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Textiles and environment in the showcase containing Saint Canute the Holy († AD 1086): Radiocarbon dating and chemical interactions

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Abstract

The cathedral in Odense, Denmark, has for nine centuries held the relics of the Danish King St Canute the Holy and his brother Benedikt. They were both murdered in the predecessor church at the site in AD 1086, and Canute was sanctified in already in AD 1100. The history of the relics has been that of turmoil at times, varying from initial worship of the Catholic believers, to being walled up and hidden away after the protestant reformation in AD 1536, and since the 19th Century on display as important heritage objects of national importance. In the present work we have characterised some of the textiles and analysed the air inside the glass showcases exhibiting the 11th Century wooden coffins holding the remains of St King Canute the Holy and his brother together with some precious textiles. Contrary to previous belief, we now prove that all the textiles analysed have the same age, which is consistent with the time of the enshrinement of the King and his brother in AD 1100. It is also shown that some of the textiles were treated with paraffin wax, most likely during attempts at conservation at the National Museum in the nineteenth century. The results of the air chemistry analyses show the problematic side of simultaneously storing of slowly decaying wood, fine textiles, and human bones in rather airtight environments. The wood continuously releases organic acids, the soaring concentrations of which are potentially harmful to the 11th Century textiles and probably also to the bones.

Keywords: Reliquaries, Medieval textiles, Radiocarbon dating, Air exchange rate, Indoor air quality, Showcase, Conservation of wood and bones

Introduction

A puzzle in Danish history concerns two very tangible objects: two coffin-shaped 1.5 m long reliquaries situated in the crypt of St Canute's Church in Odense [1–4]. One of the wooden coffins is now missing a lid, while the other has preserved the lower part of a hipped lid (Figs. 1 and 2). The two reliquaries were made of oak and were once covered by gilded copperplates of which only fragments have survived. Several Romanesque altar-frontals, retables, and crucifixes manufactured in the same technique have survived elsewhere in Danish churches and an example of these can give an impression of the original appearance of the shrines (Fig. 3) [5, 6].

Each reliquary contains the bones of a male individual. One is identified as King Canute the Holy (Kong Knud 2. den Hellige, in Danish, [7]), who was born c. 1040–45 and ruled 1080–1086; the other most likely his younger half-brother Benedikt. Several well-preserved textiles of silk and linen are present in the reliquaries. The dates of the textiles and their historical context are one of the two main research questions of this investigation, which shed new light on the complicated story of the shrines. Were the textiles specifically chosen for the enshrinement of the saint and were they contemporaneous with the enshrinement? Or do they represent a more random selection of old and contemporary textiles as has

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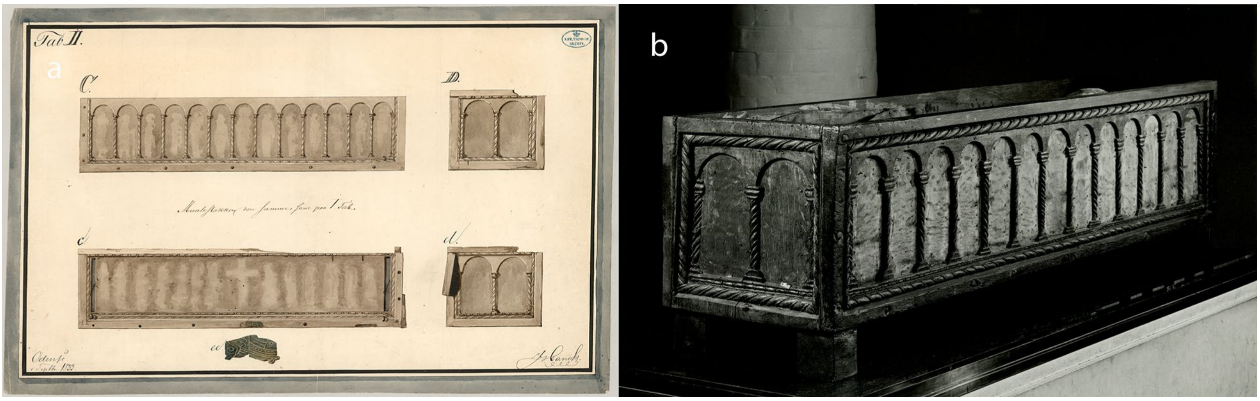

Fig. 1 **a** The shrine with the columns. Drawing by J. H. Hanck from 1833. Antikvarisk-Topografisk Arkiv. The National Museum of Denmark; **b** the shrine with the columns. Photo: Lennart Larsen 1981. Antikvarisk-Topografisk Arkiv. The National Museum of Denmark

Fig. 2 **a** The shrine with the hipped lid. Drawing by J. H. Hanck from 1833. Antikvarisk-Topografisk Arkiv. The National Museum of Denmark; **b** the shrine with the hipped lid. Photo: Lennart Larsen 1981. Antikvarisk-Topografisk Arkiv. The National Museum of Denmark

previously been suggested [8, 9]? The other research objective encompasses understanding the chemistry of the environment inside the showcases holding the reliquaries. Are the bones and the textiles well preserved and well-kept for posterity in the present configuration?

The martyrdom of St Canute and his brother Benedikt

Canute the Holy was a son of King Svend Estridsen, who reigned c. 1047–1074. Among the numerous children, which Svend had with various women, five sons became kings of Denmark one after the other. Canute was the second of them. His ideal was that of a strong royal power and his attempts to realize it in cooperation with the Church made him many enemies. In July 1086 he was killed together with his brother Benedikt and 17 housecarls by an army of unsatisfied magnates. Since the king had taken sanctuary in St Alban's Church in Odense, the killing took place on holy ground, and this was the first step towards a politically very promising sanctification instigated by other members of the royal family still ruling the country. Already in 1095 Canute's body was transferred to a stone coffin under a new large travertine church which was being erected to his honour southwest of St Alban's Church [10]. And thanks to the fourth king in the line of brothers, Erik I Ejegod, in 1100 the pope promised to canonize Canute. On April 19th in the "sixth year" of Erik's rule, i.e. either 1100 or 1101, Canute's bones were transferred from the stone coffin to a reliquary in the new St Canute's Church. Details of the killing were passed on in two brief accounts which are now only known from later copies: "*Tabula Othiniensis*" originating from the first transfer of the bones in 1095 and an "*Epitaphium St Canuti*" which was placed among the saintly bones during the transfer to the reliquary in

Fig. 3 Mary with her son enthroned in the heavenly Jerusalem. The central relief in the golden altar frontal from Lisbjerg Church, Denmark. The wooden core of the altar has been dendrochronologically dated to c. 1135. The golden altar is on display in the National Museum. Photo: Lennart Larsen 1979. Medieval and Renaissance Collection, The National Museum of Denmark

1100 or 1101 [11, 12]. Less than 40 years after the killing a detailed account of the life and death of King Canute was written by Aelnoth of Canterbury, who was a priest at the Benedictine monastery attached to St Canute's Church which had recently been founded by King Erik I Ejegod with inspiration from England [13]. In his "*passio gloriossimi Canuti regis et martyris*" Aelnoth described among other things how the royal bones were wrapped in silk and placed in a marvellous shrine forged of yellow shining metal and decorated by precious blue and yellow stones. He states that Edel, Canute's widow, who had married Duke Roger I of Apulia and Calabria in Southern Italy, contributed to the furnishing of the shrine with rich gifts. The reliquary was placed "on the life-giving altar table", either the high altar or more likely an altar in the crypt which is more consistent with Aelnoth's additional information that Canute the Holy in this way was "displayed to all who sought his protection" [14]. The entrance to the choir with the most holy high altar was reserved for clerics only. Both a Russian prayer from c. 1135 [15] and an anonymous legend about Canute from 1220–1250 [12] mention that not only Canute but also his brother Benedikt were venerated as saints, and the Icelandic Chronicle "Knytlinga-saga" from c. 1250 tells that both brothers were enshrined [16]. But for the next centuries only the veneration of Canute is mentioned in the historical sources, especially in connection with his day of martyrdom in July, when his shrine as well as a separate reliquary for his skull and other reliquaries of the church were carried in a procession around the town of Odense. Since the end of the 13th Century, the travertine church was gradually replaced by a Gothic brick cathedral, which as an unusual feature for its time got a crypt similar to the one in the old Romanesque church, undoubtedly due to the cult around the reliquaries [10].

The fate of the reliquaries after the reformation

In connection with the Danish civil war 1534–1536 the leader of the rebellion Count Christopher of Oldenburg in October 1534 sent a letter to the prior of St Canute's monastery in Odense, asking him to deliver all gold, silver, and precious objects present in the cathedral, except for four chalices. The order may not have been obeyed. But in 1536 a proper silver tax was imposed by King Christian III who was about to win the war and needed payment for his mercenaries. This time the monastery in Odense was obliged to pay 4000 "lod" silver, c. 62 kg. The prior paid up and mentioned in a letter that with royal permission he had taken part of the silver from a shrine in the church. Among the silver was also a gilded copper picture [17]. The shrine in question is likely to have been a reliquary. But an indisputable mention of a reliquary shrine in St Canute's Church in Odense does not actually occur until 1582.

In 1582 the church was being rebuilt, encompassing the demolition of both the crypt and a chapel to the north side of the church. During these works a well-preserved large reliquary was uncovered, made of oak with metal mounting that according to some sources were gilded and had a decoration with rock crystals [1]. All sources agree that this was the reliquary of St Canute, and in their descriptions, they also quote the now lost inscriptions which were made for the enshrinements of Canute, "*Tabula*" and "*Epitaphium*". One author who claimed to be an eye-witness to the find, the clerk of the now secularized St Canute monastery, Joachim Konninck, stated that the text "*Epitaphium*" was written on a piece of white parchment placed among the bones. The text was not discovered immediately since the bones were covered by textiles. According to Konninck, the reliquary was lined with several brownish silks that were still very beautiful and very rare, and it further contained a double yellow silk with yellow silk embroidery and a cotton lining as well as a golden piece of textile enclosing a linen made of smooth cotton wrapped around the bones [12]. The find aroused an interest among scholars all over Denmark, and several foreign Catholics expressed their wish to see the bones and eventually acquire some of them. Thus in

1622 two Flemish Dominican friars had the chance to see St Canute's skull.

Several decades then elapsed without any mention of reliquaries. In 1694 some minor repair works were being done in the choir, and on that occasion a small hole was noticed in the east wall behind the altar, allegedly filled up with feathers and down. The hole turned out to be opening into a niche containing two reliquary shrines which were stripped of their metal fittings except for a few fragments. They were placed vertically so that both bones and textiles lay in a heap at the bottom of each shrine. It is not known why and when the two shrines were walled up nor when they were stripped of their metal fittings. The reliquary of Canute must have lost its fittings sometime after 1582. The whereabouts of the other shrine are quite unknown, though it is a tempting suggestion that it might be the abovementioned unspecified shrine which was stripped of its silver and copper mounting around 1536. An investigation of the reliquaries was carried out in 1696 by the Odense antiquarian Thomas Bircherod. He mentions that the shrine with the hipped lid contained several pieces of silk and some pillows of wool and silk filled with down [1, 12, 18]. The textiles in the shrine with the columns were described as linen or cotton with a resemblance to altar-cloths. After the investigation both the reliquaries were once more placed in the narrow niche in a vertical position. But in 1833 they were permanently removed from their unpleasant hiding place. On this occasion, the textiles in each shrine were once more listed [19]. The shrine with the hipped roof contained a fairly large silk blanket with depictions of eagles, a couple of smaller pillows and a long, narrow, round pillow with a yellow cover which is described as cotton (it was not realized at the time that it is in reality silk), as well as a piece of red and blue "changeant"-coloured, thin silk. The shrine with the columns only contained a pillow and a fringed linen cloth [1].

