npj | heritage science

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https://doi.org/10.1038/s40494-025-01990-7

Contribution to the chronological study of the Dubrovnik Cathedral using optically stimulated luminescence

Alicia Medialdea [1], **Suzana Damiani** [2] & **Maja Zeman** [3]

The 20th century brought unexpected archaeological discoveries under the Baroque Cathedral in Dubrovnik, the historic town of Ragusa (*Ragusium*) (the UNESCO World Heritage Site). In the 1980s, a church complex older than the historically recorded Romanesque Basilica was excavated. The study focuses on the use of Optically Stimulated Luminescence (OSL) dating to mortar samples collected from the internal layers of the key structures of this oldest church, plaster from the walls and sand layers under the masonry structures. The new data indicate a different chronological development of the edifice than previously suggested, while providing a more precise chronology of its early medieval refurbishments. Advanced building practices characteristic of the Late Roman eastern Mediterranean were detected, prompting a hypothesis that the early medieval masons adapted to default conditions near the town's ancient port, while opening possibilities for future research into innovative building techniques aimed at achieving more flexible structures—potentially as a response to the region's seismic vulnerability.

The absence of historical records often leaves the scientist with only a few traditional methods and techniques to date a specific historic building, particularly when its remains were largely destructed throughout the centuries, leaving them only in the archaeological layers, and overlaid by later constructions. Since archaeometry is an inherently interdisciplinary field, collaboration among experts from various disciplines is essential to uncover evidence that may contribute to more precise dating of architectural structures. In the case of the Dubrovnik Cathedral site, one of the key archaeological sites for the understanding of the development of the historic settlement of Ragusa (*Ragusium*), which is under UNESCO protection, the project aimed to establish the chronology of the oldest structural remains located beneath the city's Baroque cathedral.

The Dubrovnik Cathedral, as it stands today, is a remarkable Baroque structure erected between 1671 and 1713 on the site of its predecessor, which was severely ruined in the 1667 earthquake[1–3]. A seismic event in 1979 also caused significant damage, after which structural reinforcement works were carried out on the Cathedral's foundations, accompanied by archaeological investigations that ultimately covered an area of approximately 1200 m^2 (Fig. 1)[4–6]. As anticipated, the excavations revealed the foundation walls of the earlier Romanesque cathedral, whose existence is corroborated by historical records[5,7–9]. A surprising discovery was made when the remains of an even earlier church—referred to by researchers as the Byzantine Basilica[4]—were uncovered within its foundations.

The investigation revealed the well-preserved architectural composition of the sanctuary, the adjoining nave, and sections of the southern and northern aisles. On the sanctuary's apsidal wall, stone-built and plastered two-levelled *subselia* with central bishops' cathedra, as well as remains of a painted scene depicting the Church Fathers, were still well preserved (Fig. 2). It was also established that during the construction of the Romanesque cathedral, the interior of this oldest basilica had been filled with rubble and construction debris, which served as the foundation for the flooring of the new church. The rubble contained numerous fragments of liturgical stone furniture and sculpted architectural elements, spanning from the Late Antique to the medieval period—including reused carved stones, fragments of pottery and ceramic ware, glass material, and various metal objects[4–7,10–14]. Among these finds, the most abundant were fragments of wall paintings, which can be classified in different historical and stylistic periods[12].

Given the extraordinary discoveries, the archaeological investigation was extended in 1983 to the adjacent square. Findings in this area revealed that the earliest church was part of a larger complex situated in a section of the settlement directly adjoining the historic harbour. Notably, a defensive

[1]National Research Centre on Human Evolution (CENIEH), Paseo Sierra de Atapuerca 3, 09002 Burgos, Spain. [2]University of Zagreb, Academy of Fine Arts, Department for Conservation-Restoration of Works of Art, Zamenhofova 14, 10000 Zagreb, Croatia. [3]University of Zagreb, Faculty of Humanities and Social Sciences, Department of Art History, Ivana Lučića 3, 10000 Zagreb, Croatia. e-mail: alicia.medialdea@cenieh.es; suzanadamiani65@gmail.com; mzeman@m.ffzg.hr

