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APPLICATION OF RADIOCARBON METHOD FOR DATING OF LIME MORTARS

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Abstract: The presented work shows the methodological problems of mortar radiocarbon dating. Dating of lime mortars is based on setting the present ^{14}C concentration of atmospheric CO_2 by mortar carbonates in the hardening process. The big difficulty is the presence of aggregate, especially carbonatious one. The application of limestone fragments as aggregate in mortar, is connected with the presence of carbon partially or completely devoid of the radioactive isotope ^{14}C. To carry out radiocarbon dating of the mortars reliably, it was necessary to remove the limestone aggregates. In this context, the application of petrographic studies that enable determination of mineral composition and the percentage of aggregate turns out to be particularly important. Such an identification allows to reconstruct mortar technology and, in combination with geological studies on the investigated terrain, helps to identify the provenance of the applied raw material. To make possible the comparison of the analysed mortar results and the verification of the applied methods, in year 2001 control mortars (mortars with established age) were used. The analyses were performed on mortars from a Romanesque castle built in the years 1177-1230 AD (Wleń, SW part of Poland) and from roman buildings with an approximate age of 140BC-68 AD (west coast of the Dead Sea,). We present the complex study of the mortar including both petrographical analyses and radiocarbon dating. The gas proportional counting technique (GPC) was applied for radiocarbon dating. Thin sections of roman mortars showed the carbonatious character of the binder and a large part of the aggregate; this was the source of the apparent age in radiocarbon dating. In spite of efforts to eliminate the lime aggregate from the mortar (by freezing, warming up, and separating under the binocular), and taking into consideration the amount of old carbon admixture derived from the carbon stable isotopes composition, there is still a great disproportion between historical and radiocarbon dating of these mortars. The results of the ^{14}C dating show, that improvement of the binder-aggregate separation process is necessary.

The mortar aggregate from the Polish castle samples does not contain limestone grits, only scarce quartz grains. These Romanesque mortars were tested successfully and the existing architectural and historical data confirm the results obtained by GPC.

1. INTRODUCTION

The presented paper concerns a still not completely solved problem of radiocarbon dating of lime mortars. Mortar is a mixture of binder and aggregate in different proportions. Thanks to the numerous works devoted to the methods of determining the age of mortars we know that the presence of aggregate (especially a carbonatious one) in the mortar has an enormous influence on the precision of dating (Van Strydonck *et al*., 1986; Sonninen and Jungner, 2001; Zouridakis *et al.,* 1987; Heinemeier *et al.,* 1997). The problems to obtain the correct radiocarbon age when dating building mortars are connected with the different origin of carbon in the carbonates. The carbon in carbonates can be originated from the air (by absorption of CO_2 by binder carbonates in the hardening process), or can be contained in the aggregates (which were added to the mortar after burning-slaking process). Much more accurate and reliable results are obtained for mortars which do not contain any admixture of aggregate.

Two groups of lime mortars with known age have been selected for the analyses: 1) the mortars from SW Poland (1177-1230 AD), and 2) the mortars from the Dead Sea coast region (140 BC – 67 AD). The age of the investigated mortars is already known from information obtained by archaeologists on the basis of found manuscripts containing time indications and from historical records. The mortars from the first group are free of almost any aggregates, whereas those from the second group contain a significant admixture of aggregate built of carbonatious fragments. Apart from one thousand years of difference in the age of the mortars from Poland and Palestine, the mortars contain a completely different amount of aggregate. The diversity between the selected groups and the knowledge of the ages make possible a comparison of the analysed mortar results with the archeological data, verification of the applied methods, and the discovery of possible systematic error sources. Because of experimental character of the presented research and because the aim of the study is connected with methodological problems, the detailed localization of the sampling sites has not been reported.

Sometimes in archaeological practice, establishing the age of particular buildings causes many problems. In such cases, the results obtained by radiocarbon dating turn out to be especially important and useful. In fact, in the case of lime mortars dating, *the real age* is the age of the binder because the carbonatious binder takes up ^{14}C from the air during the hardening process. Thus if all $CaCO_3$ is converted into CaO, the age of the binder is the age of the building erection. Radiocarbon dating of lime mortars provides a good opportunity for establishing the absolute age probably approximate to the real age of the mortars, which would supplement the results obtained from stratigraphy of the walls of investigated buildings.

Dating of lime mortars is based on setting the present ^{14}C concentration of CO_2 by mortar carbonates in the hardening process. Production of lime mortars can be written by reaction as follows:

$$CaCO_3 \rightarrow CaO + CO_2 \tag{1.1}$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{1.2}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{1.3}$$

Calcium carbonate is dissociated during the burning process (**Eq. 1.1**); then the limestone burnt to calcium oxide (CaO, so called *burnt lime*) is slaked with water. Calcium hydrodioxide is formed (*slaked lime;* **Eq. 1.2**), which after mixing with sand and water can be easily layed and shaped. After some time it sets and hardens. The mortar exposed to the action of air hardens by absorption of CO_2 and forms carbonate (**Eq. 1.3**). Exactly then, the present ^{14}C concentration in the air is set in the mortar. If the mortars are made of completely burnt lime, radiocarbon dating gives the age of construction of the building.

