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Characterization of a new protocol for mortar dating: ^{13}C and ^{14}C evidences

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Summary. — This paper reviews the present knowledge about the analysis of mortars in the framework of artworks absolute chronology determination with the aim to formulate a new methodology capable of systematically and accurately estimating the age of these constructive and/or art materials. The core of the proposed methodology is represented by a physical procedure (ultrasonication) selecting only carbonaceous materials represented by carbonates formed after the absorption of atmospheric CO_2 (carbonatation) by mortars (binder) during their setting. With the aim to evaluate the procedure efficiency in the isolation of binder signal from the most important source of carbonates, the proposed procedure was tested on a series of laboratory mortars produced, in a simplified version, in the laboratory environment. Mortar production was characterized by means of a series of measurements allowing to draw important indications about the applied procedure. The radiocarbon value of isolated binder carbonates was compared with the CO_2 signal sampled form laboratory air during mortar setting. The observed results confirmed preliminarily the good protocol accuracy for radiocarbon dating suggesting its capability for the application to real study cases.

PACS `91.80.Hj` – Radioisotope geochronology, isotopic disequilibrium dating.
PACS `29.20.Ba` – Electrostatic accelerators.
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1. – Introduction

Aerial mortars, a series of anthropogenical carbonaceous materials used for constructive and/or art manufactory, because of their production process, preserve the potential to be used for the direct evaluation of the absolute chronology of artefacts.

Mortar production process begins with the burning of a carbonatic limestone at temperatures ranging around $900\,°C$ by means of traditional lime kilns [1] according to the reaction

$$(1) \qquad\qquad\qquad CaCO_3 = CaO + CO_2.$$

This reaction, better known as calcination, removes CO_2 of fossil origin from the initial (primary) carbonate producing quicklime (Q, calcium oxide) a material virtually free of C.

Quicklime is than watered undergoing hydration, hence producing slaked lime (S, calcium hydroxide) according to the reaction

$$(2) \qquad\qquad\qquad CaO + H_2O = Ca(OH)_2.$$

Slaked lime production is a esoergonic reaction and the produced $Ca(OH)_2$ crystals (portlandite) are aged under water excess in the form of lime putty. Vitruvius [2] documented how, according to Roman habits, lime putty was aged for almost 3 years before its usage. During this period portlandite crystals are rearranged becoming smaller and foil-like [3] enhancing their future CO_2 absorption capability.

Aged lime putty is mixed, in a 1:3 to 1:4 ratio, with aggregates (*e.g.*, reworked bricks, silica minerals, marble powder) to increase workability, hydration and to avoid cracks due to drying during setting [4, 5]. Calcium hydroxide absorbs CO_2 producing calcium carbonate ($CaCO_3$) according to the reaction

$$(3) \qquad\qquad\qquad Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

Slaked lime absorbs CO_2 from the air over time periods of few years forming a secondary anthropogenical carbonate. If the burning of the primary carbonate is efficient, C composing mortars is ascribable only to the atmospheric CO_2 (*unique* C *endmember hypothesys*).

Whereas the time of setting is generally negligible with respect to the radiocarbon half-life (5730 y [6]), a procedure allowing to extract and date the C composing mortars, in principle, furnishes unbiased and direct artefact dating. This potential was initially guessed and applied by Delibrias and Labeyrie [7], in 1965, with a discrete success. Mortar radiocarbon dating represents an enormous advantage in the field of archaeology allowing the estimation of the absolute chronology of a given structure directly with no needs of coins and/or ceramics dating or indirect radiocarbon dating on organic materials found in the context of the examined structure [8]. Since 1965, different authors tried radiocarbon dating of mortars [9-12] with still unclear results about the accuracy of the measured dates.

There is a general agreement in the attribution of such lack of accuracy reproducibility to the failure of the *unique* C *endmember hypothesis*. Other sources of C, apart from the secondary carbonates, contributing to mortars preserved till present are [11]: i) primary carbonates residues survived to the Q production process leading to an ageing effect bringing to sensitive offsets in the radiocarbon age estimations; ii) carbonaceous

aggregates used as inert materials during the mortar production phases, again, ageing the mortar matrix; iii) neo-genesis carbonates (ternary) precipitated after the interaction of current water or rain, containing variable aliquots of dissolved inorganic carbon (DIC), with the structure for centuries inducing an overall rejuvenation effect.

