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Characterization of mortars of Giotto's Bell Tower for radiocarbon dating

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***Abstract* – A complete characterization of mortars of Giotto's Bell Tower (Florence) was performed in order to identify samples or portions of them suitable for dating by radiocarbon. In principle, considering at least the case of an aerial mortar, the material which can be dated is the carbon contained in the binder, since that carbon is derived from the calcite that forms in the moment of mortar hardening by interaction with atmospheric CO_2.**
Six core samples were obtained from foundation and from different levels of the Bell Tower, each of them related to a different construction phase. A multi-analytical approach was performed using X-ray diffraction, FTIR spectroscopy, thermogravimetric analysis (TGA), optical and electronic microscope to characterize binder and aggregates. Physical and mechanical parameters were also evaluated. Four samples, either from lumps or binder itself, were identified as possible candidates to be dated by radiocarbon. Obtained data have been encouraging.

I. INTRODUCTION

The Giotto's Bell Tower in downtown Florence was designed in three phases, as result of the work of different architects: the first phase took place under the supervision of Giotto, from 1334 to 1337, the second phase was realized by Andrea Pisano, from 1337 to 1343, and finally the third from 1343 to 1359, under the direction of Francesco Talenti (figure 1).

During the most recent diagnostic campaign promoted by Opera del Duomo and conducted on the Tower to investigate the history, the structures and materials of external façades and masonry, some samples of mortars were obtained. The mortar samples were taken from the foundations, from the masonry of the II and V levels of the bell tower, using a core drill.

The present research has been focused on the chemical, mineralogical, petrographic, physical and mechanical characterization of mortars in order to identify suitable samples to be dated by radiocarbon.

Among all the different types, radiocarbon dating can only be performed on aerial or weakly hydraulic mortars. In fact, the production of an aerial mortar can be summarised through the chemical reactions:

- Calcination of the original "geogenic" carbonate:

$$CaCO_3 \xrightarrow{900°C} CaO + CO_2 \quad (1)$$

- Slacking of the formed quicklime by water addition:

$$CaO + H_2O \longrightarrow Ca(OH)_2 + heat \quad (2)$$

- Setting of the mortar, after mixing with sands and other aggregates, and carbonatation:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \quad (3)$$

In this kind of mortars, we can thus isolate, collect and measure the carbon in the calcite of the binder: this is the datable fraction, as $CaCO_3$ forms by reaction of calcium hydroxide with the atmospheric CO_2 and thus that carbon is in equilibrium with the atmospheric ^{14}C concentration, until the end of the setting process. This is the fundamental hypothesis at the base of mortar dating, already introduced several decades ago [1, 2]. However,

although this method could represent a considerable progress in the archaeometric investigations that can be applied on the architectural heritage, experience has demonstrated that radiocarbon dating of this material is not as straightforward as one may expect, since there can be several different sources of possible carbon contaminations [3, 4, 5]. For example, an apparent ageing of the dated sample could be due to an incomplete separation between binder and carbonaceous aggregates, as well as to some residues of the original geogenic calcite used as raw material for the mortar production. Modern, or younger, contaminations could be introduced when the hardening process spanned over a period larger than usual.

Figure 1- The Giotto Bell Tower in the downtown Florence; different colours are used to highlight the different construction phases: Giotto 1334-1337 phase in pink; II phase by Andrea Pisano 1337-1343 in green, III phase by Francesco Talenti 1343 - 1359 in gray.

All things considering, it is clear that the measurement of the ^{14}C concentration can only come after a complete characterization of the mortar to check e.g. the composition and sizes of aggregates, the possible presence of lumps of different origin and the state of carbonation, in order to identify which can be the sample, or at least portions of it, most suitable for dating.

II. MATERIALS AND METHODS

Six core samples were obtained during recent works of restoration of Giotto's Bell Tower (figure 2).

The core samples belonged to different construction phases: CF1 belongs to the foundation, dated 1298, the core samples C2 and C3 to the V level, dated 1343, while the C4, C5 and C6 core samples to the II level, dated 1337.

A complete characterization of binder and aggregate was realized through X ray diffraction on powder, ATR-FTIR spectroscopy, thermogravimetric analysis (TGA), [6, 7, 8.9].
optical and electronic microscopy (OM and SEM-EDS).

