^{14}C dating of the lime burial of Cova de Na Dent (Mallorca, Spain), optimized sample preparation

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ABSTRACT.

Lime burials are a characteristic phenomenon of the protohistoric funerary tradition on the Balearic Islands. At Cova de Na Dent 6 samples, representing the entire stratigraphy of the lime burial, were taken for analysis. The radiocarbon dates (De Mulder et al. 2014) suggested that the lowest levels of the burial were Late Bronze Age. This is in contradiction with archaeological evidence from other sites (Micó Pérez R. 2005, 2006; Castro Martnínez et al. 1997). Therefore a new analysis strategy was put forwards, focusing more on the so-called ‘1st fraction’.

1. INTRODUCTION

In a previous paper (De Mulder et al., 2014) the ^{14}C dating and material analyses of the lime burial at Cova de Na Dent were discussed. The material analyses (on bones and lime conglomerate) confirmed earlier studies performed on museum objects (Van Strydonck et al. 2011, Van Strydonck et al.in press DOI:10.1002/oa.2307). The^{14}C results revealed however an earlier chronology than expected, in conflict with the general idea that the Balearic lime burials are a late Iron Age phenomenon. Unfortunately, no other datable material (by ^{14}C or typological) was available to validate further the obtained dates. The more recent excavation of Cova de s'Estora (cova de Can Pellicer) in Calvià (Mallorca, Spain) put however forward the need of adapting the sample preparation protocol (Van Strydonck et al in prep.). The adapted protocol was studied as well on the lime burial of Cova de Na Dent. The adapted preparation technique is discussed in the present paper and the new data are confronted with the earlier results.

Figure 1: The lime burial site of Cova de Na Dent (39°30’54.33”N, 3°18’19.92”E) is situated on Mallorca’s W-coast in the cliffs between S’estany d’en Mas and Cala Falcó, more precisely in the Area Natural De Cales De Manacor in a cliff wall overlooking the sea. It is an area is rich on karstic cave formations.

2. SITE DESCRIPTION

The site was extensively discussed in a previous paper (De Mulder at al. 2014). Important to know is that the site was not very well conserved. The 40 cm thick lime burial layer represented itself as one unit, except for a gradual change in color. 5 consecutive samples were taken in stratigraphic order: layers -1, 0, 1, 2 and 3 (from bottom to top). A minimum of 250 grams of material was sampled from each individual layer. Layer 2 was later on further separated into two layers (2a and 2b).

3. MATERIALS AND METHODS

From each layer of the lime burial a small lime lump was retrieved, being homogeneous in color and texture and not containing any bone material. The sample was dried, crushed and sieved. Samples were taken from the fraction between 70 and 125 µm. In the previous experiment four successive CO_2 fractions of roughly equal size were obtained by the titration method (Van Strydonck et al. 1982/1983; Van Strydonck et al. 2011). In the experiments described in this paper the first fraction was further split up into 4 fractions, each of roughly the same size, such that a total of 7 fractions were obtained and consequently dated: 4 smaller and 3 larger ones. The extracted CO_2 was graphitized for AMS ^{14}C measurement (Van Strydonck and Van der Borg, 1990/1991, Boudin et al. in prep). Stable isotope compositions ($\delta^{13}C$) were measured with a conventional mass spectrometer (Thermo Delta V Advantage via Conflo IV interface).

The samples retrieved for the adapted analysis (BIS and TRIS) may be considered as real duplicates, as they were extracted from the same lime lump out of each individual layer and which were, furthermore, crushed and homogenized before proceeding to any further analysis. Yet, these samples cannot be regarded as real duplicates from the samples used in the previous experiment. As the lime burial spatially grows un-orderly and intermittently when new cremation residues (bones and quicklime) are added, a very heterogeneous constitution is built up without any clear stratification. Hence, each, more or less arbitrarily chosen, individual layer is characterized by a heterogeneous composition probably combining different cremation residues spanning several generations (and decades). Although taken from one individual layer, separately sampled material (from the earlier experiments to the present paper) may exhibit important differences in cremation origin and carbonate composition. Any observed variability should therefore not only be seen in the context of the adaptation of the analysis strategy, but as well towards the heterogeneity of the material.

