# Radiocarbon dating of lime lumps: current and future challenges

Giovanni L. Pesce[1,2]

[1] Faculty of Engineering and Environment, Northumbria University; 2, Ellison Pl, NE1 8ST Newcastle upon Tyne, UK; phone: +44 (0)191 2773065; email: giovanni.pesce@northumbria.ac.uk
[2] Istituto di Storia della Cultura Materiale, Piazza Sarzano 35r, 16128, Genova, Italy

## Abstract

This paper discusses some of the main differences between the radiocarbon mortar dating technique based on the use of lumps of pure lime, and the technique based on the use of bulk mortar samples. The paper also discusses the main limitations of the current application and development of the lime lump technique, mainly related to the limited knowledge currently available of the chemical, physical, mineralogical and isotopic composition of the lumps. These limitations are supposed to be the reason why, despite the successful results obtained over the last 20 year, the lime limps technique is not yet widely used in archaeological excavation and conservation works. The paper aim at contributing to the debate on the development of the mortar dating techniques and, in the conclusions, suggests that the technique based on the lime lumps should not be considered as a substitute of the technique based on bulk mortar sample (as suggested in a recent publication) but, on the contrary, as an alternative technique. This approach will provide archaeologists and conservators with a richer and more useful toolbox for mortar dating, suitable to every circumstance.

## Keywords

Mortar dating; lime lumps; radiocarbon; mortars; plasters

## 1) Introduction

The use of lumps of pure lime for the radiocarbon dating of historic mortars was first suggested at the at the end of the 20$^{th}$ century (Van Strydonc *et al.* 1992; Heinemeier *et al.* 1997; Gallo 2001; Fieni 2002). Initially, the lumps were considered a source of radiocarbon alternative to the more common bulk mortar samples (i.e. a mixture of binder, aggregate and possible additives). Over the years the main advantage of the lumps (i.e. being naturally free from contaminants such as the $^{14}$C-dead carbonate of the sand grains) gathered the attention of various research groups interested in mortar dating. Since then, the research focused on the accuracy and precision of the technique that had to be verified, in particular when compared to the other, more common applications of the radiocarbon dating method such as those based on the use of the organic matter (i.e. pieces of charcoal) that sometimes is embedded in the historic mortars (Lindroos *et al.* 2007; Pesce *et al.* 2009).

Since the first publication, a number of papers discussing the results of the applications of the radiocarbon dating method to lime lumps were published and further advantages and limitations of the technique emerged (Pesce *et al.* 2012; Lindroos *et al.* 2014). Recently, a couple of scientific papers (Lindroos *et al.* 2018; Sironic *et al.* 2019) presented a comparison of the $^{14}$C results obtained for the same mortars using both, the lime lump technique and the technique based on bulk mortar samples. Interestingly, both publications highlight the higher accuracy of the technique based on the lime lumps. Even more interestingly, the paper published by Lindroos and colleagues (2018) specifically aimed at investigating whether the lime contained in the lumps is more suited for the radiocarbon dating than the lime contained in the bulk samples. These authors even suggested considering if time has come to abandon the analysis of bulk mortars in favour of the lime lumps

(assuming that the reliability of the lime lump is proved; LINDROOS *et al.* 2018). In the conclusions, the paper does not contain a clear answer to this question and leaves the judgment to the readers. However, considering the research question at the base of the paper, this publication represents an important milestone in the history of the development of the mortar dating and provides the occasion for an important moment of reflection. Two assumption that deserve further considerations are, in fact, implied in this research question. The first assumption is that that the technique based on the lime lumps can substitute the technique based on bulk mortar samples. The second is that two techniques for applying the radiocarbon dating method to lime mortars are not necessary.
After an initial introduction of the lime lump technique, this paper aims at discussing these two assumptions and highlights some other important issues of the current application of the radiocarbon dating method to lime lumps.

