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TITLE

Comparison of thermal decomposition and sequential dissolution – Two sample preparation methods for radiocarbon dating of lime mortars

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Mortar dating, radiocarbon dating, sequential dissolution, thermal decomposition, preheating

ABSTRACT

Dating lime mortar samples using the radiocarbon method can be difficult. This is because the contamination is similar to the primary dating material ($CaCO_3$) and consequently difficult to remove. Mortar can also have late-in-formation pyrogenic carbonate from interactions with the environment after the initial hardening phase, such as recrystallization, fire damage or delayed hardening. When radiocarbon dating a system of primary dating material, contamination and late-in-formation pyrogenic carbonate, one approach is multi-fraction dating with conclusiveness criteria. If a sample has sufficient contamination or late-in-formation pyrogenic carbonate, the criteria evaluate the result inconclusive. To improve inconclusive results from such samples, this study investigates sample preparation by thermal decomposition. Here samples that were inconclusively dated by the authors' traditional method, sequential dissolution with 85 %

phosphoric acid, are investigated further. This study finds that CO_2 thermally decomposed at low temperatures contains some late-in-formation pyrogenic carbonate. By rejecting CO_2 decomposed at low temperatures, Kastelholm castle and Kimito church in Finland are conclusively and accurately dated. Furthermore, a preheating method removes some late-in-formation carbonate, but not enough for a conclusive result. Finally, thermal decomposition finds difficulty in discerning binder carbonate from limestone and marble contamination.

INTRODUCTION

Radiocarbon dating of lime mortar is a method contributing to absolute dating in history and archaeology (Hale et al. 2003; Marzaioli et al. 2011; Ortega et al. 2012; Ringbom et al. 2014). Conclusive radiocarbon dating of a mortar sample determines the event of mortar hardening, which relates to the time of construction (Labeyrie and Delibrias 1964). For archaeological sites with mortared stone structures, mortar can be abundant and in a context that can be associated with the site's historical buildings (Heinemeier et al. 2010). Besides lime mortar, the presented radiocarbon methodologies are relevant for further anthropogenic carbonates such as ash, lime plaster and lime concrete (Toffolo et al. 2017; Toffolo et al. 2020). This study's samples are lime mortars, and the materials and methods section explains the selection of samples.

Production of lime mortar involves firing limestone, mainly made of calcite ($CaCO_3$), at temperatures near or above 900 °C, where it thermally decomposes to form quicklime (CaO). The quicklime is slaked with water to produce slaked lime ($Ca(OH)_2$). Finally, one mixes the slaked lime with an aggregate, typically sand, and wet mortar is ready to be applied as filling material between stones of the structure to be built. As wet mortar hardens, the contained slaked lime

consumes atmospheric CO_2 and binds it as $CaCO_3$, see equation 1. In doing so, the $CaCO_3$ of lime mortar binder stores the atmospheric $^{14}CO_2$ signal from the time of hardening, and this can potentially be radiocarbon dated (Labeyrie and Delibrias 1964; Stuiver and Smith 1965; Baxter and Walton 1970).

$$Ca(OH)_2(s) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l) \qquad (1)$$

Radiocarbon dating of lime mortar has challenges such as geological carbonate, recrystallization, fire damage, delayed hardening and layered double hydroxide compounds (Labeyrie and Delibrias 1964; Stuiver and Smith 1965; Baxter and Walton 1970; Sonninen and Jungner 1989; Heinemeier et al. 1997; Artioli et al. 2017; Ricci et al. 2020). Geological carbonate is several orders of magnitudes older than the ^{14}C half-life, and thus contains essentially no ^{14}C atoms. Contamination with geological carbonate can shift a mortar's ^{14}C concentration below the hardening's ^{14}C concentration. During production of mortar, the sand used as aggregate may contain grains of limestone, or limestone fragments may survive an incomplete burning of lime. In these ways, a mortar sample may have an inherent geological carbonate contamination. Recrystallization, fire damage, delayed hardening and layered double hydroxide compounds can shift a mortar's ^{14}C concentration above the hardening's ^{14}C concentration. In the presence of water, calcium carbonate is not entirely stable, and a mortar's binder may recrystallize and incorporate young CO_2 from the atmosphere. Fire damage may cause de-carbonation followed by re-activation of the binder and capture of new atmospheric CO_2 (Heinemeier et al. 2010; Lindroos et al. 2012). Delayed hardening can happen, if mortar has low permeability for CO_2 or if samples come from deeper parts in a construction. It introduces a delay between the time of construction and the time of hardening, and

it can leave unreacted calcium hydroxides (portlandite) so the sample is alkaline and absorbs modern CO_2 when sampled (Sonninen and Jungner 1989; Heinemeier et al. 1997; Michalska et al. 2017). Layered double hydroxide (LDH) compounds can form from magnesium phases in dolomitic lime mortar and ancient hydraulic mortars such as pozzolana and cocciopesto (Massazza 2003; Ponce-Anton et al. 2018; Ricci et al. 2020). LDHs can exchange carbonate anions with the atmosphere throughout the mortar's life and introduce young carbon dioxide (Artioli et al. 2017; Ponce-Anton et al. 2018; Ricci et al. 2020). This text uses the term, late-in-formation pyrogenic carbonate, to collectively refer to carbonate associated with recrystallization, fire damage, delayed hardening, alkalinity or LDHs.

