Radiocarbon, Vol 00, Nr 00, 2024, p 1–14 DOI:10.1017/RDC.2024.3
Selected Papers from the 24th Radiocarbon and 10th Radiocarbon & Archaeology International Conferences, Zurich, Switzerland, 11–16 Sept. 2022

CHARACTERIZATION AND SELECTION OF MORTAR SAMPLES FOR RADIOCARBON DATING IN THE FRAMEWORK OF THE MODIS2 INTERCOMPARISON: TWO COMPARED PROCEDURES

G Artioli[1,2] • S Barone[3,4] • M Fedi[3] • A Galli[5] • L Liccioli[3] • M Martini[5] • F Marzaioli[6] • F Maspero[5]* • L Panzeri[5] • I Passariello[6] • G Ricci[1,2] • M Secco[1,7] • F Terrasi[6]

[1]Inter-Departmental Research Center for the Study of Cement Materials and Hydraulic Binders (CIRCe), University of Padova, Italy
[2]Department of Geosciences, University of Padova, Italy
[3]INFN, Section of Firenze, Italy
[4]Department of Physics and Astronomy, University of Firenze, Italy
[5]Department of Materials Science, University of Milano-Bicocca, Italy and CUDAM (Centro Universitario Datazioni e Archeometria Milano-Bicocca)
[6]Department of Mathematics and Physics, University of Campania Luigi Vanvitelli, Italy
[7]Department of Cultural Heritage, University of Padova, Italy

ABSTRACT. For several decades, many efforts have been dedicated to enhancing the accuracy of mortar radiocarbon dating and evaluating the reliability of the results concerning the typology of the examined specimens. Several assumptions that are fundamental for the application of the method may be in many cases not fulfilled, such as (a) complete primary limestone dissociation during calcination, (b) efficient separation of geogenic carbon contained in calcareous aggregates, (c) short carbonation time, and (d) absence of secondary calcite. Many laboratories all over the world have proposed different methods to select suitable fractions of mortar.

The first intercomparison attempt, involving eight international laboratories, was organized in 2016 aiming at comparing and statistically treating the results obtained on the same materials by different laboratories with their own characterization and pre-treatment methods (Hajdas et al. 2017; Hayen et al. 2017). Following this first step, a new intercomparison experiment was proposed and set up in 2018 during the Mortar Dating International Meeting (Bordeaux, FR). A new set of three mortar samples was chosen, taking care of the selection of standardized materials (homogeneity, known mineralogical composition, absence of exogenous inclusions, known expected age).

This work describes the results of two research teams involved in the intercomparison. The samples were characterized, selected, and dated depending on each laboratory strategy. The results stress the importance of the characterization of the raw material is to better understand the mineralogical and petrographical composition of the samples. Such information can support the choice of the most appropriate strategy for the extraction of CO_2 and then for data interpretation.

KEYWORDS: calcite, chemical analysis, mortar, pretreatment, radiocarbon AMS dating.

INTRODUCTION

In 2016 eight laboratories applying radiocarbon and Optically Stimulated Luminescence (OSL) to mortars joined the first MOrtar Dating Intercomparison Study (MODIS): the aim of the project was to compare the characterization and dating results obtained by different laboratories on the same materials. Four different mortar samples were selected and distributed; however, the results obtained by the laboratories were statistically unsatisfactory in finding reliable selection and extraction methods (Hajdas et al. 2017; Hayen et al. 2017). Thus, in 2020 a second project, MODIS2, started: twelve radiocarbon research groups joined this

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*Corresponding author. Email: francesco.maspero@unimib.it

intercomparison, while three OSL laboratories conducted a separate intercomparison program, selecting samples more suitable for OSL dating (Urbanová et al. 2024).

The three samples distributed to the labs were selected for their expected simple composition and expected dating reliability. The experiment was performed in blind mode, and the participants got information about the samples only after the collection of all the results. In this research paper, the procedures and results of the two research teams were compared and discussed. One team is formed by the CIRCe laboratory (University of Padova) and the CIRCE group (University of Campania «Luigi Vanvitelli») (from now on PD-CE), the other is formed by the Lambda laboratory (University of Milano Bicocca) and INFN-LABEC (Firenze, unit of INFN-CHNet) (from now on MI-FI). This work shows the characterization and separation approaches of the involved laboratories, comparing their procedures and obtained results.

