

RADIOCARBON MORTAR DATING INTERCOMPARISON MODIS2—APPROACH FROM THE ZAGREB RADIOCARBON LABORATORY, CROATIA

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ABSTRACT. The Second International Mortar Dating Intercomparison Study (MODIS2) took place in 2020. Three mortar samples from different sites and chronologies were distributed among various research groups in form of bulk mortar and grain fraction smaller than 150 µm. This is the first time the Zagreb Radiocarbon Laboratory, with support of the Center of Applied Isotope Studies, University of Georgia, took part in the international mortar intercomparison. The initial approach of the Laboratory to mortar dating was to separate 32–63 µm grain fraction and collect three CO₂ gas portions by sequential dissolution with acid. After checking the ¹⁴C date trends of the gas portions, which should be ascending with later fractions, the one for the first and shortest gas portion was reported as the age of the mortar. However, the first gas portion might not be true age of the mortar, since it still might contain some “dead” carbon. Therefore, data extrapolation from the first two initial CO₂ portions was also conducted on the results, but not reported to the intercomparison. Though in general, all the intercomparison reported dates fit the expected historical ages, for one sample, the extrapolated result showed a better match to the historical data.

KEYWORDS: ¹⁴C, data extrapolation, MODIS2, mortar dating intercomparison, sequential dissolution, Zagreb Radiocarbon Laboratory.

INTRODUCTION

Mortar dating is of interest for many archeological and art historian studies. Radiocarbon dating of mortar binder is especially interesting, however prone to many obstacles. Though the idea of ¹⁴C dating mortar binder appeared almost at the dawn of the radiocarbon method (Labeyrie and Delibrias 1964; Stuiver and Smith 1965; Baxter and Walton 1970), only since the development of the accelerator mass spectrometry this possibility was researched more extensively (Van Strydonck et al. 1992; Heinemeier et al. 1997).

As mortar is heterogeneous and inconsistent matrix, there are different approaches to date, so the method for radiocarbon mortar dating needs systematization and verification. Therefore, the first Mortar Dating Intercomparison Study (MODIS) was conducted (Hayen et al. 2016, 2017; Hajdas et al. 2017; Michalska et al. 2017). The intercomparison showed high agreement of results among the laboratories for non-hydraulic mortars and the general conclusion was that the dating success depended on the mortar quality.

The second mortar dating intercomparison MODIS2 was conducted in 2020. Three non-hydraulic mortar samples were distributed as a 1-cm³-piece and as <150 µm grain-size fraction. The first sample (MODIS2.1) was from AD 14th century tower of the church of Saltvik on the Åland Islands, Finland, in the central part of the Baltic Sea. The church has a dendrochronological date of AD 1381 (date also provided by the organizers), which was confirmed by mortar ¹⁴C dates (Heinemeier et al. 2010; Ringbom 2011a). The second sample (MODIS2.2) was collected from the attic of the chancel of the church of Hamra located on the southernmost tip of the Swedish island of Gotland. The date of the mortar should be after 1300 AD, when the church was rebuilt (Roosval 1911) but no later than AD

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1361, since the island suffered from depression after the plague during the 1350s and the invasion by the Danish king Valdemar Atterdag in 1361. The mortar from the church was also previously dated to cal AD 1310–1360 (Ranta et al. 2009). The third sample (MODIS2.3) is from the early Christian Basilica of Santa Eulalia in Mérida, western Spain. The sample is from the basement in the inner corner of the north/northwest wall of the shrine erected in honor of Santa Eulalia that died in AD 304. Since on top of it a basilica was built in her honor in AD 570 (Mateos Cruz 1999; Pereira 2015) the sample should be dated to AD 304–570. The main focus on this intercomparison was to evaluate reproducibility of the mortar radiocarbon dating laboratories.

The Zagreb Radiocarbon Laboratory approach to mortar dating was to select and analyze lime lumps (Sironić et al. 2019). Although often reliable (Lindroos et al. 2018), lime lumps can also yield too young dates (Nawrocka et al. 2009), and not all mortars contain lime lumps. Current approach involves extraction of the “middle” grain fraction (MGF, 32–63 μm), sequential dissolution with orthophosphoric acid and collection of CO_2 gas portions (e.g. Lindroos and von Konow 1997; Heinemeier et al. 2010; Michalska 2019; Barret et al. 2020). According to Sonning and Jungner (2001), the MGF is the best grain size span for discrimination between geogenic and anthropogenic carbonate using chemical (hydrolysis) reactivity.

For the MODIS2, the dates of the first gas portions for the samples were reported as the intercomparison result. The first gas portion was collected so that the amount of produced CO_2 was maximum 20% of the amount of total CO_2 (Ringbom et al. 2011b).