Since the 1960's, the radiocarbon community has researched lime mortar as a material for radiocarbon dating (Labeyrie and Delibrias 1964; Stuiver and Smith 1965; Baxter and Walton 1970; Folk and Valastro 1976). In the 1990's and 2000's the sequential dissolution method develops, and it applies a single injection of 85% phosphoric acid to release the sample's carbonate as CO_2. Extraction of CO_2 happens in multiple fractions throughout dissolution, and several fractions are radiocarbon dated by accelerator mass spectrometry (AMS) (Van Strydonck et al. 1986; Heinemeier et al. 1997; Ringbom et al. 2014). Sequential dissolution is explained further in the associated subsection in materials and methods. Here conclusive dating results follow from conclusiveness criteria that assert agreement among multiple CO_2 fractions (Heinemeier et al. 2010; Lindroos et al. 2011; Ringbom et al. 2014). The discussion section describes conclusiveness criteria further. Heinemeier et al. (2010) compiled a successful study of lime mortars from the interior of Medieval churches. Here, 124 out of 150 samples were conclusive, and 75 out of 79 samples agreed with independent age control. There are other important approaches to radiocarbon dating of pyrogenic carbonates, and some are based on separation of a suitable dating fraction, e.g. by density separation, cryogenic-breaking, ultrasound, suspension, sedimentation or thermal treatment

(Marzaioli et al. 2011; Ortega et al. 2012; Toffolo et al. 2017; Ponce-Anton et al. 2018; Ricci et al. 2020; Toffolo et al. 2020).

Mortar is a challenging material to radiocarbon date, and sequential dissolution and other preparation methods occasionally obtain inconclusive results, especially when the above challenges are abundant (Lichtenberger et al. 2015; Hajdas et al. 2017; Michalska et al. 2017; Ponce-Anton et al. 2018).

Recently, there has been an interest in sample preparation by thermal decomposition for pyrogenic calcium carbonate, such as ash or lime mortar (Toffolo et al. 2017; Ricci et al. 2020; Toffolo et al. 2020). Thermal decomposition was actually the initial method used by Labeyrie and Delibrias (1964), but soon after acid hydrolysis became more prevalent (Stuiver and Smith 1965). The authors of this article have most often prepared mortar samples by sequential dissolution. Inspired by recent work, sample preparation by thermal decomposition revisits several challenging mortar samples. This contributes to methodological development of thermal decomposition as a preparation method for mortar dating. More broadly, it contributes to expanding the methods available to mortar dating, which may improve the conclusiveness when encountering the challenges described above. For example, sequential dissolution obtained inconclusive results for nearly all samples presented in this study, and this motivates other preparation methods.

MATERIALS AND METHODS

Samples

134 The samples come from Åbo Akademi's collection. There are three priorities when choosing
135 samples. First, samples must have a known historical context such that results from sample
136 preparation can be evaluated. The actual construction time is not known from historical sources, but
137 previous dating has yielded ages that fit into the historical context, see Table 1. Second, samples
138 must have one of the recurring challenges described in the introduction, so different preparation
139 methodologies can investigate different challenges. Third and last, samples must have previous
140 dating by sequential dissolution to compare with thermal decomposition.

141 To investigate geological carbonate's influence on ^{14}C concentration in mortar this study presents
142 mortar samples TTK005 and TTK006 from Turku cathedral in SW Finland and J13-ESM-1 from
143 Jerash, Jordan.

144 The sample TTK006 comes from the pentagonal choir of Turku cathedral. Mortar dating was done
145 in 2007, and results are presented in Lindroos et al. (2011; 2012; 2018). The sample was
146 problematic because of abundant marble contamination, which may have masked other types of
147 contamination. Sample TTK005, see Table 1, is from the same construction phase, and it has been
148 dated in five CO_2 fractions from the bulk mortar and three CO_2 fractions from a lime lump within it
149 (Lindroos et al. 2018). Sample TTK004 and TTK004Li are likewise a bulk mortar and a lime lump
150 within it and taken close to sample TTK006. They were dated in 2017 in Zürich in 3 CO_2 fractions
151 each (see Table 1), and the results have not been published earlier. The Pentagonal Choir is part of
152 the original cathedral inaugurated in 1300 AD (Gardberg et al. 2000). It may have been renovated
153 after destruction of the cathedral in 1318 AD (Gardberg et al. 2000; Lindroos et al. 2018).

154 The sample J13-ESM-1 comes from a water pipe cover in the ancient city Jerash, and Lichtenberger
155 et al. (2015) discuss the sample further. Mortar dating with sequential dissolution was tried in 2015,
156 and it proved difficult because of limestone aggregate. Lichtenberger et al. (2015) reports a charcoal

157 sample embedded in the mortar, usable for age control and radiocarbon dated to (1723±25) ^{14}C
158 years BP.

159 To investigate the contribution to a mortar's ^{14}C concentration from late-in-formation pyrogenic
160 carbonate, this study presents mortar sample Kastel09 from Kastelholm castle in SW Finland, lime
161 lump Kimito004Li from Kimito (Kemiö in Finnish) church in SW Finland and mortar sample
162 Merida003 from Mérida amphitheater in W Spain.

163 Kastelholm is first mentioned in historical documents in 1388 AD (Hausen 1910). A trial to date the
164 structurally oldest mortar with radiometric methods was made in 1985 (Sonninen and Jungner
165 1989). Lindroos et al. (2020a) performed ^{14}C dating prepared by sequential dissolution of sample
166 Kastel09, and they present calendar date spans 1285-1312 AD with 41.5 % and 1359-1388 AD with
167 53.9% probability. The age span 1285-1312 AD is interesting, because the nearby church of Jomala
168 is from the 13th century AD (Ringbom et al. 2011). Other samples show late-in-formation pyrogenic
169 carbonate either from alkalinity or fire damage. As an example of this sample Kastel10 is presented,
170 which Lindroos et al. (2020a) also dated with sequential dissolution. We make thermal
171 decomposition preparation of sample Kastel09, which is the least alkaline and has the least
172 inhomogeneous CO_2 fractions by sequential dissolution.

