

^{14}C DATING OF CARBONATE MORTARS FROM POLISH AND ISRAELI SITES

Danuta Nawrocka[1] • Justyna Czernik[2] • Tomasz Goslar[2,3]

ABSTRACT. The presented research involves the analysis and radiocarbon dating of 2 different groups of carbonate mortars, from Kraków, Poland and Hippos, Israel. Differences in composition of the mortars are reflected in different rates of their acid leaching. The Israeli mortars contain carbonate-basaltic aggregates, which may cause overestimation of ^{14}C age. Preliminary processing of these samples (choice of selected grain-size fraction and collection of CO_2 released during the first phase of the acid-leaching reaction), enabled us to obtain good agreement between the ^{14}C dates and the age derived from historical contexts. A similar method of preliminary processing was applied to the carbonate mortars of the Medieval building in Kraków. The Polish samples represent carbonate mortars with some admixture of quartz aggregates, suggesting that they would be an ideal material for ^{14}C dating. However, these samples contained white lumps of carbonates, the structure of which differed from that of the binder. These admixtures, possibly related to the hydrological conditions at the site and to the character of the ingredients, appeared modern, and if not removed prior to acid leaching, they could cause underestimation of the age of samples. The ^{14}C dates of the mortars from the walls of the Small Scales building in Kraków are the first obtained for this object, and their sequence does not contradict archaeological indications on several phases of the building construction.

INTRODUCTION

Mortars, the material applied for connecting elements of a building, are a mixture of binder, aggregate, and water, possibly containing also the coloring and sealing admixtures. Grains of the aggregate constitute the matrix of the mortar, hindering its shrinkage and cracking; while cement grout, formed after water is added to cement, coats the sand and gravel grains and fills the gaps between them.

Basically, radiocarbon dating of lime mortars requires determination of ^{14}C concentration in carbon, which was derived from atmospheric CO_2 and incorporated in mortar carbonates during the hardening process. If the mortars are made of lime that has been totally burnt, the ^{14}C concentration of the binder should indeed reflect the real age of its production and building construction. However, when fragments of unburnt limestone are present and bring in the admixture of dead carbon (carbon completely or partly devoid of ^{14}C), the ^{14}C age of mortar can be overestimated. Another problem is associated with recrystallization and the effect of rejuvenation of ^{14}C age. This problem is connected not only with the process of mortar production, but also seems to depend on climatic and hydrological conditions.

In order to estimate the ^{14}C age of a carbonate mortar sample, it was necessary to develop a proper method of sample preparation, a job that has been attempted by many authors (Heinemeier et al. 1997; Sonninen and Jungner 2001; Hale et al. 2003; Lindroos et al. 2007; Michalska Nawrocka et al. 2007).

Here, we describe some studies on sample preparation, including the selection of different fractions and the acid-leaching reaction, and show their influence on the ^{14}C dating results of mortar. This study was made using mortar samples from Hippos (Israel) and Kraków (Poland).

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ARCHAEOLOGICAL BACKGROUND

The Hippos settlement (32°47′N, 35°39′E) is located at the top of the hill, on the east side of the Sea of Galilee (Israel). For dating, mortars originating from the North-West church were taken (Michalska Nawrocka et al. 2007). Archaeological studies distinguished 3 phases of church development: I phase (6th century), erection of the church; II phase (last quarter of 6th century), related to the specific mosaic patterns on the church floor; III phase (7–8th century), enlargement of the chancel and further functioning, until the earthquake in AD 749, when the whole settlement crumbled into ruins.

Recent Polish archaeological investigations at the Kraków Market Square (50°06′N, 19°93′E), begun in 2005, exposed an area below the Square pavement containing walls of the buildings The Large Scales (Wielka Waga), The Small Scales (Mała Waga), and The Rich Stalls. For ^{14}C dating, samples of mortars from the Small Scales building were selected first. According to historical-archaeological data, the Small Scales had functioned since 14th century AD, but the localization of the original building remains unknown. The Small Scales (*super nova pensa*) is then mentioned in historical sources from AD 1405 until 1801, when it ultimately crumbled into ruins.

SAMPLE DESCRIPTION

^{14}C dates of mortars from Kraków were obtained on material derived from the Small Scales (Kr1, Kr2, Kr8, Kr9); they are the first dates published for this object. The mortars from Hippos (Hip2, Hip10, and Hip61) are used here in "opposition" to the Kraków samples, because of their totally different composition, causing different problems in ^{14}C dating. These samples were analyzed earlier and have already been described in Michalska Nawrocka et al. (2007). Here, we present some new tests of leaching reaction of those mortars, following the new method proposed by Lindroos et al. (2007).