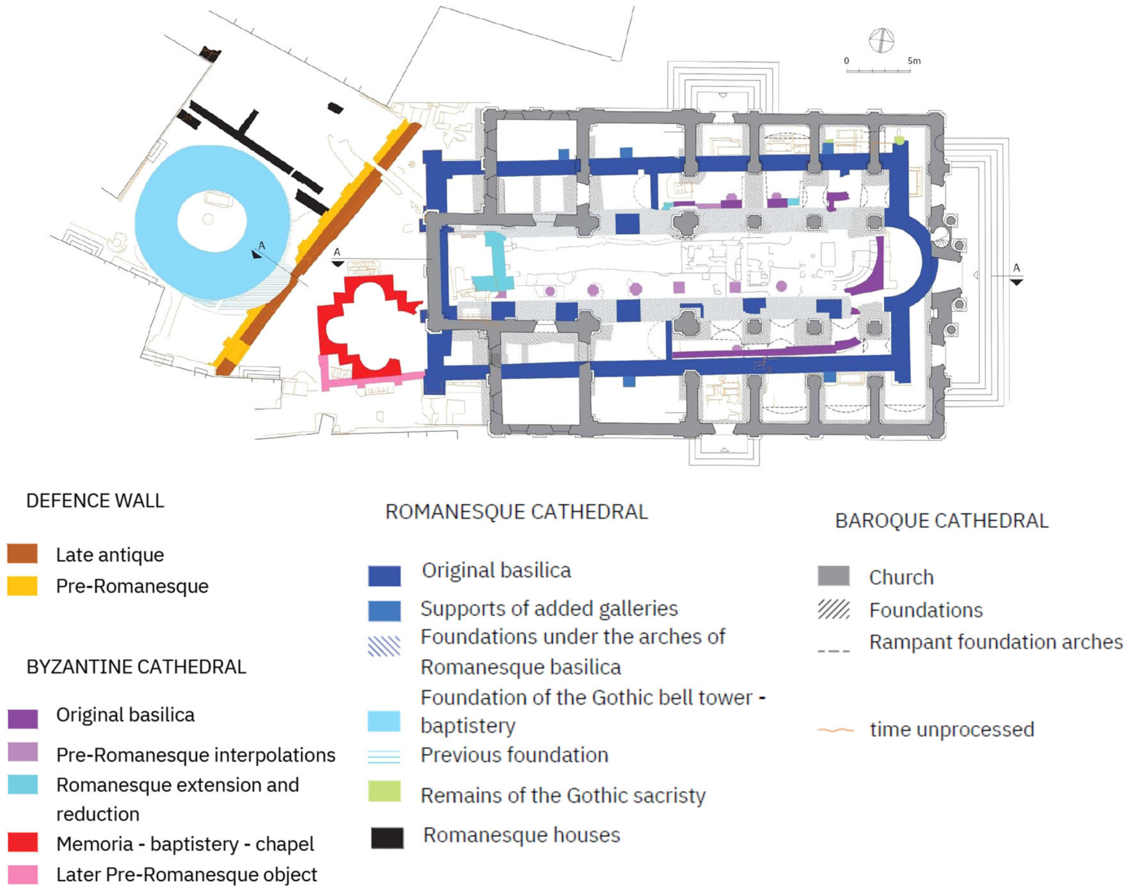

Fig. 1 | Cathedral and Bunić Square, a schematic plan representing the chronological sequence of building structures.

Fig. 2 | Remains of the apsidal wall with the wall painting fragment depicting the Church Fathers.

wall west of the church—dated by researchers to Late Antiquity—was uncovered, along with the remains of a quatrefoil structure associated with the church, which initially served as a *memoria* for housing relics and was later repurposed as a baptistery. In addition, burials from various stratigraphic layers were identified, as well as the remains of medieval dwellings and, ultimately, a Late Medieval bell tower–baptistery that formed part of the Romanesque cathedral complex[4–7,14].

By the end of the archaeological investigation, it had become clear that the excavated compound represented one of the most intricate and stratified architectural ensembles along the Croatian coast—one whose further study would significantly enrich, and potentially even alter, the understanding not only of the development of the Dubrovnik cathedral complex, but also of the earliest phases in the city's urban history. Unfortunately, all further research had to be paused at that time due to the war in Croatia (1991–1995), and the majority of the movable artefacts remained stored in the attic and underground chambers of the Cathedral for almost thirty years. Since then, the dating of the earliest church and its subsequent reconstruction phases has become a subject of ongoing debate. The proposed timeframe for its construction has expanded, ranging from the 6th–7th centuries to various periods within the Early Middle Ages—including the mid-7th to mid-9th centuries, and in some interpretations, even the 10th century[4,5,7,10,15].

It was not until 2018 that a comprehensive revision of the 1980s research was initiated through the project *Discovering the Old Dubrovnik Cathedrals*, marking the beginning of the systematic processing of all movable finds. This phase of work inevitably included a re-examination of the in situ masonry structures, carried out with full consideration of the data provided by the archaeological documentation and written records from the 1980s[16,17]. A collaborative effort was launched to conduct the first expert analysis, systematisation, and cataloguing of the material. As a result, the groundwork was laid for more detailed scientific interpretation, including natural science analyses based on physical methods, which primarily focused on material associated with the earliest church.

Physical dating methods rely on the analysis of building materials, among which mortar plays a key role, as it can provide information about the time of construction. Since the second half of the 20th century, two main techniques have been employed for this purpose: radiocarbon dating and Optically Stimulated Luminescence (OSL) dating[18]. Radiocarbon dating is used not only to date organic matter embedded in the mortar (such as charcoal and wood) but also to date the mortar's binder—lime. This technique is based on the fact that lime, acting as a binder, undergoes carbonatization shortly after being applied as mortar or plaster, incorporating atmospheric CO_2 and thus preserving the time of carbonatization. The Accelerator Mass Spectrometry (AMS) ^{14}C method has already provided crucial chronological data on historical buildings in the Dubrovnik historic core[19,20]; however, it also faces limitations due to difficulties in distinguishing between anthropogenic and geogenic carbonates[18]. Optically Stimulated Luminescence (OSL), primarily used for dating geological sediment deposition or ceramic firing, can also date mortar or plaster, often containing quartz grains. This method determines the last time the material was exposed to sunlight—a moment assumed to coincide with the time of construction. This technique has, in fact, been successfully applied previously to date the mortar used in the construction process of individual buildings[21,22].

During 2021 and 2022, several charcoal and plaster samples from the Dubrovnik cathedral site were also dated by ^{14}C Accelerator Mass Spectrometry (AMS). As mineralogical and petrographic analysis has shown the presence of quartz in some of the mortars and plasters, the chronological study was extended by using OSL, for which the possibility opened up within the IPERION HS (Integrating Platforms for the European Research Infrastructure ON Heritage Science) cooperation in 2022.

This article aims to complement historical and stylistic analyses with a refined chronological framework, primarily based on luminescence dating techniques. It outlines the key interventions and discoveries, accompanied by a detailed explanation of the applied methodology and the results of chronometric analysis of the earliest structural remains at the site. Beyond enhancing the current understanding of the construction and subsequent modification phases of the church, the obtained results also opened up possibilities for further research into potential advancements in building techniques achieved as early as the Early Middle Ages. They also offered new insights into past knowledge of material properties—possibly developed as a response to natural disasters and catastrophic events.

