THE INFLUENCE OF CONTAMINATING (FOSSIL) CARBONATE AND THE VARIATIONS OF $\delta^{13}C$ IN MORTAR DATING

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ABSTRACT. The influence of the aggregate in mortar dating is examined. Sample activity as well as isotopic fractionation approach the expected values at lower yields of the preparation reaction of the counting gas. Good results are obtained at low fossil carbonate concentration. $\delta^{13}C$ cannot give information about this concentration but preliminary visual and chemical analysis of the mortar makes prediction of sample validity possible.

INTRODUCTION

It is well known that ^{14}C dating does not date archaeologic events but only the materials found in an archaeologic context. Thus, there may be an important interval between the age of the material and the archaeologic event. A good example of this is ^{14}C dating wooden beams used in construction. The ^{14}C dated tree rings can easily be a century older than the building, itself. This problem becomes even more severe if we consider re-use of material. This problem can be avoided by using mortar as a dating material.

Traditionally mortars were made essentially of lime and sand. Different limes were used, quicklime and hydraulic lime. Quicklime (CaO) is obtained by burning $(CaCO_3)$ over a fire at ca 1000°C. When water is added it forms $Ca(OH)_2$ and hardens by absorption of atmospheric CO_2. Hydraulic lime is obtained by burning argillaceous limestone. It contains aluminates and silicates which harden with water. Younger mortars tend to be more hydraulic than older mortars. The hydraulic index framed by Leduc and Chenu (1912) provides a useful parameter to classify mortars. This index is defined as

$$\frac{Al_2O_3 + Fe_2O_3 + SiO_2 \text{ soluble}}{CaO + MgO}$$

This is, in fact, the ratio between the clay and the lime fractions. Fat limes have values up to 0.1; values > 0.5 indicate that the material is cement rather than mortar. In between are mortars which are more or less hydraulic. Besides lime, mortars also contain sand and aggregate which are used as charge. Their purpose is to enlarge the volume of the mortar and to avoid cracks.

Several laboratories have been working on mortar dating since 1964. Some obtained very good results (Delibrias & Labeyrie, 1965); others obtained dates that were far too old (Stuiver & Smith, 1965). In summary, we can say that, theoretically, mortars containing lime ought to be ^{14}C datable since hardening time is short compared to the half-life of ^{14}C. How-

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ever, contamination may occur in several ways:

1) limestone must be completely dead-burned before use, otherwise infinite old carbonate from bedrock will falsify the date. Although equilibrium CO_2 pressure of 1 atm is easily obtained in a lime kiln, it takes > 15 hours to calcinate a 20cm carbonate lump;

2) through calcareous sand;

3) through aggregate. This can be any type of material, from reworked bricks and marble to stone waste;

4) running water containing dissolved CO_2 can cause a supplementary deposit on the mortar or an exchange in carbonate ions.

By taking only samples that were not exposed to atmospheric conditions or running water and by eliminating the aggregate as well as possible, samples can be well cleaned. Despite this effort, some contaminating limestone may be present. Studies have shown that it is possible to separate "live" from "dead" carbonate by dating only the first part of the CO_2 obtained by acidification of the mortar. This procedure is based on the difference in appearance between the mortar carbonate and the rock carbonate. The former is fine-grained, powdery, and porous and tends to react more quickly to the acid solution (HCl) than the latter (Folk & Valastro, 1975, 1979; Malone, Valastro & Vazela, 1980). The favorable results obtained by this method are still questionable since the measured $\delta^{13}C$ values were corrected to the $\delta^{13}C$ value for atmospheric CO_2 ($-7‰$). If the correction is made to the standardized $\delta^{13}C$ value of $-25‰$, the age is increased by ca 300 yr (Evin, 1983).

SAMPLES

Six mortars were studied. Two of them were examined on the reproduction of the results.

1) **IRPA-296. Saint-Lambert Cathedral, Liège**

Sample taken from foundation remains, 1.8m below street level (50° 38′ 45″ N, 5° 34′ 30″ E). Archaeol age: 7th–13th century.