PD-CE approach in studying and dating historical mortars consists of combining a careful extraction and preparation of the fine binder fraction with a full mineralogical characterization of both bulk and extracted samples. The chemical, mineralogical and microstructural characterization provides useful data able to determine whether the sample is suitable for dating and which criteria are needed for a more efficient separation of the carbonate fraction of interest. In order to separate the binder fraction from other contaminant sources, as carbonate aggregates, a multistep purification protocol based on size selection by wet sieving has been developed. (Marzaioli et al. 2008; Terrasi et al. 2008; Nonni et al. 2013; Addis et al. 2019; Ricci et al. 2019, 2020, 2022).

MI-FI approach aimed at testing an ATR-FTIR characterization of the bulk mortar, based on the work of Regev et al. (2010), in order to provide a first discriminant technique to select the most suitable material to be dated. The bulk material was wet sieved to select the most suitable fractions (finest and softer grains). For graphitization, the selected fractions, after the chemical digestion process, were reduced to a partial pressure equivalent to ~50 μg of carbon and converted to graphite using the so-called Lilliput line (Fedi et al. 2020). The possibility of using this graphitization set-up for small samples represents an advantage in case of low amount of calcite minerals in the collected samples, or scarcity of mortar material. The latter, for example, can happen when samples are collected from cracks, or in case of dating of a single lump (Cantisani et al. 2021).

MATERIALS

A set of three mortar samples was chosen by the organizers, selecting materials as much standardized as possible, according to these characteristics: homogeneity, known mineralogical composition, absence of exogenous inclusions, known expected age (A. Lindroos, personal communication). The provenance and known characteristics of the materials were divulged to the involved labs only after the conclusion of the intercomparison. The three samples were:

- MODIS2.1: Church of Saltvik on the Åland Islands, AD 14th c. tower. The church was sampled in 1994 and the dating results were published in Heinemeier et al. (2010) and Ringbom (2011). The sample Saka 110 was used in this inter-comparison.
- MODIS2.2: Church of Hamra on the Swedish island of Gotland, (early) AD 14th-century attic of the chancel. The sample Hamra 002 was used in the inter-comparison.
- MODIS2.3: Early Christian Basilica of Santa Eulalia in Mérida, western Spain, inner corner of the north/northwest wall from AD 304-570. The sample Mérida 012 (MODIS2.3) was not dated, but it is a large sample from the same chronology. It was taken from the basement in the inner corner on the North-West, North wall.

PD-CE METHODS

The analytical approach is divided into different phases:

1. a chemical-mineralogical characterization of the mortars in order to assess materials' properties and the presence of dating contaminants, aimed at developing a more efficient separation procedure of the binder fraction;
2. a series of purification procedures of the binder by wet gravimetric sedimentation;
3. a characterization of the extracted fine powder in order to evaluate the effectiveness of the purification;
4. a sample treatment for the elimination of possible contaminants;
5. a final acid digestion, graphitization and radiocarbon dating of the purified fraction.

Characterization and separation procedures were performed at the CIRCe Centre in Padua (Italy), graphitization and AMS measurements were carried out at CIRCE Centre in Caserta (Italy).

Mortar Characterization Methods

Petrographic analyses were performed by OM on 30 μm thin-sections under parallel and crossed polars using a Nikon Eclipse ME600 microscope equipped with a Canon EOS 600D Digital single-lens reflex camera. The thin sections, covered with an ultrathin coating of graphite, were microstructurally and microchemically characterized through a CamScan MX2500 SEM equipped with a LaB6 electron source and an EDS used to collect elemental microanalyses through the SEMQuant Phizaf software, giving valuable information on the mineral phases and binder composition. Mineralogical quantitative phase analyses (QPAs, expressed in wt%) were performed by XRPD on fine sample powders obtained by micronization. XRPD analyses were performed using a Malvern PANalytical X'Pert PRO diffractometer in Bragg-Brentano geometry, Co–Kα radiation, 40 kV and 40 mA, equipped with a real-time multiple strip (RTMS) detector (X'Celerator by Malvern Panalytical). Data acquisition was performed by operating a continuous scan in the range 3–85° 2θ, with a virtual step scan of 0.02° 2θ. Diffraction patterns were interpreted with X'Pert HighScore Plus 3.0 software by Malvern PANalytical, reconstructing mineral profiles of the compounds by comparison with ICDD and ICSD diffraction databases. QPAs were performed using the Rietveld method (Rietveld, 1969) and refinements were accomplished using the TOPAS software (version 4.1) by Bruker AXS. The determination of both crystalline and amorphous content was calculated by means of the internal standard method with the addition of 20 wt% of zincite (ZnO) to the powders (Gualtieri 2000).