Hence, accurate dating of aerial mortars can be prosecuted by developing chemical or physical methodologies capable to prevent, by isolation, the dating of other carbonate sources different from the secondary. While aggregates and ternary carbonate contaminations can be efficiently suppressed by excluding aggregates and choosing the correct location of the sample (*i.e.* not directly exposed to the atmospheric layer but not completely isolated from the atmospheric CO_2), the suppression of primary carbonates contaminations appears to be the main cause of observed accuracy instability [11].

The dating of secondary carbonates composing mortars can be obtained exploiting their different properties of aggregation with respect to primary carbonates. Moorehead [13] found that most of the calcite composing historical mortars is characterized by a poor crystalline habit and Folk and Valastro [10] defined the secondary carbonate fraction composing historical mortars as fine grained, porous, powdery, and acid-fast-reacting. These properties allow the discrimination of the correct C signal for the accurate dating of mortars.

Following Delibries a Labeyrie [7] most of the trials in isolating the atmospheric CO_2 signal are based on the different reaction rate [14] observed when mortars are digested in acid environment. This approach (partial digestion) produces different (almost two) time-evolved CO_2 fractions, with the secondary carbonate fraction digested in the initial part of the acid reaction. In 2007, Lindroos *et al.*, [15] published a systematic study on the applicability of the partial acid digestion on different kinds of mortars of known or interpreted age. Mortar matrix is interpreted as a complex system composed by different carbonate sources characterized by different solubility constants leading to the possibility of discrimination by means of dissolution increments. This study proposes the analysis of 5 different fractions for the accurate dating of the examined structures.

On the other side, since 2005, an alternative methodology based on the laboratory isolation of secondary carbonate fractions was formulated and field tested [16]. This procedure is funded on the easily breakable and fine structure of the secondary carbonates. While in most of the examined cases (*i.e.* Romans and Dead Sea mortars) a sensitive mismatch between radiocarbon and known data was found, it is our opinion that the simplicity, in terms of applied procedure and samples to measure, constitute a promising tool having the potential, after an overall implementation, to permit accurate dating of mortars.

Moreover, the definition of the successful character of a given procedure is often defined by applying it on real study cases. The identification of C sources influencing real field mortars is laborious and the formulation of general procedures based on this comparison may not always respond to the interaction of such factors resulting in a variability of the accuracy of the proposed methodology. It is our opinion that the validation of a procedure should follow a discrete pathway where each step allows the evaluation of its applicability to a more complex matrix.

In this paper a modification of the Nawrocka [16] procedure will be tested on a series of synthetic mortars produced without adding inert materials and ageing. The successful character of the methodology on the suppression of the primary carbonate C (the most important) will be evaluated by comparing C isotopic fingerprints (*i.e.* ^{13}C and ^{14}C) of the laboratory isolated phases with the laboratory atmospheric CO_2 naturally absorbed for the carbonatation of the synthetic mortar.

2. – Matherials and methods

2˙1. *Synthetic mortar production and characterization*

2˙1.1. Limestone rock ($CaCO_3$). A 50 kg carbonatic rock was chosen as representative of the limestone (primary) carbonate. In order to verify the nature of the initial limestone, 3 pieces of about 2 g of material were randomly sampled and their mineralogy, C content and C isotopic fingerprint analyzed by means of X-Ray Diffractometry (XRD), Elemental Analysis (EA) and mass spectrometry (MS), respectively.

Five different scraps of 15–20 mg of mass and about 10 cm of maximum diameter were chosen for the mortar production process laboratory simulation.

2˙1.2. Quicklime (Q). The burning of sampled limestone was realized by means of a muffle furnace capable to reach temperatures up to 1100 °C with remote-controlled thermal cycles. With the aim to produce materials with a different tenor of residual limestone C we applied 5 different peak temperatures (700, 800, 900, 1000 and 1100 °C) for a period of 1 and 1.5 hours (700_1.5) centred in the optimum T reported for the lime kiln (*i.e.* 900 °C [1]). As soon as the limestone scrap was put in the oven at room temperature, the thermal cycle was applied: the oven temperature increased till the set peak temperature in about 30 minutes, it was maintained for the reference period, and heating was shut down so that the temperature slowly decreased to ambient temperature. An aliquot of quicklimes (Q700, Q800, Q900, Q1000, Q1100 and Q700_1.5), allowing to run 3 replicated measurements, was analysed for %C, Q700 and Q700_1.5 were analyzed for ^{14}C and the residual converted to slaked lime.

