





## UNRAVELLING THE HISTORY OF A VENETIAN ANTIPHONARY

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**ABSTRACT.** We present the results of a multifaceted study of an antiphonary—liturgical song book—presumably made in Venice in 1607, now in the Ringve, National Music Museum of Norway in Trondheim<sup>1</sup>. The book is hand-sewn on raised cords, bound in full leather on cardboard covers, originally with metal clamps. The paper block consists of pages printed in black and red that include both song texts and music scores. The red ink is based on vermilion and red lead while the black ink is carbon based. The treads and cords were made of flax. The leather used was made from goat skin. Radiocarbon results confirmed the printing date. The antiphonary shows several signs of repair including the possibility of re-binding. Animal-based glue was used for the repairs as well as for the sizing of both original and repair paper. Two potential periods were identified for reparations, 1670–1710 AD and 1782–1830 AD. This case study was conducted prior to the opening of a new permanent exhibition, Soundtracks, at the Ringve Museum where the book is displayed.

**KEYWORDS:** antiphonary, leather, paper, printed book, radiocarbon dating.

## INTRODUCTION

The development of the contextual information for a museum object that is going on permanent display is often the result of the collaboration between various museum departments and research institutions, where any additional information can play a significant role in the final narrative.

In the case of an antiphonary printed in Venice that went on display at Ringve Music Museum<sup>2</sup> in June 2022 (Figure 1), very little was known about the book from its printing in 1607 until 1955, when it was added to the museum collection. It was donated to Ringve's first museum director, Victoria Bachke, by Edith Skjerne. The book probably came from the private library of Godtfred Skjerne, who was director of the Musikhistorisk Museum in Copenhagen. When he died in 1955, his widow Edith chose to pass the book on to her close friend Victoria, and the book thus became part of the Ringve Music Museum's collection.<sup>3</sup>

The song book contains both lyrics and scores of liturgical songs. The text is in Latin and the musical score is in neumes in both C and F clefs (Figure 1B). An inscription in the lower part of the last page indicates that it was printed in Venice in 1607 (Figure 1C). The bottom part of the last page with colophon, was torn out.

Damaged to some degree, the book shows signs of rebinding, repairs, and vandalism. The level of damage to the covers and the fact that it was re-bound make it difficult to determine which parts are original. Sophisticated tools not available at the Ringve Museum were used at the

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<sup>1</sup><https://ringve.no/en/collection>; access date 03.19.22.

<sup>2</sup>Catalog number: RMT3464, <https://digitaltmuseum.no/0210210449477/antifonarium>; access date 03.19.22.

<sup>3</sup>Source : Primus - museums catalogue database.



Figure 1 (A) The Antiphonary with the names used for the parts of the book. (B) Fragment of page 31. (C) The colophon on the last page showing the place of printing, date 1607 and possibly the initials of the printer.

National Laboratory for Age Determination, NTNU University Museum, in a collaboration, to bring to light some of the facts of this particular object.

Several elements of the bookbinding that were made of reused materials might show deviations in relation to the printing date of the book, e.g., papers were produced of linen rags, headband made of reused parchment, re-bound book spine was reinforced with reused leather and paper.

The goal of this project is to analyze this complex museum object via multi-proxy research and date its separate elements in order to obtain a clearer understanding of chronological changes made to this book and provide solid background information for a better historical interpretation. Several analysis methods were used in addition to radiocarbon ( $^{14}\text{C}$ ) dating. Microscope analyses allowed us to determine the materials used for bookbinding, XRF spectra indicated the pigments used in the inks and the metals from the buckle, and FTIR showed what kind of adhesives were used.

## MATERIALS

The antiphonary is 45.5 cm high by 30 cm wide with a thickness of 6 cm and counts 180 numbered leaves printed in mainly black ink with rubrics<sup>4</sup>. The anatomy of a book and the methods used in traditional book binding are described in the supplemental material. The terminology used in this article is defined there and can be seen in Figure 1.

It has a full leather bookbinding, typical for this period. The raised cords are approximately 5 mm in diameter and, unconventionally, protrude partly above the surface of the upper leather. The handmade paper used in the antiphonary shows a consistent pattern of laid and chain lines of the wire screen indicating that all the paper probably came from the same paper mill and possibly from the same batch. There are no watermarks present on the sheets. The pages were printed recto/verso in two colors, black and red. Large sheets, containing 12 or 16 pages each, were folded into sections, marked with signatures in Latin capitals, from A to X, listed in the register<sup>5</sup> (Roberts and Etherington 1982). All 23 sections were sewn together with the aid of sewing threads to form the text block. Sewn one to another, sections were attached to the raised bands, forming the spine of the text block. The edges of the pages have been trimmed. This is seen by the narrow top margins when compared to the other margins. It is difficult to determine whether the trimming occurred originally in the early 17th century or at a later time, when the book was re-bound.

The book covers, made of cardboard, were connected to the text block by the ends of the raised bands. At both ends of the spine, headbands were created with the use of parchment strips and leather lace. Very little of the headbands is currently left. The book cover material, leather, was applied in one piece and wrapped around the edges of the covers. From inside, both front and back, covers were attached to the text block by end-papers glued to cardboards forming the so-called paste-downs. The leather cover was decorated with blind hot tool impressions without gilding. Two sets of metal clasps, mounted on both covers, originally kept the book closed. Only one of four buckle elements remains.