The situation of the reliquaries and the storing of the textiles since 1833

After 1833 the shrines were furnished with new glass lids and displayed behind an iron fence at the east end of the northern side aisle. The most important of the textiles were taken out of the shrine with the hipped lid and send to the Museum of Nordic Antiquities (*Oldnordisk Museum*), the original name of the National Museum in Copenhagen, while smaller fragments remained in Odense.

In 1875 the reliquaries with their bones and textiles underwent a thorough investigation and restauration. The reliquaries were placed on new, brickwork pedestals in the reconstructed crypt and both bones and textiles were placed inside them. The shrine with the columns got a hipped wooden lid as an imitation of the lid on the other shrine. Both shrines were fitted with a glass cover on the top. But the arrangement did not live up to the intentions expressed in the statement by the scientific commission, dated 12.12.1874, which stressed that the textiles were so fragile that they could only be saved for posterity by being hermetically sealed [20]. Most of the textiles which had been removed from the shrine with the hipped lid in 1833 were now placed in the shrine with the columns because their high quality seemed more fitting for the shrine of a king. The report from 1886 lists the following textiles:

1. A piece of red and blue, thin shot-silk cloth, which seemed originally to have served as lining inside the shrine (Table 1, sample K2/KLR-7186).

Table 1 Samples analysed in the present study

Lab No.	Field No	Present location	Sample description
KLR-7185	K1	Without lid	K1 Pillow with birds
KLR-7186	K2	Without lid	K2 Red-blue (brownish) silk "cendal"
KLR-7187	K3	Without lid	K3 Piece of silk from K6
KLR-7188	K4	Without lid	K4 Inside covering of linen in the pillow with birds, K1
KLR-7189	K5	Without lid	K5 A linen cloth
KLR-7190	K6	Without lid	K6 Yellow silk cushion/mattress
KLR-7191	K7	Without lid	K7 Inside covering of linen in silk cushion/mattress K6
KLR-7192	K8	Own showcase	K8 The Eagle Silk
KLR-7193	K9	Hipped lid	K9 Benedikt silk
KLR-7194	K10	Hipped lid	Benedikt, pillow
KLR-7195	K11	Hipped lid	Benedikt, Sheet with fringes
KLR-7196	B1	Hipped lid	Benedikt-1, Large textile
KLR-7199	B4	Hipped lid	Benedikt-4, Under-featherbed, outer part

2. A long square cushion with yellow cotton covering (Table 1, sample K6/KLR-7190 and K7/KLR-7191). The so-called yellow cotton is in fact silk.
3. Samite woven silk casing with a pattern of birds, hearts, and crosses (Table 1, sample K1/KLR-7185 and sample K4/KLR-7188, Fig. 4).
4. Into the bird silk an inside covering was placed (which had been cut from number 2 at some point, probably in 1875) (Table 1, sample K3/KLR-7187).
5. A linen cloth (Table 1, sample K5/KLR-7189).
6. A samite woven silk cloth with eagles (Table 1, sample K8/KLR-7192, Fig. 5).

   The shrine with the hipped roof hereafter only contained:
7. A long, rounded cushion with a white casing and yellow cotton outer covering (Table 1, sample K9/KLR-7193). The so-called yellow cotton is in fact silk.
8. A pillow (no samples).
9. A linen cloth with fringes (no samples).

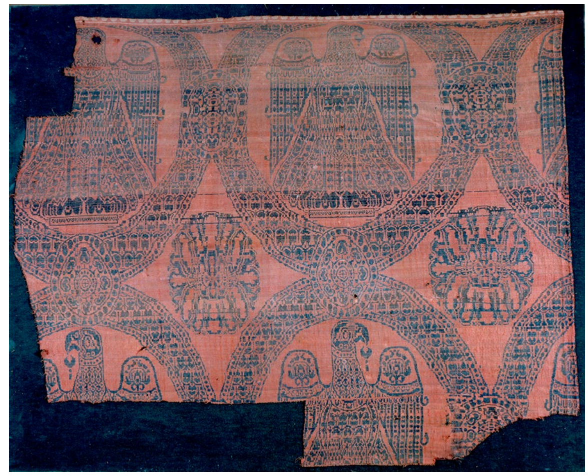

Fig. 5 The Eagle Silk. Photo: Niels Elswing 1993. Antikvarisk-Topografisk Arkiv. The National Museum of Denmark

The reliquaries were protected from the audience by panes of glass mounted in brass racks. Problems with humidity in the crypt caused mouldy growth on the coffins and their content which had to undergo repair and cleaning several times. In 1936 the reliquaries were transferred to new glass showcases designed by the architect Knud Lehn Petersen (Fig. 6). In 1956 the "eagle carpet", which had been stretched out as a cover over a part of the shrine with the columns, was removed and placed in its own, new showcase, which in 1990 was replaced with a new one [1]. The samples investigated here were taken by a conservator in 2008 and they are listed in Table 1.

The present investigation was aimed at two different aspects of the relics. First, the authenticity and the dating of the textiles was investigated, including a chronological comparison with previously reported radiocarbon dates of the bones and dendrochronological dates of the timber in the shrine with the pillars. In this connection some of the textiles were analysed to screen for contaminants in connection with the radiocarbon dates. Secondly, we performed a chemical assessment of the environment inside the glass showcases, which has bearings on the state of conservation and possible contaminants relevant for a proper assessment of the reliability of the radiocarbon dates. In addition, the possible presence of conservation materials or contaminants on the textiles was evaluated, and one

Fig. 4 The silk pillow with a bird motif from the reliquaries in Odense St. Canute's Church. Print after a drawing by Magnus Petersen 1886. Antikvarisk-Topografisk Arkiv. The National Museum of Denmark

Fig. 6 The showcase holding the wooden shrine with the columns, containing some textiles and the bones of St King Canute the Holy. Photo: Morten Ryhl-Svendsen 2009

piece of coloured textile was analysed to characterize the dyeing material used in its production.

Methods

Analyses of the organic molecules in the textiles

High-performance liquid chromatography with a diode-array detector (HPLC–DAD) for dyes analysis

The HPLC analyses were performed using a HPLC system consisting of a PU-2089 Quaternary Pump with degasser equipped with an autosampler AS-950 coupled to a spectrophotometric diode array detector MD-2010 (Jasco, Japan). The data were processed with the ChromNav software. The spectra acquisition was in the range of 200–650 nm every 0.8 s with a resolution of 4 nm.

The chromatographic separation was performed at 30 °C on an analytical reverse phase column Poroshell 120 EC-C18 column (3.0 mm × 75 mm, 2.7 µm particle size) with a Zorbax Eclipse plus C-18 guard column (4.6 mm × 12.5 mm, 5 µm particle size), both Agilent Technologies, USA. The eluents were A: formic acid (FA 0.1% v/v) in HPLC grade water and B: formic acid (FA 0.1% v/v) in HPLC grade acetonitrile. The injection volume was 20 µL, the flow rate was 0.4 mL min^{-1} and the elution program was 15% B for 2.6 min, then to 50% B in 13.0 min, to 70% B in 5.2 min, to 100% B in 0.5 min and then hold for 6.7 min; re-equilibration took 11 min. 0.462 mg of sample KLR-7199 were subjected to a mild extraction with EDTA/DMF solution. The treatment consisted in the following steps: addition of 200 µL of 0.1% Na_2EDTA in H_2O/DMF (1:1, v/v) solution, extraction in ultrasonic bath at 60 °C for 1 h, filtration with PTFE filters and injection of 20 µL of the extract in the HPLC–DAD system. Peak assignment was based on comparison with analytical standards and relevant reference materials.

Pyrolysis gas chromatography mass spectrometry (Py-GC–MS)

The analyses were performed using a multi-shot pyrolyzer EGA/PY-3030D (Frontier Lab, Japan) coupled with a 6890 N gas chromatography system with a split/splitless injection port and combined with a 5973 mass selective single quadrupole mass spectrometer (Agilent Technologies).

The samples (80–120 mg) were placed in stainless-steel cups and directly analyzed without further sample pre-treatment [21–23]. The pyrolysis conditions were optimized as follows: pyrolysis chamber temperature 550 °C, interface 280 °C. The GC injector temperature was 280 °C. The GC injection was operating in split mode and the best analytical results were obtained with a split ratio of 1:10 [24]. The chromatographic separation of pyrolysis products was performed on a fused silica capillary column HP-5MS (5% diphenyl-95% dimethyl-polysiloxane, 30 m × 0.25 mm inner diameter, 0.25 µm film thickness, J&W Scientific, Agilent Technologies), preceded by 2 m of deactivated fused silica pre-column with internal diameter of 0.32 mm. The chromatographic conditions for the analysis were: 36 °C for 10 min, 10 °C min^{-1} to 280 °C, 300 °C for 2 min, 15 °C min^{-1} to 300 °C. The carrier gas was helium (purity 99.9995%) with a gas flow set in constant flow mode at 1.2 mL min^{-1}. The MS parameters were as follows: electron impact ionization (EI, 70 eV) in positive mode; ion source temperature 230 °C; scan range 50–700 m/z; interface temperature 280 °C. Perfluorotributylamine (PFTBA) was used for mass spectrometer tuning. MSD ChemStation (Agilent Technologies) software was used for data analysis and peak assignment was based on a comparison with literature mass spectra, standard compounds previously analysed in the same conditions, and libraries of mass spectra (NIST 8.0).

Carbon isotopes and radiocarbon dating

Radiocarbon dating was performed on nine textile samples at the Groningen Center for Isotope Research in the Netherlands. The dating was performed by AMS (Accelerator Mass Spectrometry).

The samples were first decontaminated by Soxhlet extraction in hexane after which they were subjected to the standard ABA (Acid–Base-Acid) pre-treatment procedure [25]. The samples were combusted to CO_2 by an elemental analyser, coupled to a stable isotope ratio mass spectrometer (EA/IRMS) [26]. Part of the CO_2 is cryogenically trapped and subsequently transferred into graphite. The graphite was pressed into targets for the ion source of the AMS, which measured the ^{14}C content of the graphite. The AMS was based on a 2.5 MV tandetron accelerator, manufactured by High Voltage Engineering Europa. The machine is described in detail in van der Plicht et al. [27]. The ^{14}C content was measured as the $^{14}C/^{12}C$ ratio, expressed as the ^{14}C activity ^{14}a [28]. From this the ^{14}C age was calculated, expressed in BP (Before Present, defined unit for ^{14}C-time). Reporting is by convention relative to the Oxalic Acid standard, using a halflife of 5568 years and includes correction for isotopic fractionation to $\delta^{13}C = -25‰$ [28].