Methods

The objective of employing dating methods on the building materials within the site is to precisely determine the construction timelines of specific elements, enriching the historical narrative of the complex. The possibility of applying luminescence dating for this purpose was already proposed 20 years ago[23] and has been successfully applied since then[24–27], and its complexity has been previously presented[28]. The data were collected to complement ongoing investigations and serve as a supplement to the dating methods previously applied.

As part of the previous activities of the DioDuCat (Discovering the Old Dubrovnik Cathedrals) project, samples of plaster layers were examined in greater detail to determine the types of aggregates and binders, including analyses using ^{14}C AMS, conducted at the Ruđer Bošković Institute in Zagreb (Croatia)[12,29,30]. Although the results largely corroborated some of the assumptions and hypotheses proposed by researchers in the 1980s, they also provided more nuanced insights into the chronological relationships of certain masonry structures, particularly within the sanctuary and the main nave of the church.

Notably, a fine grey plaster associated with one of the earliest phases in the sanctuary apse—which likely preceded the visible painted decorations dated to the 11th–12th century[7]—was dated to the early 8th century[30]. Such a date would be at least partially expected, considering the earlier researchers' assumption that the church was erected in the earliest centuries of the Early Middle Ages.

However, a noteworthy observation of the sanctuary apse structure indicated that this presumed oldest layer of plaster—originally thought to correspond to the phase prior to the construction of the clergy bench—was applied later than previously assumed. Specifically, the initial levelling layer on the interior wall of the apse consisted of a surface mortar that closely resembled the mortar used in the construction of the apse masonry itself[12].

Based on this, the question was raised whether the layer of smoothed mortar might point to an even earlier phase of apse arrangement that should be linked to its original construction. Additionally, during the 1980s excavations, a layer of recycled marble offcuts of various types was found in the lower stratigraphic levels of the church, including fragments with polished surfaces. This opened the possibility that the surface mortar had originally served as a bedding layer for marble wall revetment—such as would be expected in Late Antiquity, i.e., the Early Christian period[31].

The layer of marble offcuts clearly points to intensive stonemasonry activity, but also suggests the availability of material that, in the Early Middle Ages, must have originated from an earlier, likely Late Antique or Early Christian edifice. Even more interesting is the fact that the layer of marble offcuts extended predominantly over a layer of red loamy earth mixed with fine sand and lay beneath structural elements in the church's nave—namely, columns—which the initial researchers proposed were constructed during the 9th–10th century phase, when the church was equipped with a dome and vaults[4].

Notably, the use of a red earth and sand aggregate has been common in the preparation of pavement subfloors since the Late Roman period. This construction technique is especially evident in the eastern Mediterranean—in public infrastructure such as roads, bridges, and harbour facilities—i.e., in structures that needed to be both flexible and resistant to compressive force[32–34]. In Dubrovnik, red earth (*terra rossa*) was also identified in the foundations of various public buildings and infrastructure projects from the 15th to 17th centuries[35–37], where its use has been interpreted as a revival of ancient Roman construction techniques and material knowledge aimed at increasing moisture resistance and long-term durability.

In line with these observations, a total of six samples were collected for OSL dating (Fig. 3). In addition to mortar samples, OSL was also used to date several sand layers located beneath masonry structures in the nave of the church. One of these layers was initially sampled for archaeomagnetic analysis due to its high iron content; however, this method did not yield usable results and will not be discussed further in this article.

Sampling

Careful consideration of sampling sites was undertaken collaboratively with the IPERION teamwork project leader, DioDuCat 2022 project coordinator, and other project collaborators, including an expert from the National Research Centre on Human Evolution (CENIEH) in Burgos, Spain, responsible for OSL sample collection and analysis. Field work and sampling

