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Original article

Ramped pyrolysis radiocarbon dating of lime lumps: Establishing the earliest mortar-based construction phase of Turku cathedral, Finland

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ABSTRACT

Ramped pyrolysis radiocarbon dating was carried out on lime lumps from what was believed to be the oldest remains of Turku Cathedral, Finland, the first sacristy. Lumps extracted from bulk mortar from five sampling locations were analysed. For each sample, 5–6 fractions of CO_2 from different temperature fractions were radiocarbon dated.

One of the five samples exhibited significant contamination for its lowest temperature fractions. For the remaining samples, the age-temperature profiles were well-behaved, exhibiting a plateau of dates that were in statistical agreement and indicative of samples where only a single carbonate source (lime binder from the construction phase) is contributing to the radiocarbon dates. For each of the five samples, the combined radiocarbon age resulted in a calibrated age with a large probability distribution mode (typically $>$ 85% probability) in the late 13th century AD. Combining the radiocarbon dates from all five samples (21 fractions in statistical agreement, χ^2-test: df $=$ 20, $T = 7.1$, 5% $=$ 31.4) provided an age of 709 ± 11 yr BP and a calibrated age of 1276–1296 cal. AD (95.4%). This result finds excellent agreement with historical sources, previous mortar dating work, and a single radiocarbon date on organic material also embedded in some of the bulk mortar.

The results demonstrate that ramped pyrolysis, applied to well-selected lime lumps, is (A) a useful diagnostic tool for establishing how reliable a sample is and (B) an accurate, precise, and repeatable technique for radiocarbon dating mortar. The results further confirm that Turku Cathedral's first sacristy was constructed from stone and mortar in the late 13th century AD.

Additionally, using Turku Cathedral sacristy as a case study, two Bayesian models were presented to illustrate how, in general, mortar dating and Bayesian statistics might, in future, be applied to examine building construction dynamics for the case of (chronologically) ordered or unordered mortar derived radiocarbon dates.

1. Introduction

The ability to directly date buildings is of considerable importance in archaeology as it can provide some of the most secure chronological information for a site [1]. Structural components composed of lime, such as mortars and plasters, have been targeted by researchers since as early as the 1960s in an attempt to radiocarbon date CO_2 trapped in those materials during hardening, and hence contemporary with the application of the mortar or plasters themselves (e.g. [2,3]). Since then, significant advances have been made in both our understanding of mortar dating and our ability to obtain reliable dates (see [4,5] for reviews); however, issues still persist with more complex mortars and there is a lack of consensus on the most reliable approach or methodology to apply to both pretreat and date them (see [6] for a discussion).

For lime mortars, most difficulties arise from trying to discern and separate anthropogenic calcium carbonate ($CaCO_3$) from geological carbonate. Lime mortars are produced by first firing limestone to temperatures typically above 900 °C for long enough to

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thermally decompose the limestone, producing quicklime (CaO) that is then slaked with water producing $Ca(OH)_2$. Aggregates (e.g. sand, rock fragments) are then mixed with the slaked lime and the mortar is ready for use. As the mortar sets or hardens it captures CO_2 from the surrounding atmospheres and reverts to $CaCO_3$. Mortar dating attempts to isolate this $CaCO_3$, and the associated CO_2 from the lime binder but problems arise where any of the following occurs:

(a) limestone was incompletely fired during production of quicklime leaving limestone residue/particles in the lime binder.
(b) the aggregate contains limestone or dolomite grains.
(c) the mortar underwent delayed hardening [7].
(d) secondary crystallization has occurred due to dissolution/weathering (e.g. due to precipitation or groundwater) or thermal decomposition events (lightning or fires, see [8]).

All of the above are problematic as they result in a contaminating source of $CaCO_3$ that is very difficult to accurately distinguish, quantify and remove with respect to the $CaCO_3$ associated with the lime binder setting.

One way to circumvent this issue is to target pure lime lumps in the mortar. These lime lumps are best described as local inhomogeneities in the mortar due to poor mixing of the quicklime during and/or after slaking, resulting in a carbonate that has an especially high binder to aggregate ratio; in many instances, the lump is pure binder, free of aggregate contamination. As lime lumps are believed to be formed during carbonation in the lime putty (i.e. before mixing with aggregate and placement of mortar mix in the construction, see [9,10]) delayed hardening issues are also minimized. These lumps have been shown to be especially promising for mortar dating [10–13] but can be mistaken for lumps that have an incompletely burnt limestone core [12]. Therefore, they also need to be treated with some caution by examining multiple fractions of CO_2 per sample.

In the past few decades, the dominant method for extraction of CO_2 from lime binder has involved acid dissolution methodologies, more specifically sequential dissolution where multiple fractions are taken from a single sample to be dated (e.g. [13–22]). Recently however, the application of thermal decomposition to mortars has also been re-examined as a means of reducing or removing contaminating components [23–25]. By exploiting differences in thermal decomposition temperatures of, say, anthropogenic versus geogenic carbonates it is possible (following suitable pretreatment) to isolate fractions of CO_2 that have negligible quantities of contaminating CO_2 present; this was demonstrated by the application of ramped pyrolysis/oxidation [26] to successfully date several medieval mortars by Barrett et al. [27].

This work examines the combined application of ramped pyrolysis radiocarbon and carefully selected lime lumps to mortar dating, more specifically by dating a series of carefully selected lime lumps from the first sacristy of Turku Cathedral, Finland. This is a structure which has undergone mortar dating previously using acid hydrolysis methods [8,12,23] and for which there is strong historical information available (discussed further below) that place the construction of the first sacristy in the late 13th century. However, this has not been completely accepted with alternative theories arguing for a late 14th or 15th century date [28–30].

2. Research aim

This work aims to:

- Explore the advantages/limitations of ramped pyrolysis radiocarbon dating of individual lime lumps. This includes how useful the technique is as a combined diagnostic and dating tool that not only provides radiocarbon dates but also information on the purity of the sample with regard to lime binder.
- Examine the reproducibility, accuracy and precision of ramped pyrolysis when applied to a series of different lime lumps from the same construction phase.
- Settle the debate on the earliest construction phase of one of the most important religious structures in Finland, Turku Cathedral.

