We are IntechOpen,
the world's leading publisher of Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Dating of Old Lime Based Mixtures with the "Pure Lime Lumps" Technique

Giovanni L.A. Pesce and Richard J. Ball
BRE Centre for Innovative Construction Materials,
Department of Architecture and Civil Engineering,
University of Bath, Bath,
United Kingdom

1. Introduction

A number of studies carried out over the last forty years describe the application of radiocarbon dating of lime mixtures such as mortars, plasters and renders (Folk & Velastro, 1976, Pachiaudi et al., 1986, Van Strydonck et al., 1992, Berger, 1992, Hale et al., 2003, Sonninen & Junger, 2001, Nawrocka et al., 2005).

To understand the basic principle of this technique we must first consider the lime manufacturing process. Lime is produced from limestone (essentially calcium carbonate of geological origin) which is burnt at around 900°C to produce carbon dioxide and calcium oxide otherwise known as "quicklime" (Norman, 1961, Oates, 1998, Vecchiattini, 2010, Rattazzi, 2007, Goren & Goring-Morris 2008).

The quicklime subsequently undergoes a slaking process where it is mixed with water. The resulting exothermic reaction forms calcium hydroxide which, in the past, was mainly produced using an excess of water which resulted in the formation of "lime putty", one of the most widely used inorganic binders for construction. Plasters, renders, mortars and other architectural parts are formed when the lime putty is mixed with a sand (aggregate).

When in place the calcium hydroxide within the mixtures hardens by carbonation resulting in the formation of new calcium carbonate. As the carbon that binds to the calcium during this reaction originates from the atmosphere, the calcium carbonate contained in the hardened mixture reflects the atmospheric radiocarbon concentration at the time of hardening. Consequently this calcium carbonate phase within lime mixtures can be used for the radiocarbon dating of mortars, plasters and other lime based materials.

Despite the fact that this method is very simple in principle, several studies have highlighted various practical challenges and factors that must be considered (Van Strydonck et al., 1986). These arise mainly from the contamination of samples with carbonaceous substances such as incompletely burnt limestone and aggregates of fossil origin including limestone sand.

However, recently studies have shown that accurate sample processing allow a significant reduction of these error sources (Sonninen & Junger, 2001, Marzaioli et al., 2011 and see also the contribution of Ortega and its colleagues in this book) and moreover adoption of a special sampling procedure based on the careful selection of lumps of incompletely mixed lime, provides an interesting alternative that avoids problems associated with contamination.

This latter technique has been discussed at an international level on several occasions (e.g. Gallo et al., 1998) and the more recent publications on this subject describe the results achieved using the latest sampling methodologies, together with the limitations and drawbacks (Pesce, 2010).

The founding principle underlying this technique is the use of the pure lime lumps. These are thought to originate from imperfect mixing and are most prevalent in mortars, renders and plasters predating mechanical mixing. Previous sampling methods for radiocarbon dating did not discriminate between pure and contaminated lime lumps. As pure lumps contain the same lime as that used in other parts of the mixtures but importantly are free of contaminants such as sand grains or under burned pieces of limestone, they can dramatically reduce the errors in the radiocarbon dating.

In the following paragraphs more details of this technique are given together with examples of some applications.
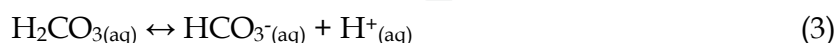
2. The radiocarbon dating of lime based materials: Basic principles

2.1 Carbonation and radiocarbon in building materials

Carbonation is one of the main reactions (if not the main reaction) of lime based materials that lead to hardening and, consequently, to an increase in strength (Van Balen, 2005, El-Turki et al., 2007).

From a chemical point of view, carbonation is the reaction between calcium ions (Ca^{2+}) and carbonate ions (CO_3^{2-}) in aqueous solution. This leads to the precipitation of a solid calcium carbonate phase, as described by the following reaction scheme:

- dissolution of carbon dioxide (CO_2) in water (Morse & Mackenzie, 1990):

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \tag{1}$$

$$CO_{2(aq)} + H_2O_{(l)} \leftrightarrow H_2CO_{3(aq)} \tag{2}$$

$$H_2CO_{3(aq)} \leftrightarrow HCO_3^-{}_{(aq)} + H^+{}_{(aq)} \tag{3}$$

$$HCO_3^-{}_{(aq)} \leftrightarrow CO_3^{2-}{}_{(aq)} + H^+{}_{(aq)} \tag{4}$$

- dissolution of calcium hydroxide ($Ca(OH)_2$) in water:

$$Ca(OH)_{2(s)} + H_2O_{(l)} \leftrightarrow Ca^{2+}{}_{(aq)} + 2(OH^-)_{(aq)} + H_2O_{(l)} \tag{5}$$

- reaction of calcium ions with carbonate ions in water solution:

$$Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \leftrightarrow CaCO_{3(s)} + H_2O_{(l)} \tag{6}$$

These reactions describe the dissolution of atmospheric carbon dioxide (CO_2) in water (reaction 1) and the subsequent reaction forming carbonic acid (2). Once in solution, carbonic acid dissociates forming bicarbonate (HCO_3^-) and a hydrogen ion (H^+; reaction 3). Subsequently, this bicarbonate ion may dissociate to form a carbonate ion and a further hydrogen ion (4). Concurrently, calcium hydroxide ($Ca(OH)_2$) dissolves in water forming calcium and hydroxyl ions (OH^-; 5).

Depending on several factors such as temperature, ion concentration and the presence of other ions in solution, a solid calcium carbonate phase precipitate (6).

Inspection of reactions 1-4 and 6 illustrates that calcium carbonate crystals precipitated from a saturated solution of lime in water (6) contain carbon atoms present in the air at the time of the reactions (1). Thus the radiocarbon analysis records the carbon contained in the air at the time of the crystal precipitation.

Moreover, as the carbon atoms in atmospheric carbon dioxide exist in at least three main isotopic forms (^{12}C, ^{13}C, ^{14}C), the calcium carbonate precipitated during hardening will contain these three forms in a similar ratio to that of the atmosphere at the time of precipitation[1].

An important consequence is that radiocarbon is incorporated within the $CaCO_3$ crystals and begins to decay from the time of precipitation. As no carbon exchange can happen in the solid phase of calcium carbonate, ^{14}C contained in lime based mortars, plasters and renders can be used to date these materials with the radiocarbon method.

Furthermore, if we assume that the time of calcium carbonate precipitation is the same as that of the buildings construction, where the lime has been used, it follows that the radiocarbon technique can be used to date old structures such as buildings, bridges and churches.