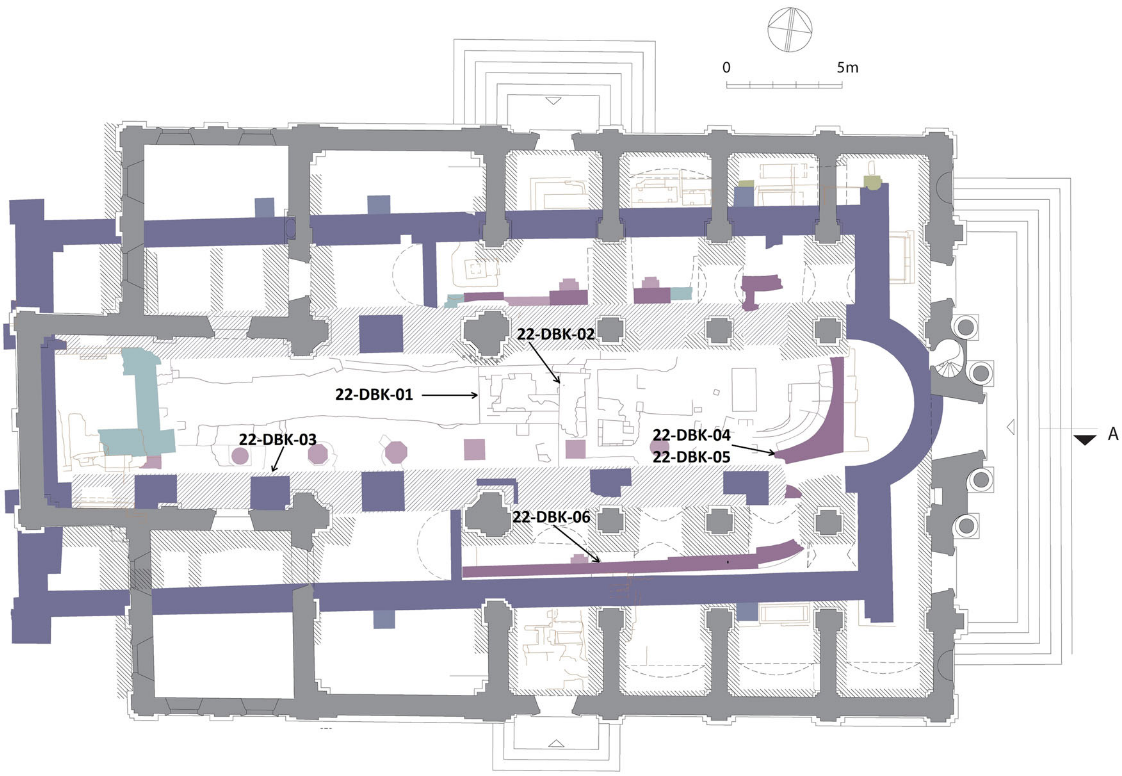

Fig. 3 | Floor plan indicating the samples' locations: 22-DBK-01,02,03 – sand samples, 22-DBK-04 – mortar sample, 22-DBK-05 – sand between construction blocks and 22-DBK-6 – plaster sample.

Fig. 4 | Sand layer sampled for OSL dating under the floor slab (22-DBK-01).

were conducted under the supervision of the Conservation Department in Dubrovnik, Croatian Ministry of Culture and Media. Samples had to meet criteria such as representativeness, size, and availability, with a focus on ensuring the surface was unpainted and devoid of significant features like graffiti. Representativeness allowed for later interpretation, and the structure from which the sample was taken had to be clearly defined concerning the entire stratigraphy.

Samples collected for OSL analysis are described here: 22-DBK-01 and 22-DBK-02 were collected from two sand layers beneath masonry structures at and below the first church's floor level, likely serving as cushioning for building stone elements (Figs. 3 and 4). These sandy layers, rich in quartz, were suitable for OSL dating since this technique could establish the last time that quartz grains within the sand were exposed to sunlight, assumed to have happened right before it was used in the construction process. Sample 22-DBK-03 was also a sand sample, but in this case, collected from an accumulation of sand at the side of the nave. This accumulation was cut, and construction elements were covering part of it. Therefore, it can be safely assumed that it was deposited before any building process.

To target the time of construction, sample 22-DBK-04 was collected from the mortar binding the blocks that form the structure of the apse wall beneath the initial masonry *subselium*, representing the earliest construction phase in the first church. In the same area, sample 22-DBK-05 was collected. This was loose sedimentary material filling the gaps left by the mortar between the blocks, most likely related to a flood dragging sediment into the structure.

The mineralogical-petrographic analysis of the grey plaster covering part of the walls and used as a base for some of the paintings showed the presence of quartz grains[12]. This material was also considered suitable for OSL dating and sampled (22-DBK-06).

The collection of sample 22-DBK-06 presented a challenge as it was a relatively thin layer (less than 8 mm) on the first church's walls, in the crucial apse area under the wall paintings. A compromise was reached, extracting a sample from the southern perimeter wall next to the existing damage. Once under the controlled light conditions of the luminescence laboratory, it was necessary to remove the outer 2 mm layer prior to any further treatment to ensure that only the grains that were not exposed to light were extracted. This work was conducted by the Conservation and Restoration Laboratory at CENIEH.

Luminescence dating

Optically stimulated luminescence dating is based on the availability of mineral grains, mostly quartz and feldspar, to store information about the ionizing radiation received from its surroundings. This radiation comes mainly from the Uranium, Thorium, and Potassium in the surrounding matrix and a small contribution of cosmic radiation[38].

The accumulated dose is estimated from the OSL response of quartz grains as it is proportional to the received dose. The burial age, i.e., the time since the quartz grains were deposited and shielded from light, can therefore

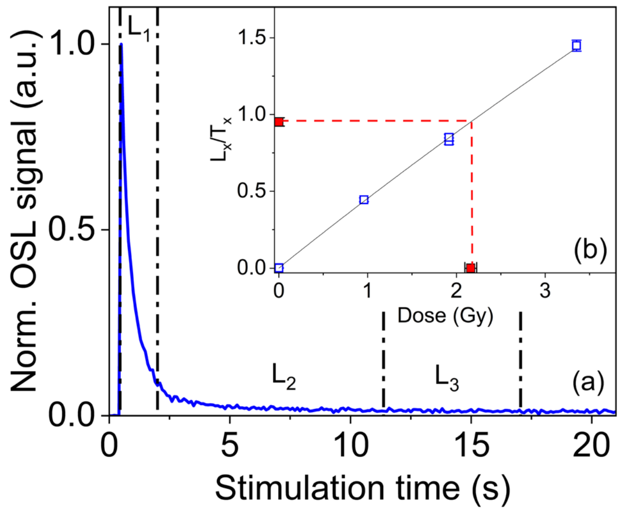

Fig. 5 | Representative OSL decay and dose-response curves. OSL decay curve of quartz grains from sample 22-DBK-04 (**a**); dose-response curve defined by the normalized OSL signal, L_x/T_x, showing the natural luminescence signal interpolated onto the curve, providing the corresponding dose. L_1, L_2 and L_3 indicate the fast, medium and slow components of the decay curve respectively (**b**).

