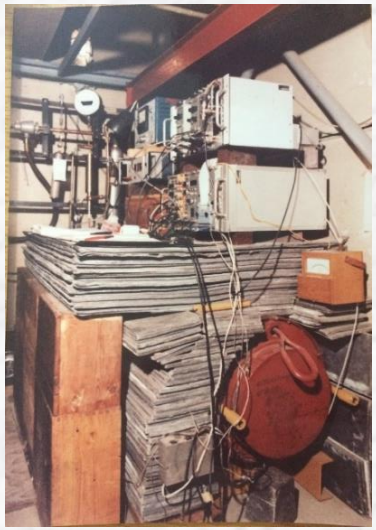
Radiocarbon dating of historical mortars

Andreja Sironić

Laboratory for Low-Level Radioactivities
Ruđer Bošković Institute
Zagreb, Croatia

1st International Conference with Workshop “Science for Conservation of the Danube Limes”
Viminacium, Serbia, June 27th – July 1st, 2022

The Zagreb Radiocarbon Lab



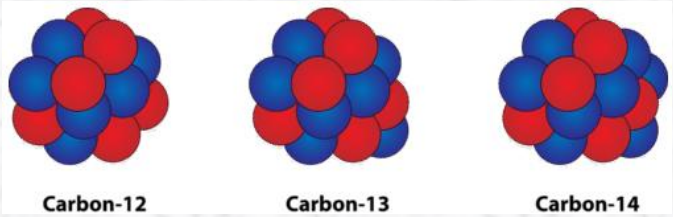
A.K.A.
Laboratory for low level radioactivities
the Ruđer Bošković Institute
was founded in **1968.**

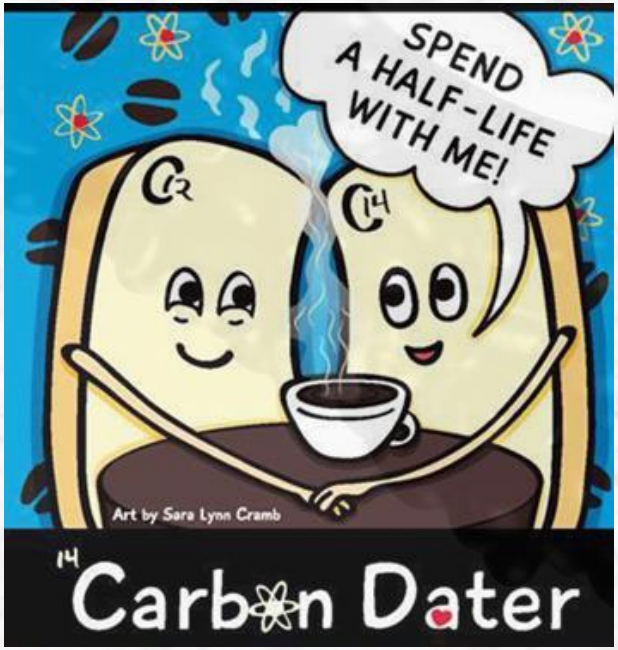
In-house equipment - **Gas proportional counter** GPC

Since 2003 - **Liquid scintillation counter** LSC

Since 2008 - Graphite preparation for **Accelerator mass spectrometry** AMS

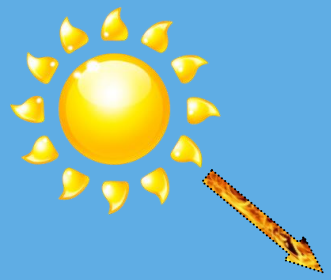
Carbon dating





- ^{14}C (Radiocarbon)
- 10^{-10} %
- Radioactive ($t_{1/2}$ = 5730 years)
- Formed in stratosphere, a part of atmospheric CO_2 and biosphere