The samples were collected by a paper conservator at Ringve museum. The sampling procedure was carried out in two rounds. A total of 22 samples were obtained, each of which was described and photographed (Table 1).

For microscopic examination, FTIR analysis and <sup>14</sup>C dating, samples were taken from both the original parts of the book and from subsequent repairs. The smallest possible amounts of material were collected to be the least noticeable and harmless to the object. In cases when elements of the book were made of possibly inhomogeneous materials, several samples were taken, e.g., in case of paper and cardboard that were produced of linen rags. Multiple samples of secondary materials like paper reparations and the adhesives used for those were also taken. Loose fragments were collected to minimize damage.

<sup>4</sup>Rubric - 1. (Printing, Lithography & Bookbinding) a title, heading, or initial letter in a book, manuscript, or section of a legal code, esp. one printed or painted in red ink or in some similarly distinguishing manner; *Collins English Dictionary – Complete and Unabridged, 12th Edition 2014*. (1991, 1994, 1998, 2000, 2003, 2006, 2007, 2009, 2011, 2014). Retrieved December 4, 2022, from <https://www.thefreedictionary.com/rubric>.

<sup>5</sup>Registrum (lat.) 2. A list of the quires or sections of a book, often printed at the end of early printed books, particularly those printed in Italy, to assist the binder in assembling and collating a complete copy in correct order; (Roberts and Etherington 1982) p. 215.

Table 1 List of samples. The results were calibrated using OxCal 4.4 and the IntCal20 dataset.

Lab code	Tra-	No.	Sample name	Sample description	<sup>14</sup> C content (pMC)	δ <sup>13</sup> C (from AMS system)	<sup>14</sup> C age (years BP)	Calibrated age ranges
18217		1.1	Leather – headband	A fragment of a headband, leather. Reused material.	95.45 ± 0.16	–26.9 ± 1.3‰	375 ± 15	68.3% probability 1467AD (48.7%) 1500AD 1600AD (19.6%) 1615AD 95.4% probability 1456AD (66.0%) 1516AD 1589AD (29.5%) 1621AD
18218		2.1	Leather – cover	A fragment of leather from the inner side of the cover. Possibly original material.	95.46 ± 0.13	–29.4 ± 1.0‰	375 ± 10	68.3% probability 1470AD (47.6%) 1500AD 1600AD (20.7%) 1615AD 95.4% probability 1456AD (65.7%) 1515AD 1590AD (29.8%) 1621AD
18219		2.2	Leather – spine reinforcement	Piece of leather from the spine reinforcement. Reused or residues of earlier binding.	97.12 ± 0.13	–26.6 ± 0.6‰	235 ± 10	68.3% probability 1650AD (48.9%) 1663AD 1787AD (19.4%) 1793AD 95.4% probability 1646AD (62.6%) 1667AD 1782AD (32.8%) 1796AD
18220		3.1	Cardboard – cover, front	Cardboard from inside the cover. Original material if it was not re-bound.	96.13 ± 0.14	–29.5 ± 0.7‰	315 ± 15	68.3% probability 1522AD (9.6%) 1530AD 1538AD (46.8%) 1575AD 1625AD (11.9%) 1636AD 95.4% probability 1508AD (77.2%) 1594AD 1617AD (18.2%) 1640AD

Lab code	Tra-	No.	Sample name	Sample description	<sup>14</sup> C content (pMC)	δ <sup>13</sup> C (from AMS system)	<sup>14</sup> C age (years BP)	Calibrated age ranges
18625		3.2	Cardboard – cover, front	Cardboard from the front cover; top part; inside layer; internal	96.29 ± 0.25	–24.2 ± 0.1‰	305 ± 20	68.3% probability 1523AD (55.8%) 1572AD 1630AD (12.5%) 1641AD 95.4% probability 1505AD (72.8%) 1596AD 1616AD (22.7%) 1649AD
18626		3.3	Cardboard – cover, back	Cardboard from the back cover; top side;	96.29 ± 0.19	–4.5 ± 0.3‰	305 ± 15	68.3% probability 1524AD (51.9%) 1559AD 1567AD (2.8%) 1570AD 1631AD (13.6%) 1641AD 95.4% probability 1516AD (73.7%) 1590AD 1620AD (21.7%) 1646AD
18627		3.4	Cardboard – cover, back	Cardboard from the back cover; lower end.	96.01 ± 0.20	–24.3 ± 0.2‰	325 ± 15	68.3% probability 1510AD (15.1%) 1528AD 1550AD (39.2%) 1592AD 1619AD (13.9%) 1634AD 95.4% probability 1495AD (76.4%) 1602AD 1610AD (19.0%) 1639AD

(Continued)

Table 1 (*Continued*)