Binder Extraction

The mortar samples were subjected to the purification treatment by wet gravimetric separation. As reported by the authors in (Nonni et al. 2013; Addis et al. 2019; Ricci et al. 2020), the purification process involves: a manual cleaning and disaggregation of the mortars; 2 ultrasonic baths for 20 minutes each in a ultra-pure water solution of sodium hexametaphosphate ($NaPO_3$) used as a deflocculant at 0.5 w/v%; 24 hours of wet sedimentation in a 500 mL cylinder in order to obtain a Stokes' Law-based dimensional separation of the particles; a sampling of the uppermost emulsion containing particles with size lower than 2 µm; a filtration of the fine grained particles (SG) using a vacuum pump system and inorganic 0.1 µm filters.

Binder Characterization and Purification

The obtained SGs were analysed by XRPD in order to evaluate the presence of contaminants for the radiocarbon dating.

If the mortars are affected by hydraulic reaction processes, layer double hydroxides (LDH), as hydrotalcite- or hydrocalumite-like compounds, may be present in the isolated binder fraction prepared for the dating process. LDHs can exchange carbonate anions with the atmosphere well after the laying of the mortar and during the life of the building, compromising the success of the dating by introducing younger CO_2 into the system (Artioli et al. 2017; Ponce-Antón et al. 2018; Ricci et al. 2020).

LDH phases can be detected by XRPD investigation allowing the evaluation of the chance to be dated of the carbonate binder and eventually a further thermal purification treatment.

In samples where LDHs were detected, a thermal treatment at 550°C for 30 min in vacuum conditions was carried out on the SG fractions in order to break down the LDH structure. The selected temperature was chosen according to the thermal decomposition temperature of LDHs and carbonates (Stanimirova et al. 1999; Roelofs et al. 2002; Trindade et al. 2009; Hollingbery and Hull 2010; Bhattacharjya et al. 2012).

Both the outcome of the thermal treatment (HT), i.e. released CO_2 of the LDHs, and the residual after thermal treatment (DR) were collected and subjected to the graphitization process for AMS measurements.

Mortar Radiocarbon Dating

The carbonate binder fraction and/or the residual after thermal treatment (DR), were digested under vacuum by means of a complete orthophosphoric acid attack for 2 hr at 80°C (Marzaioli et al. 2011). The extracted CO_2 (including the one from HT) was reduced to graphite on iron powder catalyst according to the CIRCE sealed tube reaction protocol (Marzaioli et al. 2008). ^{14}C isotopic ratios is measured (Terrasi et al. 2008) and the data are corrected for fractionation and blank according to their graphitised mass, normalised and R.C. ages are estimated and calibrated to absolute ages by means of OxCal 4.4 (Bronk Ramsey and Lee 2013) and INTCAL20 calibration curve (Reimer et al. 2020).

MI-FI METHODS

Mortar Characterization Methods

ATR-FTIR technique was chosen as characterization method to test the feasibility of a reliable radiocarbon dating of the examined samples. The ATR configuration was tested as it offers a promising tool for conducting in situ measurements. Additionally, its rapidity and minimal sample preparation requirements make it highly practical and efficient Analyses were performed using a Thermo Fisher Nicolet iN10, with a spectral range from 4000 to 675 cm^{-1}, and a 400×400 µm aperture. The spectra were firstly collected on untreated, grinded and homogenised samples in search of anomalous peaks that can be associated to functional groups characteristic of mineralogical phases different from calcite or similar. Following the separation process, the collected powder underwent further analysis by FTIR in order to detect any anomalies in the characteristic carbonate peaks, since these deviations could potentially indicate the presence of different carbonate phases. In addition, the calcite peaks associated to in-plane CO_3 deformation ($\nu4$) and out-of-plane CO_3 deformation ($\nu2$) of the selected binder material were analysed following (Regev et al. 2010) to assess their crystallinity level. The data were compared with laboratory reference datasets, which were built using a just-made calcite and a calcite crystal as boundary materials: the sets were obtained starting from the FTIR spectra acquired grinding the reference materials at different granulometries.