## 2) Basic principles of the lime lump technique

The basic principle of the radiocarbon dating of lime lumps for mortar dating, is related to the fact that historic mortars often contain lumps of pure carbonated lime that do not contain sand grains, which are one of the major source of contaminants in mortar dating (i.e. grains of carbonate sand are *$^{14}$C-dead*). Over the time, these lumps combined with the atmospheric $CO_2$ in the same manner as the surrounding mortar and, therefore, they are best suited for the radiocarbon dating method compared to generic pieces of mortar that, by their nature, do contain sand grains.
However, experience demonstrated that for a successful application of the lime lumps technique it is important to correctly identify these lumps since historic mortars have been found to contain at least five different types of lump that look very similar each other, and of which only one is suitable for the radiocarbon dating method. These comprise: 1) under-burned pieces of limestone; 2) over-burned pieces of limestone; 3) pieces of burned limestone containing high concentrations of silica (these form when the stone used for the lime production contains high quantity of Silica and Aluminate impurities); 4) lumps of re-carbonated lime; 5) lumps of pure carbonated lime (PESCE & BALL 2012). Details of these lumps are reported in Pesce & Ball (2012). Differently from the other lumps, pure lime lumps are characterised by a white, rounded and floury complexion. Furthermore, their surface hardness is very low, making them easily identifiable but also extremely delicate to handle and easy to damage. Once correctly identified and removed from the surrounding mortar, the lump surface needs to be mechanically and chemically cleaned from all pieces of sand that can be attached to it. Only after this procedure is completed, the lumps are ready for the radiocarbon dating (PESCE & BALL 2012).
Over the past 20 years, the use of lime lumps for mortar dating has proved to be successful in most cases. However, in a minority of cases (about 10%-15% estimated on the personal success of the author), the AMS results suggested contamination of the samples that was not identified during the sampling and preparation process. These cases remain nowadays unexplained and highlight an issue that represent one of the main limitation of the technique: the identification and selection of the right samples.

## 3) Lime lumps: substitute or alternative to bulk mortar sample?

Despite the frequent interference of other carbon sources such as the sand grains, the $^{14}$C extracted from the bulk mortar samples is ideally generated by the dissolution/decomposition of the carbonated lime likewise the case of the lumps of pure (carbonated) lime. However, it is undeniable that from a chemical, physical, mechanical and mineralogical point of view, the material contained in the lumps is different from the material in the bulk mortar samples. In fact, the first one is a pure polycrystalline material mostly made of calcium carbonate (usually calcite), whereas the second one is a composite material made of a variety of minerals with a substantial component of calcium carbonate of various origin (e.g. carbonate sand and carbonated binder). Therefore, the application of the $^{14}C$ dating method to the lime lumps can be evaluated either, as an alternative to bulk mortar samples if the origin of the $^{14}C$ is used for a comparison, or as a substitute if the mineralogical composition is considered.

However, irrespective of these differences, it is important to highlight that from the point of view of the sampling process (which is an important part of the whole mortar dating process) the two materials are substantially different. The number of lumps embedded in a mortar, in fact, varies depending on a number of factors including the technological process that led to the production of the mortar (e.g. hot or cold mixed; COPSEY 2017; COPSEY 2019; BROWN ADAM 2017; ARTIS 2018; VEIGA 2017)).

In some carefully produced mixes used for specific application such as bedding mortars, for instance, lumps are rarely embedded, whereas in other mixes such as core mortars for large walls, the presence of lumps can be very common. Consequence of such difference in mortar production, is that it is not always possible to collect the lumps necessary for the radiocarbon dating.

Usually, if an initial inspection of the exposed surface of the mortar shows a lack of lumps, some material can be dug out to explore the presence of the lumps immediately under the surface. This entails the destruction of a material – the mortar – with a historic value, without the certainty of finding any suitable sample for the radiocarbon dating. In such case, the value of this action is questionable and the collection and dating of a bulk mortar sample would be more appropriate since it prevents any unnecessary damage to the structure.

