# The need for a new approach to the radiocarbon dating of historic mortars

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**NOTES TO TYPESETTER:**
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**ABSTRACT.** This commentary aims at raising awareness and fostering a discussion on the need of a new approach to the radiocarbon ($^{14}C$) dating of historic mortars. Over the last decades, important advancements have been made in the application of the $^{14}C$ dating methods to lime mortar samples, including the use of lime lumps instead of generic pieces of mortar. However, a relevant number of results in disagreement with the chronological framework of the related archaeological cases are published every year without a clear understanding of the reasons for such results. This suggests that further developments to the methodology are needed. The commentary argues that to further develop this particular application of the $^{14}C$ dating method, a new, more holistic approach is needed that moves away from the very "applied" approach that dominated the last decades and focuses more on the causes of contamination and the mechanism of the reactions involved. Two actions are suggested that can immediately improve our ability to critically assess the results obtained: the publication of a chemical and mineralogical characterization of the binding fraction for the dated mortars, and the publication of sampling depth for each dated sample.

**KEYWORDS:** AMS dating, architecture, contamination, lime, mortars.

## BACKGROUND INFORMATION

The application of the radiocarbon ($^{14}C$) dating method to lime mortar samples has been the focus of several research groups for a few decades now (Marzaioli et al. 2011; Ringbom et al. 2014; Hajdas et al. 2017; Vecchiattini 2019; Daugbjerg et al. 2021a). This is because the extraction of the $^{14}C$ signal from the binder used in historic mortars has the potential of providing the most accurate chronological information on the construction time of the related buildings and structures. Such information is of great importance in various disciplines such as archaeology, building conservation, and historic studies since buildings (e.g., dwelling houses) and structures (e.g., bridges, and aqueducts) are some of the most notable evidences of past societies' activities.

The potential accuracy of this technique lies in the fact that the chronological information obtained relates to the hardening of the mortars (i.e., of the lime), which is the glue keeping together buildings and structures. Hence, the $^{14}$C dating of mortars is—in theory—the most accurate chronological information achievable on the construction time of a historic building or structure.

Other applications of the $^{14}$C method (e.g., to organic material embedded in the mortars), or the application of other dating methods (e.g., thermoluminescence, dendrochronology) can provide similar information but—practically—not as accurate as the $^{14}$C dating of the binding fraction of mortars, since they date materials and events from a different time compared to the actual construction.

The development of this particular application of the $^{14}$C dating method over the past decades is clearly summarized in some papers published by the members of one of the most experienced groups such as Ringbom et al. (2014) and Daugbjerg et al. (2021a). At the beginning, the researchers were mainly focused on a method to exclusively extract the $^{14}$C signal of the binding fraction and avoid that of other carbonate sources that are commonly part of the mix. Lime mortars are, in fact, composite materials made of various ingredients of which only one (i.e., the binding fraction) generates the necessary $^{14}$C signal. Other ingredients are, for instance, carbonate sand (which is $^{14}$C-dead) whose signal, if not properly separated, can “dilute” the binder signal. To date, no method exists to securely separate the binder fraction from the rest of a mortar and, therefore, no method exists to safely separate the $^{14}$C signal of the pure lime from that of the other carbonate sources. Consequence of this is the fact that, even today, when using pieces of mortars as a sample material, some results of the $^{14}$C dating can substantially differ from that of the related archaeological framework, making such results meaningless, with a resulting loss of money and time.

A substantial improvement was achieved in the first decade of the new millennium, when a new approach to the sampling work, led the researchers to focus their attention on the $^{14}$C signal from the small lumps of pure binder often embedded in historic mortars (Pesce et al. 2009; Lindroos et al. 2018), rather than on entire pieces of mortars (i.e., a mix of binder and aggregate). Such improvement has contributed to a risk reduction in contaminated samples compared to the previous decades but, in the literature, examples of results substantially different from the related archaeological framework are still published.

## THE PROBLEM

Arguably, the problem lies in the fact that, since the introduction of the technique based on lime lumps, researchers have learned that various types of lumps can be embedded in historic mortars (i.e., not just lumps of pure binder; Pesce and Ball 2012), and that lumps of pure lime can have a heterogeneous chemical composition due to (1) the characteristics of the lime (i.e., its chemical composition), and (2) that of the reaction leading to its setting and hardening (i.e., the carbonation reaction).

In most publications where lumps do not produce results aligned to the related archaeological framework, these are classified as “contaminated” and disregarded with little if any consideration on the possible origin of such contamination. Obviously, such an approach prevents the development of the technique since it limits any further study of the contamination process. To improve the knowledge necessary to a successful application of the $^{14}C$ dating method to mortar samples, instead, the “contaminated” samples should become the focus of the researcher’s attention. This would allow developing a better understanding on the reasons for the contamination and, in turn, on how to avoid it. More generally, a shift from the current, very “applied” approach to the $^{14}C$ dating of mortars to a more “holistic” approach would be necessary. Such approach should entail, for instance, a more focussed investigation of the reaction mechanisms leading to the fixation of the $^{14}C$ into the calcium carbonate of the hardened mortars, in a similar way as it was attempted (albeit with limited appeal to the scientific community) some years ago (Pachiaudi et al. 1986; Van Strydonck et al. 1992).

Considering the main limitations of the current approach, two, in particular, are the aspects that should be urgently introduced in presenting and discussing the results of the $^{14}C$ dating of mortars samples: the chemical composition of the binding fraction, and the sampling depth.

