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19 YEARS OF MORTAR DATING: LEARNING FROM EXPERIENCE

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ABSTRACT. Since 1994, our team has gained extensive experience applying accelerator mass spectrometry (AMS) radiocarbon analysis for mortar dating, totaling over 465 samples and 1800+ measured CO_2 fractions. Several samples have been analyzed repeatedly. The research covers both Medieval and Classical archaeology. We therefore believe our experience can be helpful when developing preparation procedures for different kinds of mortars in different areas and in varying chronologies. So far, the main areas of interest have been (a) the churches of the Åland Islands (in the archipelago between Finland and Sweden); (b) the churches in the Åboland Archipelago (SW Finland); (c) sites in the Iberian Peninsula including Torre de Palma (a Roman village in Portugal); and (d) Rome, Pompeii, and Herculaneum (Italy). Most of the analyses before 2000 were hydrolized in only two CO_2 fractions per sample, and reliability criteria were defined on the basis of how well the ages of the two fractions agree with each other. These criteria have proved most helpful in determining the reliability of ^{14}C mortar analyses. Different types of mortar have been investigated, including lime mortars made both from limestone and marble, pozzolana mortars, fire-damaged mortars, and mortars based on burnt shells. Most importantly, separate lime lumps sampled from these mortars have been analyzed sporadically and recently more systematically. The research also includes different types of hydrolysis applied in the pretreatment. In addition to using 85% phosphoric acid (H_3PO_4), the experimental research includes tests with smaller concentrations of phosphoric acid, and tests based on 2–3% hydrochloric acid (HCl) dissolutions. To characterize the dissolution process, results are presented as age profiles of 2–5 CO_2 fractions. In our experience, pozzolana mortars have been difficult to date, and HCl dissolution should be used only in special cases and in complementary tests.

INTRODUCTION

The first mortar datings were attempted in the 1960s, using radiometric methods on thermally released carbon dioxide (Labeyrie and Delibrias 1964) and later acid hydrolysis was introduced by Stuiver and Smith (1965). When acid hydrolysis is applied, differences in the solubility can be utilized to achieve accurate dating results: Anthropogenic binder carbonate grains are irregular and poorly crystalline and dissolve rapidly, while dead-carbon-bearing natural carbonate grains tend to be crystalline and dense and dissolve more slowly (Baxter and Walton 1970). Until the invention of accelerator mass spectrometry (AMS) in mortar dating (Tubbs and Kinder 1990), this chemical separation was mostly done with diluted hydrochloric acid (HCl) so that relatively strong acid (~1M) was injected into a slurry of sample powder and water. In this way, several small acid batches could be injected and the sample could be digested stepwise, or alternatively, the sample powder could be split into several aliquots that were subjected to varying degrees of digestion (e.g. Van Strydonck and Dupas 1991). The use of HCl has continued also in preparation for AMS analysis (e.g. Van Strydonck et al. 1992; Hodgins et al. 2011; Al-Bashaireh 2013). The small amount of carbon required (<1 mg) for AMS measurements made it possible to analyze only a very small fraction of the whole carbon inventory of the sample, or to take a very small piece of the sample (e.g. a lime lump without aggregate inclusions) for analysis. In the mid-1990s and onwards, it became common to use 85% phosphoric acid held in vacuum together with the sample and then tilted in excess over the sample. The CO_2 fractions were collected on the basis of reaction time (Ringbom and Remmer 1995; Heinemeier et al. 1997). In 2001, it became clear that some samples (e.g. Roman hydraulic mortars and fire-damaged mortars) have rapidly dissolving contaminants, and they must be analyzed by extracting many successive CO_2 fractions so that the mortar binder age can be read from the ^{14}C age profile. This article presents statistics on how different preparation techniques have been used on different kinds of mortars and how successful they have been. The benefits from lime lump analyses versus bulk mortar analyses will also be discussed.

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DATING METHODS

A variety of hydrolysis lines and mineral acids to extract CO_2 from the samples have been used through the years by our research group. Until 2006, all samples were prepared and analyzed at the Aarhus AMS laboratory (Heinemeier et al. 2010; Ringbom 2011). Between 2006 and 2009, some samples were prepared and measured at the AMS laboratories in Tucson, Arizona (TA, Hodgins et al. 2011) and Oxford using a similar line as in Aarhus. Since 2009, most of the samples have been converted to CO_2 at the laboratory of Geology and Mineralogy at Åbo Akademi University (ÅAU). Figure 1 is a schematic version of the preparation lines used in various laboratories. When 85% H_3PO_4 is used, the acid is let in via a burette (ÅAU) or tilted from a finger-like appendix within the vacuum system (Aarhus). In case diluted acid is used, it is either injected with a syringe (ÅAU, Figure 1; TA, Al-Bashaireh 2013) or inserted through a valve.

Initially, the first CO_2 fraction was collected within seconds, and the second fraction was collected after the reaction, a system that worked well with Åland lime mortars. Here the first fraction of several samples from the same building unit generally yielded ages in mutual agreement with independent age control, wherever available. Since porous mortar carbonate dissolves faster than the dense, contaminating unburned limestone, the first CO_2 fraction should be the purest and reflect the age of the construction (Folk and Valastro 1976).

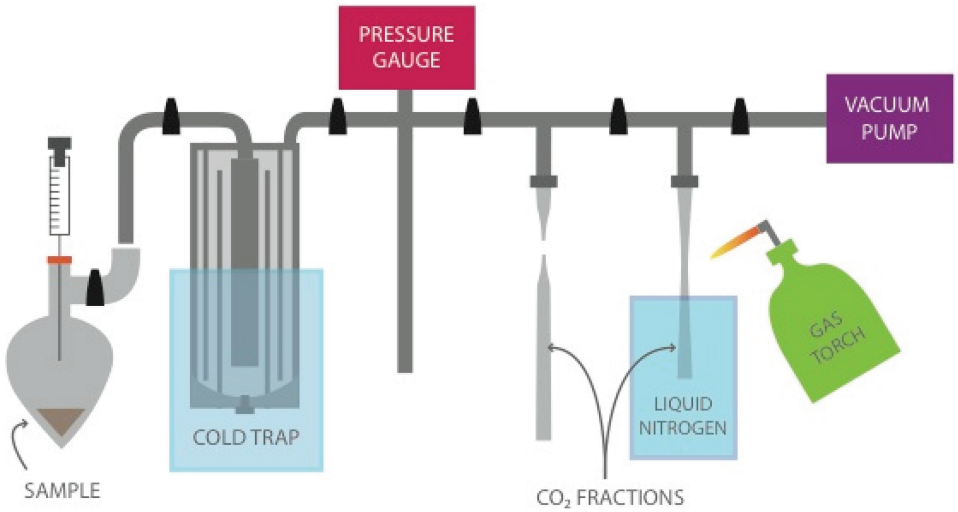


Figure 1 CO_2 preparation line. The sample is held in the reactor vessel to the left and the acid is introduced either as excess 85% H_3PO_4 with a burette or as injected batches of diluted acid (H_3PO_4 or HCl) with a syringe through a rubber septum. The cold trap contains isopropanol cooled down to −70°C. CO_2 is collected in glass vials cryogenically with liquid nitrogen (LN). Not shown in the figure is the LN cold trap in front of the vacuum pump.

