

## AN IMPROVEMENT IN PREPARATION OF MORTAR FOR RADIOCARBON DATING

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**ABSTRACT.** An error source in radiocarbon dating of ancient mortar is dead carbon of limestone mixed in the matrix. To eliminate the influence of limestone the difference in feasibility to react with acid between mortar and limestone is used. Since the rate of reaction depends on grain size use of a well-defined grain size can give a better separation between mortar and limestone. We present results for the grain size dependence of reaction rates for several mortar and limestone samples and discuss the application for dating.

### INTRODUCTION

Mortar is used for radiocarbon dating of ancient building constructions. The basic principle, on which dating of mortar is based, can shortly be described as follows: limestone (mainly  $\text{CaCO}_3$ ) is combusted to oxide ( $\text{CaO}$ ), oxide is slaked with water to hydroxide ( $\text{Ca(OH)}_2$ ), hydroxide is mixed with sand and water, and on exposure to air the lime mortar hardens by taking up carbon dioxide and forming carbonate ( $\text{CaCO}_3$ ). The actual  $^{14}\text{C}$  concentration of  $\text{CO}_2$  in air is fixed to mortar carbonate in the hardening process. If mortar is made from completely combusted oxide and the time for hardening is short, dating of the mortar should give the age of construction. But results have been varying and several error sources have been traced. Combustion of fossil limestone has not been completed, limestone lumps or other fossil carbonate materials may have been included to mortar mixture, the hardening of mortar may have been delayed or even hindered, the hardening of plaster inside a house may have been speeded by supplying carbon dioxide from an open coke fire, etc.

Further, the stability of the hardened carbonate may not be guaranteed in all environmental conditions (Van Strydonck and Waldren 1990). Some of the error sources can be avoided by careful selection of samples for dating, and by laboratory treatments. The main problem is the influence of fossil limestone in samples leading to apparently old ages. Mechanical and chemical separation methods have been developed to eliminate this error source (Folk and Valastro 1976, 1979; Van Strydonck et al. 1983, 1986). The treatment usually applied to separate limestone grains from the mortar matrix is based on the different hardness of limestone compared to the more fragile mortar. After mechanical separation the feasibility to react with acid has been used to further separate between  $\text{CO}_2$  from mortar and limestone grains. Since mortar grains react more quickly in acid than limestone grains, a gas fraction collected in the beginning of the reaction is enriched in  $\text{CO}_2$  from mortar. Van Strydonck et al. (1986) developed the method further by separating several gas fractions for activity measurements. Since the rate of reaction is dependent on surface area of reacting grains we measured rate of reaction for different grain size of mortar and limestone samples.

### METHODS

The material in the study was a set of mortar samples from medieval buildings with ages ranging from 600 to 1000 years, and calcite samples from Finnish lime stones. After the pretreatment for mortars proposed by Folk and Valastro (1976, 1979) (i.e. the mortar lumps flushed with water, gently broken into smaller pieces, which were agitated in distilled water until suspension was formed) the suspension was sieved with water to give grain sizes in the ranges 62–74, 43–62 and <43 microns. The powder was dried at about 100 °C. The  $\text{CO}_2$  was evolved with phosphoric acid (85%).

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Sample carbonate (20 mg) and acid (2 mL) were introduced to a vessel with a side arm. The evacuated vessel was turned to start the reaction. A recorder connected to a pressure gauge monitored the  $\text{CO}_2$  pressure during the reaction. The pressure for the first 60 seconds and at the end of the reaction was recorded. Reaction times were 10–30 minutes for mortar and 50–90 minutes for limestone carbonates, respectively.

## RESULTS AND DISCUSSION

The yield of  $\text{CO}_2$  against reaction time was measured for mortar and calcite samples of the grain size ranges of 74–62, 62–43 and <43 microns, respectively. The results (given as percentages of the total amount of  $\text{CO}_2$ ) for the grain size range 62–43 microns are given in Figure 1. The reproducibility was tested by measuring a few sub samples of different mortars. The relative deviation between repeated runs was less than 10%. In general, mortar reacts quicker than limestone. The difference in reaction rate between mortars was higher than between limestone calcites, probably due to variation in consistency of mortars of different origin.