The IRMS provides a measurement of the stable isotope ratio $\delta^{13}C$. This is expressed in a delta value, which is a measure of the difference of the $^{13}C/^{12}C$ isotope ratio of a sample and that of a standard (or reference) material:

It is expressed in permille. For ^{13}C, the reference is an international standard limestone known as Pee Dee Belemnite (PDB) which has an accurately measured absolute ^{13}C concentration [29].

Climate monitoring

The temperature and relative humidity of the air was monitored inside the showcase, in the crypt, and outside the church, by use of electronic climate sensors integrated in battery-driven dataloggers. For indoor measurements Tinytag Plus 2 loggers were used (Gemini Dataloggers, Chichester, United Kingdom), while the outdoor conditions were monitored using a weather station grade datalogger mounted in a sun and rain screen and placed on a light pole at 2.5 m height (HOBO Pro v2, Onset Corp., Bourne MA, USA). The accuracy of such sensors is typically within ± 0.3 °C and ± 3% RH. The climate parameters were recorded at one-hour intervals for a full year.

Showcase leakiness

The air exchange rate of the glass showcase for St Canute was established by using CO_2 as a ventilation tracer gas [30]. The analysis was performed using two Bacharach CO_2 2810 Analyzers (range 0–10,000 ppm); one located inside the showcase and one located in the open air of the crypt (Bacharach Inc., New Kensington PA, USA). CO_2 was released from a compressed gas cylinder and into the showcase up to a concentration of c. 3,000 ppmv, after which the showcase was quickly closed. The CO_2 concentration was recorded each minute inside and outside the showcase for half a day (the battery lifetime of a fully charged instrument). Although a longer measurement period could be desired, the 12-h monitoring was found sufficient, as the indoor environment was very stable. The air exchange rate between the showcase and the room air was calculated based on the decay rate of the CO_2 concentration inside the case using the formula: Air Exchange Rate $= \ln(C1/C2)/(T2-T1)$, where C1 and C2 are the concentration surplus above ambient ($C_{showcase} - C_{room}$) and T1 and T2 the two times.

Air pollution

Passive sampling

Several sampling methods were used for detecting traces of compounds emitted from indoor materials, from human activity, from outdoor pollution, and de-gassing from the reliquary objects. The methods were all characterized by using passive sampling, where the compound was collected onto the sampling media over long time (several days or weeks), as the gas diffused through a sampling tube or membrane at a rate proportional to its concentration. Although slow and less sensitive than active sampling methods (by air pump), passive sampling was preferred because it caused less disturbances of microenvironments in the showcase, and allowed that average concentrations to be determined rather than a short-term incident measurements [31, 32]. For all passive samplers, commercial analytical services were used. Samplers were mounted in an aluminium clip rack and placed at three sampling locations: inside the showcase, on a shelf in the crypt, and under the outdoor sun- and rain-screen used for the climate sensors. All compounds were measured by duplicate samplers at each location, except Volatile Organic Compounds (VOCs), which was not monitored outdoors. The reported values are the mean concentration of two samplers. The uncertainty of passive sampling methods was typically about ± 25% relative accuracy.

VOC screening

For a broad screening of VOCs Tenax TA tubes were used as samplers and analysed by Automated Thermal Desorption Gas Chromatography Mass Spectrometry (ATD-GC–MS). This was performed twice. The first time it comprised of 18.8 days of exposure. The Tenax tubes were analysed by the commercial company Eurofins A/S (Galten, Denmark). The second time, a year later, the analysis was performed with 8 days of exposure time and analysed by Norwegian Institute for Air Research—NILU (Kjeller, Norway). At the same time as the first sampling a short-term qualitative screening of the showcase air was performed by exposing (for 10 min) a solid-phase micro-extraction (SPME) glass fibre needle with a highly absorbing coating (85 µm Carboxen®/Polydimethylsiloxane) to the inside of the showcase while the lid was slightly open. The fibre uptake was analysed by Solid Phase Micro Extraction Gas Chromatography Mass Spectrometry (SPME–GC–MS) at the Conservation Laboratory at the National Museum of Denmark (Kongens Lyngby, Denmark).

Specific compounds

Passive VOC screening by Tenax TA constitutes a broad but semi-quantitative method. The main organic component found in this way, acetic acid, was subsequently re-sampled twice at all locations using a passive sampler specific for organic acids (sampler and analysis by IVL Swedish Environmental Research Institute, Gothenburg, Sweden). The exposure time was 28 days. At these two incidents the ambient pollutants nitrogen dioxide and ozone was measured as well by passive sampling tubes provided with analysis by Gradko Environmental Ltd. (Winchester, United Kingdom).

Corrosion test

As a dosimeter for determining the microenvironment's corrosivity a 20 × 50 mm coupon of pure lead was exposed inside the showcase for 1 year (Merck lead foil 0.25 mm, no. 1.07365.0500 pro analysis). Before exposure, the coupon was polished with P-800 grinding paper and rinsed and degreased in acetone. The amount of corrosion was quantified by weighing the coupon on a microbalance before and after the exposure, and normalising to the weight-gain per square meter of metal surface [33].

Results

Analyses of organic molecules in the textiles

The HPLC–DAD chromatogram of the blue thread of the sample B4/KLR-7199, extracted at 600 nm, is reported in Fig. 7. The chromatogram revealed the presence of only one peak, whose retention time and UV–Vis spectra match with those of indigo. This indigoid compound is the molecular marker for the identification of *Indigofera* o *Isatis* vegetal species [34, 35].

The Py-GC–MS chromatogram obtained for the sample B4/KLR-7199 is shown in Fig. 8. The pyrolytic profile was characterized by the presence of pyrrole and phenol derivatives, together with diketopiperazines (m/z 154, 168, 194 [36]) characteristic of the pyrolysis of the proteinaceous portion of the material. This specific pyrolysis profile agreed with that obtained for a reference silk fibre. The analysis also allowed to identify the presence of several aliphatic hydrocarbons compatible with the presence of a paraffine wax, a petroleum derivative introduced in 1830′s. This material is commonly applied during restoration attempts.

The Py-GC–MS chromatogram obtained for the sample K11/KLR-1195 is shown in Fig. 9. The Py-GC–MS chromatogram was characterized by the presence of laevoglucose and furan derivatives. This profile suggested the presence of a cellulose-based fibre. The comparison with the reference material database allowed to hypothesize the use of jute. The analysis also showed traces of several aliphatic hydrocarbons compatible with the presence of a paraffin wax.

The Py-GC–MS chromatograms obtained for the samples K10/KLR-7194 and B1/KLR-7196 are shown in Fig. 10. Both the profiles feature the pyrolysis markers of a cellulose-based material. The comparison with the reference materials database allowed to hypothesize the use of jute fibres.

Radiocarbon

The results of the radiocarbon dating are listed in Table 2.

Calibration

The ^{14}C dates are calibrated into calendar ages using the latest calibration curve, IntCal20 [37]. This curve is annual for the time range under investigation. Hence the dates are not rounded. Both 1- and 2-sigma calibrated age ranges are shown in Tables 2 and 3. The code used for