4. RESULTS

The ^{14}C results of the different fractions of each sample are represented in table 1 and figures 2 till 6. Layer 2b was not considered in this experiment. The figures combine the new data with the earlier results as presented in De Mulder et al. 2014. The consensus value is calculated according to the extrapolation method (Van Strydonck et al. 2011) and represented in table 2. Table 3 represents the ^{14}C activity (F) of the entire sample (all fractions together), calculated according to (1).

$$F = \sum(\frac{n}{100}).f \qquad (1)$$

n = % sample in each fraction; f = ^{14}C activity of each fraction

Layer	Sample	Lab code: RICH-	Fraction	% sample by weight (n)	^{14}C age (BP)	Activity (f) (%)	δ ^{13}C (‰)
-1	BIS	20822	1	5.50	2839±33	70.23±0.29	-21.9
		20823	2	6.28	2848±34	70.15±0.29	-25.7
		20824	3	5.79	3031±33	68.57±0.28	-26.4
		20825	4	7.07	2923±33	69.50±0.29	-21.9

		20826	5	24.83	2996±33	68.87±0.28	-20.4
		20827	6	24.83	2996±32	68.87±0.28	-23.6
		20828	7	25.71	2934±41	69.40±0.36	-22.4
	TRIS	21085	1	7.18	2927±34	69.46±0.29	-23.1
		21086	2	7.30	2977±34	69.03±0.29	-23.9
		21087	3	7.86	3024±35	68.63±0.30	-24.5
		21088	4	6.51	2990±37	68.92±0.32	-23.6
		21089	5	28.06	3014±34	68.71±0.29	-23.7
		21090	6	27.72	2990±33	68.92±0.28	-22.9
		21091	7	15.38	2930±34	69.43±0.29	-23.2
0	BIS	21175	1	6.56	3574±34	64.09±0.27	-26.7
		21176	2	7.69	2903±33	69.67±0.29	-23.8
		21177	3	6.26	2869±33	69.97±0.29	-25.1
		21178	4	6.97	2910±33	69.61±0.29	-25
		21179	5	27.49	2877±33	69.90±0.28	-22.7
		21180	6	29.13	2839±33	70.23±0.29	-22.6
		21181	7	15.90	2852±32	70.11±0.28	-21.1
	TRIS	21194	1	6.31	2751±32	71.00±0.29	-27.5
		21195	2	7.20	2873±33	69.93±0.29	-24.8
		21196	3	6.51	2835±32	70.26±0.28	-23.8
		21197	4	6.51	2894±32	69.75±0.28	-25.4
		21198	5	25.25	2910±32	69.61±0.28	-22.1
		21199	6	28.11	2788±33	70.68±0.29	-22.6
		21200	7	20.12	2777±32	70.77±0.28	-22.6
1	BIS	21036	1	6.28	2650±33	71.90±0.30	-27.3
		21037	2	7.83	2832±33	70.29±0.29	-23.3

