Accelerator mass spectrometry ^{14}C dating of lime mortars: Methodological aspects and field study applications at CIRCE (Italy)

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ABSTRACT

Centre for Isotopic Research on Cultural and Environmental heritage (CIRCE) has, recently, obtained some promising results in testing the feasibility of mortar radiocarbon dating by means of an ad hoc developed purification procedure (CryoSonic: Cryobreaking, Sonication, Centrifugation) applied to a series of laboratory mortars. Observed results encouraged CryoSonic accuracy evaluation on genuine mortars sampled from archeological sites of known or independently constrained age (i.e., other ^{14}C dates on different materials).

In this study, some ^{14}C measurements performed on genuine mortars will be discussed and compared with independently estimated (i.e., radiocarbon/archaeometrical dating) absolute chronologies of two Spanish sites. Observed results confirm the agreement of the CryoSonic mortar dates with the archaeological expectations for both examined cases.

Several authors reported the possibility of obtaining accurate radiocarbon dates of mortar matrices by analyzing lime lumps: binder-related particles of different sizes exclusively composed of calcium carbonate.

In this paper, preliminary data for the absolute chronology reconstruction of the Basilica of the cemetery complex of Ponte della Lama (Canosa di Puglia, Italy) based on lime lumps will also be discussed. Dating accuracy will be quantified by comparing ^{14}C data on mortar lime lumps from a funerary inscription of known age found near the Basilica, in the same study site. For this site, a comparison between absolute chronologies performed by bulk and CryoSonic purified lime lumps, and charcoal incised in mortars (when found) will also be discussed.

Observed results for this site provide evidence of how bulk lime lump dating may introduce systematic overestimations of the analyzed sample while CryoSonic purification allows accurate dating.

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1. Introduction

Mortars represent a class of construction materials virtually ubiquitous at archeological sites from the Neolithic period on [1]. Mortar matrix can be schematically divided in two portions: the binder and the aggregates.

Based on the process determining the setting, the binders can be distinguished in aerial or hydraulic form also if intermediate classes are produced by adding different aliquots of inert materials (e.g., pozzolana, crushed bricks) [2].

Aggregates used to produce mortars vary both in size and type of material (e.g., crushed bricks, silicate minerals, marble powder). They are usually mixed with the lime putty (aged slaked lime) with the aim of increasing material workability and avoiding cracks due to drying during setting [3,4]. Usage of materials characterized by sensitive concentrations (>15%) of aluminates and amorphous silicates [5] (i.e., pozzolana, volcanic ashes, crushed bricks) confers light hydraulic properties to lime mortars. This constituted, since Roman times, a breakthrough in mortar production technology

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allowing the speeding up of mortar hardening and increasing mortar mechanical resistance [6].

While hydraulic mortars mostly harden because of hydration reactions, aerial binders hardening is due to the process of carbonation: the multistep reaction of atmospheric CO₂ with the slaked lime (Ca(OH)₂) to produce calcium carbonate (CaCO₃). This process makes the binder of aerial mortars an interesting proxy preserving, virtually unvaried, the signature of the atmospheric CO₂ absorbed over the period of mortar hardening.

Binder carbonates can be used to date artifacts:

- i) If the hardening period (usually a few years) is negligible with respect to the radiocarbon decay constant (5730 a [7]) and the expected uncertainty on the measured radiocarbon age (few decades for our laboratory [8]);
- ii) if the calcination (Carbonatic rock → quick lime) was performed attaining high efficiencies (i.e., no C residuals (calcinations relics) survived in the quick lime).