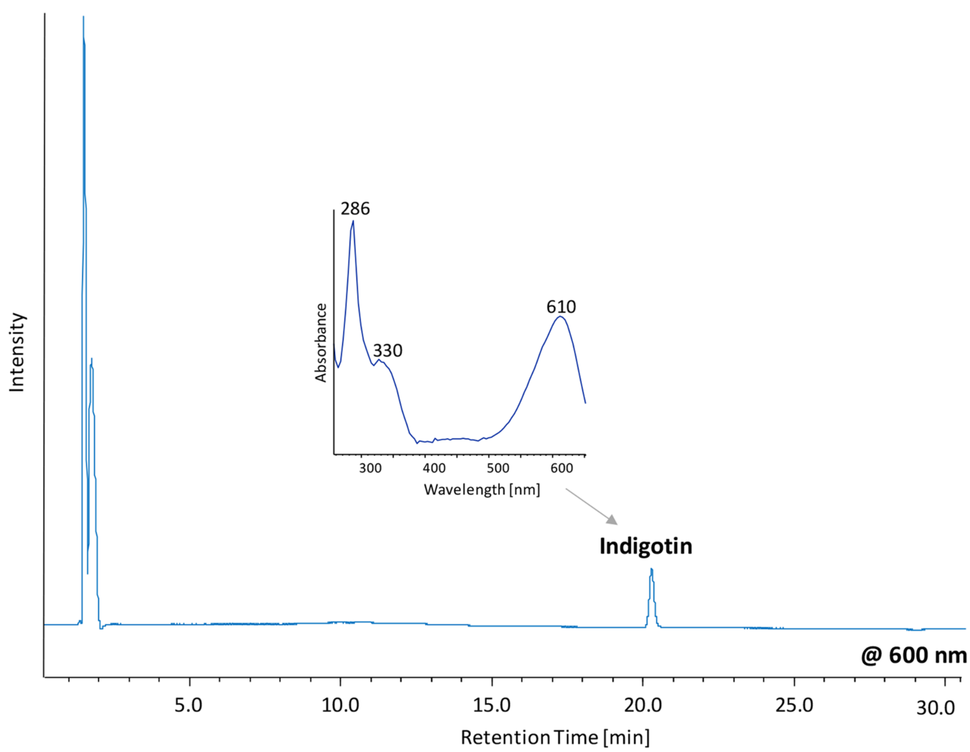

Fig. 7 HPLC–DAD chromatogram (extracted at 600 nm) of B4/KLR-7199 extract

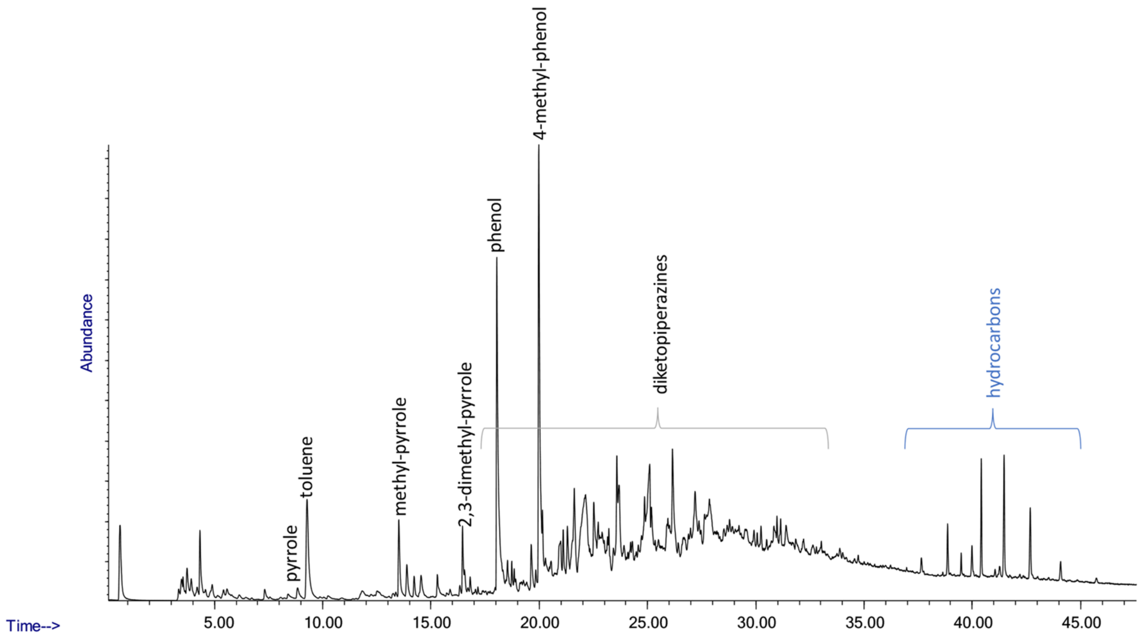

Fig. 8 Py-GC–MS chromatogram of B4/KLR-7199

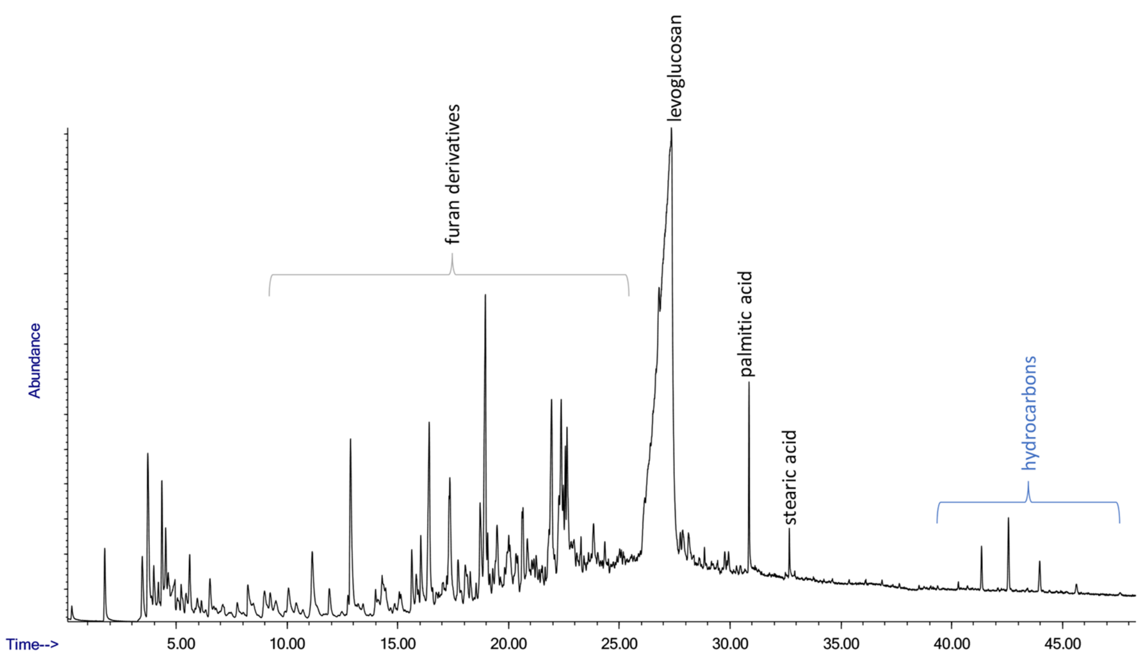

Fig. 9 Py-GC–MS chromatogram of K11/KLR-7195

calibration is OxCal (OxCal v4.3.2) [38]. The calibrated dates are shown in Fig. 11.

The $\delta^{13}C$ values for two of the samples were more negative than normally expected for textiles (KLR-7188/K4 with $\delta^{13}C = -26.3$ ‰, and KLR-7191/K7 with $\delta^{13}C = -26.4$ ‰). No explanation can be given for this slight deviation from the normal −25 ‰. However, the ^{14}C ages were corrected for isotopic fractionation and thus not affected by this. The organic chemistry analyses revealed only one unexpected component, that of

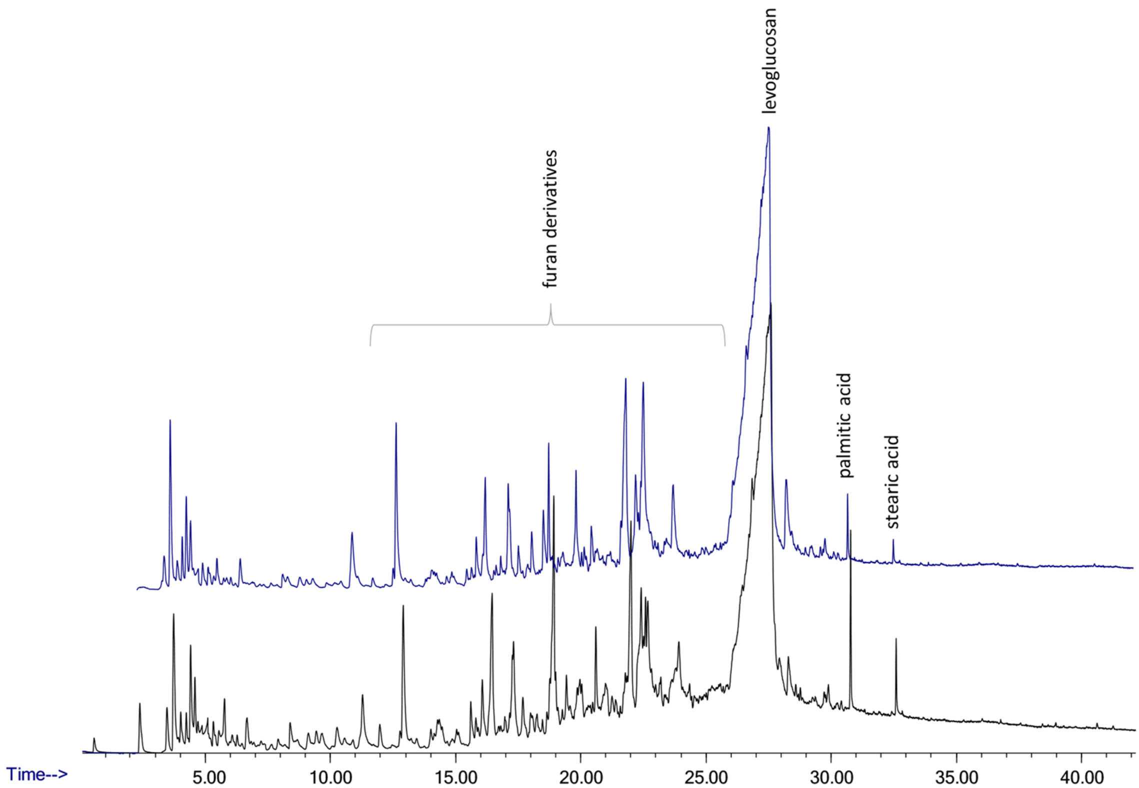

Fig. 10 Py-GC–MS chromatograms of samples K10/KLR-7194 (upper blue curve) and B1/KLR-7196 (lower black curve)

Table 2 Results of radiocarbon analysis of the 9 textile samples

GrA No	KLR No	Sample	^{14}a (%)	σ	δ^{13}C (‰)	Age (BP)	σ	Calibrated (AD, 1σ)	Calibrated (AD, 2 σ)
53,279	7185	K1 Pillow with birds	89.06	0.37	− 23.59	930	33	1045–1160	1031–1206
53,276	7186	K2 Red-blue silk "cendal"	88.68	0.37	− 23.15	964	33	1031–1151	1022–1160
53,280	7187	K3 Piece of silk from K6	88.99	0.38	− 23.33	936	34	1044–1157	1029–1199
53,278	7188	K4 Inside covering the pillow K1	89.34	0.37	− 26.34	905	33	1048–1211	1041–1217
55,270	7189	K5 A linen cloth	88.64	0.37	− 24.95	968	34	1030–1150	1021–1160
53,268	7190	K6 Yellow silk cushion/mattress	88.56	0.38	− 23.25	976	35	1025–1151	995–1160
53,269	7191	K7 Inside covering in silk K6	88.68	0.38	− 26.39	965	35	1031–1151	1021–1162
53,281	7192	K8 The eagle silk	89.20	0.39	− 22.55	917	34	1045–1171	1037–1211
53,270	7193	K9 Benedikt silk	89.41	0.39	− 23.26	898	34	1050–1214	1041–1220

Table 3 Radiocarbon dates reported by Rasmussen et al. [7]

Lab.No	Other Id	Description	Age BP	σ BP	δ13C o/oo VPDB	Calib 1σ Cal AD	Calib 2σ Cal AD
K-6141	NNU A7348 AAR1494	Femur Benedikt	860	120	− 19.0	1045–1270	900–1390
K-6142	NNU A7348 AAR1495	Tibia S Canute	985	100	− 18.3	980–1200	777–1265

The calibrations are performed by the calibration program WinCal25 from Groningen using the intcal04 High Res curves reported by Reimer et al. [37]; the outer boundaries of the 1σ respectively 2σ intervals are given to the nearest 5 years paraffine wax, probably used in the restoration of the textiles. This material is completely soluble in hexane and indeed its removal was ensured by the Soxhlet extraction procedure of the samples.

Climate conditions

The indoor temperature was uniform in the crypt and in the showcase, with an annual average of 18 °C (Fig. 12). Daily temperature variations were tiny, while the temperature seasonally varied between 16 °C in the winter and 21 °C during summer. The moisture content of air (absolute humidity) inside the showcase was constantly 9 g m^{-3}, resulting in an almost constant 60% relative humidity (RH) year-round. In the church room, the annual average humidity was c. 9 g m^{-3}, but with larger seasonally fluctuations causing the relative humidity to vary between c. 50% and 70% RH for the main part of the year (with short-term spikes between 35–77% RH) (Fig. 12). During summer, the indoor air had the same moisture content as the outdoor air. However, during winter the indoor air contained a surplus of water vapour of about 4 g m^{-3}.

Air exchange rate

The CO_2 injected inside the showcase decreased by 500 ppmv in concentration over 10 h, which corresponded to an air exchange rate between the showcase and the church room of 0.8 showcase volumes per day.

Air chemistry

While the air of the crypt contained a mixture of trace gases originating from outdoor and indoor sources, the showcase only contained internally generated compounds (Fig. 13).

