The mortars of Giotto’s Bell Tower (Florence, Italy): raw materials and technologies

Emma Cantisani a,⇑, Sara Calandra a,b, Serena Barone c,d, Samuele Caciagli e, Mariaelena Fedi d, Carlo Alberto Garzonio b, Lucia Licioli d, Barbara Salvadori a, Teresa Salvatici b, Silvia Vettori a

a Institute of Heritage Science - National Research Council of Italy, Sesto Fiorentino (Florence), Italy
b Department of Earth Sciences, University of Florence, Italy
c Department of Chemistry Ugo Schiff, University of Florence, Italy
d National Institute for Nuclear Physics, Unit of Florence, Italy
e Opera di Santa Maria del Fiore, Florence, Italy

HIGHLIGHTS
- The first multi-analytical analyses of mortars of Giotto’s Bell Tower (Florence).
- Knowledge of building technologies and raw materials used in the past.
- The use of natural hydraulic lime to obtain mortars with good performance.
- Radiocarbon dating of mortars.

ABSTRACT
Giotto’s Bell Tower is known as one of the most important religious buildings of the 14th century in Florence (Italy). Its different construction phases have been well documented over time. The possibility of analyzing mortars collected from different construction phases, allowed us a complete chemical, mineralogical, petrographic, physical and mechanical characterization of these materials, improving the knowledge of building technologies and raw materials used at different times. In addition, knowing the approximate time of production of the mortar samples, it was possible to verify if they are suitable for radiocarbon dating.

© 2020 Elsevier Ltd. All rights reserved.

1. Introduction

The study of ancient mortars plays a relevant role in the knowledge of historical buildings and structures. Numerous researches dedicated to the characterization of mortars and plasters belonging to archaeological [1–7] and architectonic heritage [8–12] highlighted the relevance of these materials to acquire detailed information on the construction phases.

The production of mortars is a very complex process, involving knowledge of materials and manpower skills. The identification of raw materials and the process of production provide also information on “material culture” of the people that manufactured those mortars [13].

Chemical, mineralogical, petrographic methodologies [14–19] can be applied in order to obtain useful data for a complete characterization of the binder, aggregate and possible additives, but often the amount of available samples is not enough to perform physico-mechanical tests [20,21].

In this paper, for the first time, core samples, belonging to different construction phases of Giotto’s Bell Tower, have been collected and analyzed through a multi-analytical approach.

A complete chemical, mineralogical, petrographic and physico-mechanical characterization of mortars belonging to different construction phases was carried out in order to identify similarities or differences among phases, improving the knowledge of building technologies and raw materials used at different times.
Moreover, a feasibility study of dating these mortars by radiocarbon was performed.

In fact, even though, in principle, aerial mortars can be dated by radiocarbon, it is only thanks to an accurate analytical characterization of the collected materials that it is possible to estimate whether the selected samples can be good candidates. In an aerial mortar, the datable component is represented by calcite that results from the reaction of calcium hydroxide with the atmospheric CO$_2$ during the hardening of the material. It is thus mandatory a complete separation of the binder with respect of the aggregates. However, different possible sources of contamination can alter the true radiocarbon concentration and can thus make the mortar appearing either older or younger [22–24].

A further challenge is represented by the fact that dealing with mortars for dating often correspond to work with very small samples, even of few tens of micrograms.

2. Giotto’s Bell Tower

Giotto’s Bell Tower is located in Piazza del Duomo in Florence (Italy), where Santa Maria del Fiore Cathedral and San Giovanni Baptistery are also present. The tower is considered a masterpiece of Gothic architecture and the output of exceptional artists, architects and sculptors such as Giotto di Bondone, Andrea Pisano, Francesco Talenti and, later on, the sculptors Donatello and Nanni di Bartolo.

At the beginning of the 14th century, many religious and civil buildings were built in Florence. The bell tower took the place of many private towers, becoming a symbol of the spiritual and political stability of the Guelf republic [25]. It represented the new monument, which overlooks the entire city.

Its foundations were excavated around 1298. All the historical events of its construction can be summarized through the three phases reported by the historic archives. Each phase was led by a different architect (Fig. 1). The first architect was Giotto di Bondone, who worked between 1334 and 1337 (when he died). Giotto designed the entire construction of the bell tower, characterized by a square plan, embellished by marble covering, sculpture and spire roof. However, he only realized the first part of the project, up to the height of the hexagonal panels. The second architect was Andrea Pisano, who repeated Giotto’s style at the second band and changed the design in the next two floors. He worked until about 1343, when he was replaced by Francesco Talenti who built the top three levels, with the large windows (double and triple-arched windows), completing the bell tower in 1359 [26].