Carbonation test using a phenolphthalein indicator was also performed.

Further investigations (physical and mechanical tests, i.e. evaluation of effective porosity, ultrasonic and penetrometric tests) were carried out to correlate/differentiate the samples belonging to the different construction phases.

Figure 2 An analysed core sample.

Radiocarbon measurements were performed by Accelerator Mass Spectrometry (AMS) at 3 MV Tandem accelerator of LABEC, Florence, one of the laboratories of INFN-CHNet [10].

To ensure the complete collection of the suitable carbonaceous fraction to be dated as gaseous CO_2, sample acidification by H_3PO_4 was performed, according to the reaction:

$$3CaCO_3 + 2H_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 3CO_2 + 3H_2O \quad (4)$$

For this reason, a new simple interface was added to the graphitization line: the sample to be processed is

inserted in a quartz vial and the acidic solution is pumped in it by a syringe through a PTFE/silicone septum. While the reaction is proceeding, the undesired water is trapped in a cold finger kept at low temperature thanks to a Peltier-based device. Reaction times have been adjusted according to mass and provenance of treated samples (either lump or binder), typically spanning between few minutes up to 30 minutes at maximum.

Considering the treated mass of about few milligrams (and carbon is only 30% wt of calcite) and that in the case of binder we are generally interested only on the CO_2 evolving as first from the reaction, after extraction of carbon dioxide, samples were graphitized using the new CHNet_Lilliput graphitization system, specifically designed to prepare samples as small as 50 micrograms of carbon (figure 3) [11].

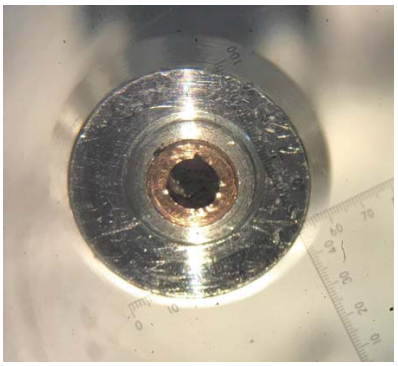

Figure 3 Detail of the microgram-sized graphite pellet prepared for the ^{14}C-AMS measurement.

During the AMS beam run, standard samples with certified ^{14}C concentration (NIST Oxalic Acid II and IAEA C2, as primary and secondary standards, respectively), and blanks samples (to evaluate the chemistry and machine backgrounds) were measured. ^{14}C ages were converted to calibrated ages using the IntCal13 curve [12] by means of the software OxCal v.4 [13].

III. RESULTS

A. *Mineralogical and petrographic characterization*

The mortars of the Bell Tower consist of a natural hydraulic lime binder obtained burning a marly limestone, identified by remains present in mortars as Pietra Alberese (figure 4). In fact, semi-quantitative chemical analyses by SEM-EDS and ATR-FTIR spectroscopic analyses suggested the presence of hydraulic phases in the binder. Also the thermogravimetric analyses performed on samples of enriched binder (disaggregated fraction <63 μm) confirm these data. This excludes the possibility of a pure aerial mortar, which would have been the perfect candidate for radiocarbon dating.

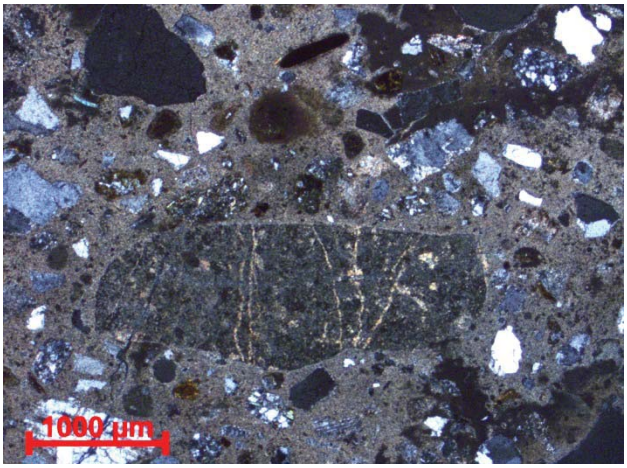

Figure 4: Microphotograph of thin section of sample 2 under OM (n ⊥).

