Mortar dating: A new procedure in the Zagreb Radiocarbon Laboratory

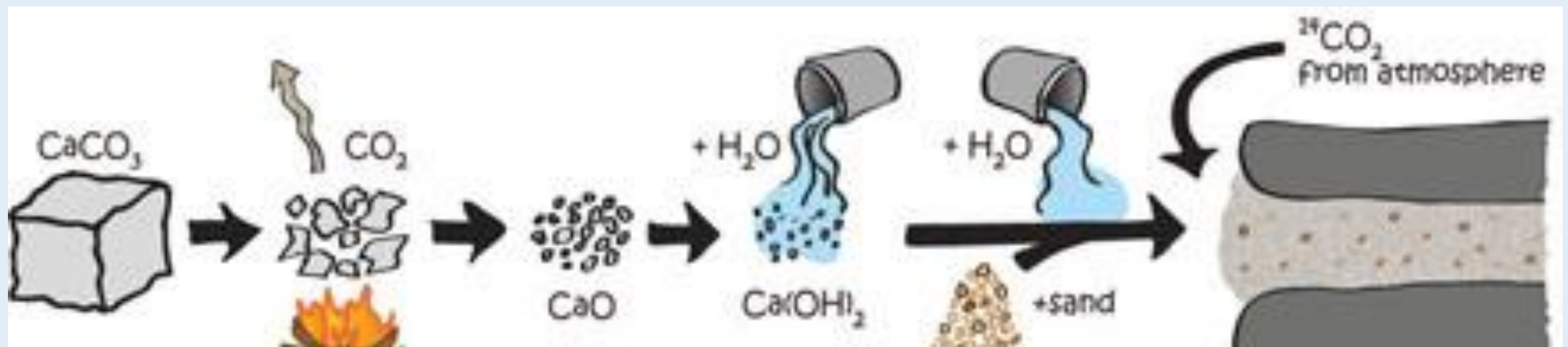
AMS-15

Andreja Sironić[1], Alexander Cherkinsky[2], Damir Borković[1], Suzana Damiani[3], Jadranka Barešić[1], Ines Krajcar Bronić[1]

[1]Laboratory for Low- Level Radioactivities, Ruđer Bošković Institute, Zagreb, Croatia; [2]Center for Applied Isotope Studies, The University of Georgia, Athens, Georgia, USA; [3]Academy of Fine Arts, Zagreb, University of Zagreb, Croatia

Basis for ^{14}C mortar dating

Mortar can be **dated** by radiocarbon dating of **binder carbonates** created during mortar hardening. However, the most prominent problem in mortar dating is selecting the carbonates from binder without impurities used in mortar production that lead to overestimated ages. To this day there is no consensus on the unique way of sample preparation that would always provide the true date.