The 2 groups of mortars were analyzed to enable observation of differences, e.g. in the rate of the acid-leaching reaction. The Israeli samples contain limestone, quartz, basaltic rock, and other aggregates (Figure 1), each in different proportion, whereas the Polish mortars consist of carbonate binder and quartz aggregate.

Samples from Poland generally contain less $CaCO_3$ than the mortars from, for example, the Dead Sea region. This is associated with the region's lack of carbonate aggregates, the large amount of quartz aggregate, and the lime-silty character of the binder. In these samples, white lumps were observed (Figure 1e), composed of soft material of young carbonates.

PREPARATION OF CO_2 FOR ^{14}C DATING

After preliminary selection based on petrographical observations, samples from Kraków and Hippos were subjected to acid-leaching reaction tests, in different fractions and time intervals (Figures 2–5). New tests of carbonate dissolution were also made on a few, already dated samples from Hippos, following the method proposed Lindroos et al. (2007). On the basis of the conducted test, it was possible to indicate different stages of this process and to find different generations of carbonates in the analyzed sample (Figures 3, 5).

The method of leaching carbonate mortars in different granulations and in different time intervals is based on the relationships between the reaction rate and the type and size of grains in the mortar. Usually, limestone aggregates react more slowly than those of the binder, so in ^{14}C dating of archaeological mortars, it is worth utilizing this difference and thus discriminating limestone carbon in the collected CO_2.

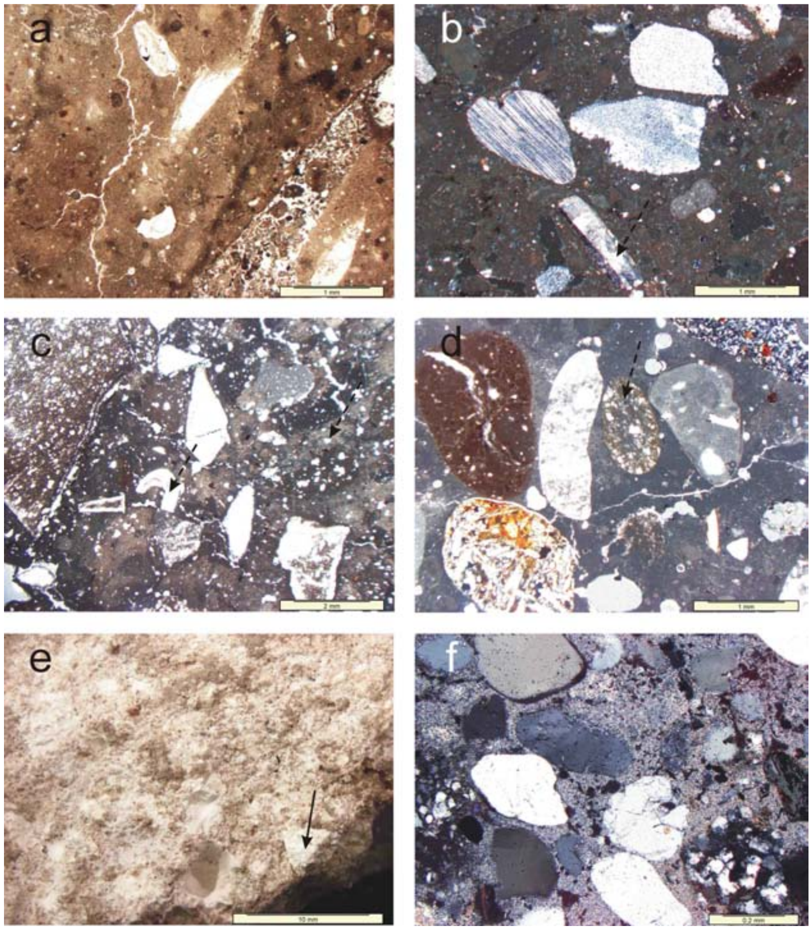

Figure 1 Petrography of different samples of mortar. a–d: samples from Israel (Dead Sea region and Sea of Galilee); e–f: samples from Kraków. (a) Hip10, 1N, pure lime plaster with voids after straw; 91% of $CaCO_3$; (b) M1, XN, carbonate mortar with different kinds of aggregate in fraction ~1 mm, among others, limestone, flints; 86% of $CaCO_3$; (c) Q6, XN, lime mortar with a different size and kind of aggregates (limestone, flints, shells fragments), especially important are fine fragments of foraminifera shells; 64% of $CaCO_3$; (d) Hip61, XN, lime mortar with coarse carbonate-basaltic sands >1 mm in diameter; 64% of $CaCO_3$; (e) macrophotograph of sample MW8, with visible white lime lumps, 11% of $CaCO_3$; (f) microphotograph of Kr8, XN, carbonate mortar with quartz grains as aggregate, 11% of $CaCO_3$. XN-crossed polarizers, 1N parallel; (optical microscope). Exemplary components, which influence the measurement of ^{14}C, are indicated with arrows: dotted arrows indicate components causing overestimation of age, while solid arrows, the effect of rejuvenation.