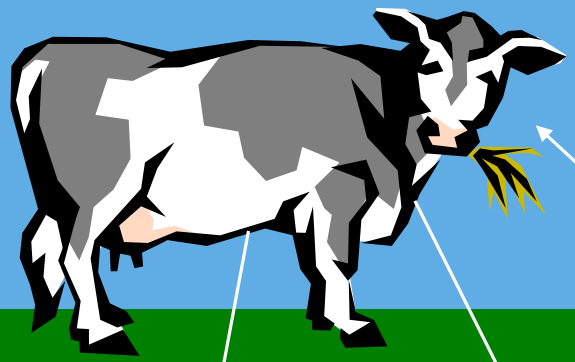
Cosmogenic ^{14}C



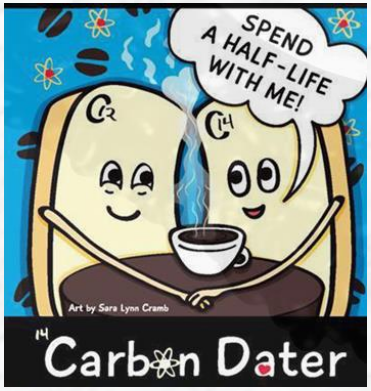
$^{14}N + n \rightarrow {}^{14}C + p$

O_2

$^{14}CO_2$



Radiocarbon dating: basics



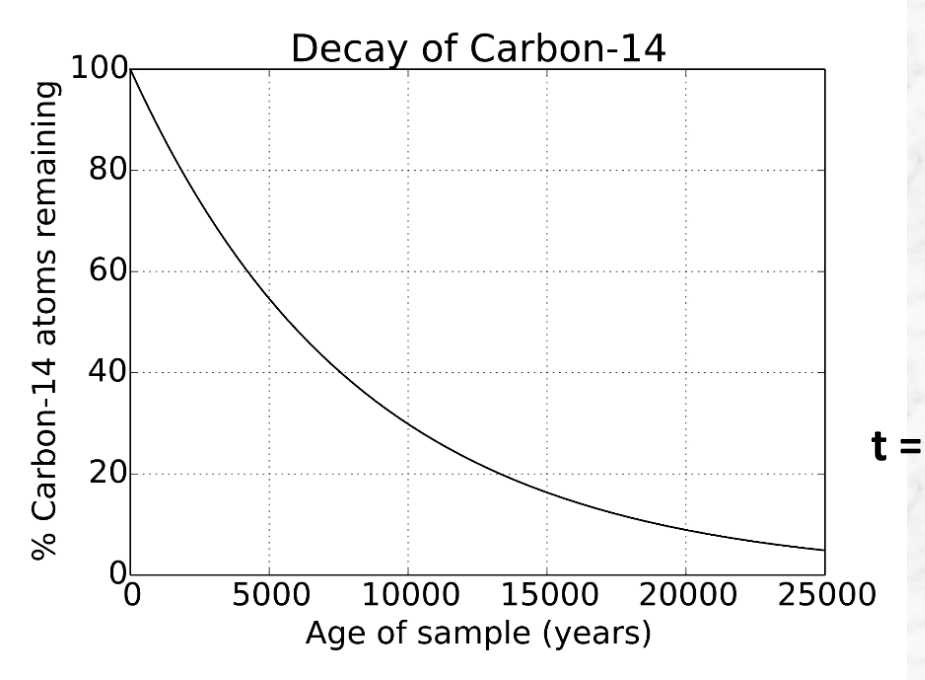
$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + \beta^{-} + \bar{\nu}$$

$t_{1/2}$ = 5730 years

$^{14}C/^{12}C = 10^{-12}$

$a^{14}C$ = 100 pMC = 226 Bq/kgC

Max. age ~ 55 000 years



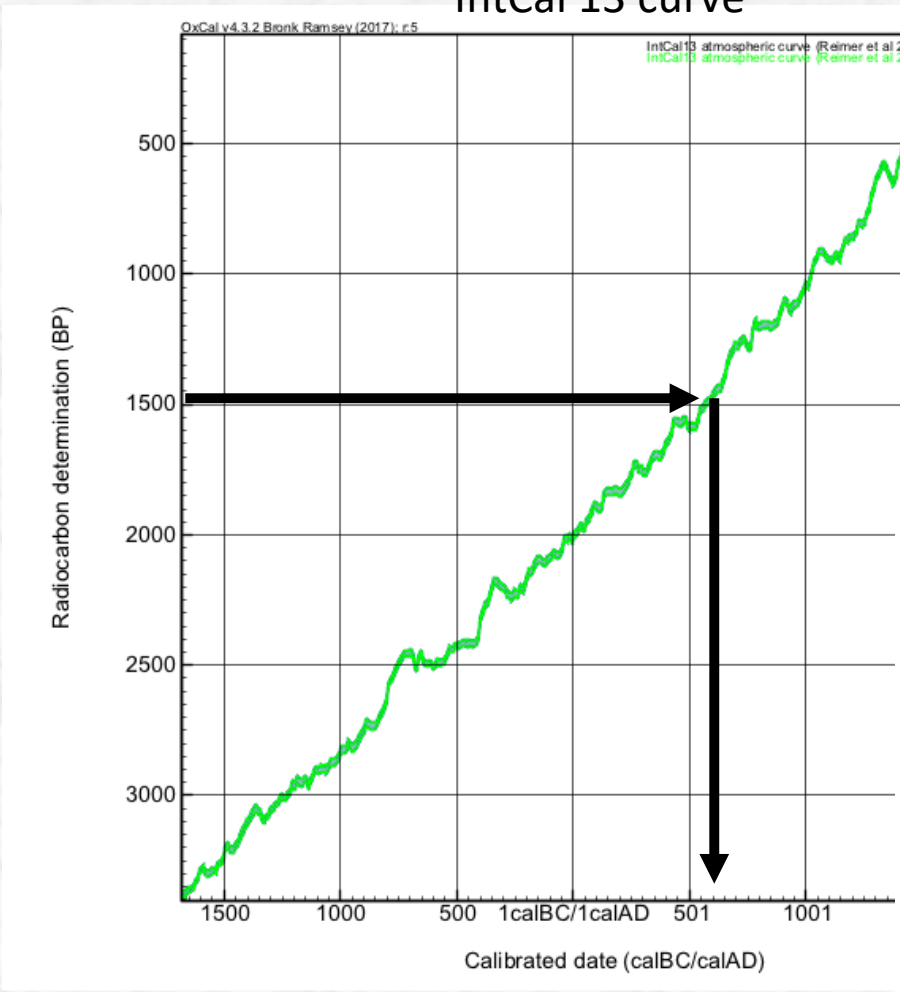
$$t = -\frac{t_{1/2}}{\ln 2} \cdot \ln \frac{a^{14}C}{a_0{}^{14}C}$$

