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Radiocarbon Dating Lime Lumps and/or Binder carbonate in Historical Mortars?

Alf Lindroos,[1] Åsa Ringbom,[2] Jan Heinemeier,[3] Greg Hodgins,[4] Pia Sonck-Koota,[1] Pia Sjöberg,[2] Lynne Lancaster,[5] Riikka Kaisti,[6] Fiona Brock,[7] Heikki Ranta,[8] Marta Caroselli,[9] Stefano Lugli.[9]

Abstract

Lime lumps and bulk mortars show different kinds of ^{14}C contamination when analyzed in several CO_2 fractions isolated from the effervescence of an ongoing hydrolysis reaction. Age profiles of both materials are therefore highly complementary and together they can provide a reliable dating. Furthermore, they can also reveal the complexity of the ^{14}C distribution and thus prevent over-interpretation of the data. The lime lump vs bulk mortar dating data presented here has been collected over 22 years and only a small fraction of the results has so far been published internationally. Since there has been an increasing interest in mortar dating over recent years with a special focus on lime lumps and since many laboratories have just started with mortar dating experiments, we want to present some of the extensive data that already exist. Earlier published data from 15 lime lumps including 34 ^{14}C measurements from sequential dissolution and new data from 17 lime lumps with 43 ^{14}C measurements will be presented. The samples are from Medieval Finland and Sweden, from Classical Rome and Medieval Italy and from the Roman Jerash (Gerasa), Jordan.

Introduction

Dating of small selected samples of historical mortars became possible after the introduction of accelerator mass spectrometry (AMS) in the field of ^{14}C mortar dating (Tubbs and Kinder 1990). Several studies have shown that lime lumps may potentially be a better material for ^{14}C dating than bulk mortars (Strydonck et al. 1992, Ringbom and Remmer 1995, Heinemeier et al. 1997, Lindroos et al. 2007, Pesce et al. 2009, 2012). Since fewer ^{14}C measurements may be needed, dating lime

[1] *Department of Geology and Mineralogy, Åbo Akademi University, Finland alindroo@abo.fi*
[2] *Art History, Åbo Akademi University, Finland, aringbom@abo.fi*
[3] *AMS Centre, Department of Physics and Astronomy, University of Aarhus, Denmark, jh@phys.au.dk*
[4] *AMS Laboratory, Department of Physics, University of Arizona. USA, ghodgins@physics.arizona.edu*
[5] *Department of Classics and World Regions, Ohio University, USA, lancaste@ohio.edu,*
[6] *Turku and Kaarina Parish Union, Finland, riikka.kaisti@evl.fi*
[7] *RLAHA, University of Oxford, Oxford, OX1 3QY, UK & Cranfield Forensic Institute, Cranfield University, Defence Academy of the United Kingdom, Shrivenham, SN6 8LA UK, f.brock@cranfield.ac.uk*
[8] *Diocese of Lund, Church of Sweden, Sweden, heikki.ranta@gmail.com*
9 Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Italy, luglis@unimore.it

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lumps may also provide more economically sustainable solutions in the future. If lumps form by clodding of the lime putty already before it is mixed with the aggregate they should be free from contamination of radiocarbon-dead geological carbonates from the filler. However, there are many kinds of lime lumps and not all of them are suitable for identifying the age of the mortared structure (Van Strydonck et al. 1992, Pesce et al. 2009, 2012, Lindroos et al. 2014). The lump may be a misidentified, weathered aggregate limestone fragment, or it may be incompletely burned and disintegrated and still contain limestone relicts that have survived the lime burning process. Due to their soft and porous nature it is also common to have weathering and re-crystallization with secondary calcite within the lumps if they have been in contact with ground water or percolating water in the masonry work at later stages (Lindroos et al. 2007, 2011a). Pesce et al. 2009 describes in some detail what kind of lime lumps are suitable for ^{14}C dating in archaeology: the best lumps are soft, white and have a flour-like surface. In the beginning the potential of dating lime lumps was only tested sporadically on centimeter scale lumps by the laboratory of Geology and Mineralogy at Åbo Akademi University in Turku (Åbo), Finland and the AMS laboratory in Aarhus, Denmark. Some of the tests were done in Tucson, Arizona in 2008. When a new line (Fig 1) dedicated to mortar dating was built 2008 in Åbo Akademi University, millimeter scale samples could be processed and lime lumps were dated more frequently.

