Mortar, plaster and brick dating:

The case study of the Modena Medieval UNESCO site

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ABSTRACT

The determination of the age of the structures is one of the most important issues in the study of historical buildings and their evolution. The UNESCO World Heritage Site of Modena, unique for its historic and artistic value, has been chosen as case study. Few historical documents revealed the dates of the beginning of the Cathedral (1099) and the completion of the Ghirlandina tower (1319), but no agreement exists about the timing of construction phases. AMS radiocarbon and OSL dating of mortars, and TL dating of bricks represent the only way to obtain scientific data about the site chronology. The aims of the research were to i) verify scientific dating techniques; ii) investigate the building phases chronology.

The petrographic characterisation of 150 mortars has provided new elements to identify the sources of supply of raw materials and to differentiate construction phases. The results suggest the lime supply sources were gravels taken from rivers and not from specific quarries. SEM-EDS, XRD quantitative phase analyses and TG analyses indicate the variable hydraulic character of the mortars by inconstant content of hydrated phases (CSH and CAH) and clinkers.

Two main construction phases were recognized for the Cathedral. The mortars of the 12th cent. show lower binder content and the sand supply was probably from a single source, the Panaro River. The Campionesi (13th cent.) performed a more refined mortar preparation technique with a higher percentage of binder and an aggregate with selected grain size from the Secchia River. Very similar mortars to those of the firsts phases of the Cathedral with similar petrographic characteristics were found in the first two floors of the tower.

For the first time a comparison of two accredited sample preparation procedures of mortars for radiocarbon dating was carried out: Cryo2sonic and sequential dissolution. Due to the high percentage of carbonate aggregates, binder related particles and secondary calcite, these mortars represent an experimental test particularly indicative of exogenous carbon sources suppression. Historical temporal constraints and mortar clustering based on petrography have been applied to define a chronological framework.

The results show that when the percentage of contaminants is very high, their suppression is not always complete. In these cases the dating of separate CO2 fractions by progressive dissolution time rates appears to yield better results by discriminating the contribution of contaminants.
In many cases the sample preparations worked in reducing the dead carbon, therefore the major building phases were dated. The dating of the Campionesi mortars, led to different results with the two different preparations of the bulk. The Cryo2sonic procedure achieved an older age date close to the 1000 AD. The CO₂ fractions method identified the large amount of contaminants getting an older age with the last two fractions. The expected age (1184-1220) came within the 2σ range (1039-1206 AD) result of the first fraction.

The date of the foundation of the tower together with the cathedral, which was only an assumption, has been confirmed by three different dating procedures. Our contribution to the controversial issue of the tower chronology suggests that the main construction phase should be postponed to the first half of the 13th cent. and not at the end of 12th cent., as assumed by previous studies.

OSL on mortars and TL on bricks were used to test the radiocarbon outcomes using independent methodologies. Unfortunately the mortars proved to be unsuitable for the OSL dating because of the uncompleted bleaching of quartz grains. The TL results confirm the large re-use of Roman bricks. Moreover, it was possible to discover and date a previously unknown renovation in the Cathedral apse area (16th cent.).

The result of this study indicate that petrography represent a fundamental tool for the identification of the most suitable dating technique of radiocarbon dating of mortars and for the correct interpretation of results.
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1. INTRODUCTION AND AIMS

1.1 Introduction

The UNESCO World Heritage Site of Modena, unique for its historic and artistic value, has been chosen as case study for the identification of construction phases, by means of absolute dating of building materials. Nevertheless, this is only part of a wider project carried out for many years by the Department of Chemical and Geological Sciences of UNIMORE, concerning the study of the local historic building materials.

My research has pursued in parallel with the restoration of the Cathedral of Modena and after the restoration of the tower Ghirlandina. The conservation work has involved several specialists of the conservation science, university students and professionals (as architects, restorers, engineers) who have been committed to the realization of an ambitious plan. All together we have contributed to the creation of a multidisciplinary project resulting in a forthcoming publication containing all the new findings about the Cathedral (the volumes concerning the restoration of the Ghirlandina have been already published in 2009 and in 2011).

In additions to this research, I have contributed to other areas of the restoration project, all linked by a common thread: the study of the two monuments, their constituent materials and the history of their restorations. In this framework, I focussed on the study of the mural paintings of the Cathedral, both those fragmentary (preserved in situ) and those detached and stored in museum environment (best suited for protection reasons) (Baraldi et al., in press). I also personally handled the archival research aimed to reconstruct the recent history of restoration works on the Cathedral. The archive material was ultimately loaded onto an online database for wider accessibility and use in the future (Caroselli and Oreni, in press; Oreni and Caroselli, in press).

In general, while studying a monument it is of vital importance to consider all construction phases as chapters of its history and a particular eye should be kept also on demolitions, reconstructions and additions. An in depth analysis should include the study of the masonry stratigraphy that allows relating the noticeable phases with the buried or hidden or unknown phases (for example by coring or archaeological excavations). The results of these investigations are of interest in archaeology, for architectural restoration and for monument preservation. The support of scientific tools can play in this sense, a fundamental role: when historical-artistic research leaves unclear issues they must be experimentally analysed and verified.
In this study, for instance, the detailed characterisation of a large number of samples of mortars and plasters allowed an in-depth technical knowledge on the production and application of the mortars in the Modena area. However, even if important efforts have been done to determine the physical, chemical and mineralogical characteristics of ancient mortars and of their components, many questions remain open on the meaning of these results. Therefore a further deepening of insight into the issue of mortar analysis is of general interest.

Beside the relevance of further research on the practical handling of mortar samples to extract pertinent information, the present study is also concerned with more specific archaeological and historical questions. The phases of construction of the Cathedral and the tower have been previously studied by several authors who have stressed the complexity of their determination, given the numerous modifications that these buildings have had over the centuries. The data that have been collected are an additional contribution to this controversial issue.

The absolute dating methods of building materials are, in part, still experimental, and they should be evaluated in their reliability. The varying success in the dating and the usually poor precision achieved by traditional decay counting on limited samples resulted in reluctance to use the method and it has not been fully accepted as an archaeological tool. Unfortunately, it seems that the awareness of the many possible problems has had a discouraging effect on the development of the method and only a few systematic studies of the problems and how to control them can be found in literature (Lindroos, 2005).

The possibility of adopting for the first time on the same set of samples, from such important case study, different experimental techniques has given a significant value to this research. The comparison of different absolute dating techniques also provided important considerations on the state of the art in that topic, at this moment in a very delicate phase. While the level of accurate dating reached today has come further, on the other hand there is still very widespread scepticism among insiders.

This thesis presents how different preparation techniques have been used and how successful they have been. The benefits from lime lump analyses versus bulk mortar analyses will also be discussed. The dating of multicomponent mortars and hydraulic mortars (as most problematic topics) addressed the experiments in this direction. Once identified the most suitable techniques to properly date mortars with such a level of contamination and complexity, then it will be possible to date other samples, from a wide range of environments.

A reliable dating of mortars would also provide information about the history of the restoration and strengthening of the structures damaged by earthquakes. The dating of these interventions is a
fundamental contribution to the update of the catalogue of ancient earthquakes and to understand the evolution of the seismic sequences of the past, mostly unknown or poorly documented. For this important future implication this research has found the support by UNESCO.

1.1 National and international collaborations

The chemical, mineralogical and petrographic characterisation of mortars and plasters has been carried out at the Department of Chemical and Geological Sciences, of UNIMORE. In particular, Prof. A. F. Gualtieri, his PhD students and Prof Galli actively collaborate to the study of the binder hydraulicity.

Many different scientists from other institutions have generously contributed to the work:

National collaborations

a) The Research Centre for Isotopic Cultural and Environmental Heritage (CIRCE) of Caserta provides their method and their laboratory for sample preparation (Cryo2sonic) and the $^{14}$C dating via AMS (Accelerator Mass Spectrometry).

b) The Department of Materials Science of the University of Milan Bicocca and the Department of Physics and Astronomy, University of Catania offers for Optically Stimulated Luminescence (OSL) dating of mortars and Thermo Luminescence (TL) dating of bricks.

International collaborations

a) Dr. Alf Lindroos from the Åbo Akademi University, Turku in Finland, worked with me for the extraction of binder materials and in the application of their method of sample preparation.

b) Dr. Jan Heinemeir as director of the Centre for AMS $^{14}$C dating of the Danish University of Aarhus, dated the prepared samples.

c) Prof. Johannes Weber, University of Applied Arts of Wien, Department of Conservation Science and Dr. Farkas Pinter, Federal Office for the protection of monuments (BDA) of Wien have participated in the study of mortar hydraulicity.

1.2 Aim and problem definition

1.2.1 Objectives

This study aimed to achieve the following objectives:

- Get more information on the technology of production, raw material sources and features of
the building materials used during the construction of the monuments of the UNESCO site of Modena.

- Provide new considerations about the relative dating of the walls, in order to better understand the phases of construction of the Cathedral and the tower and to verify what has been suggested by previous researches.
- Perform the absolute dating of the phases of construction of the main monuments of Modena UNESCO site.
- Test if the techniques in use for separation of the binder from contaminants can be applied to the particular characteristics of this type of mortars.
- Check the experimental absolute dating methods available on a specific case study.
- Find out which absolute dating method is the most suitable for this case, highlighting capabilities and limits of each technique.
- Integrate the results obtained to reduce the intrinsic errors of dating methods.

### 1.2.2 Problem definitions

This research can be divided into two main areas: the first part has been dedicated to the detailed characterisation of mortars and plasters and the second to the absolute dating of the building phases of the Cathedral and the Ghirlandina tower of Modena.

In the first part, a long process of systematic sampling, microscopic textural and compositional studies are presented. Mortars and plasters provide important information on local raw materials and the history of the building techniques. Classifying the types of mortars allow to understand the relationships between the various architectural units and mortars with specific functions. This characterisation requires the identification of the constituents and the determination of their relative proportions (Lugli et al., 2009 and Lugli et al., 2010).

This part has included a parallel study on the mortar binder. The idea has come because in many samples were recovered fragments of binder related particles that have allowed us to identify the sources of supply of limestones. This impure material by its nature has provided to the ancient workers a hydraulic binder, little known and used up to that time. This finding led us to investigate this topic, a complex issue from a chemical mineralogical and technological point of view.

The study of the historic natural hydraulic limes is challenging because of several issues: (i) the frequent impossibility to separate the binder from the aggregate; (ii) the high variability in composition of ancient mortars; (iii) the rapid change in composition that may affect hydraulic minerals over time (Elsen et al., 2010).
The second part is the main intention of the work: the application of the absolute dating techniques of building materials to a real case study, the UNESCO site of Modena. According to art historians the Cathedral and Ghirlandina tower of Modena were built in at least five phases (Labate, 2009; Peroni, 1984; Silvestri, 2013; Lomartire, 2010; Quintavalla, 1965). The dates known from historical documents have been used to constrain the results of the absolute dating methodologies.

The stratification of plasters and the analysis of mortars can be a useful tool to learn more about the age of the structures (Labate, 2009). The problem of absolute dating of individual building periods can be partially solved by studying the elements that contain dateable material (e.g. pigments, organic fragments, inscriptions, archival documents) and those with unknown chronology. Nevertheless, it is frequently difficult or even impossible to exactly know the relationship with the building construction time. The absolute dating of the setting of a lime mortar by means of radiocarbon represents a great advantage and an important improvement for historic reconstructions (Labeyrie and Delibrias, 1964; Stuiver and Smith, 1965; Van Strydonck et al., 1986; Heinemeier et al., 1997; Lindroos et al., 2007; Nawrocka et al., 2009; Heinemeier et al., 2010; Marzaioli et al., 2011).

The radiocarbon dating technique now permits to directly date mortars and plasters of historical buildings with a standard deviation of a few tens of years. This methodology may be used only if samples are adequately prepared, avoiding the contamination of components of different ages, such as, for example, the sand added to the lime to obtain the mortar. Furthermore, it is not yet possible the dating of multicomponent and hydraulic mortars and still many experiments in this direction should be made. In this research is proposed the comparison between two different sample preparation procedures for the radiocarbon dating of mortars.

The luminescence dating techniques have been applied on mortars and bricks to test with independent methodologies the results of radiocarbon dating. The same samples were divided between two laboratories in order to compare the results because, in particular the OSL dating of mortars, is still an experimental procedure.

Far from having exhausted all the topics covered, this work has resulted in several interesting findings that would contribute to the debate.

1.3 Structure of the thesis

Step 1 - Literature search - State of the art
The literature research aimed to i) briefly retrace the history of the use of lime mortars, focusing on the natural hydraulic lime; ii) define the mortar constituents, consulting the European norms (RILEM and UNi-Normal); iii) describe the historic process of production and the features and/or the characteristics that this induces in historic mortars; iii) review the recent scientific literature concerning the characterisation and the absolute dating of mortars and plasters.

**Step 2 - Case study: the UNESCO site and the studies on construction phases**

The art historical literature search was mainly focused on the history of the construction of the Cathedral and the tower Ghirlandina. In addition to many publications on the subject, even previous thesis of the University of Modena and Reggio Emilia have been consulted (Tintori, 2009; Rossetti, 2009; Maiorano, 2010; Melloni 2010; Pedrazzi, 2006).

**Step 3 - Sampling**

The restoration works permit the access to the scaffolding holes, reopened for the occasion. This has ensured the collection of sufficient quantities of mortar.

Samples in order to represent the different construction phases of the Cathedral and the tower were collected for radiocarbon dating. The sampling for OSL and TL dating were specifically conducted with the extraction of cores avoiding the exposure to sunlight that would invalidate the OSL measures.

**Step 4 - Petrographic characterisation of mortars**

The methodologies for the petrographic analysis of the mortars were the same applied for the study of other buildings in the area of Modena from the same workgroup (Lugli, 1996; Lugli, 1997; Lugli, 2000; Lugli, 2010; Lugli et al., 2013). From the samples of mortar and plaster were prepared standard thin sections to be observed with the petrographic microscope. Point counting analysis and image analysis aimed to determine quantitatively the mortar parameters in order to identify distinct groups (Lugli et al., 2007).

The characterisation of the binder itself have required a thorough analysis and the use of different scientific techniques for those constituent parts that could not be identified by standard microscopy.

The preliminary mortar characterisation is also a fundamental step for the correct application of the radiocarbon dating.

**Step 7 – Absolute dating of mortars**

With the aim to verify the relative chronology and to provide some absolute dates, experimental methodologies have been applied in the second part of the thesis. Firstly, the radiocarbon dating of
the lime binder and the test of the two most accredited sample preparation procedures: Cryo2sonic and sequential dissolution.

The luminescence dating techniques have been applied on mortars and bricks to test with independent methodologies the results of radiocarbon dating.

**Step 8 - Contribution to the definition of the phases of construction**

Combining previous studies by art historians, the distinction of the mortar typologies that characterised each construction phase, the results of the radiocarbon dating and the OSL dating on mortars and the results of TL dating of bricks it has been possible to contribute to the definition of the construction phases of the Cathedral and the Ghirlandina tower of Modena.
2. MORTARS AND PLASTER DATING: STATE OF THE ART

From a historical perspective, lime has been one of the most important materials used in construction. The oldest example of its use, dating back to 12000 BC, was found in Palestine and Turkey (Kingery et al., 1988). Other archaeological studies of ruins excavated in Çatalhüyük (Turkey), dating between 10000 and 5000 BC (Von Landsberg, 1992; Kingery et al., 1998), showed the use of lime in the construction of floors and paving (Mellaart, 1967). The earliest known concrete is that of a floor discovered in 1985 in southern Yiftah in Galilee (Israel) dated to 7000 BC (Bensted, 1997; Bensted and Coleman, 2004).

These archaeological findings, along with the remains of 4500 years old lime kilns found in Khafaje, Mesopotamia, confirm that lime was a common building material during Neolithic. In Egypt there are a few evidences of the use of lime before the Ptolemaic period (Davey, 1961). However, Egyptians used more frequently gypsum due to the lower firing temperature and thus for a lower fuel consumption (Pecchioni et al., 2008). Nevertheless it is only with the Roman period, at the end of the third century BC, that this material was systematically used in architecture and widely spread (Cagnana, 2000).

Romans hydraulic binders, prepared with the addition of pozzolans, are deeply studied, whereas hydraulic limes made from natural impure clay-limestone are not so well documented. The first type of lime in use, the “air lime”, hardened when exposed to air, but Greeks and Romans discovered that the calcination of marly limestones, yielded a binding material hardening underwater (hydraulic setting) and with improved mechanical properties (Malinowski, 1981; Navarro, 2004). In Romans treatises there is not any mention of the hydraulic properties obtained by burning marly limestones, which is documented only from the middle of the 16th century with the work of Philibert Delorme: “Architecture”. Although the official birth of NHL (Natural Hydraulic Lime) is usually connected to John Smeathon’s product, which was used to rebuild the Eddystone lighthouse in 1756 in England, there are also several well-known examples from the Middle Ages where the application of lime binders with natural hydraulic characteristics can be supposed. However, the deliberate use of these materials cannot be inferred. From the late 18th until the mid 19th century, a continuous development of the hydraulic limes can be observed, leading to the invention of Portland cement (Callebaut et al., 2011).

The following are the basic terms concerning mortars and plasters as defined by UNi – NORMAL and RILEM committee.
2.1 Mortars and plasters: definitions and technology

Mortars and plasters are defined as artificial building materials because they have acquired structural and textural characteristics similar to natural stones through a technological process. Since they are heterogeneous materials, they are subjected to large variations as regards components (raw materials) and structure (manufacturing and setting). The mixture is composed of binders, aggregates, water and, eventually, other organic or inorganic components in order to obtain a suitable workability of loose material and high resistance once hardened.

Even if mortar is used as a general term to indicate a binder/aggregate mix used in construction, more specifically it refers to a mix used to bed masonry blocks (pointing) or to fill a cavity between two masonry leaves (wall core). Conversely, the term plaster indicates a wall covering which, in addition to the protective function, commonly assumes an aesthetic function. Commonly plaster refers to internal surfaces, while render refers to external surfaces. Internal plasters can contain gypsum (calcium sulphate hydrate) as a component of the binder. The external covering can be smooth (and it can be also called plaster) or it can have an application of gravel as the outer layer.

2.1.1 Binders

The binder is defined as a material (or a combination of two or more) that, mixed with water, forms a plastic mass. It serves to connect the various materials used in a building construction (bricks, stones blocks). Once hardened, it forms a structure able to withstand mechanical stress. The most important feature used to classify a binder is the environment in which it can solidify: it can be called aerial or hydraulic depending on whether the process of setting and hardening take place, only in air or even in underwater environment. Lime and gypsum are typical air binders; hydraulic lime and cement are typical hydraulic binders.

Lime (non-hydraulic): general term to indicate pure lime, containing only calcium hydroxide (Ca(OH)\(_2\)), also known as fat lime, air lime, or high lime.

Quicklime: is composed primarily of calcium oxide (CaO), produced by burning calcium carbonate at a temperature of approximately 950°C.

Slaked lime or Hydrated Lime: consists of calcium hydroxide (Ca(OH)\(_2\)), mineral portlandite), which has been obtained by adding water to the quicklime. Depending on the amount of water it gives rise to lime hydrate, slaked lime or lime putty. The slaked lime is the raw material for mortar preparation.

Dry hydrate: in which calcium oxide (quicklime) has been hydrated with a stoichiometric amount
of water sufficient to form calcium hydroxide in the form of a dry powder.

**Lime Putty:** a form of non-hydraulic lime in which calcium oxide (quicklime) has been hydrated with excess water to form a soft white paste, thick and oily, easily workable.

**Hydraulic lime:** material obtained by burning, at a temperature of about 1000 °C, marly limestones or impure lime, containing clays or other materials. The hydraulic properties are derived from compounds that are formed between the silica and the alumina (derived from the clay) and quicklime (CaO). In this case, the chemical set of the mortar is commonly quicker than the carbonation of pure, non-hydraulic lime. The strength of the chemical set can depend on the quantity of clays but also on the conditions of manufacture. Natural cement is a particularly strong variant of a hydraulic lime. Hydraulic limes cannot be stored in the form of putty as in the aqueous environment the chemical set will take place.

**Roman cement:** natural hydraulic limes produced by the burning of limestones containing clay materials and/or nodules of silica. The name was adopted because the distinctive brown colouration resembled mortars of the Roman period.

**Natural cements:** hydraulic cements produced by mining and burning deposits of limestone and clay with a specific chemical composition within a narrow range. Strength and uniformity of natural cements are lower than for Portland cements. Natural cements were common in 19th and early 20th century construction until superseded by Portland cement.

**Portland cement:** the product of the milling of Portland clinker and calcium sulphates. The Portland clinker is the product of firing a mixture of limestone and an alumino-silicate rock (clay or shale) in order to obtain, at a temperature exceeding 1400 °C, the complete transformation in dicalcium silicate (C₂S) tricalcium silicate (C₃S), tricalcium aluminate (C₃A) and tetra-calcium alumino-ferrite or simply ferrite (C₄AF). Portland cement is the most common form of binder used in concrete architectures. The colour is usually grey and it has been used in Italy since 1870. There are many forms of Portland cement and it is commonly possible to distinguish using petrographic thin sections: ordinary Portland cement, sulphate-resisting Portland cement, pozzolanic cement (obtained by grinding Portland clinker, calcium sulfate and pozzolan), cement blast furnace (obtained by grinding Portland clinker, calcium sulphate and slag), white cement (obtained from raw materials free of iron and manganese), aluminous cement, quick-hardening (obtained leading to melting a mixture bauxite and limestone).

### 2.1.2 Aggregate

The aggregate of a mortar is added to the binder in order to reduce the effects of mortar shrinkage,
to enhance the mechanical properties and there is also an economical aspect, because it is an inexpensive way to increase the volume of a mortar. The aggregate can come from incoherent sedimentary material resulting from the weathering of rocks as a result of natural processes or by mechanical crushing of rocks. Aggregate can vary in grain size from a fine powder (<0.1 mm) filling 1-2 mm joints, to coarse gravel (>50 mm) in wall core. The study of the composition of the aggregate provides information about the supply sources.

**Gravel:** sedimentary material in particle size of between 254 and 2 mm.

**Sand:** sediment grain size between 0.063 and 2 mm.

**Pozzolans:** siliceous or siliceous/aluminous materials which, in the presence of water, react chemically with calcium hydroxide to form compounds possessing cementitious properties. They differ from “hydraulic” or “latently hydraulic” materials, which due to sufficient amounts of calcium have the ability capable to form these compounds in the presence of water alone. The potential of a given pozzolan to react with calcium hydroxide, i.e. the pozzolanic activity, depends on several factors, amongst which are the lack of crystallinity, the fineness of the powder, the chemical composition and the degree of chemical weathering, all of which play major roles. Generally pozzolanic materials are poorly crystalline, amorphous or vitreous silicates and alumino-silicates of various origins. Thus, many volcanic tuff materials form natural pozzolans, commonly referred to as “pozzolana”. Diatomaceous earth is another natural pozzolan, while the powder of brick and pottery fired at low temperatures is an artificial pozzolan that has been used since ancient times. In the case of lime mortars, pozzolans introduce a hydraulic factor, which contributes to increased final strengths and higher durability, especially under the action of water.

### 2.1.3 Historic mortars: process of production

Historic mortars are a mixture of lime, Ca(OH)$_2$ (calcium hydroxide as the mineral portlandite) an aggregate, usually gravel or volcanic pyroclastic material. The mortar hardens when calcium hydroxide reacts with atmospheric carbon dioxide (CO$_2$) to form a binder of calcium carbonate (CaCO$_3$, the mineral calcite) and water:

$$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \quad (1a)$$

(portlandite + carbon dioxide $\rightarrow$ calcite + water)

Several steps are involved in the process:

a) Limestones were selected, collected (or quarried) and crushed for burning.

b) The limestones are fired in a kiln. A typical kiln was divided into two parts: the fireplace
and the upper part, consisting of a vault of stones for the calcination. The overlap of the kiln was a delicate phase as the limestones were laid in balance, without binder. Once completed, the fire had to be lit so that the flame crossed the layers of stones homogeneously. The entry for feeding the furnace with the fuel was located in the lower part. Calcination lasted some days and nights and thus, during this period, the workers alternated to maintain a constant temperature of about 800-900°C or exceeding. As a result of calcination, the calcium carbonate (mineral calcite) is transformed into quicklime or calcium oxide (CaO) developing carbon dioxide. The burning usually leaves calcite residues.

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 = \text{calcination}
\]

c) The calcium oxide is converted afterwards to calcium hydroxide (mineral portlandite) by water uptake, trough the slaking process, which is a strong exothermic reaction. There are different forms of slaking:

- wet slaking: the quick lime is thrown in water, convert to calcium hydroxide and stays as a lime putty in the wet environment. The longer the storage lasts, the smaller and finer are the calcium hydroxide particles and the quality of the slaked lime improves. The carbonate crust formed in the external layer of lime putty during the storage period can be a cause for lime lumps formation (Bruni et al., 1997).

- dry slaking or hot lime: stacking sand layers and quick lime. The slaking process starts and due to this process lime lumps are formed in the mortar fabric (Hughes et al., 2001 and successive).

- a third method is to mix quick lime with sand in a bucket, add a little water and use this mixture immediately. The slaking process starts while the mortar is applied to the wall and still there continues. A porous structure due to released water damp is the result.

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 = \text{slake}
\]

d) The lime is mixed with geological material or reused inorganic building materials. If this filler material or aggregate is sand or gravel (inert) the mortar is non-hydraulic. If the aggregate reacts with the strongly alkaline lime, other binder minerals than calcite are formed and the mortar is hydraulic. Reactive fillers are e.g. volcanic glass, burned clay minerals and ceramic splinter.

e) After preparation and application the mortar starts to set by drying. The portlandite reacts with atmospheric CO₂ to regenerate calcite (reaction 1a= set).
2.1.4 Binder related particles (BRP)

One of the most distinctive features of historic mortars is the presence of binder related nodules, “phenograins” according to the nomenclature by Diamond and Bonen (1993) or binder related particles (BRPs) according to Elsen (2006). In the case of lime mortars three types of BRPs, reflecting their respective grades of calcination, can be distinguished: i) underburned fragments, ii) overburned fragments and iii) lime lumps sensu stricto. However, the boundaries among the groups are fluid to some extent. As mentioned above, this is due to the particularities of the historic process of production. After the slaking phase, lime putty was filtered through a grille that could stop only the larger limestones relicts, which were not completely reactive. Furthermore, the raw feed of the traditional kilns was normally a fist-sized rock material with all its natural impurities and inhomogeneities. The temperature gradients in the furnaces were followed by temperature variations within every single stone, so that the result covered different grades of calcination and it favoured uneven conditions of reaction. The finer over- or underburned material was probably not removed manually from the lime putty and the final product was a blend of differently reacted lime grains (Gadermayr, et al. 2012).

The BRPs are generally coarse particle size, frequently up to millimetres, remaining well visible to the eye of the observer. Their study is nowadays considered with increasingly importance because it bequeaths significant information about the historic process of production as well as on the nature of the raw feed. Their surplus, however, indicates a poor production technology (lack of sieving) or even a difficulty in the calcination of the stone because of its composition (e.g. too marly) (Pecchioni et al., 2014).

The underburned fragments normally maintain the original rock structure and texture providing information about the type of limestones used for lime production and its hydraulicity. They commonly show micritic reaction edges that fade into the surrounding binder because in the external part the stones can be weakly reactive (Elsen, 2006; Lugli et al., 2013).

The overburned particles are formed in the hottest zones of traditional kilns where the temperatures are sufficient to melting or sintering the carbonates. The glassy structure totally erases the original structures and textures of the limestones. When the lime is sintered or vitrified it might be poorly reactive and thus it slowly participates to the processes of hydration and carbonation. Inside the mortar these fragments will slowly carbonate with the formation of minute calcite crystals of neoformation concentrated in particular areas. Mineralogical analyses on overburned fragments can provide information about maximum burning temperatures inside the kilns and the degree of hydraulicity of the mortar (Elsen, 2006 and references therein).
The most frequent binder-related particles are the so-called lime lumps *sensu stricto*. They are easily recognisable even with naked eye, because they are whitish, fluffy and soft. They consist of lumps of calcium carbonate with a porous microcrystalline structure and rounded edges. The most debated topic within the study of lime lumps is their formation. At present, most authors are divided into two schools of thought: those that believe the cause is related to the process of dry slaking, and those that believe the cause is related to slaking (Elsen, 2006). Dry slaking is at present the most popular theory within academics (Hughes et al., 2001; Callebaut and Van Balen, 2000; Carran et al. 2010). According Bruni et al. (1997), they would be fragments that result from not perfect mixing of the binder due to residues of the carbonate crust formed on the lime putty in the process of maturation. However, whatever the cause of their formation, lime lumps can provide information on the nature and the provenance of the raw materials and on the historic technologies, which were used in lime production and mortar preparation (Elsen, 2006). Their identification and selection becomes crucial in the case of mortar dating, as it will be explained in the next paragraphs.

2.2 Recent studies: understanding the problems

In this section recent publications are examined, regarding previous experimental studies about mortars and plasters characterisation and dating. The information gathered was useful to have a clearer picture on the state of the art.

2.2.1 Hydraulicity of ancient mortars

As it was mentioned in the previous chapter, the use of hydraulic limes in mortars is well known from ancient times. But ancient hydraulic limes made from natural impure clay-limestone are not so well documented. The study of the historic natural hydraulic limes is challenging because of several issues: (i) the difficulty of separating the binder from the aggregate; (ii) the high variability in composition and in the degree of hydraulicity of mortars due to the traditional production techniques; (iii) the rapid change in composition that may affect hydraulic binder materials over time (Elsen et al., 2010).

