AMS ^{14}C DATING OF BALEARIC LIME BURIALS

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ABSTRACT. The Balearic quicklime burials of the Iron Age have been radiocarbon dated. Because the bones found are unsuitable for dating, lime was dated using the titration method, with results indicating that in some samples there is still fossil limestone carbonate present, while other samples suffered from recarbonation. Nevertheless, ^{14}C dates on lime and organic matter agree when both are present. The titration method allows calculating a consensus value.

INTRODUCTION

Lime Burials

The Balearic Islands (Mallorca and Menorca, Spain; see Figure 1) are the only place in the Mediterranean region where during the Iron Age people were systematically buried in quicklime (CaO). This practice was very common during the Balearic Iron Age (Stuiver and Waldren 1975; Van Strydonck and Waldren 1990, 1995), although it is still debated whether this rite started early or later in the Iron Age (Micó Pérez 2005; Micó 2006). Given that these kinds of deposits are often found in natural caves or rockshelters and thus are not very visible, some are not catalogued as archaeological sites, but the presence of about a hundred of these deposits can be estimated for Mallorca and Menorca. This burial practice lasted until the early Roman occupation, but its origin is unknown.
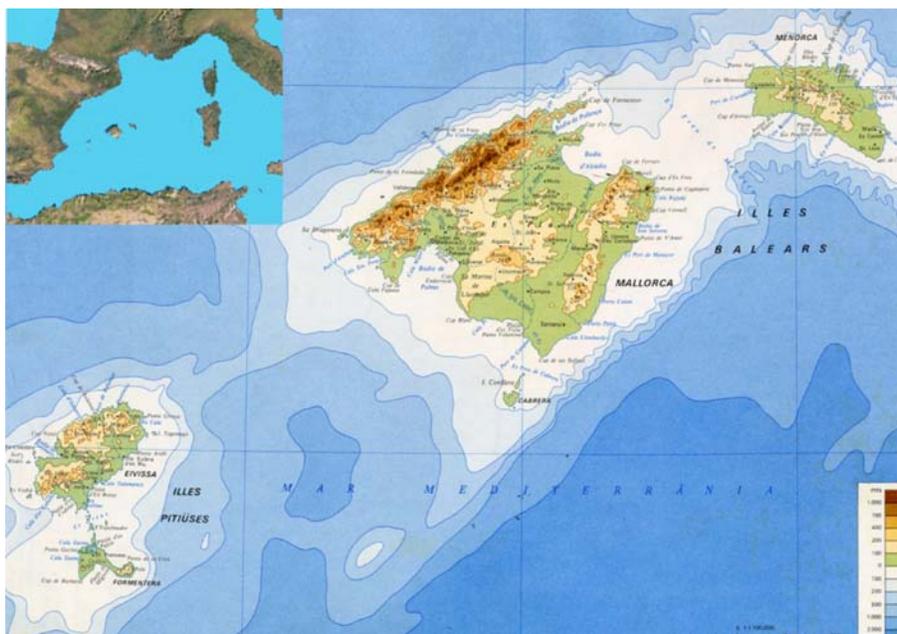

Figure 1 The Balearic Islands

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Some of the bones found are very white and well calcined, while others are black. Bone fragments are found very disorderly (Figure 2), out of any anatomical order in the lime conglomerate, as are the artifacts (offerings and personal objects like hair pieces). The lime conglomerate can be very dense or cinder-like, similar to popcorn. The lime burials can be very large, containing up to 480 m³ of lime mixed with bone fragments and artifacts (Waldren and Van Strydonck 1995).
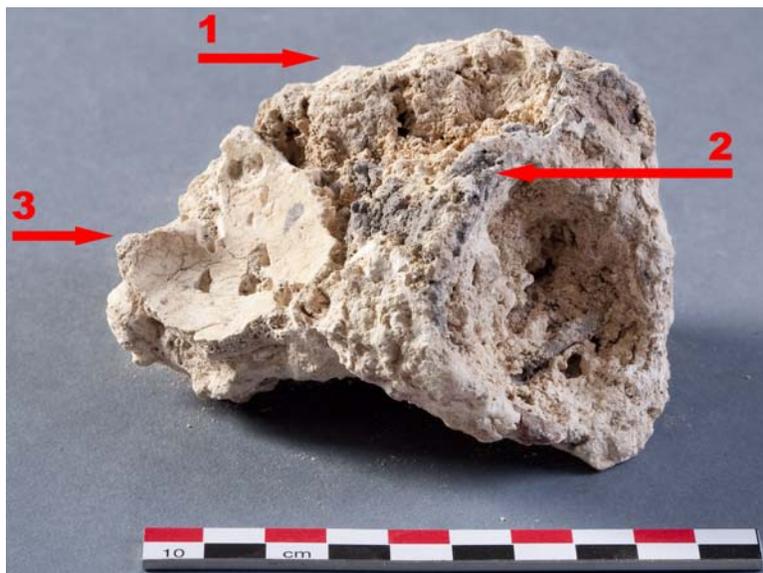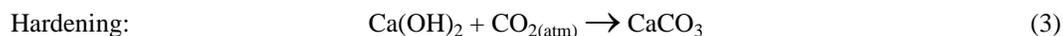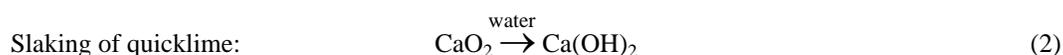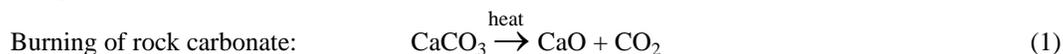

