

New Strategies in Mortar Characterization and Radiocarbon Dating

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Abstract – Radiocarbon dating was used on mortars exploiting the C uptake during the carbonation process, where the atmospheric CO₂ signal is absorbed by reaction with lime putty, and then it is converted back into CaCO₃-binder containing the signature of the construction time. The CaCO₃-binder must be isolated from other carbonate sources and contaminants such as delayed hydraulic and secondary alteration products which could affect the dating process [1]–[3]. An appropriate mineralogical characterization of the mortar greatly enhances the understanding of the reaction history of the material allowing the preliminary assessment of the “dateability” of the binder, and afterwards, the choice of the needed pre-treatments for a reliable radiocarbon dating. In this paper, our procedures in mortar characterization, binder isolation and innovative treatments of the fine binder fraction in order to obtain a suitable dateable material are shown.

I. INTRODUCTION

Since centuries, mortars were used in building technology and their dating is often requested in order to establish the chronology of different mortared constructions in archaeological and historical contexts.

Radiocarbon dating (¹⁴C) of archeological sites is mostly based on dating organic materials and, in the last 60 years, the utilization of mortars as dateable objects improved the possibilities of chronological characterization of archeological events investigated at a particular site [4]–[6].

¹⁴C methodology applied on mortars is based on the principle that the carbonate binder (Ca(OH)₂) absorbs CO₂ from the atmosphere, which contains the isotopic signal of ¹⁴C, to produce calcium carbonate (CaCO₃). The hardening

process makes mortars potentially suitable for radiocarbon dating fixing ¹⁴C to the carbonate binder [2], [7]. The formed anthropogenic carbonate must be isolated from other carbonate sources as well as other contaminants which could affect the dating process and then it has to be subjected to radiocarbon dating. Even if the principle of the method seems to be simple, radiocarbon dating of the carbonate binder is a strategic though difficult area of research and problems in obtaining the correct age estimation are common. They are often related to the selection of the pure binder fraction avoiding contaminants and to the velocity of the hardening process. The most common contaminants are: i) geologic or fossil carbonate, which could affect the dating incorporating dead carbon and overestimating the age; ii) secondary alteration processes, delayed hydraulic reactions and formation of long-term phases containing carbonate, which could be responsible of an underestimation of the age [8]–[12]. Furthermore, particular attention has to be taken in sampling strategy considering the thickness of the walls: the mortar binder may take years or decades to reach the complete carbonation due to the poor air penetration inside the voluminous structures, causing the fixation of younger carbon dioxide [7], [13], [14].

Despite large efforts devoted by the scientists to find an efficient binder isolation method and control, dedicated studies in this peculiar field are still needed.

In this frame, we present our procedures in dating mortars which includes, in brief: i) a multi-analytical approach to characterize the material in order to evaluate the materials' properties and the presence of potential dating contaminants; ii) a careful binder extraction and characterization in order to avoid aggregate contaminants and evaluate the dateability of the extracted binder; iii) radiocarbon dating of the purified fraction.

Furthermore, a representative case study showing the effectiveness of our procedures in radiocarbon dating is presented in this paper [15].

II. PROCEDURES IN DATING MORTARS

The analytical process aiming at obtaining the carbonate binder fractions suitable for ^{14}C dating, is composed by different steps: a) a chemical-mineralogical characterization of the mortars in order to assess materials' properties and the presence of potential dating contaminants, and to develop a more efficient separation procedure of the binder fraction; b) a series of purification procedures of the binder by wet gravimetric separation; c) a characterization of the extracted fine powder in order to evaluate the effectiveness of the purification; d) a sample treatment for elimination of possible contaminants; e) the final acid digestion, graphitization and radiocarbon dating of the purified fraction.

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

A. Mortar Characterization

The characterization provides useful data helping in determining whether the sample is suitable for dating and which criteria are needed for a more efficient separation of the carbonate fraction of interest. Petrographic analyses are 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, are microstructurally and microchemically characterized through a CamScan MX2500 SEM equipped with a LaB_6 electron source and an EDS probe 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) are 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, $\text{Co-K}\alpha$ radiation, 40 kV and 40 mA, equipped with a real-time multiple strip (RTMS) detector (X'Celerator by Panalytical). Data acquisition is performed by operating a continuous scan in the range $3-85^\circ 2\theta$, with a virtual step scan of $0.02^\circ 2\theta$. 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 [16] and refinements were accomplished using the TOPAS software (version 4.1) by Bruker AXS. The determination of both crystalline and amorphous content is calculated by means of the internal standard method with the addition of 20 wt% of zincite

(ZnO) to the powders.