The aggregate is likely to have been obtained from the Arno's river bed, as it is mainly constituted by silicatic grains (quartz, feldspars, micas and rock fragments). Although all the core samples are made with rather similar raw materials, the samples belonging to different construction phases differ in the technological characteristics: binder / aggregate ratio, sieving and dimensions of grains of aggregate, macroporosity.

Furthermore, physical-mechanical tests indicate that these are mortars with good performance and rather high mechanical strength.

In most of the collected cores, lumps with a yellow to white colour and an inconsistent appearance were found. The presence of lumps indicates that the mortar was produced with traditional technology [14, 15]. Their formation is due to the non-uniformity of heat in the kiln used for burning or to the unsuitable size of the limestone, or to the choice of material that cannot be completely burnt. The lumps have been subjected to a deep characterization with optical microscope, through XRD and ATR-FTIR in order to discriminate their origin, thus selecting those most suitable for dating. Indeed, the lumps that are suitable for radiocarbon dating are those due to remains of binder not mixed in the mixture, which carbonated simultaneously with the binder itself, and of course not those derived from uncomplete burning of the original limestone.

From the performed full characterization, only three samples, all of them from second level of the tower, were isolated for the radiocarbon measurement: a lump from the core C5 and its binder, and the binder from the core C6. The lump mass was large enough and thus it was split into two separate samples.

B. *Radiocarbon data*

Radiocarbon measurements allowed us to draw some

interesting considerations:

- $CaCO_3$ samples as small as 2 mg at maximum (see the processed lumps) can be successfully dissolved and measured by AMS using the set-up developed at our laboratory;
- the injection of the ortophosphoric acid into the dissolution vial can be a quite critical operation and particular care has to be taken to minimize the possibility to introduce modern contaminations;
- generally speaking, the obtained data are satisfying since they are compatible with the construction phases of the tower, thus demonstrating the validity of all the preliminary characterization measurements. Figure 5 shows the calibration graph for sample C6(0.70m), whose conventional radiocarbon age was measured as 830 ± 150 yrs BP. The IntCal13 calibration curve, with its experimental uncertainty, is drawn in blue; the measured radiocarbon age is reported on the y axis, in red, and treated as a Gaussian distributed random variable (the experimental error corresponds to the width of the Gaussian distribution); the distribution of probability for the calibrated age is shown on the x axis in dark grey. Since this obtained distribution of probability cannot be clearly described through analytical expression, the final calibrated age can only be given indicating an interval corresponding to a certain level of probability, or confidence. In Figure 5, calibrated age is reported at 68% and 95% level of probability.

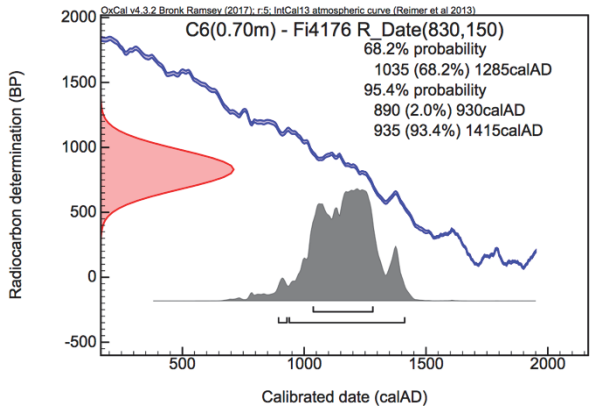

Figure 5: Calibration of the conventional radiocarbon age 830 ± 150 years BP that was measured for sample collected form core C6.

IV. CONCLUSION

The data collected during this research made it possible to enlighten how much essential the inclusion of a characterization phase of the mortar prior to the radiocarbon measurement is. The chemical, mineralogical and petrographic characterization of binder and aggregates, the identification of technology used for making the mixture allow us to determine the origin of the mortar. For instance, we can thus reject those samples that are mainly hydraulic, since in that case we could not exclude a possible contamination due to water during hardening. Only a multi analytical approach using different techniques (i.e. XRD, FTIR, TGA, OM, SEM-EDS, physical and mechanical tests) allows us to guarantee a correct knowledge of the material.

V. ACKNOWLEDGEMENTS

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