173 Sample Kimito004Li is a lime lump in a mortar from the attic of the sacristy in Kimito church, and
174 it yielded an inconclusive result with sequential dissolution. On stylistic grounds, the famous mason
175 *Petrus Murator* is considered the mason who vaulted the nave of Kimito church (Nikula 1975). It is
176 documented that Petrus Murator was payed for finishing the vaulting of Turku cathedral in 1466
177 AD (Hausen 1890; Nikula 1973), and the nave of Kimito church was most likely vaulted before
178 1466 AD (Nikula 1975). Structurally, the sacristy is the oldest part of Kimito church, and it is
179 stylistically attributed to the first half of the 15th century (Nikula 1975). Radiocarbon dating of

charred wood planks from the nave yielded variable ages from 889 AD to 1620 AD, see samples Kimito002W, Kimito003W and Kimito013W in Table 1. Furthermore, there are coin-finds from the early 14th century AD at Kimito church (Nikula 1975).

The Mérida Amphitheatre is either Augustan, early 1st century AD, or Flavian, late 1st century AD (Capello and Galán 1995; Mateos 2001). Mortar dating results from Mérida, including sample Merida003, have been published and suggest a late Flavian age (Hale et al. 2003; Ringbom et al. 2006; Lindroos et al. 2020b). The Flavian dynasty spans from 69 AD to 96 AD (Jones et al. 2002). The Merida samples are very hard, have dolomitic chemistry, delayed hardening and shows abundant late-in-formation pyrogenic carbonates that dissolves before the binder carbonate (Lindroos et al. 2020b).

TableSamplesAndDates

Sample pretreatment

The sample pretreatment starts by gently crushing a sample with pliers (Heinemeier et al. 2010; Lichtenberger et al. 2015; Lindroos et al. 2018). The crushing is intentionally careful, i.e. not using too much force, as this can produce small grains of aggregate material, which may contain contaminating limestone (Heinemeier et al. 2010). Sieves with meshes from 100-500 µm dry sieve the mortar into several grain size fractions (Van Strydonck et al. 1986). The dry sieving takes approximately 20 minutes using a mechanical sieve shaker, and the shaking promotes further crumbling of soft binder material. The grain size fraction <100 µm is wet sieved into several

fractions from <20 µm to 100 µm. According to Heinemeier et al. (2010), grain size fractions <100 µm filter out large aggregate grains that may be contaminants, and this study uses these grain size fractions for thermal decomposition and sequential dissolution.

Characterization methods

Alkalinity screening, cathodoluminescence microscopy and thermal gravimetric analysis, are used to characterize the mortar samples. The characterization methods are presented below.

Alkalinity screening

Alkalinity is an indicator for late-in-formation pyrogenic carbonates (Labeyrie and Delibrias 1964; Ringbom et al. 2011; Lichtenberger et al. 2015). Roughly 10 ml of deionized water suspends roughly 200 mg of the 300–500 µm grainsize fraction. Strips of pH indicator paper and two drops of 2 % phenolphthalein in alcohol assess the samples' alkalinity. For alkaline samples, the phenolphthalein gives a strong purple color after 5 minutes, and alkaline samples are usually rejected for AMS dating. However, this study works with some alkaline samples to study late-in-formation pyrogenic carbonates.

Cathodoluminescence microscopy

223 The 46–75 µm grain size fraction is characterized with a stereomicroscope combined with a
224 Cambridge Image Technology Ltd (CITL) CL8200 MK4 cold cathode cathodoluminescence (CL)
225 device and a camera (Marshall 1988). In CL mineral grains with luminescence light up in specific
226 colors that enable mineral identification, e.g. limestone and marble are often bright orange-red
227 (Götze 2012; Al-Bashaireh 2013). If abundant grains of limestone or marble are identified by CL
228 the sample may have problems with geological carbonate. Such samples are usually rejected for
229 AMS dating, but this study works with some samples with geological carbonate. Though not done
230 in this study, CL with a polished sample surface can study late-in-formation pyrogenic carbonates
231 (Marshall 1988; Götze 2012).

232

233 Thermal gravimetric analysis

234

235 Before thermal decomposition, samples are characterized with thermal gravimetric analysis (TGA)
236 (Bakolas et al. 1998; Toffolo et al. 2017; Ponce-Anton et al. 2018). The analysis takes around 10
237 mg of the grainsize fraction 46–75 µm, and places it in a furnace equipped with a precision scale
238 and nitrogen atmosphere. At increased temperatures, an increasing fraction of the solid sample
239 thermally decomposes to gaseous products. TGA measures loss of sample weight as function of
240 temperature. This study uses the TGA instrument, Tainstruments SDT Q600, at the department of
241 Inorganic Chemistry at Åbo Akademi University. Notice that the TGA instrument cannot collect
242 CO_2 for radiocarbon dating, so the TGA is made on a small aliquot of the grain size fraction, and
243 the actual thermal decomposition for radiocarbon dating on a larger aliquot. The result from the
244 TGA method establishes the temperature interval where a mortar sample's carbonates thermally
245 decompose and release CO_2. This is important information when operating the temperature and CO_2

collection of the thermal decomposition preparation method (explained below). The result section on TGA elaborates further on different stages of mass loss during thermal decomposition of mortar samples.

Preparation methods

Sequential dissolution (SQ)

This project uses the well-tried sequential dissolution (SQ) method as comparison to thermal decomposition. In short, the method works by a single injection of excessive 85% phosphoric acid on a powder prepared from the sample (Ringbom et al. 2014; Lindroos et al. 2018). The pre-treatment section describes production of powders, and we use several grain size windows below 100 µm and lime lumps, see Table 1. Late-in-formation pyrogenic carbonate, binder carbonate and geological carbonate dissolve with different reaction rates, and contribute differently to different CO_2 fractions collected throughout the dissolution. For example geological carbonate dissolves more slowly, and its contribution increases in the later fractions of SQ. Ringbom et al. (2014) describe the SQ method in more detail.