In this paper we present the results from testing of lumps in well preserved medieval non-hydraulic mortars made from pure marble in SW Finland and from lime mortars made from Ordovician limestone in the Åland Islands between Finland and Sweden and from Silurian or possibly Mesozoic limestone in South Sweden. We will also complement the Nordic material with data from lime lumps embedded in Classical Roman pozzolana mortars. So far we have analyzed 57 lime lumps, usually in several CO_2 fractions. Some of the results will be published elsewhere in their archaeological context. We will, however, not present a penetrating mineralogical and chemical study of the lime lumps; instead, we concentrate on the vital question – whether lime lumps embedded in the mortar are a more reliable material for dating than bulk mortar, and if the time has come to abandon the analyses of bulk mortars in favor of lime lumps.

Sample preparation

The preparation procedure of bulk mortars is described by Hajdas et al. (2017). The mortars are carefully crushed and sieved into decreasing grain-size fractions (see e.g. Lindroos et al. 2007 for details). A sample >50 g is usually sufficient to produce several hundreds of milligrams of material representing a narrow grain- size window, e.g. 46-75μm (see appendix) for the AMS dating. Lime lumps are prepared in a similar way. It is, of course, not necessary to crush a large sample, as the lump can be picked out of the mortar with a sharp tool already at the sampling site or later in the laboratory. Because lime lumps are often relatively small, it may be necessary to widen the grain size window to get enough material. Theoretically 1 mg of carbon could be recovered from 8 mg of lump material, but in practice the smallest lump we have dated was 15 mg in weight. In this case the lump powder was not sieved, but the whole lump was crushed and hydrolyzed. Lumps large enough to yield at least two successive CO_2 fractions are preferable in order to have some control of the homogeneity of the ^{14}C distribution. It is also possible to collect material from several

separated small lumps, but it is important to ensure that they are homogeneous and representative of the original mortar.

The hydrolysis system

To monitor any possible contamination, the lime lumps were processed using the same dissolution system as the bulk mortars. Figure 1 illustrates the relevant elements of the CO_2 preparation line.

Figure 1.

The result of several ^{14}C measurements from successive CO_2 fractions can be presented as an age profile of the sample, which is formed by plotting the consecutive ^{14}C ages of the fractions obtained in sequential dissolution (Fig. 2). The theoretical modelling of contamination is described in Lindroos et al. (2007) and a formalized categorization of age profiles produced with H_3PO_4 hydrolysis is presented in Heinemeier et al. (2010). The true archaeological age forms a horizontal baseline and the contamination causes deviation from this baseline. Usually the first CO_2 fraction is the least affected by the contamination. In the present paper, however, the lines drawn between the points in the plots are not mathematical models of contamination, they are only guide-lines connecting the data points from the individual hydrolysis runs to visually separate the different profiles in a plot. The calibration of the ^{14}C ages to calendar years was done using the IntCal 13 (Reimer et al. 2013) calibration curve and the OxCal 4.3 program (Bronk Ramsey 2017). All calibrated results are reported at 95.4% confidence level (2 sigma).

Figure 2.

If the age profile is more or less horizontal, with overlapping ages, then it demonstrates absence of contamination and is considered a very reliable result, or a Criterion I (CI) result according to the classification in Heinemeier et al. (2010). The CI criterion still applies if the first two CO_2 fractions of an age profile agree within the given error margins. For Criterion II (CII), another reliable result, independently dating a mortared structure, age profiles for three or more samples per building unit are needed. If all these age profiles yield overlapping results in their first CO_2 fractions, then the combined calibration is assumed to give the true date of the mortar.

Results and discussion

In the appendix we have listed our previously published lime lump dating results from the literature and as yet unpublished results from more recent studies. Here we will revisit some important lime lump datings and their interpretation and present data that have not been published before or only appeared in conference volumes of a regional character. For comparative reasons, we have included age profiles of the surrounding bulk mortars, sometimes generated several times and with both HCl and H_3PO_4 hydrolysis. In the plots we have used the following abbreviations and marks to denote bulk mortars, lime lumps and different hydrolysis used: Sample identification and number = bulk mortar. Extension Li after the number denotes lime lump (in some

early publications L has been used instead of Li). Bulk mortars are denoted with diamonds and lime lumps with dots. Filled symbols denote H_3PO_4 and open symbols denote HCl hydrolysis.