Indoor air pollutants

All sampling methods determined acetic acid to be the main organic component inside the showcase. In the IVL sampler, acetic acid was above quantification, i.e. in excess of 2500 μg m^{-3}, followed by formic acid quantified at 270 μg m^{-3}. Also detected, by passive sampling on Tenax TA (NILU and Eurofins methods), were furfural, acetone, acetonitrile, pinene, propanoic acid, tridecane and tetradecane, and a large amount of unidentified hydrocarbons (VOC sum c. 6000 μg m^{-3}, toluene equivalents). Acetic acid were by Tenax collected at a lower (less complete) amount; about

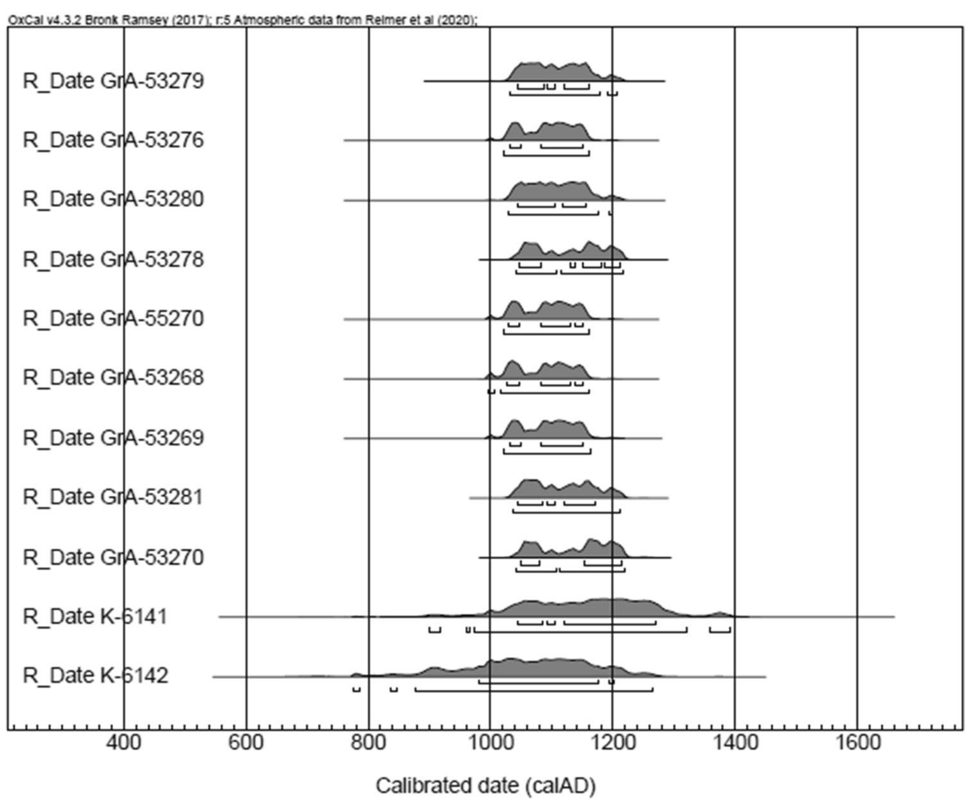

Fig. 11 Calibrated radiocarbon dates in the present study. The upper nine are dates of the textiles from the present work, the two lowermost are the bone dates of Canute the Holy and his younger brother Benedikt (Rasmussen et al. [7]), see Table 3 below

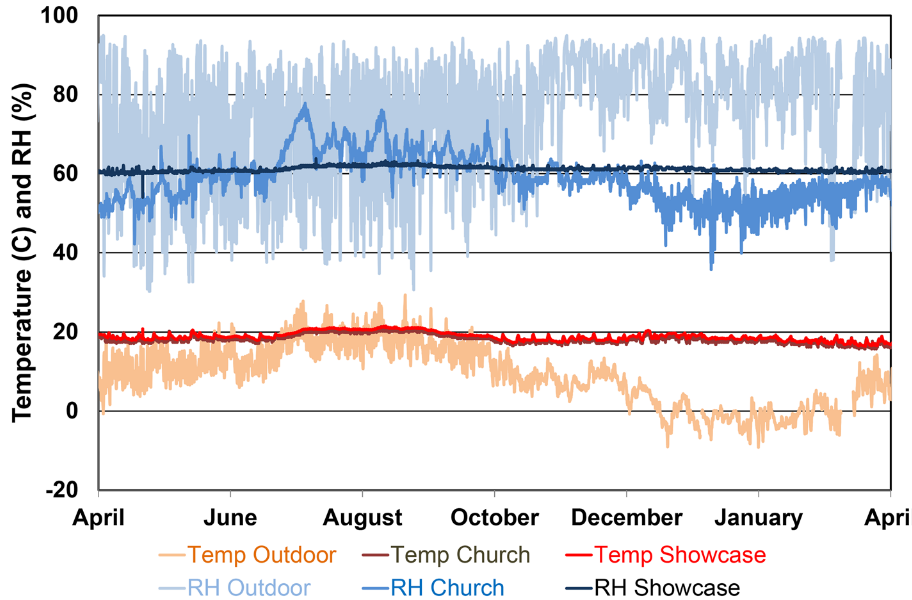

Fig. 12 Temperature (red/brown) and relative humidity (black/blue) for a 1-year period in the crypt and inside the showcase. The corresponding outdoor parameters are superimposed in pale colours

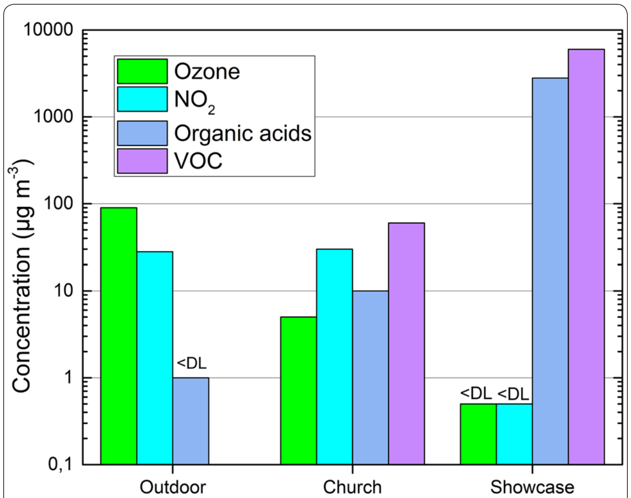

Fig. 13 The distribution of compounds in air between the showcase, the crypt of the church, and outdoors. VOC was not measured outdoor, < DL = measurement below detection limit

1400 µg m^{-3}, than by the dedicated organic acid sampler by IVL, which could indicate an even higher total VOC concentration inside the showcase. By the qualitative sampling on SPME were, besides acetic acid, also detected monoterpenes and phenoxy derivatives.

The air of the crypt contained 15 µg m^{-3} organic acids, and c. 60 µg m^{-3} other VOCs including acetone. The outdoor air contained traces of acetic acid, which, however, was below the detection limit (< 1 µg m^{-3}).

Ambient pollutants

The church is situated in an urban environment with much car traffic. Nitrogen dioxide, which is abundant in car exhaust gasses, was present inside the church room at about the same level as outdoors, 30 µg m^{-3}, while the much more reactive pollutant ozone was diminished indoors to 5 µg m^{-3} (6% of the ambient level). Inside the showcase both nitrogen dioxide and ozone were below the detection levels, i.e. < 0.5 µg m^{-3}.

Corrosion test

The lead coupon was, after 1 year's exposure inside the showcase, completely covered by grey-white corrosion, and had gained weight corresponding to 8.4 g per m^2 surface (Fig. 14).

Discussion

The average date of the nine textiles dates is 940 ± 15, and the calibrated age interval is 1045–1155 (1σ) and 1040–1158 (2σ), which is a large interval due to the nature of the calibration curve in the eleventh and twelfth centuries. However, within this uncertainty the nine textiles are all in accordance with a manufacture

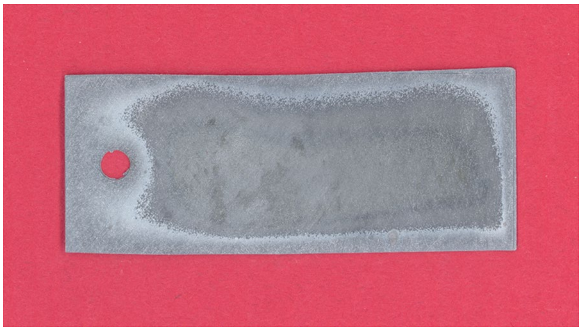

Fig. 14 A lead coupon (20 × 50 mm) with a whitish corrosion layer after 1-year exposure inside the showcase

date close to the enshrinement of the brothers AD 1100. All the tests conducted, individually and averaged, are in accordance with the expected time of AD 1100, and all the objects investigated are therefore as such authenticated.

Samples of the tibia of St Canute and the femur of his half-brother Benedikt were radiocarbon dated in 1999 [7]. According to historical sources mentioned above, Benedikt was murdered at the same time and on the same occasion as St Canute. The radiocarbon age and present-day calibrations are listed in Table 3. Even if the dating uncertainties are high, the dates agree with a death of both men in AD 1086 within the 1σ calibrated interval, and the dates are also in accordance with the textile dates of the present work. However, there are more complications to the history of the shrines and the textiles than that.

The wood of the coffin with the columns now holding the skeleton of St Canute has been dendrochronologically dated to after c. 1074 [39]. No bark or sapwood were present, so it is likely that the year of harvesting the tree was up to c. 25 after the year of the last year ring, 1074. This makes it probable that the timber was harvested c. 1100, the year of the enshrinement of St Canute.

Earlier investigations and a possible displacement of the textiles

The restoration of the reliquaries in 1875 included relocations of some smaller bones as well as most of the textiles. It was based on investigations by an expert commission which had been set up the previous year and which in 1886 on the 800th anniversary of the martyrdom of St Canute published a report about its results [20]. The members of the committee did not, however, all agree in the interpretations, and the discord has stimulated several later investigations of the reliquaries and their content of bones and textiles.

Dendrochronological investigations of the shrines and anthropological analyses of the skeletons have been carried out leading up to the 900th anniversary of the martyrdom in 1986 [40, 41] and as a preparation for the publication of "Odense Sankt Knuds Kirke" (St Canute's Church in Odense) in the thorough inventory "Danmarks Kirker" in 1995 [1, 7, 39]. This has answered two of the most discussed questions which emanate from the chaotic find history of the reliquaries.

When the two shrines were found in 1694 the main informant, professor Thomas Bircherod (1661–1731), thought that the shrine with the hipped lid contained the remains of St Canute since only this shrine showed traces of mountings with rock crystals/precious stones as described when the shrine of the king was uncovered in 1582 [42]. Since Medieval sources state that King Canute himself had acquired relics of the two well-known English saints St Alban and St Oswald, Bircherod concluded that the other shrine, which had no lid and had been decorated with columns, must contain the remains of one of these. The identification of the bones in this shrine was already challenged by the son of Thomas Bircherod, the antiquarian Jacob Bircherod (1693–1737), who instead suggested Benedikt. Yet the idea of St Alban as the other saint remained viable even up to the new investigations in the 1990′s. As late as 1992 a new suggestion was put forward: namely that the other buried person might be the nephew of St Canute, King Erik 3. Lam, who became king of Denmark in 1137 but abdicated in 1146 and retired to become a monk in St Canute's monastery in Odense where he died [43].