http://www.mortardating.com/; The Mortar Dating Project

Principle how the atmospheric ^{14}C gets into mortar, enabling mortar dating

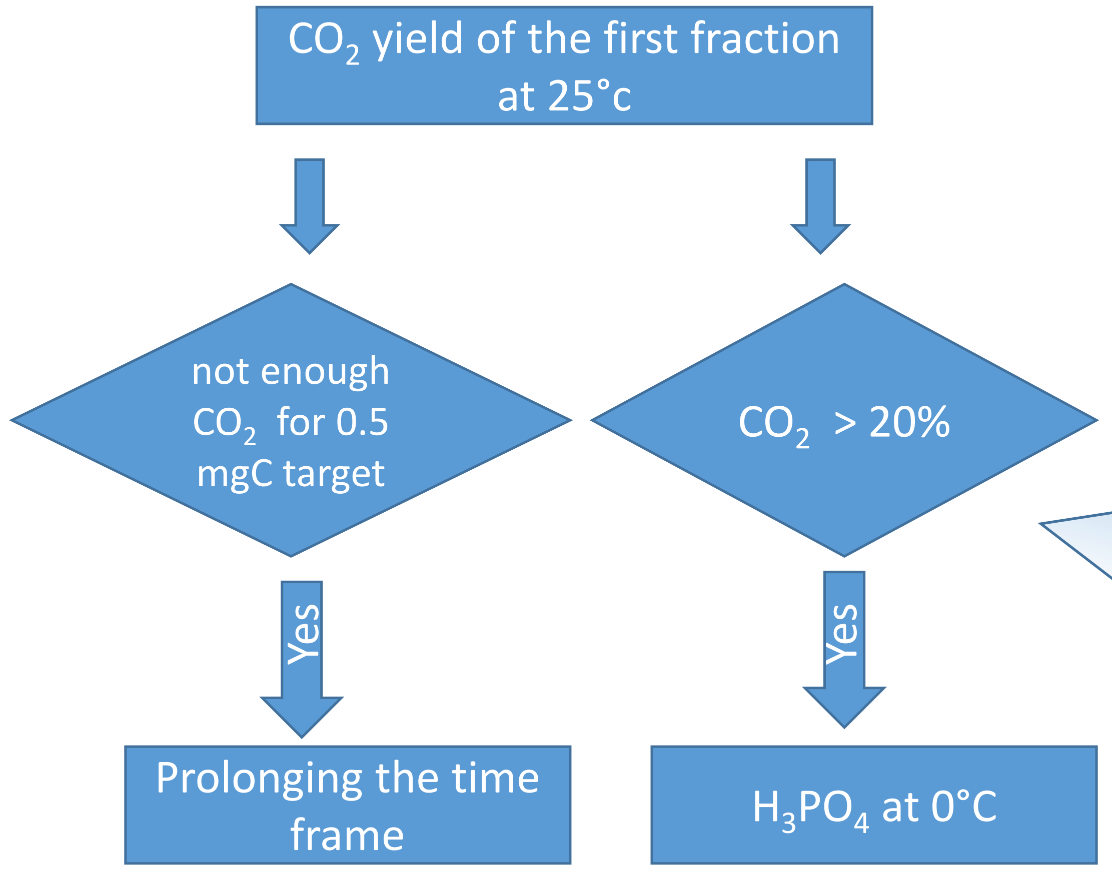
At the **Zagreb Radiocarbon Laboratory**, Croatia, we established a procedure for graphite preparation for AMS radiocarbon dating of non-hydraulic mortar that we find simple and cost-effective. The ^{14}C activity of graphite samples prepared in the Zagreb Radiocarbon Laboratory is measured at the **Center for Applied Isotope Studies** (CAIS), USA.

Method description:

-test on phenolphthalein
-"freeze-thaw" treatment of mortar and "gentle" crushing
-sieving the fraction 32 - 63 μm
-hydrolysis by H_3PO_4 (85 %) and collecting 3 to 4 CO_2 fractions (at 3, 10 and 15 s)

Rules for the acceptance of the result

-the first fraction is the reliable for date of mortar and the second one is the control*
-the first fraction should not exceed 20 % of total CO_2
-*control also by δ^{13}C trend



Mortar dating: A new procedure in the Zagreb Radiocarbon Laboratory

The 15th International Conference on Mass Spectrometry (AMS-15), 15 – 19 November 2021 (on-line)

Tests for method validation

In order to validate the procedure eight original archaeological mortars were used to which the true date could be obtained from other source (Table 1)…

