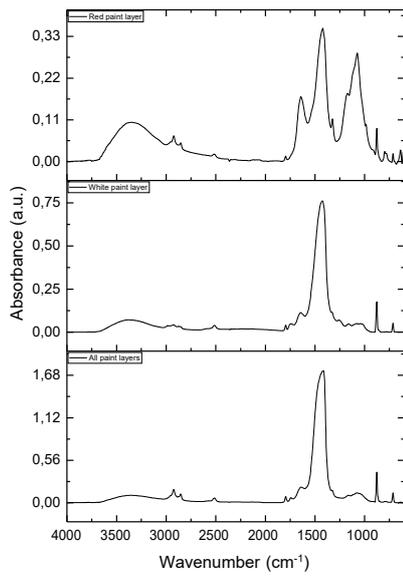
E1c



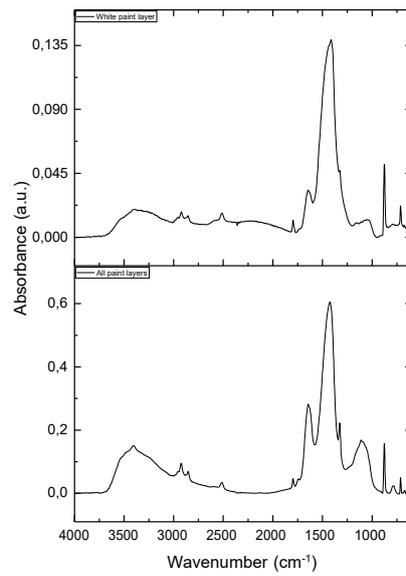
E1d

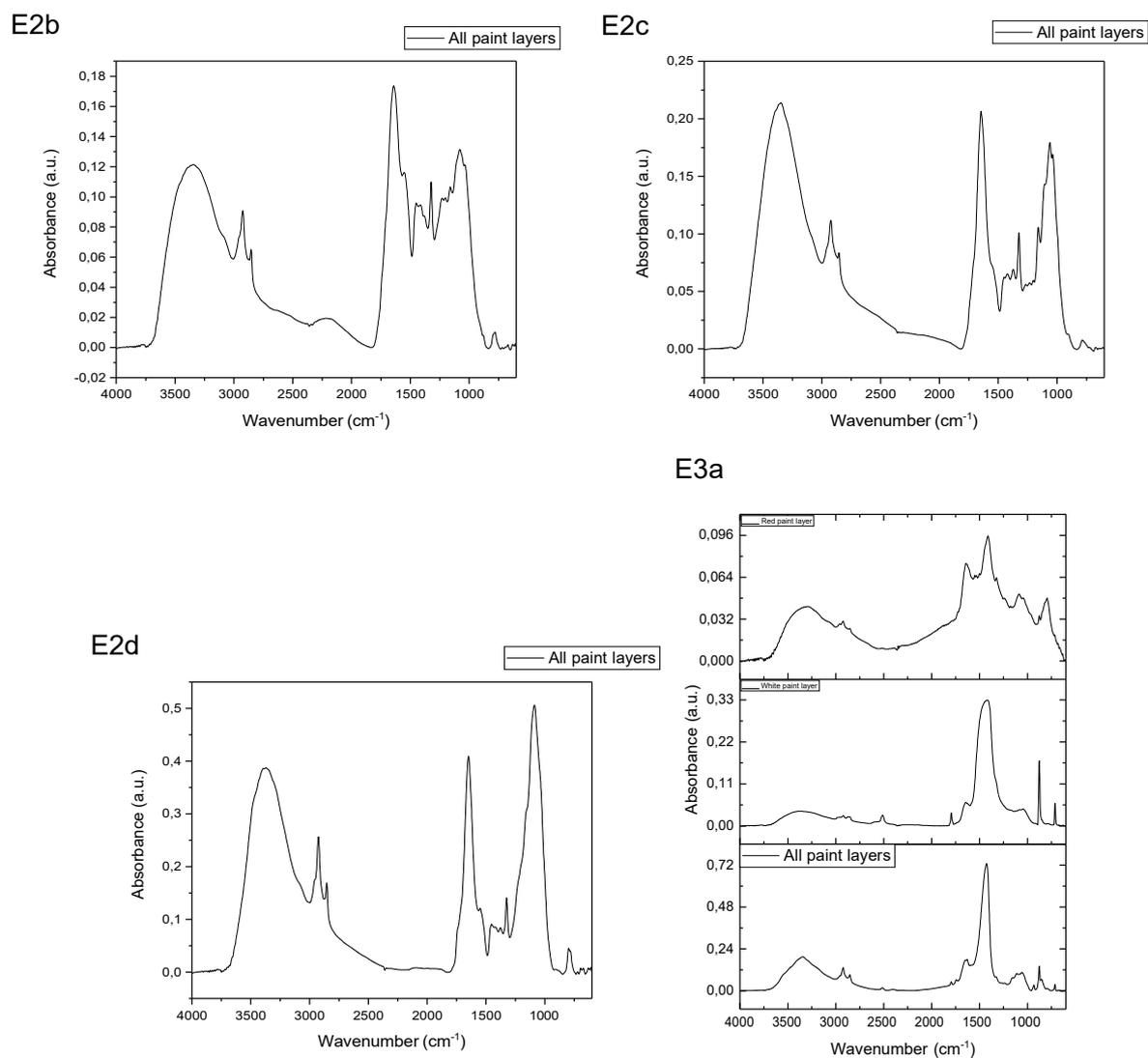


E1e



E2a





**Figure S 6:** FT-IR spectrum in the region 4000–600  $\text{cm}^{-1}$  for all samples, with layer isolation when possible.