The tower has six levels recognizable by the external banded partitions and marked by stylistic differences. The structure is supported by angular buttresses in the shape of polygonal pillars that reach up to the roof and by pillars positioned in the center of the double and triple-arched windows.

The construction method is rubble masonry, the wall was realized with two outer layers and an internal core that connects the internal lining with the external one, destined to be covered [27]. A detailed examination of masonry shows a cortical wall made with squared stone (sandstone) and the inner part filled with a coarse aggregates (mainly stone elements and in some level also in bricks) and mortars. Externally, the cladding is made up of polychrome carved slabs of marble, "green" marble (serpentinites), red limestone and marly limestone.

3. Materials and analytical methodologies

During recent restoration works of Giotto’s Bell Tower, six core samples were collected. In Table 1 a brief description of samples is reported.

The core samples belong to different construction phases: CF1 to the foundations, dated 1298; the C2 and C3 core samples belong to the fifth level, dated 1343; the C4, C5 and C6 core samples belong the second level, dated 1337.

In Fig. 2, the macroscopic aspect of the core samples is reported.
3.1. Chemical, mineralogical and petrographic characterization

The chemical, mineralogical and petrographic characterization was carried out for each sample, using the following analytical methodologies [28]:

– Optical Microscopy (OM) was used to observe macroscopic features of the mortar samples, as well as by the naked eye, also by means of a stereomicroscope up to 200 magnifications;
– Petrographic investigation was carried out through observation in transmitted light of thin sections (30 \( \mu m \) thickness) with an optical microscope. In case of mortars, the petrographic approach permits accurate characterization of binder, aggregate and inorganic additives and admixtures [29–33]. The study of binder in an ancient mortar can be performed directly on the binder itself or on “lumps”. Lumps are described as grains with “a whitish appearance, sometimes inconsistent” [34,35]. In some cases, the observation of lumps in thin section, as reported by several contributors, allows us to recognize the type of carbonate rock burnt in the kiln. Lumps, indeed, can be due to binder not well mixed in the paste, to underburnt fragments (remnants of underburnt limestone), to overburnt fragments of limestone, or to hydrated and carbonated overburnt fragments after the setting reaction of the mortar [36–38].
– X-ray Powder Diffractometry on powders (XRPD) was employed to determine the mineralogical composition using a powder X-ray diffractometer (Cu anticathode (\( \lambda = 1.54 \) Å)), under the following conditions: current intensity of 30 mA, voltage 40 kV, explored 2\( \theta \) range between 3 and 70\( ^\circ \), step size 0.02\( ^\circ \), time to step 50 s. The XRDP analyses were performed on bulk samples and on selected lumps;
– Fourier Transform Infrared Spectroscopy (FT-IR) was employed for the determination of composition of selected lumps and sifted samples through a spectrometer equipped with a diamond ATR system. The spectra obtained from the analysis of the powdered sample were acquired and processed using OPUS 7.2 software. The acquisition was carried out in the spectral range between 4000 and 400 cm\(^{-1}\), with a resolution of 4 cm\(^{-1}\) for 24 scans;
– Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM-EDS) was used for morphological and elemental microanalysis evaluation of intergranular binder and lumps, with an acceleration voltage of 20 kV, 700 pA of beam current and work distance of 9.5 mm;
– The carbonation tests were carried out using a phenolphthalein indicator [39]. Phenolphthalein is often used as an indicator in titrations: it results colorless in acidic solutions and pink in basic solutions (over pH 8.5). This method captures the color change boundary among uncarbonated, partially carbonated or fully carbonated concrete, where pH is about 9;
– Thermogravimetric analysis (TGA) was employed for binder characterization. Some fragments of each sample were disaggregated using a porcelain pestle, and the fraction passing through a sieve with 63 \( \mu m \) openings (ISO R 565 Series) was considered as a binder-enriched specimen. TGA was used to evaluate the presence and the amount of volatile compounds (essentially H\(_2\)O, CO\(_2\)) in the samples. TGA was conducted in the range 110–1000 \( ^\circ \)C on about 5 mg of sample, dried (silica gel as drying agent) at room temperature for at least a week under the following experimental conditions: open alumina crucibles, heating rate of 10 \( ^\circ \)C/min and 30 ml/min nitrogen gas flow. TGA was used for classifying the studied samples as non-hydraulic mortars or hydraulic ones as suggested by most authors [16,40,41].

3.2. Physico-mechanical tests

For each sample, five specimens of 2x2x2 cm were prepared to determine the water accessible porosity (effective porosity, Pw%) and the water absorption coefficient (I.C. w%), selecting the por-
tions of core samples without very coarse aggregate [42]. A hydro-
static balance was used applying Archimede’s law:
\[
V_w = \frac{(W_w - W_d)}{g_w}
\]
\[
V_a = \frac{(W_w - W_h)}{g_w}
\]
Where: \( W_d \) is the dry weight, \( W_w \) is the wet weight at the saturation point, \( W_h \) is the hydrostatic weight, \( V_a \) is the volume of sample, \( V_w \) is the volume of water inside the pores, \( g_w \) is the density of water at the measurement temperature.