Table 1. Mortars from archaeological context

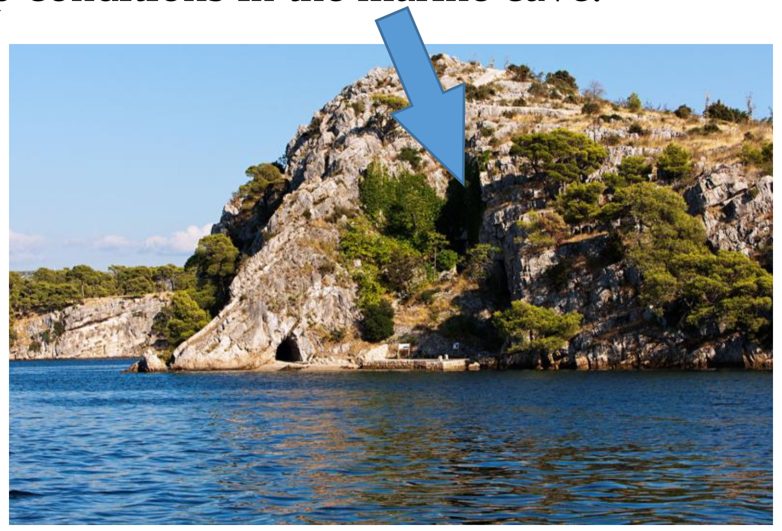
No	Sample name	Id No Z-	Origin of the mortar	Expected age	Source of expected age	No. of CO_2 subsamples and time splits (in s)*	Comment	a^{14}C (pMC)	Calibrated date range (68.3 %)	Agreement achieved
A1	Sv. Mihovil P1 U1	7431	Medieval fortress	After 970 AD, both samples are of the same age	Customer's evaluation and ^{14}C date of charcoal from another sample	2 (3, 15)	1st -24 ‰, 2nd -10 ‰	92.2 ± 0.3	cal AD 1294 – 1387	Yes
	Sv. Mihovil P4 U4	7434				2 (3, 15)	1st -21 ‰, 2nd -9 ‰	91.7 ± 0.3	cal AD 1278 – 1376	Yes
A2	Dubrovnik cathedral	7394	Early medieval church	1273(22) BP and 1299(23) BP	Two charcoal samples assigned to the mortar	3 (30, 60, 120)	2nd 85.1 ± 0.3 pMC; **Lime lump also dated!**	85.3 ± 0.3	cal AD 678 – 771	Yes
A3	ALU Romanička	7470	Fragments of medieval church	~15 century	Customer's evaluation	4 (9, 20, 60, 960)	2nd 94.4 ± 0.3 pMC	94.9 ± 0.3	cal AD 1441 – 1471	Yes
A4	Gerard	7471	Grave	1132 AD	Inscription on the grave	3 (8, 20, 60) 3 (3, 10, 30)	In duplicate	89.0 ± 0.3	cal AD 1045 – 1157	Yes
A5	Sv Ante #1	7483	Altar in a cave	~10 century, both samples are of the same age	Customer's evaluation	3 (3, 10, 30)		106.9 ± 0.3	-	No
	Sv Ante #2	7484				3 (3, 10, 30)		102.5 ± 0.3	-	No
A6	Radošević palace	7727	Antique wall	~2 century	Piece of Roman sigillata ware found in wall	2 (4, 8)	1st -23.6 ‰	79.1 ± 0.2	cal AD 130 – 202	Yes

*numbers in brackets indicate time points for split of each fraction, e.g. „3, 15" means that fractions were taken in periods 0-3 s and 3-15 s

Case A2 Lime lump
(following Sironić et al. 2019)
Fractions:
1st (0 - 3 s) 98.3 ± 0.3 pMC; -19.6‰
2nd (3 - 15 s) 97.9 ± 0.3 pMC; -15.1 ‰
3rd (15 s – end) 98.6 ± 0.3 pMC; -11.3 ‰
Not in agreement with expected result and 1150 years too young compared to the particle fraction dating!

Lime lump (A2) was around **2 cm** in diameter. The sample was taken from the middle part of grey mortar. The three obtained dates are the same proving that there was no "seed" of geogenic carbonate. Also, younger dates than for the 32 – 63 μm fraction point to delayed hardening.
So, dating lime lumps should be done with caution, if lumps are too big!

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.