Natural hydraulic lime binders are obtained by the burning at temperature 800-1200°C of marly limestones or siliceous limestones. During the calcination of impure limestones, clays dehydroxylate, at 400 to 600°C. The resulting silica and alumina combined with CaO formed after the decomposition of CaCO₃ produces calcium aluminates and silicates (Callebaut et al., 2001). The setting and hardening of such mortars occurs both through carbonation of calcium hydroxide and through hydration of calcium silicates and calcium aluminates (Pecchioni et al., 2014). Dicalcium silicate (C₂S) is the main phase that reacts with water causing their hydraulic setting, unlike in the
case of cement where tricalcium silicate ($\text{C}_3\text{S}$) is the main hydraulic phase (Callebaut et al., 2001; Navarro, 2004).

Calcination

$$\text{CaCO}_3 + \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \rightarrow \text{CaO} + \text{CO}_2 + \text{SiO}_2 + \text{Al}_2\text{O}_3 \text{Fe}_2\text{O}_3$$

$$\text{CaO} + \text{SiO}_2 \rightarrow 2\text{CaO} \cdot \text{SiO}_2 \, (\text{C}_3\text{S})$$

$$\text{CaO} + \text{Al}_2\text{O}_3 \rightarrow \text{Ca-alluminates} \, (\text{C}_2\text{AS}, \text{C}_{12}\text{A}_7 \text{etc.})$$

$$\text{CaO} + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \rightarrow \text{brownmillerite, ferrite} \, (\text{C}_4\text{AF})$$

Hydration:

$$\text{C}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{CSH}$$

$$\text{C}_2\text{AS} + \text{H}_2\text{O} \rightarrow \text{C}_2\text{AH}_8$$

$$\text{C}_4\text{AF} + \text{H}_2\text{O} \rightarrow \text{C}_4\text{AFH}$$

Understanding the hydraulic properties of a lime binder caused by silica components and clay impurities in the raw material is commonly a difficult task, especially in the case of historic binder because they underwent to many changes and alterations during their centuries-old life. The general reactions occurring in the setting of hydraulic lime are known but determining the presence of the reaction products and identifying the mineral phases is not easy (Charola et al., 1999).

The main limitation is the impossibility to separate the binder from the aggregate. Generally, most authors (Maravelaki-Kalaitzaki et al., 2005; Bruno et al., 2004; Miranda et al., 2008; Elsen et al., 2004; Adriano et al., 2008; Santos Silva et al., 2008) achieved by dissolving a part of the mortar, or a previously disaggregated fraction of the mortar, in hydrochloric acid (HCl). Among different laboratory procedures, the best results were obtained by the hydrochloric acid hot attack. This procedure was successful for a great number of different types of mortars, but except for those types with limestone aggregate, because the chemical differentiation with the binder phase is impossible and a significant contribution of the aggregate can never be ruled out (Alvarez et al., 1999).

Other studies (Yücel and Gülmez 2005; Bonilla et al. 2008; Starinieri et al., 2008) mention the analyses of the bulk mortar or a smaller grain size fraction after gentle disaggregation and sieving. The binder-enriched fraction, passed by a 63µm sieve, in theory would contain a majority of binder but it cannot be considered as pure because of contamination from fine aggregate.

The main analytical technique for mineral phases identification is XRD, but, for example, it cannot
distinguish between calcite of the aggregate from that of the binder (Middeldorf et al., 2005).

Furthermore, XRD can only successful detect the crystalline phases that result from carbonation and hardening. Most CSH phases, formed after the hydration of calcium silicates, are calcium silica gels, with a very low crystallinity degree and thus they cannot be clearly identified with this technique. In addition, a small amount of C\textsubscript{2}S (<2-3\%) is also not detectable with XRD, because it only clearly identifies phases when they are present in sufficient quantities, usually a few wt% (Middeldorf et al., 2005).

The most common classifications to attempt the measure of the hydraulicity are done by the ratio of the chemical oxides compounds using the CI (Cementation index) or the HI (Hydraulicity index) (Elsen, 2011), but these formulae have no sense in the cases in which the contribution of the aggregates is not negligible.

\[
CI = \frac{2.8SiO_2 + 1.1Al_2O_3 + 0.7Fe_2O_3}{CaO + 1.4MgO}
\]

\[
HI = \frac{SiO_2 + Al_2O_3}{CaO}
\]

The hydrated hydraulic phases in hydraulic lime mortars are amorphous and they cannot be identified with conventional petrographic microscopy and XRD, as previously stated. SEM-analysis at higher magnifications allows the recognition of the microstructure of such hydrated hydraulic phases and with EDS analysis, the chemical composition of the phases can be determined (Eckel, 2005; Franzini et al., 2000; Biscontin et al., 2002; Pinter et al., 2009). However, a first important observation is that the binder can be very heterogeneous within one mortar sample (Elsen, 2011). By looking on a smaller scale, Elsen (2011) and Mertens (2009) noticed that the hydraulic binder does not consist of a single phase, but it appears to be composed of at least two distinct components that are intimately intermixed. A composition close to pure Ca-carbonate is intermixed with phases rich in Si, but the composition of the different phases is variable. The hypothesis put forward from the authors is that segregation occurred in the C-S-H phase, whereby Ca and Si have moved into separate phases. This consideration is validated by the calculation of the Ca/Si ratio that result to be similar to those of CSH. The spatial distribution of the Ca-rich phases appears to be consistently located on the outside, adjacent to the pores and enclosing the zones richer in silica. Unfortunately, microprobe analyses can only reflect the chemical composition at specific point in the binder and the quantification of the oxides is not accurate, and thus it does not necessarily reveal the exact mineralogy of the different components. For this reason, the authors integrated SEM results with X-ray diffraction pattern of the binder-enriched fraction. Calcite was found in each sample but also
vaterite (CaCO₃) and aragonite (CaCO₃), other Ca-carbonate polymorphs, were observed in many samples. Remarkably, their occurrence appears to be related to the hydraulicity of the samples. Vaterite and aragonite are generally considered to be less stable compared to calcite at atmospheric pressures and near-room temperatures. Therefore, they do not occur upon carbonation of pure lime (portlandite). However, these two polymorphs were proven to form upon carbonation of CSH. This phase evolution might have consequences for the bulk chemical analyses, since the dissolution of these neo-formed phases might differ significantly from that of the phases initially present. This phenomenon was named “vanishing hydraulicity” (Mertens, 2009; Elsen, 2011). Lindroos at al. (2012) also found vaterite in fire damaged mortars.

Another technique widely used to the study of mortars hydraulicity is the TG/DTA analysis. Some authors contend that it is possible to distinguish between different mortar and binder types based on data derived from thermal analysis (Böke et al., 2006; Genestar et al., 2008; Maravelaki-Kalaitzaki et al., 2005; Moropoulou et al., 1995; Bakolas et al., 1995a; Bakolas et al., 1995b). However, according to others (Middendorf et al., 2005) the identification of hydrated hydraulic components in historic mortars using thermal analysis has not been convincingly demonstrated.

The TG-patterns can be divided in specific temperature ranges delimiting distinct processes. Some authors (Genestar et al., 2008; Bultrini et al., 2006) have suggested that a weight loss of hydraulic water (between 200°C and 600°C) over 3% indicates that the binder is hydraulic. However, this assumption must be considered with great care, as the amount of binder in the binder-enriched fraction is variable and dependant on the success of the binder/aggregate separation process. Lower amounts of binder in the <63µm fraction, will automatically result in lower weight losses. However, for an aggregate fraction that is mainly composed of quartz and feldspar, the proportions between the weight losses of the different dehydration/decarbontation processes will remain similar (Elsen, 2011).

The weight loss from a sample during thermogravimetry between 200-600°C represent all the structurally bound water in hydraulic components. Therefore, the ratio between the weight loss due to carbonation (>600°C) and the loss associated with the expulsion of hydraulic water is probably a better indication for the hydraulicity. Lower ratios are an indication of a strong hydraulic character, whereas high ratios point towards the presence of a pure lime binder. Whereas the samples classified as non-hydraulic generally yield ratios around 5 or higher, the samples classified as hydraulic, give ratios below 5. The TG analyses can therefore give an indication of the hydraulicity of a binder. Generally, the results of the TG analyses should be correlated with the results derived from the chemical and/or X-ray diffraction analyses (Mertens, 2009).
However, it is important to underline some limitations regarding the interpretation of TG results. Water loss from calcium-silicate-hydrates phases (CSH) takes place at a similar temperature to some clays (Ellis, 2000). The main hydraulic clinker phases C₃S and C₂S undergo phase transitions at a range of discrete temperatures from 500°C to 1425°C. This in principle permits the identification of unhydrated C₃S and C₂S in hydraulic mortars. However C₂S, which is likely to be more common in natural hydraulic lime and mortars found in historic buildings due to the lower temperatures required for its formation, undergoes its phase transitions at temperatures in excess of 693°C (Taylor, 1997). It is at approximately this temperature that calcite begins to disassociate. As calcite is generally a dominant phase in historic mortars, it may mask the identification of C₂S (Middendorf et al., 2005).

Schäfer and Hilsdorf (1993), who correlated the compositions of historic mortars to the physico-mechanical properties, used a completely different approach. New formulations were also tested using lime putty, hydrated lime, semi-hydraulic lime and hydraulic lime. From the correlation of open porosity (dependent on the original water-binder ratio) and the mechanical strength of the mortar it was possible to determine if the binder contained some hydraulic components or not. On the other hand, the correlation also made it possible to estimate the mechanical properties of a historic mortar knowing its binder nature and the open porosity. This approach may well serve as a guideline for matching new mortars to existing ones in historic structures (Charola, 1999).

It is however difficult to determine whether the hydraulicity of a mortar is induced by the addition of the supplementary materials, or by the use of natural hydraulic lime. An analysis of the Binder Related Particles can be therefore useful. The chemistry of the BRPs is expected to be identical to that of the limestone used to prepare the lime (Elsen, 2006). Even for 19th century NHL mortars is difficult to determine the hydraulicity because their texture exhibits characteristic appearance of a pure air lime binder (micritic structure, shrinkage cracks, etc.). Thus, also in this case it is suggested the use of microscopic study of the residual hydraulic phases in the form of lumps, containing different hydrated, unhydrated or unreactive phases such as belite, gehlenite, wollastonite or calcite. Normally, hydraulic residual components are surrounded by a diffuse and carbonated hydration rim (Pinter, 2014).

In conclusion, it is possible to say that even though petrographic analysis cannot precisely quantify mortar hydraulicity, it enables to discern whether a mortar is hydraulic or not and the source of its hydraulicity. The presence of both crystalline and amorphous C-S-H, portlandite crystals, relicts of unhydrated clinkers, hydration layers and pozzolanic reaction rims as well as the identification and arrangement of amorphous silica and alumino-silicates can be determined with petrography.
providing evidence of hydraulicity (Pavia, 2008).

2.2.2 Dating of mortars and plasters by radiocarbon

The $^{14}$C dating of lime mortars is a useful tool in archaeological and architectural research, because the carbon dioxide absorbed from the atmosphere during mortar setting can be used to assess the construction timing of a building. The radiocarbon dating, however, could be distorted by contaminants that can commonly occur in historic mortars: fragments of binder related particles or limestones of geological origin mixed as aggregate may provide older age. On the other hand, younger dates can be acquired if later exchange with the atmospheric CO$_2$ occurred after the construction, producing the formation of secondary calcite within the calcareous binder.

Dating mortar is principally based on rather simple inorganic chemistry. Considering the equation (1a) radiochemically, it is written as:

$$\text{Ca(OH)}_2 + [^{14}\text{C}]\text{CO}_2 \rightarrow [^{14}\text{C}]\text{CaCO}_3 + \text{H}_2\text{O}$$

Fig. 1: The CaCO$_3$ cycle from limestone to binder calcite. From Hale et al. (2003).

The carbonate formed can be dated with $^{14}$C because it has captured atmospheric CO$_2$ and fixed it to a mineral. These basic principles are, of course, well known (Fig. 1). Problems arise when other carbonate phases affect the $^{14}$C system so that it may not date the carbonate binder accurately (Lindroos, 2005). These problems have been described extensively (e.g., Van Strydonck et al. 1983a,b; 1986; 1989; Van Strydonck and Dupas 1991; Ambers, 1987; Heinemeier et al. 1997 with further references). The method has not been fully accepted as archaeological tool because not always the dating have brought reliable results and they are commonly characterized by poor accuracy, especially if derived from traditional counting decay on a limited number of samples taken. Unfortunately it seems that the many problems that have been highlighted have hampered the development of the method and only few systematic studies of the problems and their control can
be found in the literature (e.g. Pachiaudi et al., 1986; Ambers, 1987; Van Strydonck et al. 1989; Van Strydonck and Dupas, 1991).

The first mortar dating, using radiometric methods, were attempt in the 1960s, by thermal decomposition at 900°C of crushed mortar samples (Labeyrie and Delibrias, 1964; Delibrias and Labeyrie, 1965). The carbon dioxide was precipitated in a barium hydroxide solution. After acid hydrolysis of barium carbonate the CO$_2$ released was collected for decay counting measurement.

Later, the acid hydrolysis, with diluted HCl at different temperatures, was introduced directly on crushed samples (Stuiver and Smith, 1965). Baxter and Walton (1970) were the firsts to understand that when acid hydrolysis is applied, differences in the solubility among different carbonate phases can be exploit to achieve accurate dating results. Carbonate binder is irregular and poorly crystalline and it dissolves rapidly, while dead-carbon-bearing natural carbonate grains tend to be crystalline and dense and they dissolve more slowly. Folk and Valastro (1976; 1979) try to identify and remove the contaminating carbonates and they developed a dating method that utilized the difference in carbonate solubility. This chemical separation was mostly done with diluted hydrochloric acid (HCl). A relatively strong acid (~1M) was injected into powdered samples and water. Several small acid batches are injected in order to digest the sample stepwise, or alternatively, the sample powder could be split into several aliquots that were subjected to varying degrees of digestion. The so-called “Texas method” (Ambers, 1987) was tested and developed further by Van Strydonck et al. (1983a,b; 1986; 1989) and Van Strydonck and Dupas (1991). The dating were performed on a uniform grain size fraction of the sample by letting it react for only a short time with the acid and isolating the early fractions of effervescing CO$_2$ for dating. The CO$_2$ emanating from the residue was dated separately to monitor the degree of contamination. They have increased the number of dated CO$_2$ fractions from one sample by splitting it up into several aliquots, and using different partial dissolution for the aliquots. They faced the problem of increasingly larger samples and suggested that further work should be done with accelerator mass spectrometry (AMS).

The introduction of AMS was tried for the first time in mortar dating by Tubbs and Kinder (1990), and some datings were made in 1992 by Van Strydonck et al., but in general, there has been little interest in developing mortar dating by AMS. The method has two definite advantages compared to traditional decay counting: i) the sample size can be reduced from kilograms to grams; ii) the counting statistics are still better. Thus, less material is needed and the samples can be studied in more detail. The AMS radiocarbon dating offered the possibility to use very small mortar samples because it made possible to separate a rare isotope from an abundant neighbouring mass (as for
example $^{14}$C from $^{12}$C). The use of HCl has continued also in preparation for AMS analysis (Hodgins et al., 2011; Al-Bashaireh, 2013) but from the mid-1990s and onwards, it became common also to use 85% phosphoric acid (Heinemeier et al., 1997).

The small amount of carbon required (<1 mg) for AMS measurements made it possible to analyse only a very small fraction of the whole carbon inventory of the sample, or to take a very small piece of the sample (e.g. a lime lump without aggregate inclusions) for analysis. Lime lumps were frequently found in ancient mortars formed by the process of production (Hughes, 2010). Recently the potential of lime lumps dating have been studied and implemented (Pesce, 2011) but the contribution of calcination relics inside the lime lumps cannot be excluded because the petrographic observation cannot be done directly on the same sample.

The main problem is the elimination of the contamination (aggregate, calcination relics or crystallization of new calcite) that must be separated from the carbon belonging to the original binder. The methods, nowadays, most commonly used for samples preparation consist of a mechanical pre-treatment (Nawrocka et al., 2005; Marzaioli et al., 2011 and successive) or a chemical treatment (Heinemeier et al., 1997 and successive).

### Sequential dissolution (Lindroos group)

The method, used by Lindroos (2005) for the Århus AMS laboratory, is based on the principle presented by Folk and Valastro (1976) and developed by Van Strydonck and Dupas (1991). The method was completed with cathodoluminescence inspection and with a further developed incremental CO$_2$ extraction during dissolution (Lindroos, 2005).

The first step in this procedure is the alkalinity test using phenolphthalein dissolved in alcohol. An alkaline reaction may indicate the presence of calcium hydroxide, which will react with modern CO$_2$ in the atmosphere. Modern CO$_2$ will result in dating at a younger age than the archaeological age of the sample. Thus, alkaline samples are not usually dated (Lindroos, 2005).

The samples are broken into small pieces avoiding hammering because it will produce splinter from the aggregates considered as contaminants. The crushed material is vibrated in a sieve series. A fine-grained and relative narrow grain-size fraction window (the routine method uses either 46-75 or the 76-150µm grain size) is selected for washing, drying and homogenization (Lindroos, 2005).

One larger piece of intact mortar is saved for preparation of a thin section for mineralogical microscopy and cathodoluminescence (CL). The latter is especially sensitive when it comes to distinguishing between carbonate phases with slightly different crystallinity and trace element chemistry (e.g. Marshall, 1988). It is possible to inspect mortar pieces directly or after preparation
of cut and polished surfaces. The CL analysis is normally also carried out on the grain size fractions after sieving. The fine grains of the mortar after sieving are spread over a glass backing glued with a polysaccharide. It is possible to assess how many contaminants are in the grain-size fractions but the results are at best only semi-quantitative due to many problems (e.g. variable luminescence, segmentation problems, etc.; Lindroos, 2005). The most important factor determining the colour and intensity of the luminescence is the Mn$^{2+}$/Fe$^{2+}$ ratio in the calcite (e.g. Habermann et al., 2000).

The dissolution is done in a vacuum system and phosphoric acid is used because it has a low vapour pressure. Standard 85% commercial acid at 0°C is held in vacuum together with the sample powder and then tilted in excess over the sample. The CO$_2$ fractions were collected on the basis of reaction time (Heinemeier et al., 1997).

The phosphoric acid reaction is usually written:

$$\text{CaCO}_3 + H_3\text{PO}_4 \rightarrow \text{CaHPO}_4 + \text{CO}_2 + H_2\text{O}$$

Successive CO$_2$ increments during the reaction are extracted. Typically five increments from about 200 mg sample powders. At 0°C the reaction is relatively slow and the first fraction is usually produced in tens of seconds. The next three increments are collected during the following hours and the last increment after the sample has reacted overnight. The parameters $t$ (dissolution time) and $P$ (CO$_2$ pressure) are monitored and registered. $P$ is determined for each increment and the amount of C it contains is calculated. Thereafter it is split up into two parts. One part is collected in a glass ampoule and sent for MS and the other part is left for reduction to graphite for AMS (Lindroos, 2005).

![Diagram](image.png)

**Fig. 2:** graphic schematic presentation of the CO$_2$ extraction line used in the laboratory of the Abo Akademi (image from Ringbom, 2011).
Fig. 3: 14C profiles showing either convex or concave curvature. The horizontal grey bars along the x-axis denote the size of the extracted CO2 fractions relative to the total carbon yield (=1). If the sample includes rapidly dissolving mortar binder and slowly dissolving contaminants it will yield a concave curvature and the first CO2 to be released will have a 14C age close to the right archaeological age and any possible charcoal inclusions. A convex profile dipping steeply near the y-axis indicates the presence of rapidly dissolving young contaminants. The right age is difficult to read from the graph (figure by Lichtenberger et al., 2015, modified).

The contaminant activity in relation to the binder activity is well revealed in the 14C profiles (Fig. 3). If the sample includes rapidly dissolving mortar binder and slowly dissolving contaminants it will yield a concave curvature and the first CO2 to be released will have a 14C age close to the right archaeological age (the two “good mortars in figure 3). A convex profile dipping steeply near the y-axis indicates the presence of rapidly dissolving young contaminants. In such case the right age is difficult to read from the graph and it is usually rejected as unreliable (“bad mortars” in figure 3) (Lichtenberger et al., 2015).

Dating pozzolana mortars is less straightforward. In these cases, age profiles revealed a more complex pattern including contamination from young carbonates (Ringbom, 2014).

Even if mortar may be the only datable material present at the site of investigation, it may be possible to check the obtained mortar dates against other sources of information. Different reliability criteria (listed below) have been defined for the interpretation of the results (Heinemeier et al. 2010; Ringbom 2011). Criteria I and II can be used independently when there is no age control from other sources.

**Criterion I**

“The 14C ages of the first two CO2 fractions are the same (one sample per building unit is in principle sufficient for a conclusive result). The rationale behind this criterion is that if there is no age gradient (i.e. no increase in limestone contamination) from fraction 1 to fraction 2, then both
fractions are most likely free of contamination and therefore date the time when the mortar hardened. The quoted date of the mortar sample is based on fraction 1 only in order not to exaggerate the precision of the result (Heinemeier et al. 2010).

Most age profiles show an increase of contamination in later CO$_2$ fractions. If, however, the first fractions from the same building unit consistently yield the same age, the result is considered successful according to Criterion II (CII)

**Criterion II**

“Mutual agreement between the dates of the first CO$_2$ fractions in a series of three or more samples from one single building unit. The rationale behind this criterion is the following: although the age gradient indicates a degree of contamination in fraction 2 (and therefore possibly also in fraction 1) it is more likely that all first fractions have insignificant limestone contamination than all of them having the same amount of significant contamination, leading to the same age excess for all samples.

Many samples yield valuable data that are not sufficient for conclusive dating, but when put into a context it may help to clarify the chronology. However, they are not independently valid for dating, but need support of age control from other dating methods and other materials, such as dendrochronology and $^{14}$C analysis of organic materials embedded in the mortar”.

**Criterion III**

“Mutual agreement between the dates of the first CO$_2$ fractions in two samples from a single building unit” (Heinemeier et al., 2010).

**Criterion IV**

“Criterion IV describes a situation where the first CO$_2$ fraction from one sample in a building unit yields a date that fits into a relative chronology” (Heinemeier et al., 2010).

As stated in Ringbom et al. (2014) the following conclusions have been drawn:

“a) From pozzolana concrete results, only around 50% can be considered successful. However, most importantly, it has been learned why some analyses went wrong and what to avoid in the future. It has been demonstrated that mortars buried under volcanic masses are not suited for dating (Lindroos et al. 2011). The same applies to mortars taken from deep within the walls or from under marble slabs, where the hardening has been delayed. To be avoided are also mortars with crushed brick in the aggregate to make them water resistant (*cocciopesto*), e.g. for use in water cisterns (Ringbom et al., 2014).
b) Some of the unsuccessful results came from an early stage of the research, when only two CO₂ fractions were analysed, whereas a profile from analysis in five fractions would have been more informative (Ringbom et al., 2011). Experiments have further been carried out with mortars based on burnt shells, mainly with positive results (Orsel 2012a,b; Lindroos et al. 2014).

c) H₃PO₄ hydrolysis of non-hydraulic lime mortars, in age profiles of 2, or 4-5 CO₂ fractions, has generally been successful. Here, the expected age, as known from age control, was reached with the first CO₂ fractions of the age profile. The criterion discussion is useful and valid with H₃PO₄ hydrolysis of non-hydraulic lime mortars. H₃PO₄ hydrolysis of hydraulic pozzolana mortars has been less successful. Age profiles are hard to interpret, since several types of age profiles can be represented within the same building unit.

d) HCl hydrolysis of lime mortars results in confusing age profiles, where the plausible age is not necessarily reached at the beginning of the age profile, and should therefore be avoided. Yet, we have sporadically been able to identify the correct age at the first CO₂ fraction, and occasionally HCl is better than H₃PO₄ for pozzolana mortars. The reason for this variable behaviour so far remains unknown; we therefore discourage the use of HCl hydrolysis also for pozzolana mortars. HCl results cannot be interpreted with the same reliability criteria as H₃PO₄ results.

e) Most important, however, is the high percentage of success noted in the analysis of lime lumps embedded in the mortar, both in the case of lime mortars and pozzolana mortars. Here, the first CO₂ fraction tends to provide the most plausible results, which have generally supported our earlier interpretations of analyses based on the mortar proper. Lime lumps usually contain very little contamination by unburned limestone or marble, thus requiring fewer CO₂ fractions to obtain reliable dates. Above all, for dating Roman constructions, analysing lime lumps embedded in pozzolana mortar may be the solution” (Ringbom et al., 2014).

**Mechanical separation (Cryo2sonic, CIRCE group)**

The mechanical separation is based to the fact, that the limestone of aggregate is stronger and more resistant than the more porous mortar binder carbonate. Results of ¹⁴C dating show that improvement of the binder-aggregate separation process is necessary (Nawrocka et al., 2005).

The Centre for Isotopic Research on Cultural and Environmental heritage of SUN (Second University of Naples) has recently obtained some promising results in the radiocarbon dating thanks to the development of a procedure aiming to eliminate contamination that may occur in a mortar with cryobreaking, a double step of ultrasonication with different time-evolved suspensions and centrifugation (Nonni et al. 2013). The carbonate belonging to the binder fraction is characterised by a more easily breakable structure compared to the dead carbon. For this reason the binder goes
into suspension after the ultrasonication, whereas the limestone fragments remain at the bottom of the container. Only the suspended fraction collected after centrifugation is used for the \(^{14}\)C dating (Marzaioli, 2013).

The main advantages of the Cryo2SoniC methodology are i) the complete digestion of the laboratory isolated mortar fraction, avoiding difficulties in handling time-evolved fractions, and ii) the limited number of analyses per mortar to be performed that, after methodology accuracy evaluation, can be reduced to just one for each mortar sample.

The datable-fraction-isolation procedure is based on the development of a previously applied mechanical/physical procedure (Nawrocka et al., 2005). In this study mortars were delicately crushed, and then repeatedly frozen and thawed. Most of the soft mortar carbonate was separated from the aggregate grains. After that, with binocular observations, the required amount of sample material was collected.

![Schematic representation of the Cryo2SoniC procedure.](image from Nonni, 2014)

The new procedure, described by Marzaioli et al. (2011), was first applied to lime lumps (CryoSoniC) and, successively, laboratory mortar samples were prepared according to the traditional production process. In this case, it was known the isotope signature of laboratory CO\(_2\) and it was guaranteed the absence of any other contaminant sources (e.g., lack of added aggregates). The only contaminant sources left were residues of underburned limestone. The dead carbon
suppression efficiency was tested comparing the ages of CryoSonIC isolated fractions of laboratory mortars with air CO₂ signature of the laboratory (Marzaioli et al., 2011). Results obtained from laboratory mortars, encouraged testing CryoSonIC on historic mortars sampled from archaeological sites with known age. The aim was to try the suppression of eventual aggregates related effects. Results highlighted the necessity to make some change the CryoSonIC procedure that was developed in Cryo2SonIC (Marzaioli et al. 2013; Nonni et al. 2013).

The key step assumed for CryoSonIC was the ultrasonication that enables to select the right fraction to date. Different ultrasonication time intervals were applied (from 10, 30, 45 up to 60 minutes) on the same sample. The resulting suspended fractions were isolated and dated. The 10 minutes fraction reached an age older than the others, which however show all similar results. The hypothesis put forward was that a first very old fraction suddenly enters the suspension and is mixed with younger fractions. The first produced fraction was related to fine aggregates contribution (and possibly to incompletely calcinated material mixed with Fe, Mg hydroxides or possibly to secondary calcite crystallization), so that the original ultrasonication procedure (Marzaioli et al. 2011) was split into two sub-phases obtaining a fraction called “sand” from the first ultrasonication of 10 minutes and fraction called “susp” from the second step of 30 minutes (Fig. 4) (Nonni et al., 2013). According to this theory the first fraction including fine and/or diagenetic calcite, should be more easily affected by contaminations than the second, which, on the contrary, should reach an age closer to the real value.

Cryo2SonIC can be resumed as follow:

1. **Cryogenical breaking.** According to Nawrocka al. (2005) about 5 g of mortar is submerged in liquid nitrogen, till the achievement of thermal equilibrium, and immediately transferred to an oven at 80°C. This cycle is repeated almost three times and mortars are broken by means of gentle hammering in order to avoid the production unwanted fine grain-size particles not belonging to the binder.

2. **Size selection.** The resulting material is sieved under 500 µm and deionized/decarbonated water (~40 mL) is added.

3. **1st ultrasonic selection.** After complete sedimentation (~12 hr), the powder is rewetted and ultrasonicated for 10 min. The suspended mortar particles are totally removed and transferred to a Falcon 50-mL centrifuge tube. This fraction of binder represents the fraction potentially affected by dead carbon contamination and/or diagenetic calcite (sand) due to the probable presence of very fine carbonaceous grains sands entering the suspension easily and before binder particles.
4. 2\textsuperscript{nd} ultrasonic selection. Residual powder, decanted on the bottom of the beaker undergoes to another ultrasonication for 30 min in excess (~40 mL) of distilled water. About 30 mL of water are collected by siphoning and stored in another Falcon centrifuge tube, taking great care not to induce a new suspension of the sediments. This last fraction, according to our experimental experience, represents the suspension guaranteeing accurate dating (susp).

5. Centrifugation. The Falcon centrifuge tube containing susp carbonates and the other containing the sand fraction, are centrifuged at 8.0 krpm in a rotor of 10 cm mean radius for 5 min and ovendried overnight (80 °C).

The selected fractions (susp and sand) are weighed and prepared for AMS measurement. About 40 mg of powders from selected fractions and carbonate standards samples (i.e. IAEA C1 and C2; Rozanski et al. 1992) are digested under vacuum to develop CO\(_2\), by means of a complete orthophosphoric acid attack for 2 hr at 85 °C.

The developed CO\(_2\) is cryogenically purified from other gasses, reduced to graphite on iron powder catalyst according to the CIRCE sealed-tube reaction protocol (the zinc process) following Marzaioli et al. (2008), and analyzed to measure \(^{14}\)C isotopic ratios using the CIRCE AMS system (Terrasi et al. 2008).