18221	4.1	Paper – lining (pastedown)	Pastedown, inside the cover. Can be from an earlier date if the book was re-bound.	95.68 ± 0.14	–31.0 ± 1.0‰	355 ± 15	68.3% probability 1486AD (33.8%) 1516AD 1590AD (34.5%) 1620AD 95.4% probability 1474AD (45.1%) 1524AD 1560AD (1.0%) 1564AD 1571AD (49.3%) 1631AD
18222	4.2	Paper – lining (pastedown)	Pastedown, inside the front cover. Can be from a later date if the book was re-bound or repaired.	97.69 ± 0.13	–27.0 ± 1.7‰	185 ± 10	68.3% probability 1667AD (18.5%) 1681AD 1740AD (16.7%) 1753AD 1763AD (29.2%) 1783AD 1940AD (3.8%) 1944AD 95.4% probability 1663AD (21.2%) 1684AD 1735AD (52.5%) 1786AD 1792AD (7.7%) 1804AD 1929AD (14.1%) 1950AD
18223	4.3.A	Paper – text block p.125	Printed paper block, p.125 in the edge (should be original).	95.62 ± 0.15	–27.5 ± 1.3‰	360 ± 15	68.3% probability 1478AD (37.4%) 1511AD 1592AD (30.9%) 1619AD 95.4% probability 1462AD (50.7%) 1524AD 1572AD (44.7%) 1630AD

Lab code	Tra-	No.	Sample name	Sample description	<sup>14</sup> C content (pMC)	δ <sup>13</sup> C (from AMS system)	<sup>14</sup> C age (years BP)	Calibrated age ranges
18224		4.3.B	Paper – text block p.132	Printed paper block, p.132 in the edge (should be original).	95.57 ± 0.15	–30.9 ± 1.0‰	365 ± 15	68.3% probability 1476AD (39.0%) 1508AD 1594AD (29.3%) 1618AD 95.4% probability 1459AD (55.0%) 1522AD 1577AD (40.5%) 1625AD
18225		4.3.C	Paper – text block, final page	Printed paper block, final page in the edge (should be original).	95.57 ± 0.15	–30.0 ± 1.2‰	365 ± 15	68.3% probability 1476AD (39.0%) 1508AD 1594AD (29.3%) 1618AD 95.4% probability 1459AD (55.0%) 1522AD 1577AD (40.5%) 1625AD
18226		4.4.A	Paper – repair patch p.109	Reparation patches on the p.109, right, material of later date.	97.61 ± 0.18	–29.4 ± 0.6‰	195 ± 15	68.3% probability 1663AD (19.8%) 1680AD 1740AD (12.6%) 1753AD 1763AD (28.5%) 1787AD 1792AD (7.4%) 1800AD 95.4% probability 1660AD (22.9%) 1684AD 1734AD (60.8%) 1804AD 1929AD (11.7%) 1950AD

(Continued)

Table 1 (*Continued*)

18227	4.4.B	Glue – repair patch p109	Glue from reparation patches on the p.109, right, material of later date.	97.69 ± 0.14	–28.1 ± 0.4%	185 +15/–10 BP	68.3% probability 1667AD (17.1%) 1681AD 1740AD (15.5%) 1753AD 1763AD (26.8%) 1783AD 1940AD (8.8%) 1950AD 95.4% probability 1663AD (21.0%) 1685AD 1734AD (51.9%) 1787AD 1792AD (8.1%) 1804AD 1928AD (14.4%) 1950Ad
18228	4.5	Paper – spine reinforcement	Spine reinforcement between paper block and leather. Reused material.	97.75 ± 0.14	–30.5 ± 1.0%	185 ± 10	68.3% probability 1668AD (15.9%) 1681AD 1740AD (16.7%) 1753AD 1763AD (25.5%) 1782AD 1940AD (10.1%) 1950AD 95.4% probability 1665AD (19.4%) 1685AD 1732AD (51.9%) 1785AD 1793AD (7.5%) 1805AD 1927AD (16.6%) 1950AD



Lab code	Tra- No.	Sample name	Sample description	<sup>14</sup> C content (pMC)	δ <sup>13</sup> C (from AMS system)	<sup>14</sup> C age (years BP)	Calibrated age ranges
18628	4.6	Paper – repair patch p.22	Reparation paper from p. 22; lower part.	97.32 ± 0.24	−24.2 ± 0.3‰	220 ± 20	68.3% probability 1652AD (31.7%) 1671AD 1779AD (36.5%) 1798AD 95.4% probability 1645AD (40.3%) 1681AD 1739AD (5.7%) 1754AD 1762AD (46.7%) 1800AD 1939AD (2.7%) 1950AD
18629	4.7	Paper – repair patch p.38	Reparation paper II (over the older reparation) p. 38 verso, lower edge.	97.23 ± 0.19	−23.9 ± 0.5‰	225 ± 15	68.3% probability 1654AD (34.3%) 1666AD 1784AD (34.0%) 1795AD 95.4% probability 1643AD (50.5%) 1674AD 1768AD (45.0%) 1800AD
18630	4.8	Paper – repair patch, last side	Reparation paper; last side/above “Augusti”; Tabula Antiphonarii de Sanctis.	97.28 ± 0.34	−24.0 ± 0.4‰	220 ± 30	68.3% probability 1645AD (32.2%) 1675AD 1744AD (3.0%) 1749AD 1765AD (33.2%) 1799AD 95.4% probability 1640AD (39.6%) 1685AD 1733AD (49.4%) 1805AD 1928AD (6.4%) 1950AD

(Continued)

Table 1 (*Continued*)