In other circumstances, instead, the use of lumps is preferred because it causes very limited damage to the historic fabric compared to the sampling of a piece of mortar. This is the case of plasters and renders where the removal of a small lump from a large surface can be easily carried out with very limited damage to the structure.

Considering the sampling process, it is clear that the technique based on the use of the lime lumps should not be considered a substitute of the one based on bulk mortar samples. On the contrary, the two techniques should be consider alternatives, since each one is suited for specific applications. As a consequence, the idea suggested in Lindroos' paper (LINDROOS *et al.* 2018) of abandoning the technique based on bulk mortar samples because of the reduced accuracy of the results compared to the lime lump technique should be replaced with the idea of improving both techniques in order to create of a more useful toolbox for archaeologists, that is suited to every circumstance.

## 4) Improving the lime lumps technique: the need to develop the appropriate knowledge

The short history of the technique based on lime lumps and the limitations emerged in recent research (PESCE *et al.* 2012; LINDROOS *et al.* 2014) suggest that it needs further developments before being adopted on a much larger scale.

One of the main problems emerged over the last 20 years is the limited knowledge currently available on the origin and characteristics of the lumps used for dating the historic mortars. It has already been pointed out (PESCE & BALL 2012; LINDROOS *et al.* 2018) that various kind of lumps are embedded in the mortars produced in the past centuries and that, among these, only a very specific type is suitable for the radiocarbon dating (i.e. the lumps made of pure carbonated lime). The application problem of the lime lump technique lies in the difficulty of identifying the right (or "good") lumps among the others (that may have different $^{14}C$ content). This is due to the fact that, currently, no non-destructive tests are available to investigate the origin of the calcium carbonate contained in it before the $^{14}C$ extraction and count.

This methodological gap is probably related to our limited knowledge of the characteristics of the various types of lumps embedded in the historic mortars, which is often based on empirical rather than scientific evidence (BAKOLAS *et al.* 1995; TENCONI *et al.* 2018; ELSEN 2006; MIRIELLO *et al.* 2010; BRUNI *et al.* 2007; VEIGA 2017). For instance, currently we assume that both, the "good" and most of the "bad" lumps are mostly made of calcium carbonate (usually in the form of calcite) and, therefore, are difficult to distinguish. The only characteristic that has been used as an indicator of

the quality of the lump (with good but not perfect results) has been the softness of the material. However this characteristic cannot be easily quantified at such small scale (i.e. 20 mg of material) and, consequently, the decision if a lump is “soft” enough to be “good” is based on the skills and expertise of the operator collecting and preparing the sample, not on objective, measurable values. The scientific literature reports other various methods to identify the origin of calcium carbonate (CHU *et al.* 2008; GUETA *et al.* 2007) but the current research is far from providing an easily applicable methods that can be widely used for screening the samples before the $^{14}C$ analysis.
Demonstration of this lack of knowledge is the fact that most of the scientific publications describing the results of the radiocarbon dating of lime lumps do not contain information regarding the physical, mineralogical or chemical characteristics of the dated lumps. Exception are some papers containing the results of the cathodoluminescence (CL) analysis of the samples (LINDROOS *et al.* 2007; GLIOZZO & MEMMI TURBANTI 2006). Cathodoluminescence petrography is a common tool used to investigate diagenesis of carbonate rocks. CL colours and intensities are related to trace elements such as $Mn^{2+}$ and $Fe^{2+}$ and used to interpret conditions of the environment in which the precipitation took place (MACHEL 2000). However, even in these cases the characterization is far from being complete. For the situation to evolve, every time a lump is dated using the radiocarbon dating method, a detailed characterization of the material should be provided independently from the correctness of the radiometric results.