Several drawbacks [9] have been observed since the beginning of the experiments on ¹⁴C dating of mortars [10]. These fluctuations are related to the partial failure of the mortar radiocarbon dating working hypotheses. For example, the presence of exogenous carbonate contaminations affecting the sample and low efficiencies in isolating the binder from calcareous aggregates can lead to sensitive biases resulting in a contamination effect altering the measured age of samples. Hence, mortars sampled from the surface of a wall can be affected by exogenous carbonate contaminations (i.e., running water depositing dissolved inorganic carbon over centuries) while mortars sampled too deep can be affected by low carbonation velocities both leading to ¹⁴C rejuvenation. Nevertheless the most recalcitrant source of contamination affecting mortars is represented by the calcination relics of limestone surviving into the mortar and preserving a Dead Carbon (DC) fingerprint. An innovative methodology aiming to suppress calcination relics C by means of a sequence of physical separations (i.e., Cryo-SoniC) has been recently developed and tested at CIRCE [11]. Cryo-SoniC showed its overall effectiveness for laboratory samples produced at *T* ranging from 800 to 1100 °C simulating only the binder phase with no aggregates interactions.

With the aim of checking the effectiveness of the methodology on field samples, including the suppression of eventual “aggregates effects”, in this paper we applied our procedure to genuine mortars from two sites in Spain.

Lime lumps radiocarbon dating has been reported as an accurate methodology for mortar radiocarbon dating [12,13]. Lime lumps *in sensu stricto* are binder-related nodules often rounded and porous, appearing distinctly in the mortar matrix [14]. Their origin is not agreed upon: (i) some argue their genesis comes from a poor mixing of the lime putty with aggregates [13]; (ii) some attribute their development to dry slaking (i.e., the mixing of wet sand with burnt lime fragments (quick limes)) [15]; (iii) some others attribute lime lumps development to the carbonate crust that forms on top of lime putty when maturing [16]. The evident advantage of dating lime lumps is that they represent the binder already purified by aggregates. Eventual contributions of calcination relics in the lime lumps cannot be inferred in advance on the sample to be analyzed since (i) they appear in the same mineral form (calcite) as the lime lump; (ii) the Optical Microscopy (OM) methodology cannot be directly applied to the sample to be dated. In this study some data regarding lime lumps dating will be discussed and compared with dating of charcoal encased in mortar. These kinds of charcoal have been used to study artifact chronologies by Berger [17]. Moreover the application of the CryoSoniC procedure to lime lumps will be discussed in terms of its accuracy evaluation for one Italian study site.

2. Methods

2.1. Study sites description

2.1.1. San Julian e Santa Basilisa di Aistra

The church of San Julian e Santa Basilisa in Zalduondo represents one of the most ancient and best preserved medieval churches of the Álava province in the Basque country (Spain). The chronology of this structure is mostly based on formal and stylistic analyses of windows and walls, and it is still contradictory. Over the 2006–2009 period, the church underwent deeper analyses allowing the better constraining of its chronology in the framework of the Aistra village archaeological project performed in collaboration with the Institute of archaeology UCL (University College London). Thanks to a series of ¹⁴C dates (mostly bones, 20 of them are showed in Fig. 1) and other archaeological evidences, church construction was attributed to the fourth phase of the Aistra village (i.e., 10th century A.D.) [18].

Two samples belonging to the external walls of the church of San Julian were sampled (AISTRA 1 and AISTRA 2). Stratigraphic interpretation of the structure and comparison with available data, guided the choice of two samplings for this site: AISTRA 1 was sampled from the north eastern corner of the structure and supposed to belong to the first phase of development of the church; AISTRA 2 was sampled from the south eastern facing wall of the church and hypothesized to be of a later age [19].

2.1.2. Santa Maria di Zornotzegi

The Santa Maria di Zornotzegi village is also situated in the eastern Álava province. This archeological site developed continuously in the period from the 5th to the 14th century with a first settlement during the bronze age [20]. Santa Maria di Zornotzegi is characterized by the presence of the so called “fallen chapel”, a religious building, nowadays mostly dismantled because of its materials re-use. The fallen chapel is founded on a previous structure by means of a basement of filling raw materials. Pottery analysis, applied architectural styles and several radiocarbon measurements on organic materials (mostly charcoals and bones, 20 of them shown in Fig. 2) found at the study site during archaeological sample processing (i.e., flotation), allowed the precise constraint of the chronology of the structure in the first half of the 12th century A.D.