18229	5.1	Cord – raised bands	Sewing cord (first joint) between cover and paper block. Original if was not re-bound.	98.06 ± 0.14	–29.2 ± 0.9‰	155 ± 10	68.3% probability 1677AD (12.7%) 1691AD 1728AD (13.8%) 1742AD 1751AD (12.6%) 1764AD 1799AD (9.3%) 1809AD 1922AD (19.9%) 1942AD 95.4% probability 1669AD (16.7%) 1695AD 1724AD (37.6%) 1780AD 1796AD (11.6%) 1813AD 1838AD (5.6%) 1878AD 1915AD (23.9%) 1950AD
18230	5.2	Thread – sewing p.145	Sewing thread, loose p. 145, original if was not re-bound.	95.79 ± 0.14	–32.2 ± 1.2‰	345 ± 15	68.3% probability 1494AD (28.4%) 1522AD 1576AD (25.8%) 1602AD 1610AD (14.1%) 1625AD 95.4% probability 1480AD (36.8%) 1526AD 1556AD (58.7%) 1633AD

Lab code	Tra- No.	Sample name	Sample description	<sup>14</sup> C content (pMC)	δ <sup>13</sup> C (from AMS system)	<sup>14</sup> C age (years BP)	Calibrated age ranges
18631	5.3	Thread – sewing p.86	Sewing cord, p. 86, section K, lower end.	98.43 ± 0.23	–24.5 ± 0.6‰	125 ± 20	68.3% probability 1689AD (9.2%) 1705AD 1721AD (5.0%) 1729AD 1808AD (5.4%) 1817AD 1833AD (38.6%) 1891AD 1907AD (10.1%) 1924AD 95.4% probability 1683AD (24.5%) 1736AD 1802AD (71.0%) 1937AD
18632	5.4	Thread – sewing p.93	Sewing cord, p. 93, section L, lower end.	98.17 ± 0.24	–25.6 ± 0.5‰	150 ± 20	68.3% probability 1678AD (10.9%) 1695AD 1725AD (10.6%) 1742AD 1751AD (7.5%) 1764AD 1799AD (8.0%) 1812AD 1839AD (3.7%) 1847AD 1852AD (11.3%) 1877AD 1916AD (16.3%) 1941AD 95.4% probability 1669AD (15.1%) 1703AD 1721AD (27.0%) 1780AD 1796AD (10.0%) 1817AD 1832AD (22.7%) 1891AD 1907AD (20.7%) 1950AD

## METHODS

In order to provide better understanding of the combination of materials and the changes to the construction of the book, both visual and microscopic examinations combined with XRF and FT-IR techniques were carried out.

The different elements of the book were subjected to visual inspection to gather initial information about the book's construction and the changes made to it, along with determining the type of bookbinding, the possible presence of watermarks and inscriptions. In addition, measurements and photographs were taken to document the construction of the book and its state of preservation.

Optical microscopy, in both transmitted and reflected light, was used to determine the morphology of natural materials that were used in the book, such as paper, plant fibers, leather, and parchment. This technique has also been applied to evaluate the color and shape of the pigment particles in the printing inks.

Identification of the fibers was carried out based on their morphological structure using a reflected light microscope (Olympus BXFM) and transmitted light microscope: (JENAMED 2 Zeiss Jena). Polarized light was also used. A digital microscope (Q-scope, model QS. DERMO) was used for the identification of leather species.

FTIR analyses of papers, cardboards, and adhesives were performed as a non-destructive part of the research on the samples prior to chemical treatment for  $^{14}\text{C}$  dating. Infrared spectra were obtained in the Attenuated Total Reflection (ATR) mode using a Fourier Transform Infrared Spectrometer Thermo Fisher Nicolet iS50. The analyses were carried out at room temperature and ambient humidity. All the spectra were acquired between  $4000$  and  $400\text{ cm}^{-1}$  with a spectral resolution of  $4\text{ cm}^{-1}$  and 32 scans. Spectragryph Version 1.2.16.1, 2022 was used for interpretation of the spectra. In the case of paper with traces of glue present, both sides of the sample were measured. The main purpose of the FTIR analysis was to confirm what kind of adhesive was used for the sizing of the paper and for secondary repairs.

Elemental analysis of the printing inks, both red and black, and the metal fragments of the buckle with nails were performed by X-ray fluorescence (XRF) with the portable Thermo Scientific Niton XL3t GOLDD+ analyzer. Measurements were taken within standard analytical range (Mg -U) and a measurement time of 60 seconds. Various modes were used depending on the type of material. Pigments and paper were tested with the analytical mode Test All Geo whereas General Metals mode was applied for the metal elements.

The  $^{14}\text{C}$  samples were first cleaned of organic contaminants using an eluotropic sequence consisting of tetrahydrofuran (THF), chloroform, petroleum ether, acetone, methanol, and  $\text{H}_2\text{O}$  in a Soxhlet type apparatus (Bruhn et al. 2001; Seiler et al. 2019) prior to an acid-alkali-acid (AAA) treatment. This sequence uses solvents from non-polar to polar ones and each solvent will dissolve its predecessor in the series. The standard treatment keeps the samples in boiling solvents for  $3 \times 20$  min and then the next solvent is applied. Although the samples were never exposed to the elements, finger grease must have accumulated over the years on the surfaces and this sequence is intended to remove it.

The cleaned samples were combusted in an elemental analyzer and graphitized in an automatic system using a  $\text{H}_2$ -Fe-reaction (Seiler et al. 2019). The graphite was measured at the Trondheim 1 MV AMS system following our standard procedures (Nadeau et al. 2015).