Binder Extraction

Binder separation is based on gravimetric separation as well as in the case of the PD-CE approach. It just differs for the initial crushing step (according to Ortega et al. 2012).

In particular, the overall procedure follows these steps:

- hammering the material until disaggregation of the bulk structure and formation of a coarse granulate phase,
- ultrasonic bath for 10 minutes in deionized water,
- collection of the suspended fraction,
- resuspension of the collected fraction and further ultrasonic bath, centrifugation for 1 minute at 8000 rpm and collection of the suspended fraction.

Mortar Radiocarbon Dating

The selected materials were chemically digested (about 5 mg each) collecting different fractions every 20 seconds (when possible). The CO_2 collected from each of the fractions was reduced to graphite optimizing the partial pressure of gas to fit the graphitization reactors optimized for micrograms-sized samples (Lilliput experiment, Fedi et al. 2020); the pressure was reduced for every sample by ~66%. The prepared samples were measured at the INFN-LABEC AMS facility in Firenze (Fedi et al. 2007). Radiocarbon ages are estimated and calibrated using OxCal 4.4 software (Bronk Ramsey and Lee 2013) and INTCAL20 calibration curve (Reimer et al. 2020).

RESULTS AND DISCUSSION

PD-CE Characterization

The characterization obtained by PD-CE team using the complementary techniques, summarized in Table S1 and Figures S1-2-3-4 in the supplementary materials, showed the following results:

- MODIS2.1: the mortar is characterized by the use of aerial lime as binder material and (mainly) silicate aggregates with no identified reaction edges. Sporadic hydraulic lime lumps with a chemical composition (Ca and Si) compatible with C_2S phases are identified, probably due to the accidental presence of marly limestone during the calcination process (Supplementary material, Fig. S1). The XRPD on the SG fraction (Figure 1a) highlights the presence of LDH phases, formed probably due to a partial and accidental hydraulic reaction as suggested by SEM-EDX analysis; the sample may be contaminated by young carbonate, therefore, according to lab experience, a thermal treatment to eliminate the LDH phases was necessary;

- MODIS2.2: the mortar is characterized by the use of aerial lime as binder material, silicate and large carbonate aggregates and no reaction edges are identified (Supplementary material, Fig. S2). The SG is a pure calcium carbonate binder (Figure 1b), and it seems to be a good candidate for radiocarbon dating;
- MODIS2.3: the mortar is characterized by a 1:3 binder-to-aggregate ratio, aerial lime and the aggregates consist of: mainly silicates (as quartz and feldspars) and dolomite. Stages of alteration/degradation of the silicate and dolomite aggregates are observed, probably due to the establishment of hyperalkaline condition (Weber et al. 2015). The presence of Mg in the system promotes the precipitation of aragonite, as detected by XRPD, and the formation of magnesium silicate hydrate (M-S-H) phases (Secco et al. 2020; Ricci et al. 2022) (Supplementary material, Fig. S3). The XRPD of the SG (Figure1c) includes low aliquots of dolomite and aragonite (contaminants in radiocarbon dating) probably in very fine particle size difficult to be removed by gravimetric separation. Unfortunately, this sample should not be suitable for radiocarbon dating. The presence of other carbonate contaminants, dispersed in the binder fraction as dolomite and aragonite, could severely back- or post-date the ^{14}C results.

MI-FI Characterization

The characterization obtained by MI-FI group using the ATR-FTIR technique on the bulk material can be summarized as follows:

- All samples show a broad peak at 1000–1050 cm^{-1}, probably due to the presence of silicate phases;
- MODIS2.1 shows a broad peak at 1650 cm^{-1}: this peak cannot be associated to a single phase, but it can be interpreted as the deformation mode of water molecules (δ_{OH}) (Costa et al. 2008).