Thermal decomposition (TD)

Figure 1 illustrates the experimental setup for sample preparation with thermal decomposition (TD). The system is similar to systems used for SQ, with the laboratory furnace replacing the dissolution reactor flask (Heinemeier et al. 2010; Ringbom et al. 2014). TD places the selected grain size fraction in a quartz tube and fixates it with a lump of quartz wool. A hose connects the quartz tube and the vacuum system. When the system's vacuum is sufficient, the furnace slowly increases the temperature of the sample. When the preparation's start-temperature is reached, the pressure gauge monitors the release of gaseous products from TD. Characterization by TGA establishes sample-specific start-temperatures, usually around 550-650 °C, where the mortar's carbonates start releasing CO_2. Other studies report TD of anthropogenic carbonate starting in the range 500-550 °C (Toffolo et al. 2017; Ricci et al. 2020). Chemistry literature describes the release of CO_2 by TD of calcium carbonate with equation 2, and that it happens at temperatures in range 680-875 °C (Murthy et al. 1994; Rao 1996; Karunadasa et al. 2019):

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g) \qquad (2)$$

FigureThermalSetup

When the amount of CO_2 is sufficient for AMS dating (in range 0.1 mgC - 1.0 mgC), liquid nitrogen freezes out a fraction and a blowtorch seals the fraction in a glass vial. The furnace is thermostat regulated, and it holds a set temperature. As long as the sample continues to release CO_2 the temperature is kept constant, and only when CO_2 release stops the temperature is carefully increased to resume TD. In this way, the early fractions contain CO_2 from sample phases that

thermally decompose at lower temperatures, while later fractions contain CO_2 from sample phases that thermally decompose at higher temperatures. This aligns with Toffolo et al. (2020) and Ricci et al. (2020) discussing TD of different mortar phases in different temperature ranges, for example organic phase up to 500 °C, LDH phase around 500-550 °C, pyrogenic carbonates (e.g. lime mortar binder) in the range 500-650 °C and marble in range 700-800 °C. In our TD preparation a typical start-temperature is around 550-650 °C, the temperature increments are around 10-20 °C, it takes 5-15 min to produce a fraction, and a sample is exhausted somewhere between 800-900 °C. As a variation sample Merida003 has start-temperature at room temperature, see the results section.

Calcite backgrounds are also thermally decomposed. The backgrounds are compiled to a background correction used for TD radiocarbon determinations (Donahue et al. 1990; Brown and Southon 1997; Toffolo et al. 2020).

Preheating followed by sequential dissolution (P+SQ)

Ricci et al. (2020) discuss a thermal treatment at 550 °C to break down the LDH structure and release the associated carbonate anions, e.g. in a magnesium-rich mortar. Inspired hereof, preheating followed by sequential dissolution (P+SQ) is attempted for sample Merida003, which is a dolomitic mortar somewhat similar to the magnesium-rich samples discussed by Ricci et al. (2020). The sample is preheated to 620 °C and the temperature is maintained for half an hour. This temperature was chosen for sample Merida003, because it is the lowest temperature producing enough CO_2 from preheating for a datable fraction. The sample then cools to room temperature while still in vacuum, see Figure 1. One then breaks vacuum, quickly transfers the sample to a

reactor flask in the SQ setup and reapplies vacuum. SQ then prepares the preheated sample as described in the materials and methods section on sequential dissolution.

Graphitization and AMS dating

Graphitization reactors convert the produced CO_2 fractions to graphite using hydrogen and an iron catalyst (Vogel et al. 1984). A pneumatic press presses the graphite into AMS-cathodes, and they are radiocarbon dated at Aarhus AMS Centre using the centre's HVE 1MV accelerator (Olsen et al. 2017), except for samples TTK004, TTK004Li and Kimito004Li by SQ that were dated in Zürich using the MICADAS machine at the Laboratory of Ion Beam Physics (Synal et al. 2007). For each sample multiple fractions are dated, so one can evaluate conclusiveness as described in the discussion. The online program OxCal 4.4 with the IntCal20 calibration curve calculates calendar date from radiocarbon determinations (Bronk Ramsey 2009; Reimer et al. 2020).

RESULTS

This section presents results from characterization and radiocarbon dating of the selected samples. Radiocarbon profiles illustrate the dated CO_2 fractions, and the incremental heating method in potassium-argon dating inspires the style of plotting in Figures 5-7 (Foland 1983). Each box illustrates a radiocarbon-dated CO_2 fraction. The horizontal extent of a fraction illustrates the cumulative CO_2 fraction released prior to the fraction and after the fraction. The vertical extend of a

fraction illustrates the 68 % confidence interval of the determined $F^{14}C$ (^{14}C age = -8033·ln $F^{14}C$). Text annotates the temperature reached during production of the corresponding TD fraction.

Characterization

Figure 2 shows CL images screening for limestone or marble aggregate that may carry geological carbonate contamination. Figure 2B shows the CL image for sample J13-ESM-1. Unfortunately, some types of limestone at Jerash do not have the typical red-orange luminescence (Al-Bashaireh and Hodgins 2012; Lichtenberger et al. 2015). Therefore, CL cannot rule out geological carbonate for sample J13-ESM-1. Alkalinity screens samples for late-in-formation pyrogenic carbonates, and Table 2 summarizes the characterization results for CL and alkalinity. There are potential problems with most samples, and usually one would reject these for AMS dating. However, the aim is to investigate TD for recurring challenges in mortar dating.

FigureCathodoluminescence

TableCharacterization

Figure 3 shows the results from TGA, where samples loose mass through TD. The samples show drying of pore space water and water of crystallization for temperature below 200 °C (Bakolas et al. 1998; Paama et al. 1998). From 200-600 °C, the TGA curves decrease further because of

352 decomposition of OH^- groups, which may come from unhardened slaked lime or hydraulic mortar
353 minerals, e.g. calcium silicate hydrate (Dodson 1990; Massazza 2003; Ponce-Anton et al. 2018).
354 Near 640-650 °C the TGA curves start a dramatic loss of weight, and much of this is attributed to
355 TD of $CaCO_3$ (Bakolas et al. 1998; Paama et al. 1998; Ponce-Anton et al. 2018). It is interesting
356 that this loss of mass starts below the temperature interval (680-875 °C) reported for TD of $CaCO_3$
357 in chemistry literature, and the discussion elaborates further on this. Just below 800 °C, the
358 samples' carbonate is exhausted and decomposition ceases. The TGA curves helps decide the start-
359 temperatures reported in the below sections on TD of selected samples.