To avoid weather exposure contaminations, one sample situated few centimeters from the surface of the north facing wall of this structure (ZOR07) was sampled and analyzed.

2.1.3. Cemetery complex of Ponte della Lama

The cemetery complex of Ponte della Lama, discovered in the beginning of the '50s, is found near the city of Canosa di Puglia (Apulia, Southern Italy). It developed in a period ranging from 2nd to 6th century A.D. along the *via Traiana*. The complex is composed of different structures, among them (i) the catacombs representing one of the most important examples for the Apulia region for extension and preservation [21]; (ii) the Basilica founded around the 4th century A.D. This artifact plays an important role in the cemetery complex and some questions regarding this structure are still unsolved. First of all the chronology of the Basilica development/usage is not very well defined and, secondly, an abrupt discontinuity in the usage of raw building materials regarding the north-facing side of the structure requires deeper analyses. Radiocarbon dating of mortars, combined with chemical and petrographic analyses, were applied for the definition of the Basilica development. Basilica lime mortars contain (i) calcination relics of biomicritic limestone origins; (ii) carbonate aggregates (a sensitive fraction of total aggregates) whose dimensions vary from medium to fine sand sizes.

Fig. 1. Measured calendar ages (age distributions and 2σ ranges) for the Aistra susp fractions (AISTRA *susp_1* and AISTRA *susp_2*, first two age distributions) compared with the Aistra site average age (weighted average of measured ^{14}F values, AISTRA weighted) and the measurements of organic samples from the same site (AISTRA 1–20). Dashed lines represent 2σ intervals for the *susp* fractions.

Two Wall Stratigraphic Contexts (WSCs) of the Basilica were sampled: CPLM 12L and CPLM 18L and lime lumps extracted. Bulk lumps (CPLM 12L_lump and CPLM 18L_lump) underwent CryoSonic procedure (CPLM 12L_susp_lump and CPLM 18L_susp_lump). Inside CPLM 18L mortar encased charcoal was also found which underwent sample processing and measurement according to Berger [17].

An epigraph with an inscription engraved upon fresh mortar applied during the grave sealing was discovered in the catacombs belonging to the same archaeological context. Thanks to the inscription: “*Sine collega Flavius Rufius Placidus*” the epigraph was attributed to 481 A.D. Epigraph mortar manufacture appeared grosser with respect to the Basilica ones. With the aim of procedure accuracy evaluation, one lime lump (CPLM1_lump), its Cryo-Sonic produced fraction (CPLM1_susp_lump) and one encased charcoal sample extracted from the same WSC were extracted and radiocarbon dated.

2.2. Samples pretreatment and ^{14}C measurement

The main goal of the CryoSonic procedure for mortar radiocarbon dating is the isolation of the carbonate fraction merely attrib-

utable to the carbonatation of slaked lime. Sampled mortars underwent:

1. **Cryogenical braking:** Following Nawrocka et al. [22], mortar pieces (about 5 g) were submerged in liquid nitrogen until they reached thermal equilibrium and transferred immediately into an oven at 80°C . This cycle was repeated almost three times. At the end of these freezing/thawing cycles mortars were broken by gentle hammering.
2. **Size selection:** Fractured material, spanning over a wide range of particle size, was wet filtered, in decarbonated/deionized water (DDW), at $500\ \mu\text{m}$.
3. **Ultrasonic selection:** Filtered particles after complete sedimentation and water removal, were re-wet with 40 ml of DDW and ultrasonicated for 30'. Only materials being suspended (*susp*) by the induced ultrasonic shock (i.e., finer and more fragile particles) were selected by siphoning about 30 ml of the water into a centrifuge tube.
4. **Centrifugation:** Centrifuge vials containing *susp* carbonates were centrifuged @ $7874g$ for 5' and oven dried ($T = 80^\circ\text{C}$) overnight.