In practice, there are frequent discrepancies between the isotope dating age and the age expected from the archaeological and historical context. The problem appears when there are some unburnt fragments of carbonate rocks in the mortar. In such cases, not all the $CaCO_3$ is converted into CaO and the mentioned fragments give the so called „dead carbon" effect, which is the reason of significant overestimation of the absolute age. The other difficulty is the presence of aggregate, especially carbonatious one, which is hardly separable from the binder which is also a carbonate. Application of limestone fragments as aggregate in mortar is connected with the presence of carbon partially or completely free of radioactive ^{14}C. It causes that the age determined by dating is older than the real one. In this context, the application of petrographic studies that enable determination of mineral composition and percentage of aggregate turns to be particularly important. If in mortar the presence of limestone fragments, which are the source of dead carbon, is identified, the limestone needs to be eliminated in order to make the dated sample for dating possibly clean. Practice shows that limestone fragments in aggregate can be very small in size and difficult to eliminate, so despite efforts to separate them, some amount may remain in the sample. Dating results of carbonate mortars give variable ages, sometimes close to expectations, sometimes too high. It is mainly connected to the above-mentioned difficulties (Folk and Valastro, 1979; Zouridakis *et al.,* 1987). Several laboratories which have been working on mortar dating propose the procedure of separation of pure carbonatious aggregate by hydrochloric acid application. The difference of solution rate between limestone and carbonate binder is utilized in this method (Folk and Valastro, 1979; Soninen and Jungner, 2001). The reaction with HCl is much faster in the case of fine, porous binder. During the application of the radiocarbon method in dating of mortar samples one should also remember taking into consideration the δ^{13}C correction (Van Strydonck *et al.,* 1986).

The presented work is an attempt to determine the radiocarbon age of lime mortars by applying ^{14}C gas proportional counting method. As benchmarks there were used samples of mortars with the approximate age established by archaeological research.

2. GEOLOGICAL BACKGROUND

One of the most important problems in lime mortar dating is the application of limestone fragments as aggregate. In our project that problem is reported only in the group of samples from the Dead Sea region. A short characteristic of the rocks occurring in the region (their types and ages) is presented in **Fig. 1**. The map shows basic rock divisions of the Dead Sea region and the localisation of the Essenian settlement.

Determination of mineral composition of aggregate in combination with geological studies of the investigated terrain helps to identify the provenance of the applied raw material. The raw materials for lime production were probably Cretaceous rocks of Turonian Shivta formation