		21038	3	7.61	2917±33	69.55±0.28	-23.3
		21039	4	7.39	2847±33	70.16±0.29	-20.8
		21040	5	24.81	2950±33	69.26±0.29	-21.3
		21041	6	29.55	3112±33	67.88±0.28	-20.3
		21042	7	16.54	3426±33	65.28±0.27	-22.6
	TRIS	20192	1	5.86	2675±33	71.68±0.29	-24.1
		20193	2	7.20	2845±33	70.17±0.29	-25.5
		20194	3	7.10	2810±33	70.48±0.29	-23.1
		20195	4	5.76	2808±33	70.50±0.30	-22.8
		20196	5	24.79	2919±33	69.53±0.29	-20.7
		20197	6	28.60	3080±33	68.15±0.28	-21.7
		20198	7	20.68	3281±33	66.46±0.27	-21.8
2a	BIS	21164	1	7.33	2205±31	76.00±0.29	-20.8
		21165	2	7.62	2320±31	74.91±0.29	-18.9
		21166	3	7.62	2380±31	74.36±0.29	-18.1
		21167	4	7.52	2544±32	72.85±0.29	-18.8
		21161	5	25.90	2751±32	71.01±0.28	-17.5
		21162	6	26.67	3197±33	67.16±0.28	-19.8
		21163	7	17.33	3425±33	65.29±0.27	-21.0
	TRIS	21168	1	5.21	2202±31	76.02±0.33	-23.3
		21169	2	6.63	2282±32	75.27±0.29	-19.2
		21170	3	5.02	2392±32	74.24±0.30	-19.7
		21171	4	5.97	2452±32	73.70±0.29	-18.1
		21172	5	22.06	2565±32	72.67±0.29	-18.6
		21173	6	24.24	2883±32	69.85±0.28	-18.3
		21174	7	30.87	3390±33	65.57±0.27	-20.1
3		21113	1	5.63	2670±33	71.72±0.29	-19.4

	BIS	21114	2	7.14	3194±34	67.19±0.27	-19.9
		21115	3	5.84	3432±33	65.23±0.27	-18.9
		21116	4	6.54	3718±33	62.95±0.27	-21.6
		21117	5	23.04	4044±33	60.44±0.26	-20.5
		21118	6	22.23	4441±32	57.53±0.24	-21.2
		21119	7	29.58	4880±34	54.47±0.23	-20.3
	TRIS	21124	1	5.94	2677±34	71.66±0.30	-19.1
		21125	2	7.60	3080±34	68.15±0.29	-19.0
		21126	3	6.46	3389±35	65.58±0.28	-18.3
		21127	4	8.13	3696±37	63.12±0.27	-20.5
		21128	5	28.02	4065±34	60.29±0.26	-19.1
		21129	6	26.88	4597±33	56.42±0.25	-20.0
		21130	7	16.98	4836±34	54.77±0.24	-21.1

Table1: Radiocarbon dates from 7 fractions of a lime sample from each level.

Sample layer	-1	0	1	2a	3
4 fractions	2990±30	2883±30	2746±33	2586±30	1950±30
7 fractions BIS	2830±33	2880±33 (*)	2580±33	2178±33	2179±33
7 fractions TRIS	2900±33	2720±33(†)	2600±33	2164±33	2120±33
Average (BIS &TRIS)	2865±23	2801±23	2590±23	2171±23	2150±23
χ^2 test (BIS & TRIS) Df=1; T(5%)=3.8	T=2.2	T=11.8	T=0.2	T=0.1	T=1.6
χ^2 test (previous	T=11.0	T=4.7	T=15.1	T=122.0	T=24.5

test / this test) Df=1; T(5%)=3.8					

Table 2: Consensus value (BP) of each sample. (*): not including first fraction; (†): the average is used in graph 3 although T>3.8.