The water accessible porosity \( P_w \%) \) was calculated as:
\[
Pw\% = \left( \frac{V_a}{V_w} \right) 100
\]

The water absorption coefficient I.C. \( w \%) \) was calculated as:
\[
I.C.w\% = \left( \frac{W_w - W_d}{W_w} \right) 100
\]

For the mechanical characterization, ultrasonic (UPV) and pen-
etrometric methods were used.

The UPV testing were realized through an ultrasonic instru-
ment, characterized by two 54 kHz transducers. In the setup
method (Fig. 3), the gel was employed for obtaining an adequate
acoustical coupling between the sample and the face of each trans-
ducer. Calibration of the UPV instrument was tested using Pundit
calibration rod to ensure the accuracy of the readings [43].

The time of flight (the time it takes for the pulse to pass through
the path length (L, m), ToF in \( \mu s \)), was measured. The pulse velocity
(\( v \) in m/s) is calculated as:
\[
v = \frac{L}{ToF}
\]

The penetrometric test is based on penetration depth measure-
ments of a steel needle in a mortar joint subjected to the repeated
loading of strikes generated by a known mass [44]. The instrument
used is a penetrometer with the following technical characteris-
tics: impact energy of 4.55 Nm; impact mass of 835 g and stroke
of 82 mm. The obtained result is the needle penetration depth
(\( R \), mm), after a number of impacts defined according to the
type of procedure used (in the study case 10 impacts). It is possible
to calculate the compressive strength \( R \), in MPa) with a correlation
curve and equation of the instrument:
\[
R = 4.489e^{-0.106RPMs}
\]

3.3. Radiocarbon dating

The possibility to date an aerial mortar by radiocarbon relies on
the feasibility to precisely separate the binder from all the aggre-
gates (once provided that no possible sources of contamination
from the external environment are present and that full carbona-
tion has occurred). Indeed, the binder constitutes in calcium car-
bonate that forms during the reaction of \( Ca(OH)_2 \) with
atmospheric \( CO_2 \) and thus keeps the information about the date
of the carbonation itself [22, 23]. Many papers are present in the lit-
erature discussing the achievability to apply \( ^{14}C \) to mortars, evi-
dencing the limitations of the method, due to the presence of
many possible sources of contamination, and suggesting possible
experimental strategies to overcome those sources (see for example
[24]), even though general and commonly agreed procedures have not been established yet.

As a proof of principle, two of the samples collected from Giot-
to’s Bell Tower were dated by radiocarbon, choosing among both
the bulk material and the extracted lumps. The choice of sample
was based on the analysis of the material, considering as discrim-
inating factors, for example, the presence and the size distribution
of aggregates, the carbonation level, the lump provenance (see the
following section Results and Discussion).

Carbonate samples were first gently grinded by hammer and
then sieved (63 \( \mu m \) mesh). Extraction of carbon from the finer resi-
dues was performed by acidification adding \( H_3PO_4 \) to \( CaCO_3 \). The sample
is inserted in the so-called “dissolution” vial, which is con-
ected to the rest of the preparation line, where \( CO_2 \) evolving as
consequence of acidification is collected, purified and finally con-
verted to graphite (graphitization). After evacuating the line,
\( H_3PO_4 \) is introduced in the vial by a syringe through a silicon/PTFE
septum. Different dissolution times are chosen in the case of the
bulk material or the lump. In fact, while processing the bulk mate-
rial, it cannot be excluded, a priori, that some possible interfer-
ences, due to some residual aggregates, are still present. A
possible solution to overcome this issue is the collection of only
the first \( CO_2 \) fraction evolving after adding the acid to selectively
extract only the carbon dioxide originated from the binder and
minimize the possible contribution from the aggregates. This pro-
cedure is based on the experimental observation that molecular
bonds in the carbonate binder are expected to be weaker than
those in the carbonate aggregates. In our set-up, in the case of
the sample from the bulk material, the gas evolving after 180 s
from the beginning of the acidification process was collected. In
the case of the lump, considering that the material is expected to
be as purest as possible, all the gas produced in the chemical reac-
tion was collected. In our set-up, after being cleaned from possible
water traces passing through a thermal trap, the \( CO_2 \) is collected in
the graphitization reactor and there converted to solid graphite
reaction with hydrogen in the presence of iron as catalyst (at a
temperature of 600 °C). Since very low mass from the processed
samples was expected, a new so-called Lilliput graphitization reac-
tors, which had been optimized to prepare samples as small as
50 \( \mu g \) of carbon, was used [45].