Early lime lump dating was done using the Aarhus multipurpose preparation line, which required relatively large samples preferably >100 mg. There was also another problem: it turned out that the dissolution was difficult to plan in advance, since the carbon yield could vary considerably between a preliminary test and the actual hydrolysis. The first application of lime lump dating was from the church of Hammarland in the Åland Archipelago between Finland and Sweden, which was sampled in 1994 soon after adopting AMS in our mortar dating (Ringbom and Remmer 1995). At that time the samples were usually dated in two CO_2 fractions and several different grain size windows were tested (e.g. 21-150μm or un-sieved material). The potential of lime lumps became obvious when dating the vault of the church. Here the age profile of Haka 044Li (Fig 3, Ringbom and Remmer 1995, Heinemeier et al. 2010), a lime lump embedded in the mortar and dated in two fractions, appears horizontal – thus possibly without contamination, although the errors are large and partially overlap the results of the bulk mortar.

Figure 3 a, -b.

Lime lumps in classical archaeology

Figure 4.

The age of the monumental *Temple of Jupiter Anxur* in Terracina, Lazio, is considered to be one of the early pozzolana structures in Italy from the first century BC (Coarelli 1982). The bulk mortar of sample Terracina 001 was analyzed using both H_3PO_4 (Århus) and HCl dissolutions (Tucson, Arizona, USA), each time in several CO_2 fractions. The age profiles coincide at the beginning if the H_3PO_4 profile is extrapolated further towards the y-axis. The lime lump Terracina 001Li embedded in the mortar was analyzed in two CO_2 fractions. The result was an almost horizontal profile and the first CO_2 fraction supports the interpretation of the bulk mortars, yielding an age of 1909 ± 35 BP, corresponding to a calibrated age cal. AD 20-214 (2σ).

Pozzolana mortar from the very top of *Torre delle Milizie*, a medieval addition to Trajan's Market in Rome, erected by Pope Innocence III between 1198-1216 (Roma, Guida d'Italia 1999), was sampled in 1998. Different types of dissolution, H_3P0_4 and HCl have been applied, and several laboratories involved: Århus, ORAU, Oxford, and Tucson, (Hodgins et al. 2011). In an earlier dating attempt (Ringbom et al. 2006) based on hydrolysis with phosphoric acid in Aarhus and Oxford a 13th century date was proposed mainly based on the least contaminated sample Rome 009 (in appendix) with the first CO_2 fraction at 750±35 BP.

Figure 5.

Sample Rome 007 (Fig 5), which reveals extreme contamination by dead carbon, was tested further in Tucson with both H_3PO_4 and HCl. The H_3PO_4 result for the first CO_2 fraction, 735±30 BP, is similar to that of sample Rome 009. The relatively horizontal age profile created by HCl displays somewhat older BP ages in the beginning. The result from the lime lump Rome 007Li is in agreement with our earlier interpretation. Unfortunately, it was only possible to date only one CO_2 fraction because the lump was very small, only 15.7 mg.

Sant'Agnese: At the time of emperor Constantine the Great, 312- 337 AD (Frutaz 2001) the horseshoe shaped basilica of Sant'Agnese (Fig. 6) was erected outside the walls of Rome in connection to early Christian catacombs, in Via Nomentana. Adjoined as a secondary addition to the basilica is the rotunda of Santa Costanza (Fig. 7).

Figure 6.

The bulk mortars from this construction (Fig. 6 and Santa Costanza, Fig. 7a) appear to be unreliable because they display both dead carbon contamination and variable results for the first CO_2 fractions (see sample Rome 044 in appendix). The sample Rome 045/45Li (Fig. 6) provide a reasonable dating, but the lump was only 23.6 mg so there is no homogeneity control from a second CO_2 fraction.

Santa Costanza: The exact date of this rotunda, outside Rome, is unknown. Still, the building is most certainly Constantinian (Ringbom 2003, Ringbom et al. 2006). It was originally a mausoleum for Costantina and Helena, daughters of Constantine the Great, either erected by Constantina around AD330 or by her brother-in-law Julian the Apostate AD350-360, who owned the land and who was married to Helena (Mackie 1997, Ringbom 2003). We have tried to date the construction several times: First using H_3PO_4 hydrolysis in Århus and Oxford (Ringbom 2003, Ringbom et al. 2006) and later using H_3PO_4 and HCl in Århus and Tucson (Hodgins et al. 2011). Here we present the results from sample Rome 042 including a dateable lime lump (Fig 7a).