Since the first gas portion (no matter how small) can still contain a portion of “dead carbon,” here we also use extrapolation of the data principle (based on Folk and Valastro 1976, similar to one described in Van Strydonck et al. 1986, 2015) and report the extrapolated results as well. We used first two gas portions for obtaining extrapolated result. They were collected so they conformed to conditions established experimentally (Sironić et al. 2023). The conditions were derived from the MGF hydrolysis kinetics in a way that is described in the Methods section. We also used the last (third) CO_2 gas portion to evaluate geogenic carbon influence and, in comparison with the first two gas portions, to indicate presence of recrystallization, shown as significantly ^{14}C younger fractions.

An array of analysis can be used for characterization of mortar matrix (Daugbjerg et al. 2020 and references therein). For the prescreening/characterization of the samples we use carbonate content expressed as CaCO_3 , kinetics curve of mortar hydrolysis with H_3PO_4 , and FTIR. Some authors (Toffolo et al. 2019; Calandra et al. 2022) use FTIR also for determination of the extracted binder carbonate purity of the grain fraction used for ^{14}C dating. The shape of ^{14}C content vs. CO_2 -gas amount curve (e.g. Lindroos et al. 2018) in case of sequential dissolution also gives insight into possible problems with recrystallization and amount of “dead carbon” content in analyzed grain fraction (Daugbjerg et al. 2020).

Here we compare our reported and extrapolated results to the known dendrodated and historical data provided by the intercomparison organizers, and not to the results obtained from the other radiocarbon laboratories that took part in the MODIS2. We use the method applied in the Zagreb Radiocarbon Laboratory that we find to be most cost and time effective.

METHODS

Sample Preparation

The obtained samples in form of <150 µm particle size fraction were sieved and 32–63 µm particle size (MGF) was used for further processing. The MGF was analyzed by Fourier-transform infrared attenuated total reflection (FTIR-ATR) for purity, and also for carbonate content expressed as CaCO₃.

For the method used for reporting the results, MGF was reacted with 85% H₃PO₄, at room temperature (23–27°C) on vacuum unit. Three successively formed gas portions of CO₂ were collected using liquid nitrogen in 0–3 s, 3–15 s and from 15 s until the end of the reaction. Each CO₂ gas portion was split for δ¹³C analysis and graphitized for ¹⁴C AMS analysis. The first gas portion were reported as the true age taking into account the course of reaction of sequential dissolution (Figure 2).

Extra steps were performed for the method using extrapolation principle. Hydrolysis kinetic curve of MGF with H₃PO₄ (85%) was created by monitoring pressure increase in time during reaction of sample conducted at 25°C or with reaction vessel immersed in ice cold water. The cumulative CO₂ yield (p_C/p_{tot} , p_C —cumulative pressure at time point, p_{tot} —total pressure when the whole batch of sample is reacted) at which the curve changes slope (starts to stagnate) (p_C/p_{tot-k}) was determined. The time span for the collection of the first gas portion was selected so that the amount of produced CO₂ is <25% p_C/p_{tot-k} and, for the sum of the first and second CO₂ portion, <100% p_C/p_{tot-k} . If the time span for collecting first gas portion was considered to be too short at 25°C (< 2 s for the first portion), it could be extended by performing the reaction with vessel immersed in ice water. The third gas portion (until the end of the reaction) was also collected. All collected gas portions were prepared for ¹⁴C and ¹³C analyses. For ¹⁴C analysis graphites were prepared by using Zn reduction on Fe (Krajcar Bronić et al. 2010; Sironić et al. 2013).

FTIR Analysis

FTIR-ATR spectra were recorded using a PerkinElmer UATR Two spectrometer in the range 450 cm⁻¹ to 4000 cm⁻¹, with a spectral resolution of 4 cm⁻¹ and total of 8 scans accumulated. Automatic ATR correction algorithm was applied to account for relative intensity shift in the collected FTIR spectra. The ν_2/ν_4 peak intensity ratio of the out-of-plane bending ($\nu_2 = 873$ cm⁻¹) and in-plane bending ($\nu_4 = 712$ cm⁻¹) of calcite was calculated by drawing the baseline between the closest minima on the sides of these two peaks and reading the peak intensity values (Chu et al. 2008).

¹⁴C and ¹³C Analysis

Carbon isotope analysis of CO₂ gas (δ¹³C) and of graphites (¹⁴C/¹³C ratio) were performed at the Center for Applied Isotope Studies, Georgia (CAIS). The δ¹³C values, measured on Isotope Ratio Mass Spectrometer (IRMS), are expressed in per mill relative to Vienna Pee Dee Belemnite (Brand et al. 2014) and have uncertainty of 0.1‰ that was calculated based on multiple measurements of the secondary standards. ¹⁴C/¹³C values were measured on 0.5 MeV accelerator mass spectrometer (AMS) at the CAIS (Cherkinsky et al. 2010). ¹⁴C values are normalized to δ¹³C of −25‰ and expressed as fraction modern ($F^{14}C$) and as age before present (BP; Stuiver and Polach 1977; Mook and van der Plicht 1999). ¹⁴C conventional ages were calibrated by OxCal 4.4 software (Bronk Ramsey 2009; Bronk Ramsey and Lee 2013) and IntCal20 calibration curves (Reimer et al. 2020).