2.2 Drawbacks and limitations of radiocarbon dating of lime mixtures

Despite the simplicity of the carbonation process previously described, in practice the radiocarbon dating of lime mixtures is not so simple. Several studies have recognized the drawbacks and limitations of radiocarbon dating of lime based materials. These are mainly attributed to contamination of samples from carbonaceous substances such as incompletely burnt limestone or grains of carbonate sand.

Carbonate rocks are in fact mainly made of calcium carbonate that, at the beginning of the sedimentary process, contained all the carbon isotopes contained in the earths' atmosphere at the time of the precipitation. However, in contrast to the carbon contained in the lime mixtures of archaeological interest which have a lifetime shorter than the radiocarbon, calcium carbonate of geological origin comes from times far earlier than that equivalent to the decay time of radiocarbon. This means that any isotope contained in carbonate rocks is "^{14}C-dead".

---

[1]This is only an approximation because of the kinetic fractionation of isotopes during the calcium carbonate precipitation. An example of this fractionation is described, among the other scientific references, in: Turner, 1982 or Emrich et al., 1970.

Importantly, this means that any piece of carbonate rock that may contaminate a hardened lime such as grains of carbonate sand added as aggregate to the mixture or pieces of under burned limestone[2] can affect the result of radiocarbon dating.

Presence of aggregate or pieces of stones would not be a problem if it were possible to separate these phases from the binder phase in lime mixtures. But, even if under the microscope it is possible to distinguish between binder (lime) and aggregate (sand), from a practical point of view, it is almost impossible to separate all the aggregate from the binder when both are made of calcium carbonate.

In fact, if sand contained in the mixtures is only made of silica, there are already available chemical procedures to separate the calcium carbonate of the binder from that of the aggregate. However, this case is not frequent and, moreover, there still remains the problem of under burned pieces of stone that behave in a similar manner of the binder under acid attack.

Improved methodologies have been developed to allow similar procedures with mixtures containing carbonate sand but, despite this, there still remains some uncertainty in the radiocarbon dating of these types of mortar (Folk & Velastro, 1976, Van Strydock et al., 1986, Sonninen & Junger, 2001).

Looking more carefully to the limitations of radiocarbon dating of lime based mixtures, it is noteworthy that the previous statement about the immutability of carbon contained in calcium carbonate crystals is subject to an exception. Sometimes, in fact, lime contained in building materials can be affected by a dissolution and re-precipitation process of calcium carbonate that can lead to an exchange of carbon atoms.

Typical water sources of archaeological and building sites such as rain (mainly for renders), backwater or rising dump (for plasters, renders, and mortars), can lead to the dissolution of calcium carbonate. Calcium carbonate has a specific solubility in water[3] and, consequently, binder contained in the mixtures can dissolve in very wet environments such as foundations and underground floors. Binder dissolution in old lime based mixtures can be described as follows:

$$CaCO_{3(s)} + H_2O_{(l)} \leftrightarrow Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)} + H_2O_{(l)} \tag{7}$$
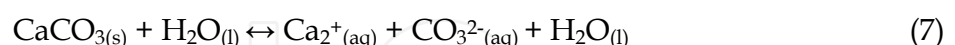
Once in solution calcium ions can react with carbonate ions in the manner already described (equation 6), to produce new calcium carbonate crystals. However, in this case the carbonate ion population dissolved in solution can be made of both, ions from the carbonate dissolution and ions from the atmosphere. But carbon concentration in the atmosphere at the dissolution time of the lime can be different from the carbon concentration at the hardening time of the original lime.

For this reason, the radiocarbon dating of a lime sample containing even a small amount of re-precipitated calcium carbonate can be affected by errors due to the radiocarbon contents of the new calcium carbonate phases.

---

[2]Pieces of the same stone used to produce the lime that have not been completely decomposed during the productive process.

[3]Even if the solubility of calcium carbonate is less than other building materials such as gypsum.

To avoid this problem it is necessary to analyse the sample used for the dating before submission to the laboratory were the radiocarbon counting is carried out. Re-precipitated calcium carbonate in lime mixtures can be recognised under the microscope with the cathodoluminescence technique (Gliozzo & Memmi Turbanti, 2006) or by other more common techniques such as X ray diffraction (XRD) and infrared spectroscopy (FT-IR).

Finally, to assume that the hardening time of lime is the same as the structure construction time is only an approximation, sometimes not verified.

Carbonation is a very slow process that depends on several factors such as temperature, moisture content and pore structure which dictates the accessibility of CO_2. As all these factors are quite changeable from site to site and also inside the same site, the hardening time of lime mixtures can be variable.

Carbonation can stop if the environment where the reaction occurs is too dry or if the CO_2 access is inhibited (Van Balen, 2005). Under these conditions carbonation can only start again following a change in the conditions such as a break in the wall or a small fracture in the mortar due to shrinkage.

Investigations of old buildings have already highlighted that the inner part of thick walls, such as the city walls, can contain calcium hydroxide centuries after their construction. This means that the results of radiocarbon dating of old lime mixtures depend not only on the purity of the sample itself, but also on the depth of the sample within the analysed structure.

For this reason, if the radiocarbon dating of a sample of lime mortar is carried out to date the building process of the wall where the sample was picked up, a superficial sample is more desirable than a deep sample.

But in this case the sampling procedure should avoid lime applied to the walls after their construction such as joint sealing whose date of origin postdates the building time of the wall.

Renders and plasters should not be affected by the problem of delayed carbonation because they are in direct contact with the atmosphere and their structure is porous thereby permitting diffusion of carbon dioxide. However, in this case, it must be verified that these layers, often considered expendable materials, have not been subject to demolition and reconstruction. If this has happened, obviously, their radiocarbon dating can not be assumed as the radiocarbon dating of the wall but simply as the date of the re-plastering.

3. The pure lime lumps technique

3.1 Advantages in the use of lime lumps

Summarising the problems previously listed, it is possible to state that errors in the radiocarbon dating of old lime mixtures mainly arise from three factors:

- re-carbonation of the lime binder;
- delay in carbonation;
- contamination from external sources of calcium carbonate.

Errors resulting from the first two types of problem can be easily mitigated by correct sample selection and accurate analysis before the radiocarbon dating. The third type of

error, instead, can be avoided by applying the "pure lime lumps technique". That is selecting a specific part of the mixture where lumps of pure lime are found embedded.

It is known that during the older manufacturing process of lime mixtures, some lumps of lime putty not mixed with sand, could remain embedded within the mixture matrix.

