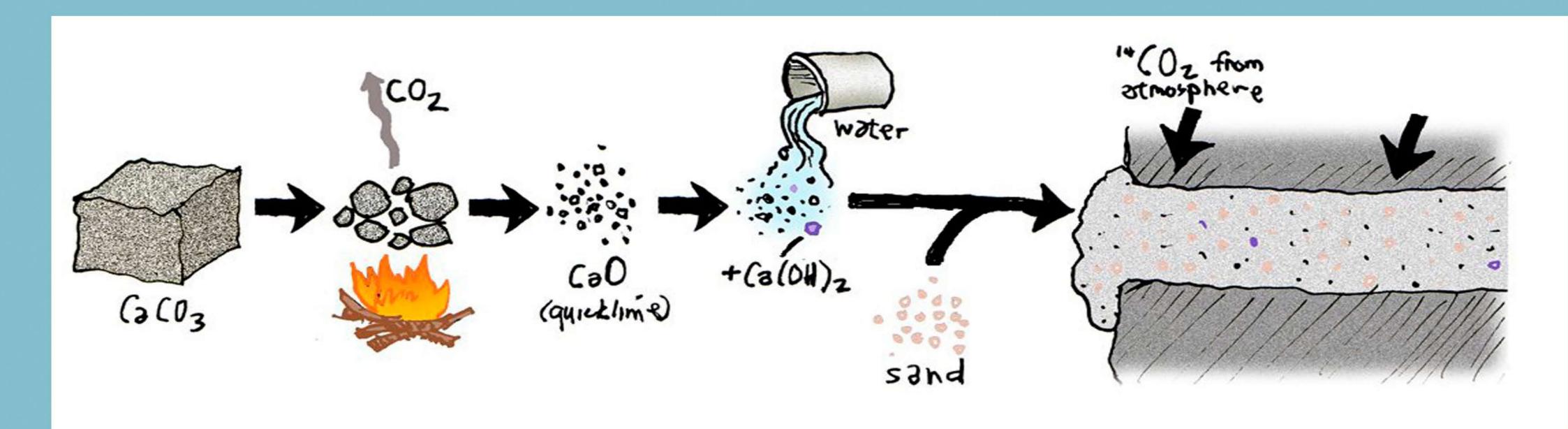
# The principle of <sup>14</sup>C AMS-analysis of mortar

This poster presents the state of research in developing a method which ideally could work on mortars of different types and different dates. The focus is on mortared structures, hydraulic and non-hydraulic, in the Mediterranean and the territory of the Roman Empire. The methodological development of <sup>14</sup>C AMS [Accelerator Mass Spectronomy] dating of mortar began in 1994, with encouraging results from Medieval Scandinavia. An interdisciplinary collaboration to develop techniques for AMS dating of concrete and other lime mortar construction materials was formed in 1997, with the aim of introducing the method into classical archaeology and defining potentials and limitations of the technique.

### Mortar absorbs carbon dioxide from the atmosphere when hardening, which makes it potentially suitable for normal <sup>14</sup>C dating.