2) **IRPA-490. Onze-Lieve-Vrouw Cathedral, Antwerpen**

Sample from brick column embedded in sandstone, 6m above street level (50° 13′ 16″ N, 4° 23′ 60″ E). Archaeol age: AD 1420–1435.

3) **IRPA-496. Heilige-Kruis Church, Vrasene**

Powdery sample from Romanesque bench surrounding a pillar (51° 13′ N, 4° 12′ E). Archaeol age: AD 1150–1183.

4) **IRPA-497. Heilige-Kruis Church, Vrasene**

Sample from lime slaking at street level (51° 13′ N, 4° 12′ E). Archaeol age: ca AD 1350.

5) **IRPA-574, Ly-3175/80. Saint-Jean Church, Lyon**

Sample from pillar foundation; sample divided in two parts (45° 16′ N, 4° 50′ E). Archaeol age: 12th or 13th century.

6) **IRPA-625 (outside), IRPA-626 (inside). Karbonkel House, Antwerpen**

Two samples from brick wall, 3 to 4m above street level. One sample is from front, one from inside house at same level (51° 13′ 16″ N, 4° 23′ 60″ E). Archaeol age: mid-16th century.

TABLE 1

Appearance*

IRPA no.	Color	Homogeneity	Solidity	Nodules	% charge	Preparation
296	Gray-beige	(+)	(+)	(−)	27.1	(−)
490	Pale-beige	+	+	(−)	1.7	(−)
496	Beige	(+)	−	−	7.2	(+)
497	Pale-yellow	−	(−)	+	10.4	(−)
574	Gray	−	(+)	(−)	46.9	−
625	Pale-yellow	+	(+)	(+)	1	+
626	Pale-yellow	+	+	(+)	1	+

*+ = very favorable conditions for sample preparation
(+) = favorable conditions
(−) = unfavorable conditions
− = very unfavorable conditions
Parameters used were color, homogeneity (+ = very homogeneous), solidity (+ = very compact), presence of nodules (+ = absent), % charge by weight, difficulty in sample preparation (+ = easy to prepare).

PROCEDURE

Pretreatment

To obtain a first separation of the live mortar from the rest of the sample, Folk and Valastro (1976) proposed a wet sieving method. In this study an alternative pretreatment was used because a shift in the $\delta^{13}C$ values due to successive wetting and drying periods was feared. The mortar lumps were gently broken with a small hammer. The aggregate grains and questionable elements were removed as completely as possible. The remaining mortar was ground, sieved through a 250μm sieve, and dried.

Chemical Treatment

A small amount of each sample was chemically analyzed by routine methods (Dupas, 1981). The rest was divided into 4 or 5 parts depending upon the amount of mortar available. From each part the CO_2 was released by a standard HCl solution. The reagent was added slowly to the mortar powder, which was held in suspension in CO_2-free water while constantly stirring. The reaction and evacuation of the released CO_2 never took longer than 5–10 min. CO_2 was released completely ($\eta = 100$) from the first part. The amount of acid added to the second part was just enough to release

TABLE 2

Chemical analysis

IRPA no.	CO_2 (%)	$CaCO_3$ (%)	$MgCO_3$ (%)	Water & organic (%)	Insoluble (%)	Hydraulic index
296	19.74	43.97	0.76	2.69	48.90	0.10
490	16.12	35.76	0.76	2.64	47.00	0.32
496	8.02	17.82	0.35	1.52	78.00	0.15
497	30.00	67.50	0.65	2.85	25.10	0.07
574	13.75	30.45	0.69	1.98	62.20	0.12
625	12.09	26.80	0.58	1.71	67.00	0.16
626	12.00	26.70	0.50	2.07	67.60	0.12