Tests with leaching reactions of the Hippos samples (Figures 2, 3) reveal some tendency in the reaction rate of all fractions. For the majority of the samples, at the very beginning the acid-leaching reaction runs very fast and with high intensity. CO_2 collected in the initial time intervals originates mostly from the binder. Further on, the reaction rate decreases.

The selected samples represent lime mortars consisting of carbonate binder and basaltic-carbonate aggregate (Hip2, Hip61), or composed of pure lime plasters, with some void spaces after straw (Hip10).

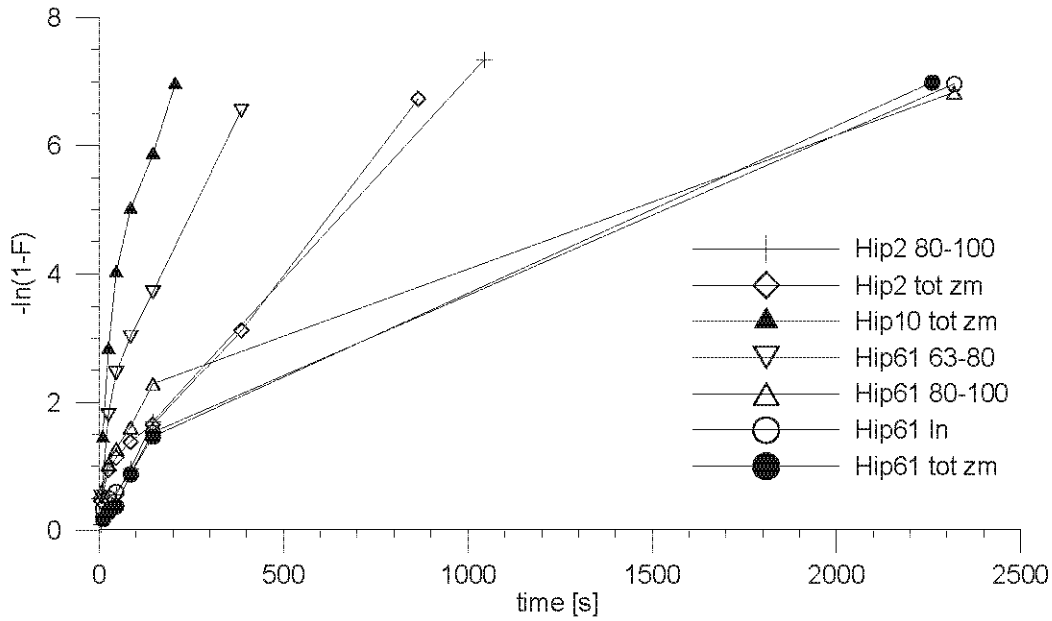

Figure 2 Leaching reaction of different samples from the NW Church in Hippos. Cumulative CO_2 pressure is represented by $-\ln(1-F)$, where $F = p/p_{tot}$ and plotted versus time, and p_{tot} is the pressure of CO_2 at the end of the reaction.