A feature of this process was that when the pieces of burned limestone (calcium oxide) were removed from the furnaces, they were immersed in pools containing water where the slaking process took place forming lime putty (i.e. calcium hydroxide). Slaking was assisted by a continuous manual mixing carried out with traditional tools. Once the quick lime was completely dissolved, the lime putty was then filtered and stored in pits dug in the ground or immediately mixed with sand and other aggregates to produce mixtures such as mortars, plasters and renders (Oates 1998, Vecchiattini, 2010, Rattazzi 2007).

However, during this process, some small lumps of lime putty could remain compact and fail to intimately mix with the sand grains (probably because they were not well slaked or mixed[4]) even though they were able to combine with the atmospheric CO_2 in the same manner as the remaining matrix. According to results of research into this topic the composition of these lime lumps is similar to that of the surrounding matrix (Franzini et al., 1990, Bruni et al., 1997, Bakolas et al., 1995) with only differences in micro-morphology[5]. These differences are described by Bakolas and colleagues as: "*The matrix of the mortar surrounding the lumps appear to be of compact texture with smaller porosity in respect to the lumps*" and, moreover, "*in many cases the growth of the binder crystals is greater than of the lumps*" (Bakolas et al., 1995, p. 814). The same observations have been made by other researchers including as Bugini and Toniolo (Bugini & Toniolo, 1990).

For this reason the lumps of pure lime embedded in old lime mixtures are the most suitable samples for the radiocarbon dating of lime based materials. With their use the contamination problem previously described is greatly reduced. The only contaminants remain on the external surface where the lump was originally jointed with the mortar matrix and these are easily removable.

3.2 Lumps in old lime based mixtures

For successful application of the "pure lime lumps" technique it is important to identify these lumps and distinguish them from several other types commonly found embedded within old mixtures. The internal structure of historic lime mixtures has been found to contain at least five different types of lump, each of which can be recognised individually. These comprise:

-    unburned pieces of limestone (Leslie & Hughes, 2002, Ingham, 2005, Elsen, 2006);
-    over burned pieces of limestone (Leslie & Hughes 2002, Ingham, 2005, Elsen, 2006, Elsen et al., 2004);

---

[4]There is not a general agreement about the formation process of these lumps but the above mentioned hypothesis is one of the most common (Bugini & Toniolo, 1990).
[5]For this reason, some authors hypothesize that crystals in these lumps developed over a shorter time period compared to the crystals of the matrix (Bruni et al., 1997).

- pieces of burned limestone containing high concentrations of silica (these arise when the stone used for the lime production contains high quantity of impurities; Elsen et al., 2004, Bakolas et al., 1995);
- concretions of recarbonated lime;
- lumps of pure calcium carbonate due to the carbonation of lime putty (Leslie & Hughes, 2002, Franzini et al., 1990, Bugini & Toniolo, 1990, Ingham, 2005, Elsen, 2006, Elsen, et al., 2004, Bakolas et al., 1995).

Among these only the lumps belonging to the latter group are suitable for radiocarbon dating. Over-burned pieces of lime contain sintered calcium oxide which is less reactive with water (Elsen, 2006). Consequently, if carbon is contained within these samples, it must not be considered representative of the atmospheric carbon dioxide at the time of the building process. Unburned pieces of limestone contain carbon dioxide of geological origin, while calcium contained inside the lumps of silica is mainly bonded to the silicon rather than to the carbon dioxide (Bakolas et al., 1995). Problem connected to the concretions have already been discussed previously (par. 2.2)

3.3 Recognition and sampling of the pure lime lumps

Lumps of pure lime are easily identifiable in old lime mixtures as they exhibit a white, rounded and floury complexion (Fig. 1). Surface hardness of this type of lump is very low making them extremely delicate to handle and easily damaged. To facilitate extraction of these lumps in an undamaged condition a two-step procedure is used:

1. on site sampling of a small amount of mortar containing the lump;
2. extraction of suitable pure lime lumps for the laboratory analysis.

Fig. 1. Pure lime lumps in a specimen of air lime mortar (left hand side; scale bar: 1 cm) and detail of the lime lump (right hand side)

3.3.1 The on site sampling procedure

On-site sampling must be tailored to reduce problems arising from the re-carbonation of lime described previously. Moreover, sampling should be carried out to accommodate the individual requirements of the structure from which the sample is taken. Buildings out of the ground, underground walls, frescos layers, mosaic substrate, all require slight variations in technique.

In the field of building archaeology, for instance, it can be difficult to reach the inner part of walls, especially if the thickness of mortar joints is not large enough to allow selection of suitable samples[6].

When the inner part of the masonry is accessible, it is always important to consider the possible re-carbonation of lime lumps and the depth from which samples within the wall should be taken. Care is also needed to avoid unusual situations such as water pockets and mixtures non belonging to the original structure such as pieces of plaster applied after its construction.

In the same manner samples taken deep inside the wall, where incompletely or delayed carbonated lime may be present, should be avoided. In this case it is useful to remember that the carbonation process initiates from the external surfaces of a structure and progresses towards the inner region at decreasing speed.

When a suitable depth of sampling is reached, a lump containing sufficient material for the radiocarbon dating must be identified. Where an Accelerator Mass Spectrometer (AMS) is used in the radiocarbon dating, at least 20 milligrams of calcium carbonate will be required.

In the case that a single lump does not contain sufficient material, multiple lumps from the same region of the masonry can be used (in archaeological terms this means from the same stratigraphic unit).

3.3.2 Sample extraction inside the laboratory

Following on-site sampling and before treatment and analysis at the AMS laboratory, it is necessary to examine the samples under an optical stereo microscope to confirm the lump nature and mechanically remove particles of aggregate that may be still attached to the surface.

On-site it is difficult to distinguish lumps of incompletely burnt limestone or rounded grains of milky quartz from pure lime lumps. However under a magnifying glass, even at low magnification, it is possible to distinguish between these types. The surfaces of lime lumps have a floury appearance (Fig. 1 right hand side) while those of under burned lumps and sand grains appear denser resembling stone.

Evaluation of the superficial hardness is a useful method for distinguishing between these different types of lump. Even performing a crude test, by hand, using a needle point, allows these different types of lump to be effectively distinguished.

Following successful identification, all pieces of sand still attached to the surface of lumps must be removed using tools such as scalpels or needles. In order to remove as many pieces of sand as possible, this work should be done under the stereo microscope.

Great care should be taken in this phase as the sample is very delicate and easily damaged.

When the sample is clean, it must be weighed to check that the mass matches the requirements for the radiocarbon dating process (usually 20 mg). It can, then, be stored in a box with rigid walls to avoid damage during transit to the laboratory.