TABLE 3

Activity and $\delta^{13}C$

Fraction %CO$_2$	IRPA-296		IRPA-490		IRPA-496		IRPA-497		IRPA-574		Ly-3175/80		IRPA-625		IRPA-626	
	$\frac{A_{ON}}{A_{SN}}$	$\delta^{13}C$ ‰	$\frac{A_{ON}}{A_{SN}}$	$\delta^{13}C$ ‰	$\frac{A_{ON}}{A_{SN}}$	$\delta^{13}C$ ‰	$\frac{A_{ON}}{A_{SN}}$	$\delta^{13}C$ ‰	$\frac{A_{ON}}{A_{SN}}$	$\delta^{13}C$ ‰	$\frac{A_{ON}}{A_{SN}}$	$\delta^{13}C$ ‰	$\frac{A_{ON}}{A_{SN}}$	$\delta^{13}C$ ‰	$\frac{A_{ON}}{A_{SN}}$	$\delta^{13}C$ ‰
10			1.067	−17.1			1.110	−21.0	1.784	−14.53	1.525	−17.0	1.037	−12.38	1.040	−14.9
20	1.332	−20.09	1.087	−13.3	1.220	−19.69	1.116	−21.14	1.809	−11.85	1.506	−16.3	1.053	−11.04	1.039	−14.2
30	1.372	−19.85	1.094	−12.8	1.220	−19.60	1.110	−20.09	1.943	−9.84	1.506	−16.2	1.046	−11.40	1.058	−11.7
43									2.046	−10.48						
47			1.100	−13.0	1.230	−19.60	1.112	−19.1			1.656	−14.0				
50	1.457	−17.83											1.049	−11.72	1.055	−12.8
100	1.677	−16.13	1.133	−12.9	1.222	−20.08	1.115	−18.1	3.294	−5.56	2.218	−11.3	1.063	−9.84	1.055	−12.2

50% of the total CO_2 ($\eta = 50$). For the other parts, the amount of acid was decreased so that only 30% ($\eta = 30$), 20% ($\eta = 20$), and 10% ($\eta = 10$) of the CO_2 was released from the carbonate. The CO_2 was transformed into CH_4 and counted in a proportional counter.

RESULTS

Table 1 provides information on the appearance of the mortar. The results of the chemical analysis are listed in Table 2. The activity of the different fractions, corrected for $\delta^{13}C$ (Stuiver & Polach, 1977) and the $\delta^{13}C$ of each fraction are listed in Table 3.

DISCUSSION

The graphs (Figs 1–8) show that there is no first fraction as suggested by Valastro (Folk & Valastro, 1976). The measured age approaches the archaeologic age more as the yield of the acidification decreases (η). The best fit for the real age is obtained by extrapolation to $\eta = 0$, the theoretical point at which fossil carbonate no longer reacts (Table 4). Not only the activity but also the $\delta^{13}C$ values tend to shift to the theoretical equilibrium atmospheric CO_2 and carbonate.

Close examination of the graphs (Figs 1–8) shows several types of mortars. One group of mortars comes from an alluvial plain (IRPA-490, -496, -497, -625, -626) with a non-calcareous soil. The slope of the activity line is poor, indicating that the separation between fossil and mortar carbonate was not effective or that the quantity of fossil carbonate was very low. The $\delta^{13}C$ curve provides information on this. The measured $\delta^{13}C$ is the weighed mean between fossil and mortar $\delta^{13}C$. The $\delta^{13}C$ of the mortar carbonate is ca −21‰ (Van Strydonck, Dupas & Dauchot-Dehon, 1983), although this value is slightly temperature-dependent. If we consider the evolution of the $\delta^{13}C$ values in IRPA-497 (Fig 6), a decrease from −18.1‰ at $\eta = 100$ to −21‰ at $\eta = 20$ is observed. This indicates a decreasing influence of the fossil carbonate. At $\eta = 20$ the equilibrium $\delta^{13}C$ is reached. IRPA-490 (Fig 4) shows a similar evolution, although even at $\eta = 10$ the equilibrium $\delta^{13}C$ is not yet reached. The kink in the curve can be explained by kinetic effects. Although the phenomena involved with the CO_2 absorption on $Ca(OH)_2$ are not completely understood, a shift in $\delta^{13}C$ is observed as long as the equilibrium $CO_{2atm}/CO_{2carbonate}$ is not attained (Pachiaudi *et al*, 1986). Since the conversion from CaO to $Ca(OH)_2$ provokes the formation of small nodules, we can assume that the surface of these nodules will attain equilibrium conditions more easily than the interior. This can be the $\delta^{13}C$ shift in the left