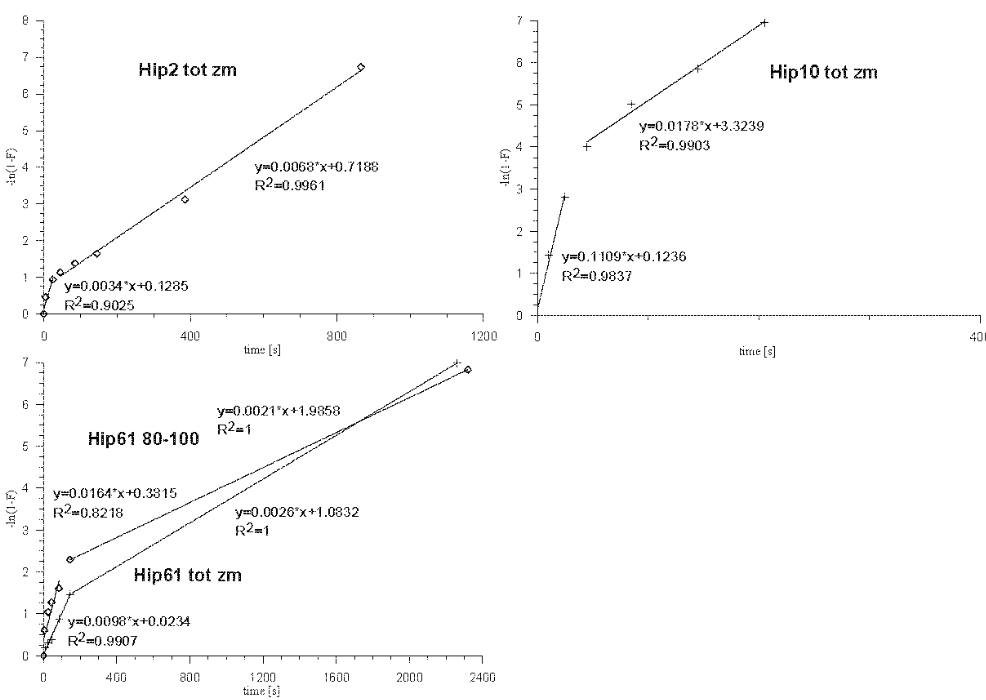

Figure 3 Single plots of the leaching reaction for the mortar samples from Hippos selected for ^{14}C dating. Hip2 tot zm, Hip10 tot zm, Hip61 tot zm—samples of totally ground bulk material.

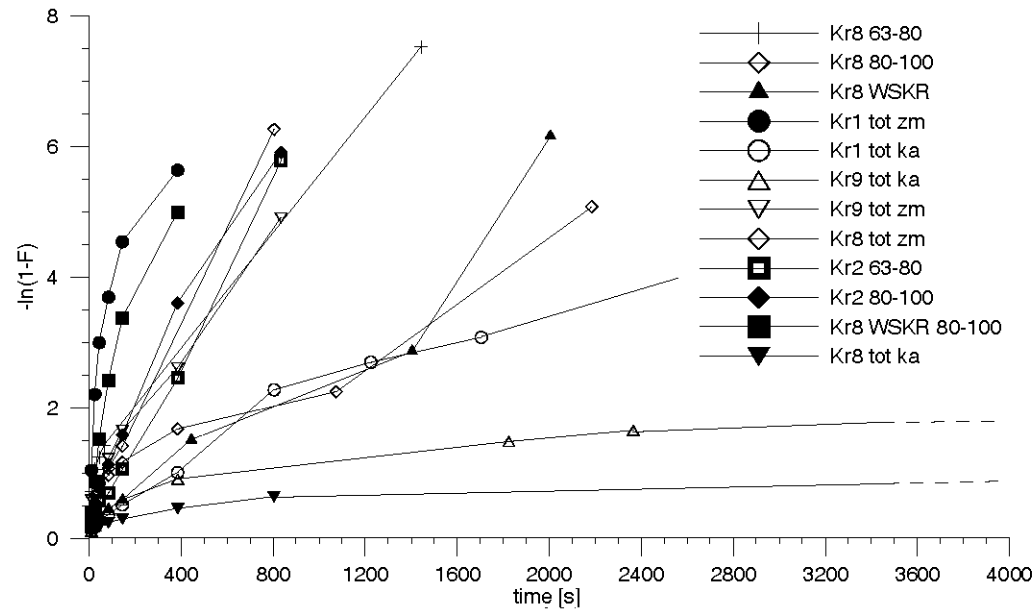

Figure 4 Leaching reaction of different fractions of mortar samples from the Small Scales in Kraków (descriptions of the fractions are given in the text). Like in Figure 2, the cumulative CO_2 pressure is represented by $-\ln(1-F)$.