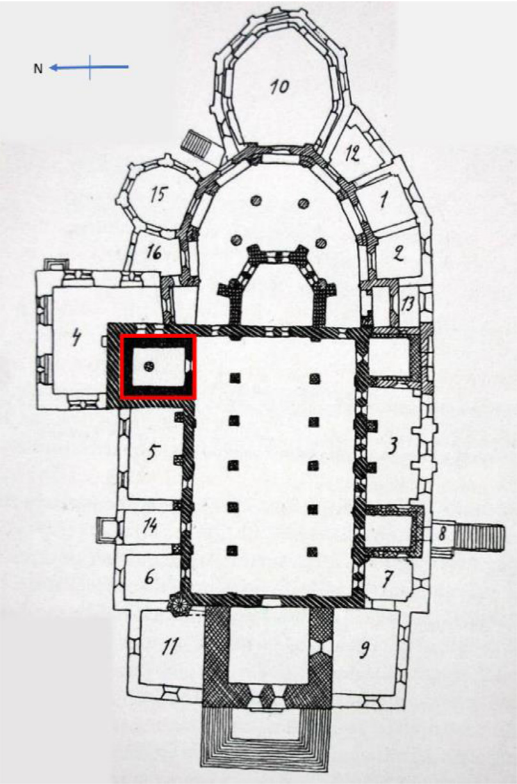

Fig. 1. Plan of Turku Cathedral with first Sacristy highlighted in red. Adapted from Rinne et al. ([33], p. 184). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Further to this, using the results from Turku cathedral as a case study, the article will also illustrate simple Bayesian modelling approaches that can be used to examine the construction dynamics (e.g. construction duration, start and end of construction) of mortared buildings where a series of samples from different sampling locations are analysed. The general approaches described provide a guide that can be applied elsewhere to more suitable sites than Turku; in particular, they are of use in scenarios where samples are unordered (no prior information regarding chronological ordering of samples is available) or ordered (prior chronological ordering information is available) and can also be used to examine how robust the chronological interpretations are for different underlying assumptions regarding construction.

3. Materials and methods

3.1. Samples – Turku cathedral

3.1.1. Background

Turku Cathedral was the primary church of the diocese of Turku from the 13th century to 1809 AD, during which Finland was part of Sweden. The earliest component of the building is believed to be the first stone sacristy (see Fig. 1), the south gable of which is still fully visible. From written source evidence, it has been dated to around 1300 AD [31] and there is reference to the election of a new bishop, overseen by Canon Laurentius, in the sacristy in 1291 AD (Diplomatarium Fennicum: 201 [32]).

Mortar dating has also been applied to the sacristy using sequential dissolution methods on both bulk and lime lump samples [8,12]. The bulk samples were interpreted as producing a calibrated age range of 1282–1302 (78.3%) cal. AD and 1369–1379 (17.1%) cal. AD (recalibrated using IntCal20 [34] and OxCal 4.4 [35]). The lime lump provided a calibrated result of 1285–1318 (43.4%) cal. AD and 1359–1389 (52%) cal. AD. These results find agreement with the historical written sources regarding a late 13th century date.

Despite this, a theory that the cathedral was not built until the late 14th/15th century persists with the earlier dating results not yet finding widespread acceptance [29,30].

3.1.2. Samples

The samples used in this study are from five bulk mortar samples (TTK007–011) taken from the south gable of the first sacristy. The samples were taken across a vertical range of approx. 3.5 m and a horizontal range of 0.6 m. There was at least 0.35 m horizontal spacing between sampling locations. Samples were taken no deeper than 4 cm to avoid any potential delayed hardening issues in bulk mortar ([7], for lime lumps extracted from bulk this should not be a problem as carbonation is believed to occur at the lime putty stage, discussed earlier). From each of these bulk samples, following gentle crushing, lime lumps were identified and extracted (labelled TTK007Li-011Li). Multiple lime lumps were sometimes taken from a bulk sample to provide enough material for dating. The lime lump samples ranged from 46 to 93 mg of material for ramped pyrolysis (RP) analysis. No pretreatment was carried out on samples before RP was applied.

A small fragment (3.75 mg) of wood/straw (TTK008W), embedded in the same bulk mortar TTK008Li was taken from, was also submitted for radiocarbon dating and was pretreated using an ABA treatment.

3.2. Ramped pyrolysis

The ramped pyrolysis method is summarized below with a more complete description of the system and method provided elsewhere [26]. The only significant difference in the current work is that, unlike Barrett et al. [27] where ramped pyroxidation was used (where oxygen is introduced into the lower furnace to enhance conversion of CO products to CO_2), only pyrolysis was used; for carbonates introduction of O_2 is not necessary and only serves to enhance CO_2 produced by other potential contaminants, e.g. organic matter or charcoal.

Lime lump samples are loaded into a pre-cleaned (baked at 850 °C) quartz glass reactor with a bed of quartz wool. This is loaded into a pyrolysis furnace. The sample is heated under a constant flow of helium gas (35 mL/min) from 200 °C (drying temperature) to 600 °C (approximate lower temperature range for onset of calcium carbonate decomposition) over a period of 20 min (20 °C/min). The sample is then held at this temperature for 20 min (or earlier if the CO_2 signal has returned to background) to ensure removal of potential lower temperature contaminants, such as organic matter or layered double hydroxides (LDHs, [24,36]). After the soaking phase ramping continues from 600 to 800 °C over a period of 1.5 h (2.2 °C/min).

The gas and CO_2 produced from thermal decomposition of carbonates passes through a water trap (ethanol/dry-ice slush), then a CO_2 detector (datalogged using LabVIEW and National Instruments software and hardware), before reaching liquid nitrogen traps that cryogenically collect the CO_2 at targeted temperature ranges. Generally, 5–6 fractions of CO_2 (minimum of 0.25–0.3 mg carbon) are collected across temperature ranges that span the low (600–650 °C) to high (700–750 °C) thermal decomposition temperatures of the lime binder. The CO_2 fraction collected is transferred directly to a graphitization line and converted to graphite with the hydrogen reduction method [37].