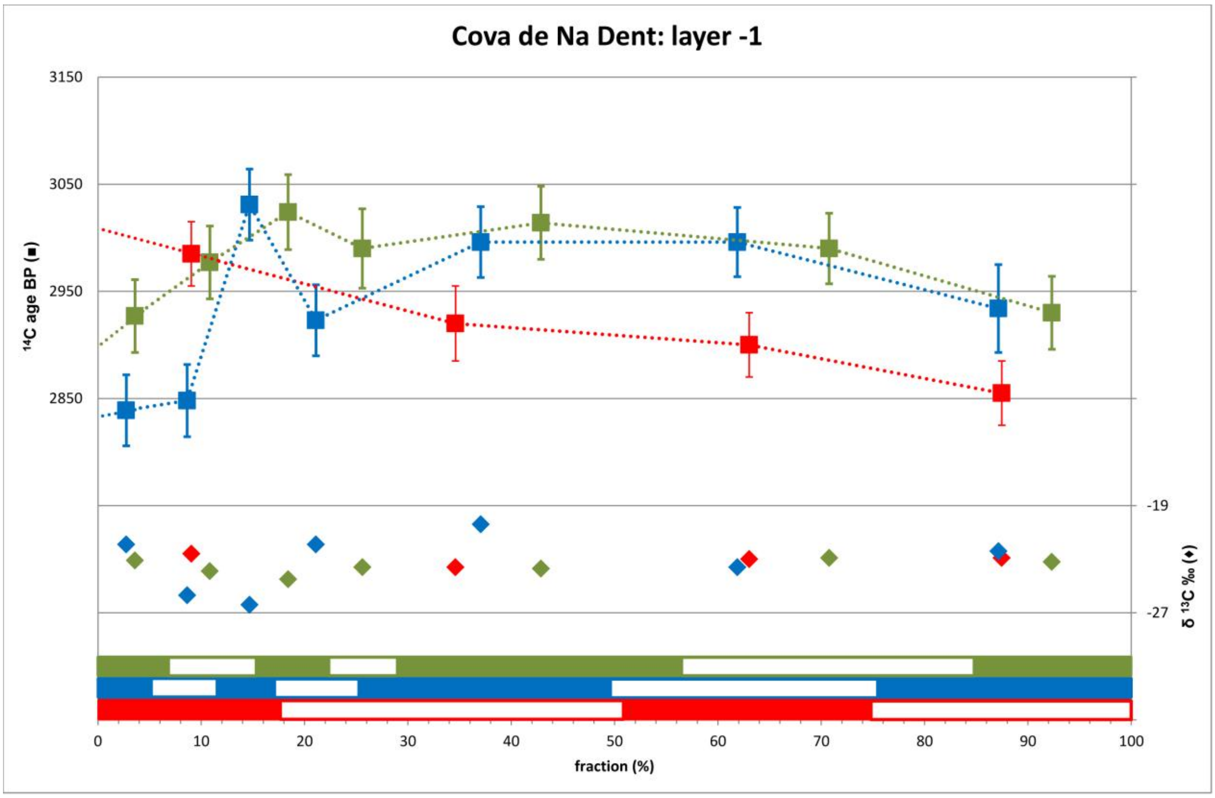

Figure 2: ^{14}C analyses of layer -1 (in red the results of the previous study, duplicates BIS and TRIS are respectively in blue and green