Principle of Date Extrapolation from Sequential Dissolution Gas Portions

Here we use idea of linear extrapolation, and it should also be pointed out that there could also be used exponential model (the Texas method, Folk and Valastro 1976; Van Strydonck et al. 1992; Lindroos et al. 2007). The ages using this principle should be considered as the minimal ages.

In order to create curve expressing changes in $F^{14}C$ with increase in CO_2 pressure in each point, cumulative values should be calculated, because the measured vales (for $F^{14}C$ and amount of CO_2) correspond only to certain extracted portion of CO_2 gas. Cumulative $F^{14}C_C$ and p_C/p_{tot} values at the end of each collected gas portions were calculated using:

$$p_C/p_{tot,n} = \sum_{i=1}^n p/p_{tot,i} \quad (1)$$

$$F^{14}C_{C,n} = \frac{\sum_{i=1}^n F^{14}C_i \cdot p/p_{tot,i}}{p_C/p_{tot,n}} \quad (2)$$

where $F^{14}C_i$ is fraction modern of each collected CO_2 portion and $p/p_{tot,i}$ are yields of each of those portions up to the n^{th} one, while $F^{14}C_{C,n}$ is cumulative activity for each CO_2 portion from zero point to the end point of that portion and $p/p_{tot,i}$ are corresponding cumulative yields. If it is assumed that with reaction development (with time and increase in p_C/p_{tot}) produced CO_2 contains more geogenic (“dead”) carbon, it can be deduced that a theoretical initial point contains pure anthropogenic CO_2 at time $t=0$ s, i.e. $p_C/p_{tot}=0$. To extrapolate the radiocarbon result p_C/p_{tot} vs $F^{14}C_C$ correlation was used. The extrapolated $F^{14}C_C$ value (at $p_C/p_{tot}=0$) was calculated as an intercept of linear equation defined by the p_C/p_{tot} and $F^{14}C_C$ values only for the first two cumulative portions, points $(p_C/p_{tot,1}, F^{14}C_{C,1})$ and $(p_C/p_{tot,2}, F^{14}C_{C,2})$. This principle of extrapolation is valid only for conditions: $p_C/p_{tot,1} < 25\%$ p_C/p_{tot-k} and, $p_C/p_{tot,2} < 100\%$ p_C/p_{tot-k} (Sironić et al. 2023). The uncertainty for the extrapolated value was assessed from uncertainty propagation of the same two points.

RESULTS

Characterization

Characterization of the samples was performed by means of FTIR analysis (Figure 1, Table 1), carbonate yields (Table 1), hydrolysis kinetics curves (Figure 2) and cumulative radiocarbon results, i.e. curve p_C/p_{tot} vs $F^{14}C_C$. (Figure 3).

The FTIR analysis is used since it can provide qualitative data in a simple, fast and reliable manner. For the more detailed mineralogical analysis, providing information about recrystallization (which can give both too old and too young results) or magnesite (in a case of dolomitic lime mortars, giving too young result) presence in mortar, petrography, XRD or SEM analysis should be used (Daugbjerg et al. 2020). The carbonate yield can imply if the mortar is non-hydraulic or hydraulic. The hydrolysis kinetic curves are mainly used for determining the time periods for collecting desired portions, however, higher p_C/p_{tot-k} values imply higher portion of anthropogenic (binder) carbonate.

The final characterization of the mortars is also checked with the cumulative radiocarbon results, i.e. curve p_C/p_{tot} vs. $F^{14}C_C$, which should generally be descending with later portions