However, dating pozzolana mortars was less straightforward. In these cases, age profiles revealed a more complex pattern including contamination from young carbonates. Therefore, new steps were taken in 2002: for pozzolana materials, 3–5 CO_2 fractions of the gas flow were isolated sequentially and analyzed separately, a system which was later applied to all mortars.

THE PROJECT AND ITS DATABASE

The state of research of *The Åland Churches Project* was published by Heinemeier et al. (2010). The article includes a thorough presentation of the method, and of the different ways of interpreting the results. It is now time to focus on the results from other areas of interest from a parallel project,

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The International Mortar Dating Project, which started in 1994, when we had replaced conventional radiometric ^{14}C dating of mortar with AMS analysis. In addition to the Medieval churches of the Åland Islands, we have also dated Medieval churches in the island of Gotland, Sweden, and in the Finnish southwestern archipelago. Classical sites, including both lime mortars and pozzolana mortars from varying types of constructions, have been investigated in Iberia and Italy (Figure 2).

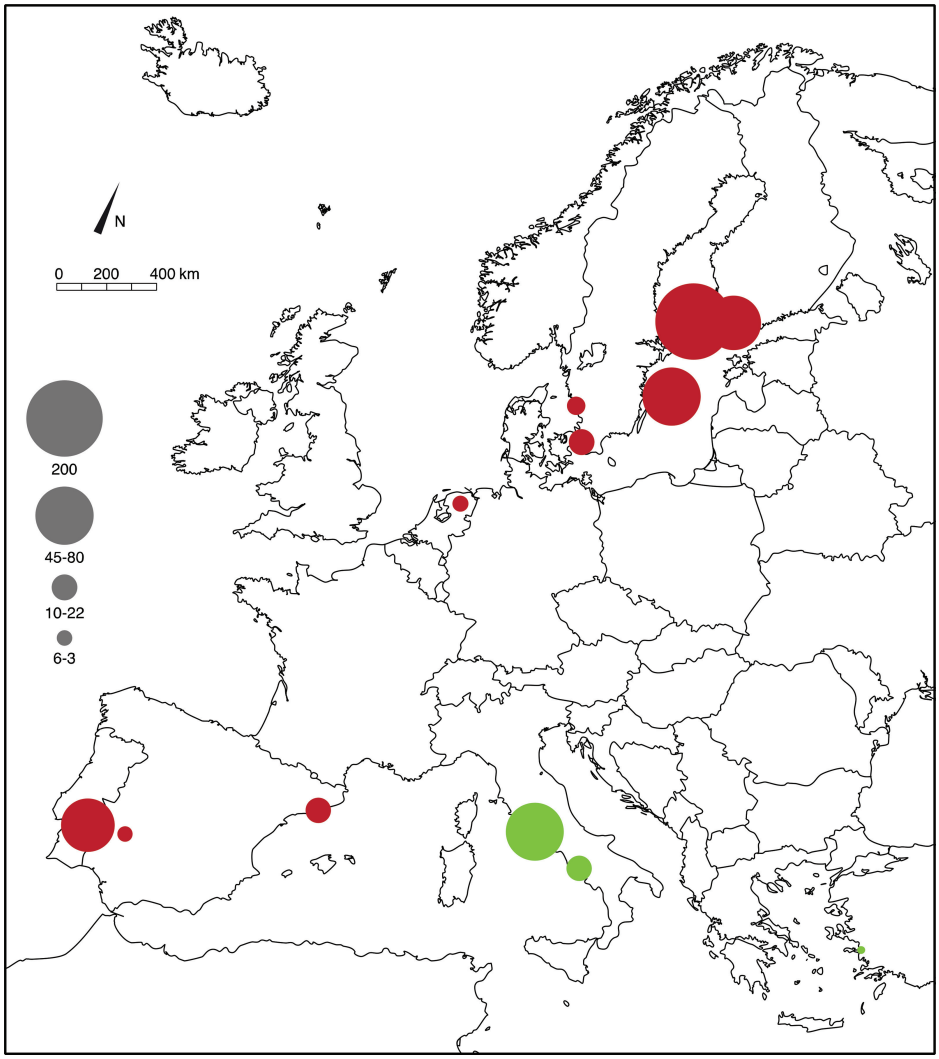


Figure 2 Map of mortar dating sites in Europe analyzed by the International Mortar Dating Project; those in red mark lime mortars, those in green, pozzolana concrete.

The vast majority of all analyses (423 samples) were performed on lime mortars. Since 1998, the database also includes 98 analyses of Roman pozzolana mortars. Most importantly, a recent focus on lime lumps embedded in the mortar has resulted in 32 analyses. For varying types of mortars, different types of chemical hydrolysis have been tested on aliquots of the same sample powder. This goes for both Medieval and Classical samples. In 480 cases, phosphoric acid (H_3PO_4) was used, whereas 65 samples were processed with hydrochloric acid (HCl). For comparison, several samples underwent both types of hydrolysis. Mortars from different chronologies were analyzed; 202 were

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Classical and 340 Medieval, mainly from the Nordic countries (Figure 3). Only six out of a total of 52 Roman samples were from the Middle Ages. Furthermore, mortars revealing fire damage have been studied carefully (Ringbom and Remmer 2005; Lindroos et al. 2011b, 2012).

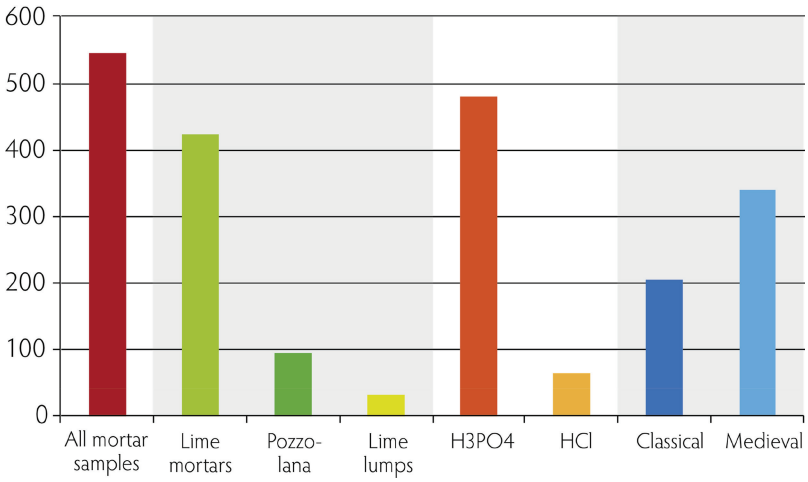


Figure 3 Diagram displaying mortar samples analyzed. The database now covers results from more than 540 analyses of some 470 individual samples. Some of the samples were analyzed repeatedly. The samples include different sorts of mortar, prepared with different types of hydrolysis, covering both Classical and Medieval archaeology.