The pellet obtained at the end of the graphitization process,
consisting in a mixture of graphite from the original sample and
iron, was inserted into the accelerator ion source for the measure-
ment of the radiocarbon concentration by Accelerator Mass Spec-
trometry (AMS). Measurements were performed at the AMS
beam line of the tandem accelerator installed at INFN-CHNet Flo-
rence [46]. Samples prepared from NIST OxAcII (SRM4990C) and
from IAEA C-2 were used as primary and secondary standards,
respectively. \( ^{14}C/^{12}C \) isotopic ratios were corrected for isotopic
fractionation by measuring \( ^{13}C/^{12}C \) in the accelerator too, and for
background counts. Calibration of conventional radiocarbon ages
was performed using IntCal13 [47] as reference calibration curve,
using OxCal v.4.3 software developed by the Oxford Radiocarbon
Unit [48].

4. Results and discussion

In the Fig. 4 some stereomicroscope images of analyzed mortars
are reported.

4.1. Chemical, mineralogical and petrographic characterization

The main mineralogical and petrographic characteristics of ana-
yzed core samples are summarized in Tables 1SM and 2SM.
The two different portions of CF1 core sample are characterized by similar macroscopic aspects: hazel color (Fig. 4), coarse aggregate made of arenaceous rock fragments and numerous lumps. The observation of thin sections under optical microscope allowed the identification of a binder with heterogeneous structure and micritic/microsparitic texture (Fig. 5a). Lumps are present both as remnants of binder not well mixed and as remnants of underburnt limestone fragments (Fig. 5b). The aggregate is abundant, well selected, with an unimodal grain size distribution (mean grain size 200–250 μm), a sub-angular/sub-rounded shape and a mainly silicate composition (mono and polycrystalline quartz, plagioclases, arenaceous rock fragments, siltstones). The ratio binder/aggregate (B/A) is 1/3. The phenolphthalein test confirmed the complete carbonation of even the deepest portion of core sample. Diffractometric analyses suggested the presence of vaterite in the bulk samples (Fig. 6) and in some lumps as well; the ATR FT-IR analyses identified amorphous silicates. The occurrence of metastable polymorphs of CaCO₃, in particular vaterite, may be due to the action of amorphous silica, which slows down the transformation in the stable form calcite [49]. Other studies [50–53] suggested that the pH, temperature, pressure, degree of supersaturation and the presence of organic substance, such as protein, in the mortar mixture could facilitate the formation and the stabilization of vaterite and inhibit the transformation in the stable calcite and aragonite. In the mortars of Giotto’s Bell Tower the presence of organic additives can be excluded (cf FT-IR analyses). On the other hand vaterite was frequently found in the binder obtained, in the laboratory tests, firing marly limestone [54,55].

The C2 and C3 core samples were taken from the fifth level of Giotto’s Bell Tower, III construction phase, built around 1343. Although the mortar is always made up of a light brown binder, the different portions of CF1 core sample are characterized by similar macroscopic aspects: hazel color (Fig. 4), coarse aggregate made of arenaceous rock fragments and numerous lumps. The observation of thin sections under optical microscope allowed the identification of a binder with heterogeneous structure and micritic/microsparitic texture (Fig. 5a). Lumps are present both as remnants of binder not well mixed and as remnants of underburnt limestone fragments (Fig. 5b). The aggregate is abundant, well selected, with an unimodal grain size distribution (mean grain size 200–250 μm), a sub-angular/sub-rounded shape and a mainly silicate composition (mono and polycrystalline quartz, plagioclases, arenaceous rock fragments, siltstones). The ratio binder/aggregate (B/A) is 1/3. The phenolphthalein test confirmed the complete carbonation of even the deepest portion of core sample. Diffractometric analyses suggested the presence of vaterite in the bulk samples (Fig. 6) and in some lumps as well; the ATR FT-IR analyses identified amorphous silicates. The occurrence of metastable polymorphs of CaCO₃, in particular vaterite, may be due to the action of amorphous silica, which slows down the transformation in the stable form calcite [49]. Other studies [50–53] suggested that the pH, temperature, pressure, degree of supersaturation and the presence of organic substance, such as protein, in the mortar mixture could facilitate the formation and the stabilization of vaterite and inhibit the transformation in the stable calcite and aragonite. In the mortars of Giotto’s Bell Tower the presence of organic additives can be excluded (cf FT-IR analyses). On the other hand vaterite was frequently found in the binder obtained, in the laboratory tests, firing marly limestone [54,55].