Based on the experience gained from the PhD research of Sara Nonni (2014), the following conclusions were drawn:

“a) A mortar with a sandy aggregate made of quartz and feldspar will be generally successfully dated using Cryo2SoniC pre-treatment.

b) A mortar with a pozzolanic aggregate will be generally successfully dated using Cryo2SoniC pre-treatment. To balance low availability of CaCO\(_3\), in pozzolana mortars (because the binder is full of hydraulic components), it is recommended to collect a larger amount of material.

c) A mortar with a calcareous aggregate will be dated using Cryo2SoniC pre-treatment only if the size of aggregate grain is coarse. Hardness is also a fundamental feature to avoid the grains breakage during protocol steps. If pure lime lumps are found in this type of mortar it is suggested to prefer them for dating.

d) A mortar with a fine-grain calcareous aggregate can give unreliable results even after Cryo2SoniC pre-treatment. Accurate datings are only obtained if performed on lime lumps.”

Some general behaviour should be avoided:
“a) Sampling of sections of wall so much deeper than the original surface (i.e. the inner part of a core drilling). Deeper mortars set more slowly than superficial ones. This could lead to a rejuvenation phenomenon on radiocarbon dating, from few to hundred years (Sonninen et al., 1985).

b) Sampling surfaces directly exposed to weather action. It should be preferred the sampling of an immediately closer inner layer to the superficial one. The outdoor surfaces of mortar could show a rejuvenation effect on final radiocarbon age due to secondary calcite.

c) Sampling on layers directly exposed to flowing waters, groundwater or involved in flooding episodes. It is recommended to get information about the presence of floods or groundwater risings at interested areas, in order to avoid bias in radiocarbon dating. Meteoric water will rejuvenate while groundwater will increase the age of the mortar.

In conclusion, the use of Cryo2SoniC as separation method has shown a satisfactory level of applicability, reaching a good degree of dating reliability.”

2.2.3 Dating of mortars and bricks by luminescence techniques

The idea of using the phenomenon of stimulated luminescence, and in particular of thermoluminescence, for dating pottery dates back to the early 60s (Tite and Waine, 1962). However, first articles about dating were published 20 years later (TL: Aitken, 1985 and OSL: Huntley, 1985). Soon after thermoluminescence became a dating tool for archaeological ceramics, its potential for dating brickwork was discovered by Fleming (1979). This study was followed by extensive researches to improve the measurement protocols (Goedicke et al., 1981). Architectural historians very much welcomed the new absolute dating method, as conventional methods such as stylistic investigation, documentary research and dendrochronology have limitations, whereas the error of radiocarbon dating commonly exceeds the required precision of architectural research. As a major advantage, this new method also includes secular buildings, for which documentary evidence is usually lacking.

Only in the last decade, the dating of historic buildings through TL analysis became a routine technique for the study of different chronological historical sites (Bailiff and Holland, 2000). Nevertheless, thermoluminescence cannot solve all the problems concerning the dating of historic buildings, because of the problem related with the frequent reuse of bricks (Martini and Sibilia, 2006). Furthermore, there are structures that are made with unfired brick or natural materials such as natural stones and mud bricks that can obviously not be dated with thermoluminescence.
In order to overcome these limits in dating historical buildings, the attention was recently dedicated to mortars. They represent a class of materials prepared just before its use. The possibility to use mortars to evaluate the time of construction, repair works or modification of a structure represents a great improvement in dating historical building. The application of dating methodologies based on luminescence emissions of crystalline fractions requires the identification of the inclusions that could play the role of dosimeters. In this case, the fine-grained quartz crystals contained in the aggregates can be used as dosimeters for which the exposure to daylight during mixing and laying acted as bleaching event (Bøtter-Jensen et al., 2000).

Luminescence investigation on the minerals in mortars started for retrospective dosimetry application (Bøtter-Jensen et al., 2000) using the OSL emission of sand-sized quartz (90–180 µm). They confirmed that the grains were bleached to a considerable degree during mixture. This evidence highlighted the potential of using mortars for dosimetric purposes. The low levels of dose involved in this kind of investigations required the use of quartz inclusions larger than 350 µm (Göksu, 2003). A first attempt to perform optical dating on mortars was carried out by Zacharias et al. (2002) on 90–250 µm quartz inclusions extracted from samples taken from two Byzantine churches. The authors also performed TL dating on brick fragments associated with the mortars. The results were characterized by quite large uncertainties and the lack of material prevented more extensive researches (Zacharias et al., 2002).

In recent years have been conducted systematic studies on the analysis of the OSL signals of mortars, the different techniques of sample preparation (Fine Grain, Coarse Grain and Single Grain) (Gueli et al., 2010; Stella et al., 2013) and the different types of light stimulation (Blue-LED, IR, Green-LED). It was recognized as a more reliable analysis the luminescence of small amounts of quartz grains and recommending the use of the Single Grain technique on quartz with green light if there is a low, and not homogeneous, level of bleaching of the sample (Goedicke, 2011).
3. CASE STUDY

The construction history of the Modena site represents a challenging case study for the application of absolute dating methods. First of all, because building materials have been fully investigated (Lugli et al., 2010) and a relative chronology among the construction phases was determined. The true dates, given from the few historical documents available, were used as time references to validate the different absolute dating results.

3.1 The Modena Medieval UNESCO site

The monumental complex that includes the Cathedral, the Civic tower Ghirlandina and the buildings facing square “Piazza Grande” in Modena, was listed as UNESCO World Heritage site since 1997 (Fig. 5). These buildings are considered masterpieces of Romanesque architecture as the result of the work of exceptional artists: the architect Lanfranco (11th – 12th cent.), the sculptor Wiligelmo (11th–12th cent.) and the Campionesi Masters (from the end of the 12th cent.), the latters native of the north of Lombardy (Italy). The two major monuments were built at the behest of the Modenese community between 1099, date of the Cathedral’s foundation, marked on a stone on its façade, and 1319, when the construction on the Ghirlandina was completed (Piccinini, 2009).

![Fig. 5: the UNESCO site of Modena.](image-url)
Cathedral

Lanfranco and Wiligelmus are the names written on the famous inscriptions on the stonewall covering of the Cathedral and they are, respectively, the main architect and the sculptor, authors of the project and its realization. All the historical events of the construction of the Cathedral can be summarized by the three dates reported by inscriptions: the oldest one (re voxlated in the beginning of the thirteenth century) is on the major apse (Fig. 6) and it is referred to the translation of the relics of Saint Geminianus from the old to the new Cathedral, in May 30th, 1106. It is also celebrated the architect Lanfranco as the work supervisors.

Fig. 6: the oldest inscription on the major apse. It is referred to the translation of the relics of Saint Geminianus from the old to the new Cathedral, in May 30th, 1106. It is also celebrated the architect Lanfranco as the work supervisors.

The leading role of Lanfranco is highlighted even from the “Relatio de innovatione ecclesiae Sancti Geminiani” a book of miniature with exceptional documentary value, written by the canonical Aimone of Modena. This text describes the building construction. Probably the inscription comes first this document, because in the stone plaque it is not remembered the consecration by Pasquale II that took place in 1106. Thus, it probably dates back to the first five years of the construction of the Cathedral (Campana, 1984). The construction of the new Cathedral was strongly supported by
the citizens of Modena to replace a previous church, finished just thirty years before.

The other epigraph, succeeding the first, is placed on the front. It indicates the date of the excavation of foundations (23 May) and the laying of the first stone (June 6, 1099). It is mentioned with admiration the sculptor Wiligelmus: “Inter sculputores, quanto sis dignus onore, claret scultura nunc Wiligelme tua”. He was also the person who made the text of the epigraph, as shown by Campana (1984). This stone plaque refers to an advanced stage of the work on the facade, certainly after 1106 (Lomartire, 1989).

The third inscription mentions the year 1184 and it remembers the dedication of the building. The text is carved on some blocks of the southern side (Lomartire, 1989). It is related to the consecration of July 12, and the parting of the Pope Lucio III, in July 14. This suggests that in 1184, the construction of the Cathedral was completed; Galavotti (1972) argues that already in 1170 the work could be concluded, as written sources indicate that from 1171 to 1179 the Cathedral was the seat of the meeting of the General Council of Modena. This does not necessarily imply that the Cathedral was completed, but it certainly indicates an advanced state of construction.

This third date is already part of a new phase, in which the active “magistri Campionesi” coming from the north of Lombardy. Their family worked in the construction of the Modena site continuously for several generations. Most of the changes in the architecture and in the sculptures of the Cathedral can be fixed at this time. Exactly between the 1160 and 1230, the fundamental aspects of the idea set by Lanfranco were deeply subverted and it was completely rethought the internal asset managed by Wiligelmus. These changes are due to new liturgical requirements aimed to adapt the building to a Gothic style, more updated at that time (Quintavalle, 1964).

**Ghirlandina**

Unlike the Cathedral, the Ghirlandina lacks written documentation of its initial construction. The two epigraphs, in the main apse and on the façade, of the Cathedral do not mention other buildings. Nor does the other important source of information about the Cathedral’s construction history, the Relatio, make any direct reference to the tower. The first written reference is the famous and controversial 1169 inscription found beneath the second cornice on the western façade, which, among other problems, surely does not refer to the foundation date of the building (Peroni, 2011).

Since its origins, the tower has served both as the Cathedral’s bell tower and as a civic tower. The Torresani, who were the custodians, rang the bells to mark the events of the city’s life and sounded an alarm in the case of danger (Piccinini, 2009).

Between the middle Ages and the Modern Age, Ghirlandina has had, in addition to the strictly
religious role, an additional civil function. The most important public papers were kept in a room of the tower, where it was located the archive of the City. This seat was maintained for a long time, at least up to 1578 (Piccinini, 2009).

3.2 Historic-artistic introduction

Cathedral

The Modena Cathedral is liturgically oriented, with three naves and three apses and a semi-circular crypt. Its general form has no transept and large columns space out the internal area. The external aspect reflects the interiors: a series of openings at the same high of the women’s gallery, with semi-column linked by blind arcades enclosing a three-light window, surround the perimeter of the Cathedral. This design gives rhythm to the building by dividing the space with areas of lights and shades. The exterior of the Cathedral is covered by stone slabs of 20 different typologies (Lugli et al., in press).

The façade has a pitched roof, reflecting the internal shape of the aisles, with ceilings at different heights; two large pilasters divide the facade into three parts. In the centre there is the main door characterised by porch with a barrel vault, which is supported by two lions from the Roman era. In the façade the role of the sculptures is predominant, moving and articulating the architectural elements and enriching the portals. The four panels with the stories of the Genesis carved by Wiligelmo are the most precious and famous. In all the sculptures is evident, the remind to the classical antiquity, but also an expressive power due to the new communicative role of images in this period aimed at an immediate impact (Quintavalle, 1965). The large rose window was added in the thirteenth century (Pedrazzi, 2006) along with the two side doors, which led to the displacement of the panels of Genesis of Wiligelmo.

Noteworthy are the side doors, two on the south side facing “Piazza Grande” and one on the north side. The Campionesi masters added the so-called “Porta Regia” within 1209 and 1231. At this time they were also working on the presbytery. The “Porta Regia” is in Rosso ammonitico stone, with different red and pink nuance that stands out of the clear surface of the Cathedral (Rossetti, 2009). Its sculptural decoration is of less artistic value if compared to the other doors, but its importance lies to its architectural grandeur: it is bordered by a series of columns, all different. The first two are of a larger diameter and they are supported by two lions. The animals grab a prey in the bows that for the medieval iconography represent the struggle between the devil and man or between the devil and God. An imposing porch surmounts the whole.

The smallest, “Porta dei Principi”, which name is derived from the presence of two princes in the
The decoration of the architrave, is adorned with a bas-relief depicting scenes from the life of St. Geminianus.

The “Porta della Pescheria” is on the north side, it is topped by the porch supported by two columns on lions. The bas-reliefs are inspired to the twelve months of the year and plants inhabited by real and imaginary animals.

Inside, the church has three naves, each ending with an apse, and it has a presbytery in elevated position, suggesting the presence of the crypt. The central nave has four large spans, twice as long as those in the aisles (which are then eight). The walls separating the naves are divided by arches, which simulate a women’s gallery that does not exist. The use of alternating pillars and columns is usually functional to the vaults construction, because the vaults of the central nave, which normally are larger and heavier, resting on pillars, while the vaults of the minor aisles are resting on smaller columns. In the case of the Cathedral of Modena, at the time of construction, the choice was purely stylistic, because a truss roof covered it. The skilful decorative effects are expressed with the only use of bricks (Quintavalle, 1965).

**Ghirlandina**

The tower was called Ghirlandina for the balustrade that rings the top of the lantern similar to a garland (Ghirlandina means “little garland” in Italian). It is approximately 90 meters high, with six floors topped by an octagonal tambour and a high cusp. The construction is made of bricks covered with ornamental stone slabs, in harmony with the Cathedral design.

Through the current entryway on the south side of the tower, there are eight steps leading up to an atrium, which serves as a visitors’ welcome centre. But this was not the original entrance due to the settling of the terrain, which has affected the Cathedral and the tower (Lancellotta, 2009). These studies show that the tower has sunk for a total of about two meters into the ground, although the settling of the terrain was not uniform, but more prevalent on the south and southwestern sides, conditioning the convergent settlement of the ground beneath the Cathedral by about 60 cm (Peroni, 2011).

Over the course of two centuries, at least three hundred and fifty sculptural elements were added to the architectural structure of the Ghirlandina during various renovation campaigns, most of them linked to the phases of construction of the first and fifth external levels. The decorative elements of the remaining portions, while sculpted, are much simpler in design. In addition, there are the columns, the basis of which display marginal decorative details, as well as moulded elements such as the ashlars, pointed archivolts and the interior shelves and cornices, which make up unique elements of the tower’s decorative complex (Lomartire, 2011).
As similar type of Romanesque towers, the mass is more compact at the base whereas in the upper floors the windows bring light into the interior space and they lighten the structure. They are single-lancet windows on the third floor, double lancet on the fourth and triple lancet on the fifth and sixth floor (Piccinini, 2009).

### 3.3 Previous studies on construction phases

The chronological sequence of the construction of these monuments is still difficult to interpret and it has stimulated an interesting debate among art historians. Several authors noted the complexity of the determination of construction phases given the lack of documentation and the many changes these buildings were subjected over centuries. Many hypotheses have been put forward, but based solely on historical and artistic studies (Peroni, 1984; Silvestri, 2013). The building of the Ghirlandina raised an extensive critical debate, with conflicting theories about the chronology of the first five floors of the tower’s square section. It was not possible to reference the oldest sources about these phases because the documentation had been destroyed (Dieghi, 2009).

### Cathedral

Concerning the Cathedral, the hypothesis of Porter (1917) is the most widely accepted. Porter claimed the presence, starting from 1099, of two opposing sites, initiated respectively by the apses and the front, then reunited in the centre. The reason was the presence of the previous cathedral, which was maintained during the early stages of the new construction. In 1927 Frankl (1927) strengthens the supposition of Porter in identifying in the anomalies on the sides of the church the junction points of the two construction sites. Salvini (1984) confirms the thesis of Porter supporting the contemporaneity of the two building site of the apse and the façade and gathering a possible dating of the work of Wiligelmo. Already in 1984 Peroni supports this reading because of the irregularities and asymmetries in the fourth span from the west, where probably the discrepancy of the two parts were corrected (Peroni, 1984).

Quintavalle (1991), Gandolfo (1989) and Montorsi (1984) advanced objections, questioning, in particular, that the head of the previous cathedral could prevent the excavation of a single continuous foundation.

Studies of Peroni (1989) and Lomartire (1989) on the sculptures, on masonries and on the letters carved on some stone blocks, lead to identify with precision three phases A, B, C that represent a fundamental contribution to the research about the Cathedral. These phases seem to fit with the reading of Porter:
- Phase A identifies the first phase that begins from the apses and proceeds westward with the first arches of the sides. On the south side, continues until the “Porta dei Principi”. Based on cited studies, it is recognized at its internal three distinct phases: A, A’, A”’. Among the phase A and A”’, along the south side, an anomalous discontinuity is visible. The phase A with its variants A’ and A”’ is identified as the “Lanfranco” phase.

- The phase B identifies the second phase, which starts from the façade, and then proceeds on the sides eastward. On the south side, is reunited with the construction site of the apses where the “Porta dei Principi” is placed. On the north side, because of substantial restoration, the “Porta della Pescheria” and arcades from sixth to ninth from the west cannot be attributed with certainty to the phase B, being still present sporadic similarities with Phase A. The Phase B is identified with the activity of Wiligelmo.

- Phase C is the one of completions and anomalies. The nave is completed with the construction of its top (clerestory). The side elevations are concluded and the remaining discontinuities are linked up. At this phase is attributed the work of the so-called “Maestro delle Metope”.

According to the newest theory (Silvestri, 2013) the interruption after the first phase, on the north and south side, can find an explanation in structural failure occurred during construction. The medieval workers have tried to separate the construction from the inclined apse and they have restarted from a new verticality. The C phase would have wait the settling of subsidence and it has
occurred in a second moment, joining two disconnected bodies. The compositional anomalies in the side elevations found in this theory a new justification, as a resolution of a connection between two bodies differently rotated. The debated architectural choices are then legitimized by structural reasons. In light of this reading, the chronology of the various phases varies. The presence of an anomaly, in the centre of the facade, seems to be the evidence supporting this thesis. Twenty-eight centimetres of difference, at the centre of the façade, between the two frames on the right and left of the porch, could correspond with the collapse of the apses in the first phase of construction. So the façade is more easily the point where the sidewalls are closing and where their inconsistencies are redressed.

The Campionesi Masters, between the 12th and 13th century, directed the last major phase. These workers were called to complete the Cathedral and to build the body of the bell tower. They changed the original project of Lanfranco through the addition of architectural elements of Gothic inspiration. The dating of these modifications is complex because a complete historical documentation is not available. Numerous assumptions have been proposed: according to De Francovich (1952) Anselmo da Campione, the founder, began to work on the Cathedral around 1184. Around 1200-1220 the modification of the presbytery had been completed (Autentrieth, 1984).

Ghirlandina

The building phases of the tower Ghirlandina have not definitively clarified. The destruction of the documents, which occurred in the 15th century because of a fire, has compromised the completeness of the historical reconstruction. The most debated topic is the chronology of the first five floors. The opening of the construction site probably dates back to the Lanfranchian period, in the same epoch of the Cathedral’s construction, but this assumption is not validated by any official document. Most researchers agree with the theory that it was started together with the Cathedral, between 1099 and 1106, with the same workers on both projects. But the theories about the end of the first construction phase are more disparate. Some recognize a substantial uniformity in the forms of the decorations of the first five floors and they attribute the whole construction of the body of the tower in a single phase by the hands of the Campionesi workers. Others distinguish the first floor, which would be built together with the Cathedral, from the remaining four floors, built later by the Campionesi. Furthermore, a much-debated element is the writing on a stone element on the third floor that has given rise to different interpretations and therefore to different chronological hypotheses. Someone read it as 1159, but the most recent theories see in it 1169 or 1179.

Of the first idea is the canon Dondi (1896), who thinks that the first phase would have been
continued until the construction of the fifth floor, finishing in 1159. As a proof, the interruption between the fifth and sixth floor, that can be seen just by observing the outside of the Tower, showing at that height an attempt to correct its leaning. The dating proposed by Dondi is due to the interpretation of the inscription scratched on the stone slab in the second cornice that would attest the completion date of the first phase (Dieghi, 2009). This thesis is supported also by the studies of the art historians Adolfo Venturi (1904).

According to De Francovich (1952), the date of the writing is 1179 and, by this date, the tower had been built up to the fifth floor. Moreover he recognises a similar style in the sculptures of the fifth floor, with the ones of the Campionesi gallery’s inside the Cathedral that should have been made within the 1160-1175 (Dieghi, 2009).

According to Roberto Salvini (1984), the Campionesi Masters, between 1160 and 1179, have constructed the first five floors of the Tower as a whole. This hypothesis is also embraced by Orlandini e Ceccarelli (1975).

The work by the Modenese art historian William Montorsi in 1976 theorizes that in 1106 the Tower has come to the fourth floor and he identified 1169 as the year of construction of the fifth floor.

In his reconstruction, Quintavalle (1964-65) gives a completely different interpretation to the inscription, which, according to him, would have been referred to another building. He maintains that the first floor was finished in 1106 and the forth floor around the 1130. The differentiation between the first four floors and the fifth floor, which was added by the Campionesi Masters around 1160-1170, is supported by the lack of pilasters on the fifth floor, as well as the fact that the capitals of the triple-lancet windows are more recent than those of the twin-lancet windows beneath them (Dieghi, 2009).

According to Labate (2010, Fig. 8) after the construction of the first floor, there was a long interruption, due mostly to problems of subsidence in the terrain beneath the tower and the lack of ornamental stones (Lugli et al., 2011). The Campionesi Masters, at a later stage, have elevated the structure from the second floor up to the Torresani Room (fifth floor). A distinctive element of the second phase is the sculptural decorations at the second and fourth cornice. They have been attributed to the Campionesi Masters, as were the capitals in the first loggia. Their dating to around 1184 is based on stylistic and palaeographic connections to the Campionese gallery inside the Cathedral. Another evidence is given by the inscription at the second cornice, which gives 1169 as the date for the construction of the Tower’s third floor. Thus the second phase can be dated to a period between 1169 and 1184 (Labate, 2010).

A similar theory has been proposed by Saverio Lomartire (2011), who emphasizes that though the
1169 (or 1179) date was always considered the time of completion of the first five floors of the Tower, it could instead actually attest the beginning of the construction of the third floor. According to him, all evidences seem to indicate that the second floor cornice was the work of one particular workshop, distinct from that of the first phase of the tower’s construction. So the cornice of the second floor constitutes the conclusion of the first phase and the 1169 (or 1179) date could refer to the production of the sculptures of this area. Indeed, at this height the corrections to the tower’s inclination began to be made (Lomartire, 1994). Contrary to the opinion of others, who think that much of the tower was already been constructed in 1169, he asserts that in the 1170s the construction work must have only reached about halfway of the bell tower. Apart from the content of the inscription, Lomartire wonder why the inscription is located in an area of the structure so far away from the object it is commemorating.

Fig. 8: construction phases of the Ghirlandina proposed by Labate (2010).

Regarding the last phases of construction some documents are available, as the “Cronache Modenesi”, which supply with further information, mostly indirect, on the state and use of the tower. In 1214 a bell seized during a raid on the Castle of Ponte Duce ends up in the tower; in 1217 one of the turricellum on top was struck by lightning. In 1261 the structure was raised of 12 “braeccia” (local unit of measurement) “a quadro supra” (meaning from whatever was the highest floor at the time, probably the fifth) so that the 6th floor was added (Labate, 2010).
In 1319 the structure was crowned with the octagon spire designed by Enrico da Campione, and a gilded copper sphere placed on top. By 1338 structures connecting the Ghirlandina and the Cathedral were built (Lomartire, 2011). The activity of the Campionesi Masters continued for three generations until, in 1322, the internal pulpit of the Cathedral was made. From the sixth floor, the outside face is made with the Veronese Ammonite stone and no putlog holes are seen. For the wall system of the spire a new type of brick was used with a 27.5 x 12.5 x 4.7 cm module that is slightly smaller than the one used for the Cathedral and the first loggia.
4. MATERIALS AND METHODS

In the first part of this chapter, the analytical methods for the study of ancient mortars are described. For the petrographic analysis, a proven method carried out by the working group of the Department of Chemical and Geological Sciences of the University of Modena and Reggio Emilia for the study of the Ducal Palace in Sassuolo (Lugli, 1996; 2000) and the Formigine Castle (Lugli, 1997) is proposed. This method has demonstrated to be particularly suitable for the identification of groups of mortars in order to distinguish the construction phases of historic buildings. The proposed methodology can quantitative determine the composition of ancient mortars as well as the grain size distribution of the aggregates used in the mortars. Also the adopted chemical and mineralogical characterisation methods are presented.

The second part of the chapter concerns the application of the analytical methods for mortar dating. The possibility to use the lime mortar binder as the carbon bearing for \(^{14}\text{C}\) measurements represents a great advantage for architectural and archaeological research. Actually, the carbon dioxide absorbed during the setting of a lime mortar reflects the content of \(^{14}\text{C}\) in the atmosphere at that time. Two sample preparation techniques, considered essential to eliminate the contaminants that could distort the radiocarbon dating, are described and discussed in paragraph 4.3.2.

The two main luminescence techniques proved to be increasingly advantageous for geoscientists and archaeologists. With thermo luminescence dating, the setting to zero is accomplished by heating, as for bricks but bricks have commonly been reused. One of the recent applications is the optical dating of mortars because the “clock” of the grain of quartz and feldspar can be set to zero also by light exposure. For both techniques the latent signal grows as the centuries go by, until it is brought to life again for measurements by thermal or optical stimulation in the laboratory (Aitkens, 1985; 1998).

4.1 The sampling

The most important consideration in the study of cultural heritage is that, more than in others contests, the planning of the sampling is crucial. The challenge is to perform the analysis with a small quantity and a limited number of samples. The sampling phase is the moment when it is necessary to find the right compromise between the collection of the sufficient amount of material to conduct an analysis and the respect of the original materials, which should, in any case, be preserved. This is also valid for the study of large monuments. In this case study, the availability of
the material is very paltry. The mortar joints, in the interior masonry, do not reach one centimetre. Moreover, on the outside surfaces, they are concealed by the stone facing.

The possibility of takes the advantage of the restoration works allowed to access the scaffolding holes, which have been reopened for the occasion. This has ensured the collection of a bit higher quantities of mortar. It was also decisive the access to not visible areas, such as turrets apse or attics.

The choice of the type and number of samples has been made considering the materials and the problems to be solved. The portions of the bedding mortars collected must be representative, reflecting the composition of the part from which they are extracted. Their selection has been carried out systematically, in order to represent the various phases of construction, as identified by previous studies (see chapter 3).

### 4.1.1 Foundations cores

Samples have been collected from the foundations. The cores from the foundations of the Cathedral and of the tower were conducted during two different test campaigns (working group of prof. Ing. Renato Lancellotta, prof. Stefano Lugli, dr. Donato Labate, eng. Mario Silvestri, arch. Elena Silvestri, arch. Silvia Tosini): the first on the foundations of the apse of the Cathedral and the tower Ghirlandina (September 2007, Fig. 9A) and the second (July 2010, Fig. 9B) has involved the prospectus and the south façade of the Cathedral. In this circumstance, it has been tried to take the cores in order to represent all the phases of construction assumed by artistic studies, including existing structures already identified by the nineteenth-century archaeological excavation (see chapter 3).

![Fig. 9: positions of coring: A) apses of the Cathedral and tower Ghirlandina (2007); B) southern side and façade of the Cathedral (2010). Survey by arch. Palazzi and eng. Silvestri.](image-url)
The study of core samples should be considered without forgetting the impossibility of direct observation of the structures and the possible loss of parts of incoherent materials (e.g. sand).

4.1.2 Mortars from masonries

A total of 62 samples of mortars were collected from the Cathedral: 26 samples from the turrets apses (Fig. 11B), 10 from the south side using the restoration scaffoldings (Fig. 12), 11 from the north side from the putlog holes under the roof of the attic (Fig. 13) and only two from the façade in the upper part and one during the sampling for OSL (Fig. 11A). These sites have been specifically chosen where it was possible to withdraw a discrete amount of material because placed in not visible areas.
Concerning the Ghirlandina tower the samples analysed were in total 52, taken directly from masonries and when possible from scaffolding holes. Two of the samples come from the geognostic core drilling that crossed the foundations of the tower, while others have been made available by the LARM DISTART University of Bologna, which have done some micro core drilling in masonries inside the tower. The following is the height of the location of samples (Fig. 14).
4.1.3 Plasters

The Campionesi phase in the Cathedral involved the addition of painted plaster, decorated in two colours, red and white, in imitation of bricks (Baraldi et. al, in press; Fig. 15A). Some fragments are left in the attic of the nave and inside the south transept, amongst the sixteenth century vaults and the roof. This decoration, however, did not have very long life because towards the end of the thirteenth century the Cathedral was re-decorated. On the remains of the Campionesi painting were superimposed new plasters, with a floral decoration on a blue background (Autentrieth, 1984).

Samples from both the level of the decoration were collected (Fig. 15B).
4.1.4 Preparation of samples for binder analyses

To determine the hydraulicity of a mortar, which can be deduced from microscopic observations only in some rare cases, a chemical analysis is useful. However, the main difficulty resides in separating the binder from the other mortar constituents. Because of the impossibility to use the acid attack since much of the aggregate of these mortars is limestone, it has been chosen to use only the recommended procedure of mechanical separation. Thus, as mentioned by other studies (Yücel and Gülmez, 2005; Bonilla et al., 2008; Starinieri et al., 2008) the analyses have been made on the fine grain size fraction after disaggregation and sieving. However, the interpretation of the results of such analyses should be done without forgetting that a significant contribution of the aggregate can never be ruled out (Elsen, 2010).

In order to understand if it was possible to determine the hydraulicity of these mortars and to highlight any differences during the evolution of the phases of construction have been chosen only few representative samples. The dearth of material, as already explained, lean towards a test on a small number of samples, being aware of the limitations of the results that could be achieved.

The samples were selected from those of which had sufficient material left and in order to represent the different phases of the Cathedral construction. Furthermore, it was also included another sample from the tower, in which, under the microscope, some very small clinkers have been found, witnesses of a possible residual hydraulicity (Table 1).
The disaggregation has been made by gently breaking the mortar samples to avoid the powdering of the aggregate as well. The samples have been sieved for 15 minutes and the grain size <125 $\mu$m has been collected. The finest fraction <63 $\mu$m has been selected after wet sieving with distilled water.

