^{14}C DATING OF LIME MORTAR – PREPARATION OF THE SAMPLE, A CHALLENGE FOR THE GEOLOGIST AND THE MINERAL CHEMIST

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Abstract

Lime mortar from old constructions can be successfully dated using the ^{14}C method if special care is taken during sampling and sample preparation. The main problems with dating is identification and removal of fossil limestone in the filler. Especially in limestone areas contamination from filler limestone can be severe. Proper identification of the contaminants enables us to develop optimal laboratory protocols for sample handling. Contaminants including limestone and marble filler material, incompletely burnt limestone residues, and recrystallisations in the mortar can be identified in thin sections of intact mortar samples and in the fine fractions of crushed mortars using polarising microscopy and cathodoluminescense. Careful crushing and sieving of the mortar samples, however, effectively removes limestone grains and particles. The proportion of limestone contaminant in the samples can be assessed by traditional point counting or computer image analysis of luminescence micrographs. A sufficient number of samples from each construction phase are needed for statistical significance of the dating.

Introduction

There is a great need for scientific dating of historical buildings, particularly where historical records are lacking, questionable or controversial, or dendrochronological dating is not applicable. Old buildings commonly have a long building history with different construction phases spread over several centuries. Thus any dating program requires a large number of samples representing the different phases. Organic material from the building construction can be dated with the ^{14}C method, but the exact relation of the material to the building history may remain obscure. Thermoluminescence and dendrochronology face similar problems. Where the masonry consists of stone and lime mortar, ^{14}C can be used for dating the hardened, carbonated mortar, which naturally has the same age as the construction itself. This does, however, entail some serious risks, mostly related to contamination with dead carbon from limestone, if used as aggregate in the mortar. Folk and Valastro Jr (1979) described the method and some of it's problems. They emphasised the importance of careful preparation and control of the mortar samples. Since then some other attempts to date mortar have been made (e.g. Sonninen et al. 1989, Tubbs and Kinder 1990, Strydonck et al. 1992) and the problems with the method are now well known, but far from resolved. In our project "The Medieval Churches of the Åland Islands" (Ringbom 1995) we have concentrated our efforts on the identification and separation of the contaminants in the mortar. Some earlier encouraging results from this project have been reported by Heinemeier and Jungner (1994 and references therein). The actual dating of the samples, including the

chemical pre-treatment is described in Heinemeier et al. (1997). They also describe the relation of the contaminants identified by us to the age measurements. It is of great importance that the ^{14}C dated sample consists of the carbonated lime used as binder in the mortar and that the sample is more or less free from limestone fragments, fossil or marble, uncarbonated or recrystallized lime

Why dating lime mortar?

Lime mortar, used as building material already since the Roman time, is a mixture of lime and aggregate (sand). Building lime used as binder, is produced by heating limestone crushed to small particles in special kilns to above 1000° C. During calcining the limestone is transformed to CaO (quicklime) with liberation of CO_2. The next step in making building lime is to slake the burnt limestone with water. Quicklime will transfer to calcium hydroxide $Ca(OH)_2$. With excess water the quicklime will form lime putty, a wet lime mixture. Industrial controlled slaking with steam or a minimum quantity of water produces a dry powder, generally known as hydrated lime or builder's lime (Boynton 1980). Slaked lime is mixed with sand and water. Calcium hydroxide in the mortar between the masonry stones or rendering mortar on the wall reacts with carbon dioxide from the atmosphere to form calcium carbonate (Perander and Råman 1985) (Fig. 1. The lime cycle). This carbonation process hardens the mortar and absorbes atmospheric CO_2 just at time of the construction. The ^{14}C content of a mortar sample can thus give a measure of the time elapsed since the time of jointing or rendering. The simple inorganic chemistry, the abundance of dateable material and the straightforward relation of the hardening mortar to the building phase to be dated would make lime mortar the ideal material for 14C dating, but there are, however, also many problems associated with the method.

Problems in ^{14}C dating lime mortar

A. Dating may give too young age

1. The carbonation of lime can be delayed if CO_2 gas is prevented from reaching the mortar, in a thick wall construction, behind a surface with low permeability e.g. an organic paint or any solid object or in a water saturated surrounding.

Hydraulic compounds as impurities or as part of the binder in old lime mortars hydrate to form calcium silicate compounds in a series of reactions where also calcium hydroxide is formed. Under normal conditions these reactions will occur totally without risk of interference to the dating process. Mortars with cement or other hydraulic components will show an alkaline reaction, due to an incomplete hydration process of the cement. Mortar samples containing hydroxide compounds are not suitable for dating, as the exposed hydroxide will immediately react with CO_2 exposed to the air and contaminate the sample. A mortar with calcium hydroxide is alkaline and can be identified at the sampling site using a pH-indicator e.g. phenolphthalein.

