FORAMINIFEROUS LIMESTONE IN ^{14}C DATING OF MORTAR

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ABSTRACT. Mortar as a mixture of binder and aggregate can be reliably dated with radiocarbon if the applied preparation method allows one to eliminate unburnt carbonate fragments, bearing ^{14}C-depleted carbon and causing overestimation of ^{14}C age. To avoid these problems, separation of specific grain-size fractions of mortar and ^{14}C analysis of the CO_2 portions collected in different time intervals of the acid-leaching reaction is usually helpful. In the present paper, we demonstrate that the rate of the leaching reaction of mortars with dense carbonate aggregate differs from that of mortars with crumbled limestone and scattered shells (e.g. of foraminifera). Verification of the obtained ^{14}C dates against historical sources shows that for mortars rich in foraminiferous limestone, a reaction rate-based chemical elimination of "dead carbon" may appear impossible.

INTRODUCTION

Lime mortar is obtained by burning limestone ($CaCO_3$) pieces and mixing such binder with sand or—depending on particular needs—with diverse admixtures. In the burning process, calcium carbonate is transferred to CaO ("burnt lime"), after which it is "slaked" with water (as a result of which $Ca(OH)_2$ is obtained). Mixed with sand and water, this substance can be easily molded and shaped. After some time, the mortar hardens due to binding CO_2 from the air and turning into $CaCO_3$ again. Concentration of ^{14}C in carbon absorbed by the binder is the same as in the atmosphere (Folk and Valastro 1979; Heinemeier et al. 1997; Sonninen and Jungner 2001; Nawrocka et al. 2007). Then ^{14}C age of the binder obtained from entirely burnt pieces of limestone would thus reflect the age of the structure. If the mortar contains carbonate elements that have not been entirely burnt, or pieces of carbonate rocks were added to the mortar as an aggregate, such elements should be removed before the dating process. Usually, carbonate aggregate contains old, ^{14}C-depleted carbon. If the sample is not selected properly, the measured ^{14}C age may thus be distinctly older than the real age.

Based on the observation that a soft binder reacts with acid faster than a more consistent carbonate of the aggregate, Baxter and Walton (1970) proposed that CO_2 collected during the first seconds of acid leaching of mortar was the best for ^{14}C dating. That method was improved by Sonninen and Jungner (2001) who performed chemical separation on mortar fractions of well-defined grain size. This improved method was successfully applied in, for example, ^{14}C dating of mortar samples from Hippos at the Sea of Galilee (Michalska Nawrocka et al. 2007). Recently, further improvement was introduced by Lindroos et al. (2007), who deconvolved the functional dependence of the CO_2 amount on time, and distinguished individual mortar components of different rates of the acid-leaching reaction, and of different ^{14}C ages.

In the present work, a similar procedure was applied in the dating of 2 mortars of well-determined calendar age. Both these samples come from Israel: MS446 from the wall of the Western Palace erected by Herod (Masada) and AA25 from the walls of the Hasmonean Palace (Jericho). According to the archaeologists, the structure in Masada (MS446) dates to 25 BC, whereas the wall in Jericho (AA25) dates to 120–75 BC.

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SPECIFICATION OF THE MATERIAL

Before the dating process, the selected mortar samples were subjected to petrographic analyses in order to specify the type of binder and aggregate. The examinations indicated the carbonate character of the binder and of a major part of the aggregate (Figure 1).
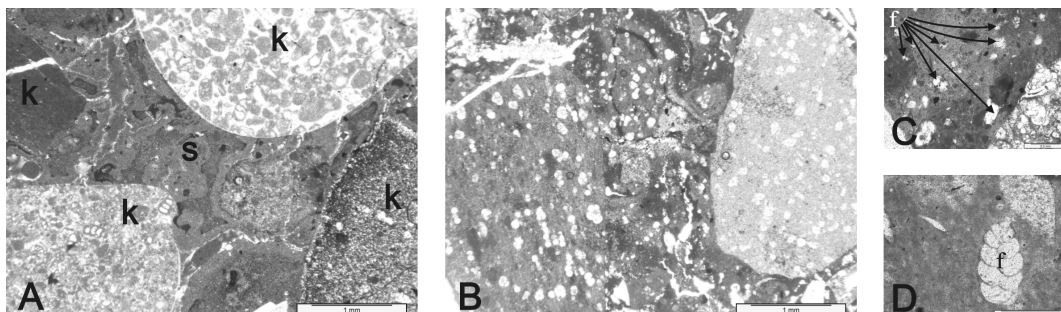