---

[6]This problem is particularly prevalent in masonry containing squared off blocks laid upon very thin mortar joints. In this case it is only possible to proceed if a cross section of the wall is accessible.

3.4 Treatment at the AMS laboratory

At the AMS laboratory the pure lime lumps are processed using the standard treatment for carbonate. Upon arrival the sample is analysed using an optical microscope to double check for the presence of macro contaminants. If necessary, further mechanical cleaning is carried out to remove these.

Once cleaned, samples are treated with hydrogen peroxide (H_2O_2) to remove the outside layer. Approximately half of the minimum amount of the pre-cleaned samples, by weight, is dried in an oven where it is also treated with H_2O_2 and converted to CO_2 using phosphoric acid (H_3PO_4).

The CO_2 extracted from the sample is, then, reduced to graphite using hydrogen (H_2) in the presence of an iron powder catalyst. The graphite is finally pressed into tablets which are used as a target in the accelerator mass spectrometer for measurement of the carbon isotopic ratios (Pesce et al., 2009; CEDAD, n.d.).

4. Applications

4.1 Literature review

In 2008 a detailed example of this sampling and dating method was presented during an international conference. This work involved the collection of two samples of lime lumps from the apses of the medieval church of S. Nicolò of Campodimonte (Camogli, Genoa - Italy) and dating with the radiocarbon method. Results obtained were evaluated and compared with the radiocarbon dating of organic material collected in the same apses. All the results were finally compared with results of other dating methods including mensiochronology of squared off blocks (Pesce et al., 2009).

Prior to this, relatively few researchers carried out radiocarbon dating of lime lumps in archaeological sites. Exceptions being Gallo, on the alto-Medieval castle of Aghinolfi (Massa Carrara – Italy; Gallo, 2001) and Fieni on the basilica of S. Lorenzo Maggiore in Milan (Italy; Fieni, 2002).

However, since 2008, additional tests have been made by the research group of the Institute for the History of Material Culture of Genoa (Italy). A total of 9 new samples taken from three different archaeological sites were dated following the procedure described earlier. Results were found to be consistent with the respective archaeological frameworks and uncertainty of radiocarbon dating was often reduced by comparison with other archaeological information. Among these samples, one was removed from the Medieval Castle of Zuccarello (Italy).

4.2 The Saint Nicolò of Capodimonte church

The San Nicolò church of Capodimonte (Camogli, Genoa – Italy; Fig. 2) is a medieval church on the Portofino Mountain with a crux commissa plan. During the most recent phase of restoration work a multidisciplinary approach was adopted to study its principal construction stages. The work also included archaeological analysis of the walls, research of bibliographic sources and radiocarbon dating of mortars.

Archaeological evidence and bibliographic sources suggested that the church existed in the 12th century, and underwent some major changes during the 12th and 13th centuries. Nevertheless, the lack of detailed documentation about the different construction phases suggested that a more direct and absolute dating method would be desirable.

Fig. 2. Medieval church of Saint Nicolò of Capodimonte (Camogli, Genoa – Italy; author Arch. Paola Cavaciocchi)

Radiocarbon dating was applied to two samples of lumps and a sample of charcoal. Sampling of lumps was possible through the large mortar joints (>1 cm thickness[7]) and damaged masonry. Samples were taken at a depth of 1–2 cm inside the wall to ensure that sufficient calcium carbonate was collected for the ^{14}C dating.

The first sample (sample n. 1 in tab. 1 and red mark in figg. 3 and 4) was removed from the wall next to the interior border of the apsidal basin, on the right-hand side of the transept. The second sample (sample 2 in tab. 1 and yellow mark in fig. 3 and 4) was removed from the external face of a wall, under the same apsidal basin. The sample of charcoal (sample 3 in tab. 1 and green mark) was removed from the internal face of the main apse.

Although the stratigraphic position of the first two samples was clear (sample n. 2 had to be older than sample n. 1), the position of the third sample (the charcoal) was not perfectly established as it could have been a part of the mortar used for the construction of wall, or a residual part of a more recent plaster applied on the interior face of the wall.

---

[7]This is a specific characteristic of the building technique of the oldest archaeological stages.

The selected samples were then submitted for ^{14}C dating at the Centre for Dating and Diagnostics at the University of Salento (Lecce, Italy). At the laboratory, the inorganic samples underwent the standard process used for carbonates whereas the charcoal sample was treated using the acid-alkali-acid protocol (Pesce et al., 2009). The 'before present' [14]C ages of the three samples are shown in tab. 1 together with the calibrated[8] and the expected ages.
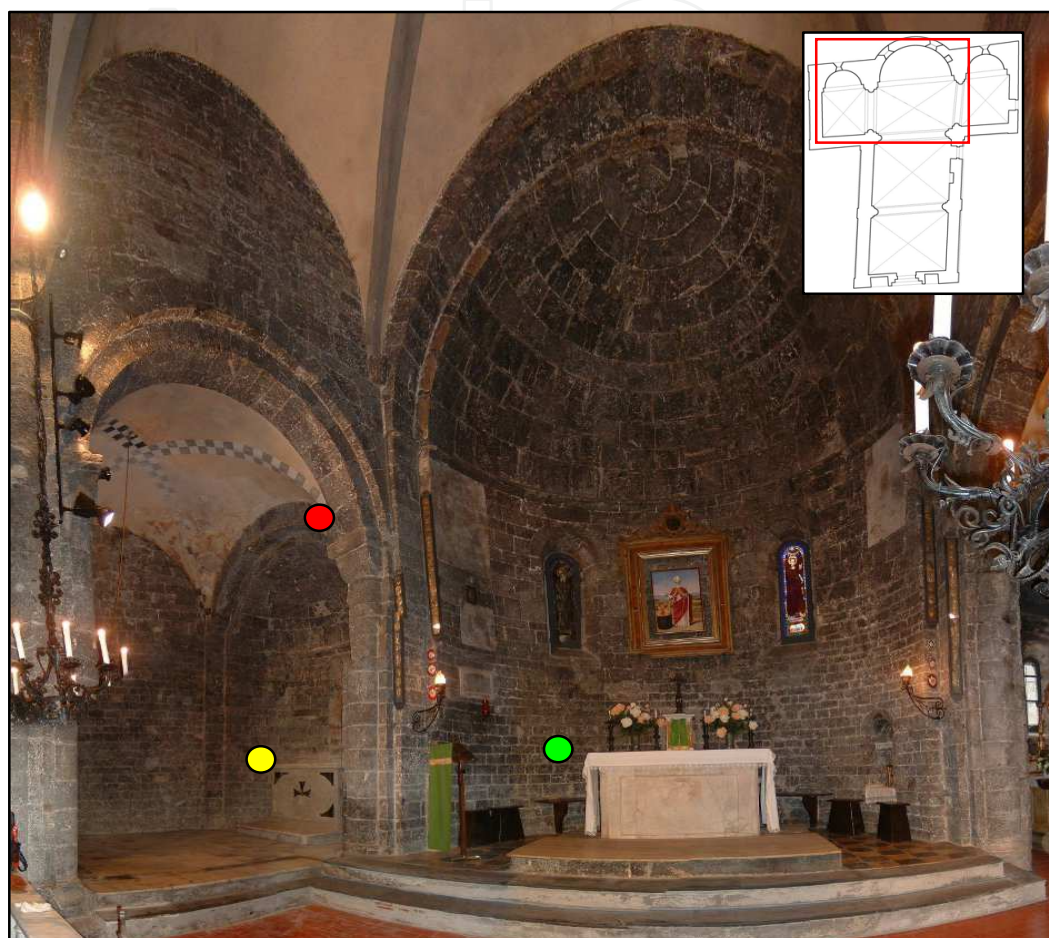