## 5) Improving the lime lumps technique: the need to overcome the limitation of the sampling work

In addition to the difficulties related to the identification of the right kind of lump, it is important to stress that the results of the radiometric dating are substantially affected by the position of the lumps within the structure. It has already been pointed out (PESCE & BALL 2012) that, because of the limited access of the $CO_2$ to the inner parts of the walls, the closer the lumps are to the surface, the closer is the result of the radiometric dating to the actual construction time of the structure under investigation, which is the main research question of any application of the $^{14}C$ method to historic constructions.
From a practical point of view it is important to stress that the ideal sampling conditions (i.e. where the right lump is close to the surface of the structure under investigation) are not always achievable and that the characteristics of the sampling work varies on a case-by-case basis. Details of who to carry out a correct sampling work were provided in Pesce and Ball (2012). However, to reduce the risk of incorrect results due to the position of the sample within the structure, the sampling work should be carried out within a planned sampling programme designed and carried out by operators with knowledge on the characteristics of the carbonation reaction and of the historic mortars. Furthermore, before carrying out any sampling work it is essential to acquire a detailed knowledge of the historic structure under investigation, including the changes that the same structure was subjected to over the time. This is because even small structures can endure several transformation over the centuries and consequently sampling the lump in the wrong part of the structure can provide an unexpected results. This result may be correct from the point of view of the radiocarbon dating technique but wrong if the sample does not belong to the phase that has to be dated.
Currently, the best methodology providing the information needed for a correct sampling work is the building archaeology. A very good example of how a detailed study of a building (or even of an individual part of a building) can support the development of the lime lump technique is presented by Vecchiattini in this very same number of the journal. In her article, Vecchiattini (2019) carries out a detailed archaeological analysis of the elevation of a medieval building located in the Italian city of Genoa that was dated using a variety of archaeometric techniques including several lime lumps. What makes this case unique is that in this case Vecchiattini is even able to highlight the accuracy and precision of the radiometric dating of lime lumps. Further details of how the building archaeology can contribute to the sampling process of the pure lime lumps are reported in VECCHIATTINI *et al.* (2013).

## 6) The contamination problem: a simple explanation to a more complex problem and the key to develop further or knowledge

In general, when the result of a radiometric dating is not in agreement with the expected result, the dated sample is classified as contaminated and the lime lump technique is considered not working. However it is important to highlight that, considering the basic principles of this technique (i.e. the $^{14}C$ is extracted from a lump of only pure carbonated lime) and the complexity of the sampling work discussed in the previous paragraphs, it can be erroneous to state that the technique does not work if the $^{14}C$ result is not in agreement with the expectations. A possible reason for such discrepancy could be, as mentioned in the paragraph 5, an error in the sampling process.

The sampling of the wrong lump such as a lump of partially decomposed limestone leads to a chronological result which is different from the actual time of the setting and hardening of lime. The difference can be minimal (few hundred years), substantial (thousands of years) or anything in between these two extremes, depending on the amount of *$^{14}C$-dead* carbon contained in the analysed sample (i.e. an unknown quantity). In such circumstance, the sample is correctly considered as contaminated. However, in this case the problem is that the dated sample should have never been used for the radiocarbon dating because it was the wrong kind of lump. Actually, any lump containing any sort of contamination is the wrong lump. This is because of the basic principle of the lime lump technique entailing that any Carbon contained in the lime lump must have been fixed in the structure of calcium carbonate at the time of the setting and hardening of the lime. No other source of carbon must be included in such kind of lump. In such context, a contamination problem of the lime lump technique can only occur when the $^{14}C$ content of the carbonated lime is contaminated by *$^{14}C$-dead* carbon such as the carbon dissolved in the water that takes part in the carbonation reaction (i.e. the water added to the lime and the aggregate when the mortar is produced). However, at the moment there is no evidence of the influence of such carbon in the results of the radiometric dating.