Table 1 | SAR protocol, used for all the OSL measurements

SAR protocol
Natural or given dose (L_n or L_x)
Preheat (200 °C, 10 s)
OSL (125 °C, 40 s)
Test Dose 2 Gy
Cutheat (180 °C, 10 s)
OSL (125 °C, 40 s)
Blue stimulation (280 °C, 40 s)

be estimated with the relation shown in Eq. (1)

$$Age\,(ka) = \frac{Burialdose\,(Gy)}{Doserate\,(Gy/ka)} \quad (1)$$

where the burial dose is based on the OSL response of quartz grains and the dose rate is based on the concentration of radionuclides in the matrix surrounding each sample. Ages were reported within 1-sigma associated error and expressed in kiloyear (ka), since sample collection, when they were removed from their location. Caution was taken to guarantee that samples, once collected, were not exposed to significant ionizing radiation.

Beta and gamma contributions to the dose rate (i.e. dose per unit time) are derived from the radionuclide activity concentration of radioelements in the sample matrix (a matrix of 30 cm radius), determined by high-resolution gamma spectrometry, applying appropriate conversion factors[28]. The alpha contribution was not included in the calculation of the dose rate received by quartz grains as the external layer of these, affected by alpha radiation in nature, was removed by hydrofluoric acid treatment (see details on sample preparation below). Radionuclide concentrations are presented in the results section. Heterogeneity of each sample matrix was considered; this refers to the cases in which there were mortar blocks or slabs next to the collected sand sample and in the case of the plaster, only the radionuclides in the wall behind it were contributing to the beta and gamma dose rates. In this case, the correction proposed by Aitken, 1985 was applied[39]. The contribution of cosmic radiation was calculated according to the burial depth, latitude, altitude and average over-burden density[40]. Samples were collected under 2 m of masonry structure (density ~2 g/cm^3) and bellow the cathedral´s roof located ~20 m above (density of the space in between 1.2 g/cm^3). Attenuation to the dose rate caused by moisture and grain size was considered. Moisture contents at the time of sampling varied between 20 and 24%. We have considered a moisture value of 22 ± 5% representative of the burial time. The additional ±5% accounts for variations in the water content during the burial period. Environmental dose rates to infinite matrix values have been calculated using the Dose Rate & Age Calculator[41].

For the measurement of the OSL signal, quartz grains of sizes 90-180 µm were extracted from each sample, following standard procedures[42]. These included wet sieving to isolate the target grain size, chemical treatment with hydrochloric acid and oxygen peroxide to remove carbonates and organic matter respectively, and density separation, keeping the fraction between 2.62 and 2.7 g/cm^3. The quartz grains extracted from each sample were etched with hydrofluoric acid for 50 min; this treatment removed the 10–17 µm outer layer of the grains[43] affected by alpha radiation; this is therefore, not accounted for in the dose rate received by the quartz grains. The final fraction was then re-sieved to guarantee that only 90-180 µm grains were kept for OSL measurement.

OSL response (Fig. 5a) was measured using an automated Risø TL/OSL reader, model DA-20 C/D, equipped with a beta source delivering ~0.09 Gy/s at the sample position, and a blue LED array (470 ± 30 nm) with a stimulation power of ~80 mW/cm^2. The derived OSL responses at a temperature of 125 °C were detected using bialkali EMI 9235QB photomultiplier tube through a 7.5 mm-thick U-340 filter. The single-aliquot regenerative dose (SAR) protocol[44] was applied for all OSL measurements (Table 1).

Dose-response curves were defined by measuring the OSL signal derived from three different given regeneration doses, the response to 0 Gy and the repetition of one of the doses to check potential variations through the measuring sequence (Fig. 5b).

The OSL signal derived from these given doses, L_x, was normalized by the OSL derived from the test dose, T_x, (i.e. a given dose that is kept constant throughout the cycle). This test dose is characteristic of the SAR protocol and makes it possible to monitor and correct for sensitivity changes throughout the measuring sequence. The dose-response curve is then defined by the normalized OSL signal, L_x/T_x, at different doses. One of the regeneration dose points was repeated, followed by infrared (IR) stimulation before the OSL detection to test the purity of the quartz extract. The derived IR depletion ratio (i.e. the ratio between the OSL of a specific given dose and the OSL of the same dose after IR stimulation[45],). In the case there were feldspar grains within the quartz extracts, these would evict part of their luminescence response during the IR stimulation leading to a ratio <1. All aliquots from all 6 samples show IR depletion ratios consistent with unity, confirming the purity of the quartz extracts.

The appropriate measuring conditions (preheat, cutheat, test dose and cleanout temperature) were determined through a series of dose recovery tests, carried out on aliquots, artificially bleached, on which a known beta dose of 2 Gy was given. Samples were bleached for 1 hour in a solar simulator and 3 aliquots were used for each different measurement condition.

Given doses were recovered successfully for preheat temperatures between 180 and 240 °C (Fig. 6). A preheat temperature of 200 °C for 10 s was used before the measurement of the natural or regenerative dose OSL signal (L_x) and a thermal treatment at 180 °C for 10 s was given before the measurement of the test dose OSL (T_x). A test dose of 2 Gy was used to measure the normalization OSL signal (T_x) and a cleanout step of blue light at 280 °C during 40 s was used at the end of each measuring cycle (Table 2).

To obtain a representative dose population for each sample, 24 quartz multi-grain aliquots of 5 mm diameter were measured. Individual estimated doses from each measured aliquot were accepted if the relative uncertainty on the natural test dose response was less than 20% and if the recycling value, excluding uncertainties, was within 20% of unity. No aliquots failed these criteria and therefore all values obtained from the 24 aliquots were used for the burial dose estimation. The burial dose was estimated from the entire dose distributions applying the Central Age Model (CAM[46],).