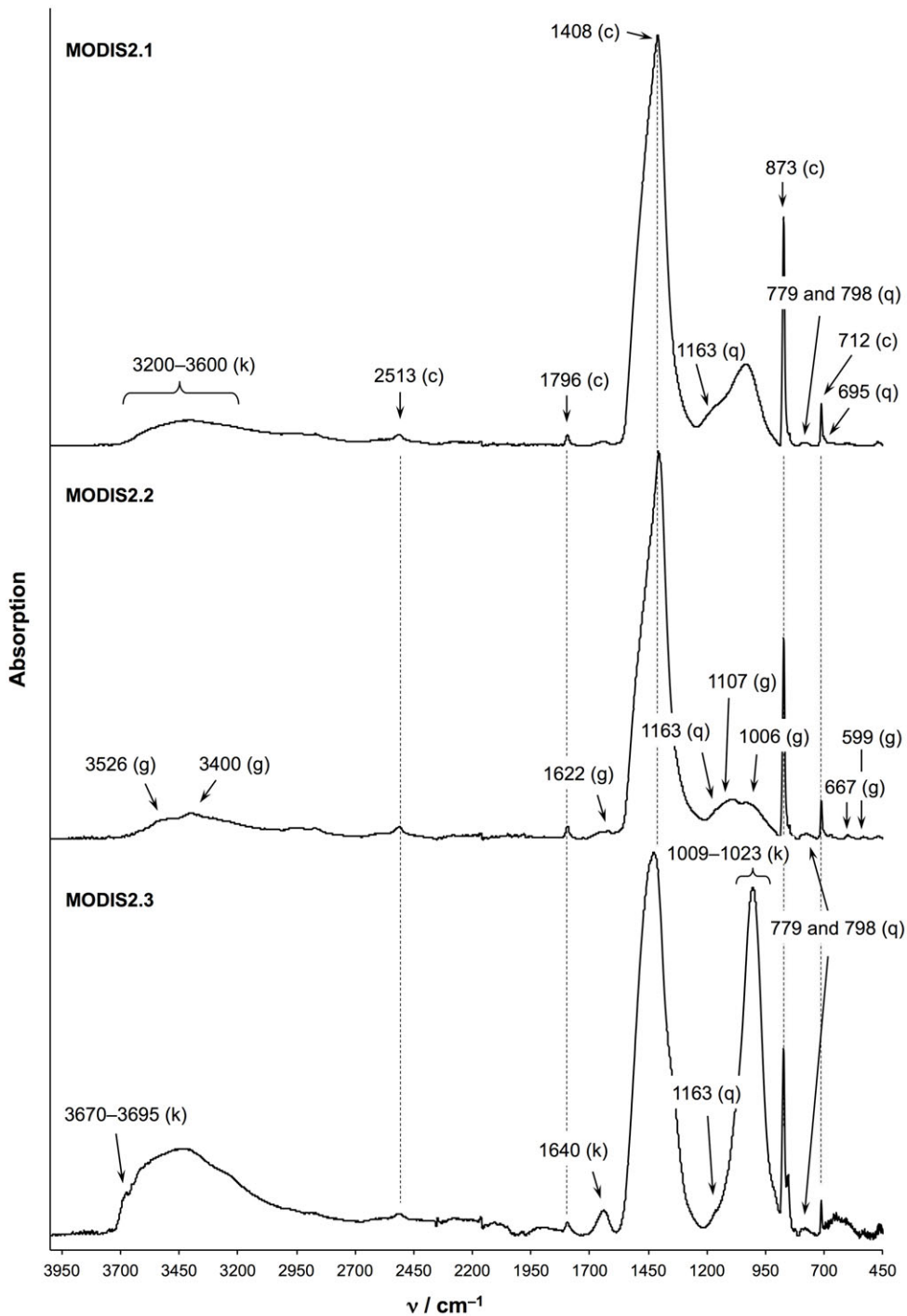


Figure 1 FTIR-ATR analysis of mortar samples with particle size of 32–63 μm : (c) calcite, (k) kaolinite, (g) gypsum and (q) quartz. Strong absorption signals of kaolinite in MODIS2.3 confirmed low carbonate content in the sample.

Table 1 Results of carbonate content (calculated as CaCO₃) of 32–63 µm grain fraction (sieved from fraction <150 µm) and FTIR qualitative mineral analysis for each MODIS2 sample and δ¹³C and radiocarbon dates of each CO₂ sequential dissolution gas portions of the three MODIS2 samples: sample ID and laboratory numbers (Z—sample id, A—graphite ID number, Zagreb Laboratory and UGAMS—graphite ID number, CAIS), step hydrolysis time fraction, *m*_{SD}—mass of sieved fraction for sequential dissolution, *m*(C_{fr})—mass of carbon in each CO₂ portion, *p*/*p*_{tot}—percentage of carbon in each individual gas portion compared to total carbon content for sequential dissolution, *F*¹⁴C—fraction modern, δ¹³C (with 0.1‰ uncertainty) and ¹⁴C date of each collected CO₂ portion.