Similarly, if the correct sample is removed from inside the structure, several centimetres from the nearest surface in contact with the atmosphere, the results of the radiocarbon dating can describe an age which is several decades (if not centuries) later than the actual construction time of the structure. Unfortunately, currently there is no experimental evidence allowing us to relate the depth of sampling with the delay time of carbonation. This is because the progress of the carbonation front depends on a number of factors such as the porosity of the mortar that are influenced by a variety of other factors difficult to evaluate such as the ratio binder:water in the original mix. A detailed analysis of the experimental results relating time and carbonation front is reported in DESPOTOU *et al.* (2016) where is also mentioned that an approximation of the development of the carbonation front with time can be described by first Fick law of diffusion represented in Equation 1. In this equation, *X* is the distance between the surface and the carbonation front, *t* is the time elapsed and *k* is a constant related to the properties of the material (DESPOTOU *et al.* 2016, p. 130).

$$X = k \cdot \sqrt{t}$$

*Equation 1 - First Fick law of diffusion*

Consequence of the difference between the experimental result and the expected result may, consequently, lead the archaeologist to wrongly consider the sample as “contaminated” (and the technique as “not working”) when the lump did not contain contaminants and the technique worked as it was supposed to do.

These two examples suggest that any time a possible contamination problem emerges it should be fully investigated because it is only through an accurate evaluation of the wrong results that our knowledge of the technique can progress further (not through the simple celebration of the correct results).

## 7) Assessing the quality of the radiocarbon dating results

As described in the latter scenario suggested in the paragraph 6, if a lump is removed from inside a structure, several centimetres from the nearest surface in contact with the air, the results of the archaeometric dating may only be few decades late compared to the actual age of the structure. Therefore, this result may appear correct, despite being essentially wrong. To overcome the problem of assessing the quality of the radiometric dating, two methods have been developed and used over the past decades that make only use of the data produced during the dating work.

The first method was developed by researchers at Abo Academy (Finland) and is based on a comparison of the results of various $CO_2$ fractions extracted from the same sample (in the latest papers the same authors suggest that even the comparison of the first two $CO_2$ fractions is sufficient to validate the results of the radiocarbon dating (LINDROOS *et al.* 2018; LINDROOS *et al.* 2007). However this method is based on the assumption that the carbonation process happens at the same time in the same manner within the whole structure of the lump. Unfortunately, considering the characteristics of the carbonation reaction, this assumption cannot always be verified, in particular if the lump is sizeable. This is because the carbonation take place at the interface between the calcium hydroxide crystals and the humid air in contact with it (CIZER *et al.* 2006). Only when the surface is fully carbonated, the reaction progresses toward the core of the crystals. The carbonation mechanism in itself may therefore introduce a delay in the carbonation time of various part of the same crystal. However, there are further problems that may an effect on the progression of the carbonation reaction. For instance, it is known that the carbonation is a self-limiting reaction. This means that it tends to slow down while progresses from the surface toward the inner part of the sample (GALAN *et al.* 2015). Besides, it is known that this reaction is dramatically affected by the environmental condition where it take places and this means that in some conditions the carbonation can temporarily stop and re-start again when the condition are once again right (DHEILLY *et al.* 2002; LOPEZ-ARCE *et al.* 2011).

So, it is possible that the surface and the bulk of the same lump, carbonate at different times and this is particularly true in big lumps (i.e. centimetre-size lumps). This, of course, has an effect on the results of the radiocarbon dating process and on the assessment procedure described above. The problem, in this case, is that, although it is known that the surface and the bulk of a lime lump can carbonated at different times, currently it is impossible to evaluate the importance of this factor on the overall results of the radiocarbon dating.

The second method that has been used to assess the quality of the results obtained with the radiocarbon dating of the lime lumps is based on the dating of various sample, each one removed from a well identified stratigraphic unit of the same structure. The stratigraphic unit from where the lumps are collected should have a clear stratigraphic relationship with the surrounding units so that the relative sequence of the units where each sample is removed is known. In this case, the chronological sequence emerging from the radiocarbon dating results should reflect the stratigraphic sequence. In this case, it is reasonable to assume that the radiocarbon dating of all lime lumps was successful. If, instead, the chronological sequences of the $^{14}C$ dating is different from the stratigraphic sequence, a critical evaluation of the results should be carried out and temporarily assume that (at least one of) the results are wrong.