Fig 2. Relative activity and isotope fractionation IRPA-490

Fig 4. Relative activity and isotope fractionation IRPA-497
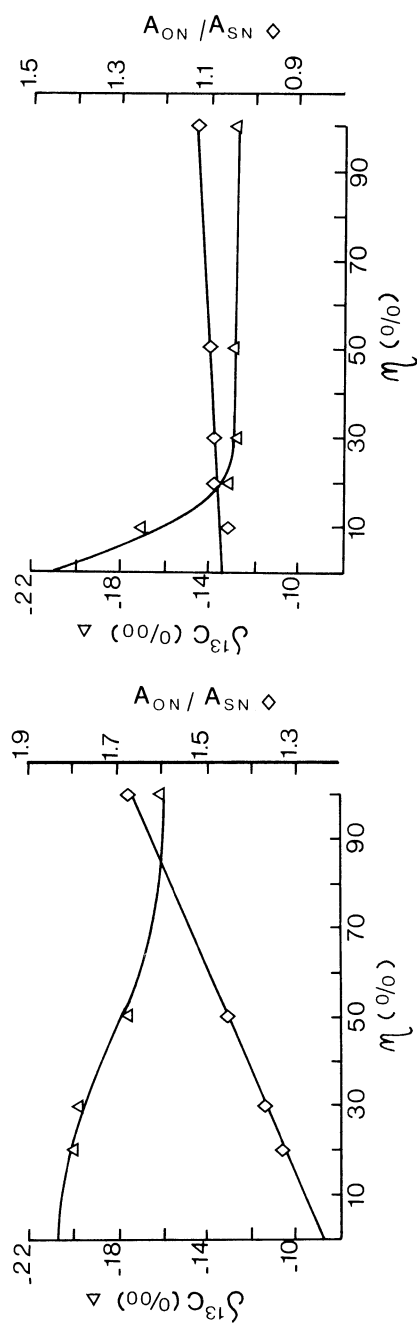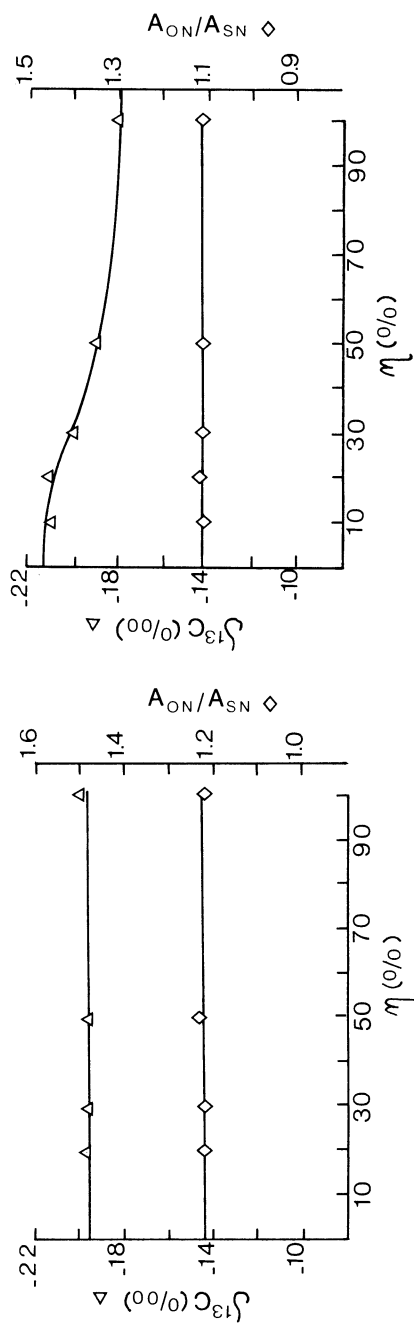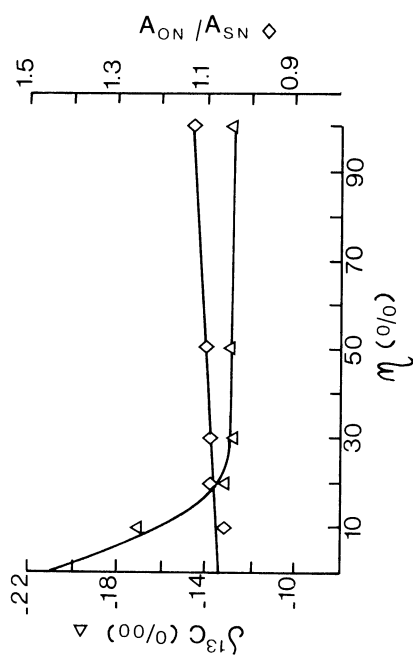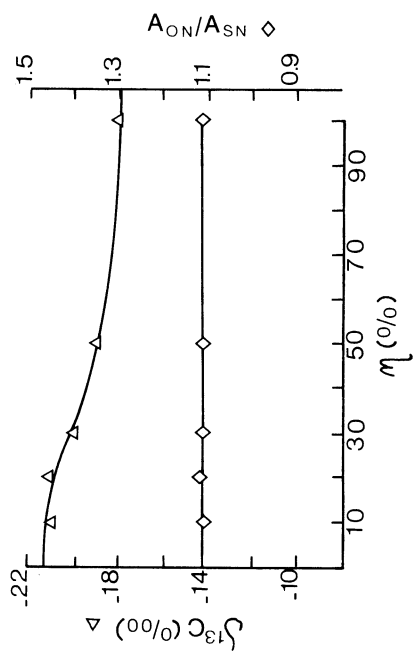