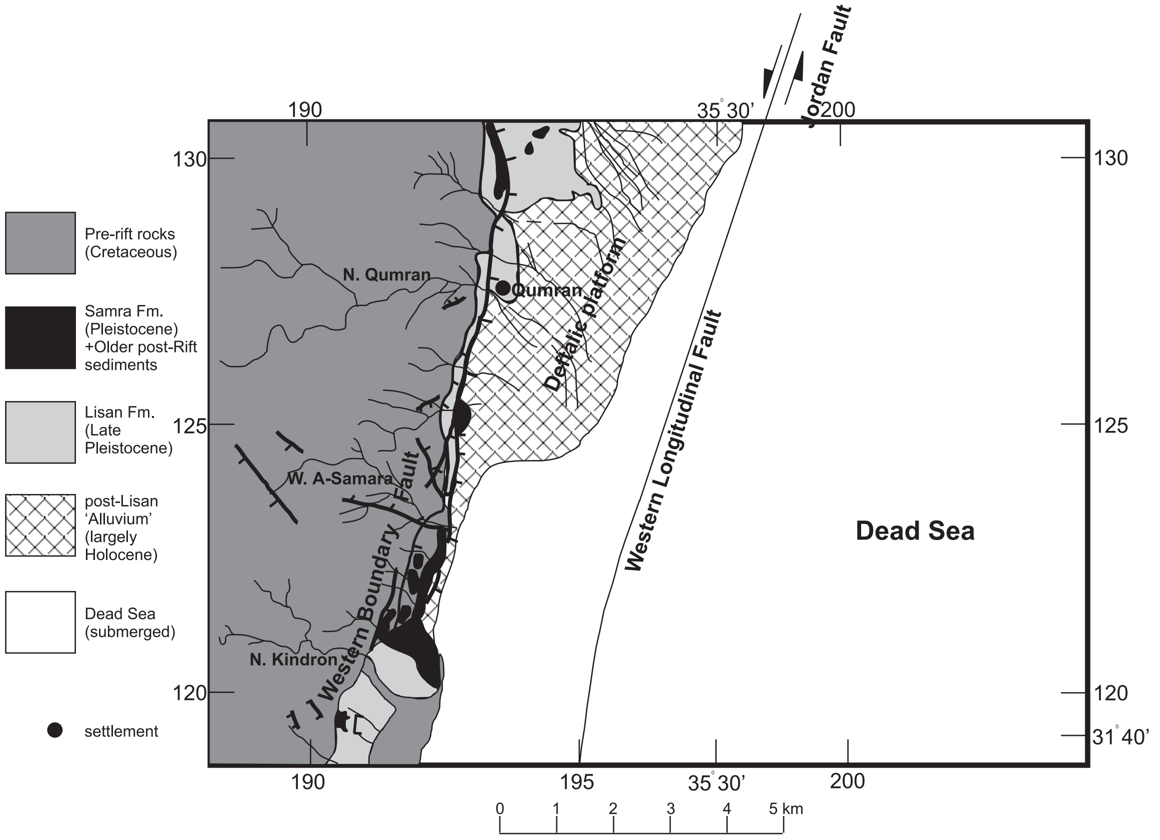

***Fig. 1**. Basic geological units of the north-western bank of the Dead Sea (Lubberts and Ben-Avraham, 2002). The raw materials for lime production were probably Cretaceous rocks.*

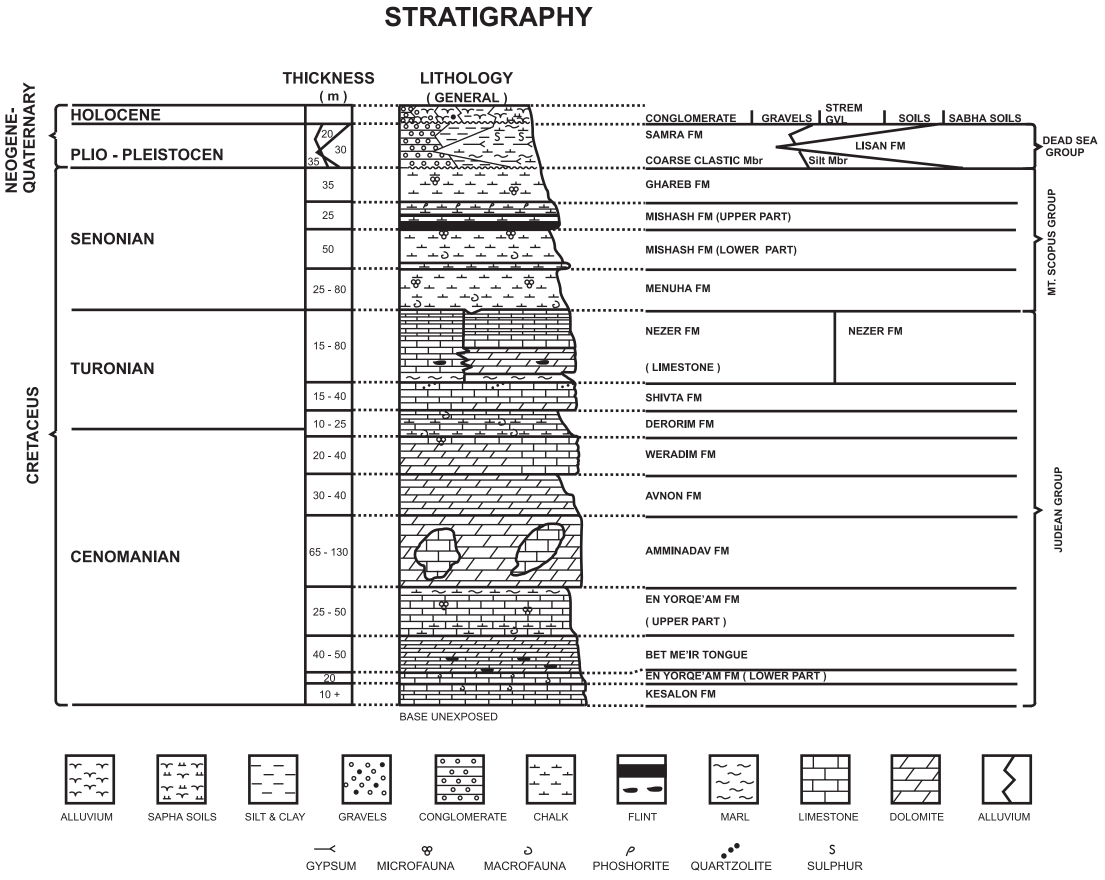

***Fig. 2**. Stratigraphy of the north-western bank of the Dead Sea, from Cenomanian to Recent (Begin, 1974; Roth, 1974). The aggregate from the Roman mortars is composed of different type of limestone and dolomites, also the fragments of flint (on the basis of petrographic studies).Such an identification in combination with geological studies helps to identify provenance of the applied raw material. The raw materials for lime production were probably Cretaceous rocks of the Turonian, Nezer or Shivta formation.*

or late Pleistocene marls of Lissan Formation (Begin, 1974; Roth, 1974). The aggregate is composed of different types of limestone and dolomites, as well as fragments of flint. They represent both, the Cretaceous rocks of the Judean Desert and sediments deposited in the Rift Valley. A special connection of the investigated mortars with the Shivta or Nezer formation is testified by numerous flints which are typical for that formation (**Fig. 2**).