Fig. 3. Sampling point inside the church (red mark: sample 1; yellow mark: sample 2; green mark: sample 3)

Sample 2 was ^{14}C dated to between the end of the 10th and the middle of the 12th century cal AD, sample 1 to the 11th–13th century cal AD, and the charcoal sample (n. 3) to the last construction phase of the building between the 12th and the 14th century cal AD.

Analysis of ^{14}C data shows that the ages obtained are consistent with each other, with their stratigraphic position (Fig. 4), and with the information obtained from historical sources. In fact, the archaeological analysis led to the identification of three main building phases, all dated to the Middle age. Bibliographic sources reveal that the church existed at least in the 12th century AD, when two congregations of monks undertook work on the building, while the last documented construction phase can be dated to the 15th century AD.

---

[8]These were obtained using OxCal v 4.0 software (Bronk Ramsey, 1995, Bronk Ramsey, 2001) and the IntCal04 atmospheric calibration curve (Reimer et al., 2004).

The first lump (sample n. 2) was selected from structures of unknown age but stratigraphically older than the 12th century building, while the second sample (sample n. 1) was selected from structures archaeologically dated to the 12th century. The charcoal (sample n. 3) has been ascribed to the last construction phase of the building dated to the 13th century AD based on the typology of the walls and on the sizes of stones[9].

Overall, the 14C results obtained confirm the expected ages of the samples and their stratigraphic position.

Sample n.	Archaeological site	Laboratory number	14C age (BP)	δ^{13}C (‰)	Calibrated age (AD)	Probability (%)	Expected age (century)
1	St. Nicolò of Capodimonte church	LTL2133A	917±55	-22,9±0,3	1010-1220	95,4	XII-XIII
2	St. Nicolò of Capodimonte church	LTL2978A	1005±45	-12,1±0,2	890-920	2,7	XI
					960-1160	92,7	
3	St. Nicolò of Capodimonte church	LTL2132A	790±60	-26,0±0,5	1040-1090	4,6	XIII-XIV
					1120-1300	90,8	
4	Zuccarello castle	LTL4756A	559±35	-4,8±0,3	1300-1370	49,9	XIII-XIV
					1380-1440	45,5	

Table 1. Radiocarbon ages obtained for samples 1 to 4
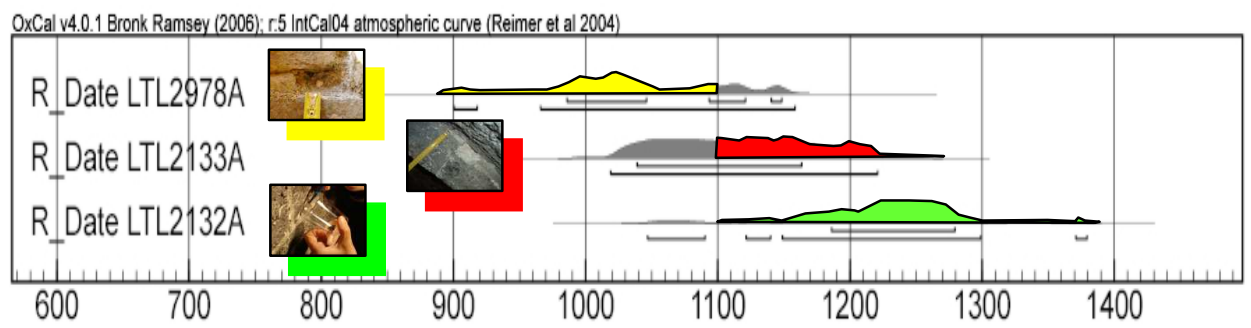
Fig. 4. St. Nicolò of Capodimonte church: comparison of the calibrated date. According to the previous pictures, red colour identifies the sample 1, yellow colour identifies the sample 2 and green colour identifies the sample 3. Coloured areas in the calibrated curve show the most likely period of time for the single result after comparison with other dating methods used in this archaeological analysis

4.3 Zuccarello castle

The Medieval castle of Zuccarello (Savona, Italy; Fig. 5) is a ruined construction built on the top of a hill in the west side of the Liguria region (North West of Italy). In recent years it has undergone restoration work and archaeological studies.

---

[9]This is a well established archaeological dating method used in this area of Italy.

In order to obtain an archaeological dating of the main walls of this building several techniques were used including: mensiochronology of bricks, chronotypological dating of door and window frames, historical and artistic dating and the radiocarbon dating of a single lime lump from one of the oldest parts of the surrounding wall (Fig. 6).

Fig. 5. The medieval Castle of Zuccarello (Savona, Italy)

Fig. 6. Sampling point of the lime lump

Uncalibrated ^{14}C and calibrated ages of samples, obtained using OxCal v 3.10 and the IntCal04 atmospheric calibration curve software, are reported in table 1 and figure 7. These results show that, even though the radiocarbon determination exhibits a normal distribution