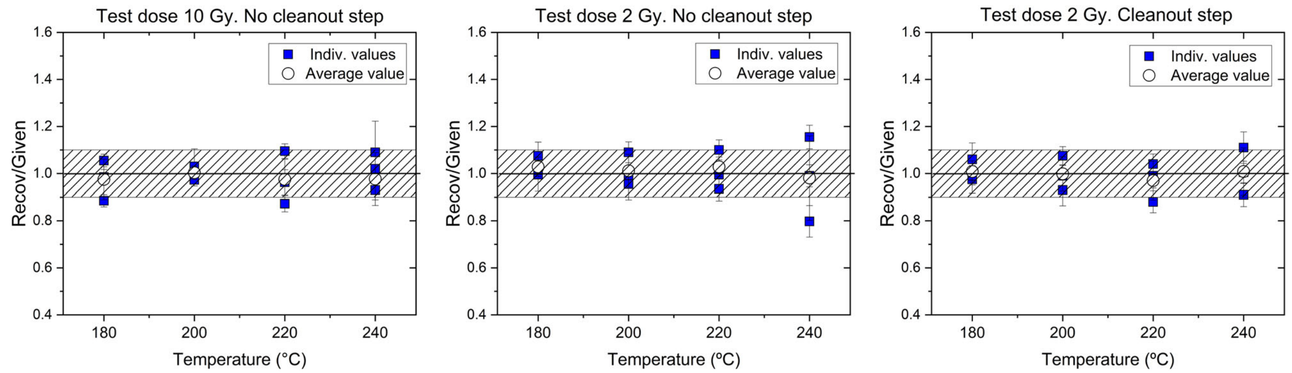

Fig. 6 | Results from dose recovery tests carried out to determine the most appropriate measurement conditions. The plot shows the individual recovered to given ratios and the average (open icons) of each 3 aliquots. The striped bar indicates the 10% error. Preheat temperature between 180 and 240 °C and cutheat temperature (heat treatment before measuring the test dose) between 160 and 220 °C have been tested. Also, the effect of using a test dose of 2 Gy or 10 Gy and the potential impact on the recovered dose of using a cleanout step at 280 °C at the end of each cycle have been checked.

Ages are reported at 1-sigma associated uncertainty and they are referred to the year of sampling, 2020. The dose received during the few months between the sampling and the moment of measurement is not significant compared to the in-situ annual dose rate and therefore, it has not been considered in the total dose rate calculation.

Results

The OSL signals from the quartz multi-grain aliquots are fast-component dominated, decaying to background level within the first 2 seconds of stimulation. This was assessed based on the fast ratio[47] and each component is shown in Fig. 5a. Also, a good signal-to-noise ratio is observed, leading to well-defined dose-response curves (Fig. 5b).

The derived dose populations (Fig. 7) are normally distributed and have low scatter with overdispersion values between 10 and 15%, except sample 22-DBK-02 which has an overdispersion of 45%. The weighted mean used by the Central Age Model, CAM[46], has been considered appropriate to estimate the true burial doses, summarized in Table 1. No different age model was applied to estimate the burial dose of 22-DBK-02, despite its large scatter as no useful information could be obtained from this sample in any case. The resulting CAM dose of 11.4 ± 1.0 Gy, equivalent to an age of over 8000 years, cannot be related to any construction phase. This anomalous age is most likely related to the sand in the sampled unit suffering from incomplete bleaching[48] (i.e. the quartz grains not being exposed to sunlight long enough to reset their luminescence signal) before it was placed in its current location and shielded from light again. This could happen if the sand, used during the construction, was transported in big quantities, preventing the exposure of a large number of grains to light.

Luckily, this behaviour is not observed for any of the other 5 samples analysed and the other dose populations do not show any anomalously large doses.

Samples 22-DBK-03, accumulated sand, partially covered by construction elements and therefore, deposited before any building process and 22-DBK-04, a piece of mortar, which could both be related to the first stages of the original construction phase, provide an age of 1600 ± 100 years, since 2020. Sample 22-DBK-05, corresponding to the loose sandy material accumulated around the mortar sampled provided an age of 1500 ± 100 years, consistent with the previous age; although, due to its position, it can be confirmed that it was deposited after the mortar (22-DBK-04). Sample 22-DBK-01, a sand layer used as a base for the floor slabs provided an estimated age of 1400 ± 100 years, indicating that it was placed slightly later than the first construction elements (the blocks bound with the mortar sampled, 22-DBK-04). The estimated ages for all these four samples (22DBK-01 to 04) are consistent with each other within a 1-sigma associated error. This indicates that the time between both events, the construction of the building's foundations and the flood happened close in time, less than can be resolved by OSL dating for these specific samples.

Results from sample 22-DBK-06, corresponding to the piece of plaster, provided an estimated age of 1100 ± 100 years from 2020, a more recent age than samples 22-DBK-01, 03, 04 and 05, therefore related to a later modification of the building.

Except for the anomalous age of sample 22-DBK-02, the other five estimated ages provide key information to understand the evolution of the Dubrovnik cathedral site.

Discussion

The results of the optically stimulated luminescence analysis confirmed that the apse structure is indeed older than previously suggested by the 1980s researchers, subsequent art-historical interpretations, and the earlier ^{14}C AMS analysis.