3.3. Radiocarbon dating and analysis

Radiocarbon dating of RP samples was carried out at ^{14}CHRONO Centre (Queen's University Belfast) using an IonPlus MICADAS. HOXII (SRM 4990C NIST) was used for normalization with background corrections carried out following Keaveney et al. [26]. The wood/straw fragment, TTK008W was dated at the AMS ^{14}C Dating Centre, Aarhus using a HVE 1MV accelerator [38]. Reporting of the results is in accordance with Stuiver and Polach [39]. Analysis, including calibration and Bayesian modelling, was conducted using OxCal 4.4 ([35], using *Phase, Sequence* and *Span* functions for modelling) with the IntCal20 dataset [34]. Outlier analysis was carried out using χ2-tests [40] and the *Outlier_Model* function in Oxcal 4.4 (Bronk-Ramsey [41]b). Where dates from the same sample are in statistical agreement weighted averages were carried out using the *R_Combine* function in OxCal 4.4.

4. Results

4.1. Radiocarbon dates and age-temperature curves

The complete RP and radiocarbon dating results are presented in Table 1 with the corresponding age-temperature curves (plots of the CO_2 profile, temperature fractions CO_2 was captured over, and radiocarbon dates obtained) shown in Fig. 2 *(left)*. With the exception of TTK009Li, the series of radiocarbon dates for each sample are very well-behaved (display a series of dates in good statistical agreement, consistent with a single carbonate source (i.e. lime binder) contributing to the radiocarbon age [27]). Outliers or suspect fractions were removed before the remaining radiocarbon dates were combined; these are presented in Table 1 and plotted in the Fig. 2 (*left*). The calibrated dates for the combined ages are presented in Fig. 2 *(right)*.

For TTK007Li, all measurements are in statistical agreement, with no dates removed from later analysis. TTK008Li is also well behaved with only fraction 1 (F1) identified as a certain outlier (age is too old). Because this is the lowest temperature fraction and might be associated with contamination from lower temperature charred organics or charcoal at lower temperatures (see discussion), to be conservative, the second fraction (F2) was also removed from subsequent analysis (this was not a problem as four fractions in statistical agreement remain).

Sample TTK009Li displayed strong low temperature contamination that is either absent or present to a much lesser extent in the other samples (see CO_2 profiles $<$ 600 °C in Fig. 2). Associated with this, the first three fractions are much older, certainly contaminated and removed as outliers. As for TTK008Li, to be cautious, the next highest fraction, F4, was also removed from subsequent analysis leaving the two highest temperature fractions, both in strong statistical agreement and with no indication of higher temperature carbonate contaminant present. TTK010Li was also very well-behaved. Outlier analysis identified F5 as a potential outlier and it was removed from subsequent analysis. Of the 29 radiocarbon dates across all samples, this is the only fraction removed as a measurement outlier, i.e. not associated with potential low temperature contamination in the sample. Finally, for TTK011Li, all dates were in statistical agreement. However, to be prudent, because TTK011Li displayed lower temperature ($<$ 600 °C) contamination that was high (but much lower than TTK009Li) the first fraction