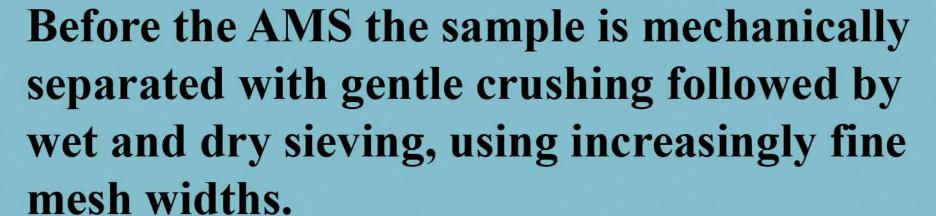


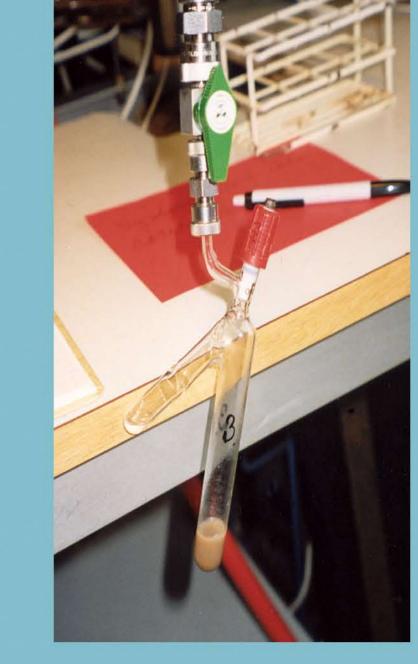
However, the method has to deal with potential problems, such as:

- Unburned fossil limestone (calcium carbonate that survived the heating, or was mixed into the filler with the sand) results in dates too ancient.
- Re-crystallization of the mortar carbonate, results in dates too recent, due to later exchange with the atmosphere.

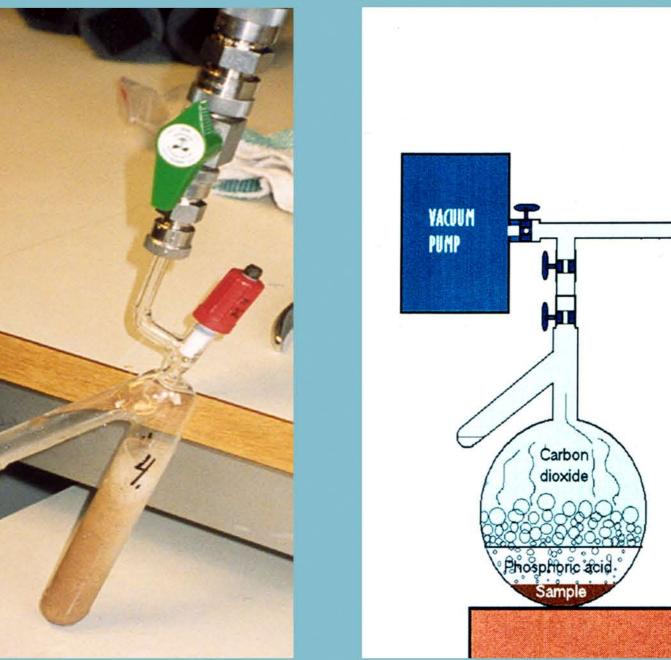
## To control these problems, both mechanical and chemical separation of the sample is required