**Table S 13:** Signals assigned to FT-IR analysis of pigments. See **Table S 12** for attributions and references.

| Sample name | Ca sulphates/<br>gypsum | Calcite                                   | Quartz         | Dolomite<br>( $\text{CaMg}(\text{CO}_3)_2$ ) | Clay mineral (general clay minerals/<br>Kaolin/montmorillonite/ degraded<br>clays/ amorphous silica) |
|-------------|-------------------------|---|----------------|--|--|
| H1a         |                         | 711, 877, 1085, 1421, 1793,<br>2512, 2873 |                |  | 788, 850, 914, 1010, 1035, 1116, 1162, 3696  |
| H1b         | 672, 1619               | 713, 877, 1085, 1415, 1795,<br>2512, 2929 | 790            |  | 1045, 1108, 1640   |
| H1c         |                         | 713, 877, 1089, 1438, 1795,<br>2510, 2873 | 779, 794, 1162 |  | 848, 914, 941, 1006, 1037, 1114, 1644,<br>3621, 3657, 3698   |

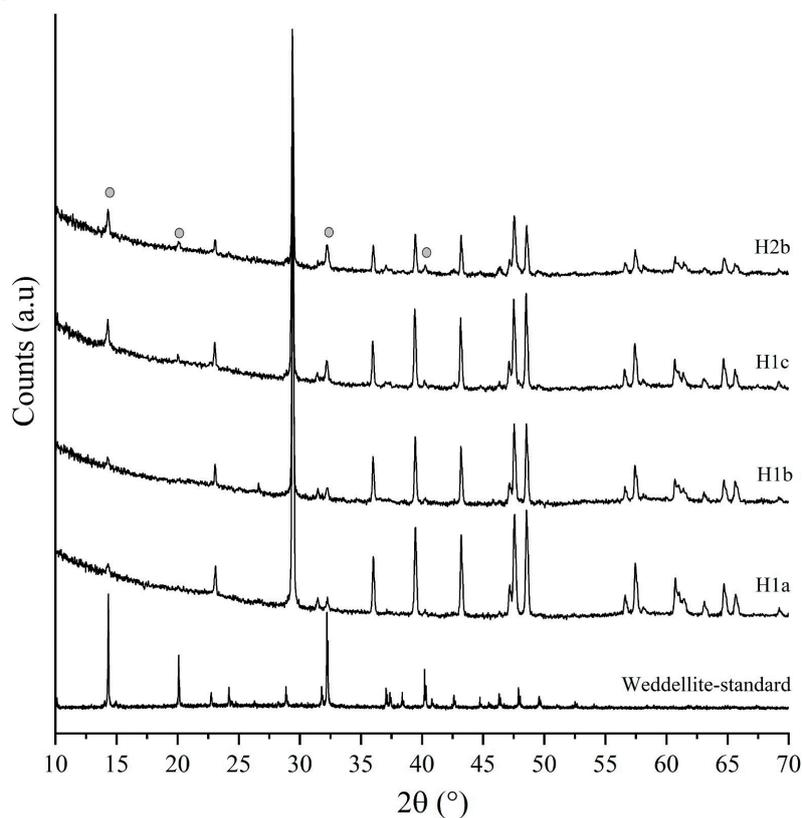
|     |   |                                |          |  |
|-----|---|--------------------------------|----------|--|
| H1d | 877, 1081 sh, 1411, 1444,<br>1795, 2512, 2877         | 794                            |          | 755,848, 914, 939, 1008, 1033, 1116, 3621,<br>3694         |
| H1e | 712, 876, 1083, 1409, 1448,<br>1795, 2850, 2875, 2929 | 784, 1153                      |          | 848, 915, 1010 sh, 1035, 1116, 1642, 3617,<br>3696         |
| H2a | 713, 877, 1079, 1403, 1795,<br>2510, 2873             |                                |          | 790, 850, 914, 1008, 1031, 1108, 1641,<br>3621, 3694       |
| H2b | 713, 877, 1089, 1423, 1795,<br>2512, 2878             |                                |          | 786, 848, 914, 937, 1008, 1035, 1114, 1640,<br>3619, 3698  |
| H2c | 711, 877, 1078, 1413, 1793,<br>2510, 2923             | 779, 800, 1162                 | 1446? Sh | 748, 850, 912, 1010, 1031, 1112, 1644,<br>3619, 3656, 3696 |
| H3a | 713, 877, 1074, 1415, 1795,<br>2512, 2921             |                                |          | 912, 1033, 1112, 1642                                      |
| E1a | 713, 877, 1079, 1417, 1795,<br>2510, 2923             |                                |          |  |
| E1b | 711, 877, 1079, 1415, 1795,<br>2512, 2875, 2923       | 780, 800, 1166                 |          | 780, 850, 1018sh, 1114, 1642                               |
| E1c | 711, 877, 1081, 1411, 1795,<br>2510, 2877, 2923       | 779, 798, 1164                 |          | 850, 1114, 1644  |
| E1d | 711, 875, 1083, 1413, 1797,<br>2512, 2875, 2923       |                                |          | 846, 1110, 1646  |
| E1e | 711, 875, 1075, 1413, 1795,<br>2512, 2923             |                                |          | 850 sh, 1116 (low), 1642                                   |
| E2a | 711, 875, 1090, 1421, 1795,<br>2512, 2923             | 696, 779, 798,<br>1056sh, 1164 |          | 846, 1112, 1643  |
| E2b | 875, 1413, 2875, 2923                                 | 779, 800                       |          |  |
| E2c |   |                                |          |  |
| E2d |   | 695, 781, 794,<br>1159 sh      |          |  |
| E3a | 712, 876, 1426, 1796, 2512,<br>2922                   | 782, 797, 1057,<br>1160        |          | 851, 1038sh, 1114, 1648                                    |