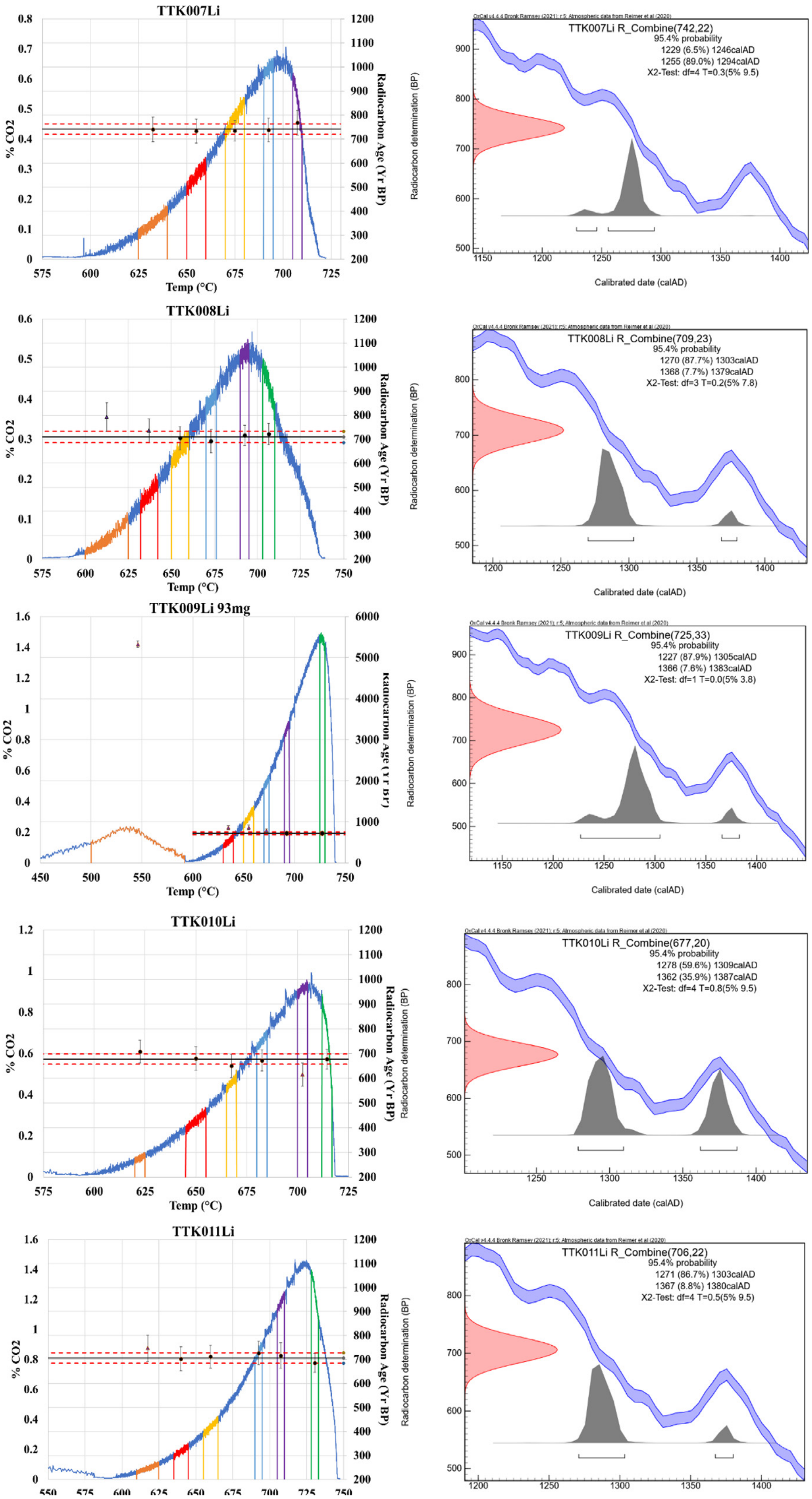

Fig. 2. Left - Ramped pyrolysis age-temperature curves for Turku Cathedral Lime lumps (top to bottom – TTK007Li, TTK008Li, TTK009Li, TTK010Li, TTK011Li). Temperature fractions for capture of CO_2 indicated by coloured lines. Radiocarbon dates presented with 1σ uncertainty. Black solid line = weighted mean of radiocarbon dates selected to be combined (see text, samples excluded are marked with a triangle). Red dashed line = 1σ uncertainty on weighted mean date. Right – corresponding calibrated ages of the combined radiocarbon dates for each sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Ramped pyrolysis radiocarbon dating results for Turku Cathedral first Sacristy lime lumps. For each sample the combined radiocarbon date is also presented together with the fractions/dates used.

Sample ID	Initial Mass (mg)	Fraction	Lab. ID	Temp. Range (°C)	Collected Mass (mg)	$F^{14}C$	σ	Age (Yr BP)	σ (Yr BP)
TTK007Li	46	F1	UBA-47707–1	625–640	0.40	0.9120	0.0058	740	51
		F2	UBA-47707–2	650–660	0.46	0.9127	0.0057	734	50
		F3	UBA-47707–3	670–680	0.58	0.9125	0.0048	735	42
		F4	UBA-47707–4	690–695	0.36	0.9122	0.0056	738	50
		F5	UBA-47707–5	705–710	0.42	0.9088	0.0058	769	51
							R_Combine (F1-F5)	**742**	**22**
							χ^2 (df=4)	***T* = 0.3 (5%=9.5)**	
TTK008Li	48	F1*	UBA-47706–1	600–625	0.38	0.9061	0.0067	792	60
		F2#	UBA-47706–2	632–642	0.32	0.9125	0.0055	735	49
		F3	UBA-47706–3	650–660	0.42	0.9161	0.0056	704	49
		F4	UBA-47706–4	670–676	0.40	0.9175	0.0055	691	49
		F5	UBA-47706–5	690–695	0.40	0.9148	0.0048	715	42
		F6	UBA-47706–6	703–710	0.46	0.9141	0.0050	721	44
							R_Combine (F3-F6)	**709**	**23**
							χ^2 (df=3)	***T* = 0.2 (5%=7.8)**	
TTK009Li	93	F1*	UBA-47705–1	500–592	0.26	0.5153	0.0050	5326	79
		F2*	UBA-47705–2	630–640	0.32	0.8979	0.0056	865	50
		F3*	UBA-47705–3	650–660	0.48	0.8979	0.0058	865	52
		F4#	UBA-47705–4	670–675	0.48	0.9066	0.0055	788	49
		F5	UBA-47705–5	690–695	0.60	0.9136	0.0050	726	44
		F6	UBA-47705–6	725–730	0.68	0.9138	0.0055	725	48
							R_Combine (F5-F6)	**725**	**33**
							χ^2 (df=1)	***T* = 0.0 (5%=3.8)**	
TTK010Li	56	F1	UBA-47731–1	620–625	0.36	0.9157	0.0052	707	46
		F2	UBA-47731–2	645–655	0.48	0.9189	0.0053	679	47
		F3	UBA-47731–3	665–670	0.38	0.9223	0.0054	650	48
		F4	UBA-47731–4	680–685	0.38	0.9198	0.0049	671	43
		F5*	UBA-47731–5	700–705	0.58	0.9263	0.0054	615	47
		F6	UBA-47731–6	712–717	0.50	0.9192	0.0046	677	40
							R_Combine (F1-F4,F6)	**677**	**20**
							χ^2 (df=4)	***T* = 0.8 (5%=9.5)**	
TTK011Li	94	F1#	UBA-47709–1	610–625	0.30	0.9112	0.0062	747	54
		F2	UBA-47709–2	635–645	0.36	0.9162	0.0057	703	50
		F3	UBA-47709–3	655–665	0.56	0.9152	0.0054	712	48
		F4	UBA-47709–4	690–695	0.54	0.9135	0.0056	727	50
		F5	UBA-47709–5	705–710	0.54	0.9147	0.0060	716	53
		F6	UBA-47709–6	728–733	0.80	0.9182	0.0045	685	39
							R_Combine (F2-F6)	**706**	**22**
							χ^2 (df=4)	***T* = 0.5 (5%=9.5)**	
TTK008W			AAR-34438			0.9139	0.0062	**723**	**54**

*Statistical outlier.

#Not an outlier but either a fraction that follows an outlier associated with lower temperature contamination or a first fraction of a sample with high lower temperature contaminant - conservatively removed.

(F1) was removed, leaving five samples in agreement that could be combined.

The radiocarbon date of the wood/straw sample TTK008W is presented in Table 1 and the calibrated result is presented in Fig. 3 *(left)*.