Fig. 2. Upper panel: observed difference in the radiocarbon age of *susp* fractions (*susp_sand* and *susp_new*) produced by the modified CryoSonic protocol for the Zornotzegi sample (ZOR07). Lower panel: comparison of the ZOR07 *susp_new* with the site average age (ZORNOTZEGI weighted) and the measurements of organic samples from the same site (ZORNOTZEGI 1–20). Dashed lines represent 2σ intervals for the *susp_new* fractions.

Due to some experimental observations (data not shown in this paper) the CryoSonic procedure was later updated in order to increase the DC contamination suppression efficiency observed in conventional CryoSonic purified samples. In detail, we split the original ultrasonication procedure (step 3) in two sub-phases: (i) the first ultrasonication was applied for 10' producing the *susp_sand* fraction; (ii) the second was applied, after a complete removal of the liquid phase and the adding of 40 ml of clean DDW, for 30' producing the *susp_new* fraction.

Weighted *susp* fractions (up to 15 mg of material) and carbonate standards samples (i.e., IAEA C1 and C2 [23]) were converted into CO₂ by means of orthophosphoric acid digestion [24] for 2 h @ 85 °C.

Charcoal samples found in the mortars were pretreated according to Berger [17] and combusted together with normalization/check standards and background samples (blank).

Produced CO₂ was cryogenically purified by other gasses, reduced to graphite on iron powder catalyst according to the CIRCE sealed tube reaction protocol [25] and measured for ¹⁴C isotopic ratios determination [26]. Measured radiocarbon ratios were converted to R.C. ages [27] and calibrated to absolute ages by means of OxCal 4.1 [28].

3. Results and discussion

3.1. San Julian e Santa Basilisa di Aistra

Fig. 1 shows results arising from the radiocarbon dating performed on organic materials found at the Aistra site. Church average age was estimated by weight averaging measured ¹⁴F abundances [27] of samples reported in Fig. 1 (AISTRA 1–20), evaluating its R.C. age and calibrating it by means of Oxcal 4.1 (AISTRA

Fig. 3. Measured calendar ages for the Ponte della Lama samples. For each sample both lump (CPLCM1_lump, CPLM 16L_lump and CPLM 18L_lump) and *susp_lump* (CPLCM1_susp_lump, CPLM 16L_susp_lump and CPLM 18L_susp_lump) calendar ages are shown, for CPLCM1 also the established age of the funerary epigraph is displayed.

weighted). 2σ ranges are also plotted as dispersion indexes for the measured distributions of the calendar ages. Measured absolute ages on the mortar *susps* (AISTRA *susp_1* and AISTRA *susp_2*) appear in agreement at 2σ level. Measured calendar ages on the *susp* fractions showed a slightly different behavior with respect to the expected age of the Church (AISTRA weighted), being AISTRA *susp_1* in agreement at 1σ level and AISTRA *susp_2* lying slightly upon 2σ . This observation indicates later ages for the AISTRA 2 sample probably attributable to a secondary stage of the structure in agreement with archaeological analyses of the San Julian e Santa Basilisa church [19] (see Section 2).

3.2. Santa Maria di Zornotzegi

Structure average age was estimated by weight averaging measured ^{14}F abundances [27] of samples reported in Fig. 2 (ZORNOTZEGI 1-20), evaluating its R.C. age and calibrating it by means of Oxcal 4.1 (ZORNOTZEGI weighted). For this site ZOR07 mortar was processed according to the conventional CryoSonic procedure. Measured radiocarbon age on ZOR07 *susp* (4122 ± 50 B.P.) compared to the expected age of the site (i.e., first half of the 12th century A.D.) indicates a failure of the CryoSonic procedure in DC suppression (i.e., older ages than expected). ZOR07 was, hence, re-processed according to the updated CryoSonic procedure with the aim of increasing the efficiency in binder carbonates selection producing ZOR07 *susp_sand* and ZOR07 *susp_new*.

A significant effect of rejuvenation induced by the procedure is evident when comparing ZOR07 *susp_new* with ZOR07 *susp_sand* (Fig 2 (upper panel)). Measured radiocarbon age on the ZOR07 *susp_new* was in agreement with the estimated average age of the site (ZORNOTZEGI weighted, Fig. 2 (lower panel)).