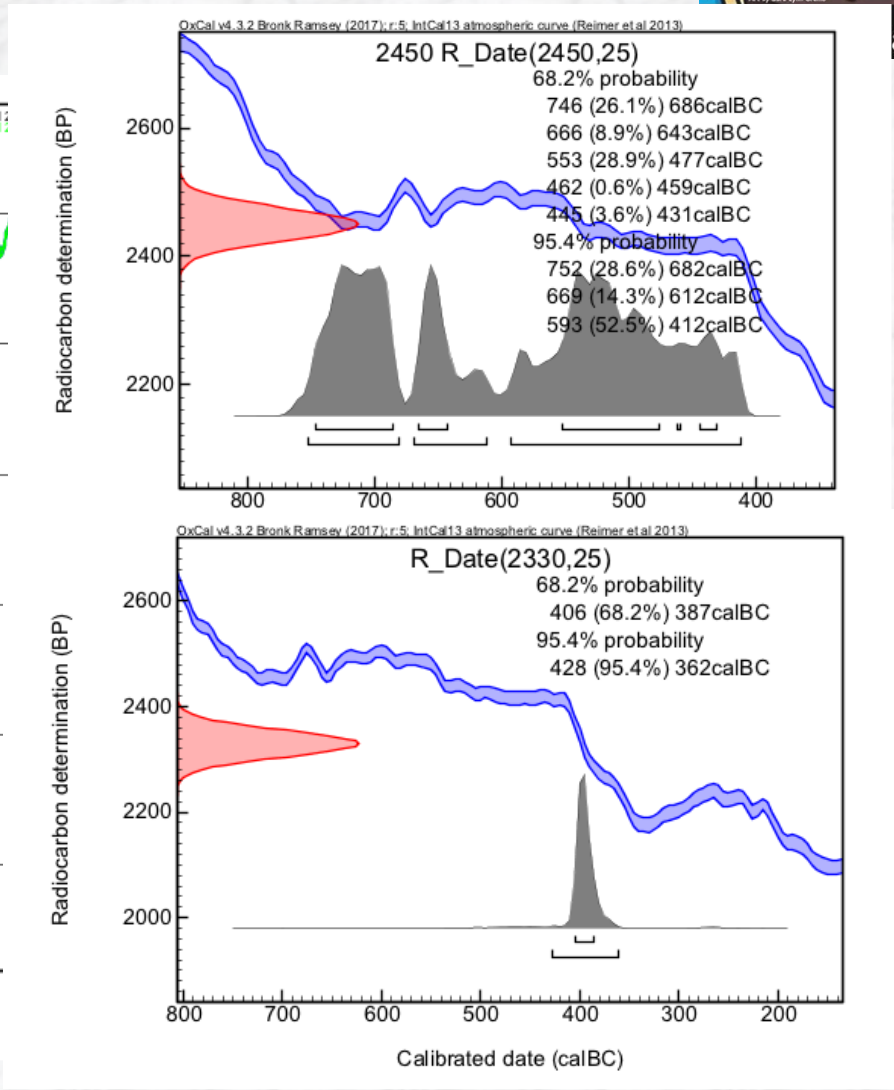
t = Conventional age [years BP]