### 4.1.5 Sampling for radiocarbon dating

Twelve samples representing different construction phases of the Cathedral and the tower have been collected, as shown in table 2 and figures 16 and 17, to be prepared for radiocarbon dating. Due to the small amount of samples available and the limited possibility to carry out numerous and expensive radiocarbon dating, only one sample from the Cathedral (DM101) and one from the Tower (GM86) were prepared following the two methodologies of sample preparation (see paragraph 4.3.2). These two samples have been dated two times, for a reliable comparison.
Fig. 17: position of samples of the tower for radiocarbon dating.

<table>
<thead>
<tr>
<th>Sample names</th>
<th>Expected age</th>
<th>Methodology followed</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>C130 lump Cathedral</td>
<td>1120-1130</td>
<td>Bulk lump (CIRCE lab.)</td>
<td>Contamination from secondary calcite</td>
</tr>
<tr>
<td>C130 susp_lump</td>
<td>1120-1130</td>
<td>Cryosonic</td>
<td>Contamination from secondary calcite</td>
</tr>
<tr>
<td>Cathedral</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DM 8 lump Cathedral</td>
<td>1099-1106</td>
<td>Bulk lump (CIRCE lab.)</td>
<td>Known date Very little quantity: more than one lump</td>
</tr>
<tr>
<td>DM 8 susp_lump</td>
<td>1099-1106</td>
<td>Cryosonic</td>
<td>Calibration date Very little quantity: more than one lump</td>
</tr>
<tr>
<td>Cathedral</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DM 101 susp</td>
<td>1184-1220</td>
<td>Cryo2sonic</td>
<td>Bulk mortar</td>
</tr>
<tr>
<td>Cathedral</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GM86B lump tower</td>
<td>1099-1106</td>
<td>Bulk lump (CIRCE lab.)</td>
<td></td>
</tr>
<tr>
<td>GM86B susp_lump</td>
<td>1099-1106</td>
<td>Cryosonic</td>
<td></td>
</tr>
<tr>
<td>tower</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GMC24 susp tower</td>
<td>1319</td>
<td>Cryo2sonic</td>
<td>Known date</td>
</tr>
<tr>
<td>GMC24 susp</td>
<td>1319</td>
<td></td>
<td>Known date</td>
</tr>
<tr>
<td>tower</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GM86B tower</td>
<td>1099-1106</td>
<td>Sequential dissolution of the bulk, three fractions</td>
<td></td>
</tr>
<tr>
<td>GM42 tower</td>
<td>1167-1184</td>
<td>Sequential dissolution of one lump, two fractions</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: list of samples prepared and dated with $^{14}$C.
4.1.6 Sampling for OSL and TL dating

The sampling for OSL and TL dating were specifically conducted using a hollow drill, to extract sandwiches composed of bricks bound by mortar (Fig. 18 A and B), in order to have samples not exposed to sunlight that can invalidate the OSL measures.

![Fig. 18: sampling for OSL dating A) extraction of cores; B) sandwiches composed of bricks bound by mortar.](image)

The samples were put in an aluminium foil, placed in a black envelope (Fig. 19 A) in order to avoid further exposure to light and stored away from sources of heat to preserve the humidity. In PH3DRA Laboratories (of Catania) under a red light, the samples were divided in parts in order to have the same samples available for the two laboratories (PH3DRA and Milan Bicocca).

The choice of the positions of the cores was made considering the different phases of construction, as shown in figures 20 and 21.

![Fig. 19: A) cores are put in an aluminium foil, placed in a black envelope in order to avoid further exposure to light; B) hole left in the putlog hole.](image)
Fig. 20: position of cores for OSL in the Cathedral.

Fig. 21: positions of cores for OSL in the tower.
4.2 Diagnostic analyses: characterisation of mortars and plasters

The analyses of the building materials have provided a scientific contribution to the studies of the monuments. The compositional and textural analyses are important to obtain information about the techniques of preparation of artificial materials and their evolution over time. Mortars cannot be reused, as bricks or stones, and their characteristics can be used to indirectly identify different building phases (Lugli, 1997; Lugli et al., 2010). Polished thin sections are probably the best choice since they can be used for full range of microscopy techniques on the same sample.

The characterisation of the binder requires, however, the integration with other scientific tools because the fine binder texture is not observable by standard microscopy. However, microscopic observation can be used to study the BRPs and directly infer about the raw rocks used for lime production. An ESEM (Environmental Scanning Electron Microscope) equipped with an energy dispersive X-ray detector (EDS) has been used to collect elemental and structural microanalyses, to have information on the composition of mortars.

Additional information on the mineralogy of the mortars can be obtained by XRD. The XRD quantitative phase analysis with the Rietveld refinement allows the identification of amorphous phase fractions that could be related to hydrate calcium silicate/aluminate phases (CSH, CAH; Gualtieri et al. 2006). The combination with thermal analysis (TG) can be used to identify the various components of the mortar.

Raman spectroscopy and XRD with Gandolfi camera have been used to identify some specific crystals.

4.2.1 Optical microscopy (OM)

The mortar samples were vacuum impregnated in epoxy resin and the thin sections were prepared according to LOGITECH standard procedures. Thin sections were observed under the optical microscope in transmitted light. The main mortars features were qualitatively described using as a reference the Document UNI-Normal 11176.

The investigations by light microscopy are typically qualitative and morphological, enabling to study details not visible with naked eye. When equipped with facilities for light transmission and reflection, a polarising microscope is a versatile tool to study many details at magnifications up to 500 times. The usual mode of observation is under transmitted light where optical parameters such as the interference colours become visible. This is valid when studying the aggregate or coarse unhydrated clinker grains, composed of large crystals. However it is worthwhile to observe the
clinker also under reflective light in the bright field, producing images of grey values according to the reflection coefficient of a phase. Thus, by simply switching between transmitted light at parallel or crossed polars it is possible to use the full range of facilities offered by the polarising microscope on one single preparation (Weber, 2013).

In contrast to Portland cement mortars, the polarising microscope is less convenient to study the precise phase composition of NHL (Natural Hydraulic Lime) mortar residual structures, since these nodules are typically composed of very fine grained clinker phases of less well defined stoichiometry and hence less significant optical parameters.

For observations by light microscopy of thin sections it has been used an optical microscope LEITZ Orthoplan polarizing transmitted light. Photographs of the thin sections were performed, both at parallel nicols that cross, via a Nikon Coolpix 990 digital camera, megapixel 3:34.

4.2.2 Point counting analysis

Point counting analyses, under transmitted light microscopy, were performed using the Gazzi–Dickinson method (Zuffa, 1985) modified to include specific mortar characteristics such as porosity, binder and binder related particles. The mortars were divided into classes according to textural and compositional parameters.

Point counting analysis with the optical microscope aimed at the quantification of the petrographic composition of mortars aggregate grains. At least 300 of aggregate grains and 200 of binder and pores were point counted (approximately 500 points per section).

Fig. 22: A) compositions of samples of sands of the modern rivers (Lugli et al., 2007) considering the parameters Q + F (monocrystalline quartz and feldspar and in rock fragments), L (fine-grained rock fragments as shales, siltstones, ophiolite fragments, etc.) and C (total carbonates, micrites, bioclastic and single crystal of calcite); B) representation of the main streams of the Modena area (Lugli et al. 2007).
The following parameters have been calculated in order to compare the composition of the sand used as aggregate and the composition of the river sands of the Modena area (Lugli et al., 2007; Fig. 22A and B):

Q = quartz monocrystalline, polycrystalline and fragments of rock, flint included.

F = feldspar microcrystalline and feldspar in rock fragments

C = CE = total carbonates

L = lithic fragments (lithic metamorphic lithic and lithic clastic ophiolite)

Statistically rigorous confidence regions of the studied samples were calculated according to Weltje (2002). Error bars in the diagrams were calculated according to Howarth (1998).

4.2.3 Image analysis

The representative samples of the different mortar categories have been studied by image analysis by means of Image J free software.

Three photomicrographs of about 5 mm per side have been analysed. The Image J software can calculate through algorithms, areas and other geometric parameters of the different mortar elements (aggregate, binder, pores, binder related particles) obtaining textural parameters (Fig. 23 A, B and Fig. 24 A, B; Carò and Di Giulio, 2004).

The binder/aggregate has been calculated according to the recommendations of the Committee for the characterization of historical mortars RILEM TC 167-COM (2001):

\[
F = \frac{\alpha \times \text{volume aggregate}}{\text{volume paste}}
\]

\[
\alpha = \frac{\text{density aggregate} \times \text{molecular mass } \text{CaCO}_3}{1.1 \times \text{density paste} \times \text{molecular mass } \text{Ca(OH)}_2}
\]

The image analysis of a thin section provides the percentages of areas (S%), which correspond to unit volumes (V%) of aggregate and binder (Delesse, 1984; Casadio et al, 2005). The first formula is a correction because it is estimated that 10% of the weight of the binder is due to water. The values used for the calculation of \( \alpha \) are: molecular mass of carbonate calcium = 100, molecular mass of calcium hydroxide = 74, density of the hydraulic binder = 1450 kg / m\(^3\) (RILEM TC 167-COM, 2001), the density of the Secchia River sand (measured) = 2516 kg / m\(^3\). The value of \( \alpha = 2.132 \).
Two values can be obtained:

- Binder-aggregate: where the binder related particles are considered as aggregate because they do not participate in the reactions. It is used to obtain the proportions to be used for restoration purposes to obtain a mortar with properties similar to those of the original mortar.

- Binder-aggregate: where binder related particles are considered as a binding agent and it is used to calculate the total amount of binder of the mortar.

Fig. 23: photomicrograph of a mortar thin section A) parallel nicols; B) crossed nicols.

Fig. 24: output of the software Image J A) skeleton of the mortar shown in Fig. 24; B) pores.

Fig. 25: A) graph of the mortar texture; B) graph of the aggregate grain size (%V/V).
In figures 25 A and B is shown an example of the two graphs in which the data obtained are summarized. In the first the main characteristics of the mortar, such as the binder quantity, the total aggregate, the BRPs and the porosity are plotted. The particle size distribution is in the second graph. The same procedure is applied on three micrographs of each thin section and the average on the three values is calculated.

4.2.4 Raman spectroscopy

This technique is based on the Raman effect according to which a sample, irradiated with a monochrome light, re-emits light at a longer wavelength. The energy output is lower because a part of it is absorbed from the functional groups of the molecules to vibrate, similar to the IR spectroscopy. The answer is visible in the form of spectrum that allows the determination of substances in a sample (Baraldi et al., 2007; 2010).

Micro-Raman spectroscopy provides a unique method for characterizing the crystal chemical properties of heterogeneous samples. The spatial resolution and ease of data collection of this technique are particularly useful for rapid identification of minerals in thin section (Mao et al., 1987). Because of the sensitivity of vibrational frequencies and scattering intensities to slight differences in crystal structures (bond angles, site symmetries, lattice vibrations), such vibrational spectroscopic methods are also well suited for distinguishing among mineral polymorphs.

Raman spectra were obtained by the use of a red laser at 632.8 nm, providing data on the molecular nature of minerals. It was used a microscope Labram of Jobin Yvon-Horiba provided with CCD (1024x256 pixels) cooled to -70 ° C due to Peltier effect, spectral resolution of 2 cm⁻¹, 1µ spatial resolution, edge filters for eliminating the exciter and objectives 10x, 50x and 100x Olympus long distance. Through the program Grams A/I were compared the spectra with a specific database.

This technique is currently widely used in the field of cultural heritage because it is completely non-destructive. In this case the Raman measurements have been conducted directly on the prepared thin sections of the mortars.

4.2.5 Electronic microscopy and microanalysis (SEM – EDS)

Despite all benefits offered by the techniques of light microscopy, SEM is as additional tool to study the binders in a historic mortar sample (Winter, 2012). A back-scattered electron detector and an X-ray analytical device (EDS) are essential in order to make useful observations. The low vacuum mode allows the study of the thin sections without the conductible layer of carbon coating. Working under low vacuum the image resolution is lower and that the chemical spot analysis by
EDS is less precise than it would be in the high vacuum mode, due to the interaction between electrons and air molecules in the chamber.

SEM investigations are useful not only to study the unhydrated portion of the hydraulic binder, but also can be employed to improve knowledge of the reacted part, which is usually of much finer grain size and hence less understandable by light microscopy.

With the image in BSE mode on polished sections the hydraulic phases have been identified in more detail and atomic ratios of the different elements have been determined semi-quantitatively. Due to the differences in atomic number, corresponding to differences in grey level displayed on the image, the different phases can be visually distinguished (Callebaut et al., 2001).

Unfortunately, as was stated in chapter 2, microprobe analyses can only reflect the chemical composition at specific point and the quantification of the oxides is not accurate. This is also why, the most common classifications to measure the hydraulicity, CI (Cementation index) or the HI (Hidraulicity Index) obtained by the ratio of the chemical oxides, cannot be calculated with the results of the EDS analyses.

For the SEM_EDS analyses it has been used an ESEM Quanta 200, in low vacuum mode, coupled with a X-EDS Oxford Inca 350 for microanalysis. HV 25,0 kV. Detector BSE SSD (Solid State Detector).

4.2.6 Quantitative X-ray diffraction, Rietveld refinement

Quantitative X-ray powder diffraction analysis has been conducted using the Rietveld method (Hill et al., 1993). The Rietveld method has been used to obtain reliable quantitative estimates (Rietveld, 1969; Hill and Howard, 1987; Bish and Howard, 1988; Bish and Post, 1993; Dinnebier and Billinge, 2008) for about 25 years. In this method, the mass fraction \( w_i \) of each \( i^{th} \) crystalline component in a mixture can be calculated from the following equation:

\[
\frac{w_i}{\sum_j w_j} = \frac{S_i(Z_i M_i V_i)}{\sum_j S_j(Z_j M_j V_j)}
\]

where \( S_i \) is the refined scale factor, \( Z_i \) is the number of formula units in the unit cell, \( M_i \) is the mass of the unit formula and \( V_i \) is the elementary cell volume of each \( i^{th} \) crystalline component. Quantitative phase analysis (QPA) using the Rietveld method relies upon the normalisation condition \( \sum_i w_i = 1 \). The content of the amorphous phase can be determined with the addition of an internal standard in the so-called combined Rietveld and R.I.R. method (Gualtieri, 2000). In this case, the refined weight fractions of each crystalline phase \( (W_c) \) was rescaled with respect to the
known weight fraction of added standard (\(W_s\)) in order to obtain the real crystalline phase weight fraction (\(W_i\)):

\[
W_i = \frac{1}{1 - W_s} \left( \frac{W_s}{W_{sc}} \right) W_{ic}
\]  

(2)

where \(W_{sc}\) is the refined weight fraction of the internal standard. Knowing the weight fractions of all crystalline phases, the amorphous content (\(W_a\)) is calculated using the following equation:

\[
W_a = 1 - \sum_i W_i
\]

(3)

Rietveld QPA

The original samples were manually ground in agate mortar. The ground material was dry-milled for 20 min using an agate mill. Final milling was performed for 40 min using a micro-mill with SiC balls as grinding media, producing a fine powder. XRPD data for both qualitative and quantitative analyses were collected using a Bragg–Brentano 0-20 diffractometer (Philips PW 1729 PANalytical, Netherlands) equipped with a gas proportional detector. A \(\frac{1}{2}^\circ\) divergence slit, 0.04 rad soller slits, and a \(\frac{1}{2}^\circ\) anti-scatter slit on the incident beam pathway, 0.04 rad soller slits and a curved graphite monochromator on the diffracted beam were used. The radiation source was an X-ray tube with copper radiation (\(\lambda\text{CuK}\alpha_1,\text{K}\alpha_2 = 1.54059, 1.54439 \text{ Å}\)) and the anode tube load was 40 kV and 30 mA. The samples were side-loaded on a quartz flat zero background holder. XRPD patterns were collected at room temperature in the 5-80\(^\circ\) 2\(\theta\) range, with a scanning rate of 0.004\(^\circ\)·s\(^{-1}\) and a step size of 0.02\(^\circ\) 20. 10 wt% corundum (NIST 676a) was added to each sample, and treated as an additional phase in the refinements for the determination of the amorphous content.

Preliminary qualitative phase analyses were performed using the X’Pert High Score Plus software (PANalytical, Netherlands). Rietveld QPAs were performed using the GSAS package (Larson and Von Dreele, 1994) and its graphical interface EXPGUI (Toby, 2000). The starting atomic coordinates for all phases in the investigated systems were taken from the literature:

- kaolinite (Bish, 1993), K-feldspar (Bailey, 1969), plagioclase (albite structure: Prewitt et al., 1976), calcite (Markgraf and Reeder, 1985); chlorite (clinochlore: Zanazzi et al., 2009), muscovite (Guggenheim et al., 1987) and quartz (Gualtieri, 2000).

The background profile was fitted with a Chebyshev polynomial function with a variable number of coefficients. The profile of the diffraction peaks was modelled using a pseudo-Voigt function with
one Gaussian and two Lorentzian coefficients in addition to an instrumental peak asymmetry component set to be equal for all phases.

Every analysis was carried out both on the bulk sample and on the sample fraction enriched in binder (<63 µm fraction of the gently disaggregated mortar sample).

Some of the hydration products (e.g. CSH, CAH) are amorphous to X-rays and so they do not produce sharp diffraction peaks. The addition of the corundum standard allows the identification of the fraction of amorphous phase that could be related to hydrate calcium silicate/aluminate phases (Gualtieri et al., 2006).

4.2.7 Thermo Gravimetric analysis (TG)

The TG/DSC analyses were carried out only on the finer part of the mortar after 63 µm sieving. The temperature range of 25–1200°C has been used with a heating rate of 10°C/min in a nitrogen/air atmosphere, with a STA 409PC Luxx Netzsch instrument.

The factor to recalculate the quantity of CaCO$_3$ from the quantity of CO$_2$ is the results of the ratio between molecular weight of CaCO$_3$ and the molecular weight of CO$_2$=100,0869/44,01=2.274.

The intrinsic limit of TG technique is the impossibility of making a chemical analysis of the binder alone and as a whole, because it is closely intermixed with the aggregate.

4.3 Absolute dating

With the collaboration of the Research Centre for Isotopic Cultural and Environmental Heritage (CIRCE) of Caserta, some samples were prepared and dated with AMS (Accelerator Mass Spectrometry) $^{14}$C. The methodology of sequential dissolution carried out by dr. Alf Lindroos of the Åbo Akademi University (Turku, Finland) has been also used.

The radiocarbon dating results have been tested using others independent absolute dating methods. The two laboratories involved are the Department of Physics and Astronomy, University of Catania and the Department of Material Science, University of Milan Bicocca. They both used optically stimulated luminescence (OSL) on mortars and thermoluminescence (TL) on bricks.

4.3.1 Preliminary mortars characterisation for radiocarbon dating

The preliminary petrographic analysis with the polarizing light microscopy (PLM) allows the identification of the different carbonate elements in a mortar: the aggregates nature (Fig. 26 E and
F), BRPs (Fig. 26 A and B), the degradation features, such as secondary calcite crystallization (Fig. 26 C) and charcoal fragments (Fig. 26 D).

Fig. 26: Photomicrographs of mortar thin sections A) at the bottom left of the image there is a lime lump with an unburned core, crossed nicols; B) at the top left a fragment of partially burned limestone and on the right a lime lump sensu strictu, crossed nicols; C) secondary calcite formed around the aggregate grains, crossed nicols; D) on the right a black charcoal fragment, parallel nicols; E) the aggregate of the mortar has high percentage of limestone, crossed nicols; F) mortar with a fine aggregate, crossed nicols.

The preliminary petrographic analyses of mortars may help in:
identifying the unburned limestone relicts, calcareous aggregates and new formed calcite, considered as contaminants;
- identifying the presence of lime lumps that could be separated from the mortar avoiding contamination from dead carbon;
- distinguishing the mortar groups by analysing the composition and texture limiting the number of absolute dating to be done;
- characterising the samples in order to select the best preparation procedure and to correctly interpret the radiocarbon data.

4.3.2 AMS Radiocarbon dating

Once the contamination is identified, it must be separated from the carbon belonging to the original binder. The methods most commonly used for samples preparation consist of a mechanical pretreatment or a chemical treatment (Lindroos et al., 2007; Nawrocka et al., 2005). Due to the high percentage of carbonate aggregates, binder related particles and secondary calcite (Fig. 26), these mortars represent an experimental test indicative of exogenous carbon sources suppression.

For the first time a comparison of these two sample preparation procedures for radiocarbon dating has been carried out on the same mortar samples: Cryo2sonic and sequential dissolution. Furthermore, each laboratory has worked both on the preparation of the bulk that of the lumps.

First, the mortars have been carefully processed and observed with a stereomicroscope in the laboratory of the University of Modena and Reggio Emilia (Fig. 27). The ones containing sufficient quantity of lime lumps have been selected. The lumps have been mechanically separated from the bulk under the stereomicroscope. This selection is very time consuming and even if it is possible to recognise the carbonate contaminants it is not always possible to completely remove them, due to their very small sizes.

Fig. 27: selection and mechanical separation of the lumps from the bulk mortars under the stereomicroscope.
**Cryo2SoniC procedure**

With the aim to test the methodology of mortar dating on a case limit, two lumps from the foundations of the cathedral (C130) have been selected. These mortars were particularly complex because they contained numerous lime lumps including lime lumps *sensu strictu*, underburned and overburned BRPs, commonly difficult to interpret correctly with naked eyes or with the stereomicroscope. In addition, it was possible to observe a phenomenon of crystallization of secondary calcite within the pores, around the grains and in the bulk. These mortars could therefore be considered as doubly contaminated by dead carbon and re-crystallized calcite.

**Bulk**

Around 10 g of mortar per sample (GMC24, DM 101) have been submerged in liquid nitrogen for few minutes and transferred into an oven at 80°C. These cycles are repeated 3 times for each sample and then the mortars have been gently crushed with a hammer (Fig. 28).

![Fig. 28: cryo2sonic mechanical preparation](image-url)
The sieved powder (under 500 µm) is put into the beaker with an excess of deionized water. The first ultrasonic bath for 10 minutes produces the so-called “sand” fraction. The water surface is collected by pipette. The sample is filled up again with distilled water. The development of the Cryo2sonic procedure involved a second ultrasonic bath of 30’ creating the “susp” fraction. This fraction is siphoned in tubes, centrifuged for 5 minutes at 8.5 krpm to eliminate the water and then it was dried overnight in an oven at 70°C (Fig. 29). The dried samples were removed from the tube with a spatula and they were weighed.

**Susp lump fraction**
Lumps from the samples C130, GM86B and DM8 were selected. One or more for each mortar have been immersed in distilled water and ultrasonicated for 30’. The suspension has been selected by syphoning immediately after ultrasonication to prevent deposits. The obtained suspension was centrifuged for 5 min. The surface water has been eliminated. Samples have been put in an oven at 80°C overnight. The dried samples have been removed from the tube with a spatula to obtain the susp lump fraction.

**Bulk lumps**
Other lumps of the samples (C130, GM86B and DM8) have been weighed and they directly underwent to acid digestion.
**CO₂ collection and AMS measurements**

About 30-40 mg of the dried suspensions (susp, susp_lump and bulk lump) and the carbonate standard samples (i.e. IAEA C1 and C2; Rozanski et al. 1992) have been attacked with 85% phosphoric acid under vacuum for 2h in a drying oven at 85 °C. The CO₂ delivered during the reaction has been collected (with the CO₂ line shown in figure 30) and cryogenically purified by other gasses, reduced to graphite on iron powder catalyst according to the CIRCE sealed-tube reaction protocol (the zinc process, Marzaioli et al. 2008) and collected. At the end the carbon is fixed on graphite tablet and dated with the CIRCE AMS system (Terrasi et al., 2008). The ¹⁴C isotopic ratios were converted to ¹⁴C ages (Stuiver and Polach, 1977) and calibrated to absolute ages with the CALIB v 6.0 program (Stuiver and Reimer, 1993) using the IntCal09 atmospheric calibration data set (Reimer et al., 2009).

![Fig. 30: CO₂ extraction line in the laboratory of CIRCE, Caserta.](image)

**Sequential dissolution**

Considering the results obtained and the limited possibility to make further dating, some samples were chosen to be dated following the sequential dissolution procedure (Åbo Akademi) in order to optimize the information gained: one sample that have obtained a date in agreement with the one expected (GM86B, foundation of the tower), one sample with an high percentage of contaminants that got an older age (DM 101, Campionesi phase of the Cathedral) and a sample never dated (GM 42, fourth floor of the tower).

The two mortar bulks (GM86 and DM101) and the lime lump (GM42) have been prepared at Åbo
Akademi University, Turku. The first step is the alkalinity test: a little quantity of mortar powder is wet with phenolphthalein (1%) dissolved in alcohol. A pale pink colour as shown in figure 31 A is considered acceptable. A second test aims to verify the dissolution rate, with one drop of diluted HCl on the sample powder (Fig. 31 B). If the sample does not show effervescence then there may be dolomite. All the samples have resulted to be with a low alkalinity and good dissolution rate and therefore suitable to be dated.

![Fig. 31: A) alkalinity test B) preliminary test with HCl to check if the sample is suitable to be dated.](image)

**Bulk**

The samples have been broken in a plastic bag using nipper pieces, not to produce fine splinter of the aggregate (Fig. 32A). The crushed material has been vibrated in a sieve series (Fig. 32B). The grain-size fraction range of 76-150µm has been chosen for both samples, because the quantity of
the finer fraction (46-75µm) was not sufficient. Then, the samples have been washed, dried and homogenized.

Fig. 33: CO₂ extraction line in the laboratory of the Abo Akademi.

The powders have been put into the reactor vessel in a specially designed preparation line, shown in figure 33. When a sufficient vacuum is reached, around 3 ml of 85% chilled at 0°C phosphoric acid has been let in excess on the powder. Samples have reacted rapidly and, after 4 and 3s, respectively, the first CO₂ fractions have been isolated, chilled out and captured in glass vials. The next CO₂ fractions have been isolated after 21s for both samples. The third fractions have been collected after 86 and 60 s, respectively. When reaction has finished and no more effervescence was visible, the total carbon yield has been calculated from the total CO₂ captured. It is important to minimize the first CO₂ fractions, collecting at least 0,5 mg of carbon, which is the requested quantity to conduct the AMS measurements. The samples behaviour during the dissolution process is summarized in table 3.

Lump
One lime lump selected from the mortar, GM 42 has been put in the reactor vessel directly. Due to the small quantity of the lump, the reaction times were longer (first fractions after 11s and 74, respectively).
<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain-size C content</th>
<th>Sample aliquot (mg)</th>
<th>CO₂ fractions (nr)</th>
<th>Diss. Time (s)</th>
<th>P in the CO₂ line (mbar)</th>
<th>F</th>
<th>Calculated C content (mg)</th>
<th>C-14 vial (mg)</th>
<th>C-13/O-18 vial (mg)</th>
<th>Dating</th>
</tr>
</thead>
<tbody>
<tr>
<td>DM0101</td>
<td>76-100</td>
<td>125</td>
<td>1</td>
<td>4</td>
<td>58,6</td>
<td>0,230</td>
<td>0,75</td>
<td>0,56</td>
<td>0,20</td>
<td>yes</td>
</tr>
<tr>
<td>H₂PO₄ 85%</td>
<td>3,52%C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25°C</td>
<td></td>
<td>2</td>
<td>21</td>
<td>136</td>
<td>0,533</td>
<td>1,75</td>
<td>1,48</td>
<td>0,54</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>86</td>
<td>95,6</td>
<td>0,375</td>
<td>1,23</td>
<td>1,03</td>
<td>0,20</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>GM86</td>
<td>76-100</td>
<td>189</td>
<td>1</td>
<td>3</td>
<td>84,8</td>
<td>0,226</td>
<td>1,09</td>
<td>0,91</td>
<td>0,18</td>
<td>yes</td>
</tr>
<tr>
<td>H₃PO₄ 85%</td>
<td>3,86%C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25°C</td>
<td></td>
<td>2</td>
<td>21</td>
<td>190</td>
<td>0,505</td>
<td>2,44</td>
<td>2,04</td>
<td>0,40</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>60</td>
<td>162</td>
<td>0,431</td>
<td>2,08</td>
<td>1,75</td>
<td>0,33</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>GM42</td>
<td>unsieved</td>
<td>44,5</td>
<td>1</td>
<td>11</td>
<td>59,1</td>
<td>0,232</td>
<td>0,76</td>
<td>0,56</td>
<td>0,20</td>
<td>yes</td>
</tr>
<tr>
<td>H₃PO₄ 85%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25°C</td>
<td></td>
<td>2</td>
<td>74</td>
<td>125</td>
<td>0,490</td>
<td>1,61</td>
<td>1,34</td>
<td>0,54</td>
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<td></td>
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<td></td>
<td></td>
<td>3</td>
<td>1350</td>
<td>19,9</td>
<td>0,078</td>
<td>0,26</td>
<td>not</td>
<td>collected</td>
<td>no</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: description of the samples to be dated and their behaviour during the preparation; it is specified: quantity (mg), number of CO₂ fractions collected, dissolution time of every fraction, pressure measured in the CO₂ line (mbar), F value calculated (F=relative fraction size. 1 corresponds to total carbon yield), carbon content calculated, mg of C for ¹⁴C measure, mg of C for stable isotope measure.

AMS measurements

All AMS ¹⁴C measurements have been carried out using the EN tandem accelerator at Aarhus University (Denmark). The ¹⁴C dating procedure for lime mortars and lime lumps has been described in detail in Heinemaier et al. (2010) and Ringbom (2011). The vessels were opened under vacuum and split into two aliquots. Part of the CO₂ gas was used for d¹³C and d¹⁸O analysis on a GV Instruments Isoprime stable isotope mass spectrometer to a precision of 0.15‰, while the rest of the gas was converted to graphite for AMS ¹⁴C measurements via reduction with H₂ using cobalt as a catalyst (Vogel et al., 1984). The calibration of the ¹⁴C ages to calendar years has been done using the IntCal 04 calibration curve and the OxCal 3.10 program (Bronk-Ramsey, 2001).