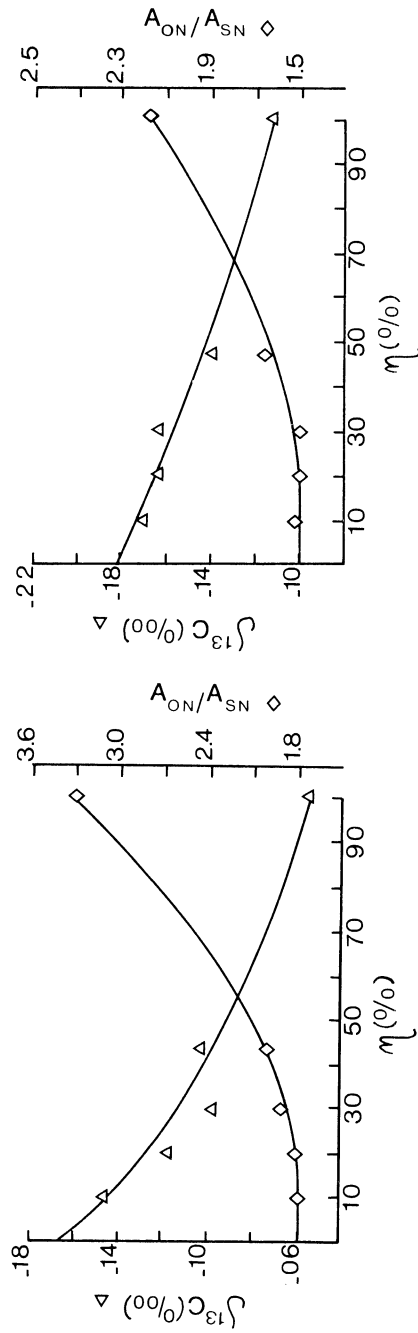
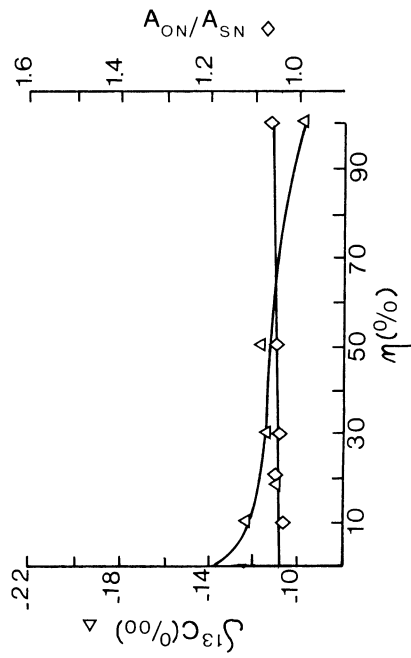Fig 1. Relative activity and isotope fractionation IRPA-296