PUBLICATIONS BY THE PROJECT

So far, the International Mortar Dating Project has published roughly two thirds of the obtained results, or 380/540 (Figure 4). Nearly all results from the dating of the Åland churches have been published by now (Ringbom and Remmer 1995, 2000, 2005; Lindroos et al. 2007; Heinemeier et al. 2010; Ringbom 2011; Ringbom et al. 2011b). Also, results from Rome and Pompeii/Herculaneum have been extensively published (Lindroos et al. 2011a; Hodgins et al. 2011; Ringbom et al. 2011a), as have the Medieval churches in SW Finland (Sjöberg 2011; Lindroos et al. 2011b), including all Criterion I samples (see next section) from Torre de Palma (Langley et al. 2011).

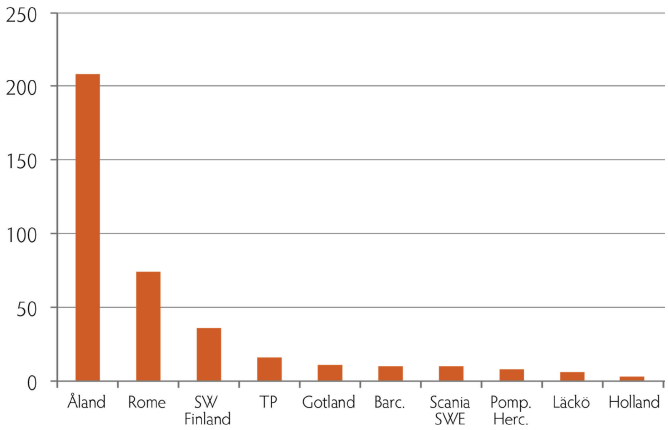


Figure 4 Sites published by the team, arranged topographically according to the number of samples.

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Experience gained from HCl hydrolysis in this project has been only partly published (Ranta and Lindroos 2009; Ranta et al. 2009; Hodgins et al. 2011; Lindroos et al. 2011b, 2012; Ringbom et al. 2011b). Concerning lime lumps, only our very first results have been published (Ringbom and Remmer 1995, 2005; Lindroos et al. 2011b, 2014a). Important mortar dating sites to be published in greater detail are Torre de Palma and the Gotland churches. The same applies to a systematic comparison between HCl and H_3PO_4 hydrolysis, and an extensive study of lime-lump analyses.

CRITERIA FOR INTERPRETATION OF MORTAR DATING RESULTS

Even if mortar may be the only datable material present at the site of investigation, it may be possible to check the obtained mortar dates against other sources of information. Different reliability criteria have been defined for the interpretation of the results (Heinemeier et al. 2010; Ringbom 2011). Criteria I and II can be used independently when there is no age control from other sources (Figure 5).

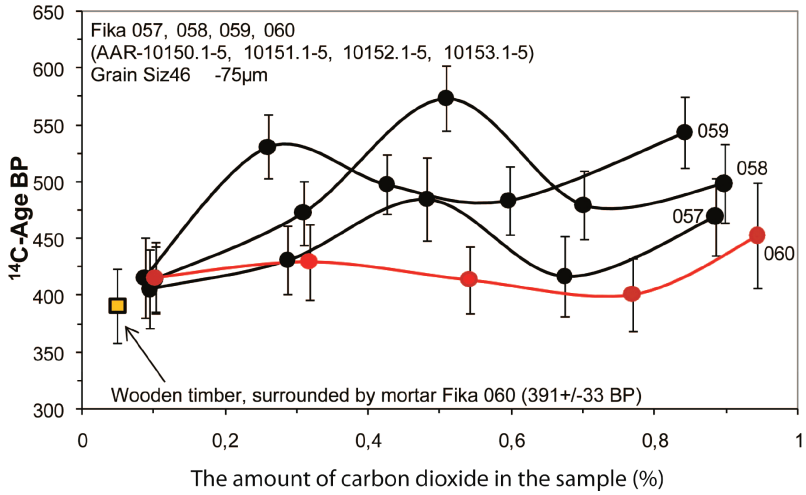


Figure 5 Examples of Criterion I and Criterion II, from Finström church, Åland. All profiles agree at the first CO_2 fractions (CII), and one of the age profiles, in red, is more or less horizontal (CI) (Heinemeier et al. 2010; Ringbom 2011).

In Åland, where we have learned the dissolution behavior of the mortars, we would consider a horizontal age profile a successful dating, giving a conclusive result. We define this type of result as Criterion I (CI).

Criterion I

The ^{14}C ages of the first two CO_2 fractions are the same (one sample per building unit is in principle sufficient for a conclusive result). The rationale behind this criterion is that if there is no age gradient (i.e. no increase in limestone contamination) from fraction 1 to fraction 2, then both fractions are most likely free of contamination and therefore date the time when the mortar hardened. The quoted date of the mortar sample is based on fraction 1 only in order not to exaggerate the precision of the result.

Most age profiles show an increase of contamination in later CO_2 fractions. If, however, the first fractions from the same building unit consistently yield the same age, we consider it a successful dating according to Criterion II (CII).

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Criterion II

Mutual agreement between the dates of the first CO_2 fractions in a series of three or more samples from one single building unit. The rationale behind this criterion is the following: Although the age gradient indicates a degree of contamination in fraction 2—and therefore possibly also in fraction 1—it is more likely that all first fractions have insignificant limestone contamination than all of them having the same amount of significant contamination, leading to the same age excess for all samples.

Many samples yield valuable data that are not sufficient for conclusive dating, but when put into a context it may help to clarify the chronology. However, they are not independently valid for dating, but need support of age control from other dating methods and other materials, such as dendrochronology and ^{14}C analysis of organic materials embedded in the mortar.

Criterion III

Mutual agreement between the dates of the first CO_2 fractions in two samples from a single building unit.

Criterion IV

Criterion IV describes a situation where the first CO_2 fraction from one sample in a building unit yields a date that fits into a relative chronology (Heinemeier et al. 2010).

TESTING DIFFERENT TYPES OF MORTARS

Results from dating lime mortar in two CO_2 fractions or in complete age profiles in the Åland churches have been successful. In cases where a comparison with other dating methods is possible, such as dendrochronology and ^{14}C analysis of organic materials embedded in the mortar, there is agreement in more than 96% of the cases (Heinemeier et al. 2010; Ringbom 2011).

The age profiles for fire-damaged mortars, however, consistently form a different pattern. Here the estimated age seems to be revealed by a horizontal plateau in the middle of the age profile, whereas the first fractions occasionally seem to indicate the date of the fire (Figure 6) (Heinemeier et al. 2010; Ringbom 2011; Lindroos et al. 2011b; Ringbom et al. 2011b).