Calibration

Dates may be expressed as either uncalibrated or calibrated years (the latter abbreviated as cal). An uncalibrated radiocarbon date is abbreviated as ¹⁴C yr BP or simply BP (before present, where the present date is considered 1950 AD). A raw radiocarbon date cannot be used directly as a calendar date, because the level of atmospheric ¹⁴C was not always constant and this fact has produced radiocarbon plateaus and deviations. The ¹⁴C level is affected by variations in the cosmic ray intensity, which is, in turn, affected by variations in the Earth’s magnetosphere (Kudela & Bobik, 2004). In addition, there are substantial reservoirs of carbon in organic matter, in the ocean, in the ocean sediments, in sedimentary rocks and in volcanoes CO₂. Changes in the Earth’s climate can...
affect the carbon flows between these reservoirs and the atmosphere, leading to changes in the atmosphere $^{14}\text{C}$ amount. These occur, for example, when some of the carbon reaches the sample by way of the oceans; because the radiocarbon composition of the oceans differs from that of the atmosphere, this can lead to erroneous dates; stable isotope measurements can be used to see if this effect is present since the stable isotope concentration of the oceans is also different. The uncalibrated date underestimates the actual age of about 10% to 20%. The 3% of that underestimation is attributable to the use of 5568 years as the half-life of $^{14}\text{C}$ in place of the more accurate 5730 years. To maintain consistency with most of published research this is still in use for all radiocarbon measurements (Radiocarbon Calibration University of Oxford, Radiocarbon Web Info, Version 143 Issued 31/10/2013). The standard radiocarbon calibration curve is continuously refined on the basis of new data gathered from tree rings, coral and other studies (Nonni, 2014).

In addition to the natural variation of the curve throughout time, in the 20th century, the radiocarbon concentration in atmospheric CO$_2$ was profoundly influenced by 2 human activities: i) the massive above-ground bomb tests of the 1950s and 1960s have led to a doubling of the pre-bomb $^{14}\text{C}$ concentration in the Northern Hemisphere (see e.g. Nydal and Lövseth, 1983 and references therein). After the Test Ban Treaty in 1963, however, this C excess decreased rapidly by atmospheric CO$_2$ exchange with the oceans and the terrestrial biosphere. Thereby, both oceanic dissolved CO$_2$ and terrestrial carbon were to some extent enriched in $^{14}\text{C}$; ii) the continuous and increasing combustion of fossil fuel delivers a load of $^{14}\text{C}$-free CO$_2$ into the atmosphere, thereby diluting the atmospheric $^{14}\text{C}$ concentration. This process, called the Suess effect (Suess, 1955), had been discovered in tree rings already in the 1950s (Meijer et al., 2006).

The raw radiocarbon dates, in BP years, are calibrated to give calendar dates. Standard calibration curves are available, based on comparison of radiocarbon dates of samples that can be dated independently by other methods such as examination of tree growth rings (dendrochronology), deep ocean sediment cores, lake sediment varves, coral samples, and speleothems (cave deposits). In late 2009, the journal Radiocarbon announced agreement on the INTCAL09 standard, which extends a more accurate calibration curve to 50,000 years (Reimer et al., 2009).

There are two main methods used for calculating age ranges from the calibration curve. The first method to be employed was called the “intercept method” because it can be done by drawing intercepts on a graph. This method tells the years in which the radiocarbon concentration of tree rings is within two standard deviations similar to the level measured (e.g. between 2940 BP and 3060 BP for the measurement 3000±30 BP). A slightly different method is now more commonly used which is called the “probability method”. This requires a computer since the calculations are
more complicated. It gives the time range, in which the confidence can be at 95% of the true value lies. A radiocarbon age, calibrated with a margin of error of 1σ means to have a 68,3% probability that a measurement repetition gives a mean value plus or minus once the error. A margin of error of 2σ means to have a probability of 95,4% if a measurement repetition gives back a mean value plus or minus twice the error. The calibration will show not a whole interval but a series of time intervals equipped with relative probability intervals. A margin of error of 2σ gives a higher reliability degree but wider chronological uncertainty. Once calibrated, a radiocarbon date should be expressed in terms of cal BC, cal AD or cal BP. The cal prefix indicates that the dates are the result of radiocarbon calibration using tree ring data. These values should correspond exactly to normal historical years BC and AD. In academic practice calibrated dates are generally presented along with their source of uncalibrated dates, as the accuracy of the presently established calibration curve varies by time period.

4.3.3 Stimulated Luminescence

The studies of historic buildings dating were normally made on bricks, employing the technique of thermoluminescence, which made it possible to date the moment of the bricks firing. The non-simultaneity between the brick preparation and the building construction commonly leads to an overestimation of the age. The dating of the mortars by means of optical luminescence (Botter-Jensen et al., 2000) represents a solution to this problem because mortars cannot be reused. The luminescence methods are applicable to mortars thanks to the fact that the mineral constituents, namely quartz and feldspars, show luminescence phenomena.

With the term luminescence are indicated processes that occur in insulators and semiconductors, in which the transition of the system from an excited state to the fundamental level is accompanied by emission of electromagnetic radiation in the visible spectrum or in the regions near to it (IR or UV). In general the term luminescence means the emission of light by a system that has been previously exposed to some form of energy. The phenomena of luminescence of interest for dating are thermoluminescence and optically stimulated luminescence, whose sources of external energy of light radiation are respectively thermal and optical.

The stimulation of crystals by visible radiation or by heating, allows the estimation of the elapsed time from the last instant of exposure of the crystals to sunlight or to high temperatures (bleaching event). These crystals are used as natural dosimeters because during the burial time, they accumulate, in the form of electrons captured by characteristic traps, the ionizing radiation from the environment. The dating of historic buildings through luminescence techniques is based on the characteristic of these dosimeter minerals (such as quartz and feldspar that normally constitute
bricks or mortars) to emit a light signal, whenever they are exposed to light or subjected to heating at high temperatures, which is proportional to the trapped charges. Depending on the type of bleaching it is possible to use different techniques of dating: thermoluminescence (TL) in the case the zero event is of thermal nature or Optically Stimulated Luminescence (OSL) if this is due to prolonged exposure to light.

The minerals used for dating, as already said, are mainly quartz and feldspar because abundant in nature and in the samples, and also because a short exposure to sunlight is sufficient to reset the luminescence signal, and then to reset the geological clock. Moreover, the traps are stable and able to maintain the signal, for long periods of time (up to 105 years). However, between these two minerals, despite the feldspars are present in larger amounts in all samples and show a strong signal, it is preferred the use of quartz as this is not affected by the phenomenon of anomalous fading (Wintle, 1973). It is the loss of the signal over time due to instability of the deep traps that can lead to an underestimation of the age.

After the bleaching event, the crystal accumulates the luminescence signal proportionally to the ionizing radiation (environmental radiation) up to a new zero event. If the new zero event is artificially stimulated in laboratory, it is possible to measure the accumulated signal and to use the fundamental age equation to calculate the time since the last event of bleaching (Aitken, 1998).

\[
\text{Age} = \frac{\text{Paleodose}}{\text{Dose-rate}}
\]

Paleodose or Equivalent Dose (ED) = total absorbed radiation (in Gy).

Dose-rate = radiation absorbed annually (in Gy / a).

The paleodose is calculated in the laboratory by comparing the intensity of the natural luminescence signal (TL or OSL) with the one provided artificially by means of a calibrated radioactive source. In other words E.D. is the amount of laboratory dose required to reproduce the luminescence signal of the natural radiation dose (paleodose).

In order to use the stimulated luminescence as a dating technique three hypotheses have to be fulfilled:

- Crystals must have been completely bleached during their last exposure to sunlight or heat.
- The intensity of the luminescence signal must have a relation with the absorbed energy (accumulated dose).
- The radiation absorbed must remain constant during the burial.
**Thermo Luminescence (TL)**

When a certain temperature is reached, the electrons from all traps of a given type are forced out very rapidly. The temperature is specific for each trap type and it is indicated by the peak emission in the glow curve (emission vs temperature). If this temperature is maintained for several seconds, or exceeded, all traps of that type are emptied. The resulting TL signal is proportional to the number of the trapped electrons and thus to the sample age.

The firing of ceramic in furnace resets TL accumulated by “geological” clay and other materials; from this moment, the TL signal starts to increase over time, the more rapidly the larger is its concentrations radioactivity and that of the environment. The amount of TL observed is therefore an indicator of the age of the object. In this case, the datings with TL refers to the last firing of bricks.

The presence of numerous traps and recombination centres at different depths (different energies) in the TL glow curves (the characteristic curve of thermoluminescence) causes several peaks at different temperatures. In general, the peaks at low temperatures are coming from unstable traps and, for this reason in the measures of dating are used only the peaks at high temperatures (Aitken, 1985).

**Optical Stimulated Luminescence (OSL)**

Whereas in thermoluminescence the dating signal of emitted luminescence is obtained by heating the sample, for optical dating the signal is obtained by shining a beam of light onto it; in both cases the signal, which is luminescence emitted by constituent mineral grains, is measured by mean of highly sensitive device, usually a photomultiplier (Aitkens, 1998). In the context of mortar dating the date refers to setting of the mortar, at which the constituent aggregate grains were expose to day light; this exposure, the bleaching event, set the latent signal to near zero and subsequently, when light is blocked by the finishing of the masonry, latent signal builds up again through the effect of exposure to weak flux of ionizing radiation. The efficacy with which the latent signal is reduced to near zero is of critical importance because for mortar grains the exposure may have been barely adequate. One strong advantage of optical dating is that any residual signal after deposition is at least an order of magnitude less then for TL (little noise).

The principal minerals used for OSL are quartz and feldspar, which are separated from the mortar bulk to obtain portions of grains of a given size range and mineral composition; it is on these portions (aliquots) that measurements are made.
The rate of eviction depends on the rate of photons arrival and on the sensitivity of the trap type to photoeviction. If optical stimulation is continued all light sensitive traps are emptied and so the integrated luminescence (sum of all the light contributions) is proportional to the number of trapped electrons and so to the sample age.

The sensitivity of a given trap to photoeviction depends strongly on the wavelength of the stimulating light: the shorter it is the more rapid is the eviction. For quartz the maximum wavelength is around 400 nm (violet). In many quartz samples it is only the trap type associated with the TL peak at 325°C that is easily bleachable. OSL signal is associated only with traps that are easy to bleach.

Evaluation of paleodose is based essentially on comparison of natural OSL with the artificial OSL induced by laboratory irradiation. If the shape of the shine-down curve is the same for all, then the ratio of natural OSL to each laboratory induced OSL will be the same and so the plot of this ratio against shine time will show a plateau. Failure to this plateau test can be due to: 1) non first order kinetics; 2) inadequate bleaching at deposition that left a residual difficult to bleach component.

Prior to measurement the grains are given sufficient heating to empty unstable traps. This is called “preheating” test and this is considered as adequate when a plateau in the ratio of natural OSL and artificial OSL is reached.

It is of critical importance the sampling moment because the grains should not be exposed to daylight. The surface layer should be scraped off and then the sample should be put in an opaque black plastic bag for transportation. The outer part should be discarded as far as for paleodose evaluation is concerned, tough this material can be used for radioactivity measurements and also for use in connection with porosity determination.

**Techniques of sample preparation**

In order to perform luminescence measurements from samples of mortars and bricks it is necessary to extract the mineral to be dated from the sample. The methods of preparation are: fine grain (FG) and coarse grain (CG) and the form of the age equation to be used is determined by the size fraction of the grains.

These are distinguished by the amount of sample used, the particle size and for the “purity” obtained at the end. Furthermore, while the Fine grain technique is mainly used for TL measures, the Coarse grain is principally used for OSL.
**Fine grain**

The Fine-grain technique (Zimmermann, 1971) consists in the selection of the grain size fraction between 4 and 11 µm. The technique normally requires a smaller amount of material. From the sample two millimetres of the surface layer is removed, in order to eliminate any contribution of the α and β radiation (radiation with a penetration capacity into the quartz respectively of µm and mm).

The two laboratories, which carried out these measures, use a slightly different approach. While the laboratory of Milan measures directly after the sieving of the material, the laboratory of Catania uses a series of chemical attacks for the elimination of carbonates, clay and organic materials.

**Coarse grain**

The Coarse grain technique consists in a first step in which the sample is sieved to a particle size between 100 and 300 µm or 300-500 µm (Q13 or Q35), in the case of the laboratory of Catania. The grain size used by the Milan laboratory is the range 150-250 µm.

Then the powder is washed in water that removes the eventual presence of clay and a series of chemical attacks for eliminate carbonates and organic materials are carried out. It is then performed a double mineralogical separation through a heavy density liquid (sodium polytungstate, $\rho = 2.82$ g/cm$^3$) to obtain a fraction of quartz as pure as possible (Fig. 34).

![Fig. 34: scheme to represent the density values of minerals, which is used to remove all except quartz.](image)

The sample thus obtained is rinsed from sodium polytungstate and sieved according to the particle size of interest. The density overlap of plagioclase with pure quartz imposes a treatment with concentrated HF, which is also needed to eliminate the α irradiated skin of quartz grains (20-30 µm). The laboratory of Milan also uses magnetic separation, to eliminate all the minerals with a magnetic behaviour. Finally, another attack in HCl is performed to eliminate the fluorosilicates produced.

It is thus obtained a powder composed of grains of “pure” quartz with a selected size.

This procedure is the standard for the measures OSL and SG-OSL (SingleGrain-OSL), and thus it is
of crucial importance that all the sample preparation phases are made in semi darkness, using a red light.

**Evaluation of the Equivalent Dose (ED)**

The evaluation of the dose absorbed by the sample (ED) consists of a comparison between the luminescence signal obtained from sample without having been subjected to any artificial irradiation in the laboratory, with the signal obtained artificially, in order to find the relation between the intensity of luminescence with the dose absorbed by the sample. This determination can be done with different methodologies: using a “single aliquot” in which both the natural and artificial luminescence is measured, or using different aliquots “multiple aliquots” for determining the natural doses and the artificial ones.

From these two analysis methods were developed several procedures: Added dose, Single Aliquot Regeneration (SAR) and double-SAR (dSAR).

*The additive method*

The additive method utilizes the “multiple aliquots” methodology. A number of equal portions (aliquots) are prepared and divided into groups, with typically 4/6 aliquots or more in each group. One group is reserved for measurement of the natural OSL and the other groups are given various doses of laboratory radiation before measurement, the same dose for each member of the same group. The use of different aliquots obtains different points of the growth curve as a function of the growth of the signal with the growth of the dose. From the first group derives the natural luminescent signal. The other groups of aliquots are artificially irradiated before being analysed, with the addition of an artificial dose to the natural dose absorbed by the sample in order to study the behaviour of the sample with increasing doses, assuming that this behaviour remains constant from the last bleaching event. The growth curve tries to approximate the signal by means of a fit, and thus to obtain the value of the absorbed dose by extrapolation to zero (Fig. 35).
Fig. 35: paleodose determination with the additive method: linear fit of data by extrapolation to zero (Aitken, 1998).

The advantage of this procedure is that the sensitivity of the sample is not altered since this is not subjected to any type of thermal stress caused by repeated cycles of read/irradiation. However, the final value of paleodose is obtained in an area where it is not experimentally known the real trend of the growth curve, but by extrapolation to zero, and then there is a strong dependence of the final result with the mathematical function chosen for the fit. The paleodose accuracy obtainable with the additive method depends both on the aliquot-to-aliquot scatter of the data points and on the degree to which the fitted curve is appropriate. Typically the uncertainty is around +/- 5-10% but it can be much worse for poor data and much better for good data and samples whose growth is linear or is well fitted by a single exponential (Aitken, 1998).

However, the additive method has disadvantages associated with the use of different aliquots for the different points of the growth curve, in fact, the sample may have undergone to a not homogeneous bleaching and the different rates may differ in the percentage of luminescent grains. Furthermore, although the sensitivity of the single rate does not vary during measurement, each of these may have a different sensitivity and therefore respond differently to the artificial radiation. It is therefore necessary a normalization, irradiating all aliquots with same dose (Duller, 1994; Wintle, 1997) and repeating the luminescence measure.

The regeneration method using SAR (Single Aliquot Regeneration)

The main advantage of the methodologies of single aliquot is the best accuracy of the paleodose value. In this case the measures are all made on the same aliquot of which the natural signal was measured, avoiding problems related to the normalization. A growth curve for each aliquot analysed is obtained and thus less amount of sample is necessary. Although, to reach the correct value of paleodose, it is necessary to increase the number of measured aliquots, obtaining an adequate statistic.
The most widely used protocol for single aliquots for OSL measurements is the Single Aliquot Regeneration protocol (SAR) that has been proposed in 1998 by Murray and Roberts and later developed by Murray and Wintle (Murray and Wintle, 2000; 2003) taking into account the various factors that could affect the soundness.

In the protocol developed by Murray and Roberts from all single aliquot the natural luminescence signal is measured and then the laboratory doses are given, with several cycles of artificial radiation and reading of the signal. The obtained values are used for the construction of the response curve for each single aliquot. Once the curve is drawn, it is possible to have the value of the paleodose by interpolation, by means the intersection of the OSL natural signal with the growth curve (Fig. 36).

The advantage of the regeneration method is that no extrapolation is involved and so erroneous paleodose values due to incorrect curve fitting are minimized. The critical disadvantage is that an error in paleodose will occur if there is a change of sensitivity between measurement of natural OSL and the laboratory regenerated OSL, after the natural OSL has been reduced to near zero.

![Graph showing the value of paleodose (P) is determined by interpolation, with the intersection of the OSL natural signal with the growth curve.](image)

Fig. 36: The value of the paleodose (P) is determined by interpolation, with the intersection of the OSL natural signal with the growth curve.

The difficult task of finding a procedure, which avoids sensitivity change, is to monitor the change and thus relate the sensitivity pertaining at measurement of natural OSL to that pertaining at measurement of regenerated OSL. Such monitoring can be done either with the SAR method or by using test doses.

The protocol has been improved by inserting, after each OSL measure, a new step of irradiation/measure with known dose the so-called “test dose” (usually 10-20% of the ED), to normalize the luminescence signal to the current sensitivity of the sample.

The presence of two tests, recuperation and recycling tests, is the huge advantage of the SAR
procedure because they monitor its consistency. The recuperation test consists of a new OSL measurement, at the end of each cycle to check if the sample has been emptied after each irradiation reaching the complete bleaching. The recycling test consists in a new measurement of a dose value already used, to check if the correction of the sensitivity done by the test dose is effective.

Finally, it is possible to perform an additional test, the dose recovery test, which consists in giving to the aliquot totally emptied a known dose, but treating it as unknown, applying again the SAR protocol. If the result of this measurement is still the same, then the parameters used for the determination of ED are appropriate. This last test then provides an estimate of the reliability of the protocol and the maximum achievable accuracy for that particular sample.

**Evaluation of dose rate**

In the fundamental age equation at the denominator there is the dose-rate, which is the radiation absorbed from a sample in a particular place, annually. This is based on the general assumption that the dose-rate is kept constant throughout the period of “life” of the tested sample.

The annual dose (or dose-rate) derives mainly from ionizing radiation emitted during the decay of radioactive isotopes present in the sample (235U, 238U, 232Th, 40K and 87Rb) and in the environment surrounding it, plus a minimal contribution by the cosmic radiation (mainly γ).

The annual dose can be written as the sum of different contributions α, β, γ:

\[ D = D_\alpha + D_\beta + D_\gamma (\text{sample}) + D_\gamma (\text{cosmic}). \]

Because laboratory dose rate are more than a hundred million times those received during burial, there is the possibility of a difference between the two.

The dose-rate is evaluated by assessment of the radioactivity of the aggregate grains, carried out both in the laboratory and on site. The dosimetric measurements are taken *in situ* and the calculation of the contributions of U, Th, K and Rb (radionuclides contained in the sample), in laboratory.

To calculate the dose rate it is necessary to consider the water content of the sample because the moisture in the interstices of sediments absorbs part of the radiation that would otherwise reach the grains. Hence, the dose rate in sediment containing moisture is low than that in the same dry sediment and if the effect is ignored, there may be an underestimation of the age. What is relevant is the average wetness over the completely burial range. For arid environments this is not relevant, otherwise estimation has to be made (Zimmerman, 1971).

The problem of measuring the on site moisture content, in the case of mortars and bricks, is that the
sampling is made by core drilling and, due to the hardness of the building materials, it should be used water to cooling, during drilling. The sample is then artificially wet and a determination of the natural water content on site is not possible. It is necessary to calculate the porosity, the fraction of the total volume that can be occupied by water, in order to estimate an upper limit for the effect on dose-rate.

Another parameter to be considered in the final calculation of the dose rate is the grain size of sample because the dimension of grains varies the capacity of absorption of the sample, as it will be explained in the next paragraphs.

*Dose rate for Fine grain*

For samples prepared following the protocol Fine grain, to measure the *paleodose* via TL, the annual dose due to radiation $\alpha$ and $\beta$ from the external environment is negligible, since $\alpha$ radiations can penetrate the quartz only of about 20-30 $\mu$m, while the $\beta$ penetrate 2-3 mm. Nevertheless, since during the preparation the 2 mm outer are removed, their contribution can be neglected. For $\gamma$ radiation, the average dose due to the sample can be considered negligible compared to that of the environment and can be eliminated from the calculation of the total absorbed dose, making a very low error (Aitken, 1985). It should be evaluated only the dose coming from radioactive nuclides within the sample, the $\gamma$ dose due to environment and to the cosmic radiation.

It is also necessary to correct the component relative to $\alpha$ particles, considering the different efficiency compared to the $\beta$ particles to produce luminescence in the sample. For this reason, it should be evaluated the efficiency, given from coefficient $k$, that must be considered to correct the contribution $\alpha$ to the annual dose.

The total annual dose for samples prepared according to the technique of the Fine grain can then be written as:

$$
Age = \frac{\text{paleodose}}{kD\alpha + D\beta + D\gamma + Dc}
$$

$D\alpha$= $\alpha$ from the sample (with humidity correction);

$k$= $\alpha$ efficiency factor;

$D\beta$= $\beta$ from the sample (with humidity correction);

$D\gamma$= $\gamma$ component of the background;

$Dc$= cosmic ray component.

The $\alpha$ contribution is due only to poor effectiveness.
Like all physical measures, ages obtained with these techniques are always accompanied by imprecision, which means it is indicated a time interval, centred on the age of maximum probability. Taking into account all the factors involved and the complexity of experimental evaluations, we come to estimate a global error average of 7-10%, reduced only in special cases to 5-6% (Aitken, 1998).

Dose rate for Coarse grain

For samples prepared according to the coarse grain technique (100µm≤∅≤500µm) the unique contributions to consider are those from $\gamma$ radiation and particles $\beta$. Indeed, the contribution of $\alpha$ particles can be neglected because they can penetrate only the outermost layer of the grains (10-50µm), which is removed during the physical-chemical preparation phase of the sample through the attack with HF. The $\beta$ and $\gamma$ contributions are predominant and their evaluations are important.

The external dose $\beta$ must be corrected with a multiplication factor of 0.90, which takes into account the grain sizes, considering the attenuation that undergoes when the radiation passes through the sample. The contribution of $\gamma$ radiation is mainly due to the dose from the background that has surrounded the sample at the site of origin, the contribution coming from grains is considered negligible since the $\gamma$ radiation that passes through them does not undergo significant attenuation.

The total annual dose for samples prepared according to the coarse grain technique is:

$$ Age = \frac{\text{paleodose}}{0.90D\beta + D\gamma + Dc} $$

Milan TL protocol

The fine-grain dating technique (Zimmermann, 1971), requiring relative small amount of material, was used for TL dating of bricks. The samples were prepared under dim red light, using the standard procedure and the polymineral fine grain (4-11 µm) fraction was deposed on stainless steel discs.

For the evaluation of the palaeodose, the TL Multiple Aliquot Additive Dose protocol (MAAD, Aitken, 1985) has been applied. In this case many aliquots (from twelve to sixteen) of the same sample are used for the construction of the luminescence vs. dose growth curve. Four aliquots are measured to get the natural signal, others are given different artificial doses superimposed to the natural signal. Plotting the luminescence signal versus the imparted dose, the palaeodose is obtained by extrapolation of the linear portion of the curve.
TL measurements were performed using a home-made system based on the photon counting technique with a photomultiplier tube (EMI 9235QB) coupled to a blue filter (Corning BG12). The samples were heated from RT to 480°C at 15°C s\(^{-1}\). Artificial irradiations were carried out by a 1.85 GBq \(^{90}\)Sr-\(^{90}\)Y beta source (dose-rate: 4.00 Gy min\(^{-1}\)), a 37 MBq \(^{241}\)Am alpha source (dose-rate: 14.8 Gy min\(^{-1}\)).

**Catania TL protocol**

The fine-grain dating technique described in Zimmermann, 1971 was used for TL dating of bricks. The preparation of the rates has been done by decantation of the sample disks of aluminium, preparing 33 disks of which 3 used for the tests to choose the temperature ramp and temperature of preheating, 24 necessary for the application of the additive method and 6 for the determination of the k\(\alpha\). All the work phases and the subsequent measurements have been carried out with controlled lighting to avoid emptying of the samples.

The instrumentation used to perform the measurements is the Risø TL-TL-DA-10. The luminescence is obtained by using a thermocouple which has a maximum temperature of 700 °C with a linear growth rate of 0.1 to 30°C/sec. Detection is made with a photomultiplier tube (PMT) coupled to a filter-Hoya U340 with a transmission curve in the range 260-390 nm, UV, and a source \(\beta\) consists of 90Sr-90Y that provides a dose rate equal to 0.017 Gy/s. The measurements have been carried out in a reducing atmosphere of nitrogen, N\(_2\), in vacuum.

**Milan OSL protocol**

The Single Aliquot Regenerative dose protocol (SAR; Murray and Wintle, 2000) has been applied. After the natural luminescence signal of the sample is registered, the very same aliquot is irradiated in laboratory with increasing doses. To overcome the problem of sensitivity changes due to the repetition of irradiation and heating, a normalizing test dose measurement is performed after each measure. The equivalent dose is obtained by interpolation of the natural signal, corrected for sensitivity changes.

OSL measurements (40 s) have been made at 125°C, after pre-heating aliquots for 10 second at 180°C. The preheat value has been experimentally derived on the basis of the results of a dose recovery pre-heat plateau test. A cut-heat of 160°C was applied to each aliquot before the test dose measurement. To evaluate the Equivalent Dose (ED), the initial part of the OSL decay curve has been used, specifically the first 0.6 s. The background has been assumed as the mean signal of the last 10 s of stimulation. The quartz extracted from mortars was checked for the absence of feldspar contamination using IR stimulation on laboratory irradiated samples. The thermal transfer was
systematically evaluated by calculating the recuperation point and the aliquots, which exceeded 5% of the natural emission, have been rejected. However all the aliquots that had acceptable recycling values, i.e. within the range of 0.90 and 1.10, have been accepted (Roberts and Wintle, 2001).

OSL measurements have been undertaken using a Risø TL-DA-20 equipped with a 90Sr/90Y beta source delivering 0.129 ± 0.012 Gy/s to quartz coarse grains. The samples have been stimulated by an array of blue LEDs (470 ± 30 nm) with a constant stimulation power of 54 mW/cm² or with IR LEDs (830 ± 10 nm) with a constant stimulation power of 360 mW/cm². Photons were detected by a bialkali photomultiplier tube (EMI 9235QB) coupled to a 7.5mm Hoya U-340 filter (280-380 nm).

**Catania OSL protocol**

First, it has been tried to use the protocol suggested by the recent literature (Geodicke, 2011), which indicates the use of the methodology Single Grain for the study of paleodose for young mortars. Furthermore, the measures for the determination of the equivalent dose on Small Aliquot, through the use of the SAR protocol have been also performed.

The quartz grains have been extracted from the samples using the coarse grain technique and obtaining about 8 grams of powder with a particle size between 100-250 µm.

The instrumentation used to perform OSL is the Risø TL / OSL-DA-15. This is provided, in addition to the classic set for the measures blue-OSL that consists of a matrix of blue LED of wavelength 470nm and IR diodes at 875 nm, of a kit for the measures Single Grain that consists of a laser source at 532 nm and a diode laser in the IR at 830 ± 10 nm. The luminescence of the sample is detected by a PMT it is coupled to a filter-Hoya U340 with a transmission curve in the range 260-390 nm, UV, and a source β consists of 90Sr-90Y that provides a dose rate of 0.1 Gy/s.
5. RESULTS AND DISCUSSIONS

In this section the results of the laboratory analyses carried out on mortars and plasters are presented. The first part concerns the characterisation of the aggregate, carried out mainly with polarizing microscopy, and the characterisation of the binder. The detailed petrographic characterisation has been used as the basic scientific knowledge for the absolute dating methodologies discussed in the second part of the chapter.

5.1 Results of the characterisation analyses

Each thin section was first photographed and then described according to the UNI 11176 Document (2006) - Petrographic description of a mortar. Considering the large number of samples, to facilitate the reading of the petrographic observations, data and photographs were organized in a summary table in Appendix. About each thin section is specified: the place of sampling, name of the sample group, type of material, type of binder, binder/aggregate ratio (L/A), maximum size of the diagonal of the largest aggregate grain (MGS), particle size fraction more represented and hypotheses on the origin of the sand. The sections marked with an asterisk are those for which it was performed the image analysis.

The petrography of mortars was used as a discriminant term to distinguish the different phases of construction of the buildings. Finally, the results have been put in relation with prior studies concerning the construction phases of Cathedral and the Ghrilandina tower.

5.1.1 Binder characterisation - Optical microscopy

The analyses of the BRPs of the Cathedral and the Ghirlandina tower show that these mortars are variably hydraulic.