(red line in the left hand side of the figure), the curve for calibrated data is divided into two parts with very similar probabilities (49.9% and 45.5%) because of the shape of the calibration curve in this time range.
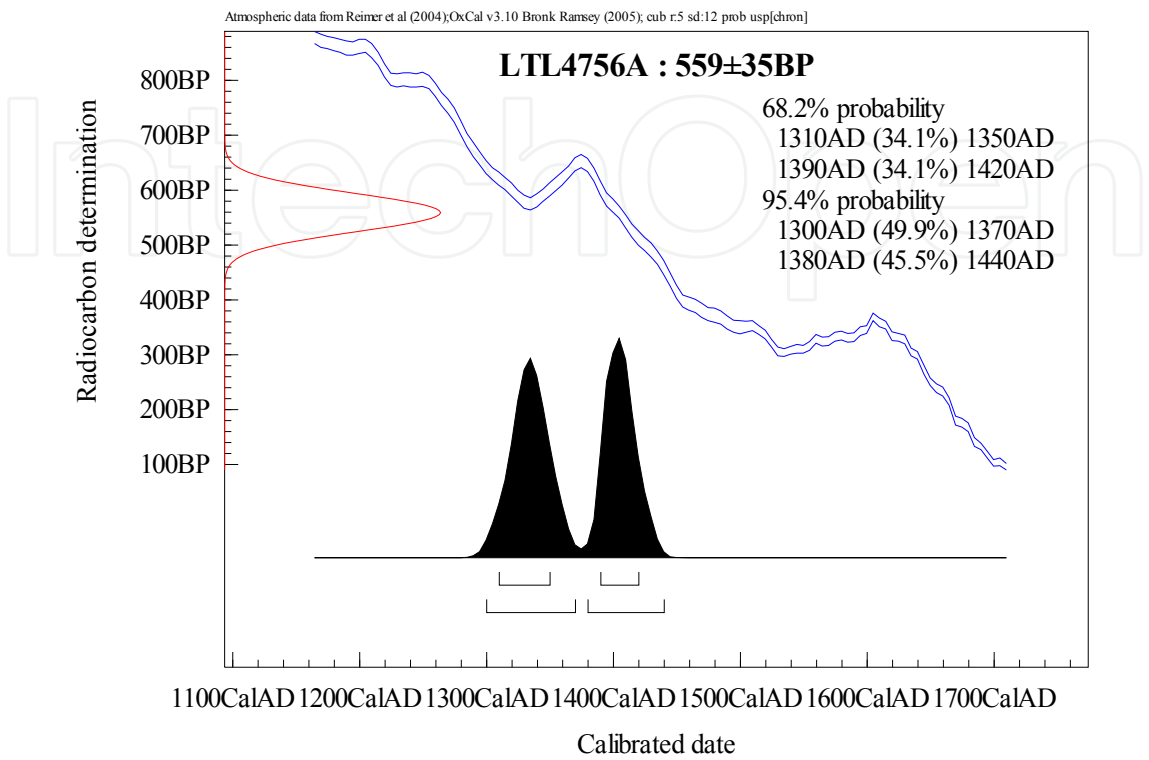
Fig. 7. Calibrated and uncalibrated age of the lime lump picked up in the lower part of the surrounding wall of the Zuccarello castle (analysis by CEDAD, Lecce – Italy)

The reliability and usefulness of this data was evaluated by comparison with results from other dating methods. Figure 8 shows collected dating estimates relative to a timeline plotted along the bottom of the figure. Each line in the figure corresponds to a specific dating obtained from different methods such as mensiochronology of bricks[10], chronotypology of doors or windows[11] and dating of artwork.

The lines corresponding to the mensiochronology method (black texture) were obtained from Five (M1-M5) groups of bricks collected in different parts of the castle. Their length represents the chronological range of production.

Above these lines the radiocarbon dating of the lime lump is reported (obliques lines on texture) and, above this, the results of the chronotypology dating (vertical lines on texture). Dating from the artistic evaluations of frescos, still visible inside the castle, are given at the top of the figure (obliques lines on texture).

---

[10]Mensiochronology of bricks is a well established archaeological dating method based on the trend of the size of bricks over the time. Its accuracy (a few tens of years) is not constant but varies over the time depending on various factors such as the amount of data available for a specific production defined in time and space.

[11]Chronotipology of door and window frames is a dating method based on the shape of frames of doors and windows with an accuracy of a few hundred years.
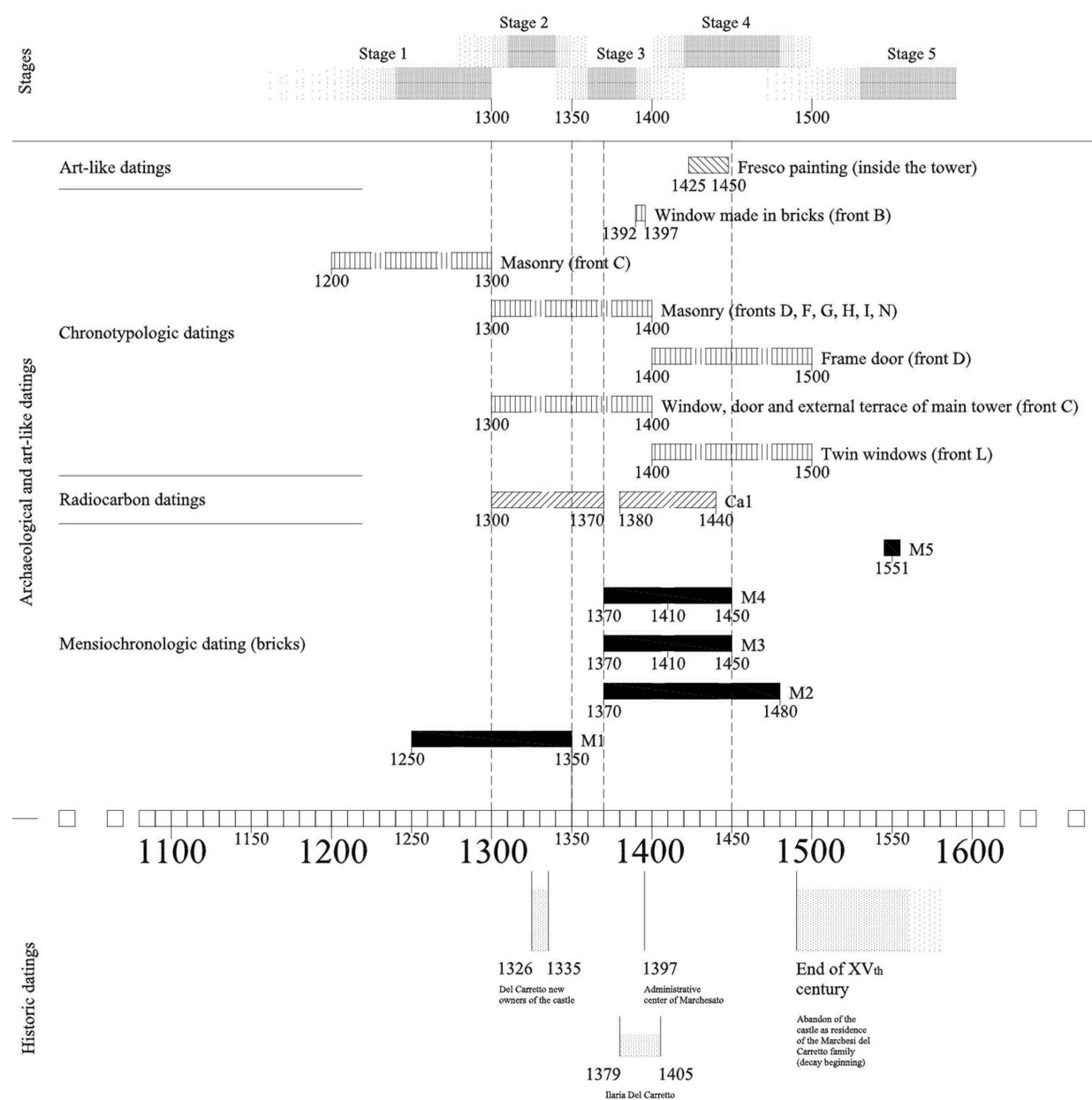
Fig. 8. Comparison of results obtained from all the different dating methods applied at Zuccarello castle