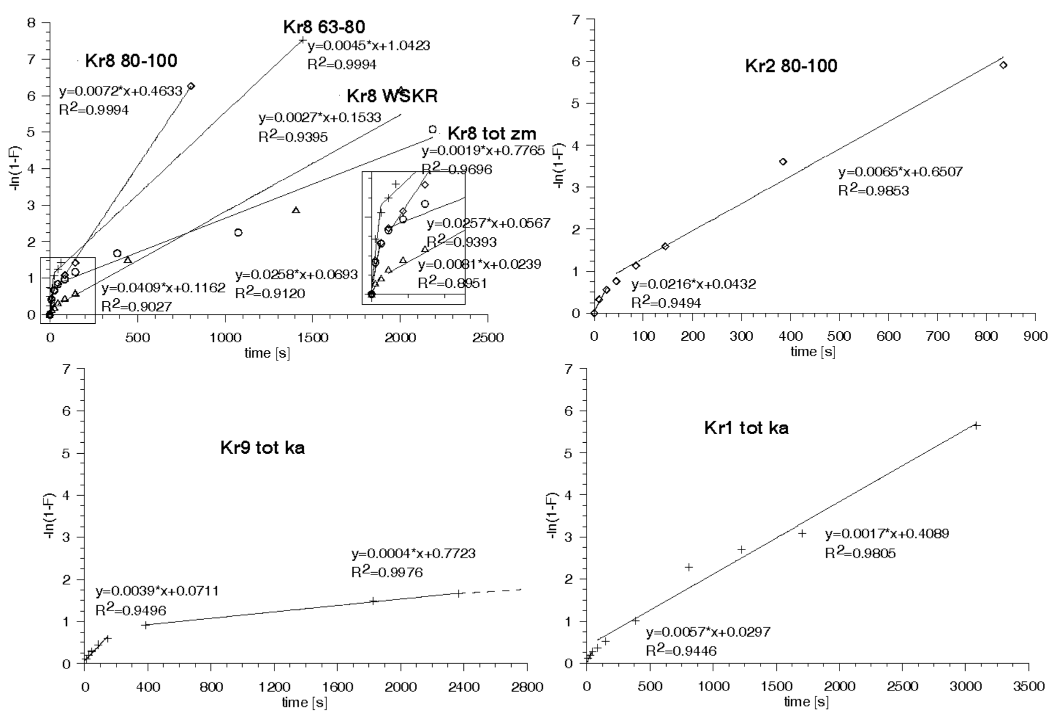

Figure 5 Single plots of the leaching reaction for the mortar samples from Kr1 tot zm, the totally powdered sample; Kr8 WSKR, white lump material from the mortar Kr8; Kr9 tot ka, fragments of the bulk sample (not powdered, with white lumps present).

Relying on macro- and microscopic observations of grain components and on test leaching, the first ^{14}C dating of Hip61 was made on the 80–100 μm fraction, using the conventional (gas proportional counting, GPC) technique of ^{14}C dating (Gd-18388, Michalska Nawrocka et al. 2007). The same technique was also used for dating powdered bulk material (Hip61 tot zm, the aggregate-binder mixture) of this sample (Michalska Nawrocka et al. 2007). From the same sample, we extracted basaltic fragments coated with a thin film of binder, and performed the acid-leaching reaction for 15 s, in order to collect an appropriate amount of CO_2 for accelerator mass spectrometry (AMS) measurement. An additional leaching test was made on the aggregate sample (not powdered bulk material, Hip61 ln, see Figure 2), and it revealed a similar course of the leaching reaction as for the totally ground sample (Hip61 tot zm).

The pure lime plaster Hip10, unlike Hip61, did not require preliminary processing. The leaching reaction of this sample was very intensive and fast. To verify the obtained results, the sample dated first with the GPC technique (where CO_2 was collected until the end of the leaching reaction, Michalska Nawrocka et al. 2007), was re-analyzed with AMS, using CO_2 collected during the first 10 s of the leaching.

The bulk material of the Hip2 sample, containing the basaltic-carbonate aggregate of a relatively big size compared to the other samples, was subjected to preliminary processing, and CO_2 was collected during the first 5 s of leaching. For comparison, a piece of charcoal retrieved from this mortar was also dated (Hip2/ch).

In the Kraków samples, considerable differences in the pace of the leaching reaction of different samples were revealed, despite the fact that all samples had similar proportions of aggregates and binder. Besides mortars, also white lumps of carbonates extracted from Kr8 were subjected to test leaching. Fragments of the lumps directly scraped from the mortar underwent decomposition within about 30 min (Kr8 WSKR), while their 80–100 μm fractions (Kr8 WSKR 80–100) decomposed in only 5 min, and during the first 10 s, 30% of the (80–100 μm) fraction was leached.

In comparison with the bulk sample, leaching of the not-powdered white lumps material (WSKR) is quite slow at the beginning of the process, but the share of the white lumps in the leached carbonate may increase with time (Figures 4, 5). However, the white lump material appears much younger than the actual mortar (Table 1) and the leaching reaction of its fine fraction (like WSKR 80–100) is very rapid. Thus, to minimize risk of rejuvenation of ^{14}C dates we decided to remove that component from the mortar samples prior to the acid leaching.