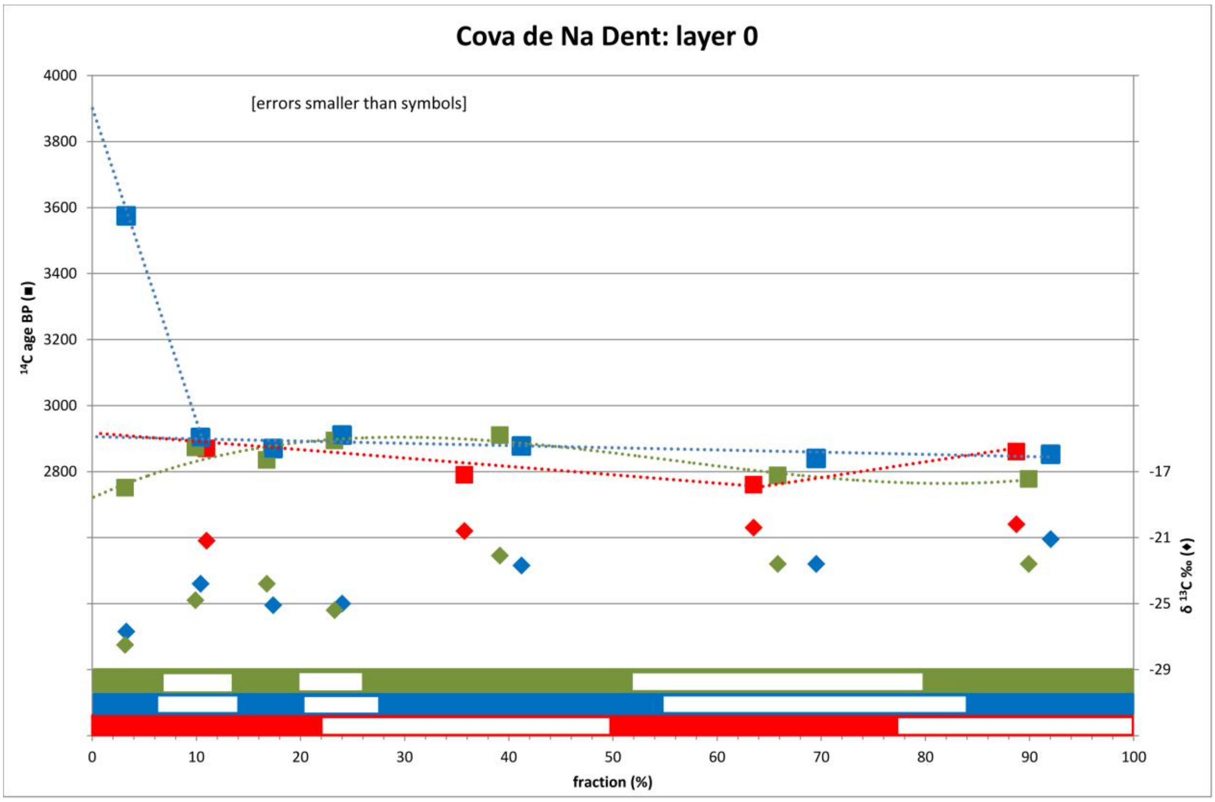

Figure 3: ^{14}C analyses of layer 0 (in red the results of the previous study, duplicates BIS and TRIS are respectively in blue and green