3. PROCEDURE

Pretreatment

The mineral composition of the mortar samples was analysed by polarizing light microscopy of thin sections. Petrographic investigations of the Roman mortars (**Fig. 3**) show the carbonatious character of the binder and large amount of limestone aggregate, which is the source of error in radiocarbon dating. The aggregate from these mortars, consist of grits of limestone and flint. Such composition is diagnostic for limestone of Cretaceous age of local provenance. In micrographs of samples from the Dead Sea area (indicated by letters Q and QA in **Table 1**) many different components of aggregates, such as quartz, foraminifera, snail shells, and limestone grains, are clearly visible.

The samples from Polish castle are made of pure carbonate, originated from burning-slaking process. The mortar aggregate does not contain limestone grits, only scarce quartz grains (**Fig. 4**). The petrographic observations are confirmed by XRF analysis.

To make the radiocarbon dating of mortars reliable, it was necessary to remove the limestone components. The first part of work was a mechanical separation based on the fact, that the limestone in aggregate is stronger and more resistant than the more porous mortar carbonate. The mortars were delicately crushed, and then repeatedly frozen and thawed (**Fig. 3c**). Finally they were also treated with microwaves. Most of the soft mortar carbonate was separated from the aggregate grains. After that, during binocular observations, the required amount of sample material was collected. The samples were prepared in the Institute of Geology, Adam Mickiewicz University, Poznań. All the ^{14}C activity measurements necessary for determining the age were performed by application of the gas proportional counting technique (GPC) in Gliwice Radiocarbon Laboratory (Pazdur *et al.,* 2000; Pazdur *et al.,* 2004).