## The importance of characterizing the binding fraction for a correct interpretation of the radiometric dating of mortar samples

Most (if not all) papers dealing with the $^{14}C$ dating of historic lime mortars assume that the only chemical reaction leading to the formation of $^{14}C$-bearing minerals is the carbonation of calcium hydroxide ($Ca(OH)_2$) represented in Equation (1) (Lindroos et al. 2007; Heinemeier et al. 2010; Ringbom et al. 2014; Daugbjerg et al. 2021a, 2021b).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (1)$$

Although in some cases this equation is just used as a “model” for all possible air-based reactions, it is often forgotten that the term “lime” (outside the domain of pure chemistry) is used to refer to a group of products and not just to a single material. This group gathers materials with substantially different characteristics, and of these only one is exclusively made of $Ca(OH)_2$: the high-calcium lime.

Admittedly, high-calcium lime has always been a rather common type of lime. However, other types of lime as well were widely used in the past centuries for the construction of buildings and structures. These included, for instance, magnesium lime which contains various percentages of magnesium oxide (MgO) or hydroxide ($Mg(OH)_2$) besides the calcium compounds (e.g., up to 50% in dolomitic lime). This type of lime was rather common in various European countries such as Italy (Vecchiattini 2019), and the United Kingdom (Pesce 2019). Upon carbonation, magnesium lime leads to the formation of a number of different anhydrous and hydrated carbonates such as magnesite and nesquehonite, respectively (Ponce-Antón et al. 2018). These minerals have chemical characteristics substantially different from those of the most common anhydrous calcium carbonates (i.e., calcite and aragonite). One of the main differences is their higher water solubility in normal conditions, which is comparable to that of $Ca(OH)_2$ (a mineral that, within the chemistry of construction materials, is considered quite soluble and, in fact, the construction industry of entire countries has been based on the transformation of $Ca(OH)_2$ into $CaCO_3$). This entails the fact that, after hardening, a mortar made with magnesium lime can easily exchange carbon atoms with the surrounding environment, if subject to water flow (as it is often the case in historic buildings). Consequently, if mortar samples from historic buildings that were built using any type of magnesium lime are dated with the $^{14}C$ dating methods, it is likely that the results are affected by the presence of much younger $^{14}C$ (compared to the construction time of the buildings), acquired by these highly soluble carbon-bearing minerals. Hence, a full characterization of the binder fraction every time the $^{14}C$ dating of a historic mortar is presented should be published and discussed in order to better assess the causes of the contamination. Without it, any interpretation of the $^{14}C$ dating result can only be very limited.

## The sampling depth as one of the main factors affecting of the results of the $^{14}C$ dating of mortars

Besides the problem of the chemical composition of lime, the carbonation mechanism of lime underpinning the setting and hardening of the mortars can frequently result in a “delayed” acquisition of carbon from the atmosphere (Lindroos et al. 2020; Daugbjerg et al. 2021a). Carbonation, in fact, is a self-limiting interface reaction (Ruiz-Agudo et al. 2013; Pesce et al. 2023) that starts as soon as the $Ca(OH)_2$ gets in contact with the $CO_2$, in the presence of water, and stops every time one of the two reagents is removed from the system. In fact, various researchers have reported the presence of $Ca(OH)_2$ in century-old core mortars (Rayment and Pettifer, 1987), and this confirms that the carbonation reaction can stop inside the walls even for a prolonged period of time. However, because of its high reactivity the $Ca(OH)_2$ can start reacting again as soon as the right conditions are reached (e.g., when a crack forms that allow new water and $CO_2$ to penetrate inside the mortar). This stop-and-go process, of course, can easily lead to inaccurate results of the $^{14}C$ dating of mortars.

Furthermore, such mechanism allows inferring that, besides unreacted material in the core of a wall, there can be sections of the mortars where the carbonation has been delayed, compared to the construction time of the building or structure. In fact, the best samples for the $^{14}C$ dating of mortars are those close to the surface of the masonry where the sample is collected, rather than any sample from the inside of it. This is because it is more likely that in such samples the $CO_2$ was fixed at the very early stage of the construction, rather than some time after it.

Hence, an important aspect that can limit the effects of the “delayed” carbonation on the accuracy of the $^{14}C$ results, is the depth of the dated sample from the nearest surface exposed to the air. Consequence of this is that it is essential for an effective discussion of the results, to provide the information related to the sampling depth every time the results of the $^{14}$C dating of a mortar is presented.

## CONCLUSIONS

Despite the important advances in the $^{14}$C dating of mortars obtained in the past decades thanks to the work of a number of research groups, further improvements to this particular application of the $^{14}$C method are required if there is a genuine interest in developing a reliable tool for dating buildings and structures.

To further improve the application of the $^{14}$C dating method to mortar samples, it is necessary to acquire a more holistic approach to it, and to focus more on the possible reasons for the sample contamination using experimental evidence. This approach has the potential to enrich and elucidate the information carried by the $^{14}$C result and, over the time, can allow overcoming the current limitation of the technique. As an immediate action, it would be extremely useful to include in any paper presenting the results of the $^{14}$C dating of lime mortars, at least, (1) the sampling depth (i.e., the depth at which the dated samples were located inside the wall), and (2) the chemical and mineralogical composition of the binding fraction of the dated mortars.

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