Figure 2 Muertos Gallard: 1) lime; 2) iron hair piece; and 3) part of a skull

Bone analyses have shown that the burial ritual consisted of a cremation of the body in contact with limestone. During this process, the limestone was burnt and transformed into quicklime (see reaction 1, below). The limestone must have been crushed because the temperature and the time needed to decompose limestone lumps is too high and too long for a normal pyre using wood as fuel (Stuiver and Smith 1965). The cremation of the bodies in contact with crushed limestone and its transformation into quicklime must have been a very elaborate task involving the consumption of a lot of firewood. Not much is known about the funeral rites that go along with this practice. It is also not clear how the quicklime was slaked (reaction 2). It is possible that this happened under natural conditions due to rainwater and dew, but it is also possible that the bones and lime were washed out of the ashes of the pyre. This could explain why hardly any charcoal is found in the lime burials except in some lenses (Waldren 1982).

Burning of rock carbonate: $\qquad CaCO_3 \xrightarrow{\text{heat}} CaO + CO_2$ (1)

Slaking of quicklime: $\qquad CaO_2 \xrightarrow{\text{water}} Ca(OH)_2$ (2)

Hardening: $\qquad Ca(OH)_2 + CO_{2(atm)} \longrightarrow CaCO_3$ (3)

Why people undertook this very complex burial rite is unknown, but the idea that it is a purification rite seems possible. Although it would not be the purification or cleaning of the burial site as has been suggested (Piga et al. 2010), but the purification of the body itself. It must be noted here that during the ritual the brown-grayish rock powder becomes bright white.

[14]C Dating of Lime Burials

The quicklime used in the burials hardens by the reaction with atmospheric CO_2 (reaction 3). If this process is relatively fast, then the ^{14}C of the carbonate in the burial reflects the atmospheric ^{14}C at the time of the funeral. Based on this assumption, Stuiver and Waldren (1975) tested some samples, but they did not consider an incomplete outgassing of the limestone (incomplete reaction 1). However, it is obvious that the ^{14}C date obtained in this way can only be valid when all carbon comes from reaction 3 and that reaction 1 was complete. Van Strydonck and Waldren (1990) measured different fractions of the same carbonate sample to identify the presence of fossil carbonate due to an incomplete outgassing (reaction 1). Unfortunately, both studies were carried out before accelerator mass spectrometry (AMS) became routinely available. The large amount of material needed to perform the tests made it very difficult to collect pure and uniform samples for β-counting analysis because lime burials are an intimate mixture of lime carbonate, rock carbonate, soil, bones, and artifacts (see Figure 2). In this study, only small homogeneous samples were analyzed and dated by AMS in order to understand the mechanism involved in the carbonate formation and to determine whether or not lime burials can be dated.

MATERIALS AND METHODS

Carbonates

In terms of their chemical behavior and composition, the lime from the quicklime burials resembles non-hydraulic lime mortars. Thus, the same ^{14}C sample preparation techniques can be used. The most important difference between both materials is that the lime fraction in the burials does not hold any carbon-containing aggregates such as sands, reworked mortar, organic material, etc., and thus can be separated well from the bones and the artifacts. The carbonate in the lime burial can originate from 3 sources: an incomplete reaction 1; CO_2 from the atmosphere (reaction 3); and from recarbonation and exchange with the environment after reaction 3 was completed.

From a small lump of lime burial material, a lime sample was taken based on its homogeneity in color and texture. The sample was dried, crushed, and sieved with a 250-μm sieve. Four successive CO_2 fractions were obtained by the titration method or sequential dissolution (Van Strydonck et al. 1982–1983). The lime sample was kept in suspension while distinct amounts of HCl (1.5%) were added. HCl was used as a reacting agent because complex equilibrium reactions can occur using phosphoric acid (3 dissociation constants). It was assumed, similar to the mortar dating method, that the acid reacts first with the softer anthropogenic-formed carbonate (reaction 3) and later with the harder remaining rock carbonate.