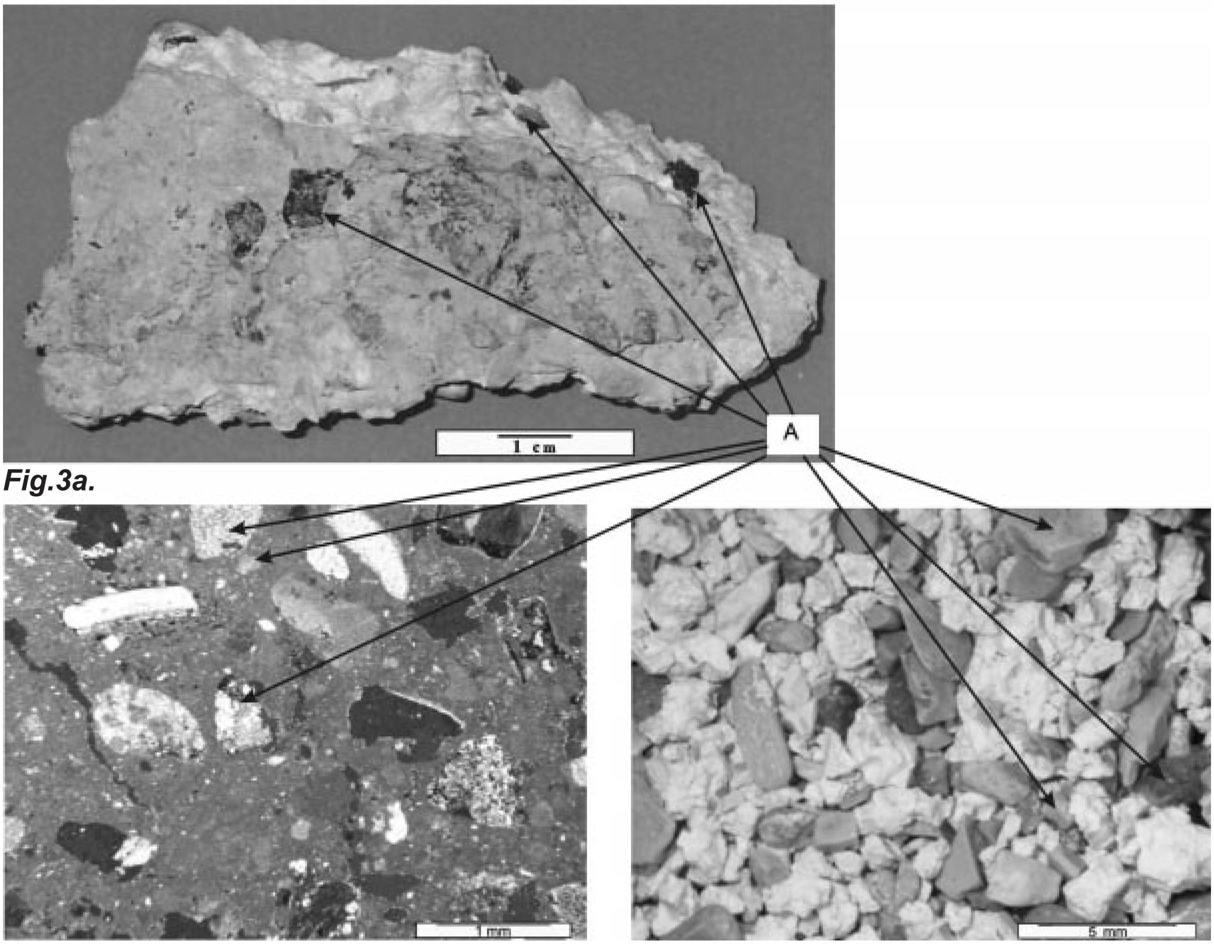

Fig.3a.

Fig.3b.

Fig.3c.

*Fig.3. Photographs of the sample from the Dead sea area; **a-** macrophotograph of the sample Q4, two layers of mortar, **b-** microphotograph of the sample QA. The variegated composition of the aggregate is visible: quartz, snail shells and limestone grains, (polarizing light microscopy, crossed polarizers); **c-** macrophotograph of the sample after the first stage of freezing-thawing process. A-aggregates.*

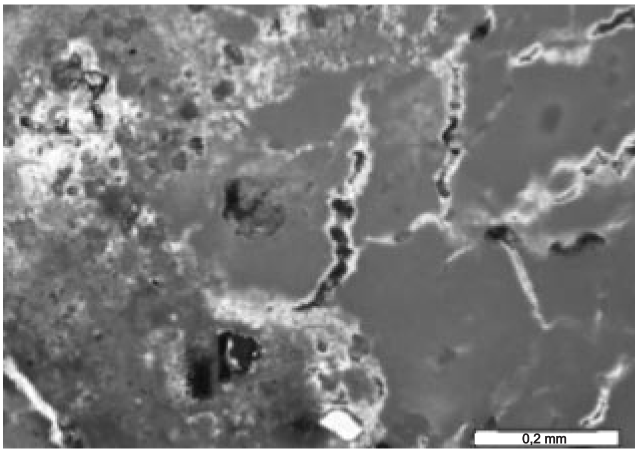

Fig.4. *Microphotograph of sample from a Romanesque castle, SW Poland (K/160/4), (the polarizing light microscopy, crossed polarizers). Carbonatious binder is contractionally fractured which was promoted by lack of any aggregate.*

Reservoir effect in mortars dating

Lime mortars contain carbon originating from two reservoirs. These reservoirs are 1) old carbonate rocks composing the aggregate, and 2) atmospheric carbon in the form of CO_2 which was caught into structure of binder in the moment of mortar setting (see **Eqs 1.1 – 1.3**). The course of setting reaction causes that there is only atmospheric carbon in the binder (while the raw material is fully burnt). Its isotopic composition is characteristic for the moment of binder forming. So one should expect, that the concentration of carbon isotopes ^{13}C and ^{14}C in that part of mortar will be the same as in the atmospheric CO_2, changed only during the chemical reactions as a result of the isotopic fractionation process. Thus, the known concentrations of these isotopes in the atmosphere at the time of binder formation and at present allow us to establish the time interval which passed since its forming. It is the so called "conventional radiocarbon age", expressed in years BP, further in the text marked as T_C.

However, not always a sufficient amount of binder can be separated from the mortar for dating. In the case of (GPC) technique applied in Gliwice Radiocarbon Laboratory, the smallest amount of a carbonate necessary for dating is a few grams. Such amount of the binder was possible to separate only from the samples Q*/1997, Q 1, Q6 /2000, and QA/1997 (compare **Table 1**). The remaining samples from the Dead Sea region were a mixture of binder and aggregate. From the point of view of the radiocarbon method, they were a mixture of old, inactive carbon present in the aggregate and binder containing ^{14}C. This fact implies, that the conventional radiocarbon age T_C determined for the aggregate-binder mixture is higher that the one established for the binder only. The overestimation of the ages of a mixture of carbonates (so called reservoir effect) can be estimated on the basis of known relative concentrations of the ^{13}C isotope whose measure is $\delta^{13}C$ quantity in the binder only and in the binder-aggregate mixture. The ^{13}C isotope takes part in a mortar setting reaction in the same way as radiocarbon does. However, it is a stable isotope and its concentration in the studied material does not change during its stay in the environment. Each of carbon reservoirs on Earth is characterised by a particular value of $\delta^{13}C$. In the case of old carbonate rocks of Cretaceous age, $\delta^{13}C$ values are close to zero. The aggregate of investigated mortars had been produced from such rocks. The estimation of the reservoir effect in the form of a suitable correction T_R (so called reservoir or apparent age; Pazdur, 1988) is possible under the assumption that:

