

VII. APPLICATIONS IN ARCHAEOLOGY

**ISOTOPIC FRACTIONATION OF CARBON DURING CO₂
ABSORPTION BY MORTAR**

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INTRODUCTION

Recent studies comparing dates from the carbon content of mortars with dendrochronologic dates for the same material have shown considerable inconsistencies related to mortar type (Van Strydonck *et al.*, 1985). Even after the best possible removal of "dead" calcite, some mortars are unsuitable for dating. We describe here our experimental study of carbon isotope fractionation during the manufacture and hardening of mortars. Preliminary experiments established overall uptake of CO₂ from the air. We then measured isotopic ratios in identical mortars at different hardening times.

PRELIMINARY TRIALS

Different quantities of CaO were exposed to the laboratory atmosphere in 100ml Erlenmeyer flasks. Absorbed CO₂ was measured after 24-hour exposure. We ascertained that the amount of CO₂ absorbed per gram of CaO diminishes with increasing weight of CaO for a constant exposed surface. This effect is still observed if the exposure time is increased to 48 hours. In a second series of experiments, constant amounts of CaO were exposed to the outdoor atmosphere in an agricultural region on a raised platform 1.5m above ground and protected from prevailing winds and direct sunlight. The samples were in beakers of three sizes and were sampled at 24 hr, 4 days, 15 days, 4 weeks, and 7 weeks after addition of air-equilibrated demineralized water at time 0. We noted considerable variation in the absorption of atmospheric CO₂, probably due to uncontrollable atmospheric effects (weather conditions, humidity, etc). Also, the layers at the bottom of the beakers were never truly uniform.

Figure 1A shows a rapid initial absorption of CO₂ followed by a slower uptake after ca 2 weeks; even after 7 weeks, we found that only 48% of the initial CaO had been transformed into carbonate. Figure 1B shows the isotopic ratio of carbon in the specimens as a function of time. Strong fluctuations in the isotopic ratio can be seen at early times, and isotopic fractionation from the atmospheric value is evident. A "surface effect" would appear to influence the value of the isotopic ratio. At present, we are unable to explain the strongly negative values of the isotopic ratio, but a detailed study of the surface conditions may provide an explanation.

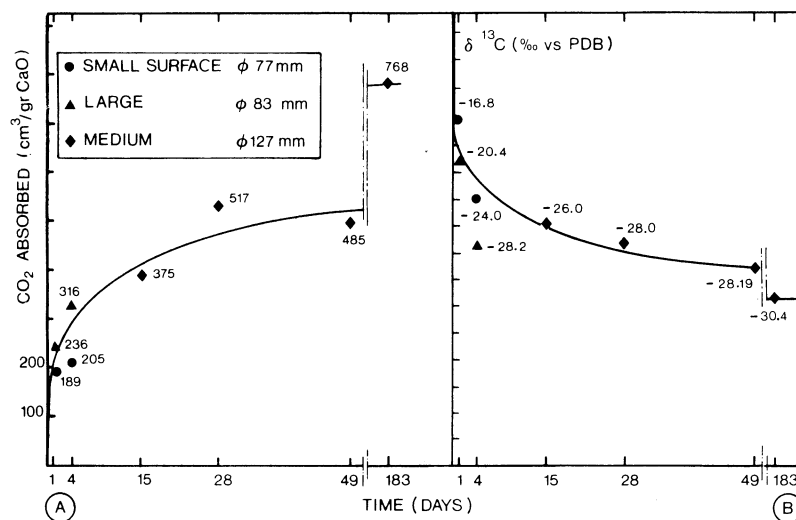


Fig 1A. CO₂ absorbed in open air at different times

Fig 1B. Isotopic ratio variation of the whole CaCO₃ formed by CO₂ absorption on CaO in open air at different times

EXPERIMENTAL PROCEDURES

To standardize surface conditions and thickness, the following experiments were performed in identical pots. Mortars were prepared as presented in Table 1. We call "charge" the part of sand or old calcite or aggregate mixed with quick lime and water to compose the mortar.