B. Purification treatment and binder extraction

The mortar samples are subjected to the purification treatment by wet gravimetric separation [17], which involves several steps: i) manual cleaning and disaggregation of the mortars; ii) 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%; iii) 24 hours wet sedimentation in a 500 ml cylinder in order to obtain a Stokes' Law-based dimensional separation of the particles; iv) sampling of the uppermost emulsion containing particles with size lower than 2 μm ; v) filtration using a vacuum pump system and an inorganic 0.1 μm filters of the fine grained particles (SG).

C. Fine fraction (SG) characterization

The obtained SGs are analyzed by XRPD in order to evaluate the presence of contaminants, such as delayed hydraulic products (layer double hydroxides, LDH) that may involve a younger age determinations [18], and cathodoluminescence-induced spectroscopy in order to evaluate the presence of geogenic carbonate fractions which may induce an old ^{14}C signal [17]. The results of these analyses allow the evaluation of the dateability of the carbonate binder and eventually of a further purification treatment for a more purified SG before radiocarbon dating.

D. SG purification process

The presence of phases related to hydraulic reactions, as LDH compounds, may perturb the original ^{14}C signal, therefore, a further purification process is applied. LDHs are flexible layered structure prone to dynamic exchanges of carbonate anions derived from atmospheric CO_2 even after the hardening process [12]. Thermal treatment at 550°C for 30 min in vacuum condition is carried out on the SG fractions in order to break down the LDH structure and release the younger CO_2 [15].

E. Mortar Radiocarbon dating

The pure carbonate binder is digested under vacuum by means of a complete orthophosphoric acid attack for 2 h at 80°C to converted into CO_2 the binder [19]. The extracted CO_2 is reduced to graphite on iron powder catalyst according to the CIRCE sealed tube reaction protocol [20]. ^{14}C isotopic ratios is measured [21] 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 4.2 [22] and INTCAL 13 calibration curve [23].

III. RADIOCARBON DATING OF COMPLEX MORTARS: THE CASE OF THE CASTLE OF CANNERO (ITALY)

The case of study discussed in this paper regards the radiocarbon dating of a series of Mg-rich hydraulic mortars from the Castle of Cannero (Lake Maggiore, Italy), from which both charcoals and mortar samples were collected. Our procedures for characterizing and radiocarbon dating the selected mortars were performed and the obtained dates were consistent with the archaeological expectations.

Historical sources [24]–[27] assess in the early 1400s the first fortress built by the Mazzardi's family for territorial defenses. The fortress was destroyed in 1414 by Filippo Maria Visconti and ceded 30 years later to Vitaliano I Borromeo. The construction of the current complex was promoted by Ludovico Borromeo in the 1519. Until 1700s it was used by the family and later it was abandoned and left as a shelter of fishermen, until 2017, when a recovery project began.

The archaeological focus was to distinguish which wall or part of the structure was originally built in the XV and which one in the XVI sec. Archaeological evidences were difficult to interpret and the archaeologists needed proofs in order to establish what has survived from the first complex attributed to Mazzardi's family.

15 mortar samples and 3 charcoal fragments found in the mortar matrices were collected and analysed. One of these mortar samples (MM_16) was collected close to a *graffiti* reporting the construction date of 1522.

A. Characterization and Radiocarbon dating

The mortar samples were at first all characterized from a chemical-mineralogical and morphological point of view, analyzing the samples by: OM, XRPD, SEM-EDX, aiming at assessing the nature of aggregates, binder and possible contaminants for the radiocarbon dating.