After the investigations in the 1980′s and 1990′s it can be concluded that the so-called shrine with the columns was made c. 1100 [39], that it has had a lining with textiles as mentioned in the description of St Canute's shrine in 1582, and that it contains the bones of the elder of the two skeletons in question, a man, who met a violent death somewhere between 980 and 1200 (1σ) at an age of 35–45 years (Fig. 15). This reliquary can safely be identified as the shrine of St Canute (Fig. 1). A trace element analysis revealed a remarkably high content of Au in the skull which could be the result of the skull being kept in a separate, gilded reliquary, precisely like the one which Queen Christine donated around year 1500 for the head of King Canute as recorded in her account book [7]. Another explanation may be that the skull had rested for centuries on pillows with golden metal threads since golden textiles were mentioned in the description of St Canute's shrine when it was recovered in 1582. The shrine with the hipped lid (Fig. 2) could not be dendrochronologically dated but has usually from a stylistic point-of-view been judged to have a slightly younger date than the shrine with the columns. There are no traces of

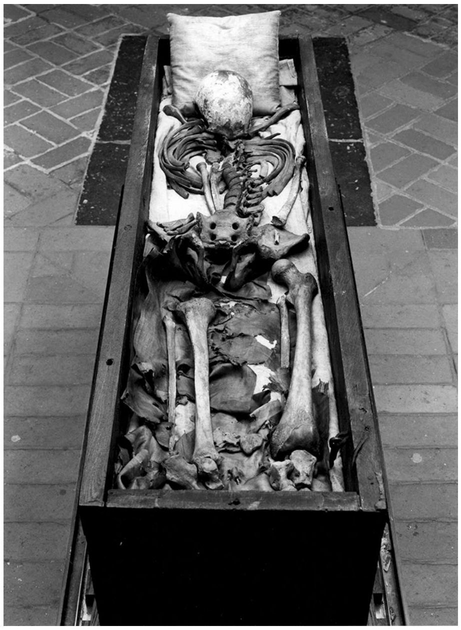

Fig. 15 The shrine with the columns and the skeleton of St Canute the Holy. Antikvarisk-Topografisk Arkiv. The National Museum of Denmark. Aage Lund Jensen Photo 1985

a textile lining inside. The skeleton in this shrine with the hipped lid is a young and strong male, who was between 18 and 25 years old when he died between 1045 and 1270 (1σ) and just like the skeleton in the other shrine showed traces of violently inflicted damages prior to death. The radiocarbon date of this skeleton rules out St Alban (died c. AD 305) and St Oswald (died c. AD 642), while the traces of a violent death contradicts the theory about King Erik 3. Lam (died AD 1146), who as far as is known died quite peacefully as a monk. It thus seems certain that the two deceased men can be identified with St Canute and his half-brother Benedikt [7].

Further investigations of the skeletons have not fundamentally changed this interpretation but have confirmed the violent death of the two men in the shrines and stressed that the structure of the bones and the skulls are so similar that it points to a family relation. Since the two men did not have the same mother it is not possible to prove the relationship with mitochondrial DNA analyses [44].

Several questions have been raised concerning the textiles in the shrines, especially their date and place of origin as well as the iconography of the two silks which are adorned with pictures: The Eagle Silk and the pillow with the bird motif [9, 45, 46]. It is the general and most likely assumption that the preserved silks must have been part of the costly gifts that were sent from South Italy to St Canute's shrine by his widow, Edel. As duchess of Calabria and Apulia Edel had access to high-quality silks from the Byzantine Empire. Perhaps the textiles were brought to Denmark by St Canute's half-brother, King Erik 1. Ejegod, who visited Italy in order to promote the sanctification of Canute and who is known to have visited Bari in Apulia on this occasion.

The textiles are the largest and best-preserved high-status textiles from the High Middle Ages in Denmark. At the time of Canute's canonization and enshrinement, silk weaving in Europe was not yet established outside the boundaries of the Byzantine Empire and silk was both a precious and a much-coveted import article. The colours, weaving, and motifs of the fabric determined its value even in a figurative sense since textiles played an important representative role in religious ceremonies as well as in the homage to rulers and princes. The preciousness of silk meant that it was considered a suitable fabric for wrapping up bones of saints, whether in tiny lead boxes hidden in the altar tables or in larger reliquaries like the ones in Odense.

The most recent technical analyses of the textiles have been published by Krag [46]. The yellow silk of the 148×35 cm monochrome pillow/mattress is linen-woven with a thin, firm warp thread and a woof of carded, loosely spun silk of a poorer quality than the one used for the warp. The appearance of the material has given it a certain resemblance to cotton, which is also the term used in older descriptions of the cloth. The yellow threads of these monochrome pillows were analysed to be dyed with Persian berries of the *Rhamnus* family [46]. The linen-woven white cloth with fringes, earlier thought to be an altar-cloth, measures 305×75 cm and has a selvage along one side. The other sides have been torn off. A number of holes placed rather at random along the edge may suggest that this cloth was once nailed inside one of the shrines as lining. The Eagle Silk (today c. 110 cm high and 133 cm wide, but originally at least 195 cm, perhaps even 230 cm wide, Fig. 5) is woven as samite, a fine weaving technique developed in Sasanid Persia (AD 226–661), in which the weft predominates so that the horizontal threads cover most of the weave without interruption creating a very smooth surface. The back of the textile is equally smooth, yet with the opposite colours. The weave of the Eagle Silk is close, and the warp is relatively coarse, z-spun, alternating in reddish-brown and undyed silk, while the weft is of unspun red and bluish-black silk in various thickness. The red threads were dyed with madder and sappanwood, while the dark blue colours were primarily achieved with woad and indigo, in agreement with the identification provided by HPLC–DAD in this study and by the data reported in Krag [46]. The pillow with birds juxtaposed in pairs consists of several pieces sewn together, of which one piece, 30×40 cm, covers the front of the pillow and about a third of the back, while the rest consists of strips about 5 cm wide (Fig. 4). They have been cut off without regard to the pattern. The material is very loose in structure. The weave is of samite type and has a closer density than the Eagle Silk. The warp consists of fine, almost unspun, undyed silk threads and the woof of similarly unspun, slightly golden- and light-blue silk threads varying greatly in thickness. It probably had three colours. The ground colour is today yellow, and the pattern appears in two faint blue shades. The yellow threads were dyed with redwood, Persian berries, indigo or woad, the blue ones with indigo or woad [46]. The organic analyses of the present work focused on samples not previously analysed (see Table 4).

The eagles on the Eagle Silk and the juxtaposed birds on the pillow, probably peacocks flanking a stylized tree or a cross, can be seen as symbols of Imperial Power and Christianity respectively, although the pattern with the peacocks originated in a non-Christian context. The production site of the Eagle Silk has been suggested as being Sicily/Southern Italy [8], Spain [47] or even the imperial workshops in Constantinople itself [48, 49]. At the base under the foot of each eagle an inscription-like pattern is to be seen. Attempts have been made to find either Greek, Islamic, Armenian, or Georgian letters in this pattern, but none of the suggestions seem trustworthy. It is more likely that it is simply an ornamental imitation of such bands with inscriptions that could be depicted on imperial Byzantine silks. The quality of the Eagle Silk does not quite live up to the high standards of the imperial workshops. But it was surely produced in an area under Byzantine influence, while the pattern on the pillow with the birds has been compared to a group of Sasanid-Persian silks. It may have been made in a town situated on the Silk Road from China to the Mediterranean, perhaps Tashkent in Uzbekistan [9]. The silk has usually been dated to c. 900, meaning that it would be about 200 years old when it was re-used for the pillow in Odense. However, such dates have not been encountered in the present work. The new radiocarbon dates reveal that all the nine dated textiles from Odense can be dated inside the same chronological framework which fits very well with the enshrinement in 1100 or 1101, and it seems clear that a fine selection of contemporary textiles was sent to Denmark to be used for the enshrinement. There is no indication of a chronological difference between the textiles. The pillow with the birds was thus not a 200 years old fabric, and the somewhat coarse way that the silk for the pillow with the birds was cut up in order to suffice should not be interpreted as a sign of reuse. Rather it indicates that various whole pieces of silk of different size were send to Denmark where they were cut out and sown into bedcover, pillow-cases etc. for the reliquaries. The sewers had to make do with the available pieces of silk and in the case of the pillow with the birds they succeed in creating a nice front while it obviously did not matter so much how the back of the pillow looked. The remaining silk was simply cut out into small strips with no regard to the pattern and motifs.

It may be questioned if the present distribution of the silks in the two shrines is valid. The textiles comprise pillows, cushion, sheets, and blankets reflecting the bedclothes of a live person yet with an exclusive character [50]. As previously mentioned, all the best silks were found in the shrine with the hipped lid as well in 1694–96 as in 1833, and it was the expert commission of 1875 that

Table 4 Comparison of previous work (Krag [46]) and this work

Lab KLR- No	Field No	Present location	Sample description	This work	Krag [46]
7185	K1	Without lid	Pillow with birds		Yellow: Quercetin, Kampherol, Rhamnetin, Indigotin Blue: Indigotin Light: Indigotin
7186	K2	Without lid	Red-blue (brownish) silk "cendal"		Indigotin, Rubiadin
7188	K4	Without lid	Inside covering of linen in the pillow with birds, K1		Quercetin, kampherol, rhamnetin
7190	K6	Without lid	Yellow silk cushion/mattress		Quercetin, kampherol, rhamnetin
7192	K8	Own showcase	The Eagle Silk		Red: Alizarin, Indigotin Blue: Luteolin, Alizarin, Indigotin
7193	K9	Hipped lid	Benedikt silk		Quercetin, kampherol, rhamnetin
7194	K10	Hipped lid	Benedikt, pillow	Jute	
7195	K11	Hipped lid	Benedikt, Sheet with fringes	Jute, paraffin wax	
7196	B1	Hipped lid	Benedikt-1, Large textile	Jute	
7199	B4	Hipped lid	Benedikt-4, Under-featherbed, outer part	Silk, paraffin wax, indigotin	

decided to place most of them in the shrine with the columns—the shrine of St Canute. The argument was that the canonized royal saint must have deserved the best possible textile equipment. In that way the textiles of the two shrines were fundamentally interchanged so that the more humble, fringed linen textile which lay in the shrine with the columns ended up in the shrine with the hipped lid instead. Yet the experts were well aware that this new distribution of the textiles rested on a feeble ground, as they declared in December 1874 in a letter to the Ministry of Church and Education: "We are not able to judge in which of the shrines the found weaved fabric belong" [20]. The only archaeologically valid argument for the new placing of the textiles concerns the so-called red and blue "changeant"-coloured, thin silk because tiny pieces of this cloth is to be found under the nails on the inside of the shrine with the columns, thus indicating that it is indeed a remain of the original lining of that shrine. In 1582 the lining of the shrine with the pillars was described as brown but that is not as strange as it sounds since the colours of this silk is not easily recognized in dim daylight inside the church and the silk even today at first glance gives the impression of being brownish. So, this textile may have been found inside the shrine with the columns and later removed from its original shrine to the shrine with the hipped lid sometime after 1582 but before the recovery of both shrines in 1694–96. The damages to the fabric seem to indicate that it was rather ruthlessly torn off. Since it was later found in the other shrine, we may deduce that the shrine with the hipped lid was accessible during or shortly after the despoiling of the shrine with the columns.