2˙1.3. Slakedlime (SL). Hydration of the Q was realized by submerging about 10 g of calcium oxide in a stoichiometric excess of deionised/decarbonated water forming lime putty in 6 different beakers. In order to increase the efficiency of hydration of the Q and simulate the ageing of the portlandite crystals, beakers were kept under ultrasonication for a period of 1 hour.

2˙1.4. Mortar (M). The produced SLs were let carbonate by exposition to laboratory air under controlled environmental (*i.e.* T) conditions to produce an appreciable carbonatation over time periods comparable to the experimental timings. To increase CO_2 absorption in the ultrabasic lime putty, environment samples were kept at 4 °C for three weeks. Then, for two other weeks, the samples were kept at room controlled T (25 °C) to accelerate drying. A fraction of the produced mortars (M700, M800, M900, M1000, M1100 and M700_1.5) was analyzed (*i.e.* %C) in 3 replicates to verify the effectiveness of carbonatation over the experimental period, and the residues were processed according to the following protocol for the isolation of the secondary carbonates.

2˙2. *Isolation of secondary carbonates*. – The procedure for the isolation of the secondary carbonates is based on the hypothesis, partly confirmed by other studies (see sect. **1** for details), that secondary carbonates are characterized by a fragile aggregation structure. Our working hypothesis is that a strong and prolonged ultrasonic attack operates a selection of carbonate materials bringing and maintaining in water, generating a suspension (S), secondary carbonates preserving the memory of the time of the setting. In details, laboratory mortars were submerged in 50 ml of decarbonated/deionized water and underwent ultrasonic attack for 1 hr. After sedimentation only the first 30 ml of suspension were siphoned in centrifuge tubes, and solid components were isolated by
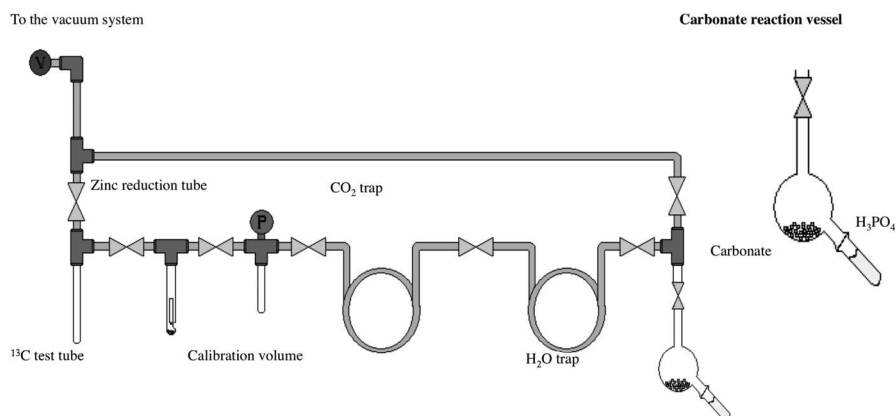
Fig. 1. – Scheme of the cryogenic purification line for the ^{13}C and ^{14}C samples pretreatment with a detailed view of the carbonate reaction vessel used for the H_3PO_4 digestion of carbonaceous materials to CO_2 and water.

centrifugation (20 minutes at 6000 rpm) and overnight drying at 70 °C. The produced suspension (S700, S800, S900, S1000, S1100 and S700_1.5) underwent ^{13}C and ^{14}C determinations.

2.3. CO_2 *isolation from laboratory air*. – During the mortar hardening period (see sect. 2.1.4) two spot samples (1st and 5th week) of laboratory atmospheric CO_2 were sampled. An amount of air (about 3 l) sufficient to ensure the sampling of 2 mg of C (7.3 mg of CO_2) were pumped through a double spiral trap cryogenic line [17] able to isolate with 100% efficiency air CO_2 avoiding also water interferences (fig. 1). The sampled CO_2 was characterized in terms of C isotopic fingerprint.

2.4. *Measurements*

2.4.1. XRD. The powdered limestone rock was analyzed aiming to evaluate possible impurities by means of a Phillips PW 1800 X-Ray Diffraction Machine and spectra acquired by using a Co K-alpha radiation.

2.4.2. Elemental analyses. Elemental analyses (C and N) were performed by means of a Thermo® flash EA 1112. For the purposes of this study, only C concentrations are used and expressed as %C:

(4)   %C = ((mass of C/mass of dried sample) × 100).