After the binder separation, additional ATR-FTIR analyses were performed to test the effectiveness of the process. The spectra are reported in Figure 2a: MODIS2.1 still shows the 1650 cm^{-1} peak; the presence of residual interlayer water molecules is a signal of unwanted phases in the selected fraction. The characterization data suggest that the obtained results could be affected by some alterations. MODIS2.2 gives evidences of no appreciable changes. MODIS2.3 sample shows a residual peak at 1000–1050 cm^{-1}, probably due to residual aggregate phases that passed the separation process. The same peak is attenuated in the other samples, suggesting a promising separation of the aggregate fractions. Moreover, the test on the characteristic peaks of calcite showed values in between the freshly made and crystalline mineral phases, according to archaeological conditions (Figure 2b). It must be stressed that an extensive study on the FTIR spectra showed some deformation of the carbonate peaks in sample MODIS2.3. A deconvolution of the $\nu 3$ peak resulted in two superimposed gaussian curves, overlapping the calcite and dolomite signals (Fig. S4). The ratio of the peak intensities revealed a high amount of dolomitic phase: this, associated to the high amount of silicate

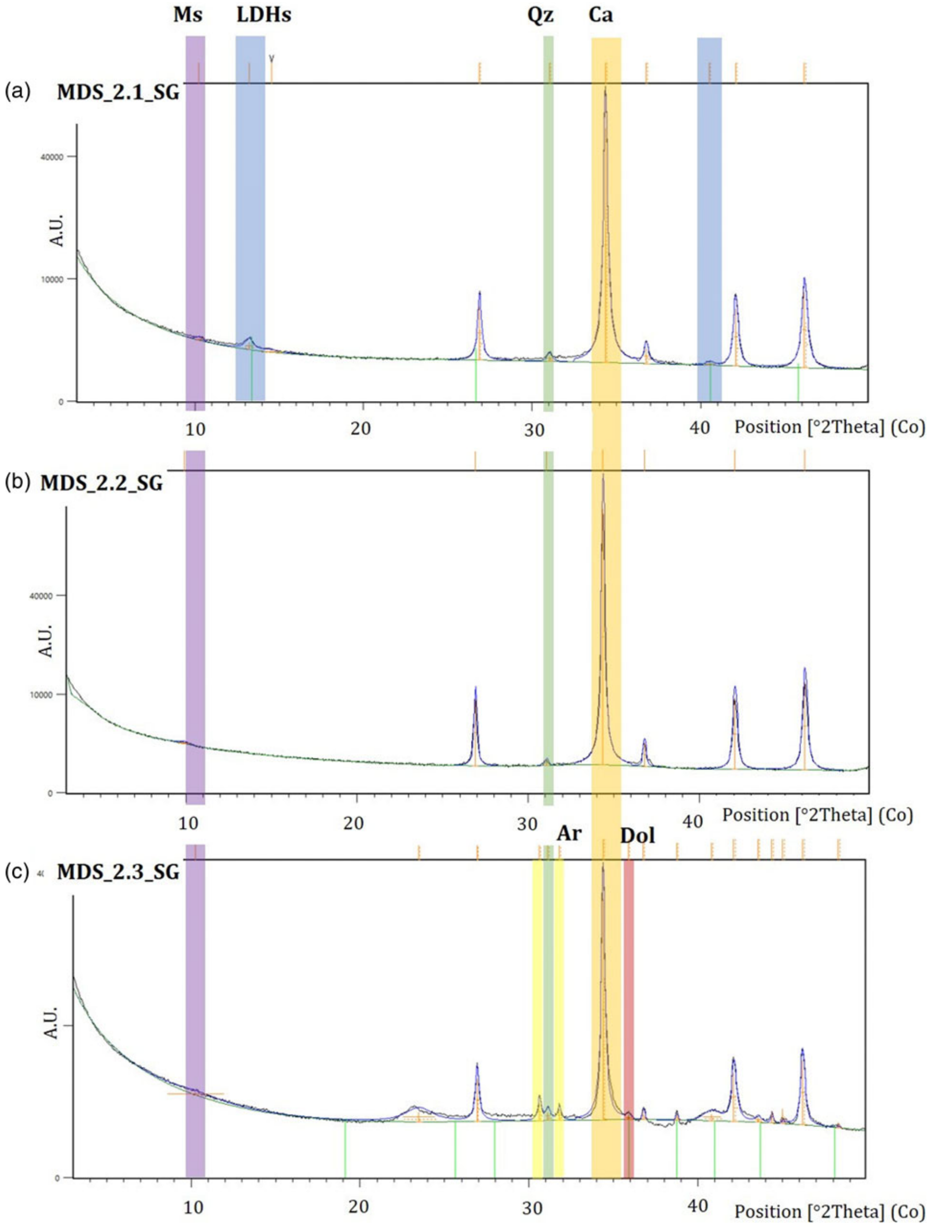
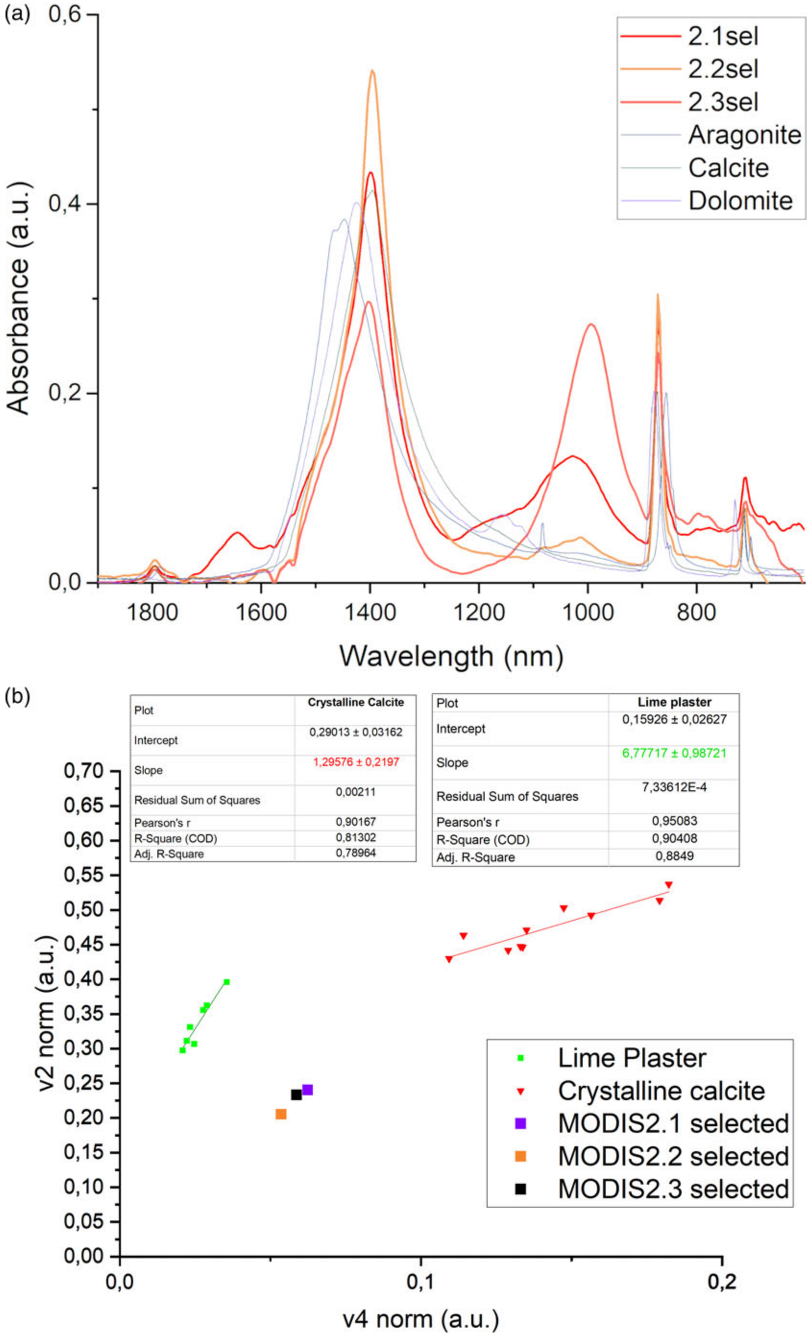