However, the 1875 argument for placing all the best silks in the shrine with the columns is not convincing. The precondition for the argument that the best silks should belong in the king's shrine is that all original textiles are preserved. That is clearly not the case. The description of the king's shrine from 1582 mentions a double yellow silk with yellow silk embroidery as well as a golden piece of textile. These silks seem to have been lost. On the other hand, the description does not mention such characteristic textiles as the Eagle Silk or the pillow with the birds. The most reasonable conclusion is that most of the preserved textiles right from the beginning lay in Benedikt's shrine where they were also found in 1694–96 and in 1833. The silks are indeed fine and suitable for a saint. But as the somewhat enforced use of the silk for the pillow with the birds indicate, Benedikt's shrine could not necessarily claim the best silks or the best handicraft. The silks in St Canute's shrine were probably of even better quality. That might explain why most of the textiles which were found in the shrine in 1582 have disappeared, probably stolen like all the metal fittings on the shrine. The shrine was clearly plundered for all valuables. It is a likely—but unverifiable suggestion—that the shrine with the hipped lid was the shrine which is recorded to have been stripped of its silver and copper fitting in connection with the large confiscations of precious metal in 1536. This would not have involved the textiles which remained relatively safely inside the shrine with the hipped lid for the next 300 years. The Py-GC–MS analyses of the white textiles in the shrine with the hipped lid highlighted mainly the use of a cellulose-based material which would correspond with the theory of a slightly humbler equipment. Since the present distribution of these textiles does not necessarily reflect the original state of things it is not, however, possible to draw any safe conclusions.

Conservation and chemistry within the showcase

The showcases—almost museum pieces in themselves—seem at first glance to be a both logical and excellent way of exhibiting the bones, the textiles, and the shrines together as a collected and coherent relic and national treasure. But is this in fact a good solution? We have investigated the protection capacity of both the church in the urban environment and of the showcase within the church.

The air exchange rate of the showcase was low compared to the surrounding room: 0.8 day^{-1}. This is not low by today's standard for modern museum showcases but signifies that the showcase offers a considerable protection from the outside air, although the objects inside the showcase are still exposed to the ambient environment to some minor degree. On the other hand, it can be assumed that the exchange of air between the church and the outdoors is about one order of magnitude higher, so the weather will influence the indoor climate of the church room, especially with regard to moisture content. Although we did not measure the air exchange of the church room, we know from other measurements in similar Danish church buildings that the natural ventilation typically provides an air change of about 5 building volumes per day [51].

Climatically this provides a "box in a box" situation: The reliquary is housed in a closed glass box, which is placed inside a church building, which again is in a temperate climate urban environment. This is reflected especially in the hygrothermal behaviour, becoming increasingly more stable inside each "boxed" micro-climate (Fig. 12).

The indoor temperature during winter is controlled by central heating (radiators), while no temperature control is turned on during summer. The high thermal inertia of the heavy construction of the church ensures a very steady temperature, with no appreciable variations between the church room and the showcase.

The synchronous trace of how the indoor relative humidity follows variations in the outdoor temperature (Fig. 12) suggests that the amount of water vapor inside the church is somewhat controlled by the outdoor air, which is also what is expected from the assumed ventilation rate of ca 5 day^{-1}. On the other hand, the relative humidity inside the showcase is almost unaffected by room-scale or outdoor humidity fluctuations; it is maintained at the same annual average level. It is well-known that hygroscopic materials act as a humidity buffer when enclosed, and the stable humidity can be attributed to the large amounts of textiles and wood in the coffin.

Despite the winter heating, the indoor relative humidity was rarely below 50% RH, even though the outdoor air was drier (4 g m^{-3} less). This indicates an additional source of water vapor indoors, which very likely could be moisture evaporating from the walls or floor of the low-lying crypt.

The analyses of the relatively well-protected air space inside the showcase show the presence of several organic compounds, but mainly acetic acid, a natural deterioration product from organic materials. It is a viable interpretation that the VOCs are derived mainly from the wood pedestal or most likely the coffin; furfural and organic acids from degassing of degrading wood – especially oak, the monoterpenes from wood resin, and the phenoxy derivatives from the deterioration of lignin. On room-scale the level of organic compounds, including organic acids, was much lower than inside the showcase, due to the higher rate of dilution by the outdoor air. The detection of acetone may be attributed to human bio-effluents.

While the showcase by its slow air exchange maintained internally-generated compounds in high concentrations, it retarded at the same time external pollutants. Both ozone and nitrogen dioxide, which were present in the church room, were diminished in concentration to below the limit of detection inside the showcase.

The corrosion of the lead coupon exposed inside the showcase was not surprising, taking the presence of organic acids into account. Corrosion of lead artifacts is a common phenomenon in wooden showcases [52], and although we did not analyse the corrosion product it is very likely basic lead carbonate; caused by acetic acid in combination with atmospheric moisture and CO_2. The corrosion rate of 8.4 g m^{-2} in 1 year suggest a highly corrosive environment [33].

Containment inside a low-ventilated showcase is a 'double-edged sword' for the preservation of heritage artefacts. The glass case clearly protects the objects from ambient air pollutants and retards the fluctuations in humidity observed in the surrounding air. As long as the temperature is kept steady at the current level the showcase ensures an overall acceptable and very stable hygrothermal environment. Likewise, it must be supposed that the showcase in the same way acts as a protecting barrier for particles; at least coarse dust, although this was not investigated.

On the other hand, acid air compounds in high concentrations could pose a potential hazard to the reliquary objects. Acetic and formic acid could deteriorate the metals (fortunately, no lead objects are present), the textiles, and the bones in the coffin. Although lower than the so-called 'acceptable damage concentration' suggested for acetic acid and bone by one study [53] we still consider the observed level inside the showcase a risk, as it have remained in an undisturbed environment for a very long time (more than a century). Probably the textiles are at the highest risk. As the source of the organic compounds is in the exhibit itself, there is no way to avoid the build-up in concentration of the organic acids other than either by an increased ventilation of the showcase, or by adding pollution scavenging materials somewhere inside the showcase. Ventilation conflicts with the protection from ambient climate factors, including the risk of soiling by dust, which could only be safely administered with a design with filtered air inlets. The use of adsorbents, e.g. activated charcoal, may be an effective mitigation strategy, however; it requires frequent control and replacement while exhausted, and it may pose a design challenge to locate the sorption media in correct positions inside the case.

Although ozone and nitrogen dioxide does not enter the showcase in any detectable amounts, the presence of either compound inside the church room still poses a risk to other, openly exposed heritage materials in the church room, such as dyes and pigments in paintings (see summary of literature by Tétreault 2003 [52]). The presence of indoor nitrogen dioxide at a level comparable to that of outside, warrants an explanation. In urban environments, nitrogen dioxide originated mainly from car exhaust, or is a reaction product from nitrogen monoxide (also from car exhaust) and ozone, which will be formed at times or places of little sunlight (at night, or indoors). The phenomenon of high indoor NO_2 concentrations was previously observed in a large art exhibition hall, not unlike the design of a church room [54]. In our case, the source of nitrogen monoxide is probably the busy roads surrounding the church, and ozone is naturally present outdoors. The indoor level of ozone is low, which, besides the loss from surface deposition may be attributed to consumption via air chemistry producing extra nitrogen dioxide indoors.

This study demonstrates how the concentration of air contaminants may increase to extreme levels inside confined spaces, if at the same time a source of emission is enclosed. This is the situation for many showcases in museums in the presence of wood.

Conclusions

The samples taken from the textiles in the reliquaries of St King Canute and his half-brother Benedikt give identical datings for all the textiles inside a 95% level of significance. The calibrated date for average of the textile dates falls in the range AD 1045 to 1155 (1σ). This fits well with the enshrinement of Canute in AD 1100. There are no indications of a chronological difference between silks from St Canute's shrine, the shrine with the columns, and the silks in Benedikt's shrine, the one with the hipped lid. As a matter of fact most of the preserved silks which are now kept in Canute's shrine—or in the case of the Eagle Silk which has now been removed from St Canute's shrine and placed in its own wooden showcase with glass lid – were probably originally not found in his shrine. They are more likely to have come from Benedikt's shrine (the one with the hipped lid) including the Eagle Silk and the pillow with the birds. A few textiles did, however, survive from the royal shrine, e.g. the original brownish/red-blue lining. All the same, there is no indication of chronological differences in the material. This supports the hypothesis that both St Canute and Benedikt were enshrined at approximately the same time. The most recent, stylistically based dating of Benedikt's shrine to 1125–1150 may on this background deserve new considerations. This date may match the engravings on the copper lists of the lid, but the shrine itself has decorative engravings of an older type. Benedikt's shrine may thus very well have been made around 1100 and have got its lid some decades later [55].

The air chemistry and the climatic parameters revealed an environment with both pro's and con's for the safekeeping of the relics: the relics are protected from ambient urban environment such as ozone and nitrogen oxide, but the slow decay of the oak wood maintains very high levels of organic acids, which can potentially be harmful to all the objects on display. So, the good intentions of the scientific commission of 1875 as well as those of more recent antiquarian authorities to preserve the historically important monuments by means of hermetically closed showcases are not entirely successful and may imply some long-term risks.

Abbreviations

ATD-GC–MS: Automated thermal desorption gas chromatography mass spectrometry; BP: Before Present, defined unit for ^{14}C-time; EA/IRMS: Element analyzer/isotope ratio mass spectrometry; HPLC–DAD: High performance liquid chromatography-diode array detector; Py-GC–MS: Pyrolysis–gas chromatography/mass spectrometry; LD: Limit of detection; RSD: Relative standard deviation; SD: Standard deviation; SPME–GC–MS: Solid phase micro extraction gas chromatography mass spectrometry; VOC: Volatile organic compounds.

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Authors' contributions

Conceived and designed the experiments: KLR and MRS. Performed the analyses: JvdP, MRS, JLN, and FS. Analysed the data: KLR, JvdP, MRS, MPC, and ID. Contributed as experts on church culture, history and art history UK and PGH. Wrote the paper, with comments from other participants: UK, PGH, KLR, MRS, MPC, JLN, ID, and JvdP. The paper was approved by all authors. All authors read and approved the final manuscript.

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Availability of data and materials

Data are available upon request from the authors.