2. Parts of the carbonated lime in the mortar can dissolve in water, that contains carbonic acid. Recrystallization or recarbonation of the dissolved binder occurs where the mortar is periodically wet and dry during long periods and well-shaped crystals are formed in cracks or pores in the mortar. If these processes take place in a closed system, no contamination with CO_2 from the air occur. Recrystallisation is more the exception than the rule, and the amount of recrystallised binder in a mortar sample is

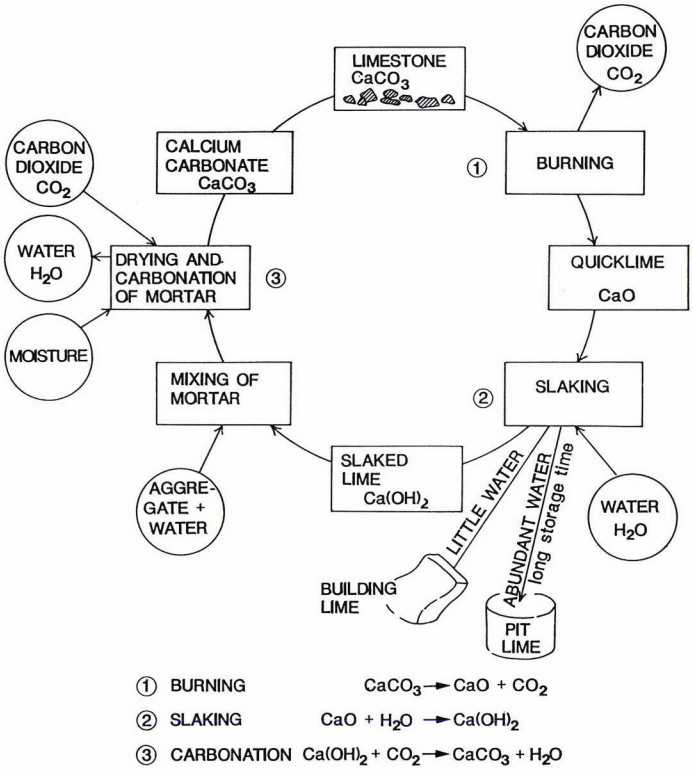

Figure 1. The lime cycle.

small compared to normally carbonated lime. The possible effect on the dating result is small and can be neglected in most cases..

B. Dating is affected by dead carbon in the mortar sample

1. Some quicklimes are incompletely burnt. The unburnt limestone grains have a calcitic or fossil carbonate residue, usually in the middle of the grain. Their optical identification is usually simple and the grains are usually large enough to be removed by sieving.

2. Sand used in traditional old lime mortars can include natural sands, gravels and sometimes crushed materials such as shells, various types of rocks and even brick. Aggregate containing limestone grains or, even worse, crushed limestone as filler (< 2 mm), may lead to severe contamination. Some fine-grained limestones can be very difficult to distinguish from lime mortar.

3. The lime was contaminated with charcoal during the burning process or the quicklime was mixed with wood ash or charcoal when the kiln was emptied.

Among these problems the contamination from the filler, particularly fossil limestone is the most difficult to tackle and is usually severe in limestone areas such as the Åland islands.

Sampling and sample preparation – methods and their development

Sampling

For proper dating of a historical building or construction many samples are needed. This is because the buildings were usually erased successively in several phases and later restorations are common. Because of the statistical nature and poor precision of the ^{14}C method it is advisable to take several samples from each construction phase (Heinemeier et al. 1997). Whenever possible the sample should be taken from the interior of buildings, because the mortar is better preserved in places where it has not beed exposed to rain, surface water and ice. The samples should be tested at the sampling site with a pH indicator for alkaline reactions from poorly carbonated mortar. At the laboratory a piece of each collected mortar sample is taken for preparation of a thin section for microscopy. The lime mortar is often soft or brittle and needs impregnation with resin in vacuum before further preparation. The thin section can be a uniform cross-section through one piece of the mortar, or through smaller fragments glued together on a glass plate. The section should not be thicker than 25 μm.

The following properties can be studied with the polarising microscope:

1. Type of binder and its degree of carbonation
2. Recrystallisations of the binder
3. Unburnt or partly burnt limestone and unslaked quicklime
4. Limestone or marble or any other carbonate matter in the aggregate.
5. Masonry- and renderings of different ages (possible repair mortars together with the original)

Sieved fractions of the mortar

An important part in the preparation of mortar samples is sieving. Our samples were crushed in an agate or porcelain mortar. It is of great importance to perform the crushing carefully and smoothly, so that only the porous binder matrix is broken, and not the individual clasts in the filler, as they may contain carbonate with dead carbon.