Fig 3. Relative activity and isotope fractionation IRPA-496

Fig 6. Relative activity and isotope fractionation Ly-3175/80

Fig 8. Relative activity and isotope fractionation IRPA-626

Fig 5. Relative activity and isotope fractionation IRPA-574

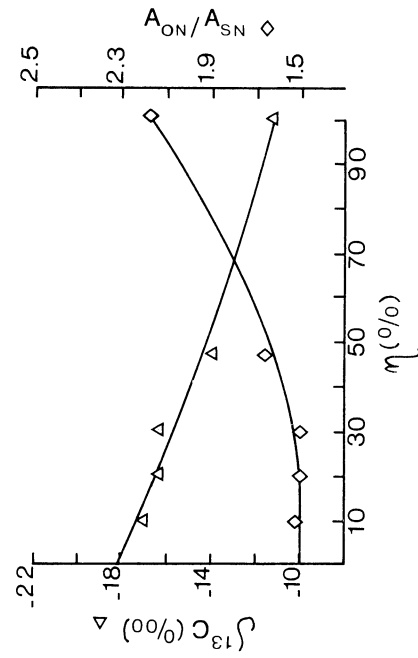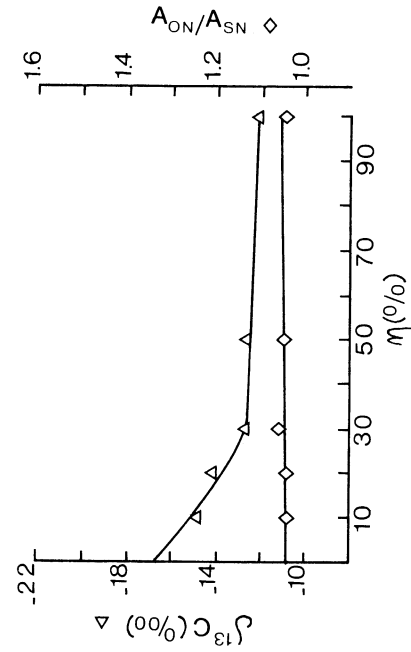Fig 7. Relative activity and isotope fractionation IRPA-625

TABLE 4
Extrapolated results

Sample no.	$\dfrac{A_{ON}}{A_{SN}}$ for $\eta \to 0$	Conventional ^{14}C date (BP)	Calibrated date (AD)	Archaeologic age (AD)
IRPA-296	1.243	1745 ± 50	260– 340	7th–13th century
IRPA-490	1.068	535 ± 50	1410–1420	1420–1435
IRPA-496	1.221	1605 ± 50	425– 435	1150–1183
IRPA-497	1.115	870 ± 50	1160–1210	ca 1350
IRPA-674	1.780	4630 ± 75		12th–13th century
Ly-3175/80	1.500	3260 ± 150		12th–13th century
IRPA-625	1.040	315 ± 50	1520–1540/ 1560–1650	16th century
IRPA-626	1.043	340 ± 50	1490–1540/ 1600–1650	16th century

part of the curve, since the acidification will first attack the surface of the nodules. This effect suggests that the δ^{13}C value for the entire sample ($\eta = 100$) cannot be a parameter for contamination by fossil carbonate, as has already been noticed by Baxter and Walton (1970) and Stuiver and Waldren (1975).