360

361 FigureTGA

362

363 **Thermal decomposition backgrounds**

364

365 TD has its own background correction compiled from calcite backgrounds of various sample sizes.
366 In Figure 4, the measured $F^{14}C$ values are plotted as a function of inverse sample mass, and the
367 fitted function is used to correct TD radiocarbon determinations (Donahue et al. 1990; Brown and
368 Southon 1997; Toffolo et al. 2020).

369

370 FigureBackground

371

372 **Thermal decomposition and geological carbonate**

373

374 Figure 5A shows radiocarbon profiles with TD and SQ for sample TTK006 from Turku Cathedral,
375 Finland. There is also a radiocarbon profile with SQ for sample TTK005, and the two samples are
376 from the same wall. Interpolation of the IntCal20 curve calculates expected $F^{14}C$ for Turku
377 Cathedral (Reimer et al. 2020), and this yields $F^{14}C=0.9212\pm0.0013$ for the inauguration in 1300
378 AD and $F^{14}C=0.9254\pm0.0012$ for the destruction in 1318 AD.

379 The SQ profiles for TTK005 and TTK006 show decreasing $F^{14}C$ for later fractions, while the 1st
380 and 2nd fractions are closer to the expected $F^{14}C$. The geological carbonate identified by CL is a
381 probable explanation for late fractions with lower $F^{14}C$, see Table 2. The first minimum (3rd CO_2
382 fraction) in the SQ profile for sample TTK005 has been interpreted as aggregate marble
383 contamination, and the minimum defined by the last (5th) fraction as calcination residues from
384 incomplete lime burning (Lindroos et al. 2018).

385 Figure 5A also shows TD for sample TTK006. The furnace heats sample TTK006 to 650 °C, as
386 suggested by TGA in Figure 3, and collection of fractions starts. The first temperature interval, from
387 650-680 °C, produces too little CO_2 for AMS dating. The TD radiocarbon profile for TTK006 is
388 also decreasing for later fractions, and it shows multiple minima and maxima as do the SQ profile
389 of sample TTK005. All TD CO_2 fractions seem affected by geological carbonate because they have
390 lower $F^{14}C$ than expected.

391

392 FigureDeadCarbon

393

Figure 5B shows TD and SQ of sample J13-ESM-1, a mortar-cover cast around a water pipe in Jerash in Jordan (Lichtenberger et al. 2015). The sample's expected $F^{14}C$=0.8070±0.0025 comes from a charcoal sample embedded in the mortar (Lichtenberger et al. 2015). According to Al Bashaireh (2013) charcoal in mortar can be used for dating, if short-lived bushes were burned and not old wood. The first fraction of SQ and charcoal are similar in $F^{14}C$, while later fractions in the SQ profile has lower $F^{14}C$ values. This behavior matches a sample influenced by geological carbonate. As explained in the characterization results section CL cannot rule out geological carbonate for this sample, because some types of limestone at Jerash are without a luminescence property. Yaseen et al. (2013) and Lichtenberger et al. (2015) find limestone sand and gravel aggregate in most Jerash mortars, and this could be the case for sample J13-ESM-1. The sample was not found alkaline, so it is unlikely that late-in-formation pyrogenic carbonates are abundant, see Table 2.

For TD, the furnace heats sample J13-ESM-1 to 600 °C, lower than suggested by TGA in Figure 3, and collection of fractions starts. The TD radiocarbon profile is also decreasing in $F^{14}C$ for later fractions, and geological carbonate is a possible explanation. Interestingly, the first fraction of TD has a higher $F^{14}C$ than expected, while the first fraction of SQ has not.

Thermal decomposition and late-in-formation pyrogenic carbonates

Figure 6A shows TD and SQ of sample Kastel09 from Kastelholm castle in Finland. Figure 6A also shows a SQ profile for sample Kastel10, and the two samples originate from the same structural unit. Interpolation of the IntCal20 curve calculates the expected $F^{14}C$=0.9253±0.0012 from the first written source on Kastelholm in 1388 AD (Hausen 1910). Allowing 10 years for construction, or a

delay from construction to first written source, the year 1378 AD has expected $F^{14}C=0.9217\pm0.0011$. Lindroos et al. (2020a) report alkalinity, fire damage and limited limestone contamination for Kastelholm mortar. ~~Lindroos et al. (2020a) found young carbonates from fire damage and reactivation in mortar from Kastelholm castle.~~ CL finds few red grains in both samples, Kastel10 is alkaline, and Kastel09 is not alkaline, see Table 2. In Figure 6A, the two SQ profiles have fractions with higher $F^{14}C$ values than expected, and late-in-formation pyrogenic carbonate from alkalinity or fire damage is a likely explanation. Notice that higher than expected $F^{14}C$ mostly affects sample Kastel10, which is alkaline.

In TD, the furnace heats sample Kastel09 to 550 °C, lower than suggested by TGA in Figure 3, and collection of CO_2 fractions starts. The first temperature interval from 550-680 °C, yields too little CO_2 for AMS dating. Comparing with SQ profiles, the TD profile is quite flat and no fractions have higher $F^{14}C$ than expected.