Figure 7 a,-b.

The first CO_2 fractions of Rome 042 (HCl) and the ages of the embedded lime lump are similar. The lime lump from the corner of the niche of Constantina's sarcophagus was analyzed twice: First in three CO_2 fractions and also in one CO_2 fraction, forming a baseline at 1716 ± 15 BP, or cal. AD 256-299 (32,4%), 319-387 (63,0%) in a combined calibration of all four lime lump measurements (X^2-Test: df=3 T=1.7; 5% 7.8). The dip in the H_3PO_4 profile at the second CO_2 fraction is irregular. Because usually younger material dissolves first, we suggest that the hydraulic mortar contained a large amount of lime lumps, which dominated the reaction at the beginning, but this particular sample also contained parts affected by delayed hardening. However, even if analyzing the lime lump proved useful, the resolution vs calibration curve was not good enough to help us pinpoint the builder of the mausoleum.

The bridge in Parma, from the Visigothic period, is located in a very humid environment and in contact with liquid water. Its mortars had plenty of lime lump inclusions. Two lime lumps were analyzed, one together with the bulk mortar. The bulk mortar and lime lump profiles (PG10, PG12Li) reveal a high level of contamination by dead carbon. The small lime lump PG10Li, was analyzed in only one CO_2 fraction, and yielded a result which was far too ancient, obviously due to contamination. The lime lump PG12Li displays on one hand a rather young first CO_2 fraction and a nearly 3000y older second CO_2 fraction. The young age for the first fraction may have been caused by new calcite crystals precipitated within the mortar pores due to weathering phenomena, as noted in thin sections. It seems that the weathering/recrystallization has affected at least the other lime lump more than the bulk mortar (the one dated in two CO_2 fractions). Only the bulk mortar resulted in an age profile where the first CO_2 fraction overlaps the beginning of the Visigothic period (starting 410 with Alarik sacking Rome), 1649 ± 28 BP, or cal. AD 332-433 (87,8%, 2σ).

Figure 8.

Jerash, Jordan. A series of mortar and lime samples from water cistern walls and water pipe joints were taken in 2013 in the ancient city of Jerash in Jordan (Lichtenberger et al. 2015). All samples were heavily contaminated with underburned limestone and they had a filler composed of fluvial limestone. The mortars contained abundant charcoal particles and small lime lumps, which were usually too small for ^{14}C dating. They had a dirty grey appearance and a closer inspection revealed charcoal within the lumps as well. The dating of the lime lumps was not successful, but it helped to interpret bulk mortar data to some extent because they showed less dead carbon contamination than the bulk mortars and similar ^{14}C ages in the beginning of the hydrolysis (Fig. 9 and 10). The lime lumps also show absence of the rapidly dissolving dead carbon contaminant seen in Fig 10, bulk mortar and in many other bulk mortar profiles reported in Lichtenberger et al. (2015).

Figure 9.

Figure 10

The lime lumps in Jerash were not typical “pure lime lumps” (Pesce et al. 2012), nor were they well suited for dating.

Lime lumps from Medieval Sweden and Finland

A study focused on lime lumps was made on the church of Dalby in Scania, S Sweden (Lindroos et al. 2014). Three lime lumps were sampled *in situ* from the supporting pillars within the church. Several hundred milligrams of lump material were peeled out from the pillars with a knife. The lime lump 010Li is iron rich and rusty and contains abundant underburned limestone contamination (Fig. 11). Lumps 012Li and 013Li are soft, bright white and flour like “pure lime lumps” (Pesce 2009). A combined calibration of CO_2 fraction 1 and 2 for sample 012Li and fraction 1 for

sample 013Li yields the ^{14}C age 944±16 BP, which corresponds to the calendar ages calAD 1028-1059 (22.5%) or 1065-1155 (72.9%; X^2-Test: df=2 T=2.1; 5% 6.0).

Figure 11.

Mortar samples were also taken from the northern wall of the church where younger plaster had fallen off and revealed the original stone masonry. Three bulk mortars and the material from two lime lumps were dated together with two charcoal inclusions (Fig.12).

Figure 12.