The mortars of the castle of Cannero seem to be very similar in terms of chemical and mineralogical composition, where the presence of phyllosilicates, micas, quartz, feldspars and calcite were identified. It was detected the presence of hydrocalumite and hydrotalcite (LDHs), which are indicators of hydraulic reaction between clays and calcic binder. Optical and electronic microscopes confirmed these evidences showing: i) quartzites, feldspars and phyllosilicates as principal aggregates; ii) Ca, Si, Mg and Al as the principal components in the elemental analyses of the matrix ascribable to the hydraulic reaction; iii) the utilization of a calcic binder, as it can be seen by the chemical analyses of the lumps (**Fig.1**).

No geogenic calcite and Ca-Mg minerals, as dolomite, considered as contaminants in radiocarbon dating of mortars, have been identified. However, the presence of the LDH phases even if in few amount in the bulk samples may represent a potential contamination in radiocarbon dating, introducing younger CO₂ in the system.

Binder extraction of selected samples was carried out by wet gravimetric separation to eliminate contaminants

(as any kind of aggregates) and extract the fine fraction mostly composed by the binder.

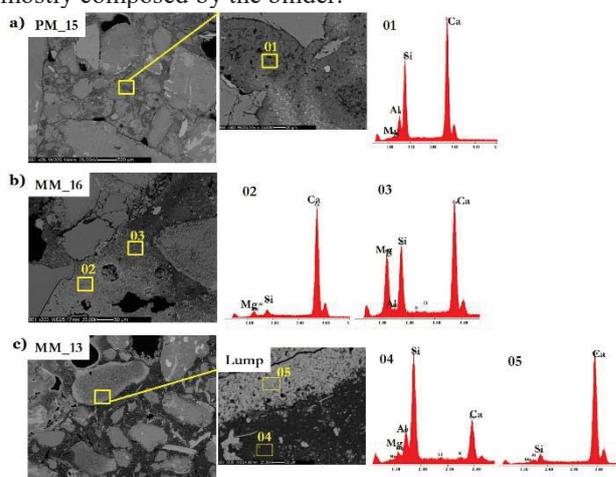


Fig. 1. SEM-EDS analyses of 3 characteristic samples: a) Sample PM_15, backscattered electron images (BSI) of the thin section and microanalyses of the matrix (01); b) A BSI of the sample MM_16 and EDS microanalyses of the highlighted points of the heterogeneous matrix (02-04); c) BSIs of MM_13 and EDS microanalyses of the matrix and lump.

XRPD quantitative analyses of the SGs showed the significant presence (up to 17 wt%) of the LDH components, and in order to neutralized possible contaminations by these phases, a thermal treatment at 550°C was performed to obtain the collapse of the LDH structure and then the discharge of the “younger” carbon anions. After the pretreatment, samples for radiocarbon dating were prepared for the accelerator mass spectrometer by converting them into solid graphite.

The dates of the graphitized CO₂ released during the thermal treatment by the LDH contaminants (OTTs) and the dates referred to the pure binders (RaTTs) are compared and discussed (**Fig.2**). The effectiveness of the used method is evident and proved in the sample MM_16 collected right above the inscription 1522. MM_16 OTT date is younger than the MM_16 RaTT, which have 98.28 (0.61) and 96.70 (0.38) pMC, respectively. This result is perfectly consistent with the inscription on the wall: 96.70 (0.38) pMC can be placed in a reliable interval between 1513 and 1600 AD, with maximum probability around 1530 AD.

Same thing happens on two other samples, PM_10 and PM_15, where the radiocarbon date of the RaTTs is younger than the OTTs. The results showed, for both the samples, dates older than 1500s, suggesting the constructions are not linked to Ludovico Borromeo. However, the dates obtained by the mortar samples (PM_5 and PM_7 RaTTs) and the charcoal fragments (CM_4, CM_7 and CM_8) are in agreement and the results reported the dates to the end of the XV - beginning of the XVI century. These last samples were collected into the

residential buildings and the obtained dates confirm that this structure is related directly to the Ludovico Borromeo fortress.