FigureYoungCarbonates

Figure 6C shows TD and SQ of the lime lump sample Kimito004Li from Kimito church in Finland. Interpolation of the IntCal20 curve calculates the expected $F^{14}C=0.9317\pm0.0012$ from the year 1400 AD, which is the beginning of the 1st half of the 15th century. Likewise, the year 1450 AD, which is the end of the 1st half of the 15th century, has expected $F^{14}C=0.9480\pm0.0012$. In Figure 6C, the SQ profile is in range of the expected $F^{14}C$, but later fractions show decreasing $F^{14}C$ values. CL rules out geological carbonates, so a possible explanation is late-in-formation pyrogenic carbonate shifting early fractions to higher $F^{14}C$. Alkalinity screening to support this is unavailable, as the lime lump was exhausted.

For TD, the furnace heats sample Kimito004Li to 600 °C, lower than suggested by TGA in Figure 3, and collection of fractions starts. The TD profile is in range of the expected $F^{14}C$, and more homogenous than the SQ profile.

Preheating followed by sequential dissolution

In relation to preheating, we test if it is possible to produce CO_2 below the start temperature suggested by TGA. Thus TD preparation of sample Merida003 starts CO_2 collection from room temperature to 620 °C.

Figure 7A shows sample Merida003 with TD and SQ. Interpolation on the IntCal20 curve calculates the expected $F^{14}C=0.7841\pm0.0014$ for the year 69 AD, which is the beginning of the Flavian dynasty, and the expected $F^{14}C=0.7859\pm0.0014$ for the year 96 AD, which is the end of the Flavian dynasty. Early fractions in the SQ profile have higher $F^{14}C$ than expected. Characterization found this sample alkaline, so late-in-formation pyrogenic carbonates are a likely explanation. The TD profile starts CO_2 collection from room temperature to 620 °C, and all fractions have higher $F^{14}C$ values than expected, especially the three earliest fractions. Again late-in-formation pyrogenic carbonates are a likely explanation.

Figure 7B shows sample Merida003 with SQ (repeated) and P+SQ (preheated to 620˚C). A considerable part of the P+SQ profile in Figure 7B is close to the expected $F^{14}C$. The CO_2 thermally decomposed during preheating was collected and radiocarbon dated to $F^{14}C=0.8437\pm0.0049$, see Table 1 for sample run no. Merida003 PSQ1.T1.

462 FigurePreheating

463

464 **DISCUSSION**

465

466 Table 2 summarizes characterization results, and this identifies potential problems with limestone,
467 marble or alkalinity for most samples. To investigate TD for problematic mortar no samples are
468 rejected for dating. As mention in the results section, CL cannot rule out geological carbonate for
469 sample J13-ESM-1 because of non-luminescent limestone at Jerash. Apart from this, the sample
470 characterization is very useful in identifying problems that enable evaluation of radiocarbon
471 profiles, e.g. fractions influenced by geological carbonate or late-in-formation pyrogenic carbonate.

472 Figure 3 shows TGA curves for mortar samples, and the dominant mass losses start around 640-
473 650°C, which is lower than the reported start temperatures for TD of calcium carbonate, e.g. 680-
474 700 °C (Rao 1996; Karunadasa et al. 2019). This compares to Ricci et al. (2020) and Toffolo et al.
475 (2020) discussing pyrogenic carbonates decomposing at lower temperatures than geological
476 carbonates. As mentioned in materials and methods, Ricci et al. (2020) employ a thermal treatment
477 at 550 °C to eliminate the carbonate fraction of LDHs, and this study experimented with preheating
478 at 620 °C. It may be possible to do a thermal treatment closer to the start temperature of the
479 dominant mass loss, e.g. 640-650 °C, without losing too much binder carbonate.

480 Figure 4 shows calcite backgrounds and the background correction for TD. The background $F^{14}C$
481 level has order of magnitude 10^{-3}. Considering that ancient and medieval samples are well above
482 one ^{14}C half-life, i.e. $F^{14}C>0.5$, the background level is satisfactory.

As seen in Table 1 the carbon yield of TD is significantly lower than SQ. At the same time, TD produces a sizeable amount of incondensable gas. TD of $CaCO_3$ in a vacuum may not happen entirely as described by equation 2. Part of the carbonate may produce carbon monoxide, which liquid nitrogen cannot freeze. Future work can investigate the carbon yield of TD with oxidizing agents such as pellets of CuO or an O_2 atmosphere. These may oxidize carbon monoxide to CO_2 and increase the yield. However, it is unknown if the addition of an oxidizing agent has an effect on TD temperatures or TD rates for late-in-formation pyrogenic carbonate, binder carbonate or geological carbonate.

Conclusiveness and accuracy

To evaluate conclusive sample ages from the radiocarbon profiles in Figure 5-7, we use criterion I defined by Heinemeier et al. (2010):

Criterion I: The $F^{14}C$ of the first two CO_2 fractions are the same.

The conclusive radiocarbon determination for the mortar sample is then the weighted average of the first two fractions. The criterion is based on the assumption that the preparation method's chemistry have different reaction rates for late-in-formation pyrogenic carbonate, binder carbonate and geological carbonate. Here they are listed in order of decreasing reaction rate. Two $F^{14}C$ determinations are considered the same, if a chi-square test for goodness of fit evaluates that the two values are well-described by their weighted average (Bennett and Franklin 1954; Bronk

505 Ramsey 2009). Accuracy is evaluated by comparing the conclusive $F^{14}C$ and an expected $F^{14}C$
506 value with the same chi-square test for goodness of fit.

507 In Figure 7, the profiles by TD, SQ and P+SQ have plateaus where 3-4 fractions show similar $F^{14}C$.
508 The plateaus in the profiles by SQ and P+SQ have $F^{14}C$ values close to the expected, see Figure 7B.
509 It may, or it may not, be possible to formulate and use conclusiveness criteria based on plateaus.
510 Perhaps, plateau criteria could be based on a chi-square test of fractions' $F^{14}C$ values, or the
511 plateau's cumulative CO_2 fraction, or agreement between multiple plateaus by different preparation
512 methods. We advise caution if one rules late plateaus conclusive because they can be inaccurate, see
513 Merida003 (TD) in figure 7A. We did not succeed in formulating simple and objective criteria that
514 simultaneously rule the accurate plateau in profile Merida003 (SQ) conclusive, and the inaccurate
515 plateau in profile Merida003 (TD) inconclusive. This study therefore avoids interpretation of late
516 plateaus.