The presence of phases containing calcium, silica and alumina was also confirmed by the SEM-EDS analysis of lumps and binder portions (Table 2). In this table, also the microchemical analyses performed on different types of lumps are reported: lumps identified as remain of stone used to prepare lime (A and B in CF1 0.40 m) and on a lump (A in CF 2.60 m) identified as unmixed lime are reported. The different micro-chemical data registered in the dark and white area are due to the heterogeneity in the composition of limestone used to produce lime.

Table 2

<table>
<thead>
<tr>
<th>Mortar samples</th>
<th>Portion</th>
<th>% MgO</th>
<th>% Al₂O₃</th>
<th>% SiO₂</th>
<th>% CaO</th>
<th>% Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF1 0.40 m</td>
<td>LUMP A</td>
<td>Under burnt limestone (Fig. 7a)</td>
<td>A white area</td>
<td>1.18</td>
<td>3.98</td>
<td>48.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>44.19</td>
</tr>
<tr>
<td></td>
<td>LUMP B</td>
<td>Under burnt limestone</td>
<td>A dark area</td>
<td>1.84</td>
<td>7.01</td>
<td>63.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF1 2.60 m</td>
<td>LUMP A</td>
<td>Unmixed lime (Fig. 7b)</td>
<td>A white area</td>
<td>–</td>
<td>2.52</td>
<td>20.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LUMP A</td>
<td>Under burnt limestone</td>
<td>A dark area</td>
<td>–</td>
<td>8.71</td>
<td>73.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>LUMP A</td>
<td>Under burnt limestone</td>
<td>A white area</td>
<td>1.16</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Marly limestone (Fig. 7c)</td>
<td>A dark area</td>
<td>1.13</td>
<td>6.60</td>
<td>46.42</td>
<td>44.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LUMP C</td>
<td>Unmixed lime</td>
<td>C white area</td>
<td>–</td>
<td>3.28</td>
<td>27.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C dark area</td>
<td>–</td>
<td>8.47</td>
<td>79.71</td>
<td>16.40</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LUMP D</td>
<td>Under burnt limestone</td>
<td>D white area</td>
<td>–</td>
<td>1.78</td>
<td>22.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>D dark area</td>
<td>1.98</td>
<td>8.87</td>
<td>75.63</td>
<td>13.53</td>
<td>1.98</td>
</tr>
<tr>
<td>C5</td>
<td>LUMP A</td>
<td>Under burnt limestone</td>
<td>A white area</td>
<td>–</td>
<td>2.38</td>
<td>29.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A dark area</td>
<td>2.39</td>
<td>4.52</td>
<td>45.75</td>
<td>43.74</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LUMP B</td>
<td>Unmixed lime (Fig. 7d)</td>
<td>A white area</td>
<td>–</td>
<td>2.26</td>
<td>24.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B dark area</td>
<td>1.23</td>
<td>4.51</td>
<td>43.67</td>
<td>49.69</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 4. Stereomicroscope images of analyzed samples.
the samples C2 and C3 present macroscopic differences due to the choice of different materials such as coarse aggregates and the presence of lumps evident only in the C2 sample (Fig. 4). The observation of thin sections evidenced that both the core samples are made of similar binder with heterogeneous structure and micritic/microsparitic texture (Fig. 5c). The ratio B/A is 1/2 and
the fine aggregate has similar composition except for the presence
of marly limestone rock fragments and some grains of calcite in C2
core sample (Fig. 5d). The aggregate has a heterogeneous grain size
distribution ranging from 2.5 mm to 250 μm and shape from sub-
angular to sub-rounded. The XRD pattern of lumps shows the pres-
ence of calcite and aragonite and traces of quartz, while the ATR
FT-IR spectra also revealed the presence of other silicate compo-
nents, probably not crystalline [56]. The presence of silicate com-
pounds in the lumps was confirmed by SEM-EDS analyses
(Table 2). Also a coarse fragment of a not burnt marly limestone
(Fig. 7c) was analyzed, confirming the heterogeneity of composi-
tion of raw material and a large amount of silica. A higher amount
of microcracks is evident in the C2 (depth 2.10 m) sample with
respect to C3 (depth 1.30 m), that is probably due to the greater

![Fig. 6. XRD pattern of sample CF1 2.60 m bulk. The main peaks of quartz, calcite, vaterite, albite and muscovite are indicated.](image)

![Fig. 7. Backscattered electron images of some mortar samples with particular of lumps: a) CF1 0.40 m, b) CF1 2.60 m, c) C2, d) C5.](image)
depth of the core sample. Furthermore, the phenolphthalein test on C2 sample showed that the carbonation process took place partially.