A quantity of sample, capable to ensure elemental peak signals statistically different from the blank (*i.e.* tin cup) background, was weighted by means of a μg balance, in a tin cup. Unknown samples were blank subtracted and calibrated by means of internal standards (*e.g.*, carbonaceous materials, soil, leaves) covering the same range of C concentration of the examined samples, precision quantified by means of replicated samples ($n = 3$) and accuracy checked by means of check standards (*i.e.* standards run as an unknown during the measurement).

2˙4.3. Isotopic measurements. [13]C measurements were performed on CO_2 by means of an isotope ratio mass spectrometer (IRMS) operated in dual inlet mode using as gaseous reference a CO_2 lab tank. After the calibration with carbonaceous reference materials ^{13}C abundances were expressed according to delta notation (‰) [18]:

$$(5) \qquad (({}^{13}R_{sample}/{}^{13}R_{VPDB}) - 1) \times 1000,$$

where [13]R is the isotopic ratio (^{13}C/^{12}C) of the sample and the standard (VPDB), respectively.

[14]C measurements were performed on the graphite developed by the CO_2 according to Zinc reduction process [19] (fig. 1) by means of the CIRCE accelerator mass spectrometer [20]. After the mass-dependent fractionation correction, blank subtraction and normalization with carbonaceous ^{14}C reference materials ^{14}C abundances were expressed according to Stuiver and Pollach [21] in percent of modern carbon (pMC) and radiocarbon age (R.C.Age):

$$(6) \qquad p\text{MC} = ({}^{14}R_{sample}/(0.95 \times {}^{14}R_{OXI})) \times \exp(\lambda \times (1950 - y)),$$
$$(7) \qquad \text{R.C.Age} = -8033 \times \ln({}^{14}F); \qquad {}^{14}F = ({}^{14}R_{sample}/(0.95 \times {}^{14}R_{OXI})),$$

where i) [14]R represents the isotopic ratio of the sample and the standard (OXI) corrected for mass-dependent isotopic fractionation; ii) λ is the true radiocarbon decay constant; iii) y is the year of measurement. Comparison of radiocarbon data is performed on calendar ages obtained by R.C.Ages by means of OxCal software [22] and INTCAL 09 [23] database.

For isotope analysis of carbonates, CO_2 was extracted by means of a H_3PO_4 (85%) complete (2 hours at 85 °C) digestion according to McCrea [24] and purified by static cryogenic procedure [19] (fig. 1).

2˙5. *Data analysis*. – Where not explicitly stated, the replicated measurements are expressed by the weighted average affected by the standard error (external error) or the weighted average error (internal error) depending on the result of a χ^2 test performed to accurately chose the best estimator for data dispersion.

Data comparison is performed by means of a t test comparison for the averages rejecting the null hypothesis (H_0 = there is no difference between the compared averages) for $\alpha < 0.05$.

3. – Results and discussion

3˙1. $CaCO_3$. – The initial limestone rock XRD analysis confirmed the overall carbonatic class for the $CaCO_3$ utilized in our study to produce the laboratory mortars. A deeper analysis of the XR diffractogram, evidencing the presence of small amounts of magnesium carbonates, allowed to classify the limestone in the class of low-magnesium calcite rocks.

The %C analyses performed on the $CaCO_3$ lead to 10.2 ± 0.2% (average ± standard error), a value fair depleted with respect to the theoretical value of the calcite (*i.e.* 12%) probably justifiable with the presence of high-mass impurities in the limestone.

The ^{13}C analyses on 3 replicated samples gave a δ^{13}C value of 2.9 ± 0.2‰. The measured ^{13}C value is in agreement with the observed range (*i.e.* from 1 to 4‰) characterizing carbonatic rocks formed for diagenetic processes in the early cretaceous [25].
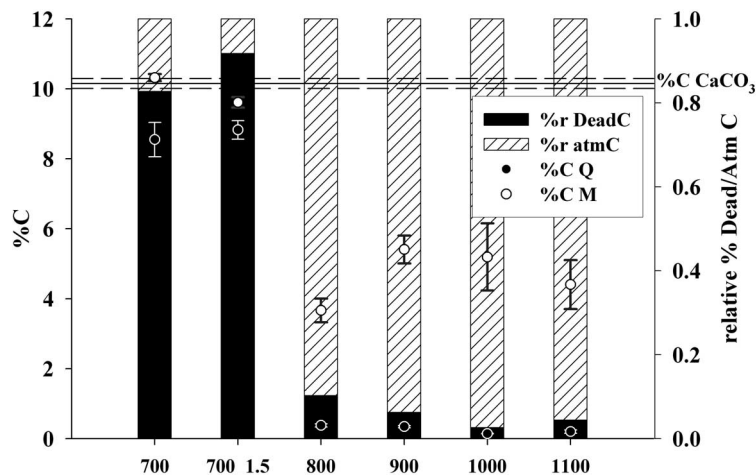
Fig. 2. – Measured (mean±standard error) C contents (%C) of the limestone ($CaCO_3$ continuous line), quicklimes (Qs filled circles) and mortars (Ms empty circles). Vertical bars to be read on the right vertical axis partition total C between primary and secondary cabonates. The horizontal axis refers to the temperature of production of the quicklime (see text for details).

