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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: *Cryo*braking, *Soni*cation, *C*entrifugation) 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 incased 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.

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 carbonatation: the multistep reaction of atmospheric CO_2 with the slaked lime ($Ca(OH)_2$) to produce calcium carbonate ($CaCO_3$). This process makes the binder of aerial mortars an interesting proxy preserving, virtually unvaried, the signature of the atmospheric CO_2 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 ^{14}C 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 carbonatation velocities both leading to ^{14}C 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., CryoSoniC) has been recently developed and tested at CIRCE [11]. CryoSoniC 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 ^{14}C 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 reusage. 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.