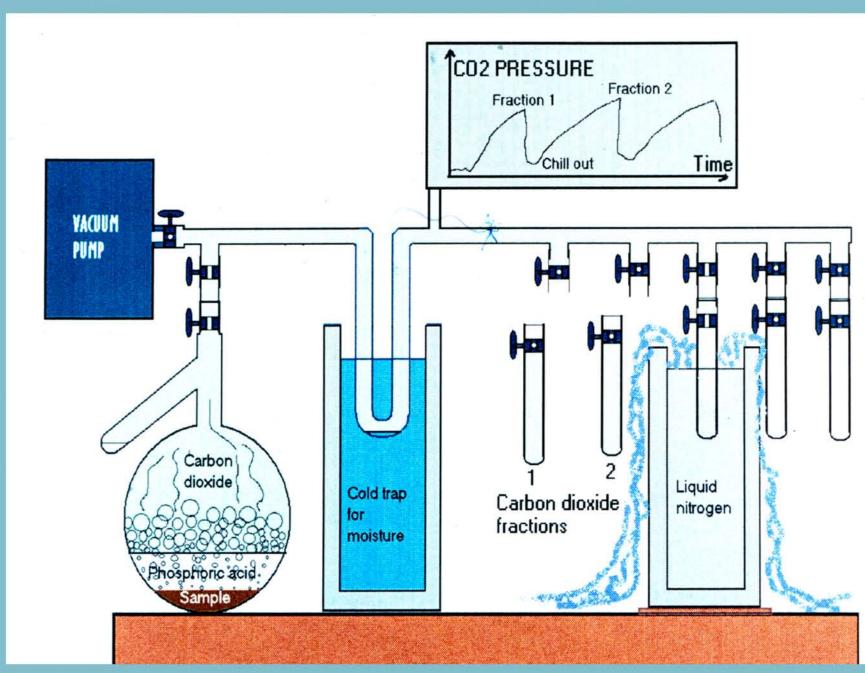






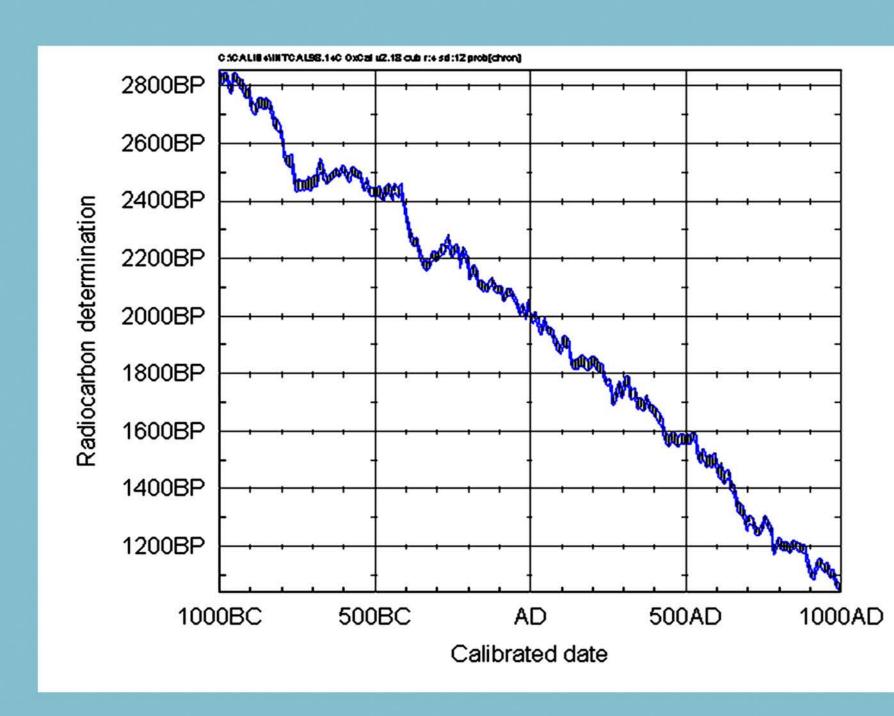
The mortar samples undergo further chemical separation by stepwise reaction with phosphororic acid under vacuum, releasing carbon dioxide gas.





The flow of the gas is interrupted into several CO<sub>2</sub> fractions. Since limestone dissolves more slowly than mortar, the first CO<sub>2</sub> fraction should in principle be free from contamination. The successive fractions are subsequently formed into graphite and analyzed separately to form age profiles.

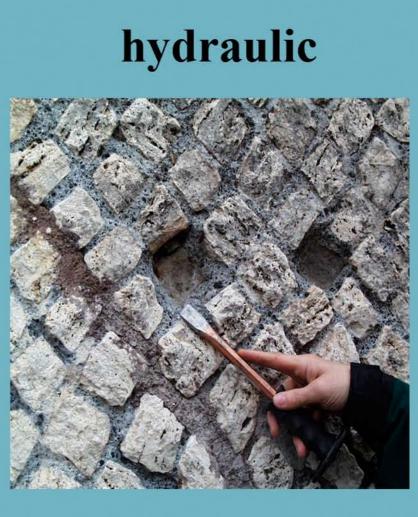
#### Radiocarbon dates must then be calibrated