**Table S 14.** Signals assigned to FT-IR analysis of organic material (wood fractions, animal protein, and linseed oil). See **Table S 12** for attributions and references.

| Sample name | Wood | Pine resin (abietic acid /<br>dehydroabietic acid) | animal protein (animal glue/<br>animal protein) | Linseed oil |
|-------------|------|--|---|-------------|
|-------------|------|--|---|-------------|

|            |  |            |                              |  |
|------------|--|------------|------------------------------|--|
| <b>H1a</b> | 1035,1116, 1162, 1326, 1643  |            | 2935, 2985, 3300             |  |
| <b>H1b</b> | 1108, 1282, 1324, 1619, 1640,<br>2851, 3388  |            |                              |  |
| <b>H1c</b> | 1037, 1114, 1162, 1280, 1328,<br>1644, 2848, 3355  | 1644, 2873 | 1644, 2873, 2891, 2923       |  |
| <b>H1d</b> | 1033, 1116, 1326, 3374   |            | 2934, 2977                   |  |
| <b>H1e</b> | 1035, 1116, 1326, 1642,2961,<br>3366, 2591   | 1642, 2875 | 1642, 2875, 2983, 2929, 3366 |  |
| <b>H2a</b> | 1108, 1162, 1641, 2967, 3386,<br>2597  |            | 2934                         |  |
| <b>H2b</b> | 1035, 1114, 1160,1326, 1618,<br>1640, 3388   |            |                              |  |
| <b>H2c</b> | 1031, 1112, 1162, 1644, 1730,<br>2850, 3380, 3397  | 2875       | 2875, 2985                   |  |
| <b>H3a</b> | 1033, 1112, 1160, 1280, 1324,<br>1642, 1731, 2851, 2961,3378                                 | 1642       | 1642,2921, 3378              |  |
| <b>E1a</b> | 1326, 2851, 3350 (low)   | 1642       | 1642, 2923, 3350             |  |
| <b>E1b</b> | 1114, 1324, 1642, 2853, 2958,<br>3395  | 1642       | 1642, 2923, 2985             | 669, 711, 1642, 1743,<br>2853, 2923 (low), 3395  |
| <b>E1c</b> | 1114, 1164, 1324, 1644, 1741,<br>2853,2961, 3351 (low), 3399                                 | 1644       | 1644, 2923, 2986, 3351       |  |
| <b>E1d</b> | 1045, 1158, 1326, 1741, 2851,<br>2958, 3320 (low)  | 1646       | 1646, 2923, 2986, 3320       | 711, 1413,1646, 1741,<br>2851, 2923 (low)  |
| <b>E1e</b> | 1047, 1116, 1162, 1324, 1642,<br>1743, 2851, 2958, 3357 (low)                                |            |                              | 711, 983 sh, 1413, 1642,<br>1743, 2851, 2923   |
| <b>E2a</b> | 1112, 1164, 1324, 1623, 1643,<br>1739, 2852, 2954, 3400, 3405,<br>3430                       | 1643       | 1643, 2923, 2985             | 711, 1143, 1228 (low),<br>1623, 1643, 1739, 2852,<br>2923 (low), 3263, 3405,<br>3430, 3430, 3482, 3538 |
| <b>E2b</b> | 1035, 1110, 1160, 1228, 1322,<br>1382, 1467sh, 1640, 1741 sh,<br>2853, 2958, 3347 (low)      |            |                              | 721, 1158, 1234, 1372,<br>1421, 1645, 1708 sh,<br>1745sh, 2851, 2924,<br>2959, 3343                    |
| <b>E2c</b> | 902, 1035, 1056, 1106,1158,<br>1234, 1323, 1372, 1421,<br>1511sh,1645, 1745sh, 2851,<br>3390 |            |                              |  |
| <b>E2d</b> | 903, 1038sh, 1159 sh, 1227sh,<br>1325, 1376, 1418, 1649,<br>1738sh, 2854                     |            |                              | 721, 1159 sh, 1227sh,<br>1376, 1418, 1649,<br>1738sh, 2854, 2924,<br>2954sh, 3009, 3347,<br>3347       |
| <b>E3a</b> | 1038sh, 1160, 1238, 1324,<br>1648, 1744, 2853,3400sh   | 1648, 2853 | 1648, 2853, 2922, 2983sh     | 1160, 1648,1744, 2853,<br>2922, 2955,3004, 3341,<br>3341, 3480 sh, 3540 sh                             |