IRPA-496 (Fig 5) shows the opposite situation. No kinetic effects nor separation between fossil carbonate and mortar carbonate are shown. This can be explained by the very powdery mortar. In this case an equilibrium situation was assumed and the δ^{13}C can be used as a parameter for contamination (Marien & Pachiaudi, 1975).

$$(\delta^{13}C)_{measured} = \frac{\alpha}{100} (\delta^{13}C)^{live}_{carbonate} + \frac{100-\alpha}{100} (\delta^{13}C)^{dead}_{carbonate}$$

since

$$(\delta^{13}C)^{live}_{carbonate} = -21.31‰ \text{ (measured on lab-made lime)}$$

$$(\delta^{13}C)^{dead}_{carbonate} = 0‰ \text{ (measured on Belgian calcareous stone)}$$

$$\alpha = \% \text{ of live carbonate}$$

we have

$$\alpha = \frac{100(\delta^{13}C)_{measured}}{-21.31‰}.$$

The activity of a mortar sample is given by

$$A_{mortar} = \frac{\alpha}{100} A^{live}_{carbonate} + \frac{100-\alpha}{100} A^{dead}_{carbonate}$$

since

$$A^{dead}_{carbonate} = 0$$

$$A^{live}_{carbonate} = \frac{100}{\alpha} A_{mortar}$$

The normalized sample activity is defined by

$$A_{SN} = A_S \left[1 - \frac{2(25 + \delta^{13}C)}{1000} \right]$$

$$A^{live}_{carbonate\ N} = A^{live}_{carbonate} \left[1 - \frac{2(25 - 21.31)}{1000} \right]$$

$$A^{live}_{carbonate\ N} = \frac{100}{\alpha} A_{mortar} \left[1 - \frac{2(25 - 21.31)}{1000} \right]$$

A feasible age can be calculated by this method (Table 5).

IRPA-625 and -626 (Figs 7, 8) show that with this type of mortar a good reproduction can be achieved.

The second series of mortars (IRPA-296, -574, Ly-3175/80) is highly contaminated by fossil carbonate. Although the steep slope of the activity line (Figs 1, 5, 6) shows an important reduction of fossil carbonate, the complete separation is not attained. The quantity of fossil carbonate is so important that the difference in reaction rate for the HCl attack is not sufficient. For IRPA-574, even a concentration of ca 66% fossil carbonate in the pretreated sample was calculated. From the chemical analyses we can deduce that in this sample 2.28% of the lime is not transformed in carbonate. This can be explained by the fact that hardening and compression of the mortar makes it completely impervious to air. This already observed phenomenon (Sonninen, Jungner & Erametsa, ms) justifies the supposition that in less compact mortars the isotopic equilibrium air/mortar has not been reached, although no free $Ca(OH)_2$ can be demonstrated. The strong inhomogeneity of the sample (IRPA-574, Ly-3175/80) makes the results irreproducible (Figs 7, 8).

CONCLUSION

The mortars in this study were not very old. This makes the slightest discrepancy between the archaeologic and the ^{14}C age visible, but also raises

TABLE 5
Calculated mean IRPA-496

η	$\dfrac{A_{ON}}{A_{SN}}$	^{13}C measured ‰	$\dfrac{A_{ON}}{A_S}$	α	$\dfrac{A_{ON}}{A_{live\ carbonate\ N}}$
100	1.222	−20.08	1.2101	94.22	1.2486
50	1.230	−19.60	1.2166	91.98	1.1273
30	1.220	−19.60	1.2066	91.98	1.1181
20	1.220	−19.69	1.2068	92.40	1.1234

Mean	1.1294 ± 0.012
^{14}C age	980 ± 85 BP
Calibrated age	AD 1030 ± 90

the relative error. The measurements show that in regions where no limestone is available, mortar dating is quite possible. Dating only one fraction is in most cases insufficient.

Since the method is very elaborate, sample selection is necessary. The data on the nature of the mortar given by the mortar-analyst, combined with information on environmental conditions of construction will make it possible to predict whether a mortar sample is suitable for ^{14}C dating.

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