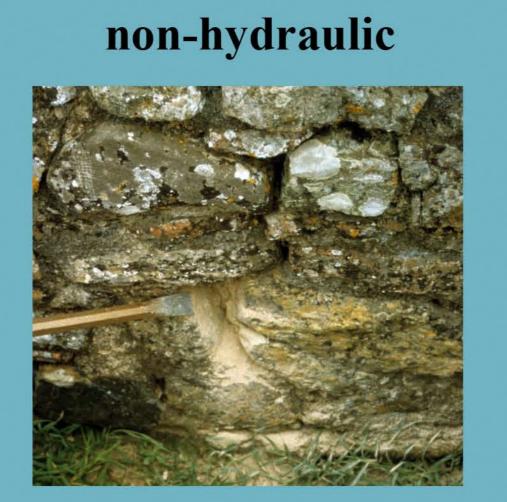


Radiocarbon measurements are by convention cast in terms of radiocarbon years "before present" (BP, meaning before 1950) using the known half life of carbon-14. The calibration between radiocarbon age and calendar age is affected by the fluctuations in the production of carbon-14 in the atmosphere over 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 affect the accuracy of the <sup>14</sup>C analysis. <sup>14</sup>C-dating can be rather precise, but variations within the radiocarbon calibration curve over time sometimes result in dates with large uncertainties, only pinpointing the right century.