$$\delta_{SK}{}^{13}C = \delta_S{}^{13}C \cdot \frac{m_S}{m_{SK}} + \delta_K{}^{13}C \cdot \frac{m_K}{m_{SK}}, \tag{3.1}$$

$$\delta_K{}^{13}C = 0,$$

$$\frac{\delta_{SK}{}^{13}C}{\delta_S{}^{13}C} = \frac{m_S}{m_{SK}}, \tag{3.2}$$

where the indices: SK, S and K denotes bulk sample material, binder material, and aggregate material respectively. Taking this assumption into account and using appropriate procedures for radiocarbon age calculations (Stuiver and Polach, 1977), the T_R correction is described by the following formula:

$$T_R = -8033 \cdot ln\left(\frac{\delta_S{}^{13}C}{\delta_{SK}{}^{13}C}\right) \tag{3.3}$$

During the derivation of this formula $\delta^{13}C$ value in the aggregate was assumed to be zero, which simplified the formula. In the reservoir age (T_R) estimations for the samples from the Dead Sea region the same $\delta^{13}C$ value (equal -8.11‰) was assumed for the binder in all the samples (**Table 1**). That value is close to the recent value in atmospheric CO_2. It must be stressed that adding the T_R correction established individually for each dated binder-aggregate mixture to the corresponding T_C values, enables obtaining the so called "corrected conventional radiocarbon age" T_{CCA}, which defines the age of the binder (**Table 1**).

$$T_{CCA} = T_C + T_R \tag{3.4}$$

`4. RESULTS

Results of dating and the calendar age of binder

A separate radiocarbon dating was made on:

1. Raw mortar samples (containing aggregate, type of dating material SK – see **Table 1**), taking into account the proportion of binder and aggregate.
2. Fragments of separated binder (type of dating material S- see **Table 1**).

The results of radiocarbon dating, i.e. the conventional radiocarbon dates (T_C), their laboratory uncertainty (ΔT_C), and the estimated binder ages in the mortars (T_{CCA}) together with the estimation uncertainty (ΔT_{CCA}) are reported in **Table 1** and **Fig. 5**. The T_{CCA} conventional dates were calibrated using the OxCal program (Ramsey, 2002) and IntCal98 curve. The results of calibration procedure, represented by probability age intervals with 68 % confidence are given.

In the case of two samples of binder-aggregate mixtures (Q 4/2000 and Q 2/2000), $\delta^{13}C$ values are much lower than in all the remaining samples (-11.0 and –10.41 per mil). In these two cases the reservoir effect correction resulted in higher values of the conventional age. It means that the assumed model of correction estimation gives incorrect results. One may suspect that low $\delta^{13}C$ values in those samples are the effect of application in the mortar production of aggregate with an isotopic composition of carbon different from the one occurring in Cretaceous carbonates, e.g. secondarily precipitated carbonates in the form of calc-sinter or lacustrine chalk. It will be possible to solve this problem after supplementary isotopic analyses of the aggregate in those samples. For more precise estimation of the reservoir effect, measurements of $\delta^{13}C$ in the binder of all the samples are also necessary. It will require a separation of ca 30 mg of binder from every sample. There is a strong correlation between the ^{14}C concentration and $\delta^{13}C$ (**Fig. 5**). **Table 1** contains also the most probable calendar age intervals obtained after performing calibration of the corrected conventional dates T_{CCA}. In the case of the samples Q 2 and Q 4, the calibration referred to the conventional ages T_C.

5. CONCLUSIONS

In the case of lime mortars dating, *the real age* is the age of binder because the carbonatious binder takes up the present ^{14}C concentration of atmospheric CO_2 during the hardening process. The problem appears when there are some unburnt fragments of carbonate rocks or limestone aggregate in the mortar. In spite of efforts made to eliminate the lime aggregate from the binder (by freezing, thawing, and separation under the binocular) and considering the value of $\delta^{13}C$, there is still a great discrepancy between historical evidence and radiocarbon dating for the Roman mortars. The obtained ^{14}C results for the Dead Sea area mortars were far from historical premises, although they revealed some regularity. It must be noted, that the age of the mixture is much more exaggerated then the age obtained for the binder (**Table 1**) confirming the enormous influence of aggregate on the radiocarbon age. The radiocarbon ages of the samples from the medieval castle in Wleń confirm the existing architectural-historical data. Further research will include AMS ^{14}C dating of the binder and charcoal present in mortars allowing a comparison of the results with those obtained by historical and radiocarbon dating methods. Separation of fractions from mortars for dating also seems to be promising (Heinemeier, 1997). The results of ^{14}C dating show that improvement of the binder-aggregate separation process is necessary.