In order to verify the applied method, we dated different fractions of the Kr8: 63–80 μm, 80–100 μm, and the totally powdered bulk material (Kr8 63–80, Kr8 80–100, and Kr8 tot zm, Table 1). The leaching reactions seem to suggest that the best elimination of limestone aggregates, and eventual rejuvenating material, would be possible during the first seconds of leaching of the 63–80 μm fraction (Figure 5). The leaching of the sample-Kr8 tot zm (the bulk sample with white lime lumps) shows some similarity to the leaching of Kr8 WSKR.

The sample Kr1 tot ka was forwarded for ^{14}C measurement in a bulk form, after white lumps had been removed. The totally powdered material (Kr1 tot zm) was not selected for dating because its leaching was very intensive and we were afraid that even the earliest released CO_2 could contain carbon from the old limestone components, which would cause overestimation of the age of mortar. The leaching process of the totally powdered Kr1 resembled that of the sample Hip61 63–80, which contained a large inclusion of carbonate aggregate.

In sample Kr2, the white lumps were removed, and the 80–100 μm fraction was selected for ^{14}C dating. The last sample (Kr9) remained in its bulk state, meaning that the white lumps were not scraped

Table 1 Results of ^{14}C dating with the description of the place of sample collection; Lab code: Gd—sample dated with the GPC technique (Michalska Nawrocka et al. 2007); Poz—sample dated with the AMS technique in the Poznań Radiocarbon Laboratory.

Sample name	Archaeological context	Material dated	Time intervals of CO_2 collection	Lab code	^{14}C age (BP)	δ^{13}C (‰)
Hippos						
Hip61 tot zm	Facade of the pastophorium northern wall, NW church	Mortar with coarse-grained, mainly carbonate aggregate; powdered bulk material	until end of leaching reaction	Gd-12824	7140 ± 90	–7.41
Hip61	—	Basaltic aggregate covered with a film of binder	first 15 s	Poz-16078	1490 ± 30	0.2
Hip61 80–100	—	Fraction 80–100 µm	until end of leaching reaction	Gd-18388	1080 ± 100	–7.41
Hip10 tot zm	Southern aisle, by the balustrade, northern face; NW church	Pure lime plaster; powdered bulk sample	first 10 s	Poz-7417	1245 ± 35	–9.5
Hip10 tot zm	—	Powdered bulk sample	until end of leaching reaction	Gd-12823	1310 ± 45	–10.35
Hip2/ch	Collection pool in the agricultural installation to the south of the akonikon	Charcoal from plaster	—	Poz-5087	1570 ± 70	–42.4
Hip2	—	Sample with relatively large size basaltic-carbonate aggregate; pieces of bulk sample	first 5 s	Poz-5016	1295 ± 30	–10.8
Kraków						
Kr8 WSKR	Western main wall	Fragments of white lumps	first 10 s	Poz-15841	100.32 ± 0.5 pMC	–31.0
Kr8 tot zm		Powdered bulk material	first 10 s	Poz-16300	505 ± 30	–18.2
Kr8 63–80		Fraction 63–80 µm	first 10 s	Poz-15881	395 ± 40	–17
Kr8 80–100		Fraction 80–100 µm	first 10 s	Poz-15885	300 ± 35	–21.8
Kr1 tot ka	Buttress in SE corner, the south part, the face from the north	Pieces of bulk sample	first 10 s	Poz-15883	400 ± 35	–25.4
Kr2 80–100	Eastern main wall	Fraction 80–100 µm	first 5 s	Poz-16270	930 ± 35	–19.5
Kr9 tot ka	Western main wall	Pieces of bulk sample	5–15 s, first 5 s removed	Poz-16156	100 ± 40	–37.6

out, and we decided to collect CO_2 in the 5–15 s interval, after the gas released in the first 5 s of leaching had been removed.

RESULTS AND DISCUSSION

^{14}C dating results for the mortar samples are given in Table 1, and calibrated ^{14}C dates are shown in Figure 6.