The obtained CO_2 was cleaned by heating for 30 min at 1000 °C in the presence of Ag and CuO, followed by an extra cleaning with $KMnO_4$. Part of the CO_2 was transformed into graphite (Van Strydonck and Van der Borg 1990–1991) and AMS dated (Nadeau et al. 1998); from the remaining CO_2 the $\delta^{13}C$ was measured using a Finnigan MAT mass spectrometer. The amount of carbon in the lime sample was calculated by comparing the weight of the dry sample with the volume of the released CO_2, measured in a calibrated volume under standard conditions, and recalculated to % by weight.

Charcoal and Carbon Black

Charcoal samples and 1 black bone were pretreated using the AAA method (1% HCl, 1% NaOH, 1% HCl–hot) to remove all carbonate, including bioapatite carbonate, and humic acids. The residual carbon was dated by AMS.

Samples

Samples were obtained from quicklime burials of the Son Matge and Muertos Gallard rockshelters on the island of Mallorca (Deià Archaeological Museum and Research Center) and from Binigaus and Sant Joan de Misa (Museu de Menorca, Maó) on the island of Menorca. One sample (Son Oms) does not come from a lime burial but from a *talayot* (a cone-shaped building) (re)used as a granary. The building was destroyed by a heavy fire and part of the cyclopic limestone walls transformed into quicklime (Figure 3) (L Plantalamor-Massanet, personal communication, 2010). The studied sample contained a large potsherd.
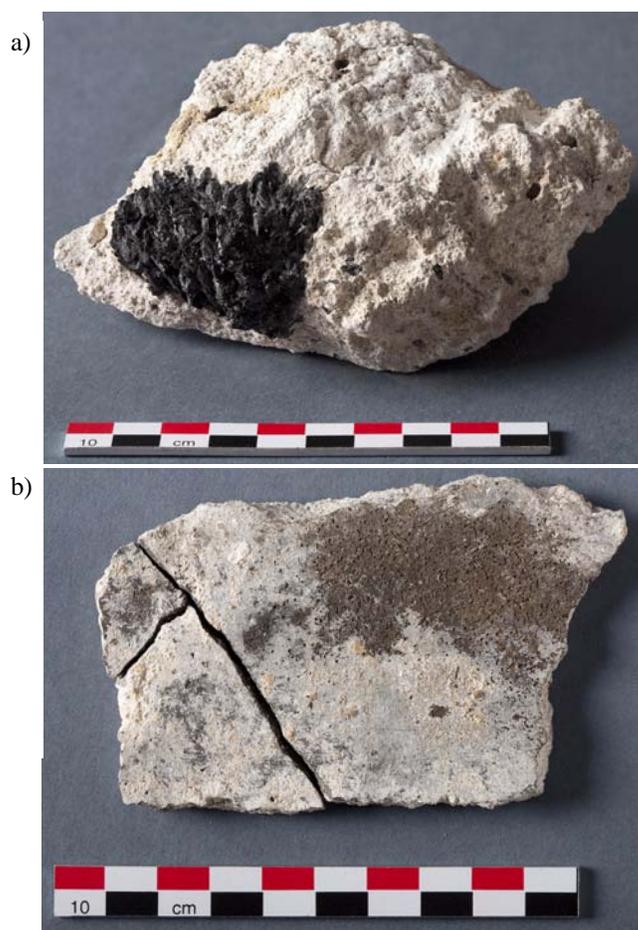

Figure 3 Son Oms: a) lime from the destroyed Talayotic wall and charred grain; b) a sherd found inside the lime lump.

RESULTS

All results are summarized in Table 1. The carbon content of the samples varied between 8.4% and 10.7%. If possible, the carbonate dates were compared with dates obtained on charcoal found in the lime. Since the entire process is basically a cremation rite, an old-wood effect was ruled out. Anthropological information as well as some rear representations and anthracological investigation have demonstrated that old wood was not commonly used for this practice (Van Strydonck et al. 2010).

Table 1 ^{14}C and stable isotope results.