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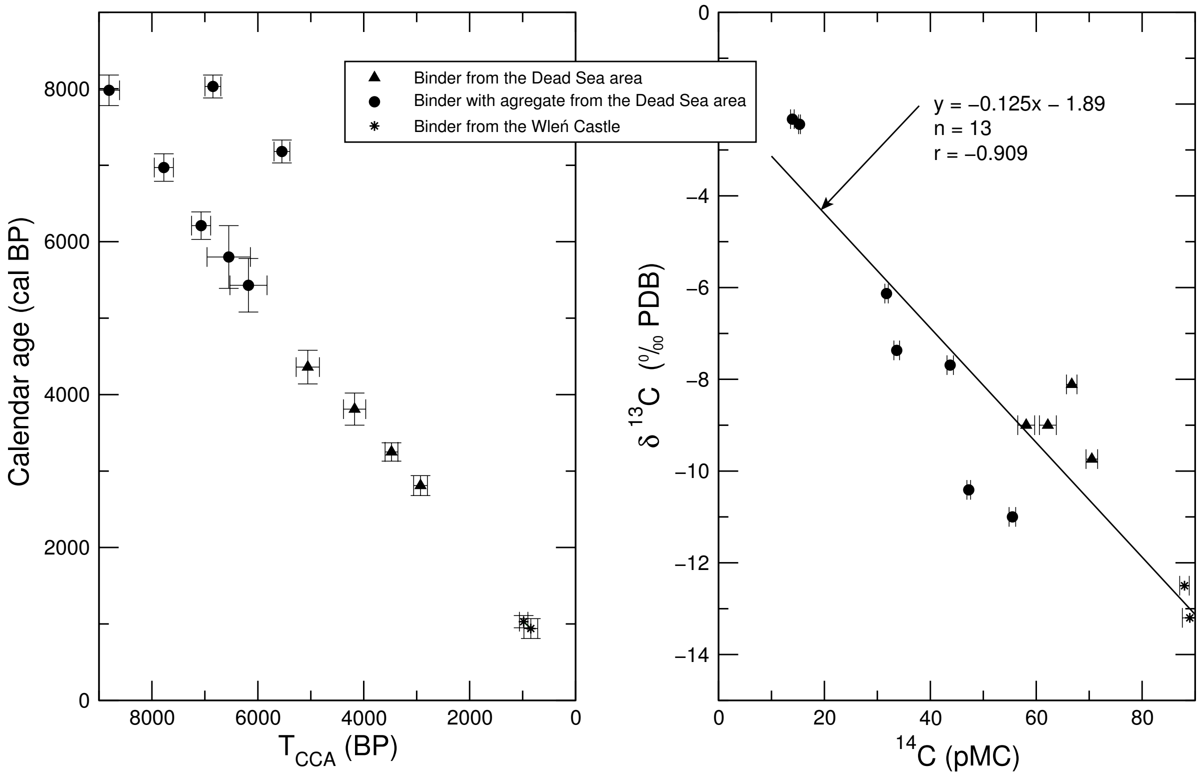

Fig. 5. *^{14}C dating results and $\delta^{13}C$ values for lime mortars from the north-western shore of the Dead Sea area and the Wleń castle in SW part of Poland.T_{CCA} is the conventional radiocarbon age of the binder, obtained after taking into account the correction for the content of „old", radiocarbon-free aggregate in the dated sample made of binder with aggregate. Vertical bars on Calendar age(T_{CCA}) graph are 68.2% confidence level intervals of the calibrated T_{CCA} age. Calibration was performed using the OxCal program and the IntCal98 curve. ^{14}C is the radiocarbon concentration in percent modern carbon (pMC) as measured in the bulk sample.*

Table 1. *^{14}C dating results for lime mortars. Approximate age established by archaeological research for Roman mortars (indicated by letters Q and QA): 140 BC - 68 AD; for Romanesque ones (indicated by letter K): 1177 AD - 1230AD.*