Sample ID	Carbonate yield (as CaCO ₃)	FTIR analysis	Laboratory number	Step	<i>m</i> _{SD} (mg)	<i>m</i> (C _{fr}) (mg)	<i>p</i> / <i>p</i> _{tot} (%)	<i>F</i> ¹⁴ C	δ ¹³ C (‰)	¹⁴ C age (BP)
MODIS2.1 Z-7093	78%	Calcite, kaolinite, quartz	Z-7176; A1989; UGAMS45016	0–3 s	101	1.5	20.1	0.9236 ± 0.0025	nm	638 ± 21
			Z-7177; A1988; UGAMS45015	3–15 s		3.8	52.0	0.9189 ± 0.0024	–10.1	679 ± 20
			Z-7178; A1987; UGAMS45014	15 s–end		2.0	28.0	0.9106 ± 0.0024	–10.0	752 ± 21
MODIS2.2 Z-7094	95%	Calcite small amount of quartz, gypsum	Z-7185; A2010; UGAMS45627	0–3 s	110	1.2	13.6	0.9204 ± 0.0025	–15.2	666 ± 21
			Z-7186; A2011; UGAMS45628	3–15 s		2.2	25.2	0.8862 ± 0.0024	–9.9	970 ± 21
			Z-7187; A2012; UGAMS45629	15 s–end		5.3	61.2	0.8014 ± 0.0023	–8.8	1778 ± 23
MODIS2.3 Z-7095	46%	Kaolinite, quartz, calcite	Z-7188; A2024; UGAMS45635	0–3 s	103	0.5	9.0	0.8043 ± 0.0022	nm	1749 ± 21
			Z-7189; A2025; UGAMS45636	3–15 s		2.2	40.9	0.7895 ± 0.0022	–21.8	1898 ± 22
			Z-7190; A2026; UGAMS45637	15 s–end		2.7	50.1	0.7757 ± 0.0021	–21.4	2040 ± 21
			Z-8173; A2805; UGAMS59884	Ice* 0–15 s	205	0.6	5.3	0.8030 ± 0.0023	–31.5	1762 ± 23
			Z-8174; A2806; UGAMS59885	Ice* 15–20 s		0.4	3.6	0.8000 ± 0.0025	–24.7	1793 ± 25

*Reaction conducted with reaction vessel immersed in ice cold water, nm—not measured.

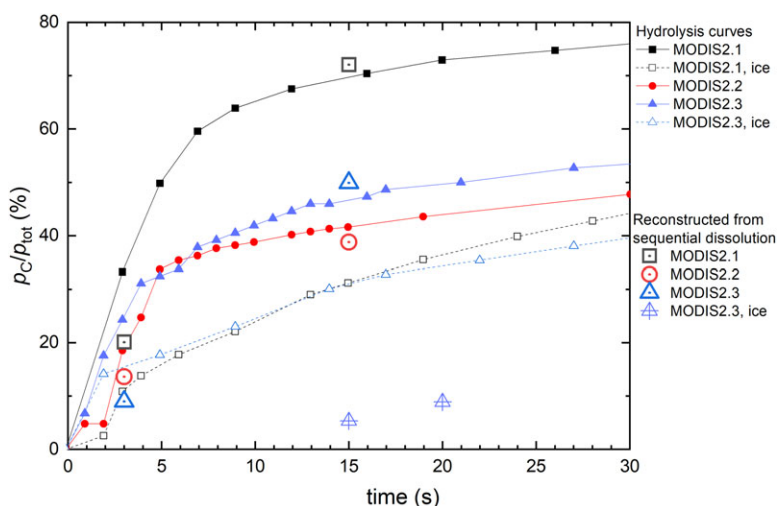


Figure 2 Hydrolysis kinetics curves for MODIS2 and points reconstructed from amount of CO_2 portions in time obtained during sequential dissolution.

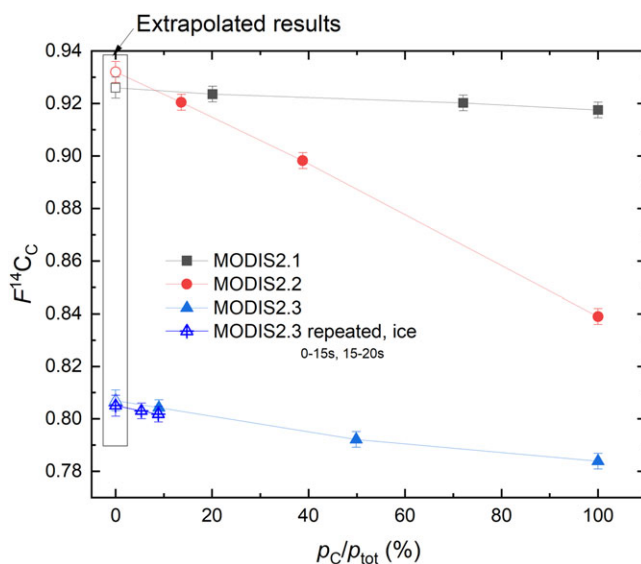


Figure 3 Cumulative $F^{14}\text{C}_C$ vs p_C/p_{tot} for all MODIS2 samples (Table S1, Supplementary data), and extrapolated result (in the black rectangle) obtained from the first two CO_2 portions. All results are obtained at 25°C , and “MODIS2.3–repeated, ice” was obtained with reaction vessel immersed in ice cold water.