## RESULTS

### Microscopic Analysis

Fibers from the sewing threads and the cords from the raised bands, as well as fibers from paper pulp, were examined under the microscope. In the case of the sewing threads, the  $^{14}\text{C}$  results revealed the presence of threads from two different periods, although they are very similar in appearance.

Microscopic studies including longitudinal and cross-sectional appearance of the fibers showed that the sewing threads and the cords from the raised bands, all were made from flax (*Linum usitatissimum*). Single flax fibers are characterized by a cylindrical shape and a smooth surface as well as thin walls and a fine lumen sometimes visible only as a thin line. In addition, on the flax fibers we can see a very characteristic thickening called nodes, which are transverse dislocations taking the shape of I, X, and Y (Strelis and Kennedy 1967). Flax fiber cells in the transverse section show a pentagonal and hexagonal shape (Catling and Grayson 1982).

In the case of the fibers from the paper pulp, the identification was based on their longitudinal appearance. It was confirmed that papers from the original printed pages, cardboards and repair patches were made of rags. Flax (*Linum usitatissimum*) fibers were found in all cases.

Species identification of the leather from the cover, the spine reinforcement, and the headband was carried out by reflected light microscopy, analyzing the hair follicles (holes) patterns on the leather surface, which are unique to each animal species (Ebsenet al. 2019; Okrağla 2013). Examinations showed that goatskin was used for the cover, characterized by double rows of hair holes of different sizes. The larger primary follicles produce guard hair and come in numbers from 2 to 5, when the smaller secondary follicles produce down and come in numbers from 4 to 8 (Duffy, 2013; Okrağla 2013). In the remaining cases of the spine reinforcement and the headband, identification was not possible due to the condition of the leather.

Printing inks consist of two main components: a binder, often linseed oil, and colorants, pigments, and dyes. A variety of additives can be added such as resins, waxes, vegetable gums, animal glues and many more. Most of the pigments used for oil painting may also be used for printing inks, if they have sufficiently fine particles (Leach and Pierce 1993; Stijnman 2000).

Microscopic observation of the red ink revealed the presence of pigment particles in two shades of red, a lighter (orange-red) and a darker shade. A small number of black and white particles are also noticeable. The latter may also be contaminants applied later on the printed surface and originating from the black ink and/or other sources.

The black pigment in the black printing ink is very fine grained and the particles are hard to discern. By observing the surface of the paint under a microscope, it is difficult to determine whether it contains one or more black pigments. The red pigment particles that are visible in the black sections most probably come from the neighboring areas with red print.

### ATR-FTIR

The ATR-FTIR spectrum of the leather cover of the antiphonary reveals a band at  $1635\text{ cm}^{-1}$  assigned to the stretching vibration of the C=O bonds, and a band appearing at  $1541\text{ cm}^{-1}$  assigned to the NH bending vibration and the CH stretching vibration. Those two bands respectively correspond to the amide I and amide II bands and are indicative of proteins. The

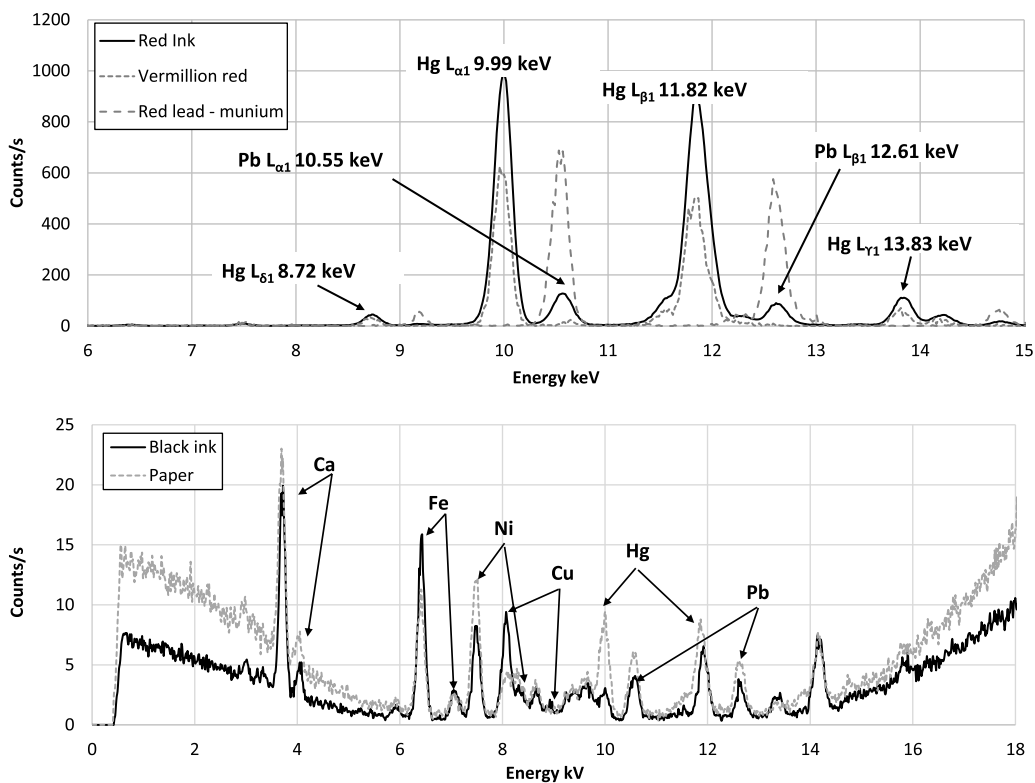


Figure 2 XRF spectra of the red ink (top) and black ink (bottom) used to print the manuscript. Comparison of the XRF spectrum of the red ink with the spectra of two pigments: vermilion ( $\text{HgS}$ ) and minium ( $\text{Pb}_3\text{O}_4$ ) shows that the red ink contains both pigments. The XRF spectrum of the black ink confirms its carbon-based nature. XRF spectra of black ink and background paper show the presence of the same trace elements in both spectra.