Sample name	**M**	**Lab. code**	**$T_c \pm \Delta T_c$** (BP)	**$\delta^{13}C$** (‰ PDB)	**$T_{cca} \pm \Delta T_{cca}$** (BP)	**Cal age 68.2% conf. intervals** (BC)
Q */1997	S	Gd-18007	3810± 210	(-9)[A]	3810±210	[2495, 1948]
QA /1997	S	Gd-15262	2810± 130	-9.74	2810±130	[1127, 829]
Q 1/2000	S	Gd-15264	4360± 220	(-9)[A]	4360±220	[3356, 2857]
Q 6/2000	S	Gd-15226	3250± 120	-8.11	3250±120	[1642, 1410]
Q 1/2000	SK	Gd-15223	6640± 110	-7.69	6210±180	[5324, 4917]
Q 2/2000	SK	Gd-15225	4730± 90	-11.0[B]	7180±150	[3634, 3555][C]
Q 3/2000	SK	Gd-15228	8750± 130	-7.37	7980±200	[7084, 6638]
Q 4/2000	SK	Gd-12312	6020± 80	-10.41[B]	8030±150	[4998, 4800][C]
Q 5/2000	SK	Gd-11609	15,080± 90	-2.44	5430±350	[4412, 4041]
Q 6/2000	SK	Gd-12313	9220± 80	-6.13	6970±180	[5933, 5719]
Q10/2000	SK	Gd-12304	15,820± 200	-2.33	5800±410	*about.* [4900, 4300]
QR 3/200	K			-0.06		
K 1/93/W	S	Gd-15369	1030± 80	-12.5		[890AD,1050AD] [C]
K160/4/W	S	Gd-17105	940± 130	-13.2		[980AD,1230AD][C]

Explanatory notes:
A = estimated $\delta^{13}C$ values
B = the estimated $\delta^{13}C$ value of the binder (-8.11 ‰) is higher than the $\delta^{13}C$ value of the dated material (binder with aggregate). It resulted in T_{CCA} value higher than T_C;
C = T_C age was calibrated
M = type of dated material
S = binder
SK = binder with aggregate
T_C = Conventional radiocarbon age of the dated mortar fraction (binder or binder with aggregate),
T_{CCA} = Conventional radiocarbon age of the binder, obtained after taking into account the correction for the content of "old", radiocarbon-free aggregate in the dated sample made of binder with aggregate. In case of the binder sample dating, the age is identical with the T_C age
ΔT_C, ΔT_{CCA} = Estimated uncertainties of the given ages
Cal age = Calendar (calibrated) age interval on the confidence level of 68.2% (T_{CCA} was calibrated)
Roman samples from the north-western bank of the Dead Sea, are indicated by letters **Q** and **QA**; Romanesque mortar from the Wleń castle by letter **K**

REFERENCES

Begin Z.B., 1974: *The geological map of Israel 1:50,000. Sheet 9-III: Jericho*. Geological Survey of Israel Mapping Division.

Folk R.L. and Valastro S., 1979: Dating of lime mortar by ^{14}C. In: Berger R. and Suess H., eds, *Radiocarbon Dating: Proceedings of the Ninth International Conference*. University of California Press, Berkeley. 721-730.

Garfunkel Z., 1988: *The pre-Quaternary geology of Israel*. Dr W Junk Publishers. Dordrecht Printed in the Netherlands: 7-21.

Heinemeier J., Jungner H., Lindroos A., Ringbom A., von Konow T. and Rud N., 1997: AMS ^{14}C dating of lime mortar. *Nuclear Insttruments and Methods in Physics Research* B 123: 487-495.

Lubberts R. and Ben-Avraham Z., 2002: Tectonic evolution of the Qumran Basin from figh-resolution 3.3-kHz seismic profiles and its implication for the evolution of the northern Dead Sea Basin. *Tectonophysics* 346: 91-113.

Pazdur A., 1988: The relation between carbon isotope composition and apparent age of freshwater tufaceous sediments. *Radiocarbon* 30(1): 7-18.

Pazdur A., Fogtman M., Michczynski A. and Pawlyta J., 2004: Precision of ^{14}C dating in Gliwice Radiocarbon Laboratory. FIRI Programme. *Geochronometria* 22: 27-40.

Pazdur A., Michczyński A., Pawlyta J. and Spahiu P., 2000: Comparision of the radiocarbon dating methods used in the Gliwice Radiocarbon Laboratory. *Geochronometria* 18: 9-14.

Ramsey C.B., 2002: OxCal Program v3.8 University of Oxford Radiocarbon, Accelerator Unit. http:/www.rlaha.ox.ac.uk/orau/06_01.htm

Roth I., 1974: *The geological map of Israel 1:50,000. Sheet 12-I: Wadi el Qilt*. Geological Survey of Israel.

Sonninen E. and Jungner H., 2001: An improvement in preparation of mortar for radiocarbon dating. *Radiocarbon* 43 (2A): 271-273.

Stuiver M. and Polach H.A., 1977: Reporting of ^{14}C data. *Radiocarbon* 19: 355-363.

Van Strydonck M., Dupas M., Dauchot-Dehon M., Pachiaudi Ch. and Marechal J., 1986: The influence of contaminating carbonate and the variations of $\delta^{13}C$ in mortar dating. *Radiocarbon* 28 (2A): 702-710.

Zouridakis N., Saliege J.F., Person A. and Filippakis S.E., 1987: Radiocarbon dating of mortars from ancient greek palaces. *Archaeometry* 29(1): 60-68.