517

518 **Thermal decomposition and geological carbonate**

519

520 In figure 5A, the 1st and 2nd fractions of profile TTK005 (SQ) pass conclusiveness criterion I, see
521 Table 3, and give conclusive $F^{14}C=0.9277\pm0.0029$. Furthermore, this conclusive $F^{14}C$ and the
522 expected $F^{14}C$ for the destruction in 1318 AD pass a chi-square test, see Table 3, so this conclusive
523 radiocarbon determination is accurate for Turku cathedral's destruction. All profiles besides
524 TTK005 (SQ) in Figure 5A and Figure 5B fail conclusiveness criterion I, and their results are
525 inconclusive, see Table 3. No TD profiles for a sample with abundant geological carbonates achieve
526 a conclusive mortar dating result. Considering these results, one can argue that TD is worse than SQ
527 at distinguishing geological carbonate and binder carbonate.

TableConclusivenessAccuracy

Thermal decomposition and late-in-formation pyrogenic carbonates

In Figure 6A, the 1st and 2nd fractions of Kastel09's TD profile pass conclusiveness criterion I, and give conclusive $F^{14}C=0.9203\pm0.0020$, see Table 3. The conclusive $F^{14}C$ and expected $F^{14}C$ for 1378 AD pass a chi-square test, see Table 3, so the conclusive $F^{14}C$ is an accurate radiocarbon determination for Kastelholm castle. Figure 6B shows calibrated date of Kastel09's conclusive $F^{14}C$, which agrees with Kastelholm castle first mentioned in written sources in 1388 AD (Hausen 1910). The SQ profiles for Kastel09 and Kastel10 fail conclusiveness criterion I, and their results are inconclusive, see Table 3.

In Figure 6C, the profile Kimito004Li (TD) passes conclusiveness criterion I, see Table 3, and yields conclusive $F^{14}C=0.9310\pm0.0019$. The conclusive $F^{14}C$ and expected $F^{14}C$ for 1400 AD pass a chi-square test, see Table 3. Thus, the conclusive $F^{14}C$ is an accurate radiocarbon determination for the sacristy of Kimito church. Figure 6D shows calibrated date for Kimito004Li's conclusive $F^{14}C$, which has some probability in the 1st half of the 15th century AD. This agrees with the expected age of Kimito church's sacristy (Nikula 1975). The expected age is based on historical context, see the samples subsection in materials and methods section, so this is actually the first dating of Kimito church.

TD of mortar samples with late-in-formation pyrogenic carbonates, and limited geological carbonate, seems to improve radiocarbon profiles in Figure 6A and Figure 6C. The causes of these

preliminary findings have not yet been studied. Figure 7A shows TD of Merida003, where CO_2 collection starts at room temperature. The first three TD fractions have the highest $F^{14}C$ compared to the expected $F^{14}C$, and likely they are affected by late-in-formation pyrogenic carbonates outgassing somewhere from room temperature to 710 °C. Secondary sodium carbonates formed in wet conditions, e.g. trona and thermonatrite ($Na_3H(CO_3)_2 \cdot 2H_2O$ and $Na_2(CO_3) \cdot H_2O$, respectively) and vaterite ($CaCO_3$) after fire damage, have lower decomposing temperatures (Maciejewski et al. 1994; Hartman et al. 2001; Lindroos et al. 2012). This can explain how Figure 6A and Figure 6C improve, as these experiments start CO_2 collection around 600 °C. Below this temperature some late-in-formation pyrogenic carbonates may drive off, and not affect fractions collected later.

Preheating followed by sequential dissolution

In Figure 7 none of the Merida003 profiles by TD, SQ or P+SQ pass conclusiveness criterion I, and their radiocarbon determinations are inconclusive, see Table 3. Many fractions have higher $F^{14}C$ than expected, and it is surprising that the entire TD profile for Merida003 has higher $F^{14}C$ than expected. The Merida samples are very hard, and Lindroos et al. (2020b) discuss poor permeability for CO_2 and delayed hardening, which could be an explanation for higher $F^{14}C$ than expected. For dolomitic mortars LDHs can contain carbonate from exchanged atmospheric CO_2 (Artioli et al. 2017; Ponce-Anton et al. 2018). Ricci et al. (2020) and Toffolo et al. (2020) find that carbonate captured by LDHs decomposes around 500-550 °C, so one would expect this to contribute to the first TD fraction only.

Figure 7B presents results from P+SQ preparation of sample Merida003. P+SQ improves the profile, which shows less late-in-formation pyrogenic carbonate than SQ. It seems that some late-in-

formation pyrogenic carbonate decomposed in the preheating, but the P+SQ profile still fails conclusiveness criterion I. It would be interestin0g to investigate preheating at a temperature above 620 °C.

CONCLUSION

TD in vacuum can extract CO_2 from a mortar sample, and TGA curves are useful for choosing the experimental parameters. TD in vacuum has a significantly lower carbon yield than SQ, and this study used larger sample aliquots for TD than SQ.

TD is not successful in preparing samples with geological carbonate. As seen in Figure 5A and Figure 5B binder carbonate and geological carbonate does not behave sufficiently different in preparation by TD.

This study finds an interesting interaction between TD and late-in-formation pyrogenic carbonates from alkalinity or fire damage. Figure 7A shows TD driving off material with higher $F^{14}C$ than the rest of the sample at temperatures from room temperature to 710 °C. In this way, Kastel09 and Kimito004Li may have had their late-in-formation pyrogenic carbonates removed below the preparation's start temperature, and the two samples are conclusively dated in Figure 6A and Figure 6C. The conclusive radiocarbon determinations for Kastelholm castle and Kimito church accurately agree with the buildings' expected ages.