The lime lumps sensu strictu are rounded, white and fluffy part of pure lime of variable size, typically a few millimetres in diameter, due to the technological process of production. Under the polarizing microscope they exhibit porous structures with the same appearance of the surrounding binder (Fig. 37D and 38A). They are the result of the partial carbonation before mixing with the aggregate. Their origin has been attributed also to the direct mixing of lime with wet sand without the addition of water (Carran et al., 2010; Callebaut and Van Balen, 2000).
Fig. 37: photomicrographs in crossed nicols of binder related particles A) at the centre of the image are three fragments of marly limestone underburned with signs of firing and brown-reddish colours. They kept the original structures and textures of the rock and show reaction edges that fade in the binder; B) a fragment of partially burned marble likely proconnesian; C) at the centre an overburned fragment created in areas of high temperature of the furnaces that have caused the sintering of the lime. They are completely extinct with crossed nicols because partially glassy and they show nuclei of recrystallization of calcite; D) at the centre a lime lump sensu strictu with porous structure with similar appearance to the binder.

Fig. 38: photomicrographs in crossed nicols of lime lumps sensu strictu; A) at the centre a lime lump sensu strictu with similar appearance to the surrounding binder; B) newly formed calcite inside a lime lumps.
Fig. 39: photomicrographs in crossed nicols of underburned BRPs; A) partially burnt siltstones; B) in the upper part and at the bottom left side of the image two underburned BRPs showing a reddish-brown coloration due to the presence of oxides and/or hydroxides of iron. They maintain the original rock structure and texture; C) at the bottom right the particle show the sign of the firing in the external part; D) the fragment on the right shows micritic reaction edges that fade into the surrounding binder.

The most frequent BRPs found in these mortars are the underburned fragments of the carbonate stones used to produce the lime, which do not completely calcine during the burning and are left inside the slaked lime as inert (Elsen 2006). They are rounded limestone or marly limestones and they showed the effect of partial burning especially in the outer part (Fig. 37A and 39 B and C). In some cases it was possible to identify partially burnt siltstones (Fig. 39A) and cherts. These fragments commonly show a reddish-brown coloration due to the presence of oxides and/or hydroxides of iron and they commonly maintain the original rock structure and texture (Fig. 39 B, C, D). Moreover these fragments commonly show micritic reaction edges that fade into the surrounding binder (Fig. 39 D).

The mixture of limestone of different composition within the same mortars indicates that the sources of supply of limestone were not quarries opened in a specific outcrop of the Apennines, which would have provided mostly homogeneous rock types, but they were gravels taken from rivers in the area of Modena (Lugli et al., 2011; 2013). The massive presence of these underburned BRPs is due to uneven calcination processes.
The use of stones from ancient Roman monuments to produce lime has been documented only in two cases: two fragments of probable proconnesian marble partially burned have been detected in the wall of a tower apse and in a foundation (Fig. 37B). The ancient ornamental stones were rarely calcined because constituted valuable sources for medieval buildings (Lugli, 2010).

The burning of impure limestones, including clay minerals and quartz grains, produces weakly hydraulic mortars. However, the quantification of hydraulic properties of these products are not easy determinable for the compositional variability of limestone and marly limestone used as raw material. Within this scope, the concept that “the key to binder identification lies in the unreacted residuals” (Walsh 2008) is particularly true for hydraulic binders. Whether or not there is a sufficient unreacted portion of binder left in a mortar is not a matter of age, but rather the quality of reactions achieved during the manufacturing process (Weber, 2013).

The overburned BRPs are formed in areas of the kiln at high temperature, sufficient to cause the partial melting or the sintering of the lime. When sintered, lime is only weakly reactive and can hydrate and participate in the carbonation reactions slowly into the mortar. The overburned BRPs appear under the microscope completely extinct with crossed nicols, because of glassy material, but sometimes they can show nuclei of calcite recrystallization, reorganizing into ordered structures (Fig. 40 A, B).

![Photomicrographs of overburned BRPs](image)

**Fig. 40**: Photomicrographs of overburned BRPs that appear completely extinct with crossed nicols because of glassy material; they show nuclei of calcite recrystallization, reorganizing into ordered structures. In both pictures is possible to observe that a reaction has occurred between the particles and the surrounding binder.

Figure 41 shows the characteristics of two residual clinker grains under the polarising microscope. Belite crystals (C$_2$S) can be identified by their rounded shape, while the interstitial phase is mainly composed of high reflecting ferrite (white in reflected light, brownish in transmitted light). While the nodule is indicative for the NHL (Natural Hydraulic Lime) nature of the sample, its fine-grained texture makes it difficult to precisely identify the phases by this method. In this case the use of SEM
is more promising.

![Fig. 41: a residual clinker grains under the polarising microscope: A) reflected light parallel polars: belite crystals (C$_2$S) with rounded shape and interstitial phase of high reflecting ferrite B) transmitted light crossed polars; transparent belite crystals and brownish ferrite interstitial phase; C) transmitted light parallel polars. Transparent belite crystals and brownish ferrite interstitial phase; D) transmitted light parallel polars. The belite crystals are transparent and the brownish interstitial phase is ferrite.}

Moreover other particles are found in these mortars. They contain prismatic crystals with high interference colour, iron-rich minerals and bubbles (Fig. 42 A, B, C, D, E, F). The optical features are in between an effusive rock (bubbles) and an intrusive one (well formed minerals).

The fragment found in the sample GM16 (Fig. 42A and B) is 4 mm in length and it is characterised by a crystalline structure, it contains rounded bubbles and it shows a reaction edge. Three crystalline phases have been identified: a phase characterised by elongated colourless prismatic crystals with one polarizer and with high interference colour with crossed nicols (green and pink). A second phase with large crystals of squared and hexagonal shape, the colour is yellowish-golden with one polarizer and with low interference colours with crossed nicols (grayish-yellowish of first order). It is also possible to observe a third interstitial phase with low crystallinity or with tiny crystals of brownish colour and with brownish interference colour.
Fig. 42: photomicrograph of particles of unknown origin A) GM16: transmitted light parallel polars: in the particle on the left possibly three phases are present: transparent elongated crystals, squared yellowish crystals, brownish interstitial phase; B) GM16: cross polars: elongated crystals with high interference colours, squared greenish crystals and brownish interstitial phase; C) DM38: transmitted light parallel polars, particle with reaction edge, prismatic crystals and bubbles; D) DM38 transmitted light cross polars, it shows elongated crystals with high interference colours and squared crystals with greyish interference colours; E) transmitted light cross polars: particle with reaction edge, prismatic crystals with high interference colour and bubbles; F) the same particle at higher magnification.

The fragment of DM38 (Fig. 42 B and C) is about 3 mm in length with bubbles and rounded edge. Even this one has three main phases: one has elongated prismatic acicular crystals, colourless with one polarizer and with interference colours from grey to pink and green. The second phase has not
well-formed crystals with golden yellow-colour (one polarizer) and grey/yellow interference colours, mostly concentrated close to the borders. The interstitial phase is not well crystallized or with very small crystals (not well resolved) green and brown with identical interference colours. There are also opaque minerals, which are mainly concentrated at the edges, parallel oriented.

Similar particles are found routinely in other buildings of the Modena area (figures 42 D and E). These fragments are quite similar to those found in the Cathedral and in the Ghirlandina tower, but they were found in the mortars from the castle of Vignola.

For these characteristics and the irregular reaction rims they can be interpreted as burning waste.

5.1.2 SEM-EDS

The SEM-EDS analyses of the binder confirm that these mortars are weakly hydraulic because the presence of silicon, aluminium and iron, however variable, has been always identified (Fig. 43 and table 4). In some cases it is possible to observe that the binder is mainly composed of Ca (CaCO₃,) but in other cases the percentage of silicon inside the binder and in the BRP is not negligible (spectra 1 and 2, table 4).

<table>
<thead>
<tr>
<th>Underburned fragment</th>
<th>CaO (%)</th>
<th>SiO₂ (%)</th>
<th>FeO (%)</th>
<th>Al₂O₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>32,1</td>
<td>58,3</td>
<td>-</td>
<td>10,2</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>23,1</td>
<td>48,3</td>
<td>18,1</td>
<td>8,9</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>59,9</td>
<td>18,2</td>
<td>7,8</td>
<td>3,3</td>
</tr>
</tbody>
</table>

Table 4: EDS quantification of the oxides compounds. The spectra have been acquired in the positions shown in figure 43.

The visualisation of elemental composition by SEM-EDS maps pointed out the variability of the BRP and of the binder, confirming that they have similar chemical composition. In the three SEM-
EDS maps shown below, it is possible to notice that in the first map (Fig. 44) there is an underburned fragment very rich in silicon and a binder with comparable composition. Around the particle, however, there is a reaction rim Ca-rich, probably testifying that a carbonation reaction between the particle and the binder has occurred.

![Fig. 44: SEM map of an underburned fragment very rich in silicon and consequently, the binder show comparable composition. Around the particle, however, there is a reaction rim Ca-rich, probably testifying that a carbonation reaction between the particle and the binder has occurred.](image)

In the second map (Fig. 45) acquired at the edge of an underburned particle containing Mg, it is possible to observe that the surrounding binder has composition Mg-rich. Conversely, in the third map (Fig. 46) it is shown the edges around a Ca-rich overburned particle, surrounded by a Ca-rich binder. In both images the silicon is confined in little roundish spot inside the particle (visible as darker areas, in the electron image).
Fig. 45: SEM-EDS map at the edge of an underburned fragment with a composition of Ca-Si-Mg. The Si is concentrated in the darker spot visible in the electron image. The surrounding binder has a very similar composition of Ca-Si-Mg, as well.

Fig. 46: overburned SEM-EDS map of the edge Ca-rich BRP surrounded by a Ca-rich binder. The silicon is confined in little roundish spot inside the particle (darker areas).
Fig. 47: BSE image of an overburned particle in which are indicated the position of the spectra that have been acquired. The quantification of the compounds is shown in table 5. The darker areas are Si-rich while the lighter ones are Ca-rich.

<table>
<thead>
<tr>
<th>Overburned fragment</th>
<th>CaO (%)</th>
<th>SiO₂ (%)</th>
<th>FeO (%)</th>
<th>Al₂O₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>24,4</td>
<td>59,6</td>
<td>2,2</td>
<td>9,7</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>50,3</td>
<td>36,7</td>
<td>4,4</td>
<td>5,8</td>
</tr>
</tbody>
</table>

Table 5: quantification of the compounds in the different phases of the overburned particle shown in figure 45.

The hydraulic phases of an overburned particle have been identified in more detail (Fig. 47) and atomic ratios of the different elements have been determined semi-quantitatively (table 5). The fragment is composed of two phases: the darker areas are Si-rich while the lighter ones are Ca-rich. The same is observed within others BRPs. In several samples, a lightly coloured zone (in BSE mode) with a composition rich in Ca (-carbonate) at that specific location, has an average composition in oxides of 50-60 wt.% CaO, 18-37 wt.% SiO₂, 3-6 wt.% Al₂O₃ and wt.% 3-4 FeO. These Ca-rich areas are intermixed with darker material rich in Si however variable, with ranges between CaO contents of 10-25 wt.% and SiO₂ contents of 40-60 wt.%.

Effectively, a closer inspection (Fig. 49 A, B, C) shows that the binder as well, in many samples, does not consists of a single phase, but appears to be composed of at least two intermixed components.

The analyses confirm the heterogeneous nature of the binder. In the example in figure 48, in both spectra the SiO₂ content is of 50 wt.%, the CaO of 40 wt.%, Al₂O₃ of 4-5 wt.% and FeO wt.% 2.
Fig. 48: BSE image of the binder in which are indicated the position of the spectra that have been acquired. The quantification of the compounds is shown in table 2. The darker areas are Si-rich while the lighter ones are Ca-rich.

<table>
<thead>
<tr>
<th>Binder</th>
<th>CaO (%)</th>
<th>SiO₂ (%)</th>
<th>FeO (%)</th>
<th>Al₂O₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>41,26</td>
<td>51,40</td>
<td>1,79</td>
<td>4,1</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>39,88</td>
<td>50,70</td>
<td>2,06</td>
<td>5,07</td>
</tr>
</tbody>
</table>

Table 6: quantification of the compounds in the binder as shown in figure 46.

The reduction of Ca ions in some cases observable in specific areas of the binder can be due to leaching effects caused by weathering (Weber, 2013) or by a carbonation reaction of the CSH phases that has produced an accumulation of Ca only some particular areas of the mortar.

The hydration rim around the clinker cores appears to be very rich in silicon, as well as spherical belite grains (C₂S) (Fig. 49 D). The pale grey zones among the C₂S grains within the clinkers contain mainly CaO. Around the clinker, in figure 49D, is shown a Ca-rich binder that indicates again a carbonation reaction between the un-hydrated particle and the binder. The phases containing more Fe e Al are the lightest coloured, so they can be clearly distinguished, and they are possibly brownmillerite (C₄AF) phases. These phases normally surround the belite grains or they are confined in specific zone of the clinker (Fig. 49 A, B, C, D).
Fig. 49: BSE images of residual clinkers found in the mortars: A) residual clinkers immersed in an inhomogeneous binder, composed of different phases with different compositions; B) the same clinker at a higher magnification, in which are appreciable the roundish pale grey belite grains; C) a clinker phase surrounded by an inhomogeneous binder. The phases containing more Fe e Al are the lightest coloured and they are possibly brownmillerite (C₄AF) phases. They surround the belite grains; D) the hydration rim around the clinker cores appears to be very rich in silicon, as well as spherical belite grains (C₂S). Around the particles is shown a Ca-rich binder that indicates again a carbonation reaction between the unhydrated particle and the binder.

In figure 51 are shown the different points of the EDS analysis (results in table 7 of the overburned BRP shown in figure 50). The roundish C₂S phases are very rich in silica. The proviso is that the calcium silicates are strongly depleted in calcium. The lightly coloured zones correspond to that of nearly pure Ca-carbonate (95,5%). Carbonation has led to the formation of a compact rim of carbonate especially outside the particle, around the pores and around the belite grains. These characteristics suggest that segregation may have separate Ca out of the C₂S grains forming a Ca-carbonate cement partially filling the pore space. The spatial distribution of the two phases confirms these results, as the Ca-enrichment (Fig. 50) is consistently located around the BRPs and adjacent to the pores (Mertens, 2009).
Fig. 50: BSE image of an overburned particle. Around the particles is shown a Ca-rich binder that indicates again a carbonation reaction between the un-hydrated particle and the binder. The phases containing more Fe e Al are the lightest coloured (brownmillerite, CaAF) phases. In this image they are confined in the external areas of the clinker. In figures 51 are shown details of this clinker with the EDS points of analyses.

Fig. 51: BSE image at higher magnification of a detail of the clinker showed in figure 50 with the indication of the points of the EDS analyses. The resulted compositions of the different spots are showed in table 7.
<table>
<thead>
<tr>
<th>Spectra</th>
<th>Ca-oxide (%)</th>
<th>Si-oxide (%)</th>
<th>Al-oxide (%)</th>
<th>Fe-oxide (%)</th>
<th>K-oxide (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>95,5</td>
<td>4,5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>14,9</td>
<td>74,8</td>
<td>4,3</td>
<td>3,1</td>
<td>1,6</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>31,1</td>
<td>58,7</td>
<td>3,5</td>
<td>4,3</td>
<td>1,5</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>37,9</td>
<td>8,4</td>
<td>10,2</td>
<td>37,1</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 7: EDS analysis results with the composition expressed in oxides of the areas as indicate in figure 14.

**Burning waste analysis**

The identification of the particles shown in figures 42 A, B, C, D, E and F turn out to be complicated. The importance to identify the minerals formed inside these fragments lead to a correct interpretation of their origin. This information is important because it can be used to determine the firing atmosphere inside the traditional kilns, in terms of temperature, pressure and environmental conditions.

The SEM-EDS analyses provided additional information regarding the nature of these particles. It is possible to observe them at a higher magnification and investigate the chemical compositions of the different unknown phases. Among several analyses performed directly on the thin sections, below are presented examples of the analyses on the fragments showed in figures 42 D and E.

The SEM-EDS maps (Fig. 52 and 53) show that the fragments are composed of two or three phases with variable crystallinity. The more crystalline phase is composed by crystals with an elongated shape composed by Ca and Si (spectrum in Fig. 54). These crystals are immersed in an interstitial phase of Ca-Si nature but with Fe, Al, Mg and Mn, in different percentages, as well (spectrum in Fig. 55). In particular, the presence of iron is the highest one.

Unfortunately the chemical composition alone is not sufficient for the identification of these minerals because they are formed by very common elements found in many crystalline compounds but also because the quantification of the elements with EDS is not exact, and it does not correspond to a unique mineral stoichiometry.
Fig. 52: composite map of a detail inside the fragment showed in figure 42 E and F. In can be noticed the presence of two distinct phases (red and green) and a third of which the composition is not so well determined (grey).

Fig. 53: maps of the single elements of the same detail showed in figure 52.
5.1.3 Raman Spectroscopy

The Raman spectra have been acquired directly on the thin sections, centred on the two fragments found respectively in DM38 (Fig. 42 C and D) and in GM16 (Fig. 42 A and B), trying to attempt a correct interpretation of the minerals.
Fig. 56: Raman spectra. Black, yellow and pink acquired on the crystals of DM38. Red/black at the bottom: reference spectrum of wollastonite, RRuf database.

Fig. 57: Raman spectra. Blue and green acquired on the crystals of DM38. Red/black at the top: reference spectrum of gehlenite, RRuf database.
Fig. 58: Raman spectra. Blue, red and green acquired on the crystals of GM16. Red/black at the bottom: reference spectrum of pseudo-wollastonite, RRUF database.

The results compared with the Raman spectra of the RRUF database indicate the presence of wollastonite in both samples. In particular, in sample DM38 wollastonite 2M and in GM16 pseudowollastonite have been identified (Fig. 56 and 58).

The CaSiO₃ formula only indicates the stoichiometry of the mineral wollastonite a triclinic inosilicate. Pseudowollastonite is the high temperature polymorph (cyclosilicate) formed from 1125°C, whereas parawollastonite is a low temperature polymorph (Taylor, 1990).

The other phase in DM38 shows a low degree of crystallinity. The spectra shapes and peak positions are similar to those of gehlenite, but the low crystallinity produces spectra with low resolution and large peaks so that unambiguous interpretation is not possible (Fig. 57). Gehlenite is a sorosilicate with the formula Ca₂Al(AlSiO₇), member of the melitite group. The discrepancy with the SEM-EDS results on the same phase, lays in the lack of iron in gehlenite.
5.1.4 Quantitative XRD, Rietveld refinement

Tables 8 and 9 report the Rietveld quantitative phase composition of the samples with the relative agreement factors (as defined in Larson and Von Dreele, 1994). The Rietveld graphical outputs are shown in Figure 59 and 60.

Fig. 59: Rietveld graphical output of the bulk of the sample MD5.

Fig. 60: Rietveld graphical output of the binder-enriched fraction of the sample MD5.
Table 8: Rietveld quantitative phase composition of the bulk samples with the relatives agreement factors (as defined in Larson and Von Dreele, 1994). In parenthesis are indicate the errors associated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcite</th>
<th>Quartz</th>
<th>Plagioclase</th>
<th>k-feldspar</th>
<th>Muscovite/illite</th>
<th>Chlorite</th>
<th>Kaolinite</th>
<th>Amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD2F_TQ</td>
<td>46,0 (1)</td>
<td>18,3 (2)</td>
<td>6,4 (3)</td>
<td>2,2 (3)</td>
<td>1,3 (3)</td>
<td>2,4 (3)</td>
<td>3,5 (4)</td>
<td>19,9 (2,0)</td>
</tr>
<tr>
<td>MD3B_TQ</td>
<td>37,2 (2)</td>
<td>25,7 (2)</td>
<td>7,7 (2)</td>
<td>6,6 (4)</td>
<td>4,6 (5)</td>
<td>4,3 (4)</td>
<td>2,2 (2)</td>
<td>10,2 (2,1)</td>
</tr>
<tr>
<td>MD5C_TQ</td>
<td>45,5 (1)</td>
<td>18,1 (2)</td>
<td>6,3 (3)</td>
<td>2,2 (3)</td>
<td>1,2 (3)</td>
<td>2,3 (3)</td>
<td>3,4 (4)</td>
<td>21,2 (1,9)</td>
</tr>
<tr>
<td>GM86B_TQ</td>
<td>42,6 (2)</td>
<td>21,8 (2)</td>
<td>9,4 (3)</td>
<td>8,6 (2)</td>
<td>0,7 (3)</td>
<td>6,1 (4)</td>
<td>5,2 (4)</td>
<td>4,6 (2,0)</td>
</tr>
</tbody>
</table>

Table 9: Rietveld quantitative phase composition of the binder enriched fractions of the samples with the relative agreement factors (as defined in Larson and Von Dreele, 1994). In parenthesis are indicate the errors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcite</th>
<th>Quartz</th>
<th>Plagioclase</th>
<th>k-feldspar</th>
<th>Muscovite/illite</th>
<th>Chlorite</th>
<th>Kaolinite</th>
<th>Amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD2F_LEG</td>
<td>70,9 (1)</td>
<td>3,8 (1)</td>
<td>0,9 (4)</td>
<td>0,7 (3)</td>
<td>0,9 (2)</td>
<td>nd</td>
<td>0,4 (4)</td>
<td>19,5 (1,5)</td>
</tr>
<tr>
<td>MD3B_LEG</td>
<td>54,1 (1)</td>
<td>6,7 (1)</td>
<td>1,0 (2)</td>
<td>nd</td>
<td>0,6 (2)</td>
<td>nd</td>
<td>1,7 (2)</td>
<td>33,2 (8)</td>
</tr>
<tr>
<td>MD5C_LEG</td>
<td>70,9 (1)</td>
<td>3,9 (1)</td>
<td>1,0 (4)</td>
<td>1,4 (2)</td>
<td>0,5 (2)</td>
<td>nd</td>
<td>0,7 (4)</td>
<td>21,6 (1,4)</td>
</tr>
<tr>
<td>GM86B_LEG</td>
<td>66,3 (1)</td>
<td>6,1 (1)</td>
<td>4,5 (1)</td>
<td>nd</td>
<td>3,2 (2)</td>
<td>1,8 (2)</td>
<td>nd</td>
<td>18,1 (7)</td>
</tr>
</tbody>
</table>

Fig. 61: Rietveld quantitative phase composition of the bulk samples.
Calcite is observed in each X-ray diffraction pattern and it results to be the main component of the binder-enriched fractions. Calcite, however, is not only the main component of the binder but, as evidenced by petrographic analysis, is also one of the main components of the aggregate (see section 5.1.8). The XRD, obviously, cannot distinguish between the calcite of the binder from the one of the aggregate.

Quartz and feldspars are also found in every bulk sample with percentages around 20% and 9-18%, respectively. They represent the other main component of the aggregate. It is possible to notice, as expected, that the sieving produces only enrichment in the binder quantity, but fractions of aggregates are always present (more than 10%).

The amorphous quantity varies from 4 to 21,2% in the bulk samples and from 18,1 to 33,2% in the binder enriched fractions. The binder-enriched fraction always contains a higher quantity of amorphous phase. It should not be forgotten, however, that the amorphous fraction could be attributed to different components present in the mortar. For example, oxides and hydroxides of iron, which are part of the aggregate, are counted as amorphous phases. But the increase in the percentage of the amorphous in the binder-enriched fraction may indicate that much of the amorphous is attributable to the binder and not to the aggregate.

In some samples was also found around 1% of dolomite, whereas gypsum (1,2%) was only present in the sample MD3B binder enriched fraction.

5.1.5 XRD single crystal analysis (Gandolfi Camera)

Some of the crystalline phases from the fragment of DM38 have been selected and extracted from the thin section for the single crystal X-ray diffraction analysis. Wollastonite 2M (parawollastonite)
and a low cristallinity phase of gehelenite have been certainly identified, although some other minor phases could also be present. The results are in agreement with Raman analysis on the same fragment.

5.1.6 Thermogravimetric (TG-DTG) analyses

Thermogravimetric analysis (TG-DTG) has been used to determine quantitatively the various compounds in the finer sieved fraction (<63 µm), which is considered to mostly constitute the binder. However a contribution from the aggregate can never be excluded, as it is shown by the XRD results.

![TG-DTG-DTA result on the sample MD2_LEG.](Image)

Fig. 63: TG-DTG-DTA result on the sample MD2_LEG.
Fig. 64: TG:DTG-DTA result on the sample MD3_LEG.

Fig. 65: TG:DTG-DTA result on the sample MD5_LEG.
Fig. 66: TG/DTA-DTA result on the sample GM86B_LEG.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight Loss (%)</th>
<th>CO$_2$/H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt; 120°C</td>
<td>120-200°C</td>
</tr>
<tr>
<td>MD3B_LEG</td>
<td>1,8</td>
<td>1,6</td>
</tr>
<tr>
<td>MD2FM_LEG</td>
<td>0,8</td>
<td>0,01</td>
</tr>
<tr>
<td>GM86B_LEG</td>
<td>0,99</td>
<td>0,25</td>
</tr>
<tr>
<td>MD5_LEG</td>
<td>0,58</td>
<td>0,16</td>
</tr>
</tbody>
</table>

Table 10: TG results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO$_2$ (weight loss ≥ 600°C)</th>
<th>Calcite from TG</th>
<th>Calcite from XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD3B_LEG</td>
<td>23,48</td>
<td>53,39</td>
<td>54,1</td>
</tr>
<tr>
<td>MD2FM_LEG</td>
<td>30,56</td>
<td>69,49</td>
<td>70,9</td>
</tr>
<tr>
<td>GM86B_LEG</td>
<td>27</td>
<td>61,40</td>
<td>66,3</td>
</tr>
<tr>
<td>MD5_LEG</td>
<td>29,52</td>
<td>67,13</td>
<td>70,9</td>
</tr>
</tbody>
</table>

Table 11: Comparison between the results from TG and the results of XRD. The quantity of CaCO$_3$ has been recalculated from the quantity of CO$_2$ derived from the TG results.

TG/DTG summary results are shown in table 10. The comparison between the results from TG and the results of XRD are presented in table 11. It is possible to observe that there is a correspondence among the quantity of calcite determined by TG and the quantity of calcite determined by XRD.

The temperatures of the TG ranges correspond to the weight loss due to: adsorbed water (<120°C), the loss of chemically bound water (200-600°C) and the loss of CO$_2$ (>600°C) due to the decomposition of carbonates.
The weight loss in the temperature range <120°C, attributed to adsorbed water is lower than 1% for most samples. This should indicate mixtures of non-hydraulic nature, because, in theory, hydraulic components are hygroscopic materials. This property turns out to be very useful in distinguishing hydraulic mortars from typical lime ones, as the latter have usually have low contents of adsorbed water (Baskolas et al., 1998). The only sample that exceeds 1% is MD3.

The weight loss in the 120-200°C temperature range, attributed to the crystallization water of hydrated salt, is less than 0.5%. Only one sample, MD3, exceeds in both temperature ranges a weight loss content of 1%. This can be attributed to the loss of crystallization water of the gypsum that was identified by XRD and optical microscopy. MD3 has in fact the characteristic peak of gypsum dehydration at 130-160°C. Moreover, as was mentioned above, another percentage rate could derive from the rehydration of clays and other minerals, contained also in the aggregate.

The weight losses in the 200-600°C range may be attributed to the chemically bound water, and could be indicative of hydraulic compounds in the binder fraction. However, in this range there might also be losses of other compounds, such as calcium and magnesium hydroxide, hydromagnesite, organic compounds, etc., that can not be excluded. The weight losses of the binder fraction in the 200-600°C temperature range varied from 3.06% to 8.07%. The presence of the hydraulic phases is indicate by the TG results because a weight loss of the bounded water is documented, even if the CSH phase do not show clear and well-delimited dehydration peak. According to Genestar et al. (2008) and Bultrini et al. (2006) a weight loss of hydraulic water over 3% indicates that the binder is hydraulic. As a consequence, all the analysed mortars are classified as hydraulic. These hydraulic compounds, probably calcium silico-aluminate hydrates, can be the result of the calcination of marly limestones. In any case, also the aggregate contains a small amount of bound water. Part of this water could therefore result from the loss of constitutional water of minerals contained in the aggregate.

The CO$_2$/H$_2$O ratio between the weight loss per cent ascribed to the CO$_2$ (>600°C) and the weight loss per cent attributed to the hydraulic water (200-600°C) is of particular interest. This ratio could give important indications on the hydraulic nature of a mixture, especially for the binder fraction (Baskolas et al., 1995; Moroupolou et al., 1995). Table 10 reports the values of per cent hydraulic water and the CO$_2$/H$_2$O ratio, showing an inverse relationship between them. In fact, the highest bound water values corresponded to the lowest value ratios whereas the lowest hydraulic water values corresponded to the highest value ratio. In the study of Mertens (2009) the samples classified as ‘non hydraulic’ sensu stricto generally yield ratios around 5 or higher, the samples classified as hydraulic, give ratios below 5 (Mertens, 2009). According to this classification only sample MD3
can be considered hydraulic. Conversely, the results obtained by Moroupolou et al. (1995) found values of the ratio CO₂/H₂O from 0,8 to 4 for cementitious mortars, from 2 to 9 for bricks mortars and from 11 to 20 for lime mortars. Following this classification all the mortars analysed can be classified as slightly hydraulic.

5.1.7 Aggregate point counting analysis

The components, which constitute the aggregate of the mortars, are generally common to the various samples analysed, although in different proportions. The main ones are:

- Angular clasts of monocrystalline or polycrystalline quartz;
- Angular clasts of feldspars (k-feldspar and plagioclase);
- Rounded fragments of carbonate microcrystalline rocks (micrites);
- Angular fragments of spathic calcite;
- Rounded fragments of ophiolitic rocks (serpentinites, spiliti);
- Bioclastic fragments of microfossils and macrofossils;
- Rounded fragments of glauconite;
- Rounded fragments of shales;
- Fragments, sometimes even of considerable size, of quartz siltstone in carbonate cement, some of which contain glauconite;
- Rounded bricks fragments.