# RADIOCARBON DATING OF MORTAR

## Case studies, testing different types of Roman mortar

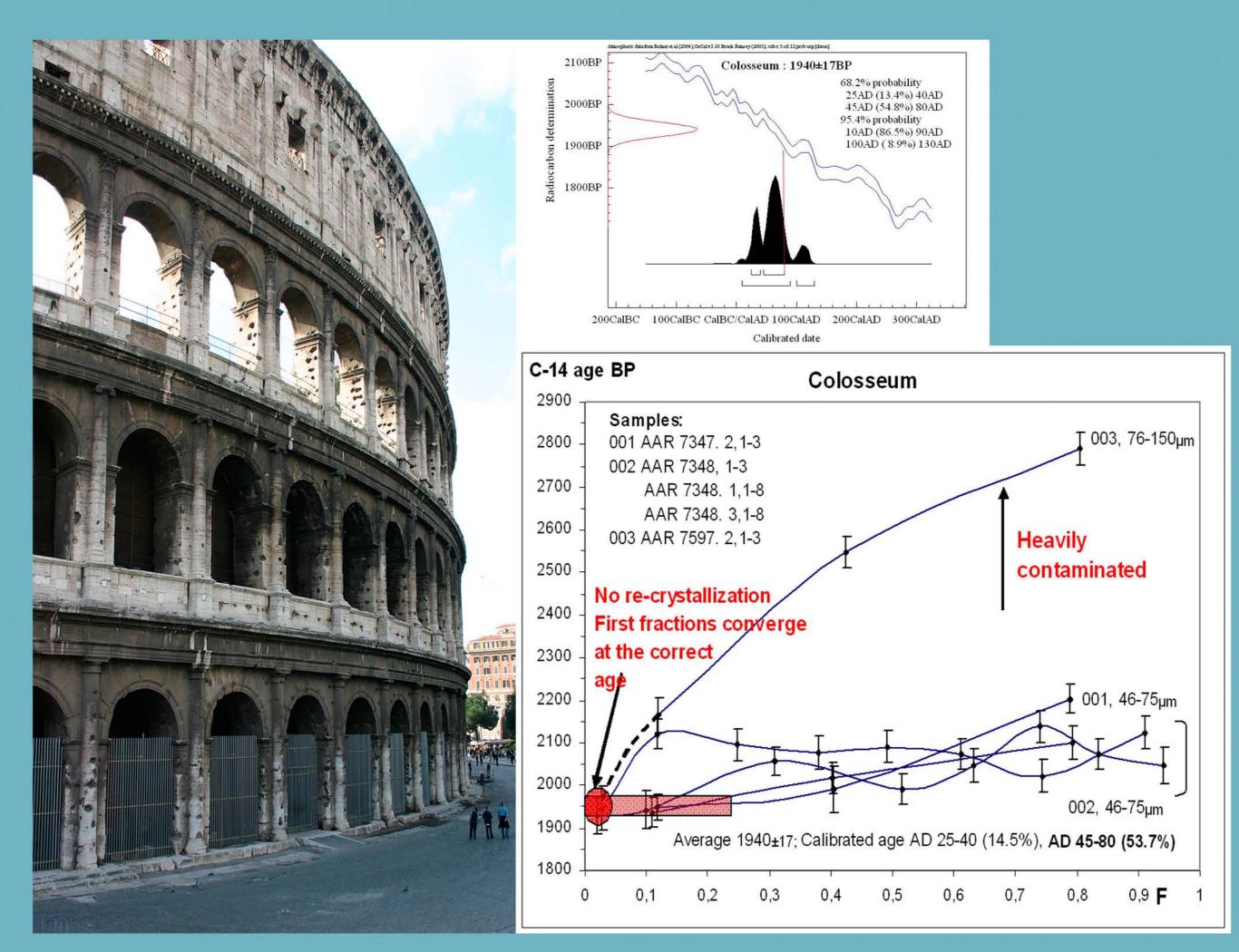




The Roman pozzolana mortar is hydraulic and can harden under water. It was in fact believed that it did not need carbon dioxide from the atmosphere for the hardening process. It was therefore doubtful if pozzolana mortar would at all be suited for mortar dating, which depends on the interaction with atmospheric CO<sub>2</sub> in the hardening process. Pozzolana is a volcanic ash mixed into the mortar. 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. Hydraulic mortars continue to be chemically active for a very long time and seem to produce readily soluble carbonates whenever exposed to atmospheric CO2. They are also full of re-crystallizations for several reasons. The impermeable hydraulic mortar will retain pockets with un-reacted Ca(OH)2. These will continue to react with CO2 and form carbonates whenever the mortar is disturbed by breaking or crushing. Testing the mortar dating method in classical archaeology, both on non-hydraulic and hydraulic samples, was a necessary stage of the developmet of the method.

> Experience shows that samples chemically separated into five different fractions create age profiles which demonstrate the successive dissolution of the mortar. In principle two different patterns of age profiles are created:

> a) an age profile where the first fraction hits the correct age, with no re-crystallization b) a pattern where the horizontal plateau of the age profile hits the correct age, revealing re-crystallization in the first CO2 fractions and contamination from unburned fossil limestone towards the end