“Present” = 1950 AD

Radiocarbon dating: basics

IntCal 13 curve



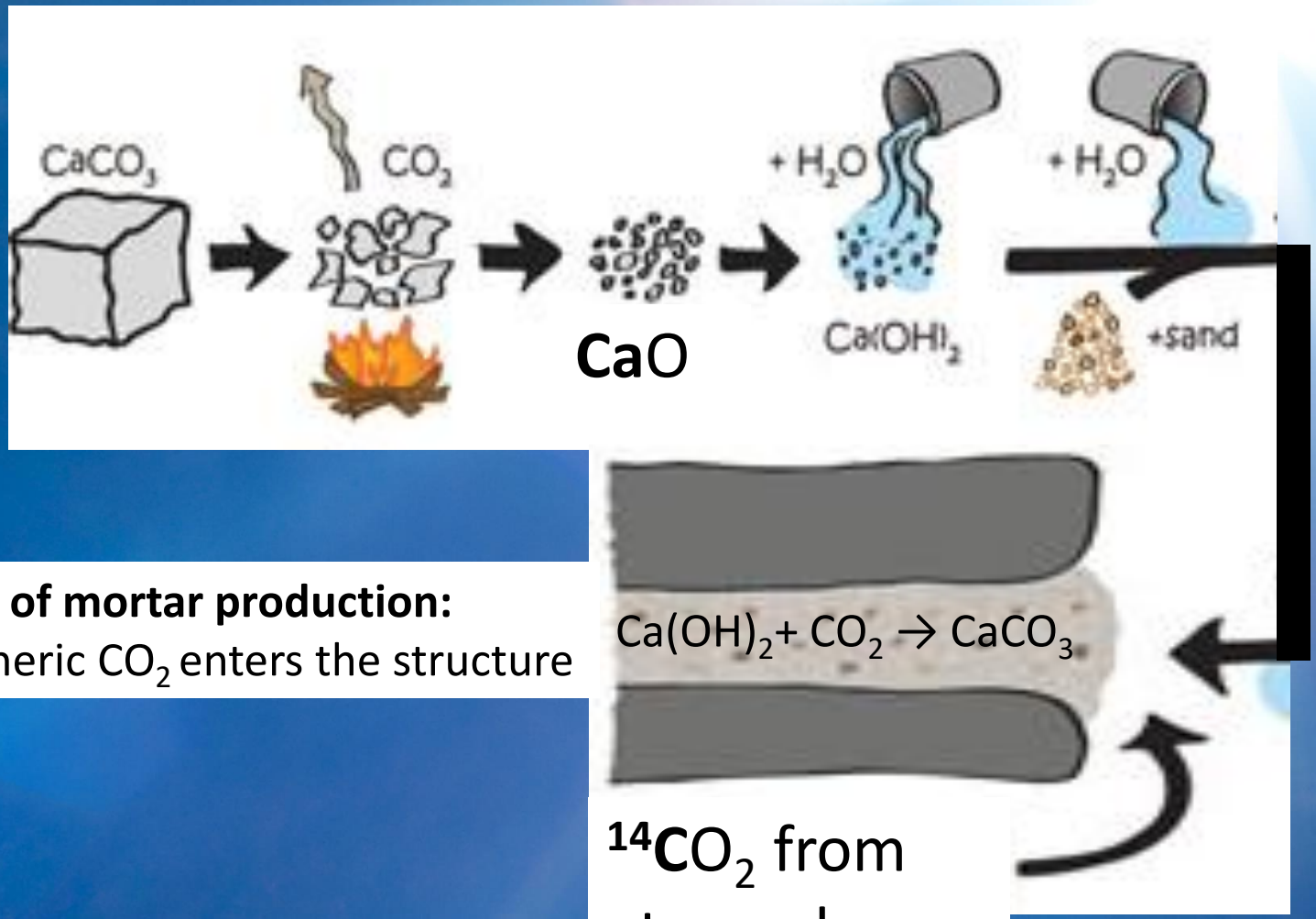


Dating of a historical construction

Stone

Mortar

Mortar production - non-hydraulic mortar

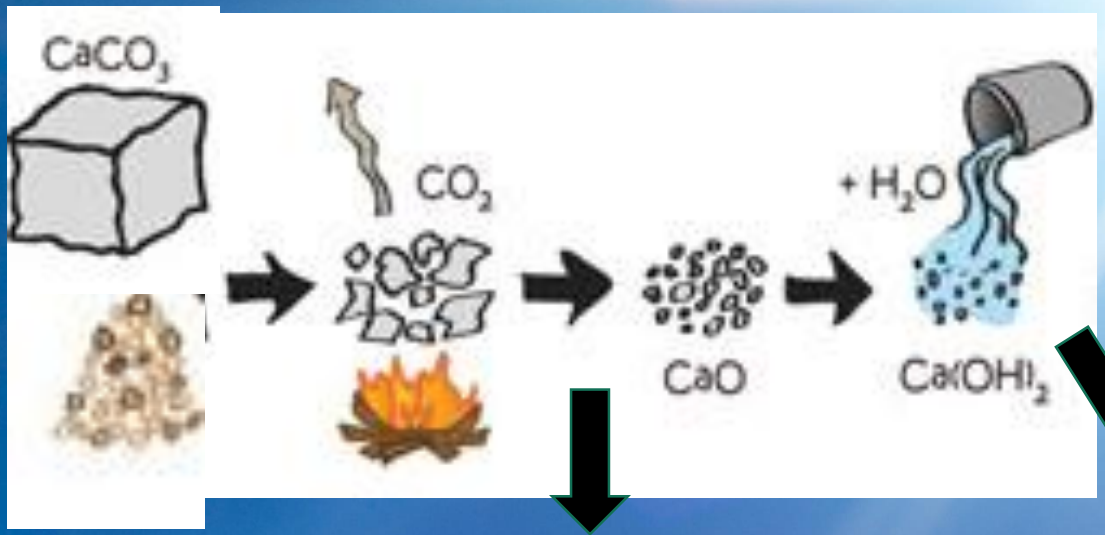


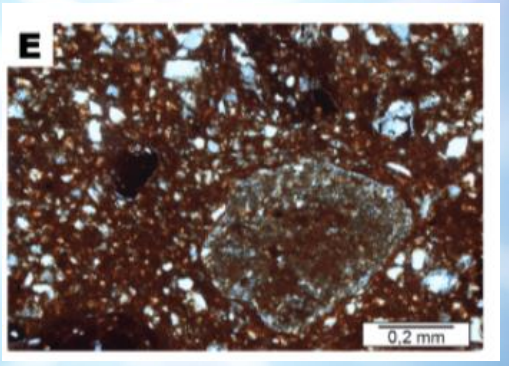
Moment of mortar production:
-atmospheric CO_2 enters the structure

www.mortardating.com/method

Mortar production - hydraulic mortar

Calacreous (Ca) and argillateous materials (Si, Al, Fe-clay, sand, fly ash)