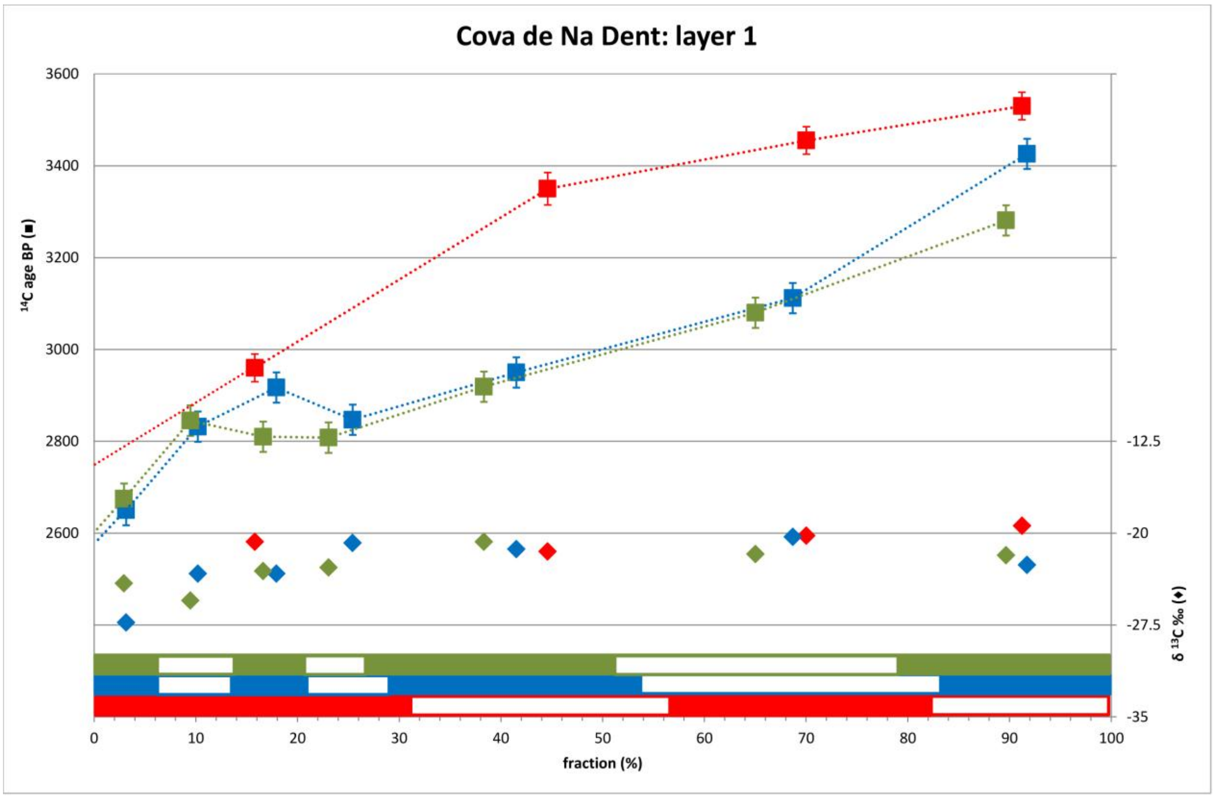

Figure 4: ^{14}C analyses of layer 1 (in red the results of the previous study, duplicates BIS and TRIS are respectively in blue and green