Sample	Fraction	% sample	Lab code (KIA-)	^{14}C age (BP)	δ^{13}C (‰)
Binigaus – Menorca					
Lime burial in rockshelter. Carbon sample ratio: 10.7% C					
Carbonate	1	21	41178	2100 ± 25	–16.42
Carbonate	2	17	40435	2120 ± 35	–14.48
Carbonate	3	28	40436	2095 ± 30	–16.55
Carbonate	4	35	40437	2105 ± 30	–16.06
Muertos Gallard (lime pit) – Mallorca					
Lime burial in rockshelter. Carbon sample ratio: 11.5% C					
Carbonate	1	25	43622	2175 ± 30	–16.39
Carbonate	2	30	43623	2220 ± 30	–16.36
Carbonate	3	28	43624	2065 ± 30	–16.65
Carbonate	4	17	43625	2030 ± 30	–18.08
Muertos Gallard (skull and hair band) – Mallorca					
Lime burial in rockshelter. Carbon sample ratio: 10.7% C					
Carbonate	1	29	43538	2305 ± 25	–22.11
Carbonate	2	28	43539	2335 ± 25	–23.60
Carbonate	3	27	43540	2355 ± 25	–24.51
Carbonate	4	16	43541	2280 ± 20	–26.58
Son Matge (ref. 2200–2204) – Mallorca					
Lime burial in rockshelter. Carbon sample ratio: 9.7% C					
Carbonate	1	34	44317	2495 ± 25	–23.30
Carbonate	2	24	44318	2455 ± 25	–27.00
Carbonate	3	20	44319	2410 ± 25	–25.80
Carbonate	4	22	44320	2420 ± 30	–25.10
Carbon black from burnt bone			45373	2580 ± 30	
Son Matge (outside Talayotic wall) – Mallorca					
Lime burial in rockshelter. Carbon sample ratio: 10.7% C					
Carbonate	1	19	44826	2160 ± 25	–16.70
Carbonate	2	24	44827	2360 ± 25	–16.40
Carbonate	3	29	44828	2545 ± 25	–15.90
Carbonate	4	28	44829	2510 ± 30	–16.60
Sant Joan de Misa – Menorca					
Lime burial in rockshelter. Carbon sample ratio: 10.6% C					
Carbonate	1	31	42762	2305 ± 30	–23.58
Carbonate	2	27	42763	2645 ± 30	–23.17
Carbonate	3	18	42764	2785 ± 30	–22.96
Carbonate	4	24	42765	3195 ± 30	–20.87
Charcoal			42767	2215 ± 30	
Son Oms – Mallorca					
Talayotic tower. Carbon sample ratio: 8.4% C					
Carbonate	1	23	42757	3025 ± 30	–15.07
Carbonate	2	27	42758	3330 ± 30	–14.95
Carbonate	3	26	42759	4020 ± 40	–15.07
Carbonate	4	23	42760	6900 ± 45	–12.56
Charred grain			42761	2450 ± 30	

Samples without Fossil Carbonate

Binigaus

Statistically, the 4 Binigaus samples have the same age (Figure 4). According to Heinemeier et al. (2010), this is a criterion 1 sample since the 2 first fractions have the same age.
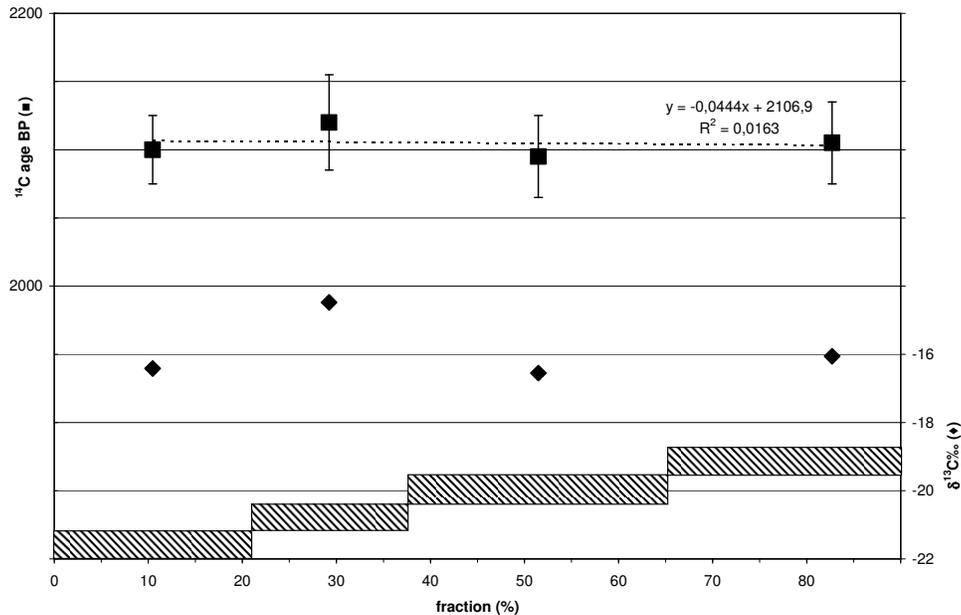

Figure 4 The 4 dated fractions from Binigaus

Samples with Fossil Carbonate

Sant Joan de Misa

The sample contains a relatively important fraction of limestone carbonate. If one considers the charcoal age to represent the real age of the lime production, then there is still 5.7% fossil carbon in the sample. Previously, it was postulated that the result that approaches most closely the real age is obtained by extrapolating the regression towards the 0% fraction point (Van Strydonck et al. 1982–1983). An exponential extrapolation seems to give the best result (charcoal = 2215 ± 30 BP, regression = 2156 ± 30 BP). Both results can represent the same true age [χ^2 test: $df = 1$, $t = 1.7(5\%$ 3.8)].