## X-Ray Diffraction



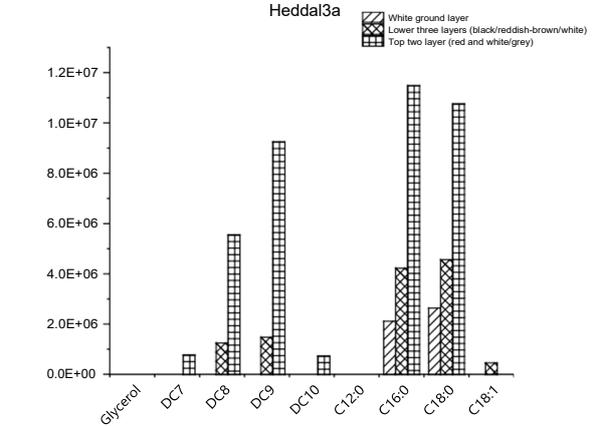
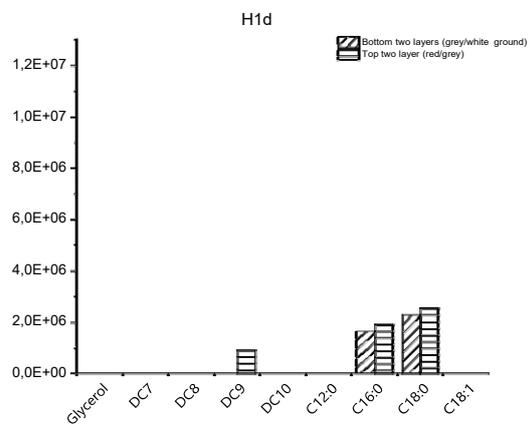
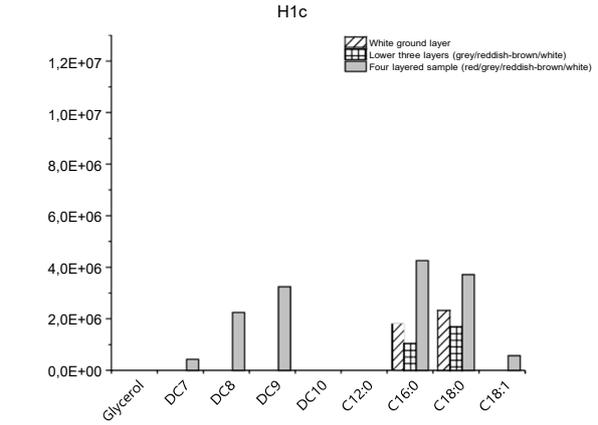
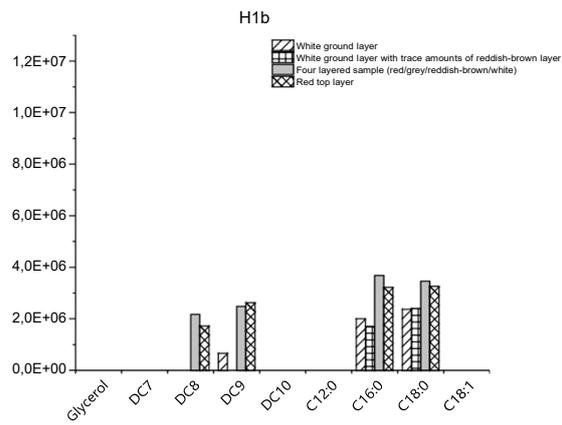
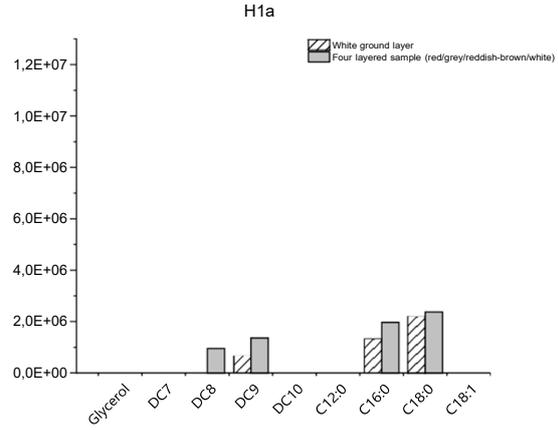
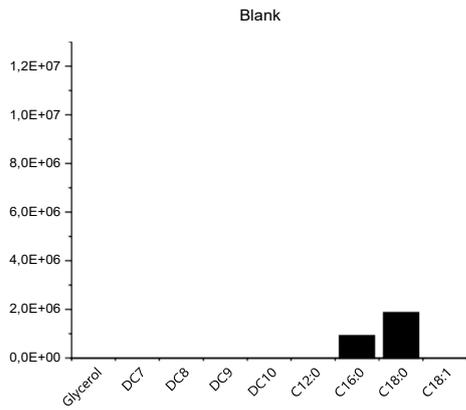
**Figure S 7:** XRD patterns of samples from Heddal. The intensity increase of weddellite's signals is shown. Considered reflections are marked with a grey dot.