Samples 001 and 003 from Dalby church show extreme dead carbon contamination while sample 009 yields a CI profile typical for a reliable dating (e.g. Lindroos et al. 2007, Heinemeier et al. 2010) and is in concordance with the ages of the charcoals (Dalby 002C, 003C in appendix). The lime lump material 008Li appears slightly older, but the whole sequence of profiles points to a similar age as the supporting pillars (Fig. 11).

The ruins of the Ås Kloster monastery, on the SW coast of Sweden, was dated in 2013 (Bjuggner and Rosengren 2015). The mortar samples were taken during excavations below the present ground level. A bulk mortar/lime lump sample pair from the stratigraphically oldest part of the monastery provided a rather convincing dating (Fig 13). Both the lime lump and the bulk mortar date the construction to cal. AD 1185-1274, which is within the expected age frame: 12-14thC.

Figure 13.

The Church of Sund, originally the largest on the Åland Islands, was dated through analyzing fire damaged bulk mortars (Fig. 14a, Ringbom et al. 2005). This was the first time when age profiles of fire-damaged mortars were identified and interpreted. In this case the horizontal plateau in the profile is believed to reflect the true age of the structure, whereas the first fractions probably reflect the time of the fire when the mortar was partly re-calcinated and re-crystallized. The horizontal parts of the two profiles from the nave agree within the error margins. A combined calibration (omitting the first fractions) yields 778 ± 16 BP or 1225-1285 cal. AD (2σ, Ringbom 2011).

Figure 14.

The data was complemented with two lime lump analyses undertaken in 2015. Suka 008Li presented an almost horizontal age profile, first and second fractions 797±27BP and 788±25BP, or combined 1190-1275 cal. AD (X^2-Test: df=1 T=0.1; 5% 3.8) supporting the earlier dates obtained from the fire-damaged bulk mortars (Ringbom et

al. 2005). Suka 009Li, however, appears younger possibly also displaying fire damage effect as indicated by the slope.

Church of Finström. Archaeological excavations in 1969-70 revealed the foundations of an earlier wooden church under the floor of the present nave in the Finström Church, Åland. In 1994 we sampled the nave of the church for mortar and undertook some of our first lime lump dating (Fig. 15, reported in Heinemeier et al. 2010).

Figure 15.

Note: Total dissolution and few CO_2 fractions can fail to reveal heterogeneous ^{14}C distribution. Theoretically all CO_2 fractions can be more or less contaminated with dead carbon and the wood may be old. In this case, however, there is ample data in Heinemeier et al. (2010) to support the interpretation presented in the text to Fig. 15. In 2004 we took another sample series of mortars, one of which contained lime lumps. The samples represent the secondary vaulting of the nave. Dendrochronological results from the roof trusses yield AD 1450 (reported in Ringbom 2011). The results from the mortar dating met the demands of both the CI and CII criteria (Heinemeier et al. 2010), and all age profiles from the same building unit agree in their first CO_2 fractions (one of the profiles, Fika 060, is entirely horizontal). A combined calibration of the first CO_2 fractions yields 1435-1485 cal. AD (Ringbom 2011).

Figure 16.

The lime lump Fika 058Li (Fig. 16) adds further support to this interpretation. The first CO_2 fraction yields 1443-1529 (54.7%) and 1543-1635 (40.7%) cal. AD. The corresponding bulk mortar Fika 058 exhibits a typical total dissolution profile in five CO_2 fractions: After an initial increasing slope the profile goes through a local maximum reflecting a dead carbon component from aggregate limestone, which then becomes exhausted and is followed by a low, positive slope due to dead carbon from slowly dissolving calcination residues.

In 1970 a hoard of coins from 1250-1285 was uncovered under the sacristy floor in Finström church, indicating that the sacristy could represent the oldest part of the stone church. To verify this hypothesis, three samples including lime lumps were gathered from the attic of the sacristy in 2015 and analyzed in age profiles with two CO_2 fractions (Fig. 17a). All of them reveal strong contamination and furthermore, contrary to expectations, all of them show that the upper part of the sacristy may even be younger than the nave. The wood sample Fika 04W from the same sample series cannot be younger (i.e. TPQ) than the lime lumps and thus the second CO_2 fractions are certainly biased. Consequently, in spite of our efforts we have not yet been able to document the oldest parts of the stone church in Finström.

Figure 17 a, -b.