Radiocarbon measurements on 3 samples gave a pMC of $0.12 \pm 0.05\%$, a value leading to an apparent R.C.Age of about $54\,$ka of the same order of magnitude of our sample preparation induced background [19]. The high radiocarbon depletion found confirms the long time spent since the formation of the carbonate happened.

3.2. *Q*. – The %C measurements on the produced quicklimes reveal a threshold behavior for the calcination of $CaCO_3$ (fig. 2, filled circles). It can be seen how quicklimes calcinated at $700\,°$C (Q700, Q700_1.5), independently of the time of application of the treatment, showed a fair depletion with respect to the others. This shallow degree of depletion can be attributed to the presence of magnesium carbonate which, being thermally decomposable at lower temperatures ($450–520\,°$C [26]), is efficiently removable also at $700\,°$C. These materials will generate a class of scarcely usable lime putty characterized by a low degree of hardening.

The Qs produced at $T \geq 800\,°$C are characterized by % of $CaCO_3$ residual C lower than 1% showing a decreasing trend with increasing T. This finding was in complete agreement with Moropoulou *et al.* [1], indicating a calcination optimum for $CaCO_3$ at T around $900\,°$C.

The measured radiocarbon abundances on Q700 and Q700_1.5, leading to an averaged value of $1.1 \pm 0.7\%$ pMC, confirm the ^{14}C depletion of the produced materials highlighting the goodness of practice (*i.e.* no contamination is added during Q production/handling/analysis) followed for the production of Q.

3.3. *M*. – The C abundances measured on the produced mortars represent an important deciphering key for the determination of the mortar laboratory production success. Our data show how the totality of the produced mortars is sensitively enriched in C with respect to their parents (*i.e.* Qs), underlying the effectiveness of laboratory air CO_2 absorption (fig. 2, empty circles).
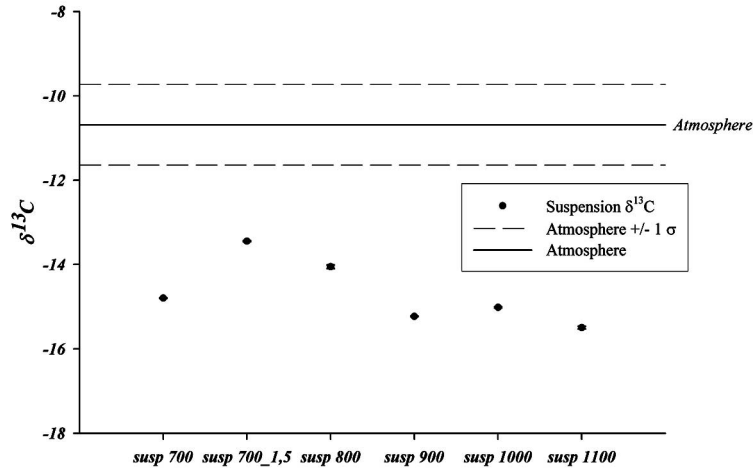
Fig. 3. – Measured $\delta^{13}C$ of the suspensions (filled circles) isolated by means of the proposed methodology for the isolation of the atmospheric signal from the mortars. The continuous line represents the measured atmospheric CO_2 signal in the laboratory air during mortar hardening.

The ratio between the measured %C in Q and M can be used to partition the C present in the mortar between primary and secondary (atmospheric origin) carbonates. It is evident how M700 and M700_1.5 originated by not completely calcinated Qs preserve the highest amount of primary carbonate C (fig. 2, column plots).

$3^\cdot 4$. *Suspensions and atmosphere* ^{13}C *and* ^{14}C *isotopic signatures*. – The ^{13}C isotopic fingerprints of the suspensions extracted by our proposed methodology show an average value of $-14.7 \pm 0.3‰$ (fig. 3).