Ethics approval and consent to participate

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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References

1. Danmarks Kirker, Odense Amt. Odense Domkirke, S. Knud. Copenhagen: The National Museum of Denmark, Forlaget Poul Kristensen; 1995, p. 424–58.
2. Vellev J. Knud 2. den Hellige og Edel (Adela). In Kryger K (ed). Danske Kongegrave I. Museum Tusculanums Forlag, Copenhagen; 2014, p. 190–205.
3. Bjerregaard MM. The archeological sources on the killing and enshrining of King Cnut IV. In Hope S, Bjerregaard MM, Hedeager Krag A, Runge M (eds.). Life and cult of Cnut the Holy. The first royal saint of Denmark. Archaeological and Historical Studies in Centrality 4:2019, Odense: University Press of Southern Denmark; 2019, p. 26–41.
4. Liepe L. Reliker och relikbruk i det medeltida Norden. Stockholm: Runica et Mediævalia; 2020. p. 100–103.
5. Nørlund P. Gyldne Altre. Jydsk Metalkunst fra Valdemarstiden. Copenhagen: H. Koppels Forlag; 1926.
6. Grinder-Hansen P. Die goldenen Altäre des Nordens aus der Romanik. Köln: Walter König; 2000.
7. Rasmussen KL, Bennike P, Kjær U, Rahbek U. Integrity and characteristics of the bones of the Danish King St Knud (II) the Holy (+AD 1086). J Danish Archaeol. 1999;13:161–70.

8. Geijer A. Sidenvävnaderna i Helige Knuts Helgonskrin i Odense Domkyrka. Aarbøger for Nordisk Oldkyndighed og Historie; 1935, p. 155–68.
9. Krag AH. Oriental and Byzantine silks in St Cnut's reliquary shrine. In: Bjerregaard MM, Krag AH, Runge M, editors. Hope S. Life and cult of Cnut the Holy. The first royal saint of Denmark. Archaeological and Historical Studies in Centrality. Odense: University Press of Southern Denmark; 2019. p. 42–49.
10. Johannsen BB, Johannsen H. Sct. Knuds Kirke. Otte kapitler af Odense Domkirkes historie. Odense: Odense Universitetsforlag; 2001.
11. Gertz MC. Knud den Helliges Martyrhistorie særlig efter de tre ældste Kilder: en filologisk-historisk Undersøgelse. Copenhagen: Universitetsbogtrykkeriet, J.H. Schultz; 1907.
12. Gertz MC. Vitae Sanctorum Danorum. Copenhagen: Selskabet for Udgivelse af Kilder til dansk Historie 1908–12;27–168,531–58.
13. Gazzoli P. Erik Ejegod's international connections and the beginnings of the Cult of Cnut. In Hope S, Bjerregaard MM, Hedeager Krag A, Runge M (eds.). Life and cult of Cnut the Holy. The first royal saint of Denmark. Archaeological and Historical Studies in Centrality 4:2019, Odense: University Press of Southern Denmark; 2019, p. 84–9.
14. Olrik H. Danske Helgeners Levned I. Copenhagen: Rosenkilde & Bagger; 1894. p. 1–110.
15. Lind J. The Martyria of Odense and a Twelfth Century Russian Prayer. Slavonic East Eur Rev Lond. 1990;68:1–21.
16. Knýtlinga Saga. Knud den Store, Knud den Hellige, deres Mænd, deres Slægt, eds. Ægidius JP, Bekker-Nielsen H, Widding O. Copenhagen; 1977.
17. De ældste danske arkivregistraturer, udgivne efter beslutning af Det kongelige Selskab for Fædrelandets Historie og Sprog… ved W. Christensen, vol. V, 1. Copenhagen. 1910, p. 202–04.
18. Knud den Helliges Historie, forfattet af Thomas Broder Bircherod, eds. Biering CG, Odense; 1773.
19. Paludan-Müller C. Om Opdagelsen af Knud den Helliges Relikvier. In Nordisk Tidsskrift for Oldkyndighed II. Copenhagen. 1833;193–223:363–68.
20. Burman Becker JG. Helgenskrinene i Sankt Knuds Kirke i Odense. Copenhagen: Ministeriet for Kirke- og Undervisningsvæsenet; 1886.
21. Orsini S, La Nasa J, Modugno F, Colombini MP. Characterization of Aquazol polymers using techniques based on pyrolysis and mass spectrometry. J Anal App Pyrolysis. 2013;104:218–25.
22. La Nasa J, Orsini S, Degano I, Rava A, Modugno F, Colombini MP. A chemical study of organic materials in three murals by Keith Haring: a comparison of painting techniques. Microchem J. 2016;124:940–8.
23. La Nasa J, Biale G, Sabatini F, Degano I, Colombini MP, Modugno F. Synthetic materials in art: a new comprehensive approach for the characterization of multi-material artworks by analytical pyrolysis. Herit Sci. 2019;7:8.
24. La Nasa J, Biale G, Colombini MP, Modugno F. A pyrolysis approach for characterizing and assessing degradation of polyurethane foam in cultural heritage objects. J Anal Appl Pyrol. 2018;134:562–72.
25. Mook WG, Streurman, HJ. Physical and chemical aspects of radiocarbon dating. PACT 8, II; 1983, p. 31–55.
26. Aerts-Bijma AT, van der Plicht J, Meijer HAJ. Automatic AMS sample combustion and CO_2 collection. Radiocarbon. 2001;43:293–8.
27. van der Plicht J, Wijma S, Aerts AT, Pertuisot MH, Meijer HAJ. The Groningen AMS facility: status report. Nuclear Instrum Methods B. 2000;172:58–655.
28. Mook WG, van der Plicht J. Reporting 14C activities and concentrations. Radiocarbon. 1999;41:227–39.
29. Mook WG. Introduction to isotope hydrology. Taylor & Francis, ISBN is 0-415-38197-5. 2006.
30. Thickett D, Frances D, Luxford N. Air exchange rate—the dominant parameter for preventive conservation? The Conservator. 2005;29:19–34.
31. Rosenberg E, De Santis F, Kontozova-Deutsch V, Odlyha M, van Grieken R, Vichi F. Measuring gaseous and particulate pollutants: instruments and instrumental problems. In: Camuffo D, Fassina, V, Havermans J (eds.), Basic environmental mechanisms affecting cultural heritage. COST Action D42. Nardini Editore, Firenze; 2010, p. 115–46.
32. Grzywacz CM. Monitoring for gaseous pollutants in museum environments (tools for conservation). Los Angeles: Getty Conservation Institute; 2006.
33. Ryhl-Svendsen M. Corrosivity measurements of indoor museum environments using lead coupons as dosimeters. J Cul Herit. 2008;2008(9):285–93.
34. Degano I, Ribechini E, Modugno F, Colombini MP. Analytical methods for the characterization of organic dyes in artworks and in historical textiles. Ap Spec Rev. 2009;44:363–410.
35. Sanz E, Arteaga A, García MA, Cámara C, Dietz C. Chromatographic analysis of indigo from Maya Blue by LC–DAD–QTOF. J Archaeol Sci. 2012;39:3516–23.
36. Orsini S, Parlanti F, Bonaduce I. Analytical pyrolysis of proteins in samples from artistic and archaeological objects. J Anal Appl Pyrol. 2017;124:643–57.
37. Reimer PJ, Austin WEN, Bard E, Bayliss A, Beck JW, Blackwell PG, Bronk Ramsey C, Butzin M, Cheng H, Edwards RL, Friedrich M, Grootes PM, T.P. Guilderson TP, Hajdas I, Heaton TJ, Hogg AG, Hughen KA, Kromer B, Manning SW, Muscheler R, Palmer JG, Pearson C, van der Plicht J, Reimer RW, Richards DA, Scott EM, Southon JR, Turney CSM, Wacker L, Adolphi F, Büntgen U, Capano M, Fahrni SM, Fogtman A, Friedrich R, Köhler P, Kudsk S, Miyake F, Olsen J, Reinig F, Sakamoto M, Sookdeo A, Talamo S. The IntCal20 Northern Hemisphere Radiocarbon age calibration curve (0–55 cal kBP). Radiocarbon. 2020; in press.
38. Bronk RC. Bayesian analysis of radiocarbon dates. Radiocarbon. 2009;51:337–60.
39. Bonde N, Bartholin T, Christensen K, Eriksen O. Dendrochronological dating at the National Museum of Denmark. Arkæologiske Udgravninger I Danmark (AUD). 1993;1994:294–310.
40. Vellev J. Helgenskrinene i Odense – fund og forskning 1682–1986. In: Nyberg T, Bekker-Nielsen H, Oxenvad N (eds.). Knuds-bogen 1986. Studier over Knud den Hellige. Odense: Fynske Studier XV; 1986, p. 123–56
41. Tkocz I, Jensen KR. Antropologiske undersøgelser af skelettet i skrinet med de snoede søjler. In Nyberg T, Bekker-Nielsen H, Oxenvad N (eds.). Knuds-bogen 1986. Studier over Knud den Hellige. Odense: Fynske Studier XV; 1986, p. 117–22
42. Bircherod T. Kong Knud den Helliges Historie … forfatted af Mag. Thomas Broder Bircherod og … til Trykken befordret af Christian G. Biering, Odense; 1773.
43. Langberg H. The Lundø Crucifix. Copenhagen: Langbergs Forlag. 1992; note 199.
44. Leth PM, Boldsen J. Skeletterne i krypten. Knud den Hellige og hans broder Benedikt. Fynske Årbøger; 2009, p. 123–36.
45. Østergaard E. Nogle mønstrede silketøjer fra danske relikviegemmer. Hikuin. 1980;6:83–92.
46. Krag AH. The Eagle Silk and other silks in the shrine of St Canute in Odense Cathedral. Herning: Poul Kristensens Forlag; 2010.
47. Muthesius A. Studies in Silk in Byzantium. London: Pindar Press; 2004. p. 294.
48. Falke O von. Kunstgeschichte der Seidenweberei. Berlin; 1913.
49. Riis PJ. Riis T. Knud den Helliges Ørnetæppe i Odense Domkirke: Et forsøg på nytolkning. KUML; 2004. p. 250–273.
50. Owen-Crocker GR. Textiles in Christian Tombs. In: Hope S, Bjerregaard MM, Krag AH, Runge M (eds.). Life and cult of Cnut the Holy. The first royal saint of Denmark. Archaeological and Historical Studies in Centrality 4:2019, Odense: University Press of Southern Denmark; 2019, p. 130–41.
51. Skytte L, Rasmussen KL, Ryhl-Svendsen M, Svensmark B, Brimblecombe P. Ammonia chemistry within Danish churches. Sci Tot Environ. 2012;417–418:13–20.
52. Tétreault J. Airborne pollutants in museums, galleries, and archives: risk assessment, control strategies, and preservation management. Ottawa: Canadian Conservation Institute; 2003.
53. Brokerhof, A., Bommel, M., Deterioration of calcareous materials by acetic acid vapour : A model study. ICOM Committee for Conservation, 11th Triennial Meeting, Edinburgh, Scotland, 1–6 September 1996. Preprints, p. 769–75.
54. Brimblecombe P, Blades N, Camuffo D, Sturaro G, Valentino A, Gysels K, van Grieken R, Busse H-J, Kim O, Wieser M. The indoor environment of a modern museum building, The Sainsbury Centre for Visual Arts, Norwich. UK Indoor Air. 1999;9:146–64.
55. Lassen E. Dansk Kunsthistorie I. Fra runesten til altertavle ca. 900–1500. Copenhagen: Gyldendal; 1972, p. 124–25.

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