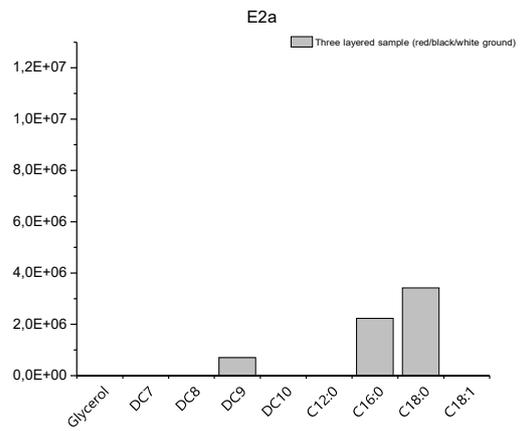
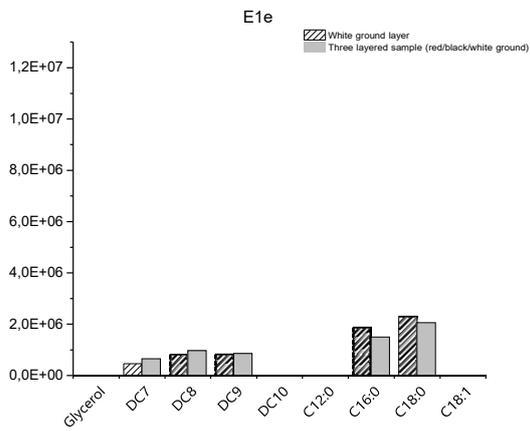
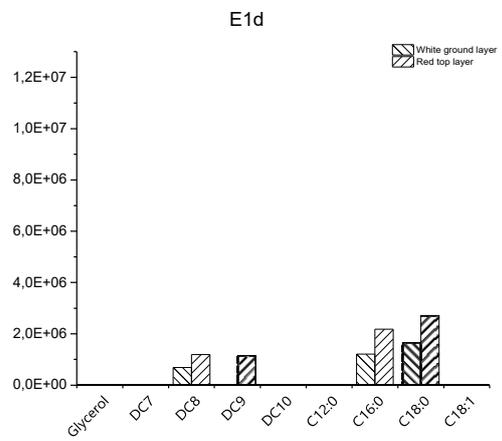
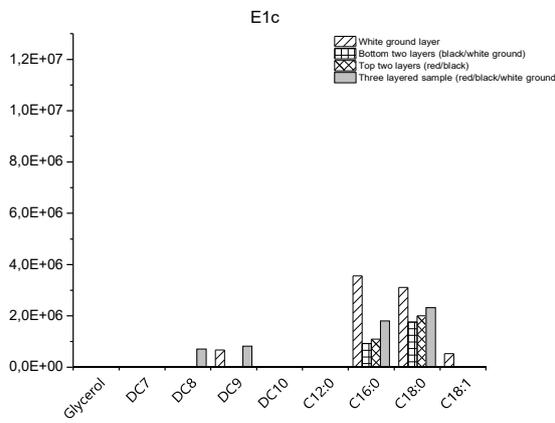
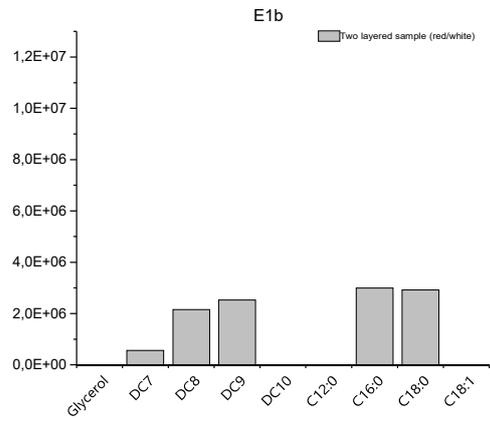
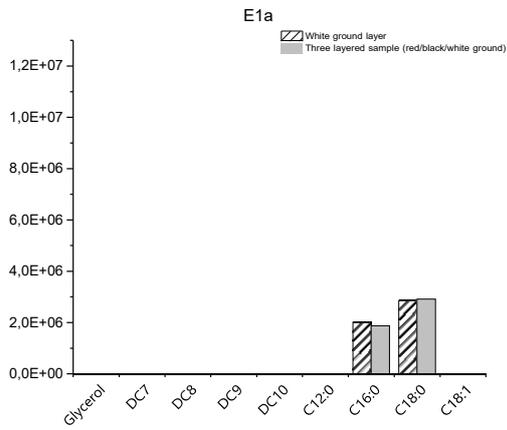
## Gas Chromatography-Mass Spectrometry and ELISA

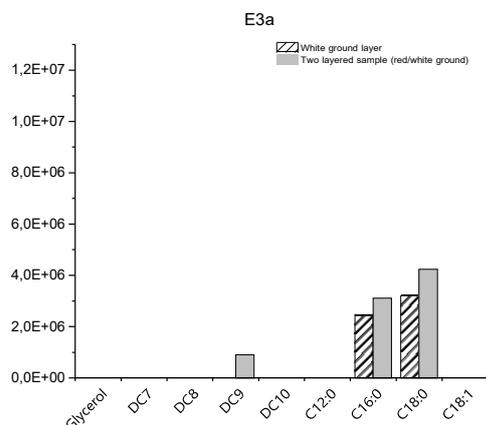
**Table S 15:** GC-MS testing configuration and parameters

| Protocol                                    | Separation column   | Oven program  |
|---|---|---|
| Meth-Prep II: natural plant resins and oils | Zebtron™ ZB-5HT (Phenomenex); 30 m x 0.25 mm x 0.10 μm<br>Helium was the carry gas (1.2 mL/min); splitless injection at 300°C and transfer line at 360 °C | 80°C for 2 min; temperature was then increased by 10°C/min until 210°C; after which the temperature was increased 20°C/min to 360°C; and lastly the temperature was increase 40°C/min to 380°C. |