The aggregates mixed with the lime for mortar and plaster production are fluvial sands taken from the rivers of the Modena area. The identification of the supply sources of the sands, shown in figure 67, was possible through the point counting analysis of the aggregate according to the classification scheme devised by Lugli et al., 2007 (Fig. 22A).
5.1.8 Groups of mortars

Cathedral

Type A

This type of mortar contains partially hydraulic lime binder and the binder related particles (both underburned and overburned) are frequent. The particles reach dimensions up to one centimetre. They were found to a greater extent and large dimension in the mortars from the foundations of the Cathedral.

The representative sample of the group, DM12 showed an average binder/aggregate ratio of 0.7. The proportions for mortar preparation is 1:2. The particle size of the aggregate is fine-medium (0.2-0.5 mm). Commonly the fragments of micritic limestone showed larger dimensions.

The porosity is generally low, but some samples were severely damaged and thus crumbled.
hindering a correct estimation of the original porosity.

The composition of the aggregate is: micritic limestones (very abundant) and sparry calcite, fossils, quartz, feldspar, argillite, siltstone, chert, ophiolite fragments, iron oxides and/or hydroxides, glauconite. The presence of silicoclastic grains in the same proportions of total carbonates suggests a provenance from the Panaro River (LUGLI et al, 2007).

Fig. 68: the textural differences of the mortars have identified four different typologies considering the more frequent size fraction in the aggregate, the aggregate composition and origin of the sand, binder type and the binder/aggregate ratio.

**Type B**

Partially hydraulic lime mortars with the presence of binder related particles (underburned and overburned) up to 5 mm in size. The representative sample of the group shows a binder/aggregate ratio about 0.8. The mortar mix proportion is 1:2. The aggregate is a medium-large grain size sand, poorly sorted.
The porosity is generally low but several samples showed disintegration phenomena jeopardizing the correct evaluation of the original porosity.

The composition is: micritic limestones and sparry calcite, quartz, feldspar, argillite, siltstone, chert, ophiolite fragments, iron oxides and/or hydroxides, glauconite. The presence of grains of quartz and feldspar in the same proportions of total carbonates indicates that the sand was taken from the same stream of group A, the Panaro River (Lugli et al, 2007).

This group includes samples from the turrets apses, from the north side attic and from the south side. Furthermore, the majority of the samples come from C1 and C3 cores of the foundations and some from C2 and C4.

**Type C**

This type of mortar is characterized by aggregate with well-sorted grain size. The representative section (MD19) has a binder/aggregate average of 1.3, corresponding to a mixing ratio of about 2:1. The porosity is low.

The composition is quartz, sandstone and siltstone, feldspar, limestone (calcite and micritic fragments spathic, shells, fossils), ophiolitic rocks, shale, fragments of brick with rounded edges, flint. The siliciclastic component prevails over the carbonate and suggests a source of sand from the Secchia River (Lugli, 2007).

This group includes samples of mortars and plasters related to the construction phase performed by the Campionese (upper part of the walls of the apses of the south and north and of the façade) and later.

**Type D**

This type of mortar has a partially hydraulic lime binder with frequent binder related particles (both underburned and overburned). The binder/aggregate ratio is variable from 0.55 to 1. The sand has a medium-coarse particle size, poorly sorted.

The composition is: micritic limestones and sparry calcite, high presence of fossils, quartz, feldspar, argillite, siltstone, chert, ophiolite fragments, abundant glauconie, iron oxides and/or hydroxides. The predominance of total carbonates amount compared with the quartz-feldspar component suggests an origin from a minor local stream e.g. Tiepido, Cerca or Guerro (Lugli et al, 2007).

The porosity in general is low except for the thin section C160-2,15 which shows strong disaggregation phenomena.

This group includes samples of mortar only from the foundations of C3, C4 and C5 cores.
Mortars from previous buildings below the Cathedral:

Porosity is low but in some areas very large pores were observed (some mm). The lime binder is characterized by abundant fragments of variable size of binder related particles (in particular overburned fragments). The aggregate is very fine (in average 0.02 mm); only some fragments (especially calcite or lime lumps) are rather coarse (from 0.5 mm up to some mm).

Porosity is low, but in some areas very large pores were observed (one mm across).

The composition is: quartz crystals in a higher percentage with coarse size and rounded shape, limestone, sparry calcite, micritic fragments and no fossils, shales, ophiolites, cherts, brick fragments, glauconia, muscovite, plagioclase. The predominance of quartz-feldspar component compared with the total carbonate fractions and the fine grain size suggests a provenance from a local minor stream, the Grizzaga River (Lugli et al, 2007).

DM 43 different from all the others

The lime binder is characterized by abundant fragments of variable size of binder related particles (in particular overburned fragments). The aggregate is very fine (in average 0.02 mm), well sorted. The binder/aggregate ratio is >1.

The composition is: micritic limestones and sparry calcite, abundant fossils, quartz, feldspar, argillite, siltstone, chert, ophiolite fragments, abundant glauconite, iron oxides and/or hydroxides. The predominance of total carbonates amount compared with the quartz-feldspar component and the fine grain size of the aggregate suggest an origin from a minor local stream e.g. Tiepido, Cerca or Guerro (Lugli et al, 2007).

Ghirlandina

Type A and Type B

In this type of mortar, with partially hydraulic lime binder, are frequent the BRP that reach dimensions up to centimetres.

The B/A ratio is generally <=1, except for the mortars from the second floor which contain a higher quantity of binder. The particle size of the aggregate most represented is that of a fine to medium sand (0,2 to 0,5 mm), but there are also a few samples with a larger grain size (type B). The aggregate size is not sorted. The porosity in general is low.

The composition is: micritic limestones and calcite, fragments of shells, fossils, quartz, feldspar, argillite, siltstone, chert, fragments of ophiolite, lumps of oxides and/or iron hydroxides, glauconite granules. The presence of siliciclastic grains in the same proportion of the total carbonates indicates
an origin from the Panaro River (Lugli et al, 2007).

This type of mortar is very similar to the mortars of the first phases of the Cathedral. The mortars from the first and the beginning of the second floor and the mortars within the 5th and the 6th floor belong to this group.

**Type C**

This type of mortar is characterized by aggregate with a grain size not well sorted, the most represented is that of a fine sand. The binder/aggregate ratio is in general >=1. The porosity is low.

The composition is quartz, sandstone and siltstone, feldspar, limestone (calcite and micritic fragments spathic, shells, fossils), ophiolitic rocks, shale, fragments of brick with rounded edges, flint. The siliciclastic component prevails over the carbonate suggests a source of sand from the Secchia river (Lugli, 2007).

This group includes samples of mortars and plasters from the tower cusp.

**Type D**

The B/A ratio is in generally greater than one. The sand has a particle size from a very fine to coarse, very poorly sorted. The porosity in general is low.

The composition is: micritic and spatic limestones, foraminifera shells, quartz, feldspar, shale, siltstone, chert, fossils and fossil fragments, fragments of ophiolite, glauconite granules, lumps of iron oxides and/or hydroxides.

The predominance of the total carbonates on quartz-feldspar component suggests an origin from a minor local stream Cerchia, Tiepido or Guerro (Lugli et al., 2007).

This group includes samples of mortars from the second to the beginning of the fifth floor of the tower.

**5.1.9 Plasters characterisation**

**Cathedral**

**DM17B - Campionesi phase**

Painted layer: lime wash painting, dark brown homogeneous colour with thickness 0.08 of mm. Two superimposed layers (not found over the entire length of the sample) with good adhesion to the support are observable. They probably were laid dry.

Plaster layer: the binder aggregate ratio is >1. The binder is calcareous. The aggregate particle size
ranges from fine to medium sand (0,2 - 0,3 mm). Only a few grains exceed 0.5 mm in size. The composition is: fragments micritic limestone, sparry calcite, fossils, quartz, sandstone and siltstone, feldspar, argillite, ophiolites, micas.

The porosity is low.

Fig. 69: Photomicrography of thin sections of the plasters A) DM 17 B two layers of lime wash are observed, parallel nicols; B) DM 17 B two layers of lime wash are observed, crossed nicols; C) DM17R painted layer od red colour, parallel nicols; D) DM17R painted layer od red colour, crossed nicols; E) DM 18 individual grains of blue pigment within the layer are observable, parallel nicols; F) DM 18 individual grains of blue pigment within the layer are observable, crossed nicols.
DM17R - Campionesi phase

Painted layer: thickness 0.05 mm, dark red uniform colour. Good adhesion. The layer was probably laid dry directly on the plaster. It is not observable the presence of pigment grains.

Plaster layer: the binder aggregate ratio is >1. The binder is calcareous. The aggregate particle size ranges from fine to medium sand (0,2 - 0,3 mm). Only a few grains exceed 0.5 mm in size. The composition is: fragments micritic limestone, sparry calcite, fossils, quartz, sandstone and siltstone, felsdpar, argillite, ophiolites, micas.

The porosity is low.

DM18 – Decoration on top of the Campionesi layer

Painted layer: thickness of 0.1 mm. The colour has been laid in a single layer probably directly on the dry plaster. There is the presence of grains of pigment by grinding of blue, green and rare red.

Plaster layer: the binder/aggregate is >1. The binder is calcareous. The aggregate particle size ranges from medium to coarse sand (0,2 - 0,3 mm).

The composition is: fragments micritic limestone, sparry calcite, fossils, quartz, sandstone and siltstone, felsdpar, argillite, ophiolites, glauconite, micas.

The porosity is low.

Comments on the decorations

The decorations in red and white bands dated back to the Campionesi master’s phase found on the walls in the attic are characterized by similar composition. They were painted with only white lime (calcite crystals and micritic calcium carbonate) for the white colour and hematite (Fe₂O₃) and magnetite for the red colour (red ochre). Under the microscope are not distinguishable any colour pigment grains, but the colours are spread over the entire painting layer (Fig. 69 A, B, C, D). Regarding these two colours no diagnostic particles permitting the dating of the paintings with sufficient accuracy have been identified. Both of them are compatible with the dating of the thirteenth century of the Campionese decorative phase because these inorganic pigments, natural or artificial, have had a wide circulation and they were used since ancient time.

The pigments found on the plaster layer above did not show any decoration, but only a dark grey black layer. The observation of the thin section by means of optical microscope in transmitted light show large crystals of blue and green pigments (azurite and malachite, Baraldi et al., in press). The relative dating of this layer was placed (Autentrieth, 1984) from the thirteenth century, the Campionese decorative phase, and the first half of the sixteenth century, when the roof was rebuilt.
with the vaults visible today.

5.2 Discussions

5.2.1 Hydraulics of the binder

To trace back the origin of the raw materials used to produce the mortar samples, petrography is the most appropriate method (Fratini et al., 2008; Lammel and Lehrberger, 2007; Lugli et al. 2013). Because impure, clay-rich or silica-bearing limestones can yield a hydraulic binder, the hydraulics of a mortar might also be an indirect indication of the source of the limestone (Mertens, 2009).

The mixture of limestone relics of different composition within the same mortar indicates that the sources of supply of limestone were not quarries opened in a specific outcrop of the Apennines, which would have provided mostly homogeneous rock types, but they were gravels taken from rivers in the area of Modena (Lugli et al., 2011). The massive presence of these underburned BRPs is due to uneven cooking processes.

Mortars are heterogeneous materials of which the constituents can be intrinsically heterogeneous. This automatically leads to variations in mortar composition. Moreover, different burning conditions can affect the hydraulics (Mertens et al. 2006 and Chapter 2 in this thesis) and the hydraulics could be affected over time (e.g. by carbonation) as well. Very old mortars with presumable natural hydraulic characteristics commonly show only indirect evidence of their original composition.

Examining the inhomogeneous binder under crossed nicols, carbonate rich zones and patches richer in silica phases are observed. However, due to alteration processes (carbonation, leaching, etc.) the original hydraulic phases are not always easy detectable. Under cross-polarized light also the BRPs have shown similar appearance.

The high amounts of Si, Al and Fe in the binder, confirm the hydraulic character of these mortars. Sometimes Ca and Si have moved to form separate phases, probably derived from an originally presence of CSH phases. The nearly pure Ca-carbonate zones around the silicon-rich BRPs are an indication that a carbonation reaction of the CSH has occurred. The distribution of the two phases confirms these results, as Ca-rich zones are located adjacent to the pores and enclosing darker zones that are richer in silica. This phenomena indicates decomposition of the original CSH and thus, indirectly, the hydraulic character of the binder (so-called vanishing hydraulics). Within the overburned BRPs, clinker phases with ferrite and belite have been identified. Similarly, belite grains are richer in silicon, not respecting the stoichiometry of the molecule. This is also possibly
due to the migration of Ca ions, producing a carbonatic cement around the grains and accumulated around the pores.

The presence of ferrite (C₄AF) and the major fraction of amorphous phase can be related to hydrate phase (CSH, CAH). Physico-chemical processes resulting in carbonatation of the CSH phase lead to the formation of new Ca-carbonate. Indeed, in these mortars only calcite is detected whereas its polymorphs vaterite and aragonite, related to the hydraulicity, are not identified. Remarkably, vaterite and aragonite are generally considered to be less stable compared to calcite at atmospheric pressures and near-room temperatures. Therefore, they probably are not present due to the old age of these mortars, so that a transformation in calcite can be occurred.

Moreover, these mortars underwent numerous transformations. Beside carbonation, dissolution and precipitation reactions are commonly observed. Even though these processes do not necessarily lead to a significant addition or removal of material (Leslie & Hughes, 2002) secondary porosity or secondary pore fillings are commonly visible especially in the mortars belonging to the lower parts of the buildings. Therefore, calculated binder/aggregate ratios might sometimes differ from those anciently adopted.

Particles of unknown origin that are systematically found in the mortars are interpreted as burning waste. These particles result containing wollastonite and gehelenite.

The evidence of carbonate-silica reaction is then preserved in the form of Ca-silicates as belite or wollastonite (the latter only in the burning waste). These minerals both result from the interaction of silica or a silica-bearing phase with calcite or lime. For higher relative concentrations of silica, the formation of wollastonite is favoured, whereas C₂S is formed from locally higher calcium oxide concentrations (Mitsuda et al., 1985). However, C₂S is not always preserved as it reacts with water to form CSH.

Two different Raman spectra on the burning waste differentiated between pseudo- and parawollastonite. Wollastonite is a single chain silicate that occurs in three polymorphic forms: low temperature triclinic form [1T], monoclinic form or the so-called para-wollastonite [2M] and the high temperature form pseudo-wollastonite, which occurs in the pseudo-hexagonal form and which is found rarely in nature. The conversion of the low temperature form to the high temperature form takes place at 1125°C (Maithan Obeid, 2014).

Furthermore, the carbonate-silica-alumina reaction is also testified by the presence of Ca-aluminates, as gehlenite. But in the interstitial phase of the fragments were also found elevated percentages of iron. In oxidising atmosphere at firing temperatures of 850°C, 950° and 1050°C Fe³⁺ has proved to incorporate in the structure of gehlenite, among other minerals. In gehlenite, the
incorporation of Fe$^{3+}$ increased the amount of ferri-gehlenite component, (Ca$_2$Fe$_2$$^{3+}$SiO$_7$) (Rathossi and Pontikes, 2010). The elevated presence of iron oxides and hydroxides among the fired limestones can have facilitated the replacement of some aluminium and calcium atoms by iron atoms in the structure of gehlenite. During the firing of carbonate with clay impurities, melilite is frequently formed in very small crystals (1–5 µm or less in size). In the literature, this phase is generally called gehlenite, however, no precise composition is available (Dondi et al., 1999).

A good calcination with no or a low amounts of under- and overburned particles, requires an appropriate selection of the raw material and its particle size distribution. Additionally, adequate heating rates, burning temperatures, duration and homogeneous heat distributions throughout the kiln are necessary. Experimental, small-scale traditional lime binder production (Schouenborg, et al., 1993; Hughes et al., 2005) has demonstrated that high temperatures gradients, from 600°C to 1400°C may exist in lime kilns and that the control of parameters such as air in- and outflow are particularly important for efficient lime burning (Mertens, 2009). The high abundance of these BRPs in the mortars of all the phases of construction of the Cathedral and of the Ghirlandina tower suggests a lack of selective removal of these particles.

5.2.2 Relative chronology of the construction phases

The petrographic analyses, carried out on samples of mortars and plasters of the Cathedral and the tower Ghirlandina of Modena, have revealed that the techniques of production and supply sources of raw materials has changed during their construction.

The most important parameters for distinguishing the different types of mortars are the origin of the sands that have been aggregated to lime and the binder/aggregate. The sands of major rivers, such as Secchia and Panaro, are distinguishable from those of smaller rivers, Tiepido, Cerca and Guerro as shown in the triangular graph (Fig. 67). It should be noted that different supply sources of sands do not necessarily indicate different and distinct phases of constructions, since it is conceivable that at certain times in the history of the monument can be activated multiple sources of sand and limestone at once (Bianchini et al., 2004)

The mortars of the oldest phases of construction of the Cathedral (12$^{th}$ cent. sec.- type A and B) are distinguishable from those of Campionesi age (13$^{th}$-14$^{th}$ cent., type C) for a low percentage of binder and the different origin of the sand used as inert. This difference may reflect local production techniques less sophisticated than those of the workers from Como.

The results of the petrographic investigations conducted on mortars of the foundations are shown in fig. 70 A and B. The samples were coloured with the colour of the group in which they are allocated.
It is possible to say that all mortars contain a low percentage of binder (binder aggregate ratio 1:3) and a high presence of BRPs. Most of the mortars contain aggregate from the river Panaro with a particle size from fine (mortar type A) to medium and coarse (mortar type B). Most of the samples of the foundations analysed are made by mortars of these two types. Our hypothesis is that they belong to construction phases very close in time and carried out by the same workers. The difference in size may be due to collection of sand in the same river but in different sedimentary areas (meander bars, longitudinal bars or terraces). The particle size differentiation could therefore indicate a collection in different times: during the minimum flow of Panaro it is possible to collect sand of larger particle size directly within the riverbed, while in other seasons the collection may be conducted only in unflooded areas that in some cases may yield different grain size sands.

![Fig. 70: foundations with coring C4 and C5. Survey modified from an original one by eng. Silvestri. In light blue are indicated type A mortars, in dark blue type B mortars (both with sands of Panaro river) and in green type D mortars with sands from Tiepido river.](image)

Only in the foundations of core C3, C4 and C5 is used sand from Tiepido river (type D). According to the studies carried out by Peroni (1984), these walls are contemporary and they would be built by Wiligelmo in the construction phase B (Peroni, 1984). This “anomaly” could be explained in two ways. The first hypothesis, to be verified by further diagnostic investigations, is the inclusion of existing mortar: it is plausible by the discovery in the foundations of the resulting material of previous Roman buildings and of the pre-panfranchian cathedral. The second hypothesis would be the manufacture of wall in which the masonry mortar in the casing of the foundation is different from the mortar filling the core of the masonry.

The foundation of the wall crossed core C4 documented the presence of a wall belonging to a previous Cathedral (as of 1913 relief of Domenico Barbanti, published by Bertoni in 1913, remains attributed by critics to the second basilica prelanfranchiana). Different types of mortars may have incorporated fragments coming from the older building (samples C460-1,4C and C460-1,8).
Fig. 71: reconstruction of the Cathedral types of mortars of the elevations according to petrographic parameters. In light blue mortar type A, in dark blue mortar type B and red mortar type C. Phases according to Peroni, 1984. From an original survey of arch. Palazzi, modified.
Figure 71 shows the reconstruction of the types of mortars of the walls divided according to the petrographic parameters and Peroni (1984) construction phases.

The mortars of group C show a higher percentage of binder ratio (binder/aggregate ratio of the mixture 2:1) and the choice of an aggregate well sorted. It can clearly represent an advanced knowledge of building material preparation and therefore a different stage, probably made by more specialized and skilled workers compared to previous phase. This group includes samples of mortars and plasters related to the Campionesi Masters (the upper part of apse walls). It was possible to find that, even in the following phases (superimposed plasters of the attic), similar types of mortars were adopted: the technological innovations made by the workers from Como have been maintained for centuries afterwards.

Fig. 72: reconstruction of the Ghirlandina types of mortars according to petrographic parameters. In light blue mortar type A, in dark blue mortar type B, in red type C mortars and in green type D mortars. From an original survey of arch. Palazzi. Construction phases according to Labate (2010).
Very similar mortars with similar petrographic characteristics (A and B type) were found in the first two floors of the tower. The hypothesis suggested by most authors (see chapter 3) that the starting of the Ghirlandina construction probably dates back to the Lanfranchian period, in the same epoch of the Cathedral’s construction, is now based on scientific observations.

The second period began later with the Campionese Masters after a long interruption and the elevation of the structure continued up to the Torresani Room (fourth floor). Indeed, the mortars from the second to the beginning of the fifth floor showed to be made all with sands from the minor rivers. There are only three mortars with different sands (Secchia river) that can be probably attributed to later additions.

Within the fifth and the sixth floor was found a group of mortars belong to type A, probably as a consequence of the construction phase which started in 1261 when the 5th floor was added to the tower (Labate, 2010).

The last phase of the elevation of the tower with the octagon is made of mortars with sand of the Secchia river and fine grain size. The others mortars form the 4th to the 6th floor with sands from the Secchia River are probably due to later restorations.

5.3 Results of AMS Radiocarbon dating

The petrographic analysis revealed some potential problems for the $^{14}$C dating. Firstly, the aggregate is rich in fine limestone clasts and this may be a problem in the case of Cryo2sonic preparation (Nonni, 2014). If the limestone sand dissolves rapidly in the hydrolysis process, problems can arise also for the sequential dissolution preparation. The carbonate sand may contribute with geological carbon yielding a $^{14}$C age that is older than the true age. Secondly, the samples resulted to be slightly hydraulic. The hydraulic minerals are micro-crystalline and they are intergrown with calcite. Any grain size fraction of the binder has mixed grains in which the insoluble or slowly dissolvable hydraulic part may shield the soluble carbonate part during dissolution. Furthermore, the possibility of the formation of portlandite during the hydraulic setting of the mortar can cause, in presence of fractures, the input of successive CO$_2$, which would cause a younger measured age than the expected one. Thirdly, the samples were in general full of BRPs. An incomplete calcination is generally not a problem, since these contaminants usually dissolve slowly and they do not go in suspension with the Cryo2sonic preparation (Marzaioli, 2011). However, if these particles are very abundant and the sand contains older limestone contaminants, the combination of the two sources may yield peculiar results that require a detailed interpretation.
The types of BRPs identification and classification is important for the radiocarbon dating because while the underburned and overburned fragments are considered sources of dead carbon contamination, the lime lumps *sensu strictu* have revealed to be sometimes fundamental because not contaminated by the aggregate.

### 5.3.1 Results of Cryo2sonic (CIRCE Lab. Caserta)

Results of measured radiocarbon age carried out at Circe lab. are listed in Table 12.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Expected age</th>
<th>¹⁴C age (BP)</th>
<th>Calibrated age 2σ</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>C130 lump Cathedral</td>
<td>1120-1130</td>
<td>1570±38</td>
<td>412-571</td>
<td>Contamination from secondary calcite</td>
</tr>
<tr>
<td>C130 susp lump Cathedral</td>
<td>1120-1130</td>
<td>444±37</td>
<td>1411-1511</td>
<td>1601-1615</td>
</tr>
<tr>
<td>DM 8 lump Cathedral</td>
<td>1099-1106</td>
<td>970±45</td>
<td>988-1167</td>
<td>Date known from documents</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Very little quantity: more than one lump</td>
</tr>
<tr>
<td>DM 8 susp lump Cathedral</td>
<td>1099-1106</td>
<td>1180±38</td>
<td>769-904 912-970</td>
<td>Date known from documents</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Very little quantity: more than one lump</td>
</tr>
<tr>
<td>DM 101 susp Cathedral</td>
<td>1184-1220</td>
<td>1055±33</td>
<td>896-923 939-1026</td>
<td>Too little lime lumps</td>
</tr>
<tr>
<td>GM86B lump Tower</td>
<td>1099-1106</td>
<td>953±33</td>
<td>1021-1158</td>
<td></td>
</tr>
<tr>
<td>GM86B susp lump Tower</td>
<td>1099-1106</td>
<td>929±38</td>
<td>1023-1186 1200-1205</td>
<td></td>
</tr>
<tr>
<td>GMC24 susp Tower</td>
<td>1319</td>
<td>743±35</td>
<td>1218-1294</td>
<td>Date known from documents</td>
</tr>
<tr>
<td>GMC24 susp Tower</td>
<td>1319</td>
<td>810±45</td>
<td>1058-1074 1154-1282</td>
<td>Date known from documents</td>
</tr>
</tbody>
</table>

Table 12: results of radiocarbon dating carried out by the Caserta lab.

![Calibrated Age Ranges](image1.png)

Fig. 73: results of radiocarbon dating by Cryo2sonic procedure carried out by the Caserta lab.
The C130_lump (1570 ± 50 B.P.) without the Cryo2sonic preparation (bulk lump) compared to the expected age of the mortars, first half of the 12th century A.D., obtained 412-571 AD calibrated age which are older dates than expected (Fig. 73 and table 12). A significant effect of rejuvenation induced by the Cryo2sonic procedure is evident comparing C130 susp_lump with C130_lump (Fig 73). Measured radiocarbon age on the C130_lump (444 ± 37 B.P.) is not in agreement with the estimated age of the masonry, first half of the 12th century A.D., in fact it has been dated to the 15th century (2σ = 1411-1511 and 1601-1615 A.D.).

Two lumps belonging to DM 8 mortars have been dated: one after the Cryo2sonic preparation DM8_susp) and the other directly as a bulk. A result in agreement with the expected age (AD 1099-1106) was obtained with the lump bulk (cal AD 988-1167), whereas the Cryo2sonic prepared lump reaches an older age (2σ = 769-904 and 912-970).

The dating of the bulk mortar DM 101, belonging from the Campionesi period, led to incorrect results. The Cryo2sonic procedure achieved a date close to the 1000 AD (table 12).

The mortars from the tower yielded satisfactory results in all cases (Fig. 73-74 and table 11). The foundation mortars (GM86B) were dated following different methodologies: one lump after the Cryo2sonic preparation (GM86B susp_lump: 2σ= cal AD 1023-1186 and 1200-1205) and one bulk lump (GM86B lump: 2σ = cal AD 1023-1186 and 1200-1205).

Fig. 74: calibrated dates of the two lumps of GM86.

Radiocarbon dating of two bulk samples GMC24 and GMC24’ prepared with Cryo2sonic procedure (2σ = cal AD 1218-1294) was in agreement with the known date of the completion of the tower cusp (1319).

5.3.2 Results of sequential dissolution (Abo Akademi Lab., Turku)

The first step in this procedure is the alkalinity test using phenolphthalein dissolved in alcohol. An alkaline reaction may indicate the presence of calcium hydroxide, which can react with modern CO₂
in the atmosphere. All the samples result with a low alkalinity and therefore suitable to be dated.

CL inspection revealed some of the aggregate limestone contaminants and the underburned limestone relicts. Fig. 75 A and B shows two CL micrographs of the sample DM101 thin section.

![Fig. 75](image1.png)

**Fig. 75**: CL micrograph of the sample DM101 thin section. The binder to be dated appears as dark brown, orange grains are limestones, blue grains are quartz aggregates and green are possibly feldspars.

![Fig. 76](image2.png)

**Fig. 76**: CL observation of the selected grain size fractions after sieving (76-100 µm) and on the same powder after sequential dissolution. A) The powder before dissolution contains carbonate contaminants and part of silicic aggregates. B) After the dissolution, are only visible the aggregates whereas the carbonate binder and contaminants were both dissolved.

The CL observation have been carried out on the selected grain size fractions after sieving (76-100 µm) and on the same powder after sequential dissolution (Fig. 76 A and B). The aim was to determine if there were any contaminants sources within the powder and whether they were dissolved during the hydrolysis. This consideration can be used to interpret the dating results. Both powders (before and after acid dissolution) were spread over a glass backing glued with a polysaccharide. As is shown in the pictures above, the powder before dissolution contains carbonate contaminants and part of silicic aggregates. After the dissolution, are only visible the aggregates whereas the carbonate contaminants were dissolved.
The $^{14}$C measurements together with hydrolysis data are presented in table 13. The impure limestones used to prepare the lime of these mortars results in binder and BRPs rich in Mg-Fe hydroxides and in hydraulic phases. This can explain the low carbon yield achieved during the dissolution process (2.83-3.86%).

![Graph](image)

**Table 13:** results of radiocarbon dating carried out at the Abo Akademi lab. Because the oxygen isotope ratios were measured after hydrolysis with 85% phosphoric acid they are not comparable with values obtained with standard methods (Craig, 1953).

The obtained dating results are evaluated from $^{14}$C profiles in Fig. 77. The two $^{14}$C profiles
represent samples with rapidly dissolving mortar binder and slowly dissolving contaminants. The curves are indeed concave and the first CO$_2$ released should have a $^{14}$C age close to the correct archaeological age (Lichtenberger et al., 2015). The horizontal profile along the x-axis of the lump GM42, indicates that the two dates obtained from the two fractions extracted at different dissolution time, are very similar ($^{14}$C age BP: 806 and 802). This result can be considered as an indication that the lump selected was free of contaminants.

In Fig. 78 the calibrated Abo Akademi results of the first fractions are shown.

A large amount of contaminants have been identified in DM 101, getting a very old age with the last fraction (from 113 to 357 BC, fig. 77). The second fraction obtained a date around the year 1000 AD (table 9). The expected age (1184-1220 AD) came within the calibrated 2σ ranges (=cal 1030-1169 AD and 1178-1182 AD) results of the first fraction (fig. 78 and table 13).