In all cases, the quantity of CaO used was 20mg. The pots were placed in a closed reactor (Fig 2) which was evacuated, and then connected to a reservoir containing 10 vol of nitrogen, oxygen, and carbon dioxide mixture of atmospheric composition. The carbon dioxide had a δ¹³C close to that of natural air, in this case, -8.20‰. The pressure was adjusted to 1atm in the reactor-reservoir assembly. At this point, slightly more than the stoichiometric quantity of water was introduced into each pot, and the reaction was allowed to proceed to the predetermined time. Duplicate samples were taken at 24 hr, 48 hr, 7 days, 1 month, and 2 months. Mass spectrometric measurements of the CO₂ liberated by acid treatment of each whole specimen are shown in Table 2. Values are the means of the duplicate specimens.

RESULTS

Nature of the Charge

The isotopic ratios of the mortars are shown in Figure 3 as a function of the nature of the charge and of exposure time.

The charge, even one of non-calcitic nature, perturbs and slows down the absorption of CO₂ by the lime. When the charge is pure calcite with δ¹³C = 0.40‰, it may be calculated that the carbonate formed from the lime after 2 months still has not attained a steady isotopic composition. In

TABLE 1
 Preparation of mortars

CaO (%)	Charge (%)	
	Sand	Calcite*
100		
50	50	
50		50
98		
90		2
80		10
50		20
50		50
40		60

* $\delta^{13}\text{C}$ (calcite) = + 0.40‰ (vs PDB).

** Equal quantities of sand and calcite

 TABLE 2
 $\delta^{13}\text{C}$ (‰) results of "mortars" produced in the laboratory (Fig 2) with various types of charge and reaction times

	24 hr		48 hr		7 days		30 days		60 days	
	% charge	‰	% charge	‰	% charge	‰	% charge	‰	% charge	‰
0		-20.87	0	-18.89	0	-21.16	0	-20.64	0	-20.64
Mix 3.3	Mix 2.4	-20.57	Mix 3.3	-16.69	Mix 3.3	-17.38	Mix 2.9	-16.78	Mix 2	-19.6
Mix 10.3	Mix 9.3	-15.4	Mix 8.9	-10.53	Mix 8.9	-15.72	Mix 9.7	-17.46	Mix 8.9	-17.03
Mix 16.5	Mix 16.8	-14.28	Mix 16.3	-10.95	Mix 16.3	-13.17	Mix 16.7	-16.27	Mix 16.7	-12.60
Mix 48.5	Mix 50	-7.36	Mix 46.8	-4.71	Mix 46.8	-8.0	—	—	Mix 49.5	-9.47
Mix 59	Mix 51.4	-3.43	Mix 58.5	-3.91	Mix 58.5	-6.62	Mix 41.3	-9.97	Mix 59.3	-7.32
Calc 48.2	Calc 51.5	-7.13	Calc 50.8	-8.13	Calc 50.8	-4.40	Calc 50.5	-2.97	Calc 50.4	-3.4
Sand 51.7	Sand 40.4	-19.6	Sand 47.8	-16.9	Sand 47.8	-18.89	Sand 50.7	-21.8	Sand 49.5	-19.0