4.2. Combine Dates and calibrated ages

In total 8 of 29 dates were removed from subsequent analysis involving combined dates. Seven of these (four from TTK009Li) were associated with low temperature contamination (see discussion). One was a measurement outlier. The 21 remaining dates were in statistical agreement and could be combined, providing a combined radiocarbon age and associated calibrated age for the first sacristy (Fig. 3).

For each sample, the results provide a calibrated age that is predominantly in the last few decades of the 13th century, typically 1260–1300 cal. AD. When combined across all samples the result is a radiocarbon age of 709 ± 11 yr BP (χ^2-test: df = 20, T = 7.1, 5% = 31.4) that calibrates to 1276–1296 cal. AD (95.4%), providing a robust date for the lime lumps and construction of the first sacristy. This, and indeed the calibrated ages of the combined fractions for each sample, finds excellent agreement with the date from wood/straw (Fig. 3, *left*).

4.3. Bayesian modelling and construction duration

Bayesian modelling results, exploring the building dynamics of the first Sacristy are presented in Fig. 4 and Fig. 5. Fig. 4 presents *Model 1* (see discussion) where the dates are unordered, i.e. no

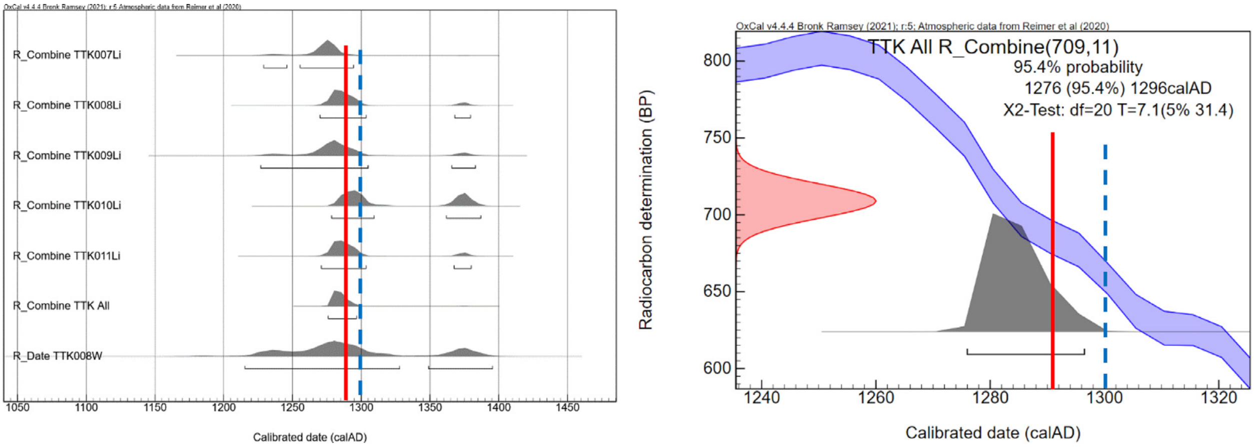

Fig. 3. Left - Calibrated combined age for each individual sample together with calibrated combined age across all samples (TTK All) and date of wood/straw sample TTK008W. Right- Calibrated combined age of all samples. Solid vertical lines: Red solid – AD 1291 date for the election of a new Bishop (Magnus I) in the cathedral sacristy (Dip. Fenn. 201 [32]). Blue dashed: Date of the cathedral sacristy from historical sources [31]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