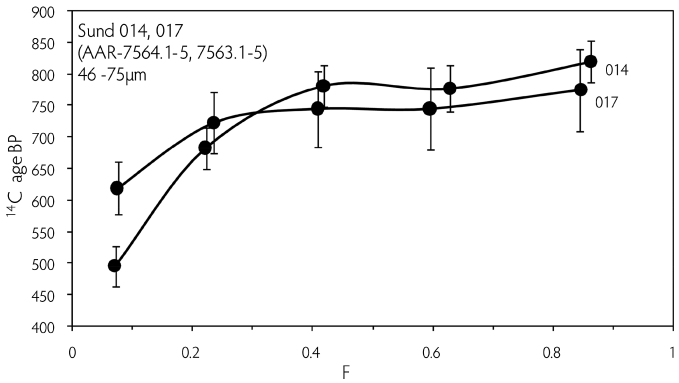


Figure 6 Two age profiles from the church of Sund, Åland. The samples are from the nave, which was repeatedly damaged by fire. The age of the construction is shown by the horizontal plateau of the age profiles. In this case, the role of the first CO_2 fractions is unclear. They may indicate Medieval fires that have remained unrecorded. The first recorded fire occurred in 1673, and the second in 1921.

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Between 1997 and 2000, AMS dating of mortar was introduced in Classical archaeology. Torre de Palma, the largest Roman villa complex on the Iberian Peninsula, meant an important extension of the project. Again, it was a case of non-hydraulic lime mortars, based on Estremoz marble (Lapuente et al. 2000) available nearby. Archaeologists from the University of Louisville (USA) had been excavating the site since the beginning of the 1980s, without a suitable method to establish the chronology of the site with certainty. Torre de Palma is of great importance, not only from an archaeological point of view, but also in a mortar-dating context. Like so many other prehistoric sites, it represents an abandoned site in ruins, left unsheltered for centuries. In addition, it was archaeologically excavated for decades. It therefore offers an opportunity to test the method in a place where the risk of disturbing erosion is obvious. Again, mortar was the only datable material present in most of the different building units. Only some of the oldest house foundations were erected in dry-wall technique, without the use of mortar.

At this stage, samples were dated in two CO_2 fractions only. Since the structures offered very little datable materials for age control, the most restrictive path was chosen—only Criterion I results were accepted as reliable dates. At Torre de Palma, 18 samples out of 64 met the demands of Criterion I (Figure 7). Independently of other materials and methods, these 18 samples could indicate the date

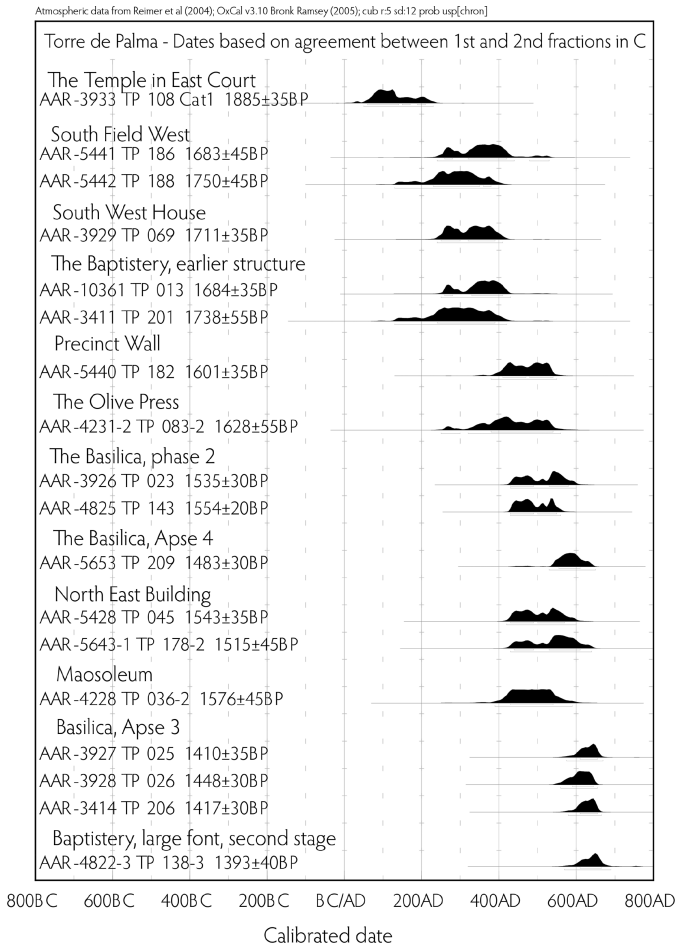


Figure 7 All these 18 samples are Criterion I samples from Torre de Palma, Vaiamonte, Portugal, outlining the chronology of the site.

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of 12 out of 21 structures, thus marking the outlines of the chronology of the site. The earliest structure was the temple in the East Court (AD 70–170), and the latest were apse 3 of the Basilica (AD 580–630) and the large font of the Baptistery (AD 570–690) (Langley et al. 2011).

It should be kept in mind, however, that the mortar analysis at Torre de Palma was introduced at an early stage of the development of the method. Analyzing only two CO_2 fractions per sample added some uncertainty to the results. Even if the 18 Criterion I samples at Torre de Palma indicate a plausible chronology for the site, continued tests representing more advanced stages of the development have already been initiated.

In Classical archaeology, dating ancient pozzolana concrete from Rome was the biggest challenge of all. The chemical difference between pozzolana mortars and lime mortars is fundamental. It was far from certain that the method would work, since pozzolana mortar is hydraulic and thus can harden even under water, without absorbing CO_2 from the atmosphere in the hardening process. Our testing of Roman pozzolana mortars was initiated in 1998. In Rome, sampling was done both in sheltered places under roofs and in exteriors exposed to weathering and erosion.

The first impression from dating pozzolana concrete was that the expected, or known, age was revealed only in the middle of the age profile, rather like fire-damaged mortars from Medieval Scandinavia (Lindroos et al. 2012). Only occasionally did the first CO_2 fractions yield the right age, as in the case of the Colosseum (Figure 8). The samples Colosseum 001-002 were taken from the entrance level, in an interior wall of the second room west of the north entrance, next to cavities where logs have been embedded. The room has always been well covered. Mortar was sampled between bricks, from the very surface some 1–3 cm into the wall (Ringbom et al. 2011a).