Figure 1 XRPD patterns of SG samples of the three mortars. Ms = muscovite; Qz = quartz; Ca = calcite; Ar = aragonite; Dol = dolomite.

phases, is a warning about the reliability of the material for dating purposes. The other two samples showed a negligible contribution from carbonate phases other than calcite.

Further considerations will be presented in the discussion section.

The initial mass of collected material after separation was chemically digested under vacuum, and the produced CO_2 collected in different fractions (every 20 seconds each), using as a



Plot	Crystalline Calcite
Intercept	0,29013 ± 0,03162
Slope	1,29576 ± 0,2197
Residual Sum of Squares	0,00211
Pearson's r	0,90167
R-Square (COD)	0,81302
Adj. R-Square	0,78964

Plot	Lime plaster
Intercept	0,15926 ± 0,02627
Slope	6,77717 ± 0,98721
Residual Sum of Squares	7,33612E-4
Pearson's r	0,95083
R-Square (COD)	0,90408
Adj. R-Square	0,8849

Figure 2 (a) Normalized ATR-FTIR spectra of MODIS2 bulk samples; (b) comparison of ν2/ν4 ratio values with experimental databases.

general rule the first fraction as reliable. Sample MODIS2.3 required a 30 seconds collection time to reach an optimal gas partial pressure, showing a lower kinetic speed.