Son Oms

The age of the charred grain found in Son Oms is representative for the destruction of the building. All the carbon in the grain comes from 1 growth season and the grain was only stored for a short time before consumption. Uncharred grain does not survive for a long time; furthermore, the large quantities found in the building demonstrate that we are not dealing with small remnants from an earlier use. The sample contains an important fraction of limestone carbonate. If one considers the age of the charred grain to give the real age of lime production, then there is still 19.2% fossil carbon in the sample. In contrast to the other samples, the lime from Son Oms does not come from a lime
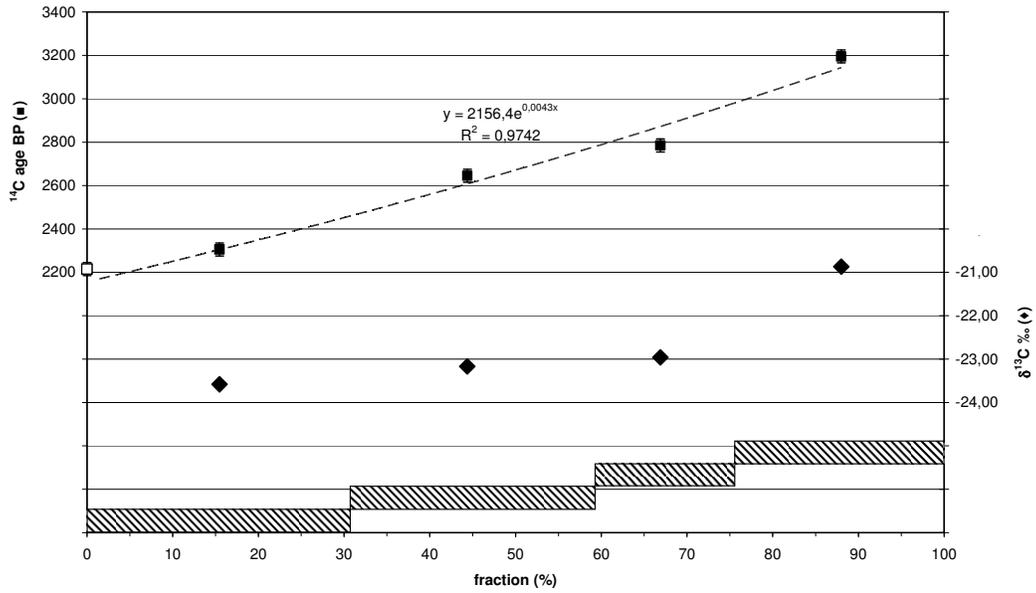
Figure 5 The 4 dated lime fractions (filled squares) and a charcoal (empty square) inclusion from Sant Joan de Misa

burial, but from a limestone building that was set on fire. In spite of the large amount of limestone in the sample, the charred grain date (2450 ± 30 BP) is in agreement with the extrapolation of the lime dates (2440 ± 30 BP) [χ^2 test: $df = 1$, $t = 0.1$(5% 3.8)].
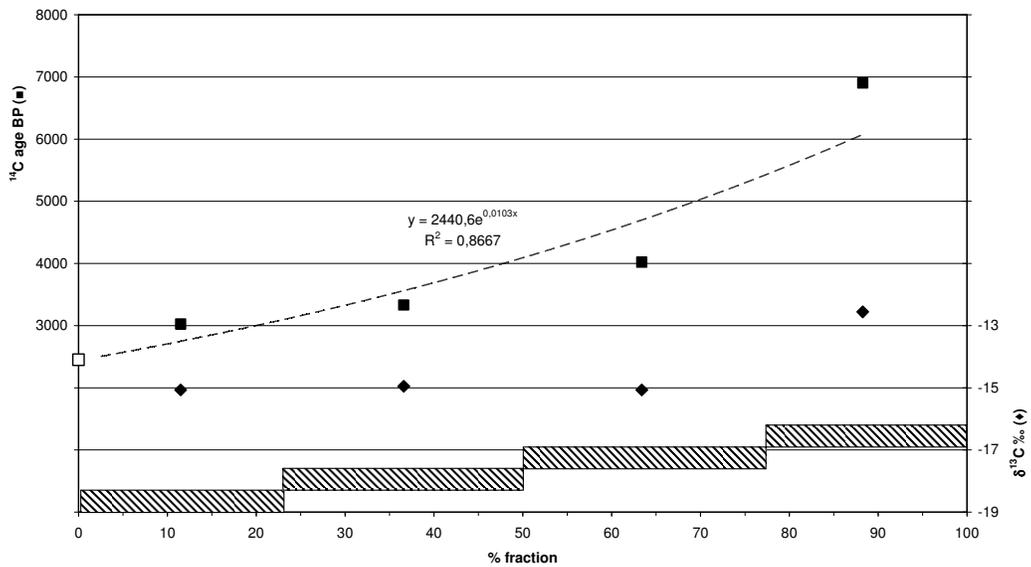