Michalska, *Nucl Instr MethB* B 2019

Hardening process

$CaO, SiO_2, Al_2O_3, Fe_2O_3$
$\rightarrow Ca_2SiO_4, Ca_3SiO_5,$
$Ca_4Al_2Fe_2O_{10}$

Major reaction

$2CaO*Al_2O_3 + xCaSO_4*7H_2O$
$\rightarrow 3CaO*Al_2O_3*xCaSO_4*7H2O$

Pozzolana – volcanic ash and slaked lime
Cocciopesto – lime and crushed fired ceramics and pottery

Only a small amount od carbonate if hardened on the air:

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3$

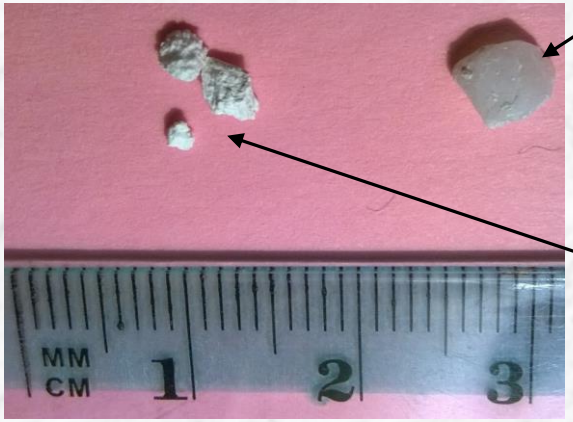
Other mortar dating possibilities...

- Radiocarbon
- SG-OSL (Single Grain - Optically Stimulated Luminiscence)
- EPR (Electronic Paramagnetic Resonance Spectroscopy)

Moment of mortar production:
-rock is heated
-sand is exposed to light
-atmospheric CO_2 enters the structure

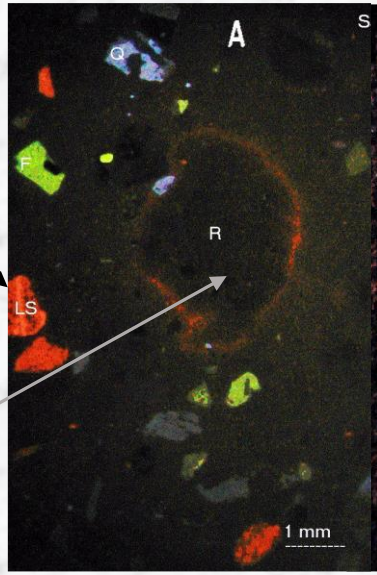
Radiocarbon mortar dating issues

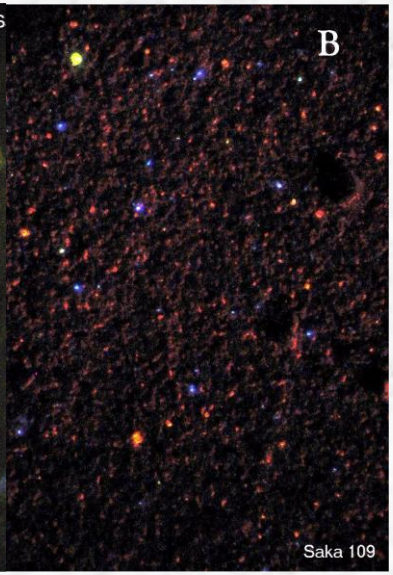
- Analyte – **lime carbonate -** $CaCO_3$
- Unreacted old carbonate – „dead carbon” contamination



Old limestone

Lime carbonate

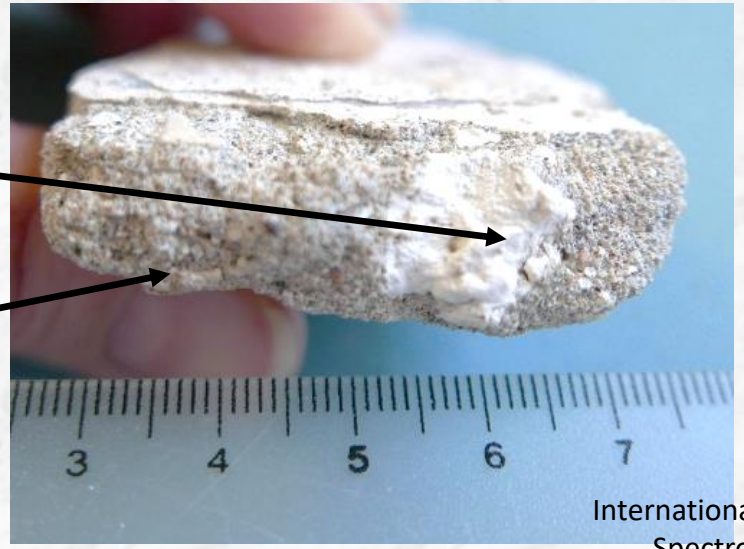




Cathodoluminiscence (CL) photo from Lindroos, A et al. (2007) Radiocarbon 49:47–67