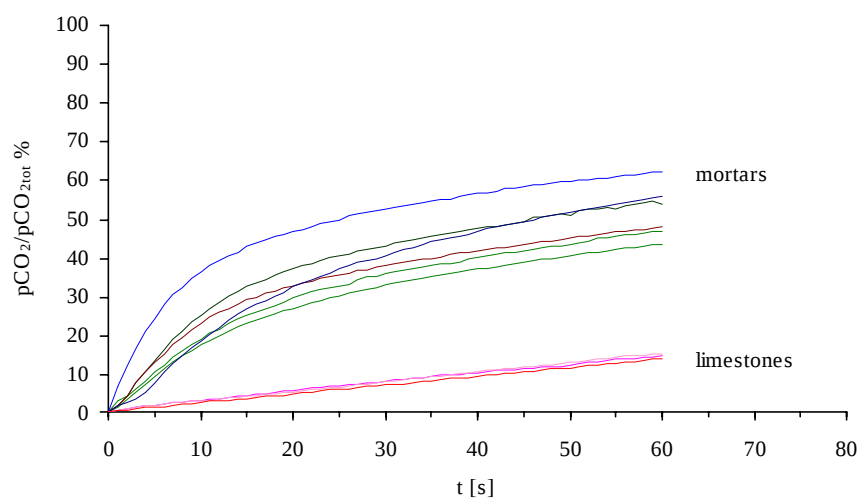


Figure 1 The  $\text{CO}_2$  yield as a function of time for six mortar and four fossil limestone carbonates. The  $\text{CO}_2$  pressure recorded is given relative to the maximum reached at the end of reaction. The grain size range is 43–62 microns.

The dependence of the reaction rate on the grain size is seen for a mortar and a limestone sample in Figure 2. The reaction rate increases with decreasing grain size. For the fine grain fraction (<43 microns) the reaction is very fast even for the limestone.

For dating two or more  $\text{CO}_2$  fractions are normally collected and their  $^{14}\text{C}$  activity compared to observe the influence of limestone. The separation between mortar and limestone at this step is more efficient if well-defined grain size is used, and the reaction curve for the sample is utilized to decide the reaction time for the first  $\text{CO}_2$  fraction. For the samples in this study (Figure 1) the first gas fraction, if collected during the first 10–30 seconds, would contain about half of the  $\text{CO}_2$  from mortar but less than 10% of  $\text{CO}_2$  from eventual limestone. The second fraction consequently would contain most of the limestone  $\text{CO}_2$  and about half of mortar  $\text{CO}_2$ . The limestone  $\text{CO}_2$  is thus enriched in the second gas fraction. When  $^{14}\text{C}$  activity is measured in the two fractions a lower value in the second fraction indicates limestone in the sample. For example, if the original sample contains 1% of lime-

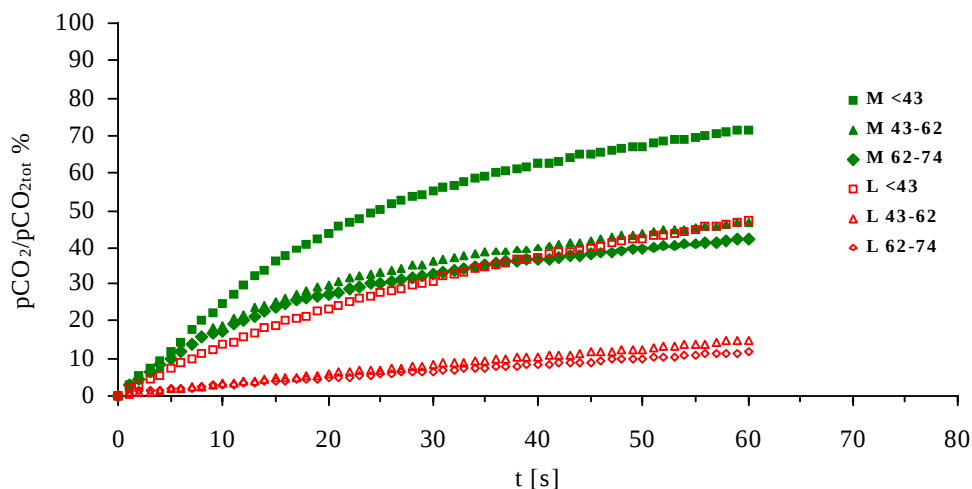


Figure 2 The dependence of the rate of reaction on grain size for a mortar (M) and a limestone (L). The grain size ranges were 62–74, 43–62 and <43 microns.

stone, the second fraction would contain around 2% and the first less than 0.1% of  $\text{CO}_2$  from limestone. If the  $^{14}\text{C}$  activity can be measured with a precision of 5‰ the activity difference of 2‰ between the two gas fractions can be observed. Based on the activities of the two fractions the amount of dead carbon in the sample can thus be estimated down to a level of about 1%. The influence of the dead carbon on the activity of the first fraction can then be estimated and an age correction made, when the amount of gases in the two fractions are known.

## CONCLUSION

In  $^{14}\text{C}$  dating of mortar chemical separation of limestone can be more efficient if well-defined grain sizes are used and very fine grains are excluded. When the division of the  $\text{CO}_2$  gas in two fractions is based on reaction curve for sample and limestone and the radiocarbon activity for both fractions is measured, a corrected age for the mortar sample can be calculated.

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