(e.g. Heinemeier et al. 2010). If changes in the trends are observed, e.g. to higher $F^{14}\text{C}_C$, or there is a steep fall of $F^{14}\text{C}_C$, recrystallization is suspected making the initial portion unreliable. Otherwise, the $F^{14}\text{C}_C$ of the first portion (amount of CO_2 portion < 20% of the amount of total CO_2 , Ringbom et al. 2011b) or the extrapolated value (Sironić et al. 2023) provide the best estimated date of the mortar.

An initial screening of MODIS2 samples by FTIR showed qualitative differences among them. The most prominent features in all FTIR-ATR spectra of analyzed mortars were absorption bands of calcite as a major component, found at 712, 873, 1408, 1796, and 2513 cm^{-1} (Chu et al. 2008; Poduska et al. 2012). Mineralogical analysis also revealed that all MODIS2 samples contained a small amount of quartz based on the presence of signals at 695, 779, 798, and 1163 cm^{-1} . Characteristic absorption signals at 3526, 3400, 1622, 1107, 1006, 667, and 599 cm^{-1} clearly correlated with gypsum as the third component in MODIS2.2 sample. However, in comparison with MODIS2.1 where kaolinite clay constitutes the rest of the composition, MODIS2.2 appeared to have the highest carbonate content in semi-quantitative terms. On the other hand, MODIS2.3 sample was made up of a substantial amount of kaolinite clay as indicated by typical absorption bands at 3670–3695 cm^{-1} and 1640 cm^{-1} , as well as a strong signal at 1009–1023 cm^{-1} , with expected low levels of carbonate content. These findings were later supported by carbonate yield (as CaCO_3) analysis (Table 1).

An anthropogenic portion of the analyzed MODIS2 samples was evaluated through calculation of the ν_2/ν_4 ratio (at 873 and 712 cm^{-1} , respectively) of the corresponding CaCO_3 vibration intensities in the collected FTIR-ATR spectra. The ν_2/ν_4 ratio values were consistently found in the range from 5.0–5.9, as opposed to pure geogenic calcite for which a value of 2.3 or similar would be expected (Chu et al. 2008).

Hydrolysis kinetics curves (p_c/p_{tot} vs. time, Figure 2) were obtained for all the MODIS2 samples at room temperature and for samples MODIS2.1 and MODIS2.3 also in ice water. The points reconstructed from the amount of CO_2 portions collected in time for ^{14}C analysis during sequential dissolution for all the samples at the room temperature and for MODIS2.3 in ice water are shown in Figure 2.

It can be observed that the steepness (change in p/p_{tot} in time) for the kinetics curves depended on the temperature of samples, largely slowing down the reaction in ice water compared to room temperature. The first two CO_2 portions from sequential dissolution fitted the desired gas portion ($<25\%$ $p_c/p_{\text{tot-k}}$ for the first and $<100\%$ $p_c/p_{\text{tot-k}}$ for the first and the second CO_2 portion) of the total yielded CO_2 for all the three samples. For the sample MODIS2.3, points reconstructed from the sequential dissolution in ice water did not coincide with curve obtained from hydrolysis kinetics obtained with the same conditions. This was probably due some error in manual measurement of time during collection of gas portions from sequential dissolution.

Carbon Isotopes and Radiocarbon Age Results

Carbonate content (calculated as CaCO_3) of all MODIS2 samples 32–63 μm grain fraction, as well as carbonate content in grain fraction, CO_2 yield of each gas portion (p/p_{tot}), carbon isotope data and radiocarbon date results for all sequential dissolution CO_2 portions are presented in Table 1. The dates for each sample that were reported to the MODIS2 organizers as the age of the mortar were all 0–3 s gas portions (first gas portions) conducted at the room temperatures (Z-7176, Z-7185 and Z-7188 for MODIS2.1, MODIS2.2 and MODIS2.3, respectively).

The curve displaying relation of cumulative p_c/p_{tot} vs. $F^{14}\text{C}_c$ (Figure 3, Table S1, Supplementary data) shows steady decrease of $F^{14}\text{C}$ for later portions for all the samples. This is generally expected behavior for samples without recrystallized carbon (Heinemeier et al. 2010; Lindroos 2018), implying that the first portion contains only anthropogenic carbon.

Extrapolated values, because of uncertainty propagation, have almost twice the uncertainty of the reported values.

All the extrapolated results are higher than for the corresponding first portions. Results for repeated analysis of MODIS2.3 sample conducted at lower temperature (reaction vessel immersed in ice cold water) agree very well to the analysis at the room temperature (Table 2).

$\delta^{13}\text{C}$ values for all the portions increase with later CO_2 portions for all the samples, which is usually observed due to kinetic effect (Nawrocka et al. 2009; Heinemeier et al. 2010), but can also be influenced by increase in amount of the dead carbon.