Helium was the carry gas (1mL/min); splitless injection and transfer line at 240 °C







**Figure S 8:** Monocarboxylic and dicarboxylic fatty acids (lauric(C12:0), palmitic (C16:0), oleic (C18:1), stearic (C18:0), and pimelic(C7), suberic(C8), azelaic(C9), sebacic acids(C10), respectively) and glycerol peaks derived from Meth Prep analysis.

**Table S 16:** List of amino acid compositions from historic paints samples by GC-MS analysis (parts per million).

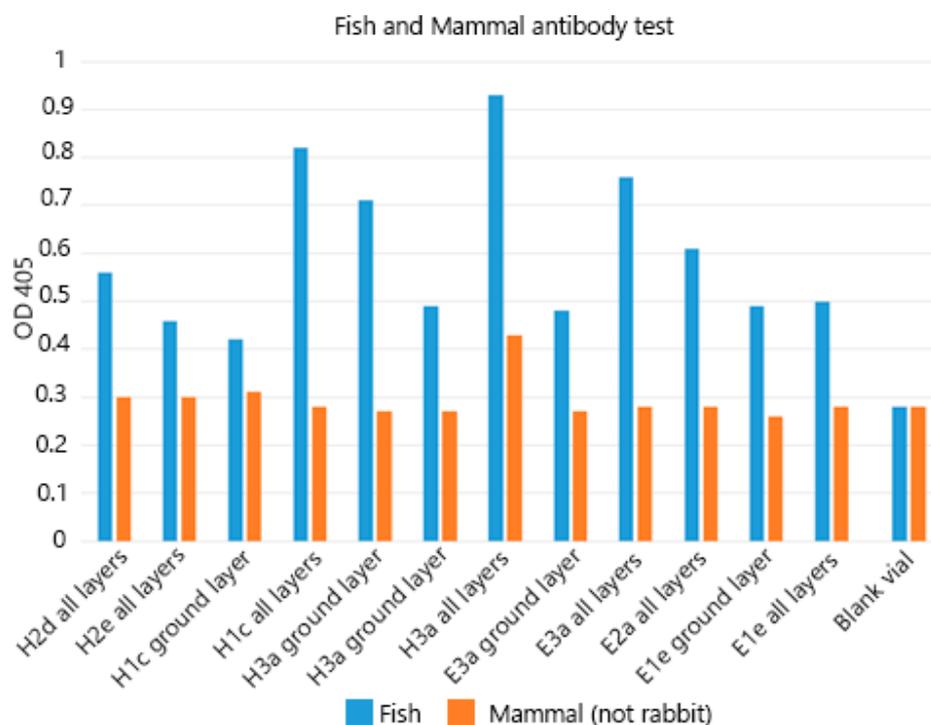
| Sample location & description |   | weight, µg | alanine | glycine | valine | leucine | isoleucine | proline | serine | threonine | phenylalanine | hydroxyproline |
|-------------------------------|---|------------|---------|---------|--------|---------|------------|---------|--------|-----------|---------------|----------------|
| E1a                           | White ground layer                            | 226.8      | 81      | 222     | 25     | 36      | 21         | 69      | 50     | 53        | 20            | 55             |
|                               | Three layered sample (red/black/white ground) | 842.3      | 158     | 483     | 42     | 59      | 40         | 164     | 97     | 81        | 37            | 92             |
| E1b                           | wood  | 515.2      | 179     | 507     | 58     | 113     | 55         | 185     | 155    | 191       | 65            | 130            |
|                               | Two layered sample (red/white ground)         | 467.6      | 140     | 366     | 61     | 86      | 49         | 139     | 109    | 82        | 45            | 77             |
| E1c                           | wood  | 225.3      | 91      | 233     | 29     | 46      | 25         | 85      | 72     | 75        | 34            | 61             |
|                               | White ground layer                            | 289.4      | 63      | 213     | 20     | 34      | 20         | 51      | 47     | 60        | 18            | 41             |
|                               | Bottom two layers (black/white ground)        | 48.0       | 7       | 17      | 2      | 2       | 1          | 6       | 6      | 6         | 2             | 14             |
|                               | Top two layers (red/black)                    | 131.3      | 15      | 34      | 4      | 4       | 3          | 11      | 17     | 19        | 2             | 34             |
| E1d                           | Three layered sample (red/black/white ground) | 585.9      | 121     | 357     | 32     | 43      | 24         | 116     | 72     | 75        | 36            | 89             |
|                               | White ground layer                            | 581.4      | 150     | 460     | 43     | 43      | 29         | 135     | 91     | 109       | 31            | 120            |
|                               | Red top layer                                 | 194.5      | 42      | 89      | 16     | 23      | 12         | 49      | 42     | 39        | 14            | 43             |
| E1e                           | Two layered sample with insect (red/white)    | 470.0      | 0       | 1       | 0      | 0       | 0          | 0       | 0      | 2         | 0             | 5              |
|                               | White ground layer                            | 368.5      | 258     | 669     | 55     | 60      | 35         | 175     | 129    | 150       | 42            | 206            |