Figure 6 The 4 dated lime fractions (filled squares) and charred grain (empty square) from Son Oms

Samples Showing Recarbonation

Muertos Gallard (Lime Pit)

At the right-hand side of Figure 7 (fraction 4), where one expects to find the hardest material that reacts slower than the anthropogenic lime, a younger date, not an older date, is found. Although this seems to contradict what is expected, this situation is similar to what was previously obtained by β-counting (Van Strydonck and Waldren 1990). This must be due to recarbonation. Waldren (1982: 180) notes that "...the conglomerate was exposed to the weather, the lime matrix was hard as limestone; a condition of weathering which seems independent of whether or not deep underlying strata existed." Furthermore, it is known that the uppermost layer of plasters applied on walls in very humid rooms tends to become extremely hard due to recarbonation (R Hayen, personal communication, 2011).
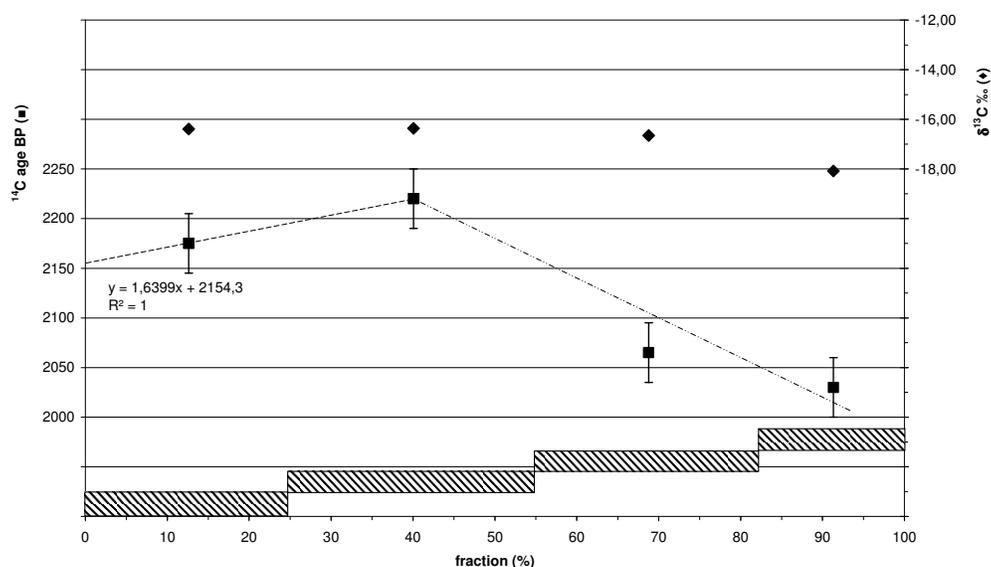

Figure 7 The 4 dated lime fractions from Muertos Gallard (lime pit)

Son Matge (Outside Talayotic Wall)

The fractions depicted in Figure 8 show the same trend as in Figure 7.

Son Matge (ref. 2200–2204)