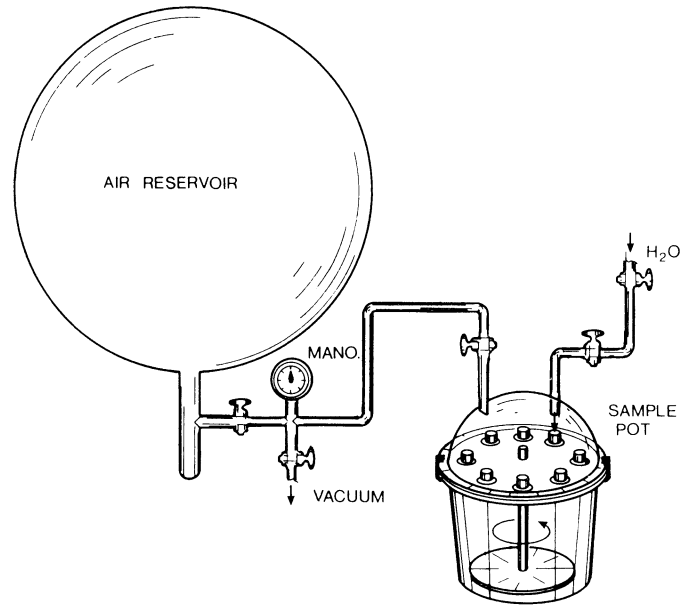


Fig 2. Experimental design

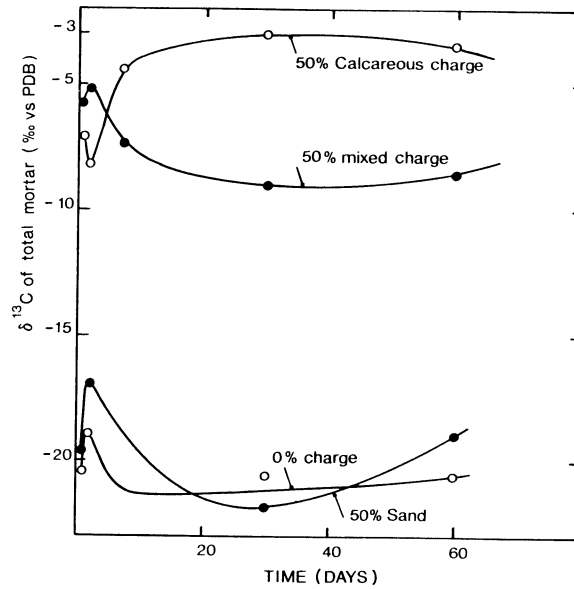


Fig 3. Isotopic ratio variation of total mortar as a function of charge type

this case, not only is the absorption slowed, but a steady state in the isotopic composition is prevented.

Quantity of the Charge

Figure 4 shows the variation in the isotopic ratio as a function of the amount of charge at fixed times of exposure. These curves might be expected to be linear, but, in fact, we observed that the quantity of carbonate formed from the lime, as estimated from its contribution to the isotopic ratio, diminishes as the amount of charge increases. This is confirmed by the yields of CO₂ obtained on acid treatment. The greater the quantity of charge, the more the absorption of CO₂ is retarded.

Time

Figure 5 shows the isotopic variation of the total carbon from mortars of the same composition exposed for different intervals. Fractionation varies considerably over the first 48 hours; similar variation is seen for the pure CaO sample over the first 24 hours. This series of similar curves show that the fluctuations are more marked in samples containing larger amounts of charge. Since transformation of the lime to carbonate is incomplete even after 2 months, we would expect the curves to decline to more negative $\delta^{13}\text{C}$ with increasing time as the CaCO₃ derived from the lime will contribute progressively to the total value. If we subtract the contribution of the added calcite, we obtain a series of curves similar to that obtained for

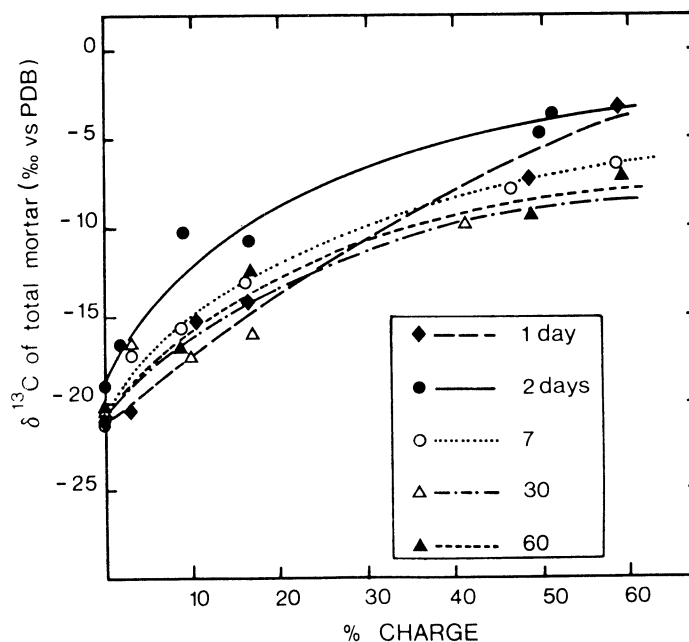


Fig 4. Isotopic ratio variation of total mortar as a function of charge percentage