|     |   |        |     |      |    |     |    |     |     |     |    |     |
|-----|---|--------|-----|------|----|-----|----|-----|-----|-----|----|-----|
| E2a | Three layered sample<br>(red/black/white ground)            | 683.1  | 241 | 684  | 45 | 39  | 26 | 168 | 119 | 172 | 45 | 165 |
|     | Three layered sample<br>(red/black/white ground)            | 191.9  | 40  | 119  | 11 | 20  | 9  | 39  | 29  | 32  | 16 | 46  |
|     | wood  | 207.4  | 69  | 189  | 17 | 8   | 10 | 69  | 33  | 39  | 15 | 80  |
| E3a | White ground layer  | 224.5  | 52  | 137  | 14 | 17  | 10 | 40  | 46  | 39  | 12 | 53  |
|     | Two layered sample<br>(red/white ground)                    | 1114.7 | 183 | 694  | 42 | 46  | 24 | 174 | 83  | 90  | 33 | 125 |
| H1a | White ground layer  | 102.1  | 17  | 34   | 5  | 8   | 3  | 14  | 16  | 15  | 4  | 23  |
|     | Four layered sample<br>(red/grey/orange /white ground)      | 511.1  | 170 | 417  | 46 | 62  | 31 | 160 | 82  | 85  | 37 | 119 |
|     | White ground layer  | 189.0  | 145 | 326  | 42 | 59  | 29 | 133 | 86  | 76  | 34 | 94  |
| H1b | White ground layer<br>with trace amounts of<br>orange layer | 123.0  | 57  | 129  | 18 | 25  | 13 | 56  | 39  | 36  | 15 | 47  |
|     | Four layered sample<br>(red/grey/orange /white)             | 636.6  | 204 | 613  | 60 | 86  | 40 | 248 | 112 | 104 | 52 | 161 |
|     | Red top layer   | 522.1  | 55  | 128  | 14 | 24  | 10 | 51  | 41  | 40  | 17 | 61  |
| H1c | White ground layer  | 123.1  | 41  | 119  | 13 | 19  | 9  | 50  | 24  | 25  | 13 | 37  |
|     | Lower three layer<br>(grey/ orange / white ground)          | 256.9  | 0   | 3    | 0  | 2   | 1  | 0   | 0   | 2   | 0  | 2   |
|     | Four layered sample<br>(red/grey/orange /white ground)      | 618.2  | 207 | 658  | 61 | 86  | 42 | 303 | 95  | 93  | 58 | 163 |
| H1d | Bottom two layers<br>(grey/white ground)                    | 392.6  | 185 | 693  | 29 | 38  | 20 | 119 | 81  | 86  | 26 | 92  |
|     | Top two layer<br>(Red/grey)                                 | 303.2  | 44  | 141  | 11 | 17  | 8  | 38  | 39  | 36  | 12 | 42  |
|     | wood  | 211.4  | 35  | 127  | 12 | 16  | 9  | 47  | 61  | 34  | 14 | 53  |
| H3a | White ground layer  | 116.2  | 33  | 70   | 10 | 14  | 8  | 31  | 30  | 21  | 9  | 34  |
|     | Lower three layer<br>(black/orange /white ground)           | 258.4  | 111 | 279  | 38 | 56  | 29 | 109 | 78  | 55  | 34 | 68  |
|     | Top two layer (red and<br>white/grey)                       | 1069.7 | 370 | 1174 | 94 | 151 | 65 | 522 | 192 | 155 | 97 | 83  |

**Table S 17:** Fatty acid content (ppm) from paint samples analysed, where ND denotes not detected or below the detection limit

| Sample location & description |  | weight, µg | Pimelic | Suberic | Lauric | Azelaic | Sebacic | Myristic | Palmitic | Stearic | Oleic |
|-------------------------------|--|------------|---------|---------|--------|---------|---------|----------|----------|---------|-------|
| Blank vial                    |  | N.D.       | N.D.    | N.D.    | N.D.   | N.D.    | N.D.    | N.D.     | 1,65     | 2,35    | N.D.  |
| E1a                           | White ground layer                               | 226.8      | 0       | 0       | 0      | 0       | 0       | 0        | 3.62     | 3.61    | 0     |
|                               | Three layered sample<br>(red/black/white ground) | 842.3      | 0       | 0       | 0      | 0       | 0       | 0        | 3.34     | 3.65    | 0     |
|                               | Wood specimen                                    | 515.2      | 4.08    | 7.11    | 0      | 12.07   | 1.81    | 0        | 11.82    | 11.43   | 2.22  |