Radiocarbon Dating

The ^{14}C dating results are reported in Table 1 and Figure 3. A short comment is worth mentioning on Mi-Fi data. The setup specifically designed for microgram-sized samples affected the uncertainty of radiocarbon concentration, due to the lower currents produced in the AMS facility; the uncertainties are higher than the ones obtained with the setup for "standard" sized samples (corresponding to about 700 μg of carbon). However, this configuration allowed us to assess the reliability of the measurements when dealing with a low amount of starting material, or with a low yield after the separation process.

The results of both the teams are generally in agreement with the expected dates of the three mortar samples provided by the organizers of the intercomparison.

In particular:

- MODIS2.1: PD-CE group thermally treated the sample, and both the outcome of the thermal treatment (HT) and residual after the thermal treatment (DR), were dated. The former shows a modern calendric date (AD 1896–1904 2σ at 95.4%), which is likely to be related to the capability of the LDHs to exchange anions introducing younger CO_2 into the system. The latter can be interpreted as the real date of the mortar (AD 1293–1395 2σ at 95.4%). MI-FI group found that the first digested fraction gave AD 1408–1451, while the second fraction gave AD 1230–1394.
- MODIS2.2: it is considered as a good radiocarbon dating candidate by both the teams, and its date is in agreement with the expected period.
- MODIS2.3: PD-CE group found an older date (AD 22–207 at 95.4%) than expected, as well as MI-FI group (BC 166–AD 537), even though in this latter case the large experimental uncertainty does not allow us to draw much comment.

Some considerations can be made after the comparison of the results obtained by the two research teams:

- MODIS2.1 is affected by LDHs contamination, that was identified with XRPD by the PD-CE group and eliminated by thermal treatment. A compatible result was obtained by MI-FI group collecting the second digested fraction, although it is not the selection rule generally adopted by the laboratory. It could be taken as a selection step in the case of LDHs contamination. The presence of LDHs, detected by XRPD, confirms the ATR-FTIR experimental evidences about the presence of non-calcitic phases. This result has to be investigated to find a fingerprint for this kind of minerals, since they affect heavily the reliability of dating.
- MODIS2.2 result reflects the mineralogical characterization as a binder made of pure and disordered calcium carbonate, matching the independently obtained expected age
- MODIS2.3 is affected by an overestimation of the age, probably due to a residual amount of dolomite mineral, detected by XRPD; with a granulometry small enough to pass the separation step. The presence of dolomite was detected by FTIR as well, after the deconvolution of the 1370 cm^{-1} peak that showed a strong contribution from the dolomitic fraction.

Table 1 Radiocarbon and calibrated ages of the collected fractions.

CIRCE Code	Sample code		$F^{14}C$	^{14}C age (BP)	Cal. age range AD (1σ)	Cal. age range AD (2σ)
DSH9815	MDS_2.1	HT*	1023 ± 0.007	—	Modern	Modern
DSH9815	MDS_2.1	DR**	—	625 ± 18	1299–1390	1293–1395
DSH9816	MDS_2.2	—	—	676 ± 18	1282–1380	1277–1385
DSH9817	MDS_2.3	—	—	1910 ± 26	70–125	22–207
LABEC Code	Sample code			^{14}C age (BP)	Cal. age range AD (1σ)	Cal. age range AD (2σ)
Fi4509	MDS_2.1	First 20 seconds	—	484 ± 47	1408–1451	1392–1490
Fi4510	MDS_2.1	20–40 seconds	—	700 ± 85	1230–1394	1175–1418
Fi4511	MDS_2.2	First 20 seconds	—	602 ± 70	1303–1405	1280–1431
Fi4515	MDS_2.3	First 30 seconds	—	1850 ± 140	22–364	−166–537

*Outcome of the thermal treatment;