In the case of Son Matge, there is hardly any fossil carbonate present. The secondary carbonate seems to be less hard than the rock carbonate, resulting in decreasing ^{14}C values from fraction 1 until 3 and a slightly older age for fraction 4. A carbon black dating from a burnt bone gave a date of 2580 ± 30 BP. A linear extrapolation of the 3 first fractions gives a consensus date of 2525 ± 30 BP. There is 95% probability that this value and the date of the carbon black give the same true age [χ^2 test: $df = 1$, $t = 1.7(5\% \ 3.8)$]. The fourth fraction is slightly older than the third fraction. This could solely be due to the statistical uncertainty of the measurement. But the $\delta^{13}C$ value of the fourth fraction shows that there is a change in composition. As an alternative option, a parabolic regression was calculated, which gave a result of 2561 ± 30 BP.
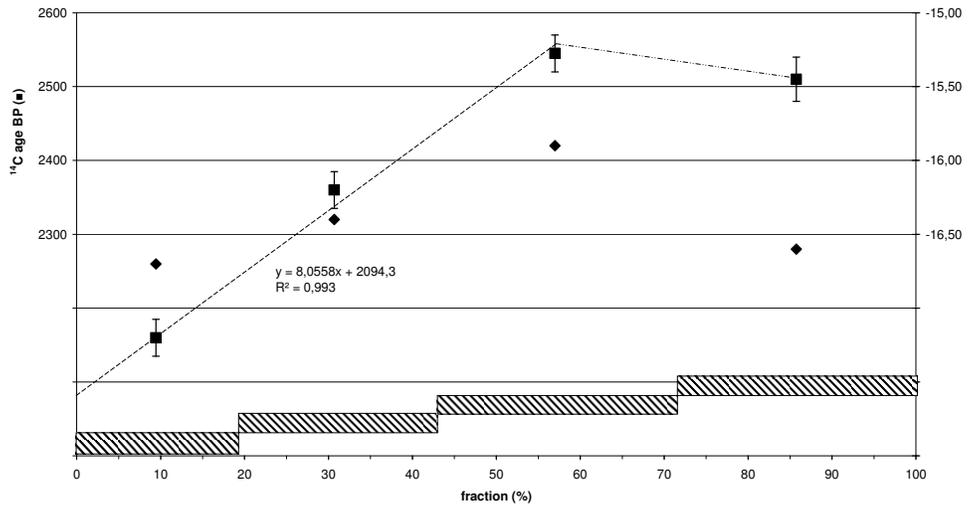
Figure 8 The 4 dated lime fractions from Son Matge (outside Talayotic wall)

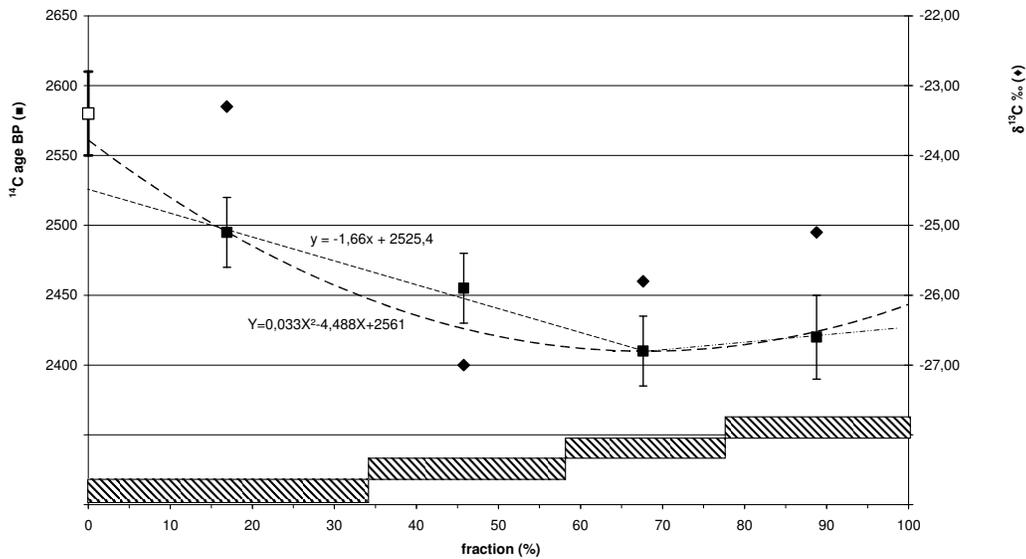Figure 9 The 4 dated lime fractions (filled squares) from Son Matge (ref. 2200–2204) and 1 carbon black sample from a burnt bone (empty square).

Muertos Gallard (Skull and Hair Band)

This sample is a real threshold case: 1) the 4 fractions can statistically have the same true age (average 2326 ± 12 BP); 2) a linear extrapolation of the 4 fractions gives a consensus date of 2327 ± 25 BP. If we consider that the date of the fourth fraction is influenced by recarbonation, a linear extrapolation of the first 3 fractions gives a consensus date of 2293 ± 25 BP.
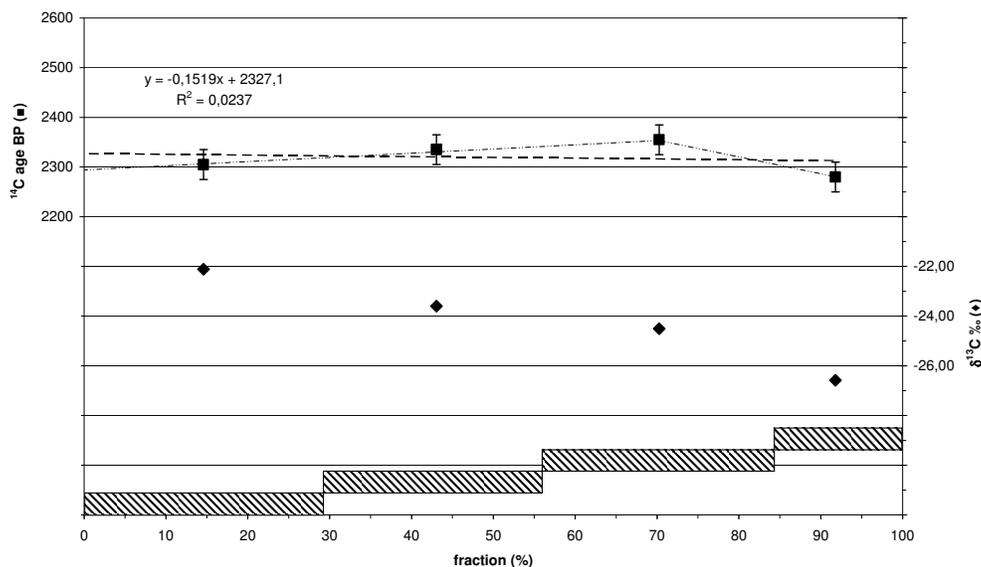
Figure 10 The 4 dated lime fractions from Muertos Gallard (skull and hair band)