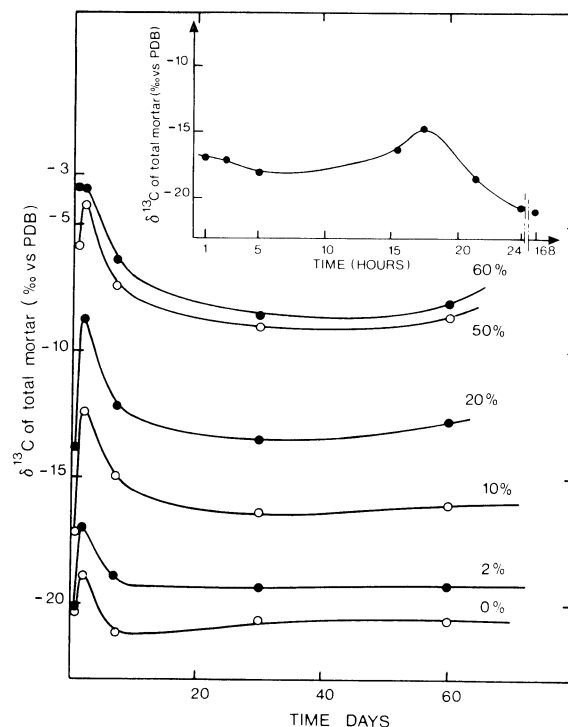


Fig 5. Isotopic ratio variation of total mortar as a function of time with different quantities of charge

pure lime, but the fluctuation of the values around the mean varies according to the amount of charge added.

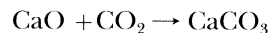
Exact calculations using the volume of CO_2 obtained on acid treatment of the total mortar and on the charge alone allow us to estimate $\delta^{13}\text{C}$ for the carbonate derived from the lime. If we assume that the $\delta^{13}\text{C}$ for the ancient calcite of the charge is 0.40‰ , *ie*, that no exchange between the atmosphere and the calcite has occurred, we obtain -21.7‰ for the newly formed carbonate. After a certain time, the measurement appears to oscillate around this value.

If we calculate the fractionation factor between the newly formed CaCO_3 in mortar and atmospheric CO_2 ($\delta^{13}\text{C} = -8.2\text{‰}$), assuming that the value of -21.7‰ represents the isotopic value for the mortar in free contact with air, we obtain $K = 1.0139$. Craig (1953) gives a value of 1.012 at 298°K and 1.016 at 273°K . Our $\delta^{13}\text{C}$ of -21.7‰ is close to -21‰ (Ergin, Harkness & Walton, 1970; Van Strydonck *et al*, 1986) for mortars formed in air containing CO_2 of $\delta^{13}\text{C} = -7\text{‰}$ *vs* PDB.

CONCLUSIONS

This preliminary study indicates that in the exceptionally favorable case of mortar containing a rather compact mixed charge laid thinly and

well exposed during hardening, the carbonate formed in mortar from the lime will have an isotopic value corresponding to the kinetic fractionation of the complete reaction



with CO₂ of free air. In this case, dating may be possible. It is known that ancient mortar often contains untransformed CaO (Sonninen, Jungner & Erametsa, 1984) but our experiments show that even under these conditions, the same δ value as with total carbonatation of CaO may be attained. This appears to depend on the nature and quantity of the charge, grain size and the compaction of the mortar. As yet, we have no results for other types of mortar, or for longer exposure times, or along a core in mortar, but our studies may help select types of mortars useful for dating.

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