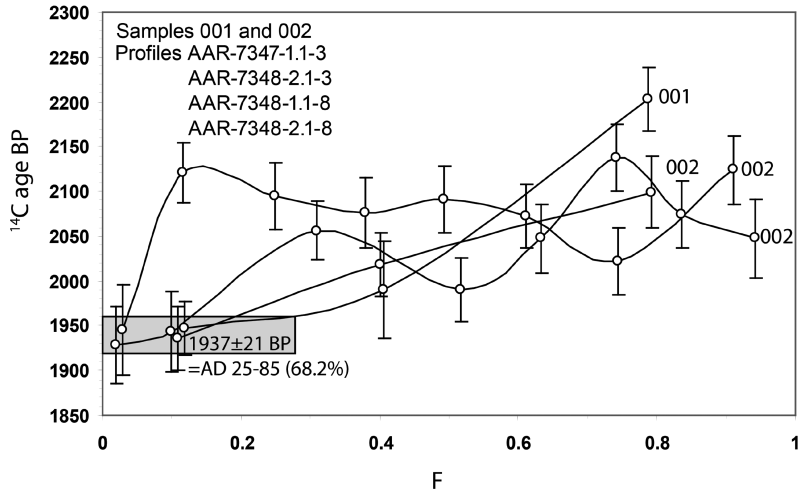


Figure 8 Results from the Roman Colosseum illustrating both CI and CII, the first CO_2 fractions indicating the date of the construction (Lindroos et al. 2011a).

As far as comparing the rate of success is concerned, analysis of Roman pozzolana concrete cannot compete with lime mortars from the Åland Islands. From all our pozzolana concrete results, only some 50% can be considered successful. However, most importantly, we learned why some analyses went wrong and what to avoid in the future (Figure 9). From eight samples taken in Pompeii and Herculaneum (Lindroos et al. 2011a), we learned that mortars buried under volcanic masses are not suited for dating. The same applies to mortars taken from deep within the walls or from

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under marble slabs, where the hardening has been delayed. Five experiments to establish early use of pozzolana mortars were unsuccessful. To be avoided are also mortars with crushed brick in the aggregate to make them water resistant (*cocciopesto*), e.g. for use in water cisterns. Also, some of the unsuccessful results came from an early stage of the sampling, when only two CO_2 fractions were analyzed, whereas a profile from analysis in five fractions would have been more informative (Ringbom et al. 2011a). Experiments have further been carried out with mortars based on burnt shells, mainly with positive results (Orsel 2012a,b; Lindroos et al. 2014b).

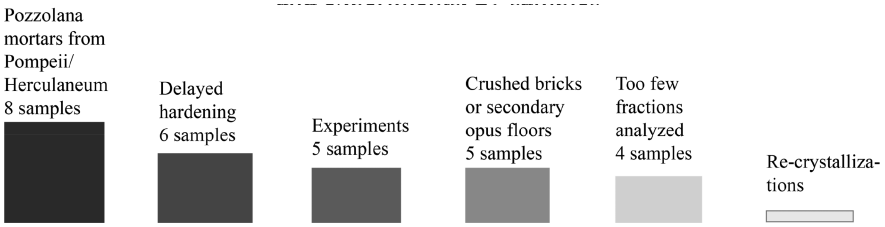


Figure 9 Diagram of unsuccessful (no reliable results yielded), yet instructive, analyses of Roman pozzolana mortars (modified from Ringbom et al. 2011a).

HYDROCHLORIC ACID USED IN THE SEPARATION PROCESS

In 2006–2010, our team analyzed altogether 63 samples using HCl hydrolysis in the separation process (Figure 10; Ringbom et al. 2006). Some 49 samples represented non-hydraulic lime mortars, while 13 were hydraulic pozzolana mortars. Only one lime lump was prepared with HCl hydrolysis. Sixteen samples came from fire-damaged constructions. Classical archaeology was represented by 12 pozzolana mortar samples; the rest of the samples were Scandinavian.

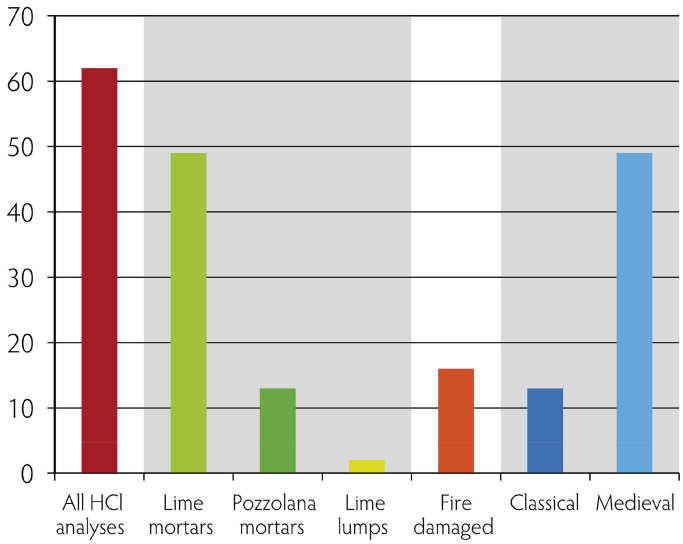


Figure 10 Diagram of samples prepared with HCl hydrolysis

Rome 007 (Figure 11), sampled at the highest point of Torre delle Milizie, from the exterior of the wall, represents Medieval Roman pozzolana mortar with an estimated age at the end of the 13th century. The sample has been analyzed repeatedly, by all three different AMS laboratories involved (Aarhus, Oxford, and Tucson), and with both types of hydrolysis—H_3PO_4 and HCl. In each individ-

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ual case, the first CO_2 yielded similar ages. Actually, in this case the HCl hydrolysis yielded the least inclined age profile, more horizontal and easier to interpret. Could HCl occasionally work better for pozzolana concrete than for lime mortars?

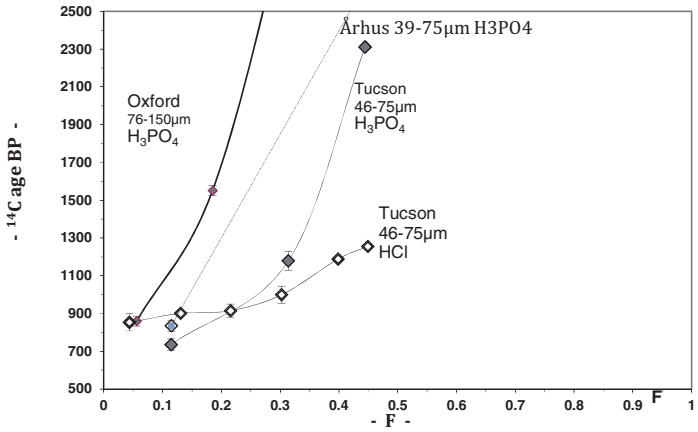


Figure 11 Plot of Rome 007, taken from the unsheltered exterior wall at the highest point of Torre delle Milizie (Lindroos et al. 2011a).

Sample Rome 004 from Basilica Ulpia was also tested with both types of hydrolysis, this time resulting in an agreement in the middle of the age profiles (Figure 12). Thus, in this case, the same type of age profile seems to be repeated with both types of acids—the HCl hydrolysis behaved much like the H_3PO_4.