Figure 1 Microscope image of components of examined mortars (polarizing light microscopy, XN): A - MS446 sample; B - AA25 sample; C, D - enlarged sections of the AA25 image: C - small, crumbled foraminifera pieces (f) in the sample; D - a whole foraminifera shell (f); k - aggregate, s - binder

The dominant component of the aggregate in samples MS446 and AA25 are pieces of limestone, but there is also flint, dolomite, and pieces of shells. Differences were observed in the degree of preservation of the mortar components. Aggregate from the mortar of Masada has a larger grain size and contains dense, solid pieces of limestone (Figure 1A). On the other hand, aggregate from the mortar of Jericho shows the distinct presence of less dense and brittle foraminiferous limestone (Figure 1B, C, D). Scattered small pieces of foraminifera shells are also visible throughout the entire binder.

METHODS

The mortar samples were softly crumbled and sieved through 45-µm, 63-µm, 80-µm, and 0.1-mm sieves, which enabled partial removal of the aggregate. Grains coarser than 0.1 mm were inspected with a microscope; pieces looking like fragments of aggregate were picked out, crushed, and sieved again, and the 63–80 µm fraction of material so obtained was also forwarded for analysis (denoted "lm 63–80"). Next, each fraction was leached with orthophosphoric acid. During the leaching reaction, several portions of CO_2 were collected, after 5–10, 25, 45, 85, and 145 seconds, and later (after 20–60 min, depending on the sample). The temporal projections of the acid-leaching reactions are given in Figure 2.

Following the method used by Lindroos et al. (2007), we tried to deconvolve the functions presented in Figure 2 and distinguish individual components of different rates of the leaching reaction. The assumption was that acid leaching of individual component resulted in the exponential rise of CO_2 pressure, and so the measured pressure could be presented by the following formula:

$$p = p_1 + p_2 + p_3 = p_{01}[1-\exp(-a_1t)] + p_{02}[1-\exp(-a_2t)] + p_{03}[1-\exp(-a_3t)] + ... \quad (1)$$

where $p_0 = p_{01} + p_{02} + p_{03} +...$ was the total pressure.