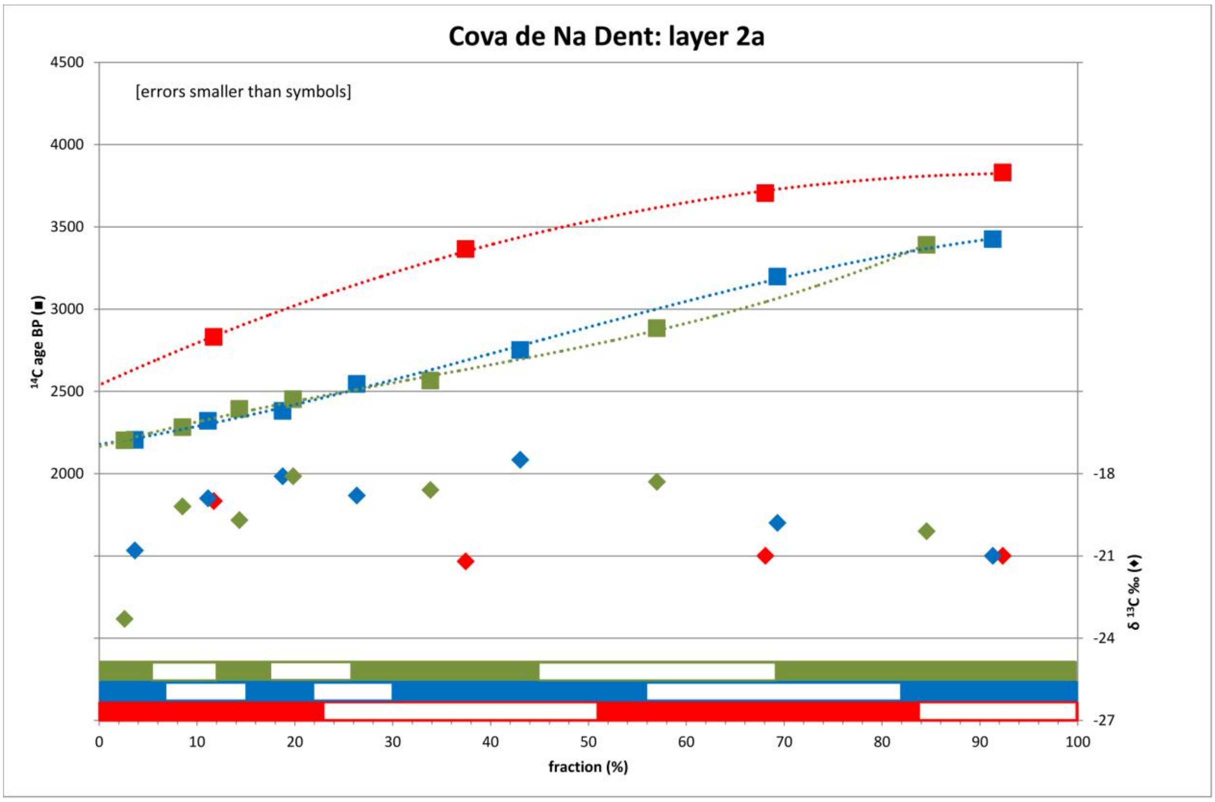

Figure 5: ^{14}C analyses of layer 2a (in red the results of the previous study, duplicates BIS and TRIS are respectively in blue and green

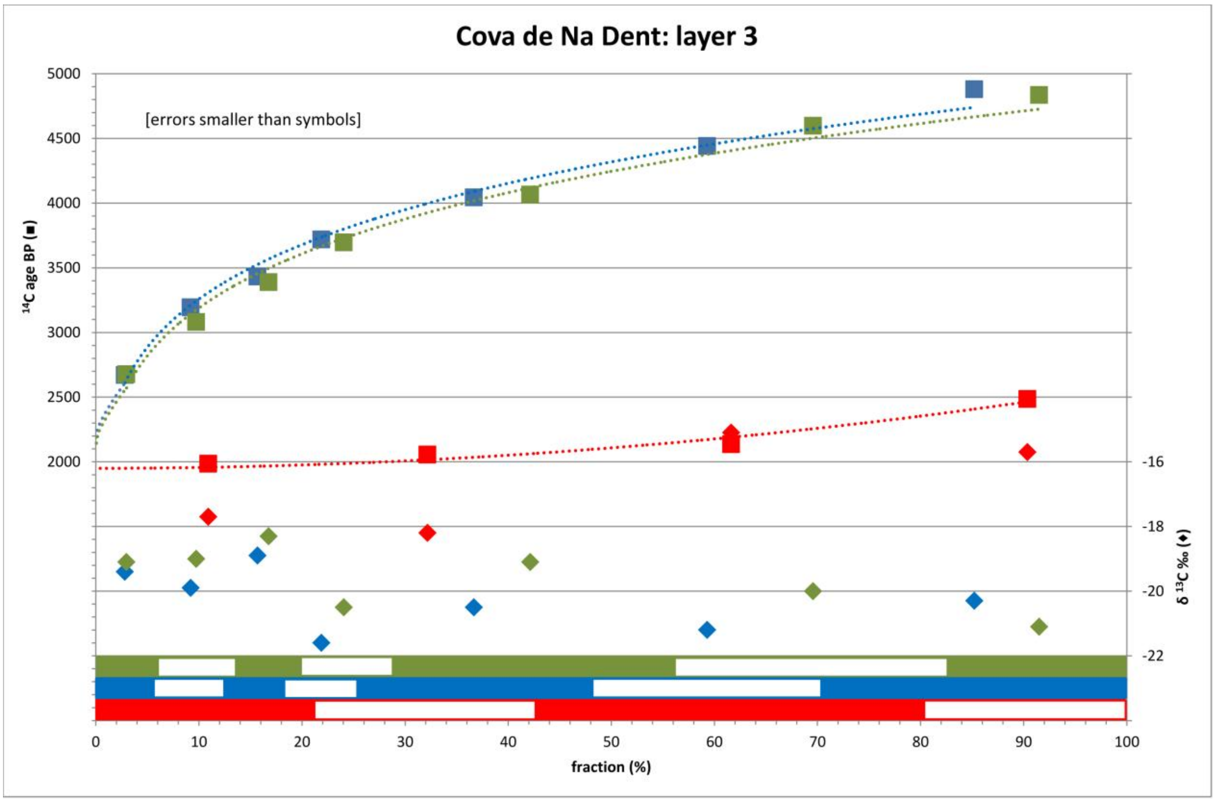

Figure 6: ^{14}C analyses of layer 3 (in red the results of the previous study, duplicates BIS and TRIS are respectively in blue and green

5. DISCUSSION

The reproducibility amongst the duplicates (BIS and TRIS) is generally very good, hence implying that the applied titration method yields reproducible results. The age profiles of the various fractions within one sample are almost identical for both duplicates of layers 2a and 3, while only minor differences in reactivity are observed in the case of the samples taken from layers -1 and 1. Finally, except for the date obtained for the first fraction of sample BIS, also both samples of layer 0 revealed comparable age profiles.