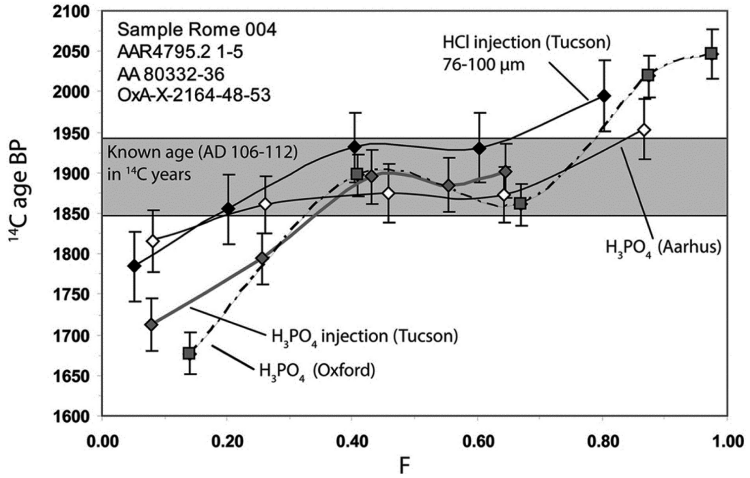


Figure 12 Rome 004 from Basilica Ulpia, erected in AD 106–112 by Emperor Trajan. It was sampled from a big chunk of pozzolana mortar from the original coffered ceiling, which had collapsed during the Renaissance.

In 2007, HCl hydrolysis was tested on lime mortars from Medieval churches in southwestern Finland (Turku Cathedral, Pargas, Nagu, and Korpo) (Lindroos et al. 2011b; Sjöberg 2011), and in the outer archipelago of the Åland Islands churches (Kökar, Föglö, and Kumlinge) (Ringbom et al. 2011b), again, in comparison with H_3PO_4 hydrolysis. As an example, we present the HCl age profile from Turku Cathedral. It starts off as much too old, only to fall abruptly (Figure 13). In the middle of the dissolution process, it reaches the horizontal level of the H_3PO_4 profile. When comparing

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HCl and H_3PO_4 hydrolysis on Scandinavian lime mortars, the pattern often repeats itself—the first CO_2 fractions of the HCl hydrolysis frequently yield too-old dates. Compared to H_3PO_4 hydrolysis age profiles, the HCl hydrolysis created almost mirror images: the first CO_2 fraction often was far too old, an experience totally new to us. But the pattern varied. Occasionally, the plausible age was yielded at the beginning, sometimes in the middle of the dissolution process, or not at all.

Yet, in spite of the confusion described above, there are Scandinavian cases where the HCl hydrolysis seems successful, such as in the church of Pargas and in the precinct wall surrounding the church of Kökar (Ringbom et al. 2011b; Sjöberg 2011). Only some 50% of all HCl samples have yielded reasonable results. For the interpretation of HCl age profiles, criteria I–IV cannot be used.

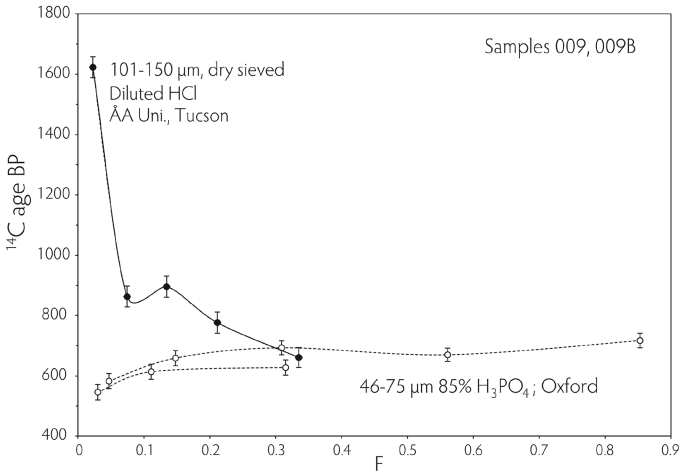


Figure 13 HCl versus H_3PO_4 hydrolysis. Plot from Turku Cathedral, lime mortar sample from the fire-damaged attic of the Sacristy. The age profile of the HCl hydrolysis yields far too high an age with the first CO_2 fractions, whereas the H_3PO_4 age profile coincides with the age suggested by written sources at the horizontal plateau (Lindroos et al. 2011b).

DATING LIME LUMPS EMBEDDED IN LIME MORTAR AND IN POZZOLANA MORTAR

When quicklime from the kiln is slaked, it is mixed with water and worked to a putty. There may still, however, survive clods of quicklime in the putty, which become slaked and carbonated possibly already before the aggregate is added. These form aggregate-free, white lumps in the mortar (Pesce et al. 2009). In principle, well-burnt lime lumps should be free from contamination. If so, they would have great potential for dating difficult mortars, such as pozzolana mortars, but also for fire-damaged mortars with age profiles equally problematic.

So far, 32 lime lumps have been dated, from lime mortars, pozzolana concrete, and fire-damaged mortars. We initiated analysis of lime lumps in 1994, at first sporadically, later more systematically. Finding lime lumps embedded in lime mortar and pozzolana mortars became a high priority. We spotted them frequently, but until now only part of them have been tested and analyzed (Figure 14).

Only a few of these lime lump results have so far been published (Ringbom and Remmer 1995, 2005; Heinemeier et al. 1997; Sjöberg 2011; Lindroos et al. 2007, 2014a). Table 1 presents some new results. The results from dating lime lumps embedded in the mortar have been promising. In fact, so far only those from Pompeii have failed completely (Lindroos et al. 2011a).

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Table 1 Lime lump dating results and data related to the hydrolysis. $\delta^{18}O$ values are not comparable with values from standard stable isotope procedures. They are included as descriptive parameters for progress of the reaction (Rome 007, Torre delle Milizie, samples Rome 042, 1-2, Santa Costanza).

Sample carbon yield (%)	Grain size µm	CO_2 fraction (%)	^{14}C age BP	± yr	$\delta^{13}C$ ‰	$\delta^{18}O$* ‰	Lab nr
Rome 007Li 1 9.8	21–150	0–98	716	40	−18.37	−9.22	AAR-15193,1
Rome 042Li 1 5.7	21–75	0–58	1683	40	−13.76	−7.36	AAR-15194,1
Rome 042Li 2	76–150	0–45	1738	25	−14.12	−7.81	AAR-115195,1
11.6		45–84	1700	30	−11.78	−8.86	AAR-115195,2
		84–100	1718	30			AAR-115195,3

*85% H_3PO_4.