The nave of Jomala church is usually considered to be the oldest known stone construction in the Åland Islands (Ringbom 2011). Unfortunately it has been heavily rebuilt and the oldest parts were demolished in the 19th century. However, the bulk mortar of the tower has been successfully dated to the 1280s (Heinemeier et al. 2010). To find out the age of the nave, lime lumps from the west gable of the nave were dated in 2015 (Fig. 18).

Figure 18.

The resulting age profile of Joka 001Li (first fraction BP 660 ± 26, cal. AD 1273-1389, 95.4%) is similar to the dates presented by analysis of bulk mortar and dendrochronology of the tower wood elements. It was sampled from the joint between the tower staircase and the west gable and could possibly date the oldest part of the nave. Thus, it is still not clear whether the west gable and the tower belong to the same building phase or whether there are still older parts of the nave in the church.

Church of Nagu, in the Åboland archipelago, SW Finland. The bulk mortar sample Nagu 009 is part of the inter-comparison project within the international mortar-dating network (MODIS, Hayen et al. 2016a, Hayen et al. 2016b). The sample has been labelled MDIC 1, SWFin 01 and Nagu 009 in different reports. The hydrolysis was done twice because CO_2 fraction 1 was lost in the first attempt (therefore the overlap of fractions 1 and 2). The mortar contains abundant amounts of lime lumps, one of them had previously been dated using both 5% H_3PO_4 and 3% HCl (Fig. 19). The sample should date the secondary vaulting of the nave, which has a dendrochronological dating at AD 1436 (appendix).

Figure 19 a-c.

The Cathedral of Turku. From the 13th century to 1809 AD Finland was part of Sweden, forming one large diocese, the diocese of Turku. The building history of Turku Cathedral is controversial. According to the traditional chronology, following the evidence of written sources, it has been dated to around 1300AD (e.g. Gardberg et al. 2000), when the sacristy and the nave were supposedly inaugurated. According to later theories the Cathedral was not built until the 15th century (Hiekkanen 2007). The south gable of the first sacristy is still fully visible as a separate part adjoining the northern wall of the nave, thus predating the nave. The Cathedral has been subject to repeated fires and the irregularity of the calibration curve in the 14th century adds further uncertainty to the interpretation. Nevertheless, analyzing bulk mortars (Lindroos et al. 2011b, 2012) and lime lumps (this study) have added clarity to dating the first three building stages: the sacristy (TTK 008Li), the polygonal chancel (sample TTK 005Li), and the tower staircase belonging to the Hemming chancel, an enlargement of the nave (TTK 031Li and TTK 033Li).

Figure 20.

The remnants of the first stone sacristy are the structurally oldest part of the building. According to written sources bishop Magnus I was elected in 1291 AD in the sacristy of the Cathedral (Diplomatarium Fennicum: 201). In 2012 we analyzed new lime lump samples from the Cathedral and from samples taken earlier. Lump TTK 008Li is from a mortar sample taken earlier (Fig 21).

Figure 21.

The bulk mortars show the usual effects of fire damage (Lindroos et al. 2012), the earliest fire recorded in 1318 when the Cathedral was devastated by the Novgorodians. The first CO_2 fractions are irregular and seem too recent, probably indicating the time of later fires, which would have caused re-crystallization. Later in the plot the profiles of the bulk mortars flatten out and this plateau may be interpreted as a baseline formed by the binder carbonate at the time of construction: We used it for dating the sacristy to cal. AD1270-1300 (84.8%, Lindroos et al. 2011b, 2012). All four CO_2 fractions of the lime lump profile TTK 008Li, agree within the error margins and support this interpretation. The combined calibration yields 659 ± 18 BP or cal. AD 1282-1313 at 46.3% probability and 1357-1389 at 49.1% respectively (X^2-Test: df=3 T=0.8; 5% 7.8), and is thus compatible with the chronology of Gardberg et al. 2000.

Remains of the foundations of an earlier polygonal choir attached to the east wall of the nave are found under the present floor, where they have been sheltered from fire. The bulk mortar of TTK 005 was analyzed in five CO_2 fractions (Fig. 22, Lindroos et al 2011b, 2012).

Figure 22.