|     |   |        |      |      |   |       |     |   |       |       |      |
|-----|---|--------|------|------|---|-------|-----|---|-------|-------|------|
| E1b | <b>Two layered sample</b><br>(red/white)                            | 467.6  | 1.31 | 3.21 | 0 | 3.89  | 0   | 0 | 5.35  | 3.66  | 0    |
|     | <b>Wood specimen</b>  | 225.3  | 2.09 | 3.35 | 0 | 5.27  | 0   | 0 | 2.73  | 2.36  | 0    |
|     | <b>White ground layer</b>   | 289.4  | 0    | 0    | 0 | 1.03  | 0   | 0 | 6.36  | 3.9   | 2.15 |
| E1c | <b>Bottom two layers</b><br>(black/white ground)                    | 48.0   | 0    | 0    | 0 | 0     | 0   | 0 | 1.65  | 2.21  | 0    |
|     | <b>Top two layers</b><br>(red/black)                                | 131.3  | 0    | 0    | 0 | 0     | 0   | 0 | 1.95  | 2.51  | 0    |
|     | <b>Three layered sample</b><br>(red/black/white ground)             | 585.9  | 0    | 1.05 | 0 | 1.26  | 0   | 0 | 3.23  | 2.91  | 0    |
| E1d | <b>White ground layer</b>   | 581.4  | 0    | 1.02 | 0 | 0     | 0   | 0 | 2.17  | 2.08  | 0    |
|     | <b>Red top layer</b>  | 194.5  | 0    | 1.78 | 0 | 1.73  | 0   | 0 | 3.9   | 3.41  | 0    |
|     | <b>Two layered sample with insect</b><br>(red/white)                | 470.0  | 0    | 0    | 0 | 0     | 0   | 0 | 1.63  | 2.01  | 0    |
| E1e | <b>White ground layer</b>   | 368.5  | 1.08 | 1.21 | 0 | 1.31  | 0   | 0 | 3.38  | 2.91  | 0    |
|     | <b>Three layered sample</b><br>(red/black/white ground)             | 683.1  | 1.53 | 1.45 | 0 | 1.32  | 0   | 0 | 2.68  | 2.57  | 0    |
| E2a | <b>Three layered sample</b><br>(red/black/white ground)             | 191.9  | 0    | 0    | 0 | 1.07  | 0   | 0 | 3.99  | 4.28  | 0    |
|     | <b>Wood specimen</b>  | 207.4  | 2.57 | 1.93 | 0 | 3.96  | 0   | 0 | 2.85  | 2.67  | 0    |
| E3a | <b>White ground layer</b>   | 224.5  | 0    | 0    | 0 | 0     | 0   | 0 | 4.46  | 4.03  | 0    |
|     | <b>Two layered sample</b><br>(red/white ground)                     | 1114.7 | 0    | 0    | 0 | 1.39  | 0   | 0 | 5.56  | 5.31  | 0    |
| H1a | <b>White ground layer</b>   | 102.1  | 0    | 0    | 0 | 1.03  | 0   | 0 | 2.38  | 2.74  | 0    |
|     | <b>Four layered sample</b><br>(red/grey/reddish-brown/white)        | 511.1  | 0    | 1.43 | 0 | 2.1   | 0   | 0 | 3.53  | 2.98  | 0    |
|     | <b>White ground layer</b>   | 189.0  | 0    | 0    | 0 | 1.03  | 0   | 0 | 3.58  | 2.97  | 0    |
| H1b | <b>White ground layer with trace amounts of reddish-brown layer</b> | 123.0  | 0    | 0    | 0 | 0     | 0   | 0 | 3.05  | 3.01  | 0    |
|     | <b>Four layered sample</b><br>(red/grey/reddish-brown/white)        | 636.6  | 0    | 3.25 | 0 | 3.83  | 0   | 0 | 6.59  | 4.34  | 0    |
|     | <b>Red top layer</b>  | 522.1  | 0    | 2.57 | 0 | 4.05  | 0   | 0 | 5.75  | 4.08  | 0    |
| H1c | <b>White ground layer</b>   | 123.1  | 0    | 0    | 0 | 0     | 0   | 0 | 3.23  | 2.92  | 0    |
|     | <b>Lower three layers</b><br>(grey/reddish-brown/white)             | 256.9  | 0    | 0    | 0 | 0     | 0   | 0 | 1.86  | 2.12  | 0    |
|     | <b>Four layered sample</b><br>(Red/grey/reddish-brown/white)        | 618.2  | 1.02 | 3.36 | 0 | 5.01  | 0   | 0 | 7.62  | 4.66  | 2.36 |
| H1d | <b>Bottom two layers</b><br>(grey/white ground)                     | 392.6  | 0    | 0    | 0 | 0     | 0   | 0 | 2.97  | 2.85  | 0    |
|     | <b>Top two layer</b><br>(Red/grey)                                  | 303.2  | 0    | 0    | 0 | 1.4   | 0   | 0 | 3.43  | 3.17  | 0    |
|     | <b>Wood specimen</b>  | 211.4  | 0    | 0.99 | 0 | 2.7   | 0   | 0 | 3.49  | 2.65  | 0    |
| H3a | <b>White ground layer</b>   | 116.2  | 0    | 0    | 0 | 0     | 0   | 0 | 3.78  | 3.31  | 0    |
|     | <b>Lower three layers</b><br>(black/reddish-brown/white)            | 258.4  | 0    | 1.87 | 0 | 2.29  | 0   | 0 | 7.56  | 5.72  | 1.88 |
|     | <b>Top two layer</b><br>(red and white/grey)                        | 1069.7 | 1.8  | 8.27 | 0 | 14.25 | 1.2 | 0 | 20.54 | 13.49 | 0    |



**Figure S 9:** Chart of plat reading results at OD45, where blue bars are absorbency reading for fish collagen and orange bars are for mammal collagen.

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