An example of such deconvolution is illustrated in Figure 3, and the parameters of individual components of all the leached samples are given in Table 1.
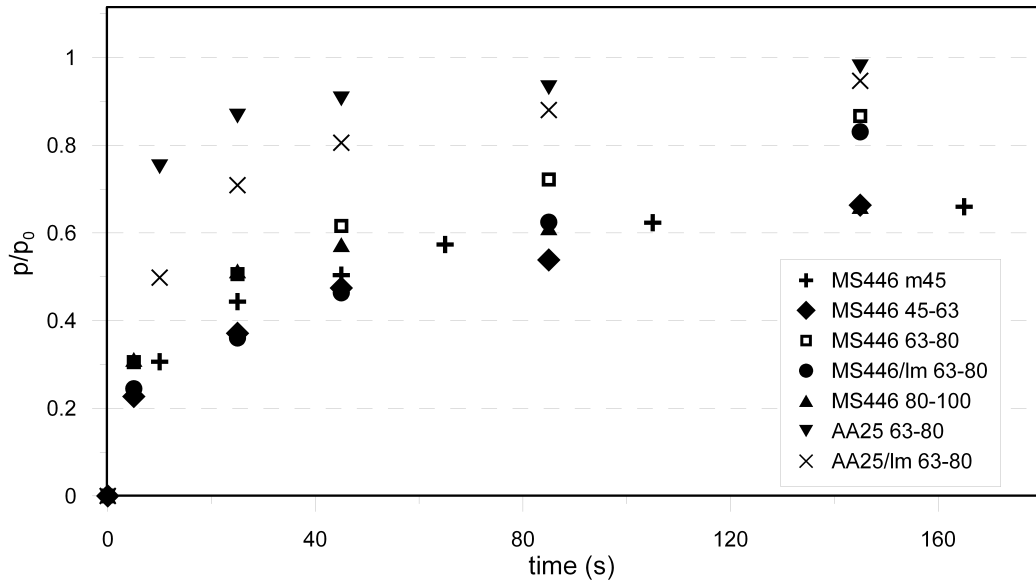
Figure 2 Leaching of individual fractions of carbonate mortars from Masada (MS446) and Jericho (AA25). MS446 63–80 µm and AA25 63–80 µm are samples of carbonate mortars in a specific fraction; MS446/lm 63–80 and AA25/lm 63–80 are carbonate aggregate from those mortars. The ordinate p/p_0 represents the proportion of pressure of CO_2 collected after time t to the pressure of the whole collected CO_2.
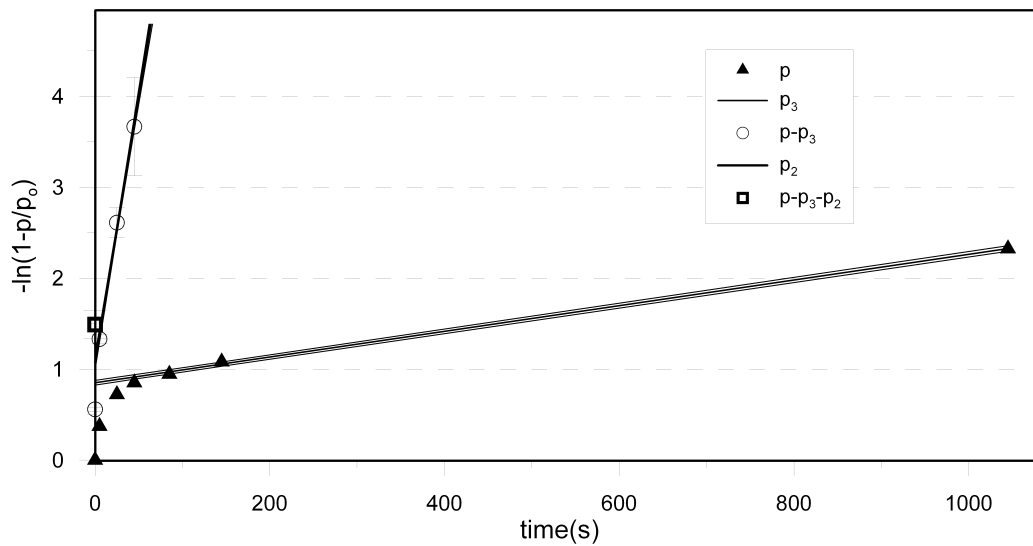

Figure 3 Leaching reaction of the sample MS446 80–100. CO_2 pressure is represented by $-\ln(1–p/p_0)$ (after Lindroos et al. 2007), for the actual pressure of the collected gas (p), and for calculated pressures of individual components (p_3, p_2, and p_1) as defined in Equation 1.

Table 1 Results of deconvolution of time dependence of the acid-leaching reactions of the mortar samples from Masada and Jericho. Parameters a_1 to a_3 denote rates of leaching of individual components defined by Equation 1; p_{01} to p_{03} represent proportions of individual components in the sample. For simplicity, these proportions have been normalized to a sum of 1000.

Sample name	Type of material fraction	a_1 (min^{-1}) p_{01} (mbar)	a_2 (min^{-1}) p_{02} (mbar)	a_3 (min^{-1}) p_{03} (mbar)
MS446 m45	binder <45 µm	? ?	? ?	0.132 ± 0.024 488 ± 22
MS446 45–63	binder 45–63 µm	? 264 ± 75	2.13 ± 0.75 300 ± 60	0.066 ± 0.012 436 ± 62
MS446 63–80	binder 63–80 µm	18.6 ± 3.8 352 ± 36	0.64 ± 0.04 648 ± 36	no component
MS446/lm 63–80	aggregate 63–80 µm	? 157 ± 44	0.64 ± 0.04 843 ± 44	no component
MS446 80–100	binder 80–100 µm	? 264 ± 74	3.39 ± 0.87 308 ± 61	0.084 ± 0.006 428 ± 12
AA25 63–80	binder 63–80 µm	14.5 ± 1.8 798 ± 30	0.89 ± 0.11 202 ± 30	no component
AA25/lm 63–80	aggregate 63–80 µm	7.9 ± 0.4 611 ± 22	0.83 ± 0.04 389 ± 22	no component