DISCUSSION

Stable Isotopes

Pachiaudi et al. (1986) have shown that due to diffusion processes within the slaked lime (regulated by the pH, compactness, and the composition of the matrix), $\delta^{13}C$ values of the newly formed carbonate in different samples cannot be compared. The stable isotope curves in this study, however, do not display the typical Z-shape that has been observed during mortar analysis (Van Strydonck et al. 1989). This is an indication that the lime burial is a much more open system than in the case of mortar. Mortar is applied in a thin but deep layer between bricks with only a small surface exposed to the atmosphere, while a lime burial is a loose and uncovered conglomerate that is compressed only by its own weight. Furthermore, the samples used in this study are so small (~200 mg) that we can consider the $\delta^{13}C$ differences due to diffusion as minimal. In other words, the observed shift in $\delta^{13}C$ comes from a mixture of different carbonates.

This is confirmed by the fact that in all samples, except that of Muertos Gallard (skull and hair band), the $\delta^{13}C$ and the ^{14}C curves have the same trend over the 4 fractions. The fractions containing more geological carbonate tend to have a higher $\delta^{13}C$ and the samples containing recarbonation a lower $\delta^{13}C$, as one would expect.

In the samples that do not contain detectable amounts of rock carbonate [Binigaus, Muertos Gallard (skull and hair band)], a heavier isotopic signature towards the end of the reaction, as described by Lindroos et al. (2007), was not noticed. This phenomenon is most likely caused by differences in laboratory setup and extraction procedure.

^{14}C Dating

From the samples containing organic material as well as lime, it can be concluded that extrapolating the ^{14}C curve to 0 point on the abscissa gives a reliable date even if relatively large amounts of rock carbonate are present. The question remains, however, which type of extrapolation should be used.

As seen from Figures 5 and 6, an exponential regression seems to be most appropriate if relatively large amounts of rock carbonate are present. These curves were drawn on the basis that they gave the best (mathematical) fit, not on any chemical criterion. In fact, the separation method is based on the assumption that the acid reacts preferentially but not exclusively with the softer component. This assumption has proven to be correct. The anthropogenic-formed lime is much softer than the limestone carbonate. However, the separation of both components as well as the shape of the curve depends on the difference in affinity for the reaction as well as on the relative amount of both components. The situation becomes much more complex if recarbonation has occurred. Instead of 2 types of carbonate, 3 types are involved, with each reaction slightly different with the acid. In Figures 7, 8, and 9, an extrapolation was made using only the data points that did not show any recarbonation. Here, it is assumed that there is a complete separation between the acid reaction involving limestone carbonate and the acid reaction involving secondary carbonate. This is of course not true since it is only a question of differences in affinity. In this case, a parabolic function seems to be more appropriate. Fortunately, if rock and secondary carbonate are present only in small quantities, a linear extrapolation will provide a good result within the statistical uncertainties of the ^{14}C measurement.

CONCLUSIONS

The titration method using HCl provides good ^{14}C dates for lime burials. Three different situations can occur: 1) only lime burial carbonate is present; 2) lime burial carbonate and rock carbonate are present; and 3) situation 1 or 2 combined with secondary carbonate. The δ^{13}C as well as ^{14}C curves are less complex in shape than in mortar dating (Van Strydonck et al. 1986; Ringbom et al. 2011) due to the fact that 1) the carbonate in the burial is formed in a relatively open system that has a large contact surface to the atmosphere and 2) that no aggregate is present that can interfere during the acid reaction. Since the final result is obtained by the interpretation of a data set (regression), the obtained result is not a ^{14}C date in the strict sense but a consensus value obtained by ^{14}C analysis.

ACKNOWLEDGMENTS

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