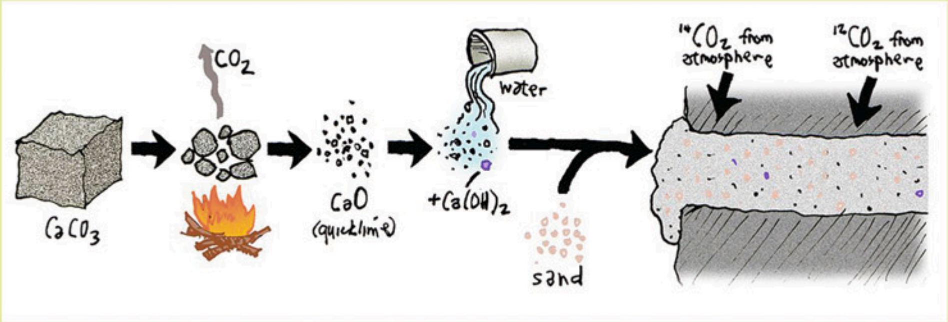
WHEN DID THE MORTAR HARDEN?

A new method for dating buildings and other structures through AMS radiocarbon analysis.

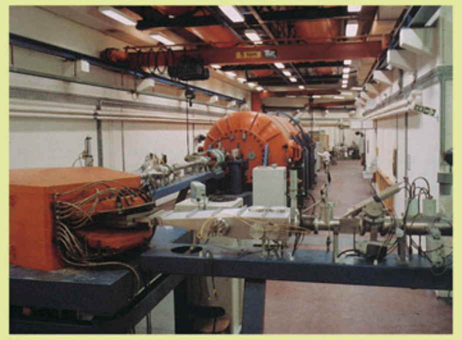
This is an account of an interdisciplinary Scandinavian-American team in the process of developing the method of dating ancient mortar. If reliable, such a method means a great step forward for studying the architecture and engineering of the Roman Empire and other ancient civilizations. For the first time buildings without diagnostic archaeological artifacts could be dated as isolated chunks of building debris. Such a method has been sought for over 30 years.

The method - Lime is the key

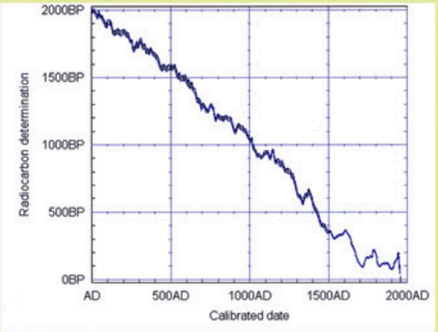


ill. 1

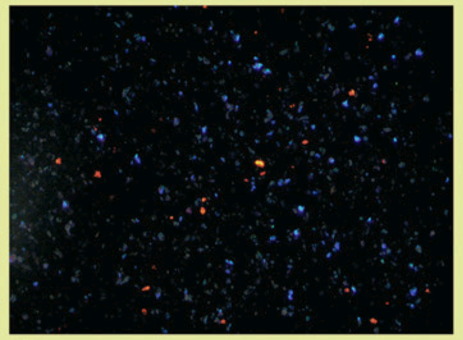
When hardening the mortar absorbs the carbon dioxide of the atmosphere (ill. 1).
Ancient mortar thus contains a sample of atmospheric carbon, which can be subjected to radiocarbon dating. Initially the ratio of ^{14}C to normal carbon in plant and animal tissues reflect the roughly constant atmospheric concentration. But after an organism dies, radioactive decay reduces the original amount of ^{14}C by half every 5.730 years. However, with mortar the presence of fossil carbon complicates the endeavor. Particles of unburned limestone (calcium carbonate that survived the heating) constitute one source of contamination. Recrystallization of calcites in the mortar causes another type of contamination.



ill. 2



ill. 3



ill. 4

The particle accelerator in the laboratory in Aarhus, Denmark (ill.2), has been used to separate carbon-14 from the more abundant isotopes of carbon (carbon-12 and carbon -13) a technique called accelerator mass spectrometry (AMS).

Before the AMS analysis the mortar samples, mechanically separated with gentle crushing followed by wet and dry sieving, using increasingly fine mesh widths, undergo a further chemical separation, where phosphorous acid is poured under vacuum over the sample prepared. This procedure creates a gas of carbon dioxide, the flow of which was interrupted in two stages. These two different gas fractions were isolated, formed into graphite and thereafter each one was analyzed separately. Of these the first fraction gave a result which corresponded with the estimated age.

The calibration curve (ill. 3).