C4, C5 and C6 core samples come from the second level of Giotto’s Bell Tower, II construction phase, dated from 1337 to 1343. The mortars of the C4 and C5 samples have very similar macroscopic appearance: compact, of hazel color and characterized by an abundant presence of lumps from centimeter to millimeter in size, from yellow to white in color. Coarse aggregates are less frequent in C5. Macroscopically, C6 sample is very compact, consisting entirely of fine portion of mortar (without coarse aggregates) and no lime lumps are present (Fig. 4). From a petrographic point of view, the samples are different: the aspect of binder range from homogeneous in C6 sample (Fig. 5e) to heterogeneous (i.e. C4 sample has a strongly crystallized binder (Fig. 5f)). Lumps, as remains of binder not well mixed (Fig. 5g) and remnants of not well burnt limestone (Fig. 5h) have been identified. In C4 and C5 core samples the aggregate is well selected, with sub-rounded to sub-angular shape and medium-fine grain size (mean grain size 300 μm). The B/A ratio is 1/3. The C6 core sample, without lumps, has an aggregate with a heterogeneous grain size distribution, grain size ranges from 0.80 mm to 100 μm. Phenolphthalein tests showed that all samples completed the carbonation process.

XRD suggested the presence of some types of lumps (in C4 and C5) suitable for dating, since in their case only calcite was detected. However, analyzing these lumps by ATR FT-IR (Fig. 8), the additional presence of amorphous silicates, probably originated from the firing of the stone rich in silicate components (e.g. clay minerals), was detected as a broad band centered at 1100 cm⁻¹. Lumps of different origin were analyzed also by SEM-EDS revealing a variable amount of silica from 24.50% to 45.75%.

In Table 3M the results of TGA analyses are reported. The temperature range and the relative weight loss represent the most significant parameters for identifying the type of binder making up the mortar mixture [40]. The weight loss in the 200–600 °C temperature range identifies the dehydration of the aluminosilicates determining the presence of hydraulic components. These data refer to hydraulic water (%) and the analyses have relatively high values ranging from 6.81% to 8.71%.

In the 600–900 °C temperature range, a weight loss due to the decomposition of CO₂ is observed. The amount of CO₂ in the sample comes from the calcium hydroxide carbonation process and the contribution of calcium hydrated silico-aluminates (they react slowly with CO₂ forming CaCO₃ and separating silica and alumina in the amorphous state). This parameter makes it possible to distinguish mortars with air lime characterized by the loss of CO₂ > 30% compared to mortars with hydraulic lime with values <30%. The analyzed samples have relatively low CO₂ values between 19.83% and 26.93%, resulting a material with a hydraulic behavior.

The CO₂/H₂O ratio between the percentage of weight loss attributed to CO₂ and the percentage of weight loss attributed to hydraulic water is particularly interesting. This parameter is related to the %CO₂ in Fig. 9a, where it is possible to better understand the degree of hydraulicity of the samples. The trend shows that the samples fall in the typical cluster of hydraulic mortars and are characterized by a rather homogeneous hydraulicity.

Fig. 9b reports the theoretical curve of the natural hydraulic lime obtained by the firing of Pietra Alberese, a marly limestone that was traditionally used for production of lime in the Florentine area [54,55,57]. The samples of Giotto’s Bell Tower fall precisely around it, confirming that the hydraulic properties of the mortar are conferred by firing this marly limestone. The samples are distributed on the left side of the curve, a portion that represents the lithotype with the greatest amount of clayey minerals and dark grey in color from the Monte Morello Formation [54].

The chemical, mineralogical and petrographic data allow to highlight differences or similarities among the three construction phases of mortars of Giotto’s Bell Tower. The raw materials used to produce mortars have been similar over time: a local marly limestone has been fired to produce a natural hydraulic lime, while the aggregate was obtained from the bed of the Arno river.

The main differences can be ascribed to the process of production of mortars. The ratio binder/aggregate ranges from 1/3 in the core samples coming from foundations to 1/2 for the core samples of III construction phase. The mean grain size and the grain size distribution of aggregates reveal a different sieving: in the core samples from the foundations a homogeneous grain size distribution and a finer mean grain size (250–250 μm) have been observed, while in the core samples belonging to III construction phase a heterogeneous grain size distribution and a grain size ranging from 2.5 mm to 250 μm have been register. For the II construction phase an intrinsic variability was observed also among samples belonging to same phase, in particular: the C6 core samples has different petrographic properties with respect to C4 and C5 samples, probably due to the employment of different manpower.

4.2. Physico-mechanical characterization

The effective porosity (Pv%) ranges from a maximum mean value (43.5%) for the CFI 0.40 m sample (foundations) to the minimum mean (27.8%) value of C6 sample (II construction phase) (Table 3). Similar trend is shown by C.I.P % that varies from 29.8% to 15.9%. A clear relationship between petrographic observation and physical data can be observed: i.e. the C6 core sample was described as very compact, with a binder with homogeneous structure and without lumps.