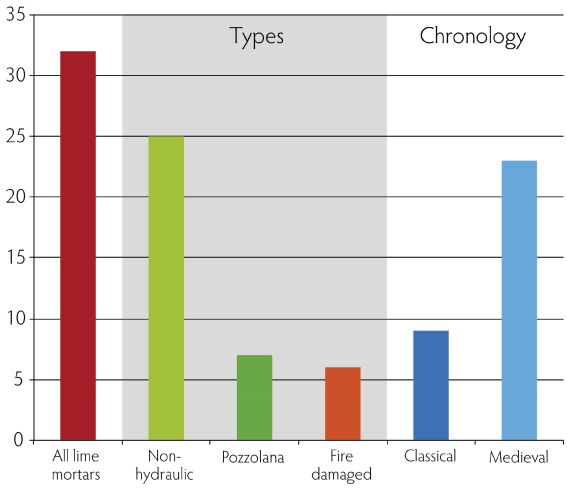


Figure 14 Breakdown of results from 32 lime lumps embedded in the mortar. Of these, 25 lime lumps were identified in lime mortars, whereas 7 were embedded in pozzolana mortars. Of the 32 samples, 7 had been exposed to fire. HCl hydrolysis was used just once. The majority come from Medieval Scandinavia.

The age of Haka 044Li (Li stands for lime lump), Hammarland Church, Åland, from a secondary vault, was obtained already in 1994. The age of the first and second fractions are similar and overlap with the age of the first fraction of the surrounding bulk mortar sample of Haka 044 (Figure 15). It was our first experience of dating lime lumps. The result is convincing, and yet, at the time the potential of dating lime lumps was not realized, because dating Åland lime mortar in two fractions seemed just as reliable (Heinemeier et al. 2010; Ringbom 2011).

Even so, it was not until 2010 that systematic search for lime lumps became the main focus of our research. At the same time, and independently of our work, Gianluca Pesce and his team had initiated dating of lime lumps. They have tested Medieval Italian mortars, with equally promising results (Pesce et al. 2009, 2012).

Depending on the small size of the samples, lime lumps are usually analyzed in just one or two CO_2 fractions. Only occasionally is there sufficient material for a full age profile (i.e. five fractions).

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Regardless of mortar type (lime, pozzolana, or fire-damaged mortar), most results reach a plausible age with the first fraction. With two or more CO_2 fractions analyzed, the age profiles often form a horizontal line, marking reliable CI results. Occasionally, the later CO_2 fractions are older, revealing insufficient burning of the limestone (cf. Marzaioli et al. 2013). But in these cases, the first CO_2 fraction seems to pinpoint the plausible age.

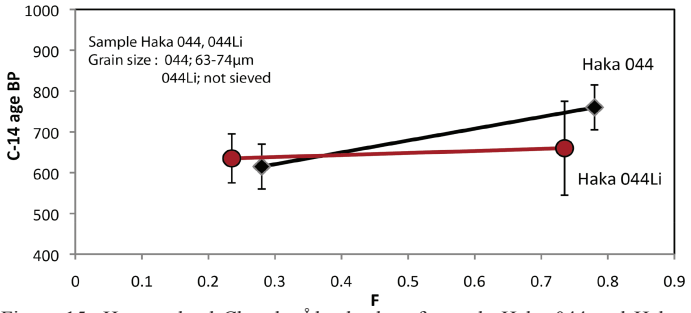


Figure 15 Hammarland Church, Åland, plot of sample Haka 044 and Haka 044Li. The lime lump profile (in red) is almost horizontal.

From the vaulting in the church of Sund, Åland, we can compare the age profile of a lime lump with that of the surrounding bulk mortar. The difference between the two profiles is striking (Figure 16). The bulk mortar presents an atypical and inconclusive age profile, with a peak at the third CO_2 fraction, after which it falls again. On its own, it would be difficult to know which CO_2 fraction in the profile dates the construction. The lime-lump profile is very different. It is almost horizontal and thus settles the question. The mortar including the lime lump obviously belongs to the repairs of the church after a fire recorded in the 1670s (Lindroos 2005; Ringbom and Remmer 2005; Heinemeier et al. 2010).

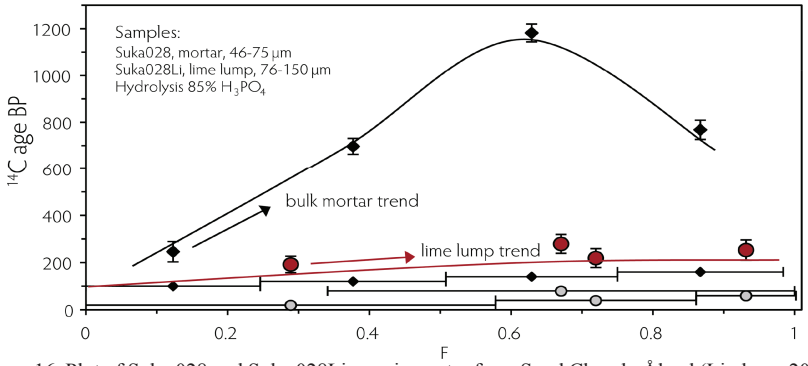


Figure 16 Plot of Suka 028 and Suka 028Li, repair mortar from Sund Church, Åland (Lindroos 2005)

A small lime lump was identified in sample Rome 007 (Figure 17), which had earlier been analyzed at three different AMS laboratories. It was dated in one CO_2 fraction at the AMS laboratory at Aarhus (because it was too small to yield CO_2 for further fractions). The result, Rome 007Li, confirms our earlier interpretations of the individual age profiles from Rome 007, especially that of the HCl hydrolysis. The calibrated result of 715 ± 40 yields two peaks at 2σ, AD 1222–1310 (81.5%) and 1360–1387 (13.9%). But even if the result from analyzing the whole lime lump in this case seems straightforward, it would be better to collect CO_2 from only the beginning of the hydrolysis process. This is because in the beginning of the process the risk of contamination from improperly burnt limestone should be minimal.

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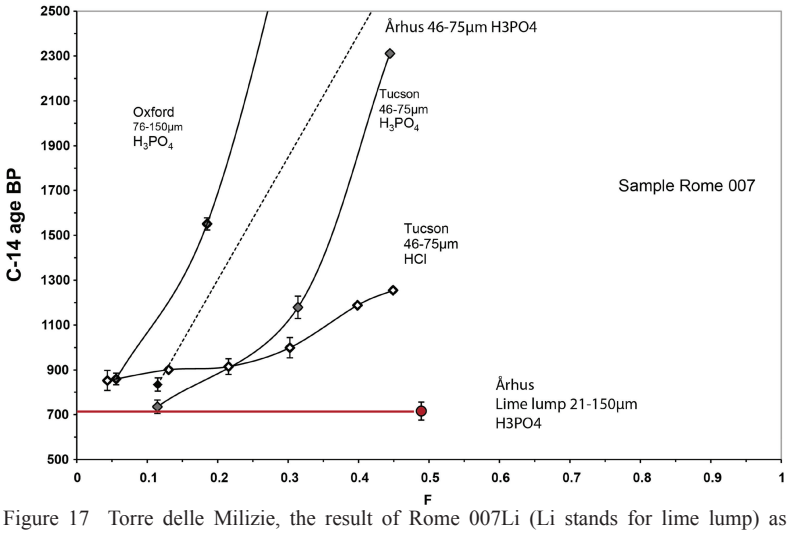


Figure 17 Torre delle Milizie, the result of Rome 007Li (Li stands for lime lump) as compared to the other samples.