Radiocarbon mortar dating issues

- Analyte – **lime carbonate -** $CaCO_3$
- Unreacted old carbonate – „dead carbon” contamination
- Natural elements - uptake of carbon in the form of dissolved inorganic carbonates – cracks
- Burning of building – yields new carbonate
- Delayed/stopped hardening - if too alkaline still uptakes CO_2 from the air (especially with pozzolana)
- Recrystallization of old carbonate over lime carbonate



Sironić et al. The 15th International Conference on Mass Spectrometry (AMS-15) 2021

Sampling rules

- Non-hydraulic mortars are the most reliable
- Avoid deep parts of masonry (poor exposure to air – hydraulic mortars- and delayed hardening)
- Avoid part near water (see above, probably hydraulic)
- Sample above water level (recrystallization from ambient water)
- Not in places with high moisture (like caves)

Sampling rules

- N
- Av
  ar
- Av
- Sa
- N

Case A5 (Sv Ante)

The only case where agreement with expected and achieved date was **not set**.

Even though the mortars were tested negative to phenolphthalein , they show delayed hardening. The samples were collected from an altar settled in a cave in close proximity to sea. This might had lead to delayed hardening due to damp conditions in the marine cave.

Sironić et al. The 15th International Conference on Mass Spectrometry (AMS-15) 2021

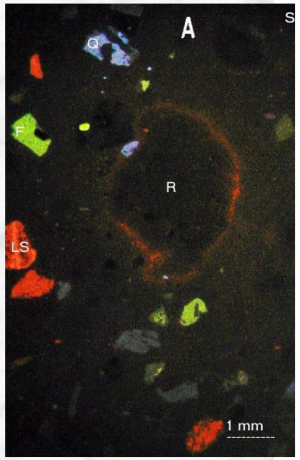
Sampling rules

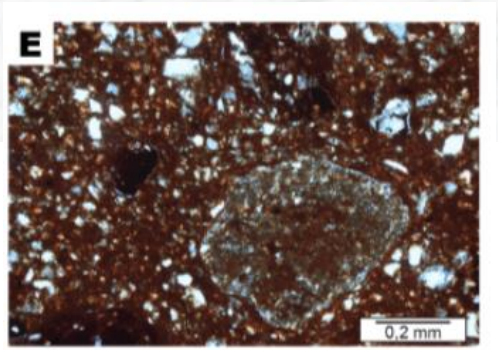
- Non-hydraulic mortars are the most reliable
- Avoid deep parts of masonry (poor exposure to air – hydraulic mortars- and delayed hardening)
- Avoid part near water (see above, probably hydraulic)
- Sample above water level (recrystallization from ambient water)
- Not in places with high moisture (like caves – delayed hardening)
- Avoid drilling tools – they crush large geologic carbonate making it difficult to remove
- Keep organic material (charcoal, wood, hairs, straws, grains or seeds)

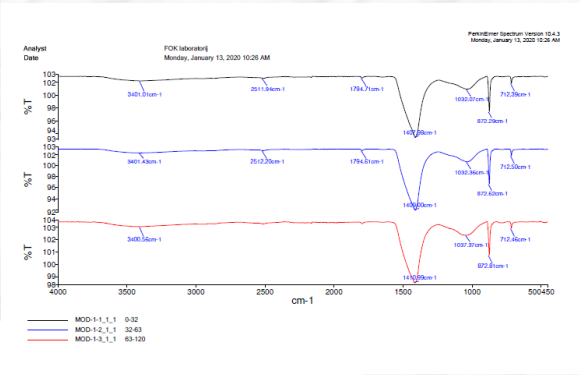
At the sampling site

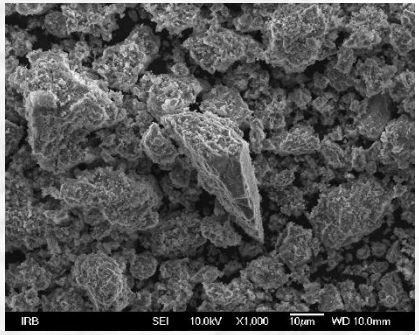
- Record the place were the sample is taken
- Watch for repairs when sampling
- Watch for proofs of fire damage
- Clean the outermost layer of mortar with a chisel and use a clean chisel to sample from the cleaned surface, avoid sampling deep into the mortar
- Sample about a fist size of mortar, closer to the surface, on standing construction if possible
- Do the phenolphthalein test on alkalinity on smaller piece of sample!
- Sample also on few places from other parts of the construction

Characterisation methods









Daugbjerg et al. 2020 *Archaeometry*

Philosophies of lime carbonate extraction for radiocarbon dating

1. Breaking of mortar and selecting fractions:

   according to morphology (lime lumps)