3.3. Cemetery complex of Ponte della Lama

For this archeological site available data includes encased charcoals, bulk lime lumps and CryoSonic purified *susp_lumps*. Accuracy evaluation in lime lumps dating, for this site, was performed by comparing measured radiocarbon activities on one lime lump extracted from an epigraph of well constrained age (CPLCM1 see methods).

Given the accurate results generally observed using bulk lime lumps [12,13] for radiocarbon dating, lime lumps from this site had been originally acid digested [24] following the protocol applied at CIRCE for carbonates. Observed results on CPLCM1 indicate a measurable DC effect affecting the radiocarbon age estimation of the mortar when bulk lump is used (CPLCM 1_lump (Fig. 3)). CPLCM 1_lump, in fact, appeared to be compatible with the 1st century B.C. Because of their formation process, lime lumps do not contain aggregates, hence observed discrepancies can be exclusively attributed to the presence of calcination relics. This experimental observation lead us to apply the CryoSonic classical procedure also to lumps. Residues (up to 10 mg) of the previously dated bulk lumps were pretreated to produce *susp_lump* fractions and measured. It can be noted how the application of CryoSonic efficiently removed the effect of calcination relics on measured radiocarbon ages leading to unbiased age for the epigraph sample (CPLCM1_susp_lump).

A similar effect (i.e., smaller but significant DC) was observed for the other two analyzed lime lumps (CPLM12L_lump and CPLM 16L_lump) compared to CPLM12L_susp_lump and CPLM 16L_susp_lump.

Also in this case the application of the CryoSonic procedure to produce *susp_lump* fractions brought all the other ^{14}C ages to values compatible with the archeological expectations for the Basilica

(4th century A.D.) reducing the lime lumps observed DC effect virtually to zero.

Difference in the DC contamination affecting the analyzed lime lumps (i.e., CPLCM1 lump appeared sensitively older than the CPLM12L_lump and CPLM 16L_lump) well matches some observations on the technology used during mortar production. CPLCM1, in fact, turned out to be produced by means of a grosser manufacturing process probably leading to higher amounts of calcination relics in the examined mortars.

Dating of charcoal intrusions in the mortar matrix revealed, again, a strong DC contamination evidenced by corresponding calendar ages of 10th century B.C. and 1st century B.C. respectively for the CPLCM1 and CPLM 18 L samples. This observation is attributable to the lack of carbonate suppression during the coal pretreatment also if ad hoc methodologies [17] were applied.

4. Conclusions

Radiocarbon dating of mortars has been attempted since the '60s with still ambiguous results. The method development can lead to sensitive improvement for the applied archaeology allowing dating of artifacts, from the Neolithic period on, with no need for organic materials and no risk of wrong age estimations because of material recycling. In this paper, after the development and testing of a new methodology for mortar radiocarbon dating (CryoSoniC) at CIRCE, some applications to genuine field mortars are shown. Observed results on San Julian e Santa Basilisa di Aistra church were in agreement with the archaeometrical expectations. Santa Maria di Zornotzegi results revealed the necessity to update the classical CyoSoniC procedure. Observed results, after the application of the updated CryoSoniC procedure led to accurate ^{14}C dating also for this site.

Our data on lime lumps revealed how the dating of this class of materials can be affected by significant offsets strictly connected to the technology applied for the calcination of the primary limestone during mortar production. For the Ponte della Lama site this effect was visible for all the analyzed lumps, and the production of purified *susp_lump* fractions efficiently removed DC contamination attributable to this interfering source.

Also if more experiments should be produced, this work shows the general applicability of the CryoSoniC procedure to extract a carbonate fraction capable of guaranteeing accurate radiocarbon dating from mortars. Data presented in this paper clearly indicate how the procedure validation must be supported by a series of geological analyses (i.e., thin sections + optical microscopy, XRD) sustaining some, otherwise assumed, scenarios for the correct data interpretation.

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