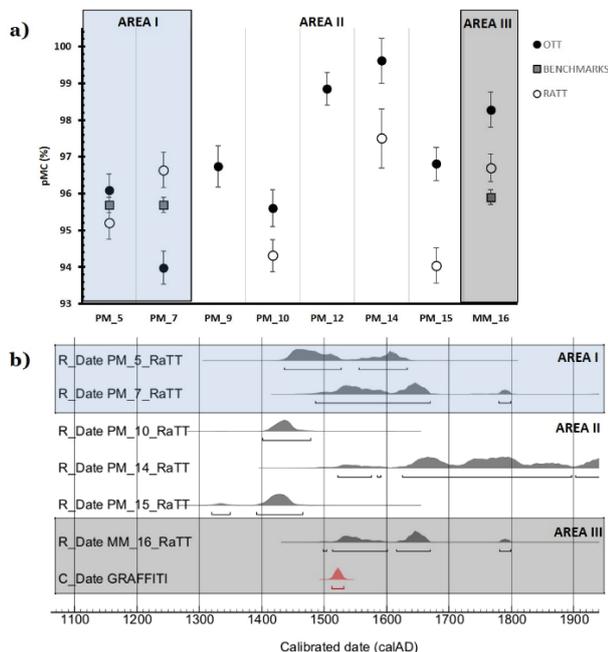


Fig. 2. ^{14}C dating results. a) Comparison between OTT and RaTT pMC \pm standard errors of each SG samples and expected date (benchmarks) converted in pMC; b) Calibrated dates of the ^{14}C measurements of mortar samples (SG_RaTT) by means of OxCal 4.2 [22] and INTCAL 13 calibration curve [23]

IV. CONCLUSIONS

The multi-analytical approach in characterizing mortar materials is crucial in determining particular phases and contaminants for radiocarbon dating. The identification of particular mineral phases as LDHs in the bulk sample and binder fraction is fundamental in a preliminary evaluation of the dateability of the samples and in planning pre-treatments in order to obtain a very pure fine fraction.

Our procedure in separating the fine fraction by wet gravimetric sedimentation and purification of the binder fraction showed very good results. Indeed, as in the presented case study, good accuracy of the applied procedure for chronology reconstruction and capability of both wet gravimetric separation and thermal treatment to further study hydraulic mortars containing LDH phases are shown.

REFERENCES

[1] A. Addis *et al.*, “New strategies for radiocarbon dating of mortars: Multi-step purification of the lime binder,” in *4th Historic Mortars Conference HMC2016*, 2016, no. October, pp. 665–672.

[2] J. Hale, J. Heinemeier, L. Lancaster, A. Lindroos, and Å. Ringbom, “Dating ancient mortar,” *Am. Sci.*, vol. 91, no. 2, pp. 130–137, 2003.

[3] R. L. Folk and S. Valastro, “Successful Technique for Dating of Lime Mortar by Carbon-14,” *J. F. Archaeol.*, vol. 3, no. 2, pp. 203–208, 1976.

[4] S. Nonni *et al.*, “ ^{14}C Mortar Dating: The Case of the Medieval Shayzar Citadel, Syria,” *Radiocarbon*, vol. 55, no. 02, pp. 514–525, 2017.

[5] J. Sanjurjo-Sánchez, “An Overview of the Use of Absolute Dating Techniques in Ancient Construction Materials,” *Geosciences*, vol. 6, no. 2, p. 22, 2016.

[6] M. J. Y. Van Strydonck, K. Van der Borg, A. F. M. De Jong, and E. Keppens, “Radiocarbon Dating of Lime Fractions and Organic Material from Buildings,” *Radiocarbon*, vol. 34, no. 3, pp. 873–879, 1992.

[7] L. A. Ortega, M. C. Zuluaga, A. Alonso-Olazabal, M. Insausti, X. Murelaga, and A. Ibañez, “Improved Sample Preparation Methodology on Lime Mortar for Reliable ^{14}C Dating,” in *Radiometric Dating*, 2012, p. 126.

[8] A. Lindroos, J. Heinemeier, Å. Ringbom, M. Braskèn, and Å. Sveinbjörnsdóttir, “Mortar Dating Using Ams ^{14}C and Sequential Dissolution: Examples from Medieval, non-hydraulic Lime Mortars from the Aland Island, SW Finland,” *Radiocarbon*, vol. 49, no. 1, pp. 47–67, 2007.

[9] G. Artioli, *Scientific methods and cultural heritage*. Oxford University Press, 2010.