The three different fractions of the foundation mortars from the tower (GM86B) showed the presence of dead carbon contaminants. The second and third fractions get a very old age (around the 9th cent. and around the 3rd cent, respectively). A date in agreement with the archaeological hypothesis was found with the first fraction: 2σ = cal 1039-1206 AD.

Unfortunately, the $^{14}$C age results and the errors associated obtained from the Ghrilandina foundation and from the Campionesi phase did not permit a distinction between these two phases. Furthermore, the horizontal shape of the calibration curve around the $^{14}$C year 900 BP results in a very large 2σ range, which includes both expected ages (Fig. 78).
5.4 Results of luminescence dating

5.4.1. OSL Results - University of Catania Lab.

A first attempt of analysing the single quartz grains have been tried, but it has not been possible to gain successful results because the percentage of quartz grains that showed a luminescence signal was lower than 1%.

Therefore, it has been carried out the Small Aliquot procedure using the SAR protocol. First, a test of preheat has been made and it has shown a good behaviour of quartz extracted from mortars as natural dosimeter for preheating temperature of 200°C. However, the results of ED show a strong dispersion, which does not allow, with that statistic, to consider the central values of the distributions as acceptable. They correspond in fact, for the majority of samples (MD1AM, MG2BM and MG4DM) to dates not compatible with the historical context. Even in the case of compatible values (MD3CM), the high dispersion associated, does not allow to calculate the age.
Table 14: results of OSL mortar dating carried out by the lab. of Catania.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>E.D. (Gy)</th>
<th>Error E.D.</th>
<th>Dose rate (mGy/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD1AM</td>
<td>13</td>
<td>8.6</td>
<td>3.18±0.04</td>
</tr>
<tr>
<td>MD3CM</td>
<td>1.5</td>
<td>1.2</td>
<td>2.27±0.03</td>
</tr>
<tr>
<td>MG2BM</td>
<td>8.6</td>
<td>3.2</td>
<td>3.49±0.08</td>
</tr>
<tr>
<td>MG4DM</td>
<td>3.4</td>
<td>1.0</td>
<td>2.57±0.04</td>
</tr>
</tbody>
</table>

5.4.2 OSL Results - Milano Bicocca Lab.

The thermal transfer was systematically evaluated by calculating the recuperation point and the aliquots, which exceeded 5% of the natural emission, have been rejected. However all the aliquots that had acceptable recycling values, i.e. within the range of 0.90 and 1.10, have been accepted (Roberts and Wintle, 2001; see column 3 in tab. 15). The calculated E.D. (see column 4 in tab.15) have been obtained using the weighted mean. The age obtained with OSL (see column 7 in tab. 15) has been overestimated and that probably means that only few quartz grains were completely bleached. The small amount of sample does not allow a significant statistic to eliminate the samples with extreme values of E.D. The only sample that showed the expected age is MG4DM (1060 A.D.), but the error is still too big to be considered acceptable.

Table 15: results of OSL mortar dating carried out by the lab. of Milano Bicocca.
5.4.3 TL Results - University of Catania Lab.

The dates obtained, compared with the assumptions from historical sources, are closed to the expected for samples MD1AL, belonging to the first phase of construction of the Cathedral, and MG2BL belonging to the second phase of construction of the tower from the second to the fifth floor. The other two samples turn out to be too recent than expected.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E.D. (Gy)</th>
<th>Dose rate (mGy/a) ± 3%</th>
<th>Age (years B.P.)</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD1AL</td>
<td>6.26±0.06</td>
<td>7.72±0.09</td>
<td>811±26</td>
<td>1203±26</td>
</tr>
<tr>
<td>MD3CL</td>
<td>1.22±0.06</td>
<td>9.20±0.15</td>
<td>133±6</td>
<td>1881±6</td>
</tr>
<tr>
<td>MG2BL</td>
<td>5.89±0.09</td>
<td>6.98±0.16</td>
<td>844±34</td>
<td>1170±34</td>
</tr>
<tr>
<td>MG4DL</td>
<td>2.40±0.04</td>
<td>8.46±0.13</td>
<td>284±9</td>
<td>1730±9</td>
</tr>
</tbody>
</table>

Table 16: results of TL brick dating carried out by the lab. of Catania.

5.4.4 TL Results - Milano Bicocca Lab.

For the Cathedral all the brick samples have shown similar TL curves, probably as a consequence of a very similar composition and firing technology. The natural TL signal is quite high in all samples but one. The ages obtained, do not refer to the building of the Cathedral, but indicate a reuse from the Roman period. They are in fact compatible, when considered with their errors, with the Modenese Roman era because Mutina was founded in 183 B.P. The only sample with low TL signal and thus with a more recent age (1565 ± 35 A.D.) is MD3, which was bound with a gypsum mortar. The hypothesis is that a renovation intervention was intercepted by the core drilling. This date is compatible with the age of the addition of the vaults, made during the 16th cent.
Similar results have been acquired for the tower, which also was built with Roman reused bricks, as well. The only sample dated in medieval period is the one of the cusp, which was a calibration sample, surely dated at 1319. Indeed the brick turned out to be 1345 with an error of 45 years. This hypothesis is also in agreement with the observed difference between the Roman and the medieval brick size (Labate, 2010).
Fig. 82: results of TL brick dating carried out by the lab. of Milan Bicocca on the sample MG2BL.

Fig. 83: results of TL brick dating carried out by the lab. of Milan Bicocca on the sample MG4DL.
Table 17: results of TL brick dating carried out by the lab. of Milan Bicocca.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E.D. (Gy)</th>
<th>Dose rate (mGy/a) ± 3%</th>
<th>Age (anni B.P.)</th>
<th>Date</th>
<th>Errors (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD1CL</td>
<td>10.0 ± 0.5</td>
<td>4.69</td>
<td>2140</td>
<td>130 a.C.</td>
<td>90</td>
</tr>
<tr>
<td>MD2FL</td>
<td>12.5 ± 0.5</td>
<td>5.73</td>
<td>2190</td>
<td>70 a.C.</td>
<td>90</td>
</tr>
<tr>
<td>MD3DL1</td>
<td>1.70 ± 0.13</td>
<td>3.79</td>
<td>450</td>
<td>1565 d.C.</td>
<td>35</td>
</tr>
<tr>
<td>MD4BL1</td>
<td>13.9 ± 0.5</td>
<td>6.32</td>
<td>2200</td>
<td>180 a.C.</td>
<td>85</td>
</tr>
<tr>
<td>MD5DEL1</td>
<td>9.00 ± 0.4</td>
<td>4.10</td>
<td>2190</td>
<td>180 a.C.</td>
<td>90</td>
</tr>
<tr>
<td>MG1BL</td>
<td>14.7 ± 0.6</td>
<td>6.82</td>
<td>2160</td>
<td>140 a.C.</td>
<td>90</td>
</tr>
<tr>
<td>MG2BL</td>
<td>10.8 ± 0.5</td>
<td>5.18</td>
<td>2085</td>
<td>70 a.C.</td>
<td>90</td>
</tr>
<tr>
<td>MG3BL</td>
<td>14.0 ± 0.6</td>
<td>6.60</td>
<td>2120</td>
<td>105 a.C.</td>
<td>90</td>
</tr>
<tr>
<td>MG4DL</td>
<td>3.2 ± 0.2</td>
<td>4.78</td>
<td>670</td>
<td>1345 d.C.</td>
<td>45</td>
</tr>
</tbody>
</table>

5.5 Discussions

5.5.1 AMS Radiocarbon dating comparison

The comparison between the results obtained from the two radiocarbon dating procedures are showed in figure 84.

The samples showing the largest difference with the expected age are the ones coming from the cores crossing Cathedral foundations (C130 susp. lump). A possible explanation is that the mortars from the internal buried walls may have delayed the carbonation reaction, resulting in a rejuvenation of the age of about 4 centuries. Voluminous structures have shown to take even centuries before complete carbonation (Sonninen et al. 1985). Residues of neoformation of secondary calcite within the carbonate binder may also have contaminated the selected lump (Fig. 85).

The evident advantage of dating lime lumps is that they are made of pure binder being potentially free of aggregates contamination. The possibility of lime lumps dating has been studied and implemented (Pesce et al., 2009; Pesce et al., 2012; Pesce and Bull, 2012) but the contribution of contaminants inside the lime lumps cannot be a priori excluded because the petrographic
characterization cannot be performed directly on the sample to be dated. For example the samples from the same foundation core mortars showed the presence of newly formed calcite inside one lime lump (Fig. 38B). This can be another possible reason for the rejuvenation of the calibrated age achieved.

Fig. 84: comparison between the results of CIRCE lab and the first fractions of the Abo Akademi method.
In these mortars, the difficulty to select unequivocally the lime lumps from the underburned BRPs is confirmed by the $^{14}$C dating of C130 lump and DM8 susp_lump because they yielded older age than expected. It can be supposed that the lumps were reactive only in the external part but they contained an underburned core inside, not easy distinguishable with a stereomicroscope. In the study of Lindroos et al. (2014) the dating attempt of an iron-rich lime lump material with heterogeneous appearance, visible by CL, demonstrated that it contained abundant dead carbon. The reason seems to be linked to the incomplete reaction of the original limestone. Within the lumps, relicts were preserved with components that have provided a significant aliquot of dead carbon. In the case of DM8 susp_lump the Cryosonic procedure has not completely eliminated the contamination by dead carbon. On the other hand, the dating of another lump from the same mortar (DM 8_lump) provided the expected age, indicating that this particular binder related particle was not contaminated by fragments of the older limestone used in the kiln.

The mortar bulk of DM 101 from the Campionesi period, appear to be very contaminated as it yielded a much older date than expected by Cryo2sonic preparation. The same sample was also subjected to sequential dissolution and the contaminants were clearly identified in the last fraction of the dissolution sequence as the calibrated age range from 113 to 357 BC. The second fraction gave a date around the year 1000 AD, very similar to the date obtained using the Cryo2sonic protocol of the Caserta Lab.. The expected age, 1184-1220 AD is close to the calibrated $2\sigma$ ranges results of the first fraction, 1030-1169 AD and 1178-1182 AD. So it seems that the dissolution method has succeeded in dissolving only the binder in the first seconds of the acid reaction, while a part of contaminants has gone in suspension despite the preparation Cryo2sonic.

Results in agreement with the expected ages have been obtained for the tower. It has been validated the historical-artistic hypothesis that the tower and the Cathedral were probably founded together in 1099, obtaining overlapping results with three different methodologies: one lump after the
Cryo2sonic preparation (GM86B susp_lump: \(2\sigma = \text{cal AD 1023-1186 and 1200-1205 AD}\), one bulk lump (GM86B lump: \(2\sigma = \text{cal AD 1021-1158}\)) and three different fractions after sequential dissolution of the bulk mortar. The first fraction date is in agreement with the results of Cryo2sonic (\(2\sigma = \text{cal 1039-1206 AD}\)). All these dating overlap with the dating of the calendar age (1099) of the Cathedral foundation (\(2\sigma = \text{cal 988-1167 AD}\)).

Unfortunately, the calibrated \(^{14}\text{C}\) ages for the tower do not permit a clear distinction with the Campionesi phase as the horizontal orientation of the calibration curve around the year 900 BP causes large overlapping \(2\sigma\) ranges.

An important contribution to the controversial issue of the dating of the main body of the tower was obtained by the dating of two fractions of one lump from the fourth floor that yielded very similar ranges in the first half of the 13\(^{th}\) century (fulfilling the criterion I as suggested by Ringbom, 2011). According to these results, the main construction phase of the tower, previously dated by art historians at the end of the 12\(^{th}\) century, could be slightly postponed.

### 5.5.2 Luminescence techniques

The thermoluminescence analysis on bricks, considered a reliable and routine protocol has evidenced some incongruence between the two laboratory results.

Of the four samples dated in Catania lab., two of them have got dates almost compatible with the historical context and two appears to be too recent.

Bricks from all phases of construction of the two buildings (9 samples) have been dated at the laboratory of Milan Bicocca. These results show that most of the bricks belong to the Roman era. This is in accordance with the historic-artistic hypothesis that had shown how the module and the surface treatment were compatible with their reuse.

Only two bricks have obtained a different dating. One in the cathedral turret apse was manufactured in the 16\(^{th}\) century. Confirmation of a restoration work also comes from the gypsum mortar associated with the same brick. Effectively, in that period is documented the construction of the vaults of the church which stands on these structures. Furthermore, several mortars from the vaults (not presented in this study) are made with a gypsum binder.

The other brick dating back to medieval times is that of the Ghirlandina cusp, which got a date in 1300, consistent with the time of conclusion of the tower (known date). In fact, even according to archaeologist Labate these bricks have different sizes from the other of the Roman times and therefore should have been produced specifically at this stage.
Considering these findings, the two laboratories are now verifying the origin of these differences between their results.

Not as useful from the point of view of the applications of OSL dating technique to mortars, which was not so reliable as expected. The Single Grain protocol has not allowed analysing the individual quartz grains due to the low percentage of the luminescent grains (less than 1%). This has shown that the technique is useful to identify the individual quartz grains luminescent but not always adequate for conducting analysis for the determination of equivalent dose, in case of low statistical. The analyses by the Small Aliquot OSL data, obtained by both laboratories, have confirmed the hypothesis of the absence of total bleaching during mortar production and application. Some ED values obtained by radial plot are in fact slightly lower than 2 Gy, compatible with the historical context but, mediated with the other values, leading to average values too high to enable the dating. Unfortunately, the small amount of sample available didn’t allowed to perform other OSL analysis.

5.6 New data for construction phase determination

Petrography of mortars and plasters contributed to the distinction of the phases of construction of the Modena UNESCO site on the basis of textural parameters, binder/aggregate, the size and composition of the sand. In particular, this study has revealed that the most important parameters for distinguishing the different construction phases are the origin of the sands that have been aggregated to lime and the binder/aggregate of mortars.

The mixture of limestone relicts of different composition within the same mortars indicates that the sources of supply for lime were not quarries opened in a specific outcrop of the Apennines, which would have provided mostly homogeneous rock types, but they were gravels taken from rivers in the area of Modena (Lugli et al., 2011). The practice of taking calcareous pebbles collected from the riverbeds for lime production has continued for all the site construction, despite the succession of different workers that followed one another. The extreme variability of the raw material therefore does not allow to distinguish the construction phases based on the use of a different binder and on the basis of a possible variation in the binder hydraulicity. Furthermore, the large amount of BRPs of all types that are found in the mortars indicates that the calcination processes, the slaking and the sieving have not changed during the construction of the two buildings.

For the Cathedral it has been possible to distinguish the two major phases of construction in which the technology of the mortar production have changed. During the first phase (12th century) the mortars (type A and B) contained a relatively low percentage of binder (binder/aggregate = 1: 3)
and a large amount of binder related particles. The supply of sand was probably made from a single source, from the Panaro river. Most of the mortar samples from the perimeter of the Cathedral, both from the foundations and from the walls, belong to these groups. The analyses show a difference in the particle size of the aggregate, which may indicate the collection in different areas of the Panaro River, possibly in different seasons. This phase was a reference date because we know that the foundation of the Cathedral occurred in 1099. The obtained radiocarbon dating cal. 988-1167 A.D is therefore compatible with this early construction phase. (Silvestri, 2013; Peroni, 1984)

The third type of mortar (type C), attributed to the Campionesi workers (13th century) located in the upper part of the walls of the church, showed a more refined technique of preparation. Indeed, it was observed the use of a higher percentage of binder (binder / aggregate =2:1) and the choice of a more sorted aggregate. The source of supply of sand is no longer the Panaro, but the Secchia river. The result of radiocarbon dating, cal 1030-1169 AD and 1178-1182 AD is close to the expected age (1184-1220 AD).

Only in the foundations of the façade of the Cathedral has been documented the use of a sand with different origin, from the Tiepido stream. Our hypothesis is that these walls have included fragments of pre-existing mortar, from earlier buildings. This hypothesis may explain also the presence of mortars that cannot be ascribed to any other of the identified groups. Unfortunately it was not possible to obtain any reliable absolute dating of the foundations because the mortars from the internal buried walls have probably delayed the carbonation reaction. Also the crystallization of new calcite may have played a role in this process.

Very similar mortars to those of the first phases of the Cathedral with similar petrographic characteristics (A and B type) were found in the first two floors of the tower. It has been finally validated the historical-artistic hypothesis that the tower and the Cathedral were probably founded together in 1099, obtaining overlapping results with three different methodologies. All these dates overlap with the dating of the Cathedral foundation in 1099.

Unfortunately, the calibrated $^{14}$C results do not permit a clear distinction between the first phase of the Cathedral (and the tower) and the Campionesi phase. The two phases are however perfectly distinguishable by petrography.

The successive phases of construction of the tower have obtained very interesting results. The second phase that began with the Campionese Masters, after a long interruption, continued up to the Torresani Room (fourth floor). Indeed, the mortars from the second to the beginning of the fifth floor are all made with sands from the minor rivers and with a binder/aggregate >1. There are only three mortars with different sands (Secchia river) that can be probably attributed to later
interventions. The dating of two different fraction of one lump from the forth floor obtained two very similar dates in the first half of the 13\textsuperscript{th} century. This phase of construction dated by art historic assumption at the end of 12\textsuperscript{th} century could therefore be slightly postponed.

Within the fifth and the sixth floor a group of mortars have been produced with an aggregate from the Panaro river. In the 1261 phase when the 5\textsuperscript{th} floor was added the sand supply source was probably changed.

The last phase of the elevation of the tower is made of mortars with sand from the Secchia river and a fine grain size. The calibration date of the completion of the tower cusp (1319) is in agreement with the radiocarbon dating of bulk samples prepared with Cryo2sonic procedure cal AD 1218-1294.

The TL results confirm the large re-use of Roman bricks except in the case of the tower cusp, in which the bricks are medieval dated at 1345 with an error of 45 years. Moreover, a previously unknown renovation phase in the Cathedral was discovered and dated to the construction of the new vaults in the 16\textsuperscript{th} century.
6. CONCLUSION

The main objective of this research was to contribute to the debate on the controversial issue of the determination of the phases of construction of the Cathedral and the tower of Modena but also to test and verify the absolute dating methods applied to mortars, plasters and bricks. The large number of samples analysed (112 from the walls and 37 from the foundation cores) has enabled to extensively study building materials and different dating techniques to provide a more complete picture on the state of the research in this field.

This study provided:

- more information on the production techniques, sources of supply and characteristics of the building materials used during the construction of the UNESCO site main buildings.
- new considerations about the phases of construction of the Cathedral and the tower Ghirlandina, verifying what has been suggested by previous studies.

It was also possible to:

- derive information that may be applied to a broad range of cases with mortars prepared with carbonate aggregate.
- apply different archaeometric methods on mortars to determine the most suitable techniques, highlighting their strengths and limitations.

It is therefore possible to say that the set objectives were achieved. In particular:

1. Considerations about the absolute dating techniques

- Radiocarbon dating comparison

This part of the research was designed to explore whether the techniques for the separation of the binder from dead carbon contaminants could be applied to the particular and extreme characteristics of the mortars of the Modena UNESCO site.

Five samples were dated after the preparation of the bulk. Three were prepared and dated according to the Cryo2sonic protocol and two after sequential dissolution. Among them, four dates are within the expected range and one is older. In particular, DM 101 from the Campionesi phase appears to be very contaminated as it yielded a much older date than expected after Cryo2sonic preparation. The
same sample was also tested with sequential dissolution and the contaminants were clearly identified in the last fraction of the dissolution sequence. Even the second fraction gave a date around the year 1000 AD, very similar to the date obtained using the Cryo2sonic protocol. The expected age is close to the calibrated 2σ ranges results of the first fraction. So it seems that the dissolution method has succeeded in dissolving only the binder in the first seconds of the acid reaction, whereas a part of contaminants has gone in suspension despite the Cryo2sonic preparation.

The other three samples, one from the foundation of the tower and two from the tower cusp, all yielded an age close to the expected one. The samples from the cusp (GMC24 and GMC24’) were the reference of comparison for checking the results because their true age is well known from historical documents as the tower was completed in 1319. Both samples were extracted from the same mortar and were subject to Cryo2sonic preparation. So, in this case it can be said that the preparation was able to separate the binder from the contaminants.

The bulk mortar from the foundation was dated after sequential dissolution and although this was an unknown date, the result reached from the first fraction overlaps with the dating of two lumps from the same mortar. This is also in agreement with the historic-artistic considerations that the foundation of the two monuments occurred at the same time.

Seven lumps have been dated by following different procedures. In theory, the evident advantage of dating lime lumps is that they are made of pure binder, being potentially free of contamination. Hence, the dating of lumps from extreme contexts has been tested. It is well known that the dating of mortars from the excavation or foundations is potentially very problematic because affected by different possibilities of contamination, especially by secondary calcite. Effectively, the samples collected from the foundation cores of the Cathedral were the ones that showed the largest difference with the expected age. To interpret this result, several hypotheses may be put forward.

Firstly, the mortars from the internal buried walls may have delayed the carbonation reaction, resulting in a rejuvenation of the age of about 4 centuries, a phenomenon known to occur in voluminous structures. Secondly, fragments of the secondary calcite belonging to the carbonate binder may have contaminated the lump. Finally, the contribution of contaminants inside the lime lumps cannot be excluded. Actually, mortars from the same core showed the presence of newly formed calcite even inside lime lumps. Anyway, in this case, the Cryo2sonic protocol failed in eliminating this type of contamination.

The same can be said about the other two lumps dated after Cryo2sonic protocol. In both cases, the samples yielded a date much older than expected. The likely hypothesis is that unreacted relicts of the limestone used for lime production were preserved inside the lumps.
Conversely, three others lumps, one prepared with Cryo2sonic and two directly dated without any preparation, yielded the expected age. It is therefore not possible to specify whether in this case the protocol worked and it succeeded in avoiding the contaminants, or whether selected lump was free of carbonate contaminant.

Very interesting results came from the lump dated after sequential dissolution, from the 4th floor of the tower. Both fractions collected after acid digestion yielded two very similar dating, which fell within the 13th century. These results allowed to limit the associated error (from ±25 to ±19) and to narrow the 2σ calibrated range. If two fractions from the same sample give the same result, then the date is considered reliable without the need for additional controls (Criterion I, Ringbom, 2011).

In light of these findings, the methodology of sequential dissolution seems to work better on the mortars of the UNESCO site of Modena, as also in the case of high contamination it was able to identify it achieving compatible results.

Unfortunately, raw radiocarbon dates that yield a year around 900BP corresponding to the calibrated age within the 12th century (which includes most of the dates of the Cathedral and the tower) do not allow a precise estimation of the ages, because of the horizontal plateau of the calibration curve in that zone.

- **Luminescence techniques**

The thermoluminescence analysis on bricks, considered a reliable and routine protocol has evidenced some incongruence between the two laboratories participating to the test.

Furthermore, these mortars result to be unsuitable to be dated with OSL. The small amount of samples available, the low percentage of quartz grains and the not complete bleaching of them made it impossible to determine the age.

**2. Production technology, sources of supply and characteristics of the building materials**

Petrography of mortars and plasters contributed to the distinction of the phases of construction of the Modena UNESCO site on the basis of textural parameters, binder/aggregate, the size and composition of the sand. In particular, this study has revealed that the most important parameters for distinguishing the different construction phases are the origin of the sands that have been aggregated to lime and the binder/aggregate of the mortars.

The mixture of limestone relicts of different composition within the same mortars indicates that the sources of supply for lime were not quarries opened in a specific outcrop of the Apennines, which would have provided mostly homogeneous rock types, but they were gravels taken from rivers in the area of Modena (Lugli et al., 2011). The supply of calcareous pebbles from the riverbeds for
lime production has continued for all the site construction phases, despite the succession of different workers that followed one another. Furthermore, the high abundance of these BRPs in the mortars of all the phases of construction of the Cathedral and of the Ghirlandina tower suggests no selective removal of these particles and that the main preparation techniques have not changed during the construction of the two buildings.

The most frequent BRPs found in these mortars are the underburned fragments of the carbonate stones used to produce the lime. They are limestone or marly limestones nodules and in some cases it was possible to identify partially burnt siltstones and cherts. The burning of impure limestones, including clay minerals and quartz grains, produce hydraulic mortars. The high amounts of Si, Al and Fe in the binder, confirm the hydraulic character of these mortars. Furthermore the presence of ferrite (C4AF) and the major fraction of amorphous phase can be related to hydrate phases (CSH, CAH).

Nevertheless, very old mortars with presumable natural hydraulic character, commonly, show only indirect evidence of their original composition. Actually, these mortars underwent numerous transformations: carbonation, dissolution and re-precipitation. Indeed, secondary porosity or secondary pore fillings are commonly visible especially in the mortars belonging to the lower parts of the buildings. All these phenomena lead to the formation of new Ca-carbonate that initially may have been aragonite and vaterite (Mertens, 2009). But these minerals are unstable and over time they will form calcite. Probably the CSH phases were mainly transformed into calcite and amorphous silicate (vanishing hydraulicity).

Unfortunately, the inability to effectively separate the lime binder from the aggregate limestone and the characteristic heterogeneity of mortars hampered the quantification of the hydraulicity index.

However, the carbonate-silica-alumina reaction has remained in the form of C2S (belite), wollastonite and gehlenite, which were all found in very small quantities in these mortars.

Mineralogy helped to determine the calcination conditions in kilns because the study of the formed minerals may indicate the maximum temperature reached inside the fire chamber. Particles, which were interpreted as burning waste, contain two forms of wollastonite: pseudowollastonite as the high temperature polymorph (cyclosilicate), and parawollastonite as the low temperature polymorph (Taylor, 1990). It is therefore possible to assume that inside the firing chamber large gradients of temperature can be occurred. Para-wollastonite and gehlenite are formed around 800-850° C, whereas pseudo-wollastonite is formed at 1125° C. They high amount of Fe found in these particles can be explained with the replacement of Ca in the mineral structures at high temperatures.
To trace back the origin of the raw materials used to produce the mortar, petrography resulted to be the most appropriate method.

3. Phase determination of the Modena UNESCO site

For the Cathedral it was possible to distinguish the two major phases of construction in which the technology of the mortar production have changed.

During the first phase (12th century) the mortars contained a relatively low percentage of binder and a large amount of binder related particles. The supply of sand was probably made from a single source, from the Panaro River. The analyses show a difference in the particle size of the aggregate, which may indicate the collection in different areas of the Panaro river, possibly in different seasons. This phase was a reference date because we know that the foundation of the Cathedral occurred in 1099. The obtained radiocarbon dating cal. 988-1167 A.D is therefore compatible with this early construction phase.

The Campionesi phase of the 13th century showed a more refined technique of mortar preparation. Indeed, it was observed the use of a higher percentage of binder and the choice of a more sorted aggregate. The source of supply of sand is no longer the Panaro, but the Secchia river. The result of radiocarbon dating, cal 1030-1169 AD and 1178-1182 AD is close to the expected age (1184-1220 AD).

Only in the foundations of the façade of the Cathedral has been documented the use of a sand with different origin, from the Tiepido stream. Our hypothesis is that these walls have included fragments of pre-existing mortar, from earlier buildings. This hypothesis may explain also the presence of mortars that cannot be ascribed to any of the identified groups. Unfortunately it was not possible to obtain any reliable absolute dating of the foundations.

Very similar mortars to those of the firsts phases of the Cathedral with similar petrographic characteristics were found in the first two floors of the tower. It has been finally validated the historical-artistic hypothesis that the tower and the Cathedral were probably founded together in 1099, obtaining overlapping results with three different methodologies. All these dates overlap with the dating of the Cathedral foundation in 1099.

The successive phases of construction of the tower have obtained very interesting results. The second phase that began with the Campionesi Masters, after a long interruption, continued up to the Torresani Room (fourth floor). Indeed, the mortars from the second to the beginning of the fifth floor are all made with sands from the minor rivers and with similar binder/aggregate (>1). There are only three mortars with different sands (Secchia river) that can be probably attributed to later
interventions. The absolute dating of the fourth floor obtained an age in the first half of the 13th century. This phase of construction dated by art historic assumption at the end of 12th century could therefore be slightly postponed.

Within the fifth and the sixth floor a group of mortars have been produced with an aggregate from the Panaro river. In the 1261 phase when the 5th floor was added the sand supply source was probably changed.

The last phase of the elevation of the tower with the octagon is made of mortars with sand from the Secchia river and a fine grain size. The calibration date of the completion of the tower cusp (1319) is in agreement with the radiocarbon dating (cal AD 1218-1294).

Unfortunately, the calibrated 14C results do not permit a clear distinction between the first phase of the Cathedral (and the tower) and the Campionesi phase. The two phases are however perfectly distinguishable by petrography. Thus, the impossibility in distinguishing different stages of construction within the twelfth century does not allow to determine what is the more likely chronology among those proposed by scholars (Peroni, 1984 and Silvestri, 2013).

The TL results confirm the large re-use of Roman bricks except in the case of the tower cusp, in which the bricks are medieval, dated at 1345 with an error of 45 years. Moreover, a previously unknown renovation phase in the Cathedral was discovered and dated to the construction of the new vaults in the 16th century.

To conclude it is possible to say that the multidisciplinary nature of this research project provided new data for the understanding of complex problems and controversial questions. The results have provided essential elements for the distinction and the timing of the construction phases and for the comparison of different methods of independent dating.
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Pesce G.L., Ball R.J., Quarta G., Calcagnile L. (2012) Identification, extraction, and preparation of reliable lime samples for 14C dating of plasters and mortars with the “pure lime lumps” technique. Radiocarbon 54(3–4) 933- 42.


Prescott J. R., Fox P. J. (1990) Dating quartz sediments using the 325°C TL peak; new spectral data, Ancient TL, 8, 32-34.


Raccomandazione NORMAL 36/92 (1994) Glossario per l'edilizia storica nei trattati dal XV al XIX secolo, Ed. CNR e ICR, Roma.


Van Der Plas L. & Tobi A.C. (1965) A chart for judging the reliability of point counting results, American Journal of Science, 263, 87-90.