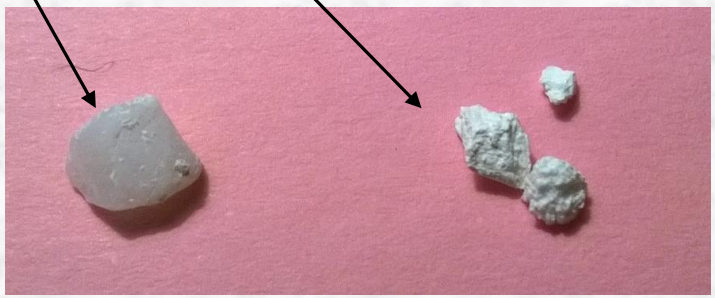
   according to particle size

   on ability to sediment in aqueous suspension

2. Selecting the first CO_2 gas fraction after **hydrolysis** (H_3PO_4 / HCl) or by **thermal decomposition** – <u>lime carbonate</u> reacts much quicker than <u>mineral limestone</u>

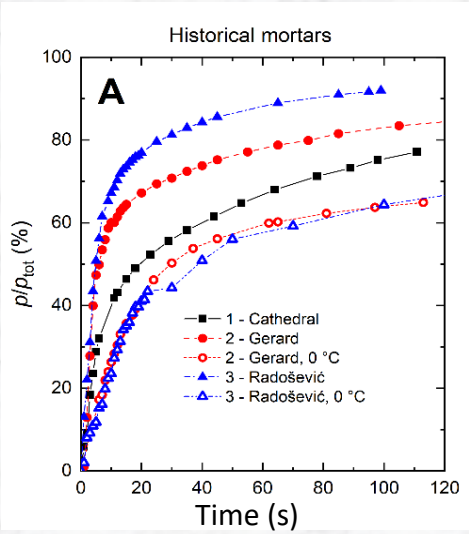
3. All the combinations…

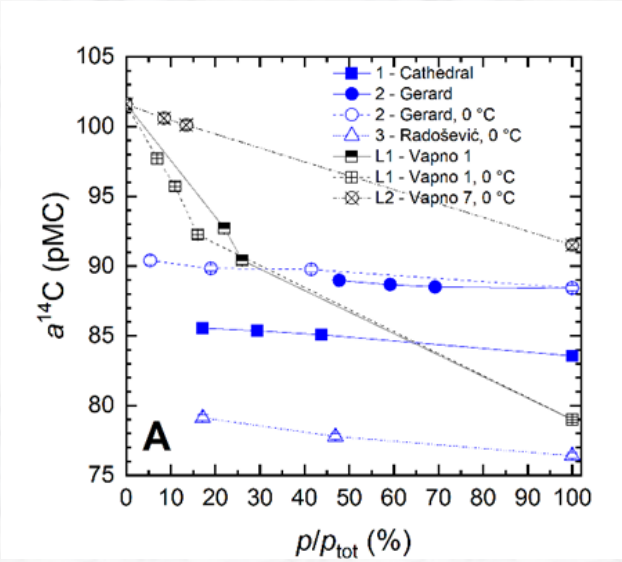
And data extrpolation.



How we prepare mortars for dating at LNA

1. Crush the mortar and dry sieve fraction 32 – 63 µm
2. Create hydrolysis reaction curve
3. Decide on CO_2 fraction collection and collect two fractions before the „knee”
4. Produce graphite target from CO_2 and measure ^{14}C activity on AMS
5. Extrapolate the data