For the fraction <45 µm of MS446, separation of individual components of the acid-leaching curve was not possible, most probably because that fraction has an enormous relative spread in grain size compared to the well-defined grain-size windows of the other fractions. In some fractions, like that of 80–100 µm of MS446, the fastest leaching component (p_1) was detected by 1 measurement only (Figure 3), so determination of its rate of leaching (a_1) was not possible.

Among the fractions of the sample MS446, the most suitable for ^{14}C dating appeared to be that of 63–80 µm, which revealed only 2 components of very different rates of acid leaching. Consequently, proportions of individual components (p_{01}, p_{02}…) in this fraction could be determined with better precision than in the other fractions of MS446 (Table 1). Relying on that observation, test leaching reactions of the sample AA25 were performed only on the fraction 63–80 µm. Also for that sample, the leaching curve revealed a simple 2-component shape.

Interestingly, the material selected as "aggregate" (denoted by "/lm" in Figure 2 and Table 1) had acid-leaching characteristics very similar to that of the "binder," with only some enrichment in the slow-leaching component at the expense of the fast-leaching one. This could partly be due to the fact that in our sample, carbonate grains of the aggregate were more irregular than those of the binder, and irregularities of the aggregate grains were easily dissolved. Secondly, our procedure of sieving and hand-picking of pieces looking like aggregate was not absolutely efficient, as some grains selected as aggregate could still be coated with a thin layer of binder.

The samples analyzed in the previous studies (e.g. Sonninen and Jungner 2001; Michalska Nawrocka et al. 2007; Lindroos et al. 2008) were carbonate mortars with pieces of mainly crumbled solid limestone as an aggregate. Our sample from Jericho has a quite different composition of carbonate aggregate, which contains a lot of soft and fragile foraminiferous limestone, making collection a "pure" sample of binder-bound CO_2 impossible, even in a very short time of acid leaching. Crumbled pieces of foraminifera shells can decompose as quickly as the binder, hence the acid-

leaching reaction in the very first seconds is very fast. The impact of foraminiferous limestone can be illustrated (Figure 2) by the difference in the volume of gas collected in the same period of time and fraction in the case of the Masada sample (MS446, containing mostly dense pieces of carbonate aggregate) and the Jericho sample (AA25, containing pieces of crumbled foraminifera shells), and also by difference in the proportion of the fast-leaching components in both samples (Table 1).

The content of $CaCO_3$ in the MS446 sample (78%) is higher than in the AA25 sample (68%), but it was the Jericho sample that decomposed quicker and more intensively. This indicates that it was not the content of carbonate aggregate, but rather the presence of foraminiferous limestone that had a major impact on the leaching process of the sample AA25.

In order to examine the influence of different aggregate composition on ^{14}C dating results, a few samples were forwarded for ^{14}C measurement. These samples were 3 portions collected during acid leaching of the 63–80 μm fraction of MS446, and 2 portions collected during leaching of the same fraction of AA25 (for details, see Table 2).

Table 2 Results of ^{14}C dating of different fractions of Masada mortar (MS446) and Jericho mortar (AA25). The pressures p_1, p_2 are given in mbar.

Sample name	Time interval of CO_2 collection	Proportion of components: p_1 / p_2	Lab nr	^{14}C age (BP)	δ^{13}C (‰)
MS446 63–80/5s	first 5 s	271 ± 4 / 33 ± 4	Poz-13580	2045 ± 30	−7.6
MS446 63–80/45s	25–45 s	1 ± 1 / 109 ± 1	Poz-13581	2405 ± 30	−4.5
MS446 63–80/145s	85–145 s	0 ± 0 / 145 ± 1	Poz-13582	2420 ± 35	−9.3
AA25 63–80/10s	first 10 s	723 ± 7 / 28 ± 7	Poz-13577	3255 ± 30	−11.2
AA25 63–80/25s	10–25 s	73 ± 9 / 34 ± 9	Poz-13579	6720 ± 40	−8.7

RESULTS AND DISCUSSION

^{14}C measurements on both mortar samples confirm that CO_2 collected at the very beginning of the acid leaching is best for dating purposes. Indeed, ^{14}C dates obtained on the first CO_2 portions (2045 ± 30 BP and 3255 ± 30 BP for MS446 and AA25, respectively) are closer to the expected values (according to IntCal04 [Reimer et al. 2004]: 2020 ± 15 ^{14}C BP and 2090 ± 30 ^{14}C BP, respectively) than the dates obtained on the portions collected later on.