The ultrasonic velocity of a rubble masonry depends on the quality of mortar, the type of coarse aggregate and the proper filling of mortar among the space of stones. The sand content in mortar increases the values of velocities [58]. There is a relation between the physical and mechanical properties of materials and ultrasonic velocities. Usually, porosity is inversely proportional with the ultrasonic pulse velocity; in other words, if a material has high porosity, its ultrasonic velocity will be lower [59]. On the other hand, in this case the masonry ultrasonic velocity depends on both the coarse aggregates and fine portion of mortars: similar values of porosity may correspond to different ultrasonic velocity values. The microfracture network inside the material, as between stones and mortar, affects the velocity. In fact, pores and cracks cause discontinuity in the stone, which results in the decreasing of ultrasonic velocity and increasing breakability under compression [59].
The results obtained from the UPV tests show values that depend on the internal variability of the mortar: the centimetric-size aggregates have different elasto-mechanical characteristics as shown by the different ultrasonic velocity, the contact of different materials can cause internal cracks and, in some cases, real textural voids. As shown in Table 3, the differences of the average velocity of the samples largely depends on presence of the aggregates. In fact, the CF1 0.40 m sample (foundations) and the C2 sample (III construction phase) have the maximum velocity recorded. The C4 sample (II construction phase) shows values of ultrasonic velocity of about 2300 m/s that consist of mortar and stone aggregates. Instead, the CF1 2.60 m (foundations), C3 (III construction phase), C5 and C6 samples (II construction phase) show low value of velocity because these are composed mainly of fine portion of mortar and the C3 sample contains fragments of brick. Any clear relationship for UPV data with the construction phases has been evidenced. It is impossible, in this case, to compare the ultrasonic velocity with the physical characteristic of mortar, as a matter of fact the effective porosity was estimated for the portions of core samples consisting entirely of finer fraction avoids the coarse aggregate fraction. Concerning the penetrometric data, should be noted that the core samples belonging to II and III phases have a high strength respect to the samples that come from the tower foundations. This outcome is due to the mortar packaging conditions that led to an optimization of the material properties. The greatest strength (4.0 MPa) was registered for C6 core sample.

4.3. Radiocarbon dating

All the chemical, mineralogical and petrographic characterization of collected mortars and lumps allowed us to select the material, which appeared to be more suitable to test radiocarbon dating procedure. In general, a partially, or full, hydraulic mortar is not a good candidate to be radiocarbon dated, because in this case the setting is not due to only reaction with atmospheric CO2. Actually, this is the case of samples collected from the bell tower, as the mortar has been analysed to be composed by a natural hydraulic lime binder, as inferred from the discussion above. Moreover, CF samples from the foundations were excluded because petrographic analysis suggested that carbonation was slower than expected and, in addition, they may have been contaminated by underground water (see also the measured Pw%). C2 sample, III construction phase, was characterized by an incomplete carbonation and was excluded as well. However, some characteristics appeared to be promising. In the C5 core sample, a lump was selected (i.e. Lump 4), because it was composed mainly of calcite (as shown by XRD and ATR FT-IR data, see discussion above) and it derived from binder not well homogenised in the mixture (as shown by OM and SEM observation). This result suggests that the lump carbonated at the same time of the binder of all core sample. C6 core sample, II construction phase, was selected because it was characterized by absence of lumps and of carbonatic aggregates, it was very compact and the carbonation of the binder resulted to be complete. A mechanical separation of binder with respect to aggregate was performed.

Table 3

Results of physical and mechanical tests of core samples.

<table>
<thead>
<tr>
<th>Mortar samples</th>
<th>Pb %</th>
<th>C. I. p%</th>
<th>Ultrasonic velocity (m/s)</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF1 0.40 m</td>
<td>43.5 ± 1.1</td>
<td>29.8 ± 1.2</td>
<td>3560 ± 500</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>CF1 2.60 m</td>
<td>35.8 ± 0.7</td>
<td>21.6 ± 0.6</td>
<td>1160 ± 570</td>
<td>1.9 ± 0.3</td>
</tr>
<tr>
<td>C2</td>
<td>37.8 ± 3.0</td>
<td>24.4 ± 3.0</td>
<td>3700 ± 450</td>
<td>3.5 ± 0.1</td>
</tr>
<tr>
<td>C3</td>
<td>30.6 ± 1.4</td>
<td>17.8 ± 1.2</td>
<td>1400 ± 250</td>
<td>3.9 ± 0.1</td>
</tr>
<tr>
<td>C4</td>
<td>30.7 ± 1.0</td>
<td>17.5 ± 1.0</td>
<td>2300 ± 500</td>
<td>3.2 ± 0.5</td>
</tr>
<tr>
<td>C5</td>
<td>31.0 ± 1.2</td>
<td>18.0 ± 1.3</td>
<td>1100 ± 270</td>
<td>2.3 ± 0.1</td>
</tr>
<tr>
<td>C6</td>
<td>27.8 ± 1.7</td>
<td>15.9 ± 1.3</td>
<td>910 ± 70</td>
<td>4.0 ± 0.1</td>
</tr>
</tbody>
</table>