DISCUSSION

Radiocarbon ages and corresponding calibrated dates for reported and extrapolated values for each sample (Table 2 and Figure 4) are compared to the expected dates. Calibrated ages are given with 68.3% probability. Radiocarbon ages are not rounded according to the convention.

Sample MODIS2.1 for both the reported and extrapolated calibrated dates agrees very well with the dendro-dated wood. Also, the whole span of both results fit into the expectation that the building belongs to the 14th century. The influence of the geogenic carbon is very low (Figure 3) and accounts to about 0.9% (calculated from $F^{14}\text{C}_\text{C}$, Table S1, Supplementary data), so the difference between the first and the final gas portion is only 100 ^{14}C years. This is the main reason that the reported and extrapolated result fit one another.

The reported date for the MODIS2.2 sample in the 68.3% posterior probability does not overlap with the expected historical span of dates. With 95.4% (2σ) probability calibrated dates for reported value are cal AD 1281–1319 (49.5%) and cal AD 1359–1389 (45.9%) overlapping the historical dates in period AD 1300–1319 and AD 1359–1361. Higher probability range (99.7%, 3σ) (calibrated dates are cal AD 1276–1327 (51.8%) and cal AD 1351–1395 (47.9%)) overlap the historical dates in periods AD 1300–1327 and AD 1351–1361. However, by moving about 100 years later, with extrapolation, extrapolated dates fit completely with 68.3% (1σ) probability, yielding overlapping date span AD 1321–1358. The difference between the extrapolated and the $F^{14}\text{C}$ of the complete CO_2 portion is 0.09, which would approximate to about 10% of the geogenic component (Table S1, Supplementary data), making the difference between the reported and extrapolated result significant for dating. The stable isotope data are influenced mainly by the kinetic effect, which is particularly emphasized in very low value (-31.5‰) for the first CO_2 portion in ice of MODIS2.3. However, the highest $\delta^{13}\text{C}$ of the MODIS2.2 value (-8.8‰) for the last CO_2 portion compared to the other samples, and the biggest difference between its first and the last CO_2 portions (from -15‰ to -8.8‰) implies largest influence of the geogenic/dead carbon contamination in the last portion.

The historical date span for the MODIS2.3 sample is quite wide; 266 years. Both reported and extrapolated dates (in 68.3% probability) overlap in about one third of the older part of the historical date span. If both dates are considered, when dating the event of erection of the St. Eulalia shrine, the date range can be shortened to from AD 305 to cal AD 375 (reported date) or to cal AD 430 (extrapolated date), both for 94.5% posterior probability. We cannot assume normal probability distribution of the true age between the set historical range AD 304–570. It would be more probable that the shrine was erected closer to the time of death of St. Eulalia, which is here implied by the reported and extrapolated results for the sample MODIS2.3.

Table 2 Reported and extrapolated radiocarbon ages and corresponding calibrated dates for 68.3% probability compared to the expected age. Ranges marked gray fit/overlap with the expected date.

Sample	Reported		Extrapolated		Expected date
	¹⁴ C age (BP)	Calibrated date	¹⁴ C age (BP)	Calibrated date	
MODIS2.1	638 ± 21	Cal AD 1300–1320 (29.6%) Cal AD 1358–1389 (38.7%)	617 ± 43	Cal AD 1303–1328, (25.5%) Cal AD 1339–1368, (27.1%) Cal AD 1380–1396, (15.7%)	Dendro date 1381 AD
MODIS2.2	666 ± 21	Cal AD 1286–1305 (34.2%) Cal AD 1365–1383 (34.0%)	566 ± 43	Cal AD 1321–1358, (38.2%) Cal AD 1390–1420, (30.0%)	AD 1300–1361
MODIS2.3	1749 ± 21	Cal AD 250–263 (12.8%) Cal AD 275–295 (19.8%) Cal AD 310–346 (35.7%)	1722 ± 51 1742 ± 50*	Cal AD 254–286 (19.2%) Cal AD 324–404 (49.1%) Cal AD 248–297 (28.9%) Cal AD 308–375 (39.4%)	AD 304–570

*Repeated reaction with vessel immersed in ice cold water, shaded calibrated dates overlap with expected ranges).