Different sieving techniques have been investigated. Dry sieving to a fraction 74–62 μm was used in the beginning, but proved inadequate as adhesion of very fine material to larger grains, complicated the mineralogical control of the fraction. The next step was a more careful, wet sieving of still finer fractions. Washing the sample during sieving with ionised water facilitated the optical analysis and minimised the risk of unknown infinite small material.

To test the amount of available calcium carbonate for AMS ^{14}C dating in different sieved mortar fraction, six fractions from 500 to < 38 μm were treated with dilute hydrochloric acid and the evaporating CO_2 was measured as the decrease in weight. Fig. 2 shows the greatest content of pure lime binder (calcium carbonate) in the 62–38 μm fraction, whereas the other fractions have more sand (aggregate),which is not soluble in acid. For further studies we have chosen the washed 38–62 μm fraction. A small sample of the fraction immersed in oil on a glass plate or as a thin sections can be studied directly with the polarizing microscope. The fraction is inspected for residual limestone, marble and other carbonate compounds. The lime binder has usually a dull brownish colour while marbles have well-defined crystals showing the characteristic birefringence and interference colours of calcite. The fossil limestone can be similar to either of these, depending on it´s crystallinity, but have more compact grains than the lime binder.

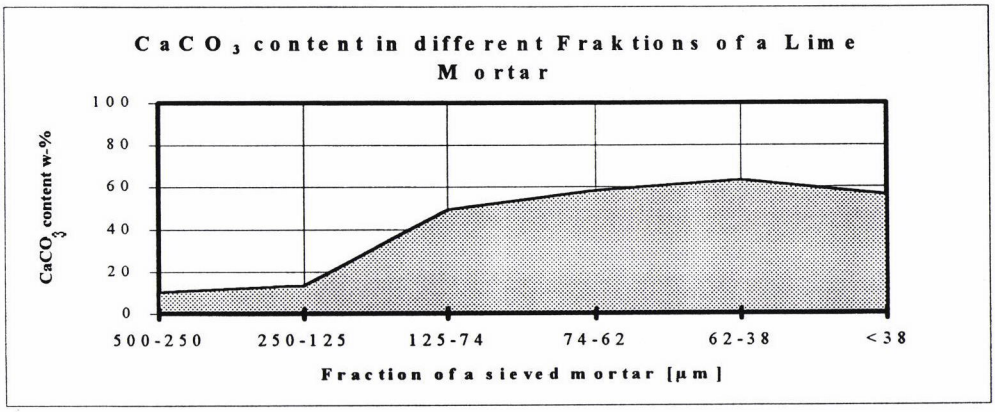

Fig. 2. Calcium carbonate content in different fractions of lime mortar.

Microscopic inspection with cathodoluminescense

A useful method for studying carbonate minerals is cathodoluminescense (e.g. Marshall 1988). The cathodoluminescense devise or luminoscope can be used in combination with the polarising microscope. At ca 10 kV accelerating voltage most natural calcites show a bright, often orange luminescence colour while binder calcite has a dull brownish or tile red luminescence. Differences in luminescence colours arise from small compositional differences and the intensity of the luminescence is related to the degree of crystallinity and the collected dose of radioactive background radiation during the history of the particular minerals. Heating the minerals to temperatures used in calcination will reset the luminescence. A grain of fossiliferous limestone will therefore have a different luminescence than a lime binder in a historical mortar even if the same kind of limestone was used as raw material for the building lime.

Results and discussion

Several preparation methods for old lime mortar samples have been controlled and developed mainly based on experience from dating churches on the Åland islands. At the present stage of development we recommend the following sampling and laboratory procedure.

- Sample mortars, that have been protected from groundwater and precipitation.
- Take several samples from each construction phase to be dated.
- Test fresh surfaces of the sample immediately with pH indicator. Reject samples showing an alkaline reaction.
- Examine the samples visually observing colour, hardness, charcoal residues and aggregate composition
- Analyse thin sections of the samples using polarising microscopy and cathodoluminescence.
- Crush the samples smoothly and carefully in an agate or porcelain mortar. Break only the binder, not the filler clasts.
- Sieve the crushed mortar. Reject fractions > 62 µm and sieve with water the fraction < 62 µm with a 38 µm sieve. Reject the finest fraction and dry the preserve 38–62 µm fraction for dating.

- Examine the sample fraction with polarising microscope and cathodoluminescence and assess the percentage of contaminants. Samples with several per cent limestone particles should not be accepted for dating.

We hope through further development to minimise the often mentioned risks with lime mortar dating and we are convinced that with careful sample preparation, the results of ^{14}C dating will be reliable.

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