Ideally both methods should be used to assess the correctness of the radiometric results however, this increases the cost of the dating process and, therefore, this may not always be a viable option. In any case, it is clear that a single radiometric result obtained with the lime lump technique, despite being less affected by the contamination problem (compared to similar techniques), does not provide the necessary assurance that the result is correct. Any time a lime lump is dated with the $^{14}C$ method, a system to evaluate the correctness of the result (such as those listed above) should be used.

## 8) Mortars made with non-calcic lime

All examples and discussions in the paragraphs 6 and 7 implied that the lime fixing the $^{14}C$ in historic mortars was made of calcium oxide or calcium hydroxide (i.e. calcium lime; BSI, 2015). However this is not always the case since magnesium lime was widely used in the past centuries (LAYCOCK *et al.* 2019; PAVIA *et al.* 2005; PESCE *et al.* 2019; PONCE-ANTÓN *et al.* 2018) as well as various kind of lime with natural hydraulic properties (FRANQUELO *et al.* 2008; ROBADOR *et al.* 2010; MARAVELAKI-KALAITZAKIA *et al.* 2005; LAYCOCK *et al.* 2019). These are two kind of lime for which our knowledge of their possible $^{14}C$ signature is very limited if not existing at all, although it is clear that their nature introduces a further level of complexity in our understanding of the radiocarbon dating of lime lumps.

For instance, it is known that during carbonation, Magnesian lime not only produces calcium carbonate as reaction product, but also various magnesium compounds such as magnesite (Equation 2) and hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$), depending on the conditions where the reaction takes places (e.g. temperature, humidity and pH) (VEIGA 2017). Little is known about the isotopic composition of these Mg-based compounds however, it is known that any magnesium carbonate is far more soluble than any form of calcium carbonate. Figure 1 shows the aqueous solubility of some common Calcium and Magnesium compounds at 25°C. In this graph it is possible to observe that magnesium carbonates have a solubility similar to the one of calcium hydroxide, whereas Magnesium hydroxide has a solubility similar to the one of calcium carbonate.

*Equation 2 - Carbonation of Brucite (from: Zhao, et al., 2010)*

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O$$

This suggests that mortars made with magnesium lime are more prone to a rejuvenation process due to the capture of fresh $CO_2$ from the atmosphere by the magnesium that, if in a form of carbonate, can easily dissolve in presence of water and re-precipitate as new soluble compound when the water evaporates. As a consequence, it is possible to suggest that mortars made with Magnesium lime are not suited for the radiocarbon dating method. However, no experimental evidence is currently available to support this statement and further research is needed.

When lime with natural hydraulic properties is used to produce mortars and plasters, the hydration of anhydrous calcium silicate compounds such as Belite (or di-calcium silicate), had the effect of producing new calcium hydroxide as by-product that is, then, subjected to a late carbonation (compared to the lime available in the material since the mixing; (HEWLETT & LISKA 2019).

*Equation 3 - Hydration of di-calcium silicate (from: Czernin, 1980, p. 42)*

$$2(2CaO \cdot SiO_2) + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2$$

The reaction is described in Equation 1 and, according to CZERNIN (1980), a unit of completely hydrated dicalcium silicate contains approximately 20% by weight of calcium hydroxide.

This could introduce an error in the results of the radiocarbon dating, in particular in cases where the hydration of silicates took place after the initial setting (i.e. if the mortar dried to quickly initially). Furthermore, there is no experimental evidence that lumps of pure lime can form in naturally hydraulic lime. Currently the scientific literature provides examples of successful radiocarbon dating of hydraulic mortars made with air lime and cocciopesto (PESCE & DECRI 2013) but not examples of mortars made with natural hydraulic lime. This may be due to a poor characterization of the binder in the mortars already dated or to an actual lack of data with regard to this kind of lime. What is relevant here is that this lack of data make even more relevant the need to provide a full characterization of the lumps when these are used for the mortar dating.