Another application is P+SQ, which preheats to remove late-in-formation pyrogenic carbonates prior to sequential dissolution. In Figure 7B, the preheating (at 620 °C for half an hour) removes

some late-in-formation pyrogenic carbonates, but not enough for the P+SQ profile to pass conclusiveness criterion I.

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CAPTIONS

Table 1: Samples, aliquots and radiocarbon dates. It was not possible to look up the sequential dissolution mass of the samples dated before 2008. Mortar samples with TD in the sample run no. column were prepared with TD, and similarly for SQ and P+SQ. SQ radiocarbon dates taken from Lindroos et al. (2011; 2012; 2020b; 2020a), Ringbom et al. (2006) and Lichtenberger et al. (2015).

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Figure 1: The experimental setup for sample preparation by thermal decomposition. Figure inspired by Ringbom et al. (2014).

753 Figure 2: CL images for the samples TTK006, J13-ESM-1, Kastel09, Kastel10, Kimito004Li and
754 Merida003. **A** TTK006, 46-75 µm. Brown-grey binder calcite and orange marble calcite. The blue
755 grain is quartz. **B** J13-ESM-1, 46-75 µm. The sample has no luminescence. **C-D** Kastel09 and
756 Kastel10, respectively, 46-75 µm. Brown grains are binder calcite and red ones limestone. Blue is
757 quartz and green is feldspar. **E** Kimito004Li, crushed lime lump. Dark red is binder calcite. **F**
758 Merida003, 46-75 µm, with marble splinter yellow and dolomite red. Blue, quartz and green
759 feldspar (and occasionally xenotime).

760

761 Table 2: Results from sample characterization. Alkaline mortars may have problems with late-in-
762 formation pyrogenic carbonates. Abundant bright yellow-orange-red grains are a marker for
763 limestone and marble that can carry geological carbonate. CL for sample J13-ESM-1 cannot rule
764 out geological carbonate, because on non-luminescent limestone at Jerash (Lichtenberger et al.
765 2015). The sample Kimito004Li was too small for alkalinity test.

766

767 Figure 3: Results from TGA for samples J13-ESM-1, TTK008, Kimito004Li, Kastel09, Kastel10
768 and Merida003. Weight loss from TD of binder $CaCO_3$ is seen from c. 640-770 °C. Pure calcite
769 decomposing to calcium oxide has its normalized weight reduced from 1.0 to 0.56. A mortar sample
770 may have a smaller reduction of normalized weight because of non-decomposable aggregates or
771 hydraulic mortar minerals (Dodson 1990).

772

773 Figure 4: Calcite backgrounds for TD. The background correction is fitted: $F^{14}C_{Background} =$
774 $(0.19\pm0.6)\cdot10^{-3}$ mgC $\cdot$ 1/mass + $(3.2\pm0.3)\cdot10^{-3}$. A $F^{14}C$ value of 0.0030 corresponds to a
775 radiocarbon age of c. 46 600 ^{14}C years BP.

776

777 Figure 5: Radiocarbon profiles for TTK006, TTK005 and J13-ESM-1, see Table 1 for further
778 information on sample aliquots. **A** TTK006 with TD and SQ, and TTK005 with SQ. The expected
779 $F^{14}C$ values derive from the years 1300 AD and 1318 AD, and geological carbonate shifts many
780 fractions to lower $F^{14}C$ values. The weighted average of the 1st and 2nd fractions of TTK005 (SQ) is
781 F14C=0.9277±0.0029. SQ data taken from Lindroos et al. (2011; 2012). **B** J13-ESM-1 with TD and
782 SQ. The charcoal sample J13-ESM-1C embedded in the mortar infers the expected $F^{14}C$, and
783 geological carbonate shift many fractions to lower $F^{14}C$ values. SQ data and charcoal data taken
784 from Lichtenberger et al. (2015).

785

786 Figure 6: Radiocarbon profiles for Kastel09, Kastel10 and Kimito004Li, see Table 1 for further
787 information on sample aliquots. **A** Kastel09 with TD and SQ, and Kastel10 with SQ. The expected
788 $F^{14}C$ values derive from the years 1378 AD and 1388 AD. SQ data taken from Lindroos et al.
789 (2020a). **B** The weighted average of the 1st and 2nd fractions of Kastel09 (TD) is
790 $F^{14}C$=0.9203±0.0020, and this is calibrated (Bronk Ramsey 2009; Reimer et al. 2020). The first
791 written source on Kastelholm is from 1388 AD. **C** TD and SQ for sample Kimito004Li. The
792 expected $F^{14}C$ values derive from the years 1400 AD and 1450 AD. **D** The weighted average of the
793 1st and 2nd fractions of Kimito004Li (TD) is $F^{14}C$=0.9310±0.0019, and this is calibrated (Bronk
794 Ramsey 2009; Reimer et al. 2020). Kimito church's sacristy is from the 1st half of the 15th century.

795

796 Figure 7: Radiocarbon profiles for Merida003, see Table 1 for further information on sample
797 aliquots. **A** TD and SQ profiles for sample Merida003. The expected $F^{14}C$ values derives from the
798 years 69 AD and 96 AD, the Flavian dynasty. Many fractions have higher $F^{14}C$ values than

799 expected, probably because of alkalinity, delayed hardening or dolomitic chemistry. SQ data taken
800 from Lindroos et al. (2020b). **B** SQ (repeated from 7A) and P+SQ profiles. More of the P+SQ
801 profile is close to the expected $F^{14}C$ value than the SQ profile, and preheating seems to remove
802 some late-in-formation pyrogenic carbonates. The P+SQ profile is also published in Lindroos et al.
803 (2020b).

804

805 Table 3: Summary of conclusiveness and accuracy of $F^{14}C$ profiles in Figure 5-7. Conclusiveness is
806 evaluated by criterion I, described in the discussion.