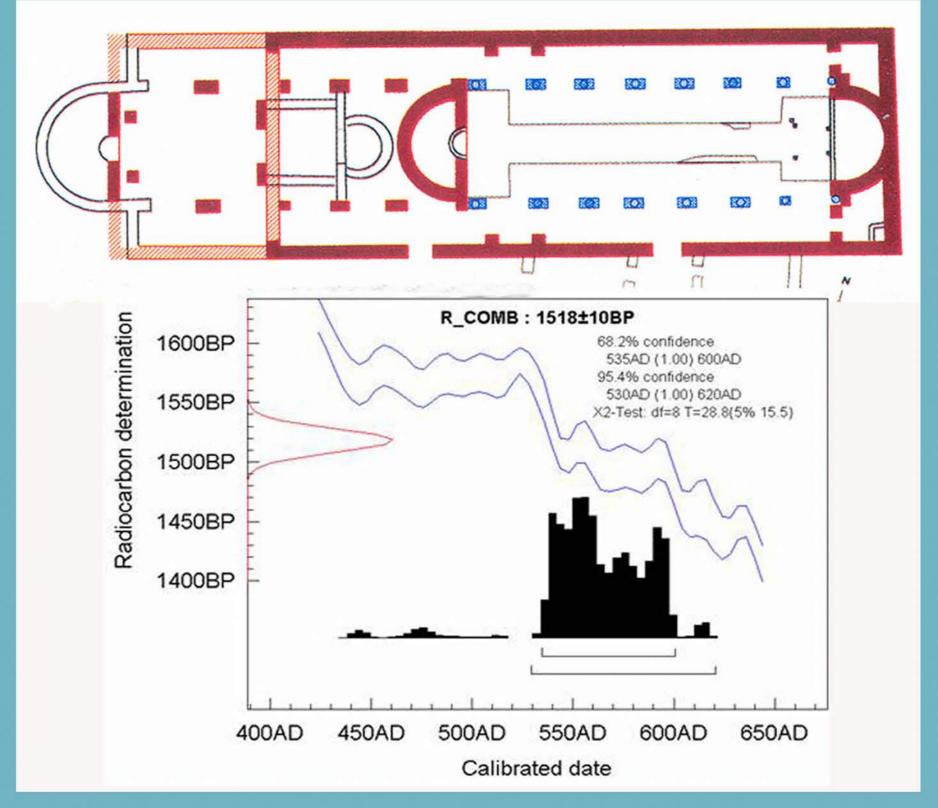
#### The Colosseum

where the pozzolana mortar is only slightly hydraulic, represents an example of pattern a): where four different age profiles agree on the same age for the first fraction. The result, the BP age of 1940 +/-17, corresponds with the calibrated age range of AD 45 - 80 and with historical sources suggesting ca AD 80.

# 68.2% probability 80AD (60.0%) 140AD 150AD (2.6%) 170AD 190AD (5.6%) 210AD 95.4% probability 70AD (95.4%) 220AD Basilica Ulpia (Aar-4795 1,2)

#### The Basilica Ulpia, Trajan's Forum

hydraulic pozzolana mortar, demonstrates pattern b): the correct age (BP 1873 +/-18) which corresponds with written sources is reached at the horizontal plateau of the age profile. The result after calibration yields the age range of AD 80-140.



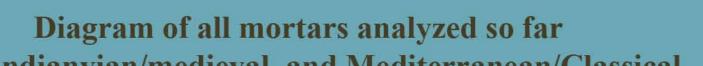
#### Torre de Palma, Portugal

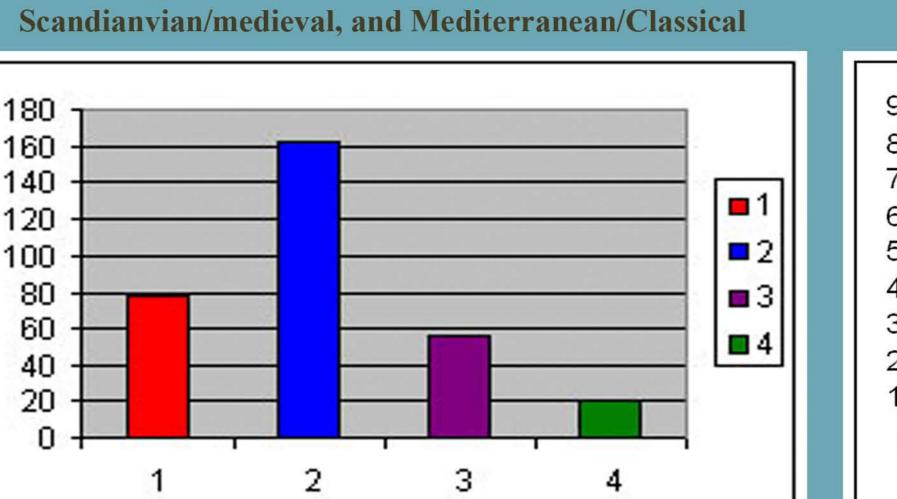
an example from the margins of the Roman Empire with non-hydraulic lime mortar of high quality, responding well to mortar dating. No written sources or archaeological artifacts are available to confirm the derived chronology.