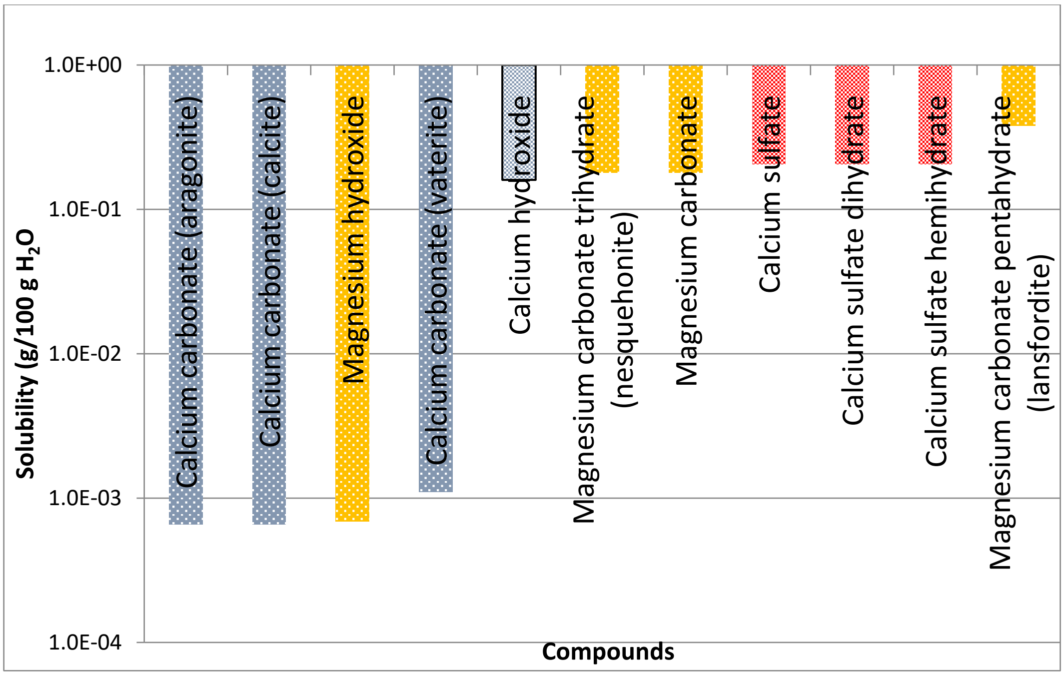


*Figure 1 - Aqueous solubility of some common Ca and Mg compounds at 25°C (data from: VV.AA., 2009)*

## 9) Conclusions

The radiocarbon dating of lumps of pure carbonated lime is a technique for mortar dating that was introduced only at the end of the 20th century. Although it provides better results than the results obtainable with the technique based on the use of bulk mortar samples, the technique is not yet fully mature and needs further development.

Currently, one of the main limitations in the development of the technique is our knowledge of the lime lumps used for dating the historic mortars (e.g. their chemical, physical, mineralogical and isotopic composition). Our current knowledge is such that, when the result of the $^{14}C$ dating is not in agreement with the expectation, the sample is generically labelled as “contaminated” and the technique is declared “not working” even if, from a technical point of view, the radiocarbon dating of that sample is correct.

Because of the importance of the sampling work on the quality of the $^{14}C$ results, the samples should be selected, removed and prepared only by operators with specific knowledge on the characteristics of the carbonation reaction and of the historic mortars. Furthermore, any sampling work should be carried out only after having acquired a detailed knowledge of the historic structure under investigation, with the application of techniques such as the building archaeology.

To increase our knowledge of the characteristics of lime lumps and, in turn, to increase the current successful rate of the technique, every time a lump of lime is dated using the radiocarbon dating method, a full characterization of the material should be produced.

Finally, despite producing better results, the technique based on the use of the lime lumps should not be considered a substitute of the technique based on the use of bulk mortar samples. On the contrary, the two techniques should be consider alternatives, each one particularly suited for specific applications. As a consequence, the idea of abandoning the technique based on bulk mortar samples should be replaced with the idea of improving both techniques to create a more useful toolbox for archaeologists, suited to every circumstance.

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