[10] D. Miriello *et al.*, “Characterisation of archaeological mortars from Pompeii (Campania, Italy) and identification of construction phases by compositional data analysis,” *J. Archaeol. Sci.*, vol. 37, no. 9, pp. 2207–2223, 2010.

[11] D. Michalska and J. Czernik, “Carbonates in leaching reactions in context of ^{14}C dating,” *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, vol. 361, pp. 431–439, 2015.

[12] G. Ponce-Antón, L. Ortega, M. Zuluaga, A. Alonso-Olazabal, and J. Solaun, “Hydrotalcite and Hydrocalumite in Mortar Binders from the Medieval Castle of Portilla (Álava, North Spain): Accurate Mineralogical Control to Achieve More Reliable Chronological Ages,” *Minerals*, vol. 8, no. 8, p. 326, 2018.

[13] I. Hajdas *et al.*, “Preparation and Dating of Mortar Samples-Mortar Dating Inter-Comparison Study (MODIS),” *Radiocarbon*, vol. 59, no. 6, pp. 1845–1858, 2017.

[14] J. Heinemeier, H. Jungner, A. Lindroos, Å. Ringbom, T. von Konow, and N. Rud, “AMS ^{14}C dating of lime mortar,” *Nucl. Instruments*

- Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, vol. 123, no. 1–4, pp. 487–495, 1997.
- [15] G. Ricci *et al.*, “The Cannero Castle (Italy): Development Of Radiocarbon Dating Methodologies In The Framework Of The Layered Double Hydroxide Mortars,” *Radiocarbon*, vol. in press, 2019.
- [16] H. M. Rietveld, “A profile refinement method for nuclear and magnetic structures,” *J. Appl. Crystallogr.*, vol. 2, pp. 65–71, 1969.
- [17] A. Addis *et al.*, “Selecting the most reliable 14 C dating material inside mortars: The origin of the Padua Cathedral,” *Radiocarbon*, vol. 61, no. 2, pp. 375–393, 2019.
- [18] G. Artioli, M. Secco, A. Addis, and M. Bellotto, “Role of hydrotalcite-type layered double hydroxides in delayed pozzolanic reactions and their bearing on mortar dating: Composition, Properties, Application,” in *Cementitious Materials: Composition, Properties, Application*, P. Herbert, Ed. Berlin: Walter de Gruyter GmbH, 2017, p. 500.
- [19] F. Marzaioli, C. Lubritto, S. Nonni, I. Passariello, M. Capano, and F. Terrasi, “Mortar radiocarbon dating: Preliminary accuracy evaluation of a novel methodology,” *Anal. Chem.*, vol. 83, no. 6, pp. 2038–2045, 2011.
- [20] F. Marzaioli *et al.*, “Zinc Reduction As An Alternative Method For Ams Radiocarbon Dating : Process Optimization At Circe,” *Radiocarbon*, vol. 50, no. 1, pp. 139–149, 2008.
- [21] F. Terrasi *et al.*, “High precision 14C AMS at CIRCE, Nucl. Instrum. Meth. B266 (10) 2221–2224,” *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, vol. 266, no. 10, pp. 2221–2224, 2008.
- [22] C. Bronk Ramsey and S. Lee, “Recent and planned developments of the program oxcal,” *Radiocarbon*, vol. 55, no. 2, pp. 720–731, 2013.
- [23] P. J. Reimer *et al.*, “Intcal13 and Marine13 Radiocarbon Age Calibration Curves 0–50,000 Years Cal Bp,” *Radiocarbon*, vol. 46, no. 1, pp. 1111–1150, 2013.
- [24] F. Lose and C. Lose, *Viaggio pittorico e storico ai tre laghi Maggiore, di Lugano e Como*. Milano: Francesco Bernuca, 1818.
- [25] M. B. Bottacchi and C. Mancini, *Storia e fantasia ai castelli di Cannero*. 2000.
- [26] C. A. Pisoni, *Pro arce della Vittaliana. Excursus storico per una fortalicium di breve vita, rudere di grand fascino, in Cannero Riviera tra lago e monti. Storia d’una terra e d’una parrocchia*. 2003.
- [27] P. Frigerio and P. G. Pisoni, *Fratelli della Malpaga: storia dei Mazzarditi*. 2006.