Here the mortar was analyzed in two CO<sub>2</sub> fractions only - a large majority of the samples from the double-apse Basilica agree on the same age with the first fractions. The calibrated age lies between AD 535 and 600, a plausible age which could only be reached using mortar dating.

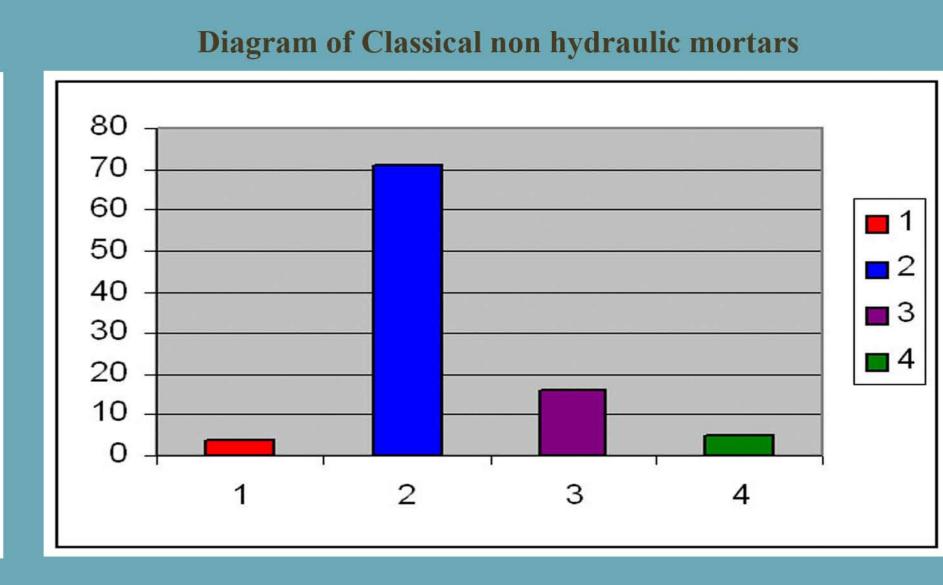


## A series of statistical diagrams to demonstrate how different types of mortar respond to mortar dating

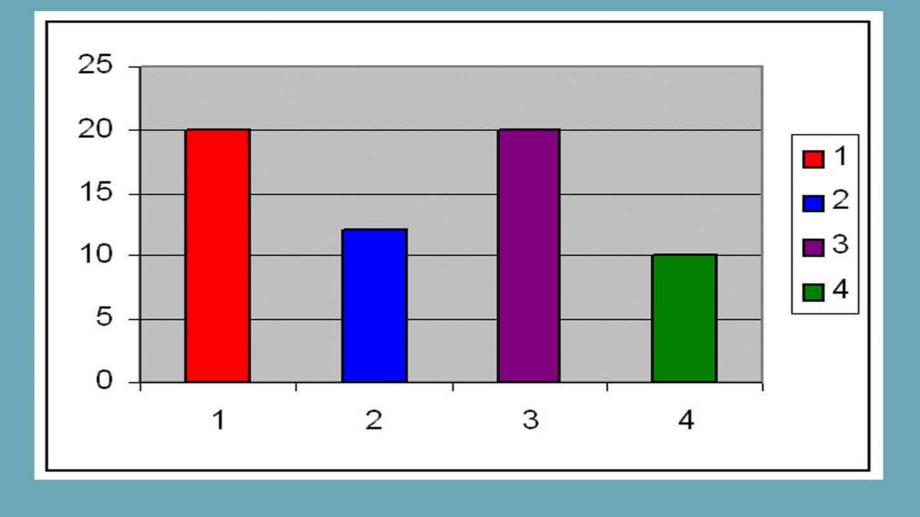




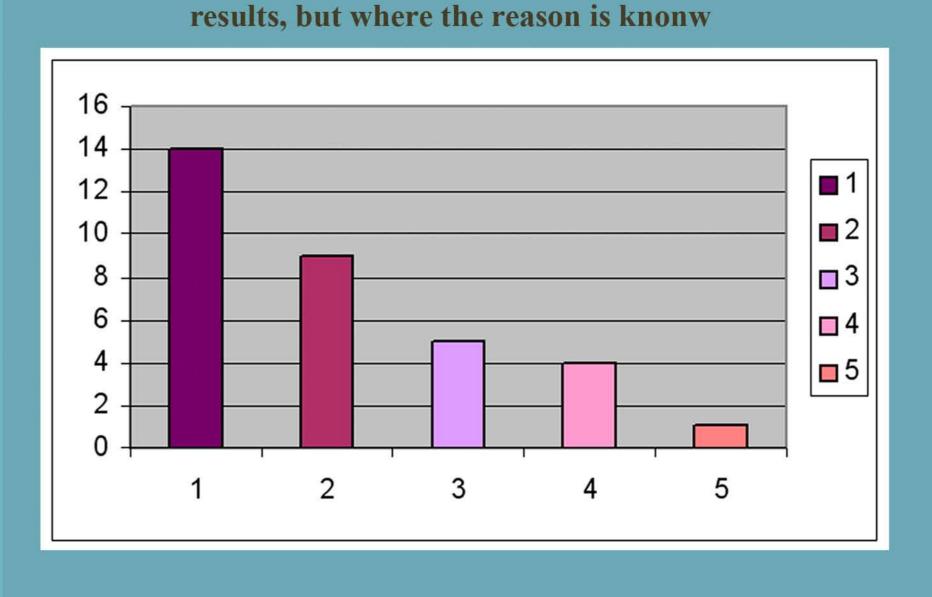
#### Diagram of all Mediterranean samples, hydraulic and non hydraulic mortars



#### Diagram of Classical Pozzolana concrete samples



#### Diagram of all Classical mortars which yielded wrong



- 1. Red the results correspond to the date known from historical sources, brick-stamps or dendrochronology.
- 2. Blue the results agree with the expected age, but objective feedback is missing. The result is reached either with the first fraction, or with the plateau of the profile. These results were only possible to reach using <sup>14</sup>C-analysis of mortar, and they show the potential of the method.
- 3. Mauve the results are wrong, but the reasons are known. 4. Green – the result is wrong or useless if the first fractions or the plateaux from several samples yield different results or if no plateau is formed.

These unsuccessful samples are among the most useful, because they forced us to ask further questions and showed us the types of samples to avoid.

- 1) Most of them were taken at an early stage of our project, when only two fractions were analyzed, whereas a profile from analysis in five fractions could have solved the problem.
- 2) We have also learnt, from trial and error, to avoid mortars that have been buried under volcanic masses,
- 3) and mortars that have crushed bricks in the aggregate to make them water resistant.
- 4) The same applies to mortars taken from deep within the walls or from under marble slabs, where the hardening has been delayed 5) unsuccessful sampling.

## What we have learnt so far:

- -Mortar is often the only datable material available from ancient constructions and we have had positive results from all types of mortar
- However, the best results are achieved with non-hydraulic lime mortar
- Pozzolana mortar is not always hydraulic
- Hydraulic pozzolana mortar can be successfully dated by mortar analysis, but the results are less certain and the interpretation is often more complex.
- Mortars that have deliberately been made hydraulic by mixing in crushed terracotta are not suitable for dating.
- The same, for some yet unknown reason, seems to apply to mortars buried under volcanic ashes.
- For a correct interpretation of the profiles, mortared structures have to be dated with profiles from three separate samples from each building unit. The dates can be established if the profiles coincide a) at the first fractions, or

b) at the horizontal plateau.

This is true of both hydraulic and non-hydraulic mortars.