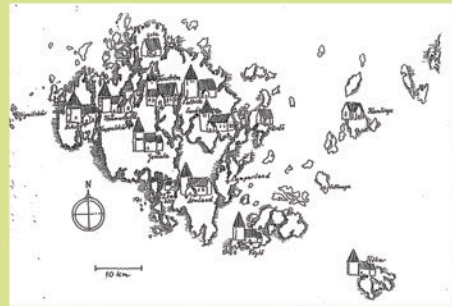
Radiocarbon measurements are by convention cast in terms of radiocarbon years "before present" (meaning before 1950) using the known half-life of carbon-14. The calibration between radiocarbon age and calendar age, varies because the concentration of atmospheric carbon-14 changes over time. In order to yield the right calendar age, this BP age therefore has to be weighted against the calibration curve, which illustrates the wiggling course of the concentrations of radioactivity in the atmosphere. These irregularities in turn effect the accuracy of the ^{14}C analysis.

Cathodoluminescence microscopy to trace contamination (ill. 4).

After mechanical separation of the mortar sample, cathodoluminescence microscopy helps to control the contamination from unburned fossil limestone. Insufficiently burnt limestone is revealed as glowing orange or red against a dull gray background. The blue spots are quartz crystals.

Implementations and results

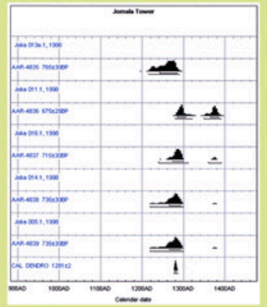
Step 1 – Testing the method against firmly dated structures in Medieval Åland.



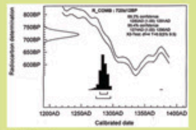
ill. 5

ill. 6 a

ill. 6 b



ill. 6 c



ill.6 d

The medieval stone churches of the Åland Islands (ill. 5).
The project was initiated in the beginning of the 1990s with the medieval stone churches of the Åland Islands, between Finland and Sweden, where the dating was an open and controversial question, since no written contemporary records survive

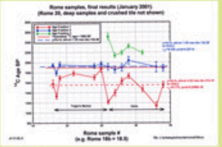
Dendrochronlogical analysis of the timber in the church tower of Jomala (ill. 6 a) **showed that the logs were felled in 1281.**
To ensure original mortar for the analysis, the samples were taken from mortar touching the timber beams, which are firmly dated by tree ring counting (ill. 6 b). The calibrated results from the first fractions of five mortar samples in the tower (ill. 6 c) - at this stage only two fractions were separated chemically, and dated separately - gave surprisingly even results, which corresponded with the known date of the timber beams. The joint calibration of the mortar samples hit a steep spot of the calibration curve, yielding ^{14}C dates of 1279-1290 (ill. 6 d), the most remarkable bull's-eye yet achieved with the newly developed method.

Step 2 - Going international, testing other types of mortar and other chronologies, Roman mortars and pozzolana.

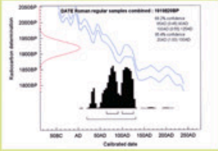
The focus was set on firmly dated structures in the Mediterranean and the territory of the Roman Empire. One big challenge was to see how the mortar from ancient Rome made with pozzolana would behave in the analysis.
In Roman pozzolana mortar volcanic ash was mixed into the aggregate. When combined with building lime, the silica and alumina of the pozzolana cause a chemical reaction resulting in a mortar much stronger than mortar made with quartz sand. The pozzolana mortar is hydraulic and it will harden under water. It was in fact believed that it did not need the carbon dioxide from the atmosphere for the hardening process.
Hydraulic mortars continue to be chemically active for a very long time and seem to produce readily soluble carbonates whenever exposed to atmospheric CO_2. They are also full of recrystallizations for several reasons. The impermeable hydraulic mortar will retain pockets with unreacted $Ca(OH)_2$. These will continue to react with CO_2 and form carbonates whenever the mortar is disturbed by breaking or crushing.

ills. 7 a-7 b

ills. 8 a-8 b



ill.9 a



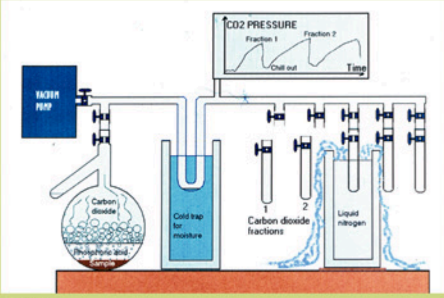
ill. 9 b

Sampling was done in the interior of **Trajan's markets** (ills. 7 a-7 b) where the date AD 106-113, is well known from historical sources and from brick stamps, and in the exterior of **Caseggiato del Giardino, Ostia** (ills. 8 a-8 b) with a slightly later age, (i.e. 118-138), equally well known.

Results from individual samples in Trajan's Market and in Ostia (ill. 9 a) show, that differently from Åland, the second fractions, (colored blue), rather than the first, came close to the estimated date. This is even more obvious in the graphical curve of the joint calibration of the second fractions (ill. 9 b).