presence of these bands in the FTIR spectra of the paper indicate that animal glue was used as a sizing agent in the production of the paper. This practice was gradually abandoned in the mid-19th (Brown et al. 2020) century with the industrialisation of paper production. FTIR analysis of the glue used for the repairs show that animal glue was used (see supplementary material).

## XRF

The XRF spectra of the red printed surface show the presence of mercury (Hg) and lead (Pb) (Figure 2 top). Comparing the spectrum of the red printing ink with the spectra of vermilion and lead red<sup>6</sup> allows us to conclude that a mixture of both pigments was used in the production of this particular ink. This does not exclude the potential presence of other pigments, e.g., of organic origin but these are not detectable by the methods used.

Vermillion is an artificial pigment based on mercuric sulphide ( $\text{HgS}$ ), which occurs naturally as Cinnabar. Natural vermilion was known already in ancient China and was produced artificially in Europe from the 8th century (Gettens et al. 1972). An orange-red lead-minium

<sup>6</sup>Source of the XRF spectra for pigments: <https://chsopensource.org/pigments-checker/> CHSOS (Cultural Heritage Science Open Source),

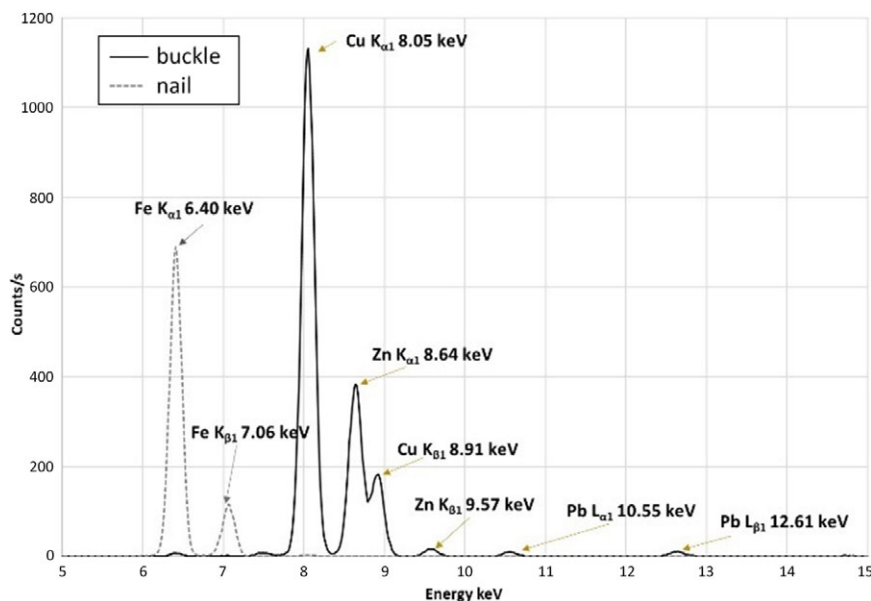


Figure 3 The XRF spectrum of the metal clasp indicates a copper alloy. The second spectrum confirms that the fastening nail was made of iron.

( $\text{Pb}_3\text{O}_4$ ) has been known since antiquity and used in the Middle Ages to decorate manuscripts (Fitzhugh 1986) and later for printing inks (Rudniewski et al. 2018).

The XRF spectrum of the black ink confirms its carbon-based nature. It shows only traces of calcium, iron, nickel, lead, and mercury. Impurities containing mercury and lead might have been trans-positioned from the neighbouring areas with powdery, unstable red ink. The similarity of both the paper and ink spectra (Figure 2 bottom) indicates that these trace elements are found both on the paper and in the black ink. Historical sources indicate that lamp black, vine-charcoal black, and ivory black were the most widely used in the production of black printing inks at that time. These pigments consist mainly of amorphous carbon, but may contain different impurities, traces of different elements (Larsen et al. 2016). Lamp black is a soot obtained during combustion of a wax candle, a tallow candle or linseed, hemp seed or olive oil lamp. Vine-charcoal black was made by charring young shoots of grape vines (Thompson 2003:ss. 83–85) and ivory black from charred animal bones (Crespo and Viñas 1985).

The XRF spectra, acquired on the metal clasp surface, shows the peaks of copper (Cu), zinc (Zn) and lead (Pb) (Figure 3). The second spectrum confirms that the clasp was attached to the book with iron nails.

### Radiocarbon Results

The  $^{14}\text{C}$  results are presented in Table 1. The results were calibrated using OxCal version 4.4 (Bronk Ramsey 2009) and the IntCal20 dataset (Reimer et al. 2020). The un-modeled calibrated results are presented in Figure 4. The distributions indicate homogeneous materials within each material type. The results of the original materials confirm the printing date of 1607 AD.