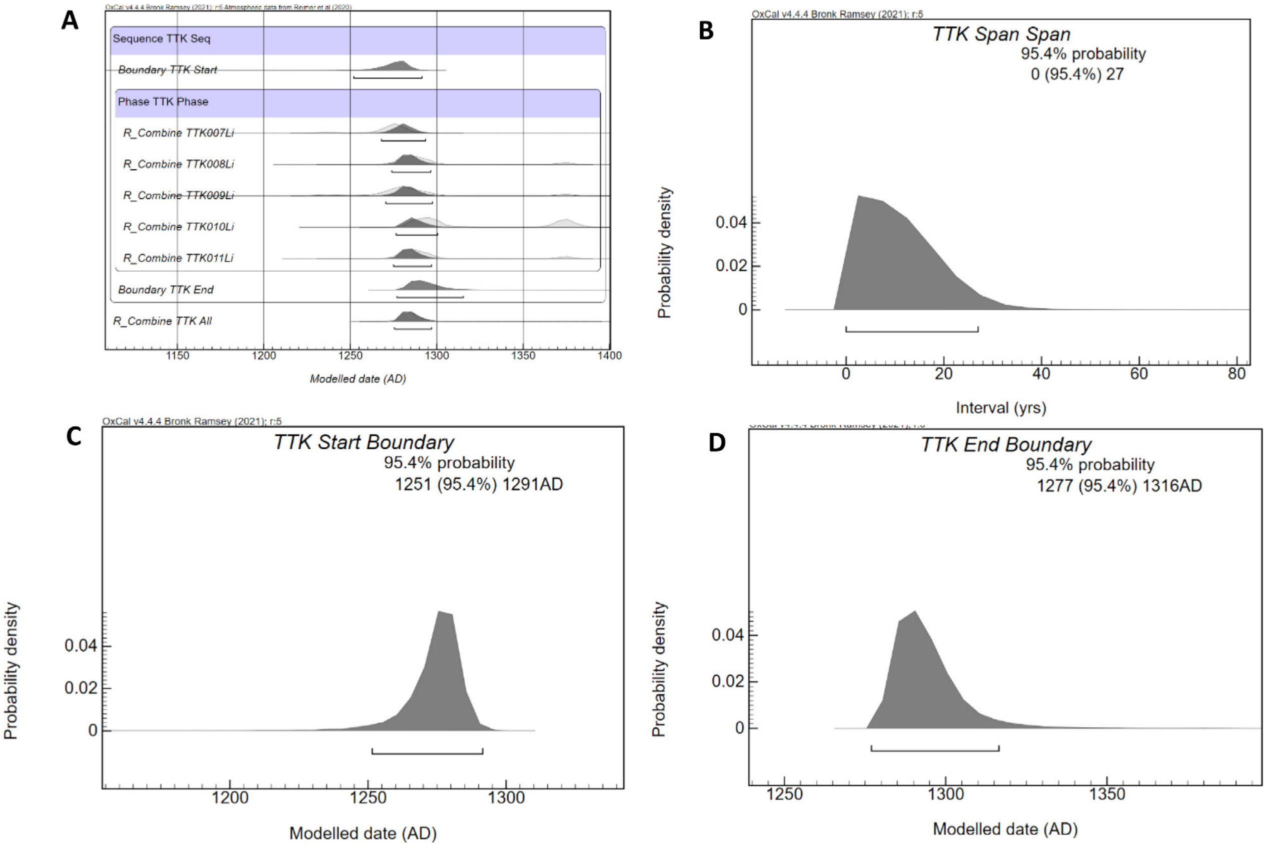

Fig. 4. (A) Bayesian modelling, Model 1, of the construction of Turku Cathedral sacristy using OxCal4.4 and the following priors: (1) a uniform probability distribution for the phase; (2) the samples correspond to a single phase of construction. (B) Modelled span of the construction phase. (C, D) Modelled start and end of the construction phase.

chronological sequencing information is available; in this case a simple *Sequence* and *Phase* model, with *Start* and *End* boundaries, was applied. Fig. 5 presents *Model 2* where the dates are treated as ordered, i.e. that there is a known construction sequence associated with the dates providing a relative chronology. In this case, the dates are arranged in a sequence based on their height in the sacristy wall (see discussion).

The results from both models are very similar and, with that, the interpreted building dynamics such as the start of construction (*Start*), end of construction (*End*), and duration of construction (*Span*), are relatively invariant to the model and assumptions applied (discussed below). *Model 1* provides a start of construction of 1251–1291 cal. AD (95.4%), an end of construction 1277–1316 cal. AD (95.4%), Fig. 4 *(C,D)*, and a duration of construction of 0 – 27

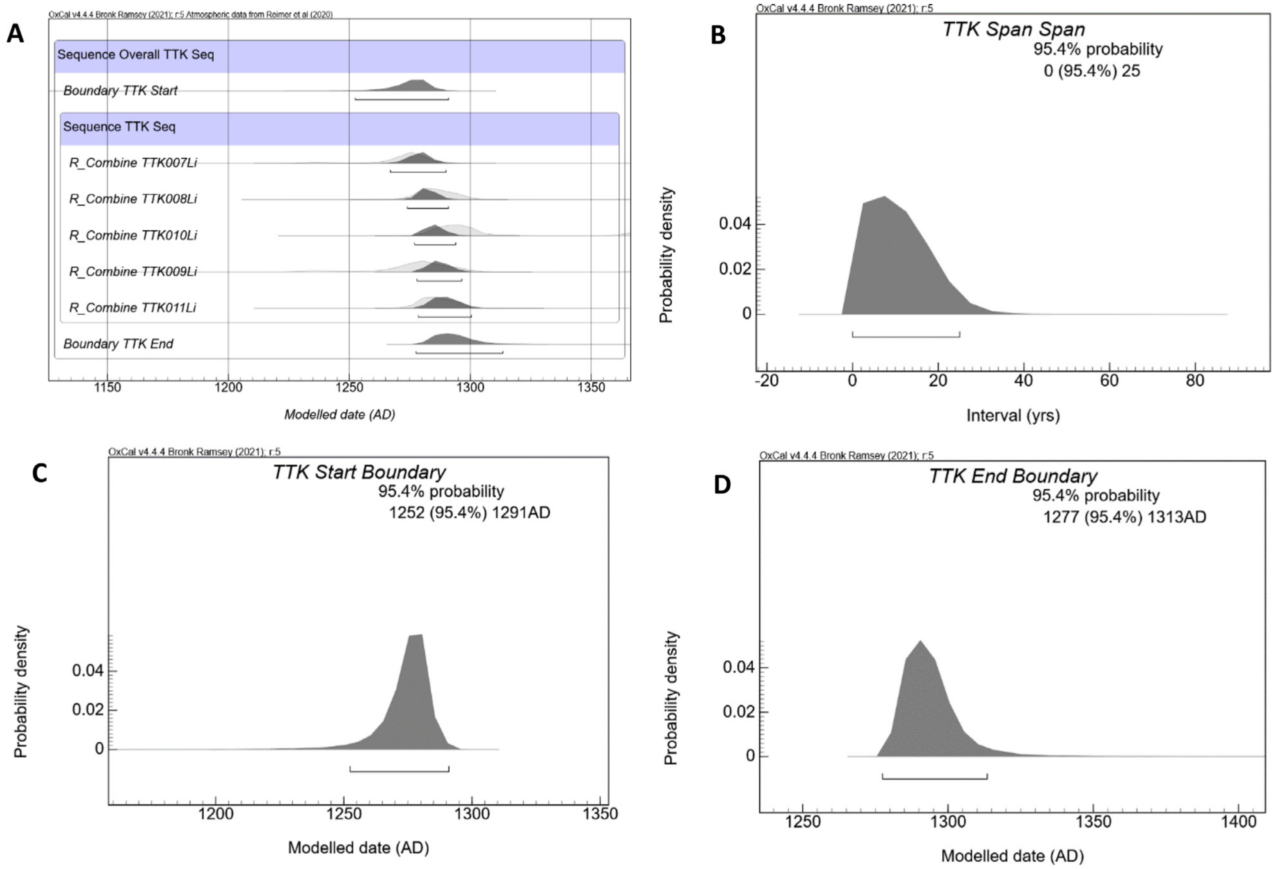

Fig. 5. (A) Bayesian modelling, Model 2, of the construction of Turku Cathedral sacristy using the Sequence function in OxCal4.4 and the following priors: (1) a uniform probability distribution for the phase; (2) the samples are chronologically sequenced according to their vertical position in the south gable, i.e. the coursing was carried out layer by layer. (B) Modelled span of the construction phase. (C, D) Modelled start and end of the construction phase.

years (95.4%), *Figure 4(B)*. Assuming sequencing of dates, based on sampling height, makes little difference to these values (*Model 2*) with adjustments on the order of only 1–3 years (Fig. 4).