The graph highlights the agreement between radiocarbon dating and other dating methods. The first peak of the radiocarbon dating curve between 1300 and 1370 matches historical records indicating that between 1326 and 1335 the historically important family of "Del Carretto" acquired the castle (at the bottom of the figure). At this time significant expansion of the main building was carried out.

However, the second peak of the radiocarbon dating curve, between 1380 and 1440, is not in agreement with archaeological records describing building techniques of this period. In particular there are anomalies regarding the size, shape of masonry unit, mortar joints and the laying technique of the wall where the lump was sampled that does not fit the radiocarbon dating (whereas the first peak does).

Therefore, after comparing radiocarbon data with other archaeological evidence, the surrounding wall of the castle where the lime lump was picked up is believed to date from between 1300 and 1370.

5. Conclusions

Experience already gained through the studies described highlight the importance and future potential of radiocarbon dating of pure lime lumps for historic constructions.

Success of the method is dependent on following an appropriate sampling methodology which involves archaeological, chemical and physical knowledge of the building and the materials being studied. Following the removal of appropriate lime mortar samples from the historic site of interest the pure lime lumps must be extracted under the view of an optical microscope. Once extracted these lumps must be weighed and properly stored before being sent to the AMS laboratory.

Despite recent advances in this technique the full potential is still to be discovered. Unknowns include the dating of mixtures containing hydraulic lime which accounts for a significant proportion of historic mortar.

Re-carbonation of calcium carbonate is expected to affect the results of radiocarbon dating (Karkanas, 2007). However few studies have been carried out to address this phenomenon in lime lumps. This is believed due to the associated difficulties in identification of primary and secondary calcite. To date, results applied to lime lumps do not suggest this problem despite their extraction from ruined walls of archaeological sites where the penetration of rising damp or rain was expected has not been carried out.

6. Acknowledgment

7. References

Bakolas, A., Biscontin G., Moropoulou A. & Zendri E. (1995). Characterization of the lumps in the mortars of historic masonry. *Thermochimica Acta*, 269/270, pp. 809-816

Berger, R. (1992). [14]C dating mortar in Ireland. *Radiocarbon*, 34, 3, pp. 880-889

Bronk Ramsey, C. (1995). Radiocarbon calibration and analysis of stratigraphy: the OxCal program. *Radiocarbon*, 37, 2, pp. 425–30.

Bronk Ramsey, C. (2001). Development of the radiocarbon calibration program. *Radiocarbon*, 43, 2A, pp. 355–363

Bruni, S., Cariati, F., Fermo, P., Cariati, P., Alessandrini G. & Toniolo L. (1997). White lumps in fifth to seventeenth century AD mortars from northern Italy. *Archaeometry*, 39, 1, pp. 1-7

Bugini, R. & Toniolo, L. (1990). La presenza di grumi bianchi nelle malte antiche: ipotesi sull'origine. *Arkos Notizie GOR*, 12, pp. 4-8

CEDAD, n.d.. Sample preparation for AMS radiocarbon dating, In: *Internet site of CEDAD*, Date of access: November 2011, Available from: http://cedad.unisalento.it/en/clams.php

Elsen, J., Brutsaert, A., Deckers, M. & Brulet, R. (2004). Microscopical study of ancient mortars from Turnay (Belgium), *Materials Characterization*, 53, pp. 289-294

Elsen, J. (2006). Microscopy of historic mortars – a review. *Cement and Concrete Research*, 36, pp. 1416-1424

El-Turki, A., Ball, RJ. & Allen, GC. (2007). The influence of relative humidity on structural and chemical changes during carbonation of hydraulic lime. *Cement and Concrete Research*, 37, 8, pp. 1233-1240

Emrich. K., Ehhalt, DH. & Vogel, JC. (1970). Carbon isotope fractionation during precipitation of calcium carbonate. *Earth and Planetary Science Letters*, 8, 5, pp.363-371

Fieni, L. (2002). La Basilica di San Lorenzo Maggiore a Milano tra età tardoantica e medioevo: metodologie di indagine archeometrica per lo studio dell'elevato. *Archeologia dell'Architettura*, 7, pp. 51-98

Folk, R.L. & Valastro, S. Jr. (1976). Successful technique for dating of lime mortar by carbon-14. *Journal of Field Archaeology*, 3, pp. 203-208

Franzini, M., Leoni, L., Lezzerini, M. & Sartori, F. (1990). On the binder of some ancient mortars. *Mineralogy and Petrology*, 67, pp. 59-69

Gallo, N., Fieni, L., Martini, M., Sibilia, E. (1998). Archèologie du bati, 14C et thermolumiscence: deux exemples en comparaison, *Actes du 3eme Congrés International 14C et Archéologie*, Lyon, 6-10 Avril

Gallo, N. (2001). 14C e archeologia del costruito: il caso di Castello Aghinolfi (MS). *Archeologia dell'architettura*, 4, pp. 31-36

Gliozzo, E. & Memmi Turbanti, I. (2006). La catodoluminescenza e l'analisi di immagine per lo studio delle malte. *Proceedings of the IV Congresso Nazionale di Archeometria - Scienza e Beni Culturali*. Pise, Febraury 2006.