The hypothesis that the apse of the church—namely the sanctuary area—constitutes the oldest part of the structure was first put forward by 1980s researchers, alongside the proposition that this space underwent multiple episodes of adaptation and structural modification. Further attention was directed toward the area in front of the sanctuary, where archaeological excavations revealed a masonry structure, possibly representing the foundations of an auxiliary altar or an ambo. This area was seen as subsequently modified through the addition of a dome[4–6]. Based on these considerations, samples were collected from the wall of the apse, from the soil (sand) directly beneath the masonry structure in front of the sanctuary, and from the interior of the nave—specifically from a location overlaid by the foundations of the Romanesque cathedral. In addition, a sample of plaster from the wall surface (grey plaster) was taken to serve as a comparative method to the already applied AMS ^{14}C.

The first four samples mentioned show a significantly earlier date than previously established. According to the results of this study, the OSL analysis dates the apse structure (sample 22-DBK-04) to the period from the last third of the 3rd to the end of the 5th century. In earlier research, this structure was dated to the 7th–8th century based on the visible wall stratigraphy, stylistic analysis of the wall paintings, and, ultimately, radiocarbon dating of the plaster using the AMS ^{14}C method. We began to question the later date proposed by previous studies due to the masonry characteristics of the apse itself, and particularly because of the presence of a smoothed mortar layer observed during analysis. The OSL results, which point to the Late Antique period, further strengthen the hypothesis that the apse was originally clad in marble revetment. This will direct future investigations toward a more detailed study of marble fragments found at the site, including a variety of marble offcuts[31].

One of the most unexpected results came from the sample taken in the nave, beneath the foundations of the Romanesque cathedral (sample 22-

Table 2 | Summary of results from luminescence dating including the dose rate of the matrix, the estimated burial dose and the derived age for each sample

Sample	Lab code CENIEH	K (%)	Th (ppm)	U (ppm)	Dose rate (Gy/ka)	Burial dose (Gy)	Age (ka)	Age (A.D.)	Sample type
22-DBK-01	FIX5LM-01	0.52 ± 0.01	3.05 ± 0.09	1.65 ± 0.03	0.97 ± 0.03	1.39 ± 0.03	1.44 ± 0.06	520–640	Sand
22-DBK-02	FIX5LM-02	0.62 ± 0.01	5.43 ± 0.20	2.57 ± 0.03	1.36 ± 0.05	11.37 ± 1.01	8.4 ± 0.8	-	Sand
22-DBK-03	FIX5LM-03	0.67 ± 0.01	2.83 ± 0.05	1.88 ± 0.02	1.14 ± 0.04	1.80 ± 0.06	1.58 ± 0.08	360–520	Sand
22-DBK-04	FIX5LM-04	0.18 ± 0.01	1.47 ± 0.13	2.01 ± 0.04	0.92 ± 0.05	1.50 ± 0.05	1.64 ± 0.11	280–490	Mortar
22-DBK-05	FIX5LM-05	0.18 ± 0.01	1.47 ± 0.13	2.01 ± 0.04	0.92 ± 0.05	1.34 ± 0.04	1.46 ± 0.11	450–660	Sand
22-DBK-06	FIX5LM-06	0.27 ± 0.01	0.69 ± 0.07	1.23 ± 0.02	0.65 ± 0.03	0.72 ± 0.03	1.12 ± 0.07	830–980	Plaster

Radionuclide concentrations derived from high-resolution gamma spectrometry are included. All errors are reported with 1-sigma-associated error. Ages are reported in kiloyears (ka) since the moment of sampling (2020) and they have been converted to calendar ages (A.D.) by subtracting the estimated age in ka from 2020. The type of sample is also given.

DBK-03), composed of compact layers of sand and red earth. Its dating to the period between the second half of the 4th and the first half of the 6th century suggests that the Romanesque foundations were laid atop significantly older deposits—possibly related to the phase of construction associated with the apse. The stratigraphy of this layer—consisting of fine sand and red earth (*terra rossa*)—points to purposeful and well-considered construction choices. This type of aggregate was commonly used in coastal environments, particularly in harbour infrastructure and for paving roads and bridges. Such material selection indicates the involvement of experienced and knowledgeable builders, as well as the planned transport of construction materials. Even the dating anomaly recorded in sample 22-DBK-02 may reinforce this interpretation, potentially reflecting the origin of a larger quantity of sand from a consistent source, leading to the incomplete bleaching of the quartz grains within the sand observed in their OSL signals.

The similar stratigraphy of the embankment beneath the foundations of the structures located at the very centre of the nave prompted the decision to date this layer using the OSL method as well. Moreover, the structures beneath which sample 22-DBK-01 was taken have not yet been fully interpreted. The analysis results, which suggest that the foundation of that yet unidentified structure was built sometime between the first half of the 6th and the mid-7th century, are of particular importance. They point to potential structural modifications to the building that have taken place even before the earliest known early medieval phases of the church. In this context, the dating of sample 22-DBK-05 is particularly significant, as it indicates a possible episode of sedimentary or alluvial deposition occurring at an as yet undetermined time shortly after the construction of the apse—an event that warrants further detailed investigation.

The dating of layers composed of sand mixed with red earth also suggests that early medieval builders adapted to the existing conditions at the construction site and made use of the materials available to them. The documented presence of a layer of marble offcuts in the church nave—recorded during excavations in the 1980s and laid uniformly over the previously described layer—opens up the possibility of investigating potential advancements in construction practices and the creative reuse of material waste. This also raises the question of whether such offcuts were used intentionally to enhance the structural strength and overall resilience of the building—perhaps even as a deliberate response to the seismic vulnerability of the Dubrovnik area[31].

The analyses detailed here indicate a time frame from the last third of the 3rd century to the last third of the 7th century. However, the time ranges for specific components (apse dated to 270–490 CE; ground around the apse 450–670 CE; nave under Romanesque foundations 360–520 CE; structure in the centre of the nave 520–640 CE) direct research to further examine whether the first church of Dubrovnik cathedral site was built earlier than previously thought—possibly as early as the late 5th century—or whether its construction began with the adaptation of an older, late antique building, with the earliest date so far established in the period from the last third of the 3rd to the late 5th century.