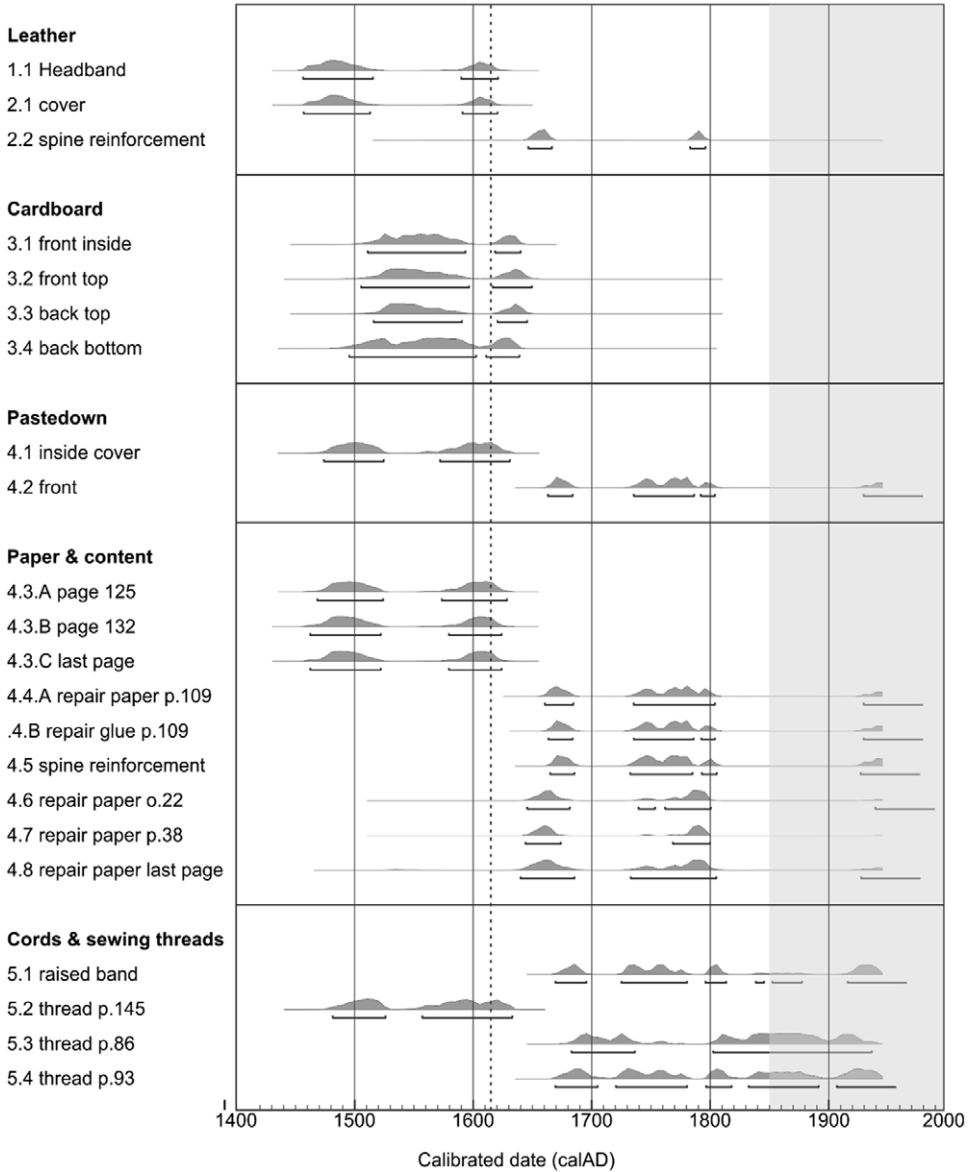


Figure 4 Unmodeled calibrated <sup>14</sup>C results. The dashed vertical line indicates 1607 AD, the printing year of the book. The gray shade indicates less likely date of repair due to the manufacture of the paper.

From these distributions, we can deduce that the leather and paper used for both the text block and the pastedown (sample 4.1) were most likely very recent at printing time, being produced within the previous decade. The thread used to sew the book might have a slightly older origin, although the data does not exclude that the thread is from the same period as the paper and leather.



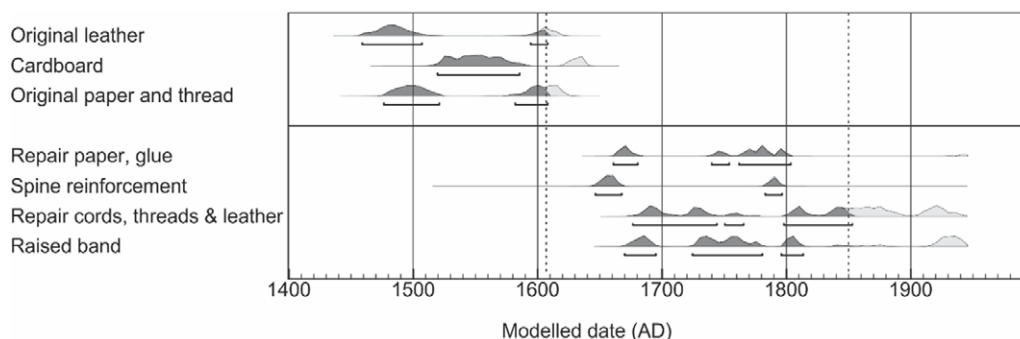


Figure 5 Modeled  $^{14}\text{C}$  results. The OxCal code is presented in the supplemental material. The dashed line indicates the printing year of the book, 1607 AD.