The rotunda of Santa Costanza is a secondary construction adjoined to the horseshoe-shaped basilica of Saint Agnese. The age of Santa Costanza has been disputed; the two options are AD 337–350 built by Constantina, daughter of Constantine the Great, or erected by Julian the Apostate in AD 361–363 (Ringbom 2003). Several samples have been analyzed from the rotunda, in all three AMS laboratories, with different types of hydrolysis, both H_3PO_4 and HCl. These results form a confusing cluster of profiles (Hodgins et al. 2011). Two analyses of one lime lump were clarifying: one analyzed in three CO_2 fractions, creating an almost horizontal age profile, supported by the other analysis in one CO_2 fraction only (Figure 18). Yet, unfortunately the chronology of Santa Costanza still remains enigmatic, since the age difference between the two options is too small to be resolved by ^{14}C dating, especially since the calibration curve at this stage is irregular, creating a chronology with a wide timespan.

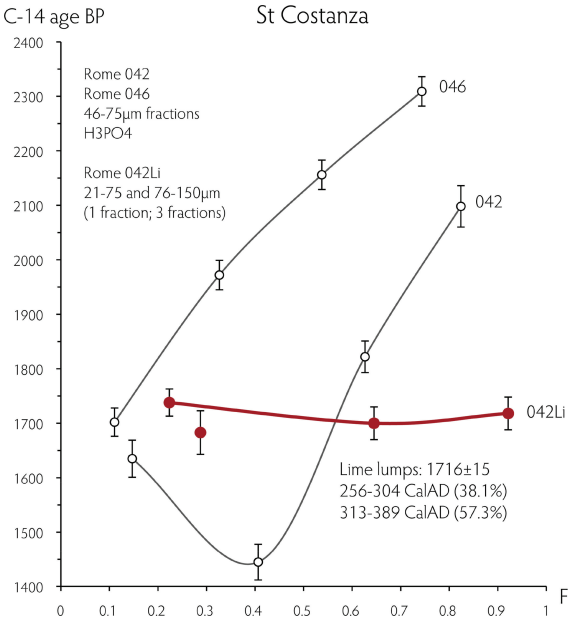


Figure 18 Santa Costanza, the well-preserved rotunda at the Via Nomentana, Rome, originally a mausoleum from the 4th century AD. The lime lump profile represents CO_2 fractions 1, 3, and 4 because fraction 2 was lost. In a secondary run only the first fraction, representing 0–58% of the carbon yield was analyzed.

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DISCUSSION

To begin with, non-hydraulic lime mortar analyzed in two CO_2 fractions and sampled from well-sheltered places like in the Åland churches seemed straightforward and easy to date using H_3PO_4 hydrolysis. Torre de Palma meant an important extension of testing the method in Classical archaeology and of defining different reliability criteria for interpretation when mortar was the only available material for dating. Our experience from Torre de Palma, with mortars exposed to weathering, also seemed to demonstrate the usefulness of these criteria in establishing reliable dates. Later, this view was confirmed when samples from Åland were analyzed in complete age profiles with 4–5 CO_2 fractions. The known age was reached at the beginning of the age profile. With mortar analysis, we have been able to solve the problem of the chronology both of the Åland churches and of Torre de Palma.

Fire-damaged mortars form different kinds of age profiles. In our experience, the estimated age is indicated by a horizontal plateau in the middle, thus enabling dating with due caution. Compared to non-hydraulic lime mortar, results from Roman pozzolana mortars are hard to interpret. The known age can be represented by different stages of the age profiles, either at the beginning or at a horizontal level in the middle of the profile. Samples from the same building unit can yield different age profiles, as in Trajan's Market (Ringbom et al. 2011a: Figures 14 and 17).

Only about 50% of all the pozzolana mortar samples have been reliably dated through ^{14}C AMS analysis. However, important observations were drawn from samples that went wrong. Among other things, it is clear that dating cocciopesto with crushed bricks or ceramics mixed into the matrix should be avoided. To avoid the effect of delayed hardening, samples should be taken from the surface, not too deep in the wall. And for some reason, pozzolana mortars covered with volcanic ashes as in Pompeii or Herculaneum have consistently gone wrong (Lindroos et al. 2011a; Ringbom et al. 2011a). Therefore, already at an early stage of testing the method on Roman pozzolana mortar it was obvious that there was still a long way to go before the method could provide reliable results. Testing Roman pozzolana mortars with HCl hydrolysis gave more straightforward results. Still, pozzolana mortars proved to be too problematic even so. Therefore, at present we focus on analyzing lime lumps embedded in mortars in general, and especially in pozzolana mortars.

Hopefully our databank covering our wide experience from different types of mortars, hydrolysis, and chronologies offers a valuable opportunity to learn from experience. Conclusions may be drawn about what to avoid and where to focus in future developments of the method.

CONCLUSIONS

Based on our experience, the following conclusions can be drawn:

a) H_3PO_4 hydrolysis of non-hydraulic lime mortars, in age profiles of 2, or 4–5 CO_2 fractions, has generally been successful. Here, the expected age, as known from age control, was reached with the first CO_2 fractions of the age profile; that is, the samples fulfill criteria I and II.

b) The criterion discussion is useful and valid with H_3PO_4 hydrolysis of non-hydraulic lime mortars.

c) H_3PO_4 hydrolysis of hydraulic pozzolana mortars has been less successful. Age profiles are hard to interpret, since several types of age profiles can be represented within the same building unit.

d) HCl hydrolysis of lime mortars results in confusing age profiles, where the plausible age is not necessarily reached at the beginning of the age profile, and should therefore be avoided. Yet, we have sporadically been able to identify the correct age at the first CO_2 fraction, and occasionally HCl is better than H_3PO_4 for pozzolana mortars. The reason for this variable behavior so far remains unknown; we therefore discourage the use of HCl hydrolysis also for pozzolana mortars.

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e) HCl results cannot be interpreted with the same reliability criteria as H_3PO_4 results.

f) Pozzolana mortars from Pompeii and Herculaneum cannot be dated, regardless of what type of hydrolysis is used, and regardless of sample type, whether it is a question of pozzolana mortars or lime lumps embedded in the mortar.

g) Fire-damaged lime mortars procure age profiles where the first fraction seems to date the fire, whereas a horizontal platform later in the profile identifies the real age of the building construction.

h) Most important, however, is the high percentage of success noted in the analysis of lime lumps embedded in the mortar, both in the case of lime mortars and pozzolana mortars. Here, the first CO_2 fraction tends to provide the most plausible results, which have generally supported our earlier interpretations of analyses based on the mortar proper. Lime lumps usually contain very little contamination by unburned limestone or marble, thus requiring fewer CO_2 fractions to obtain reliable dates. Above all, for dating Roman constructions, analyzing lime lumps embedded in pozzolana mortar may be the solution.

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