**Residual after thermal treatment.

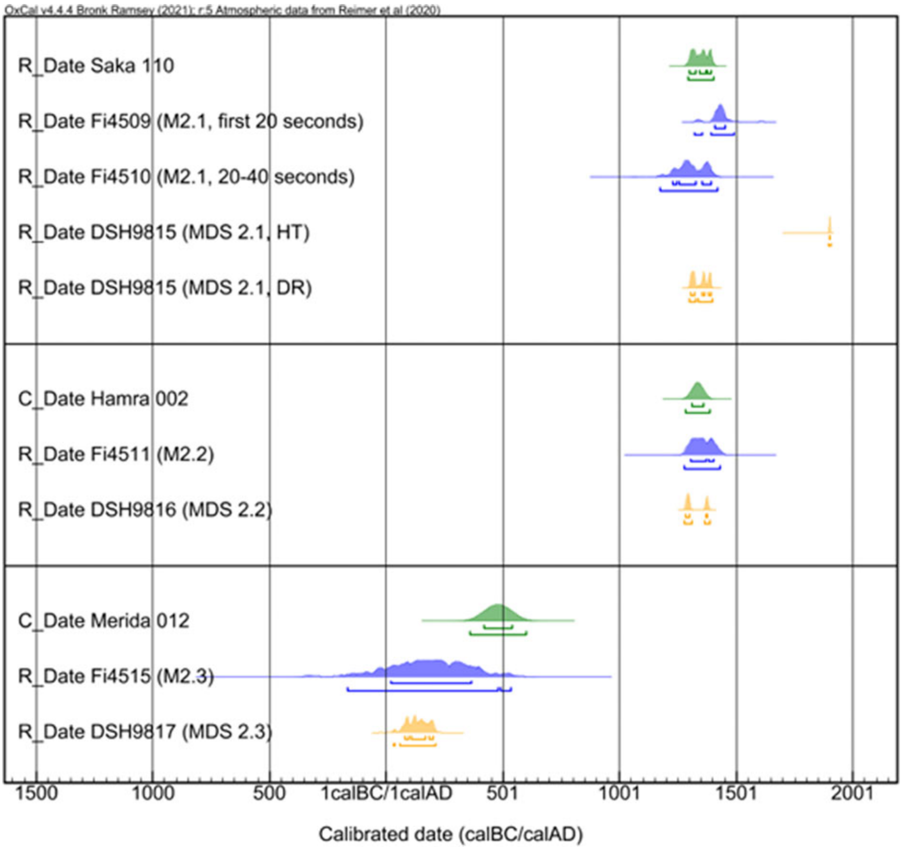


Figure 3 Probability density functions of the collected fractions, compared with the expected ages.

CONCLUSIONS

The results of both the research groups highlight the significance and necessity of a preliminary mortar binder separation procedure and mortar characterization prior the dating process in order to optimize the separation process and enhance the reliability of the analyses. In particular, Specifically, XRPD and SEM-EDS analyses were employed to distinguish the types of minerals present in the material and determine the most effective method to purify the binder. The results from these analyses were then compared with those obtained using ATR-FTIR spectroscopy, a technique also used *in situ* and capable of serving as an initial discriminating step. However, the obtained results show that further studies must be done on the correlation between FTIR spectra and the selected mineral fraction, searching for evidences of characteristic deviations from the typical calcite spectrum. In particular, the presence of dolomite and aragonite phases may be inferred by a deformation in the three carbonate characteristic peaks. It is clear that the use of such a single method cannot give us all the information we need for a fully comprehensive selection of samples. For instance, this is evident in case one needs to identify the presence of particular classes of contaminant minerals such as LDH phases. In this case specific separation treatment must be used to separate the identified contaminants. As an example, XRPD analysis, as proposed by PD-CE, have demonstrated to be a useful step able to identify radiocarbon contaminants and plan treatments in order to better purify the fraction to be dated. Nonetheless, even though certain contaminants such as other carbonate contaminants (as in MODIS2.3) were identified, finding a procedure able to effectively eliminate them remains a significant challenge. A recommended approach includes: initial characterization (even *in situ*) employing Fourier Transform Infrared (FTIR) analysis; subsequent in-depth characterization employing sophisticated diagnostic techniques such as X-ray Powder Diffraction (XRPD) and Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM-EDS); followed by meticulous selection utilizing gravimetric methodologies to isolate the most pertinent fraction; ensuing rigorous quality assessment of the selected fraction through FTIR analysis; extraction of carbon content for subsequent dating.

SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit https://doi.org/10.1017/RDC.2024.3

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