5. Discussion

5.1. Ramped pyrolysis of lime lumps

Of the five samples analysed, four (TTK007Li, 008Li, 010Li, 011Li) produced a plateau of four/five radiocarbon dates that were in excellent statistical agreement *(*Fig. 2 *(right)*, Table 1) emphasizing the internal consistency per sample and with that the consistency of the RP method on a single run. The strong statistical agreement within a sample was also the case across all samples with 21 radiocarbon dates across 5 samples in statistical agreement (Table 1, Fig. 3). This confirms that all samples are from the same construction phase and demonstrates a high level of repeatability with the RP method when applied to suitable material.

Despite this, contamination was present for some samples at the lowest temperatures, notably TTK009Li, with soaking at 600 °C for 20 min insufficient for its complete removal. This contamination is associated with a broad thermal decomposition component with a peak at approximately 540 °C and an age of 5326 yr BP (Table 1, F1 of TTK009Li, note that this is a minimum age because some of the lower end of the lime lump carbonate thermal decomposition curve will be contributing to the higher end of the temperature range trapped for F1). The source of this contamination is unclear, but the peak temperature is higher than what would be expected for simple organic matter (wood/straw) where 200–400 °C would be expected. The higher temperature peak is more likely to be the case for charred material, e.g. residual flecks of charcoal/coal or fuel, used to produce the lime, that became embedded on the surface of the lime lumps. Given the age, this seems very unlikely for charcoal unless the charcoal/graphite had adsorbed or absorbed CO_2 from the thermally decomposing limestone during the original lime burning. It is also unlikely to be coal as there is no evidence of it as a fuel source in that area at that time. Another possible explanation is that the lime was produced from marbles from SW Finland that are known to contain small grains of graphite. However, had this graphite survived the original firing associated with lime production, it then seems unlikely that it would thermally decompose under the conditions of the current RP measurements (pyrolysis).

Unfortunately, characterization (e.g. FTIR, XRD that would be carried out on binder prepared from bulk as per [14]) was not conducted on the samples. Because the quantity of material available per sample was limited and the carbon content of each sample was unknown at the outset, retaining all material to optimize the number of RP fractions and quantity of CO_2 trapped was prioritized; this also served to minimize the risk of introducing contaminants or inducing secondary crystallization by breaking up the sample and exposing unreacted surfaces (e.g. if portlandite was present). Focused characterization studies on more lumps would be necessary to elucidate the source of this contamination further.

Regardless of this, for four of the five samples the impact of this low temperature contamination was negligible or restricted to the 1st fraction only. Subsequent fractions were sometimes removed out of caution, but had they not been removed it can be shown that they would have had limited impact on the combined ages.

Without considering the accuracy of the results, the set of mortar dates presented is one of the most consistent and statistically robust sets of mortar dates for a built structure in the published literature.

5.2. Turku cathedral's earliest stone-built phase

Each sample provides a set of dates and a combined age with, in general, a large mode of the probability distribution spanning the last 3 decades of the 13th century AD. This finds remarkable agreement with historical resources (Fig. 3, *left*), particularly the 1291 AD date for the election of a new bishop that is associated with the sacristy (Diplomatarium Fennicum: 201 [32]). For some, not all, samples there is a smaller probability of a late 14th century date (typically $<$ 9% probability) but this is no longer the case when dates across the five different samples are combined. Combining the dates is considered valid for three reasons: 1) the samples are all taken from within a very small area of 2.1m^2 that is likely to have been constructed in a short window of time; 2) delayed hardening effects should be negligible for lime lumps (discussed earlier); 3) the level of statistical agreement observed would not be the case unless samples were contemporary. When the dates are combined construction of the earliest stone-built phase of Turku Cathedral is firmly set in the last two decades of the 13th century, 1276–1296 cal. AD (95.4%, df=20, T = 7.1, 5%=31.4).

This result is not only in complete agreement with the historical dating (Dip. Fenn. 201 [32]) but also in agreement with the date on organic material (wood/straw), TTK008W, that was found embedded in the same bulk mortar that TTK008Li was taken from (Table 1, Fig. 3). Note, this fragment of organic matter was very small and not characterized so the possibility of it being 'old' wood cannot be ruled out. Despite this, its contemporaneity with the lime lump and historical data is apparent.

Previously, the structure was also dated using the sequential dissolution approach on both lime binder from bulk samples of mortar (TTK009B, TTK010B, [8]) and a lime lump sample (TTK008Li, [12]). The present work agrees well with these results, particularly the interpreted combined age for TTK009B and TTK010B of 681 ± 9 yr BP (1282–1302 cal. AD (78.3%), 1369–1379 cal. AD (17.1%), recalibrated using IntCal20). The results for TTK008Li from Lindroos et al. [12] appears a little younger, 659 ± 18 yr BP (1285–1318 cal. AD (43.4%) and 1359–1389 cal. AD (54%), recalibrated using IntCal20) but there is still good overlap with the calibrated age probability distributions in the current work.

In relation to historical sources, there is also a record from 1329 (Dip. Fenn. 369 [32]) that is worth commenting upon in relation to the current dating of the sacristy. This record refers to the donation of a "mountain of limestone" to the cathedral in 1329, to "commemorate the souls of their parents". Turku and its cathedral were plundered by Novgorodians in 1318 (Dip. Fenn. 286 [32]); it therefore seems plausible that this mountain of limestone was donated for the cathedral's repair, supporting a significant portion of the cathedral having been earlier constructed.

It is worth emphasizing that in all of the above discussion what is actually being dated is the carbonation of the lime lumps from the sacristy, most likely in the lime putty prepared immediately before construction [9,10]. This is technically not the same as when the stone blocks were laid but it is difficult to envisage a situation where the two are not contemporary, at least annually.