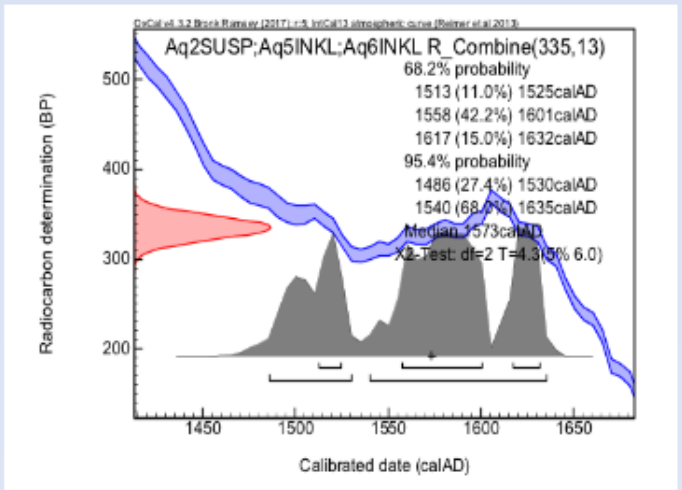




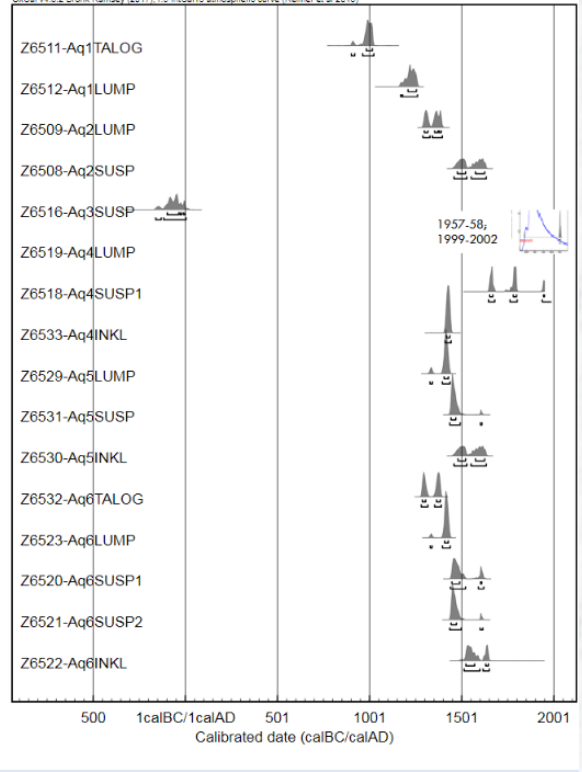
Criteria for data acceptance

Confidence of the result

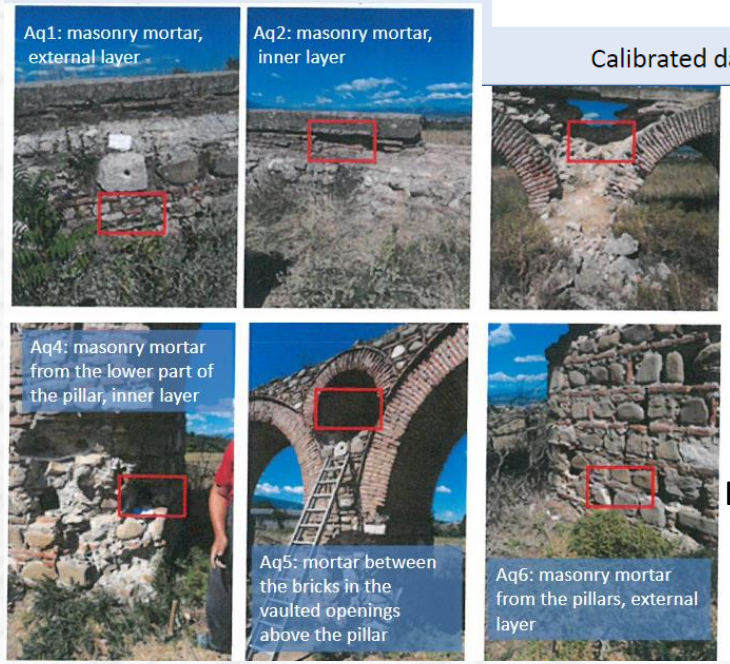
- I – both dates are the same
- II – agree from the same wall
- III – agree from the same construction
- IV – agree with historical assumption



The OxCal Combine function of Aq5 and Aq6 inclusions and Susp-1 Aq2



Calibrated dates for all the fractions



Dating of Aqueduct in Skopje, N Macedonia
Sironić et al. 2019
Radiocarbon

MODIS intercomparisons

- Mortar Dating Intercomparison Study in 2016
- 9 Labs: 7 Radiocarbon and 2 OSL labs
- 4 samples
- True ages compared to wood, charcoal and bone radiocarbon ages associated with the samples

Reported in:

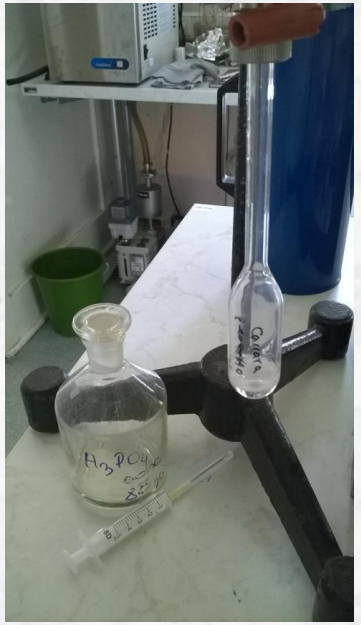
Hajdas, I, A Lindroos, J Heinemeier, Å Ringbom, F Marzaioli, F Terrasi, I Passariello, M Capano, G Artioli, A Addis, M Secco, D Michalska, J Czernik, T Goslar, R Hayen, M Van Strydonck, L Fontaine, M Boudin, F Maspero, L Panzeri, A Galli, P Urbanová, P Guibert (2017) **Preparation and Dating of Mortar Samples—Mortar Dating Inter-Comparison Study (MODIS**). Radiocarbon 59:1845–1858

Hayen, R, M Van Strydonck, L Fontaine, M Boudin, A Lindroos, J Heinemeier, Å Ringbom, D Michalska, I Hajdas, S Hueglin, F Marzaioli, F Terrasi, I Passariello, M Capano, F Maspero, L Panzeri, A Galli, G Artioli, A Addis, M Secco, E Boaretto, C Moreau, P Guibert, P Urbanova, J Czernik, T Goslar, M Caroselli (2017) **Mortar Dating Methodology: Assessing Recurrent Issues and Needs for Further Research**. Radiocarbon 59:1859–1871

Michalska, D, J Czernik, T Goslar (2017) **Methodological Aspect of Mortars Dating (Poznań, Poland, MODIS).** Radiocarbon 59:1891–1906

MODIS intercomparisons

- Mortar Dating Intercomparison Study in 2020 (MODIS2)
- 9 Radiocarbon Labs
- 3 samples (expected Medieval to Renaissance times)
- ongoing



Thank you for your attention!