Summary

Radiocarbon dating of anthropogenic lime carbonates was first developed in the 1960s, based on the assumption that ^{14}C decay would behave similarly to that in living organisms after death. The initial results were promising, and researchers highlighted the importance of microscopic analysis to check for the presence of Foraminifera, which could skew the dating results due to their ancient carbonates. Foraminifera and other carbonates may be present in lime mortars due to the mortar's formation process or subsequent alteration. For this reason, while some radiocarbon dating tests have been successful, others have failed, making the process complex and unreliable. To confirm the ^{14}C dates for mortar samples, reference materials, such as charcoal dated with ^{14}C or roof structures suitable for dendrochronology, along with contextual information, are essential.

The main objective of PALc was to verify the reliability of the radiocarbon dating of anthropogenic lime carbonates by developing a pre-screening method. To achieve this goal, a careful characterisation of the samples was linked to the way radiocarbon results matched the presumed historical dates or the ^{14}C date obtained on organic materials present inside the mortar. The analytical methods used were complementary for obtaining a wide range of parameters characteristic of each sample. A characterisation protocol was set up to determine if a sample was suitable for dating or not using the stepwise acid hydrolysis. This pre-screening protocol was implemented to be the most concise and rapid by selecting the more appropriate tools and parameters determinant for a successful dating of the samples. Eventually, this protocol will result in cost and time saving. The methodological approach of PALc consists of a meticulous process starting from the sampling to the precise description of the samples using multiple analytical techniques to the radiocarbon dating. It starts by a macroscopic description of the mortar samples, followed by Fourier transformed infrared (FTIR) spectroscopy measurements, thin section petrography and cathodoluminescence observations and thermogravimetric analysis coupled with differential scanning calorimetry (TGA/DSC). When necessary, other techniques such as Raman spectroscopy, scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) and X-ray diffraction (XRD) on powders were also implemented. These techniques were applied on 48 mortar samples from 21 sites in Belgium and abroad. A wide variety of samples was processed to obtain a range of parameters suitable for pre-screening most types of samples in the final protocol. They were composed of diverse types of lime binders (air-hardening and hydraulic), aggregates and additives/admixtures and presented a diversity of physical properties with different states of conservation. Their provenances and ages were also diverse.

While conducting the literature survey, we observed that the terminology used varied based on the dominant field of study for a given article or book. This variation led to ambiguity or confusion in the definition of certain words or concepts, particularly when applied to radiocarbon dating of ancient mortars. To address this, we aimed to provide a comprehensive overview of the components of lime mortar and their potential impact on radiocarbon dating when using stepwise acid hydrolysis. We created a diagram to summarize the various components of lime mortars and the possible phenomena that could influence the radiocarbon content during the acid reaction used to extract CO_2. The six main categories we defined are: i) aggregate; ii) binder; iii) lime inclusions; iv) organic matter; v) weathering carbonates; and vi) delayed hardening. The inorganic aggregates were further categorized into two types: inert

aggregates (mainly siliceous aggregates and calcareous aggregates), which do not participate in the chemical reaction during the mortar production process, and reactive aggregates (aggregates containing substances capable of reacting chemically with the slaked lime binder and water to form calcium silicate hydrates). The binder category was divided into (natural) hydraulic binder and non-hydraulic / air hardening binder. The lime lumps sensu lato comprise the lime lump sensu stricto (completely burned carbonated binder inclusions), underburned carbonated binder inclusions and over burned binder inclusions. The organic additions are classified into additives (mainly liquids) and admixtures / organic aggregates. Weathering processes include phenomena such as variation of conditions, secondary carbonates, dissolution/precipitation, rainfall, groundwater, microorganisms, *etc*. Recrystallisation is considered to be metastable polymorphs of carbonates which were already present within the structure of the mortar that spontaneously recrystallise in a more stable form or to a larger uniform size. In this sense, recrystallisation should not have any impact on the ^{14}C content since no new source of carbon is incorporated within the matrix. Lastly, delayed hardening depends on the depth where the mortar was sampled, the presence of uncarbonated lime (portlandite) or the hydraulicity of the mortar.

Three calculation methods were used to obtain the radiocarbon determination using the stepwise acid hydrolysis CO_2 extraction: an extrapolation method, a statistical extrapolation method and the combination of the first CO_2 fractions (1 to 4 %). We considered a date as correct when at least two of the methods provided a similar radiocarbon determination. The most effective pre-screening techniques were petrography, FTIR, cathodoluminescence, and thermal analysis (TGA/DSC). Key indicators include:

- **Petrography**: Aggregate mineralogy, lump state, and alteration (dissolution or secondary carbonates);
- **FTIR**: Presence of aragonite and other minerals / salts (clays, nitrates, gypsum) and the relative ratio between silicates and carbonates;
- **Cathodoluminescence**: Limestone presence, especially in the powdered fraction used to extract the CO_2 for radiocarbon dating;
- **Thermal Analysis**: Percentage of carbonates and apparent hydraulicity index.

The sample should be excluded from radiocarbon dating using stepwise acid hydrolysis if, at any point during the characterization process, there is a suspicion that it will not yield a reliable date.

About 33% of samples provided reliable radiocarbon dates, often those with pure siliceous aggregates, higher carbon content, containing aragonite, non-hydraulic properties, not containing limestone fragments and minimal alteration. In total, 52% of samples were unsuitable for reliable radiocarbon dating, often due to poor preservation (leached), unfavourable composition (calcareous aggregates, hydraulic mortars) or having undergone delayed hardening. Some samples (8%) produced reliable dates despite unfavourable conditions, possibly due to compensating phenomena. Other samples (6%) had a conservation state and composition that suggested they should be reliable for radiocarbon dating, but their dates fell outside the expected historical range and could challenge historical hypotheses.

Keywords:

Anthropogenic lime mortars ; radiocarbon dating ; stepwise acid hydrolysis ; thin-section petrography ; cathodoluminescence ; FTIR ; TGA/DSC.