While these data certainly do not claim to offer definitive conclusions about the earliest history of the Dubrovnik cathedral complex, they have the potential to reshape its historical narrative, and above all, to direct subsequent research activities to more specific areas of the site, as well as to more specific research questions. As a multilayered urban site, it opens up new possibilities in the study of the evolution and the changes in building technologies, including their more subtle adaptations to different conditions, using recycled materials. Situated in the seismic fault zone, at a site where construction, reconstruction, demolition, and removal of individual structures can be traced over more than a thousand years, the oldest excavated church at the site may provide new insights into the past seismic activities that have not been documented in the historic records.

This study highlights the versatility of OSL dating in the analysis of significant buildings, offering the ability to date various construction materials - from mortar and plaster to sand deposited in the foundations. Furthermore, the findings presented here demonstrate that OSL dating could play a key role in establishing not only the chronology necessary to

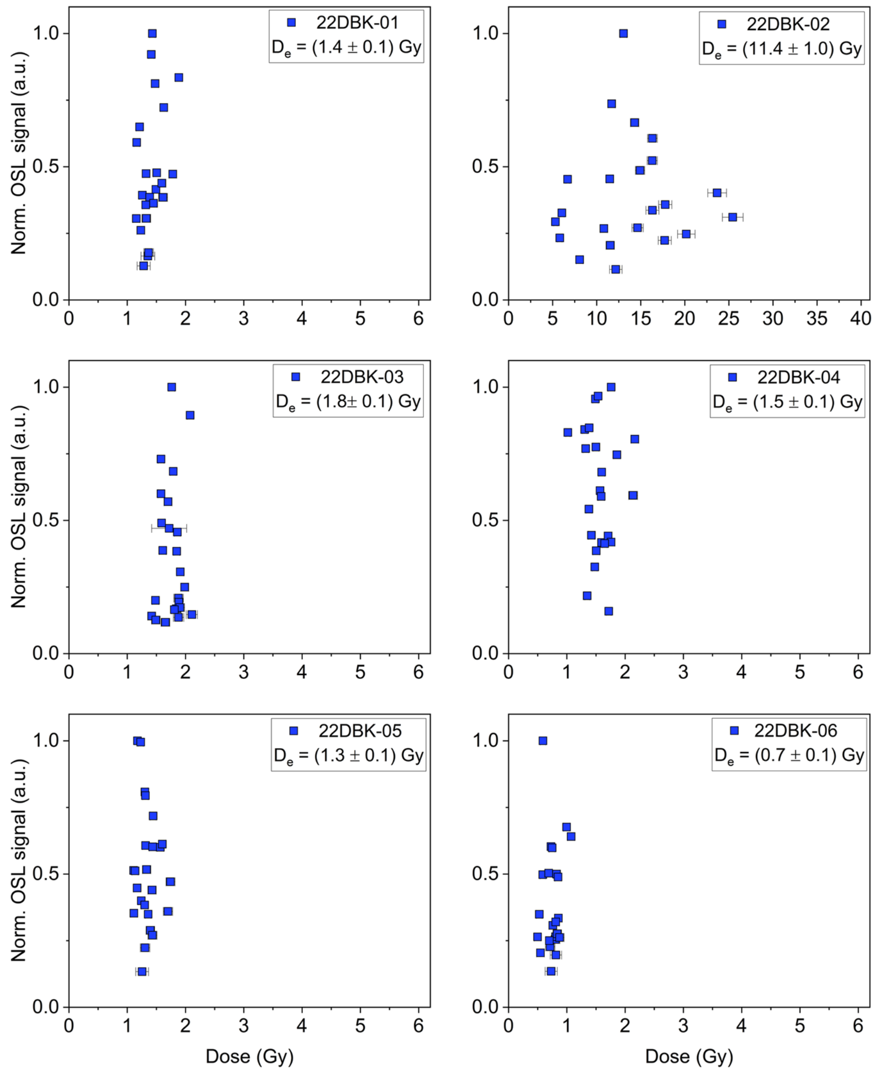

Fig. 7 | Dose distributions derived from the OSL measurement of multi-grain quartz aliquots for each sample. The OSL signal has been normalized to the highest intensity of each population to ease plotting. Please note that the x-scale of sample 22-DBK-02 is different from the rest.

understand Dubrovnik's evolution during its formative centuries but also its spatial development, even reshaping the understanding of the original 'urban core'.

Data availability

Raw Data supporting the OSL results of this study have been deposited in CENIEH's system, Gestilab, under the code Fixlab_05_Iperion_DioDuCat-F (codes FIX5LM-01 to 06). They include the individual measured doses from quartz aliquots and are available upon request at the email labs@cenieh.es and from the corresponding author.

Received: 15 July 2024; Accepted: 7 August 2025;
Published online: 25 September 2025

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Acknowledgements

Financial support by the Access to Research Infrastructures activity in the Horizon 2020 Programme of the EU (IPERION HS Grant Agreement n.871034) is gratefully acknowledged. We thank the City Parish of the Assumption of the Blessed Virgin Mary in Dubrovnik as the site and findings owner, and the Dubrovnik Diocese for their support in cooperation.

Author contributions

A.M. sampling, analysis, interpretation of the data, writing and revising; S.D. conception and design, sampling assistance, drafting, writing and revising; M.Z. historical and art historical data, writing and revising. All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Correspondence and requests for materials should be addressed to Alicia Medialdea, Suzana Damiani or Maja Zeman.