The pMC signature of the extracted suspensions, on the contrary, evidenced a more complex behaviour: the suspensions extracted by the M700 and M700_1.5 are significantly depleted with respect to the Ss extracted from the Ms produced at $T \geq 800$. These Ss (S800, S900, S1000 and S1100) are characterised by an average pMC of $98 \pm 1\%$.

Both isotopic values measured on the suspensions (the pMC with the exclusion of S700 and S700_1.5) indicate the high degree of reproducibility of the applied procedure at levels comparable to the observed atmospheric CO_2 variability (see later in the text).

The ^{13}C and ^{14}C values measured on the atmosphere during the period of hardening of laboratory mortars are $-10 \pm 1‰$ and $100 \pm 2\%$, respectively.

A real accuracy evaluation of the procedure can be performed only by looking at the comparison of C isotopes data between suspensions and atmosphere.

The comparison between $\delta^{13}C$ values of the suspension and measured atmosphere CO_2 signature indicates the fair accuracy of the proposed methodology at 3σ level independently of the temperature of production of the Q (fig. 3). The ^{13}C tool indicates the good suppression efficiency of the procedure also if it must be noted how, given the little expected gap between the isotopic fingerprint of the sources contributing to mortars, it should be less sensitive than ^{14}C.

An agreement between the $^{14}CO_2$ signature of the laboratory atmosphere and the signal extracted by mortar is attributable to the efficient suppression of the primary carbonate contamination.
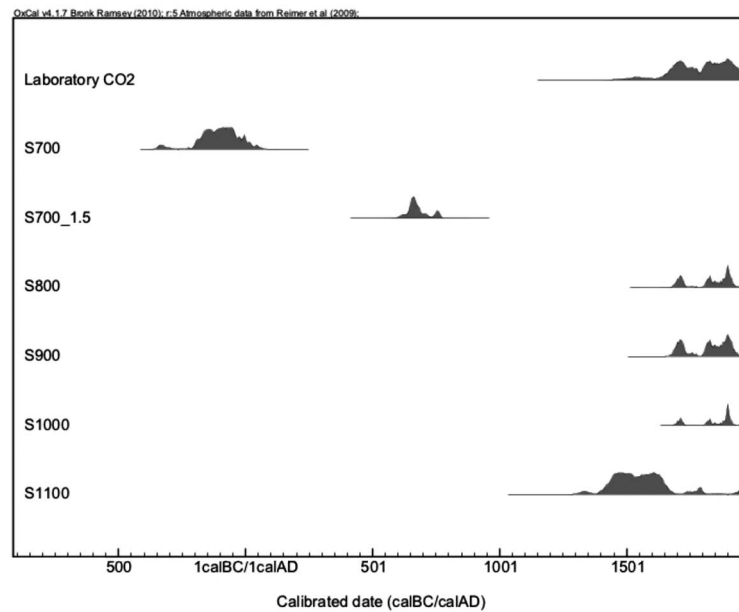
Fig. 4. – Probability distributions of the calibrated dates for the suspensions isolated by means of this study proposed protocol for radiocarbon dating of mortars. The probability distribution of laboratory CO_2 during the hardening of the mortar is also represented aiming for accuracy evaluation.

Comparison between the age measured on the laboratory air CO_2 sampled during mortars setting and the suspension extracted from mortars indicates (fig. 4):

 i) The introduction of significant aliquots of dead C of primary carbonate origins leading to a significant ageing effect of the suspension with respect to the real age of the atmosphere for M700 and 700_1.5.

 ii) The good accuracy of the procedure when mortars are produced according to the conventionally used T for quicklime production.

Also, if significant mismatches are observed in radiocarbon dating mortars by means of the proposed methodology, our results indicate a promising dead C suppression efficiency, being the observed offset attributable to the analysis of mortars characterised by a scarce probability of usage (see sect. **3**˙2).

4. – Conclusions

The radiocarbon community has attempted dating of mortars for a long time period. During this experimentation, several reasons have been found to justify observed accuracy fluctuations. Among the different causes, the presence of unburned C of primary-carbonate origin is pointed as the main cause influencing radiocarbon dating. This experiment, by simulating in laboratory a simplified production process of mortars, evaluates the efficiency in primary-carbonate suppression of a novel methodology by comparing the ^{14}C signature of the atmosphere at the time of mortar setting and the signal extracted by mortars. Overall the observed successful character of the proposed methodology opens the opportunity for future experimentations on more complex mortar matrices and real field mortars.

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