Step 3 – Profiles based on successive CO2 fractions.

The results from Trajan's Market and Ostia demonstrated the necessity to analyze the mortars samples in several fraction based on a separation system with successive CO_2 fractions (% of total CO_2 yield) from mortar carbonates during reaction with phosphoric acid (ill. 10).

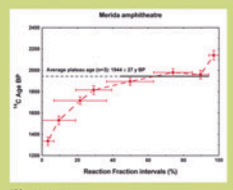


ill. 10

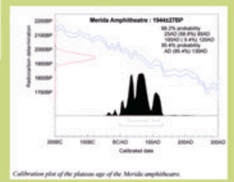
Samples were taken in the provincial city of Merida, western Spain, where the amphitheatre (ill 11 a-b) according to inscriptions was inaugurated in 8 BC. Nevertheless archaeologists want to date this amphitheatre to the Flavian period around AD 80.
The multi fraction analysis creates a profile, where the fractions seem to stabilize at the horizontal level (ill. 11 c). **The horizontal level yields an age of 1944** +/- 27 BP which corresponds with the calibrated age range of AD 25-120 (ill. 11 d) . Here the wide error margins depend on the wiggling calibration curve.

In the profile fractions with low ^{14}C ages dissolve first, where after the ages stabilize horizontally.
The first fraction yielding an age far too recent, shows the influence of the later reactions for atmospheric CO_2, due to different kinds of recrystallizations and alkalinity of the sample. The last fraction was extracted after overnight reaction. It is clearly affected by dead carbon from unburned limestone.

ill. 11 a-b



ill. 11 c

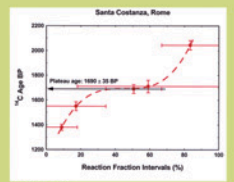


ill. 11 d

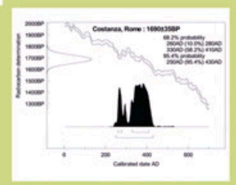
New light on Santa Costanza, Via Nomentana, Rome (ill. 12a-c)

ill. 12 a

ills. 12 b-12 c



ill. 12 d



ill.12 e

Santa Costanza is yet another enigmatic construction which remains open to debate. The common explanation is that it was erected as a mausoleum by and for Constantina, daughter of Constantine the Great, between AD 337 and AD 351. The result of the mortar analysis, so far based on one sample (Ill. 12 d-e), indicates that the building rather belongs to the second part of the fourth century. This would support the recent discovery that the mausoleum is later than the circus shaped basilica of St. Agnes.

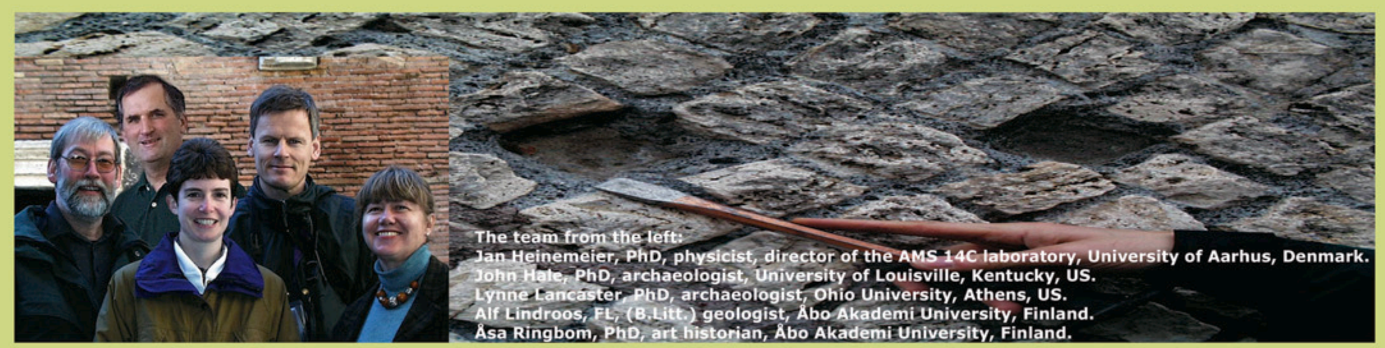
So far our project has demonstrated that:

A: Although some problems remain to be addressed, our results suggest that the foundation for a viable mortar-dating method has now been established.

B: The preparation of the samples is as important a part of the analysis of the radioactive isotopes in the AMS, as the analysis itself, for determining a correct age.

C: The horizontal level in profiles based on chemical separation of a sample in several successive fractions, gives the most accurate results. This is true wherever the sampling was done, either from the sheltered interior or the exposed exterior of a building.

D: Pozzolana does indeed, whenever possible, react with the CO_2 of the atmosphere, which makes it possible to analyze Roman mortar with the new AMS method described above.



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