In consideration of all of the above, the dates from this work provide robust and reliable dating of the first sacristy of Turku Cathedral to the last few decades of the 13th century. These results highlight the potential of RP radiocarbon dating of lime lumps as a tool for dating lime mortared constructions. It should be stated that running as many samples and fractions as in the present work should not, in general, be necessary now that the technique is becoming better validated and established. Two well-behaved samples with suitable age-temperature curves and fractions in statistical agreement ($\geq$ 3 radiocarbon dates) and agreement between samples would be sufficient.

5.3. Building dynamics and chronologies

The primary objective of the Bayesian modelling analysis in this work is to demonstrate how some general approaches for exploring building dynamics using mortar dating can be carried out. The Turku results, while far from ideal, are useful for illustrating the methods and highlighting the limited application of these approaches unless the samples are well separated chronologically.

In general, where samples have been taken from multiple locations from a building or building phase, mortar dating can provide a potential tool for exploring the dynamics of how the building was constructed. For Turku Cathedral, the samples were taken from a small area (3.5 m x 0.6 m) of a single wall (south gable) of an already relatively small structure (9 m x 9 m). As such, it is reasonably safe to assume that the mortars from these samples are relatively synchronous, probably within 1 year, and can be combined as carried out above without the need for further modelling. Regardless, we will use this set of results to explore and illustrate alternate interpretations and Bayesian modelling approaches that might be more suitably applied to other buildings. These models are also instructive for examining how robust the dating of this structure is under different assumptions regarding its building dynamics.

5.3.1. Model 1: dynamics of construction for unordered samples

For a series of radiocarbon dates on mortar samples from a building that are believed to come from a single phase of construction, but where there is uncertainty around the chronological relationship between the samples (e.g. which wall/part of the building was started first), a simple Bayesian model using the *Sequence, Phase* and *Span* functions in *OxCal 4.4 (Bronk Ramsey 2009)* can be used. This is illustrated in Fig. 4 where a uniform distribution is assumed as a prior for the phase; this is equivalent to assuming that construction was carried out at a constant rate from start to completion of the structure (alternative underlying distributions should be tried where there is doubt over the suitability of the default uniform distribution, used here for illustrative purposes). This model provides estimates of when the construction phase was likely to have commenced (Fig. 4, *C)* and finished (Fig. 4, *D*), as well as the span (Fig. 4, *B*) or duration over which construction was carried out. Applied to the first Sacristy, we have a *span* of 0–27 years (95.4%) and *Start* and *End* boundaries that allow for a maximum period of 1251 – 1316 cal. AD for start and end of construction (taking the earliest and latest values for the *Start* and *End* posterior (95.4%) distributions). The narrow duration and ranges are unsurprising given the tight agreement between all the radiocarbon dates obtained for the Sacristy. However, if we were dealing with a much larger structure, with samples taken from a broader range of locations, this same model could still be applied and provide a useful and conservative interpretation for its construction chronology.

5.3.2. Model 2: dynamics of construction for ordered samples

Where there is prior information about the chronological ordering of samples, then this can be integrated into a Bayesian model to further refine the dates. If, for example, the stonework in a multistorey building is constructed course by course over a prolonged period ($>$ annual), then the relative vertical positions of samples can be used to define a *Sequence* for the samples in a Bayesian model. For example, the samples in the current work were taken from different vertical positions on the south gable of the sacristy (TTK007Li, TTK008Li, TTK010Li, TTK009Li, TTK011Li at 1.1 m, 0.9 m, 0.85 m, 0.6 m, 0.5 m, respectively, measured down from the secondary wooden floor). While it seems highly implausible that these samples are not all broadly contemporaneous, a *Sequence* based model (Fig. 5) is useful not only to illustrate how the model might be applied for more realistic scenarios, but also to test the robustness of the assumption that the sacristy was constructed over a very short period. From the output of the *Span* and the *Start* and *End* boundary functions (Fig. 5, *B, C, D,* respectively), it can be observed that there is little shift in the results relative to the simpler phase-based Model 1. Therefore, the construction duration estimated of 0–27 years (95.4%) is relatively robust and invariant with respect to the model used (*Model 1 or Model 2*) and the sacristy was constructed over a relatively short period.

As expected, the models above are not especially enlightening for the current site, but the approaches described will be of use elsewhere at sites where samples are less tightly constrained chronologically.

6. Conclusion

Ramped pyrolysis radiocarbon dating was successfully carried out on a series of lime lump samples extracted from Turku Cathedral's first sacristy. Four of the five samples produced well-behaved age-temperature curves and a series of radiocarbon dates that were in excellent statistical agreement and combinable. One of the five samples featured strong lower temperature sources of contamination but was better behaved in the higher temperature range with the two highest temperature fractions also in agreement and combinable. The calibrated combined dates for each sample found excellent agreement with historical sources, earlier mortar dating work, as well as with the radiocarbon date on organic matter found in the bulk mortar one of the lime lump samples was also taken from. Statistical agreement between all samples was also excellent, allowing for the combining of 21 radiocarbon dates across 5 samples and a calibrated age of 1276–1296 cal. AD (95.4%) that again was in excellent agreement with historical sources, earlier mortar dates and the organic material date.

Bayesian models were also presented that illustrate how basic construction dynamics (start, end, duration of construction) can be examined using mortar dates, particularly where the radiocarbon dates obtained are unordered or ordered (i.e. where the relative chronology of samples is unknown or known). The modelled results are shown to be of limited use to Turku where the underlying chronology is already very tightly constrained but the general approach will be of use elsewhere at more suitable sites where there is greater chronological separation between samples.

Overall, the work highlights that the ramped pyrolysis technique, applied to well selected material, is accurate, precise, and repeatable. The results presented make Turku Cathedral's first Sacristy arguably the most securely mortar dated structure in the published literature and validate the future use of ramped pyrolysis as a dating tool for lime lumps extracted from bulk mortar.

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