Table 4

Radiocarbon data for the selected samples: 14C concentrations, corresponding conventional radiocarbon ages and calibrated ages. Experimental uncertainties on the measured 14C concentration and conventional ages are quoted at 1 sigma; calibrated age intervals are reported at 95% confidence level.

<table>
<thead>
<tr>
<th>Sample</th>
<th>14C concentration (pMC)</th>
<th>TRC (yrs BP)</th>
<th>Calibrated age (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6</td>
<td>90.1 ± 1.7</td>
<td>830 ± 150</td>
<td>850–1450 CE</td>
</tr>
<tr>
<td>Lump 4 in C5</td>
<td>85.7 ± 2.6</td>
<td>1200 ± 200</td>
<td>400–1250 CE</td>
</tr>
</tbody>
</table>

Fig. 9. a) Diagram of CO2 vs CO2/H2O measured on the enriched binders with representative areas of hydraulic mortars and lime-based mortars; b) diagram of CO2 vs CO2/H2O with the theoretical curve of binders obtained burning Alberese limestone is reported (modified from [57]).
sured (about 50 μg of carbon in the graphite samples collected at the end of the preparation procedure instead of the “typical” 700 μg): a smaller mass corresponds to smaller ion currents extracted and measured into the accelerator and thus to lower acquired count rates.

The obtained data are satisfying. Considering the experimental uncertainties, the two samples are consistent one with another according to statistics.

In addition, C6 sample is also compatible with the construction phases of the tower. The lump collected in C5 appears to be slightly older than C6; this can be explained considering a residual very tiny contamination connected to the natural hydraulic lime binder which characterizes these mortars. In fact, in principle, as a consequence of the chemical reactions during the hardening process, only aerial mortars can be suitable for radiocarbon dating, as also highlighted in the introduction. The results shown are particularly interesting because they suggest that radiocarbon dating of a slightly hydraulic mortar is feasible as long as a full preliminary characterization of its petrographic, chemical and structural properties is performed.

5. Conclusion

The possibility of taking samples of mortar from different construction phases of Giotto’s Bell Tower allowed us to characterize raw materials and technologies used for the preparation of the mortars and to highlight similarities or differences among mortars belonging to different construction phases. Moreover, the chemical, mineralogical and petrographic study of the samples permitted the selection of the most suitable portions of mortar and lumps to be dated by 14C method.

The mortars of the bell tower consist of a natural hydraulic lime binder, obtained burning a marly limestone identified by underburnt fragments as a marly limestone, known in the Florentine area as Pietra Alberese (Monte Morello Formation). Semi-quantitative chemical analyses conducted with the SEM-EDS and ATR FT-IR confirm the presence of hydraulic phases in the binder, which gave the dough tenacity. The aggregate was obtained from the bed of the Arno river, its composition is mainly silicatic, free of organic substances. Although all the core samples were obtained from quite similar raw materials, samples belonging to different construction phases differ in technological characteristics: B/A ratio, sieving and mean grain size of aggregates, macroscopicity. Moreover, the results of physico-mechanical tests indicate that these are mortars with rather good performance; the mechanical strength ranges from 1.3 and 4.0 MPa.

Most of the samples have lumps that show, macroscopically, a yellow to white color and an inconsistent appearance. The presence of lumps indicates that the mortar was produced with traditional technology. Their formation is due to the non-uniformity of heat in the oven used for burning the limestone, to the unsuitable size of the limestone, to the choice of material that is not able to be completely fired.

Thanks to the full characterization performed (i.e. OM, XRD, ATR FT-IR and SEM-EDS), one mortar core sample and one lump were selected for radiocarbon dating. The results of the measurements are consistent with the expected age, thus suggesting that the overall analysis was fundamental to select a material that can be expected to be free from contaminations.

CRediT authorship contribution statement

Emma Cantisani: Conceptualization, Methodology, Investigation, Visualization, Data curation, Writing - original draft. Sara Calandra: Investigation, Visualization, Writing - review & editing. Teresa Salvatici: Investigation, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to thank the management board of the Opera di Santa Maria del Fiore, Florence, for the support and the collaboration for the collection of samples.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.conbuildmat.2020.120801.

References

E. Cantisani, S. Calandra, S. Barone et al.

Construction and Building Materials xxx (xxxx) xxx