The  $^{14}\text{C}$  results were modeled using OxCal 4.4 and the IntCal20 dataset (see code supplemental data). This simple model presumes that the original materials date from prior to 1607 AD and that the repair material dates from prior to 1850. The latter is supported by both the presence of animal glue in the repair paper and the  $^{14}\text{C}$  results of the repair paper themselves. The results of the model are presented in Figure 5 and Table 2.

In the model,  $^{14}\text{C}$  results of samples of similar origin, such as two samples from the leather cover or four samples from the cardboard, were grouped together using the R\_Combine function. Each group is in a sequence in which it followed by a “Date ()” function, either 1607 or 1850, if the sample is from the original work or from the repair. This was done to remove parts of the calibration from after the known calendar dates for each sample group individually. The same could have been achieved by including the R\_combine functions in a phase which is then in a sequence followed by the calendar dates for each period (original and repair). However, including the different groups in a phase would have caused interference between the groups which we wanted to avoid. We also kept the un-modeled older part of the distributions (not using a boundary) in the sequences, as the goal was to truncate the distributions with the known historical dates but not to alter the distributions by over modeling it. The function “Date()” was used to specify the two historical dates used in the model as it provides a clearcut limit without influencing the rest of the distributions.

As can be seen from the un-modeled calibration results (Figure 4), all the distributions have a significant component before the historical date they precede. The results of the groups of samples are very homogeneous. The R\_Combine agreement indices can be found in Table 2.

## DISCUSSION

The modeled  $^{14}\text{C}$  probability distributions of the original materials have two areas, one before 1520 AD and one from ca. 1585 to 1607 AD (Figure 5). From the consistency of the results and the unlikely possibility that the book would have been produced from materials all being 100 years old, we exclude the period before 1520 AD. This indicates that the book was produced from materials grown from 1594 AD onward, which is the 2 sigma lower limit of the modeled leather samples (Table 2). The cardboard would have been produced from old rags which is supported by modeled results which place the youngest age for the cardboard at 1585 AD, 12 years prior to the printing of the book.

Table 2 Modeled radiocarbon results.

Group of samples	Modeled results (years AD)	Agreement index
Original leather	1458 (79.8%) 1506	102.9
	1594 (15.7%) 1608	
Cardboard	1519 (95.4%) 1585	101.5
Original paper and thread	1476 (61.9%) 1520	96
	1582 (33.6%) 1608	
Repair paper & glue	1660 (28.9%) 1680	94.1
	1740 (10.9%) 1754	
	1762 (55.7%) 1803	
2.2 spine reinforcement (single sample)	1646 (66.1%) 1667	95.5
	1782 (29.4%) 1796	
Repair cords, threads & leather	1676 (48.6%) 1744	90.7
	1750 (5.5%) 1765	
	1798 (41.3%) 1852	
5.1 Raised band (single sample)	1670 (24.3%) 1694	97
	1724 (55.0%) 1780	
	1796 (16.1%) 1813	

The date of the repair and the possibility of multiple repairs are harder to assess. The results of all the materials used in the repair cannot be combined into a single solution. The results indicate that the repairs cannot have been made before 1670 AD. If we assume that repair materials are not more than 30 years old, especially the repair paper and glue, we can see two potential periods when the book could have been repaired: from 1670 to 1710 and from 1782 to 1830. The possibility of multiple repairs cannot be excluded.

The raised bands are protruding through the leather cover, this can be attributed to haste or not very skilled abilities of the person making repairs. The positioning of the paper and darker leather fragments that were sampled from under the spine are from a later period, confirming that re-binding took place using the original leather cover.

## CONCLUSION

The  $^{14}\text{C}$  results confirm the printing date of 1607 AD. The results also confirm that the main elements of the book, covers and text block as well as some of the sewing threads, are contemporary to each other and their dating can be attributed to early 17th century.

The red printing ink is a mixture of two different red pigments (lead red and vermilion) with a minimal admixture of black and white. The latter two may also be contaminants applied later on the print surface and originating from black ink and/or other sources. The leather used for the cover was made from goat skin.

The results from the repair materials indicate that the repairs were not done before 1670 AD. According to the  $^{14}\text{C}$  results the most probable periods for repairs are from 1670 to 1710 and from 1782 to 1830 AD. There is a high probability that the materials used for repairs were of some age at the time when repairs took place.

Protruding at the edges of the spine on the top of the leather, offset with the decorations of the spine, raised bands from the beginning were a major sign of reparations. Their dislocated positioning can most probably be addressed to a hasty and unskilled work.

The  $^{14}\text{C}$  dating results of the paper and darker leather fragments that were sampled from under the spine are from a later period. This indicates that the book was re-bound and the original leather was reused.

The presence of the animal glue under the repairs can be explained by its addition to a mixture of starch paste with which repairs were glued. It is worth mentioning that ATR-FTIR results indicate the presence of the animal glue in both the original and the repair paper as sizing agent. Gelatin was widely used through centuries, up to the 1800s when the production of paper was industrialized (Dąbrowski and Siniarska-Czaplicka 1991; Barrett et al. 2016).

## SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit <https://doi.org/10.1017/RDC.2023.61>

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