Case A4 (Gerard)

First analysis
Fractions:
1st 89.1 ± 0.2 pMC; 54 % CO_2 yield; -14.3 ‰
2nd 87.5 ± 0.2 pMC; 12 %; -10.2
3rd 87.5 ± 0.2 pMC; 10 %; -11.9 ‰

Second analysis
Fractions:
1st 88.1 ± 0.2 pMC; 4 % CO_2 yield; -13.0 ‰
2nd 88.8 ± 0.2 pMC; 37 %; -13.6 ‰
3rd 88.3 ± 0.2 pMC; 24 %; -10.7 ‰

The CO_2 yield of 54 % (1st fraction in the 1st analysis) and of the 2nd fraction (37 %) in the 2nd analysis actually gave a date corresponding to the inscription on the grave.
This is **in contradiction to the „rules"** set for the method - that the correct date is in the 1st fraction with CO2 yield <20 %. However, **the lowest δ^{13}C values point to the true fraction**.

Sironić A et al. (2019) Radiocarbon dating of mortar from the Aqueduct in Skopje. *Radiocarbon*, 61 (5), 1239 - 1251.

Tests for method validation

…Also, two laboratory mortars containing 26 % and 48 % of binder carbonate (Šustić et al. 2012) were prepared to test the reliability of the results (Table 2).

Both laboratory mortar samples show lower $a^{14}C$ than expected - meaning that the radiocarbon dates would be up to 345 years too old!
This could be in relation to higher amount of calcite in mortar mixture.

After repeating the analysis of Vapno #1 to lower the percentage of CO_2 in the first fraction (<20 %), **$a^{14}C$ was higher** - contained lower amount of geogenic calcite.

Table 2 Mortars produced in laboratory in September 2011, analyzed in 2021

No	Name	Id No Z-	Measured $a^{14}C$ of the whole mortar	Percentage of unreacted $Ca(OH)_2$ (%)	Expected $a^{14}C$ (pMC) – for dating	$a^{14}C$ (pMC) **	$\delta^{13}C$ (‰)**	$w(CO_2)$ (%)**	Temperature of reaction	No. of CO_2 subsamples	Percentage of geogenic C	Years too old date
L1	Vapno #1	4793	26 pMC	27	99 - 102*	92.7 ± 0.3	-19.7	79	20°C	3	6.4 - 9.1	575 - 765
						97.7 ± 0.3	-33.0	13	0°C	3	1.3 – 4.2	105 - 345
L2	Vapno #7	4799	48 pMC	23		100.6 ± 0.3	-35.8	20	0°C	2	< 1.4	< 115

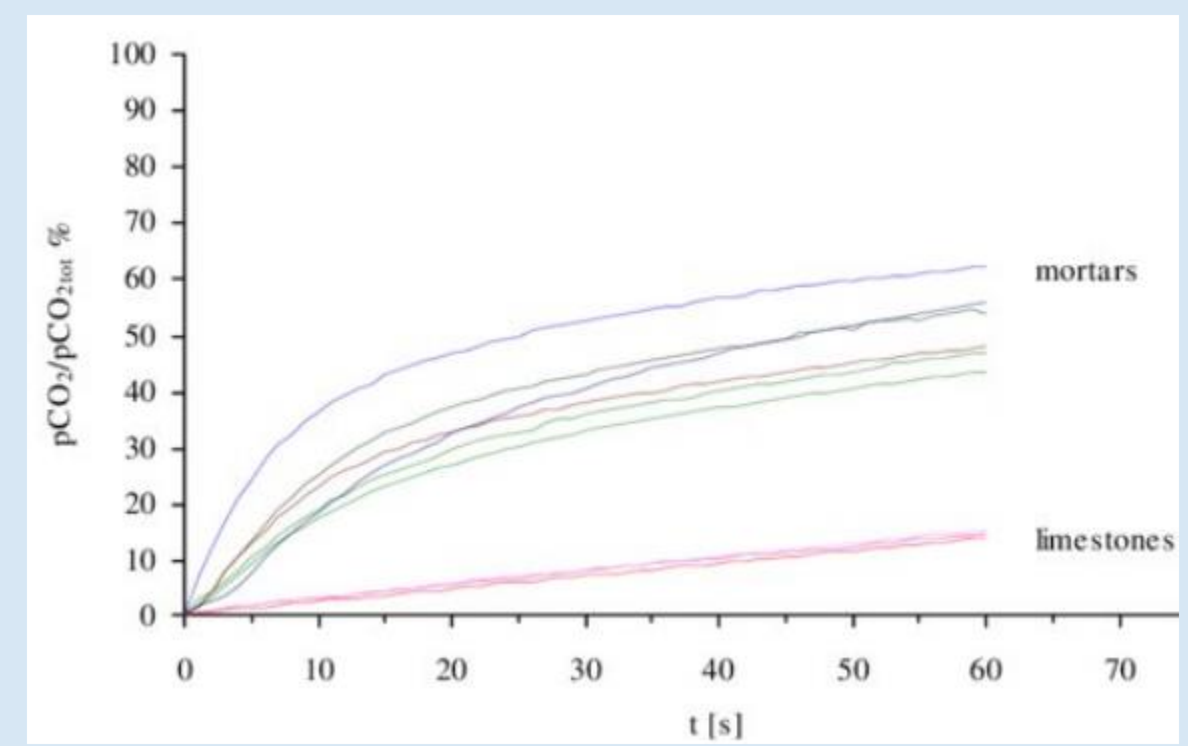
*True expected $a^{14}C$ for dating is not precise since the mortars were prepared in 2011 and analyzed in 2021, when the mortars were still active, so it can range from 99 pMC (mean $a^{14}C$ in Zagreb in 2021) to 102 pMC ($a^{14}C$ in Zagreb in Sept 2011).
**for the first CO_2 fraction in time interval 0 - 3 s