The age profiles of bulk mortar TTK 005 and its embedded lime lump TTK 005Li overlap in the beginning of the profiles. The calibration of the first CO_2 fractions in the bulk mortar profile and in the lime lump, are both affected by the irregularity of the calibration curve in the 14th century. They reveal dates, mutually very close (TTK 005: cal. AD 1300-1370; 45.4% and cal. AD 1380-1440; 50.0%; TTK 005Li: Cal. AD 1293-1405). The final fractions reveal heavy contamination with underburned marble used for lime production, whereas the increase in age at the third fraction of the bulk mortar is interpreted as contamination from marble splinter in the filler material. Note that the observed slope in the lime lump profile means that one single date based on a total or large fraction would have given a misleading date (too ancient).

Two bulk mortars (TTK 030, appendix and TTK 031) from the northern staircase belonging to the Hemming choir were analyzed in three fractions each. Sample TTK 031 contained embedded lime lumps one of which was analyzed in two CO_2 fractions. From another sample, TTK 033, we analyzed only the lime lump TTK 033Li, but we were able to extract four datable fractions (Fig. 23).

Figure 23.

Even if the age profiles (Fig. 23) behave very differently from each other, all the first CO_2 fractions coincide within the error margins. Furthermore, the profile for TTK 031Li is almost horizontal, which clearly helps the interpretation. The combined calibration of the first fractions yields 543 ± 14 BP, or cal. AD 1325-1343 (12.5%), and 1395-1425 (82.9%), which is more recent than the polygonal choir, in accordance with the structural sequence.

The church of Pargas belongs to a city located around the largest marble quarry in Finland, which has been in production since the 14th century (Boström 1986).

Figure 24a,-b.

From the secondary vault of the nave in the church of Pargas two bulk mortars were dated, one using only HCl hydrolysis and the other using both H_3PO_4 and HCl, for comparison. The HCl results were later considered unreliable in general in the marble area since the ^{14}C profiles repeatedly revealed rapidly dissolving marble contamination (see 2 examples in Lindroos et al. 2011b). Two lime lumps: Pargas 033Li and 035Li were dated using H_3PO_4 hydrolysis (Fig. 24). Both lime lumps present almost horizontal age profiles, meeting the demands of Criterion I and combined with the first fraction from the H_3PO_4 hydrolysis of the bulk mortar they yield 529 ± 19 BP dating the vaulting of Pargas church to cal. AD 1329-1341 (5.0%) and 1396-1435 (90.4%; X2-Test df=2 T=0.7; 5% 6.0).

Conclusion

In this paper we have investigated whether lime lumps, possibly even dated in one fraction only, are to be preferred to bulk mortars when it comes to dating ancient constructions using ^{14}C AMS analysis. We have presented the results of a series of lime lump dating in comparison with other materials relevant for the chronology of the structures, preferably with the very bulk mortars hosting the lumps themselves. For a broader comparison we have dated lime lumps embedded in mortars based on different types of limestone from Medieval Scandinavia and from Classical Archaeology from different sites in Europe and the Middle East. We have found that lime lumps, just like the bulk mortars, can be subject to contamination of under-burnt limestone, and that they therefore need to be analyzed in several successive CO_2 fractions to create reliable dates from age profiles, just like bulk mortars do. Our results clearly indicate that lime lumps dated using only one CO_2 fraction are not sufficiently reliable without supporting data because contamination from dead carbon or younger calcite growth cannot be *a priori* assumed to be absent, nor indeed can its possible effect on the dating result be detected. The contamination by under-burnt limestone commonly appears, however, to be less severe than in the case of bulk samples, whereas, as expected, the lumps are essentially free from contamination from the filler.

With lime lumps the same criterion guidelines apply for the interpretation of the results as with bulk mortars. While lime lumps often yield good results, especially in Medieval Scandinavia, ^{14}C AMS analysis of lime lumps should not substitute analysis of bulk mortar, but it should be seen as a valuable complementary method to validate ^{14}C AMS analysis of bulk mortars. If the two form agreeing age profiles, then the result of the first CO_2 fractions can be regarded as very reliable.

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Appendix

Dated CO_2 fractions from lime lumps and bulk mortars including them or in close connection with them. ^{14}C data of charcoal and wooden inclusions from the mortars are also reported as well as a relevant dendrochronological age.



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Radiocarbon dating historical mortars: lime lumps and/or binder carbonate?

Lindroos, Alf; Ringbom, Åsa; Heinemeier, Jan; Hodgins, Greg

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