Goren, Y. & Goring-Morris, AN. (2008). Early Pyrotechnology in the Near East: Experimental Lime-Plaster Production at the Pre-Pottery Neolithic B Site of Kfar HaHoresh, Israel. *Geoarchaeology: An International Journal*, 23, 6, pp. 779-798

Hale, J., Heinemeier, J., Lancaster, L., Lindroos, A., & Ringbom, A. (2003). Dating ancient mortar. *American Scientist*, 91, pp. 130-137

Ingham, JP. (2005). Investigation of traditional lime mortars – the role of optical microscopy. *Proceedings of the 10th Euroseminar on Microscopy Applied to Building Materials*, University of Paisley, June 2005, pp. 1-18

Karkanas, P. (2007). Identification of lime plaster in prehistory using petrographic methods: a review and reconsideration of the data on the basis of experimental and case studies. *Geoarchaeology: An international journal*, 22, 7, pp. 775-796

Leslie, AB & Hughes, JJ. (2002). Binder microstructure in lime mortars: implications for the interpretation of analysis results. *Quarterly Journal of Engineering Geology and Hydrogeology*, 35, pp. 257-263

Marzaioli, F., Lubritto, C., Nonni, S., Passariello, S., Capano, M. & Terrasi, F. (2011). Mortar Radiocarbon Dating: Preliminary Accuracy Evaluation of a Novel Methodology. *Analytical Chemistry*, 83, 6, pp. 2038-2045

Morse, J.W. & Meckenzie, F.T. (1990). *Geochemistry of Sedimentary Carbonates* (1st edition), Elsevier, 0-444-88781-4, Amsterdam

Nawrocka, D., Michniewicz, J., Pawlyta, J., & Pazdue, A. (2005). Application of radiocarbon method for dating of lime mortars. *Geochronometria*, 24, pp. 109-115

Norman, D. (1961). *A history of building materials*, Phoenix House, London

Oates, JAH. (1998). *Lime and limestone: chemistry and technology, production and uses*, Wiley-VCH, 3-527-29527-5, Weinheim

Pachiaudi, C., Marechal, J., Van Strydonck, M., Dupas, M., & Dauchot-Dehon, M. (1986). Isotopic fractionation of carbon during CO_2 absorption by mortar. *Radiocarbon*, 28, 2A, pp. 691-697

Pesce, G.L.A., Quarta, G., Calcagnile, L., D'Elia, M., Cavaciocchi, P., Lastrico, C. & Guastella, R. (2009). Radiocarbon dating of lumps from aerial lime mortars and plasters: methodological issues and results from the S. Nicolò of Capodimonte Church (Camogli, Genoa – Italy). *Radiocarbon*, 51, 2, pp. 867-872

Pesce, G.L.A. (2010). Radiocarbon dating of lumps of no completely mixed lime in old constructions: the sampling problem, *Proceedings of 2nd Historic Mortar Conference*, Prague, September 2010

Pesce, G.L.A., Ball, R., Quarta, G., & Calcagnile, L. (2012). Identification, extraction and preparation of reliable lime samples for the ^{14}C dating of plasters and mortars with the method of "pure lime lumps", *Proceeding of the 6th International Symposium on Radiocarbon and Archaeometry*, Cyprus, April 2011

Rattazzi, A. (2007), *Conosci il grassello di calce? Origine, produzione, impiego del grassello di calce in architettura, nell'arte e nel restauro*, Edicom Edizioni, 978-88-86729-70-3, Monfalcone

Reimer, PJ., Baillie, MGL., Bard, E., Bayliss, A., Beck, JW., Bertrand, CJH., Blackwell, PG., Buck, CE., Burr, GS., Cutler, KB., Damon, PE., Edwards, RL., Fairbanks, RG., Friedrich, M., Guilderson, TP., Hogg, AG., Hughen, KA., Kromer, B., McCormac, G., Manning, S., Bronk Ramsey, C., Reimer, RW., Remmele, S., Southon, JR., Stuiver, M., Talamo, S., Taylor, FW., Van der Plicht, J. & Weyhenmeyer, CE. (2004). IntCal04 terrestrial radiocarbon age calibration, 0–26 cal kyr BP. *Radiocarbon*, 46, 3, pp. 1029–58

Sonninen, E. & Junger, H. (2001). An improvement in preparation of mortar for radiocarbon dating. *Radiocarbon*, 43, 2A, pp. 271-273

Turner, JV. (1982). Kinetik fractionation of carbon-13 during calcium carbonate precipitation. *Geochimica et Cosmochimica Acta*, 46, 7, pp. 1183-1191

Van Balen, K. (2005). Carbonation reaction of lime kinetics at ambient temperature. *Cement and Concrete Research*, 35(4), pp.647-657

Van Strydonck, M., Dupas, M., Dauchot-Dehon, M., Pachiaudi, Ch. & Maréchal, J. (1986). The influence of contaminating (fossil) carbonate and the variations of $\delta^{13}C$ in mortar dating. *Radiocarbon*, 28, 2A, pp. 702–10

Van Strydonck, M.K., Van der Borg, A.F.M., & De Jong, E.K. (1992). Radiocarbon dating of lime fractions and organic material from buildings. *Radiocarbon*, 34, 3, pp. 873-879

Vecchiattini, R. (2010). *La civiltà della calce. Storia, scienza e restauro*, De Ferrari, 978-88-6405-089-8, Genoa
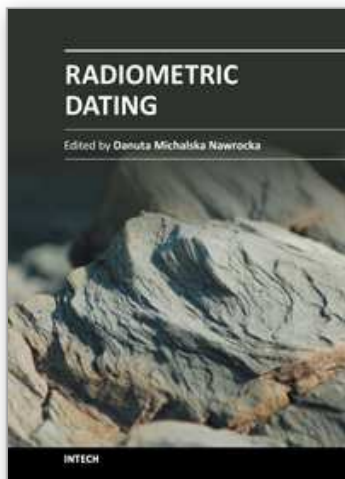
Radiometric Dating

Edited by Dr. Danuta Michalska Nawrocka

This book explores a diversity of topics related to radiometric dating, with particular emphasis on the method of radiocarbon dating and a cross-check of its results with luminescence measurements. Starting from the chapter on Methodology the book includes, among other topics, the description of the problem of preparation of samples for 14C measurement, a wide application of the radiocarbon method and a comparison of results obtained by various methods, including the radiocarbon method, the method of OSL, TL and palynology. The issue of radiocarbon dating of mortars and plasters is thoroughly discussed in the book. Chapter Two, Applications, and Three, Luminescence and Radiocarbon Measurements, provide examples of the application of the radiocarbon method in the study of archaeological, geological sites, from the analysis of soils, loesses, to the study of organic deposits filling the depressions in the Morasko Meteorite Nature Reserve. A wide range of studies reveals the great potential of the radiocarbon method, and the presented papers reflect interdisciplinary research.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

INTECH
open science | open minds