Mortar preparation
The mortars were prepared in 2011 by mixing of commercially available hydrated lime ($Ca(OH)_2$) with calcite (geogenic $CaCO_3$) and water at 20 °C in:
2 : 5 : 1.8 mass ratio for Vapno #1 and
5 : 5 : 4.9 mass ratio for Vapno #7.
They were left to dry and $a^{14}C$ was determined fort the bulk mortars by liquid scintillation counting – benzene synthesis.

Mortar samples Vapno #1 and Vapno #7 vials with particle fractions: >3.35 mm, 3.35 mm – 63 µm , 63 – 38 µm and < 38 µm, and pieces of hardened mortars

Phenolphthalein test
The mortars tested positive in 2020 when they were prepared as unknown mortar samples for dating.

This is in accordance to the findings of Sonningen and Jungner (2001):



The CO_2 yield as a function of time for six mortar and four fossil limestone carbonates. The CO_2 pressure recorded is given relative to the maximum reached at the end of reaction. The grain size range is 43-62 µm.

Sonningen E, Jungner H (2001) An Improvement in Preparation of Mortar for Radiocarbon Dating *Radiocarbon*, 43(2A), 270 - 273
Šustić I, Barešić, J, Šipušić J (2012) Determination of hardened binder initial composition. *Zement - Kalk - Gips international*, 65 (10), 70-78.

AMS-15

Summary

Five out of six archeological mortars yield expected dates.
Mortars from damp ambient and lime lumps should be dated with caution.

Laboratory mortars showed <4 % influence of geogenic calcite which can lead up to approximately 350 years too old date!

- **First fraction** does not necessary yield true date and **percentage of CO_2 yield (<20 %)** in hydrolysis is not unambiguous marker for the true date – the RULES should be modified
- $\delta^{13}C$ points to the mixing of geogenic and binder carbonate - it should be used as indicator of the reliable fraction for dating (however, fractionation should always be considered)
- Influence of geogenic carbonate in laboratory mortars is relative to its amount in the mortar mixture

- Implement in the procedure routine measurement of:
  - -the total amount of CO_2 in mortar
  - -the velocity of CO_2 production during the hydrolyses
- Run more tests with **laboratory mortars** in controlled environment

Acknowledgment for the contribution of archeological mortars and their expected dates:
J. Pavić – Fortress of Culture Šibenik, Croatia (A1)
E. Podrug – Šibenik City Museum, Croatia (A5)
E. Visković – Kantharos d.o.o., Hvar, Croatia (A6)