Having ^{14}C dates obtained on portions collected at different time intervals of the acid leaching, and knowing the proportions of different components (p_1, p_2) in the given portion, we calculated ^{14}C dates of individual components of the leached mortars (Table 3). We were satisfied to see that calibrated ^{14}C date of the fast-leaching component of MS446 63–80 perfectly agreed with the date of the wall (25 BC) determined by archaeologists. Therefore, the method used by Lindroos et al. (2007) appeared to work also for the mortar from Masada. It is worth pointing out that because the rates of leaching of the 2 components of our sample differed so much, the second and third CO_2 portions we have collected were both practically free of the first component ($p_1 \sim 0$). This fact was additionally confirmed by the fact that ^{14}C dates of these 2 portions appeared identical. Thus, the ^{14}C ages of the individual components of that samples could be determined with high accuracy.

Table 3 ^{14}C ages of individual components of the samples MS446 63–80 and AA25 63–80, differing by the rates of the acid-leaching reaction.

Sample name	Component	^{14}C age (BP)	Calibrated ^{14}C date
MS446 63–80	p_1	2000 ± 40	110 BC (95.4%) AD 90
MS446 63–80	p_2	2410 ± 30	740 (11.7%) 680 BC
			670 (2.6%) 640 BC
			550 (81.2%) 390 BC
AA25 63–80	p_1	2890 ± 60	1270 (95.4%) 910 BC
AA25 63–80	p_2	>16,000	—

However, the ^{14}C date of the first component of the sample from Jericho (AA25 63–80) appeared much older than the wall from which the sample came (120–75 BC). In the case of the Jericho mortar containing large amounts of crumbled foraminiferous limestone as aggregate, and many pieces of foraminifera shells scattered in the mortar, even the fast-leaching component is "contaminated" with old carbon from the aggregate.

One might be puzzled that the ^{14}C age of the second component was determined with such a large uncertainty (>16,000 BP). Judging by significant difference in the ^{14}C dates obtained on the 2 portions (.../10s and .../25s), one can surely expect the second component to be very old. More precise determination of its ^{14}C age would require ^{14}C analysis of subsequent portions, which for technical reasons was not possible. Nevertheless, as the .../10s portion contained <5% of the second component, the large uncertainty in its ^{14}C age did not affect dating of the first component too much. Thus, we can conclude that in our mortar sample, the reaction rate-based chemical separation was inefficient for the elimination of the effect of foraminifera, and the correct ^{14}C date of this mortar was impossible to obtain.

CONCLUSION

Our studies on the mortar samples from Masada and Jericho, whose age was known *a priori*, indicate that obtaining correct ^{14}C ages requires the selection of the appropriate fraction and time of the leaching reaction. Acid leaching of different fractions of carbonate mortar in different periods of time enables selection of a fraction most appropriate for dating. In terms of time characteristics of the acid-leaching reaction, such a fraction should contain components of clearly defined and quite different rates of leaching.

Deconvolution of the acid-leaching curve of the sample from Masada (MS446 63–80) allowed for reliable ^{14}C dating of this mortar. However, similar processing of the mortar from Jericho (AA25) did not result in a correct ^{14}C date. With a large amount of aggregate present in the form of crumbled limestone and shells scattered in the mortar, chemical elimination of "dead carbon" turned out to be impossible. ^{14}C dating results of mortars containing such aggregate can be significantly too old, even after separation of the most suitable fraction and ^{14}C dating of several CO_2 portions collected in different time intervals. It thus appears that the presence of small, crumbled pieces of foraminiferous limestone and shells scattered in a sample may practically preclude its ^{14}C dating.

ACKNOWLEDGMENTS

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