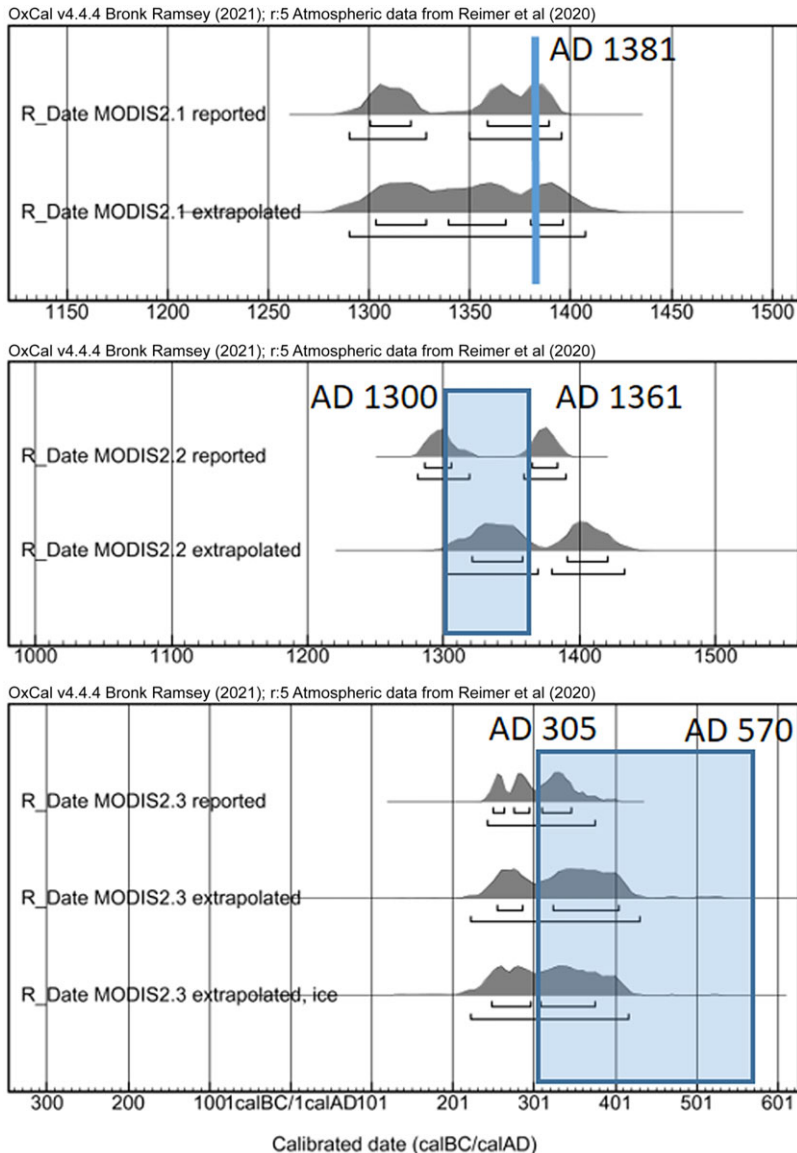


Figure 4 Calibration curves of the reported and extrapolated results for MODIS2 samples in comparison to the expected dendrodated and historical dates (blue line and rectangles, respectively).

Similar to MODIS2.1 sample, the amount of geogenic carbon of MODIS2.3 is low, 2.9% and 2.6% at the room temperature and in ice-water, respectively (Table S1), and so the difference between the reported and extrapolated values is not crucial. The difference of this sample compared to the samples MODIS2.1 and MODIS2.2 is visible in the carbonate content (which is only 46%) and in amount of other material present as visible in FTIR spectra.

Another feature that makes the extrapolated values more reliable than the reported ones is wider uncertainty that considers both information from the first and the second gas portion.

CONCLUSION

We present the Zagreb Radiocarbon Laboratory, Zagreb, Croatia and Center for Applied Isotope Studies, University of Georgia, USA, radiocarbon results of the three mortar samples from the second international mortar dating intercomparison MODIS2. We compared our results to the expected historical age spans provided by the organizer.

The characterization of the samples was performed by FTIR, carbonate composition, hydrolysis kinetic curve of the 32–63 μm grain fraction and trend of radiocarbon results of three successive CO_2 portions obtained by sequential dissolution of 32–63 μm grain fraction by phosphoric acid. We reported the date of the first CO_2 portion as the date of mortar. All reported results for all three MODIS2 samples fitted the expected historical and dendrodated results. We also used the MODIS2 samples to test the principle of extrapolating results obtained from sequential dissolution. This approach is currently applied for mortar dating in the Zagreb Radiocarbon Laboratory. All the extrapolated results also fitted the expected historical ranges, and in case of sample MODIS2.2 the overlapping in calibrated extrapolated calendar dates with the historical period was better than for the reported one. This implied that the extrapolation principle can be used for eliminating dead carbon contamination in samples with higher contribution of geogenic carbonate.

The reported approach for radiocarbon mortar dating works for non-hydraulic mortars without recrystallization. Although the trend in radiocarbon activities for collected successive CO_2 portions implied no presence of recrystallization, only three gas portions are not enough as definite proof, and, in the future, use of petrography and XRD analysis will be required prior to dating.

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SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit <https://doi.org/10.1017/RDC.2024.75>

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