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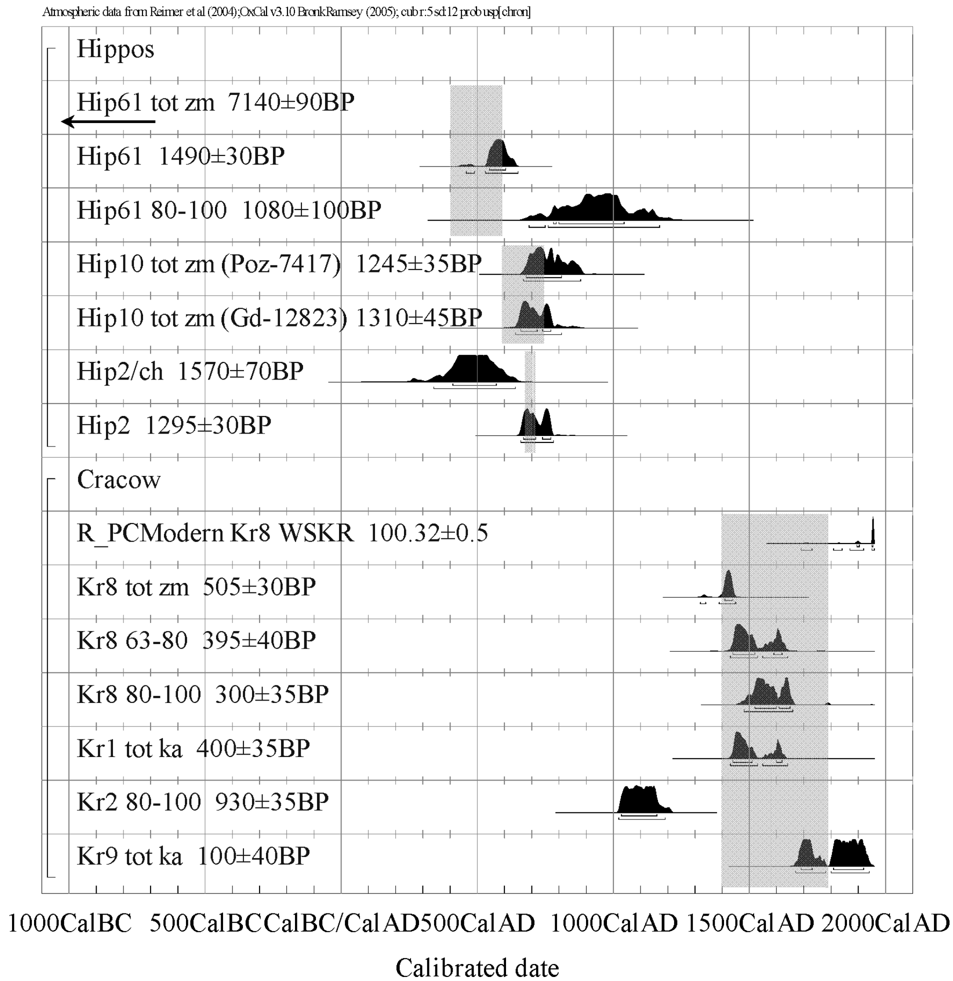

Figure 6 Calibration of ^{14}C dates of the Hippos and Kraków mortar samples, obtained with OxCal v 3.10 (Bronk Ramsey 1995, 2001) and IntCal04 atmospheric data (Reimer et al. 2004). Time intervals of archaeological estimations are marked in gray color.

In general, the ^{14}C dating results of mortars from Hippos are in good agreement with the expected calendar ages (Michalska Nawrocka et al. 2007), due to a relevant fraction selection and relevant time intervals of the leaching reaction. However, during analysis of these samples, different problems were encountered. For instance, in the case of Hip61 there is a puzzling discrepancy in the ^{14}C measurement results obtained by the 2 techniques (GPC and AMS). When the clearly outlying date of the whole powdered bulk material (Hip61 tot zm, CO_2 collected until the end of the leaching reaction, cf. Table 1) is ignored, the difference between the remaining results is still significant. Taking into account the composition of Hip61, one would not expect a rejuvenation effect in this material, so it was the older date, which could be easier treated as wrong. However, the AMS date, obtained on fragments of the coated aggregate, agrees with archaeological expectations, while the GPC dating result for the 80–100 µm fraction (Michalska Nawrocka et al. 2007) appears too young. In this aspect, we must say that we do not know the actual reason of rejuvenation of that sample.

When compared to archaeological background, the ^{14}C date of the carbonate fraction of Hip2 appears reasonable, while the date of charcoal (Hip2/ch) is too old, suggesting that the dated fragment originated from some older part of a tree. Based on the date of the mortar carbonate, attribution of the sample Hip2 to a particular (second or third) phase of existence of the NW church is, however, impossible, because its calibrated date interval is too wide. For sample Hip10, dated with the 2 techniques, 2 very similar results were obtained, irrespective of the time of the leaching process, and both ^{14}C dates appear correct.

The mortar samples from Kraków, coming from the Middle Ages, were found to contain carbonates of a structure different from that of the binder (compare the photos of samples from Hippos and Kraków, Figure 1). The presence of these admixtures (white lumps) might be connected with the mortar production process, but also with later precipitation, incorporating carbon derived from dissolution of other mortars, and eventually from overlying soils. Thus, in ^{14}C dating of mortar, not only the ingredients of the mortars but also hydrological conditions in the site appear significant. In fact, the mortars in Kraków were buried in very humid conditions.

Direct ^{14}C analysis of the white lumps (Kr8 WSKR) indeed confirmed that the component contained modern carbon. Therefore, most samples from Kraków were dated after the white lumps had been removed, and most of their dates appear reasonable. The ^{14}C date of sample Kr9—leached together with the white lumps but with removal of CO_2 collected during the first 5 s—is younger than the other dates, but relying on the archaeological background alone, this result cannot be treated as an outlier.

Differences between samples originating from Hippos and Kraków are visible in the rate of leaching reaction. As discussed in Michalska Nawrocka et al. (2007), the most accurate dates are usually given when CO_2 forwarded for ^{14}C dating is collected at the beginning of the leaching reaction. For the Kraków samples, however, it is difficult to determine the correct fraction of the sample and the time of CO_2 collection. This problem seems responsible for the overestimation of age, revealed for sample Kr2.

Archaeological observations suggest that samples Kr1, Kr2, Kr8, and Kr9 may represent several phases of construction of the Small Scales building, and so their ages would follow a sequence. This, and additional information (*terminus post quem* (TPQ) at AD 1405; *terminus ante quem* (TAQ) at AD 1801), have been used in the calibration of combined ^{14}C dates (Table 2, Figure 7). The result of this calibration demonstrates that the group of analyzed mortars may indeed represent a large part of the period of existence of the Small Scales building, although we still cannot exclude that the young age of the sample Kr9 was caused by rejuvenation. This problem needs to be resolved by ^{14}C analysis of additional samples.

Table 2 Results of calibration of combined ^{14}C dates of the mortars from Kraków (Figure 7).

Lab #	Date	Calibrated age (68.2% confidence interval)	Calibrated age (95.4% confidence interval)
Poz-15883	400 ± 35	AD 1440 (57.6%) 1510 AD 1600 (10.6%) 1620	AD 1430 (70.7%) 1530 AD 1550 (24.7%) 1640
Poz-15881	395 ± 40	AD 1490 (23.3%) 1530 AD 1550 (44.9%) 1640	AD 1470 (95.4%) 1640
Poz-15885	300 ± 35		
R_Combine	342 ± 26		
Poz-16156	100 ± 40	AD 1690 (17.9%) 1730 AD 1810 (50.3%) 1920	AD 1670 (30.8%) 1780 AD 1800 (64.6%) 1940

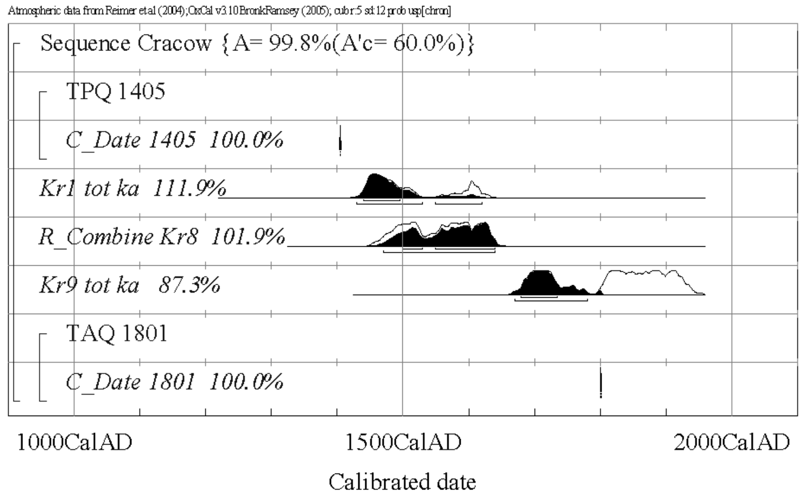

Figure 7 Calibration of combined ^{14}C dates of the mortars from Kraków. Sample Kr2, giving an outlying age, was ignored.

CONCLUSION

Test acid-leachings of mortars appear very helpful when selecting material for ^{14}C dating. On the basis of these tests, coupled with petrographic observations, it is usually possible to select an appropriate preparation method. These observations are also very helpful when interpreting dating results. These techniques do not fully eliminate the risk of aging or rejuvenation, but they certainly bring us closer to the real ages and allow for better chronological interpretation of the analyzed material. ^{14}C dates obtained for the mortars from Kraków constitute the first absolute dating of the walls explored after 2005 in the Kraków Market Square.

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