Most of the radiocarbon age profiles evidence a similar development over the first few fractions: the first 2 to 3 fractions show a gradual ageing effect, followed by a slightly younger or more or less similar age (within the margin of error of the measurements). Such a behavior can be attributed to the presence of various phases with varying dissolution rates. Fragments of incompletely burnt limestone, a partially recrystallized crinoid biosparite still containing crinoid columns, were identified and described in the previous paper (De Mulder et al., 2014).

Overall, the behavior is similar to the modeling of the contamination effect of readily-soluble calcitic limestone and slowly dissolving unburned limestone residues on the radiocarbon age of the various lime fractions, as presented by Lindroos et al. 2007, although the experimental conditions differ from the theoretical principles of the modeling approach. The modeling approach is strictly valid for spherical grains of uniform size and chemistry, while the grain size fraction applied here (70-125 µm) is rather non-uniform. In addition, sampling of the various fractions was not time-domain related from a continuing chemical reaction but instead fractionated by titration. Despite this different approach, the basic modeling approach can be considered valuable for the interpretation of the experimental data as even in the case of titration-based sampling the phases reacting fastest, will also be the first to be consumed and therefore contribute to the first fraction.

The observation that reaction differences occur within the first 30% evidences that i) a highly reactive contaminant should be present within the lime burial and ii) the anthropogenic carbonate is not characterized by a unique reactivity coefficient in order to obtain both an initial reaction of the anthropogenic carbonate at the first fraction and a somewhat delayed reaction towards the 3rd and/or 4th fraction, in order to account for the age development over the consecutive fractions. The nature of the highly reactive contaminant is unclear.

In the case of layers 2a and 3, which contain larger amounts of fossil contaminants, the above described effect could still be present but masked by the ageing effect of the slowly reaction fossil contaminants.

Sometimes outliers occur (especially the 1st fraction of sample BIS from layer 0). Such outliers, as well as most probably the minor differences observed amongst the various samples of an individual layer (e.g. the 3rd fraction of samples BIS and TRIS from layer 1 and of sample BIS from layer -1), are to be considered as anomalies in the gradual evolution of the age profile. After all, the age profiles are influenced by the variability of the fossil carbonate origin and presence within the sample as a result of small scale heterogeneities. Since these inclusions are so small (<1 mg) it is possible for them to appear in only one of the two duplicate samples, yet strongly influencing the radiocarbon age profile.

The radiocarbon age profile of layer -1 evidences the influence of secondary carbonation deposits within the lime burial, where rejuvenation occurs towards the last fractions. This observation is opposite to observations made elsewhere, which indicate an influence of recrystallized calcite on the first fraction only (Lindroos et al., 2007). Hence, instead of a highly reactive contribution, the secondary carbonation deposits are characterized here by a very low reactivity coefficient.

The data demonstrate that the age variation amongst the different fractions is influenced by various phases, characterized each by a different dissolution reactivity. Instead of the first series of fractions being entirely free of fossil carbonates, a variable influence of the presence of fossil carbonates is observed certainly from the second fraction onward. If the first fraction would entirely be free of the influence of fossil carbonates cannot be attested and should therefore not be assumed. This implies that, at least when lime burials are concerned, the choice of the first fraction is arbitrary and that the sample preparation should be focused on the actual onset of the acid reaction. Extrapolating the age profiles to the acid reaction onset, the obtained consensus values of the BIS and TRIS samples are within statistical uncertainties to be considered equal (Table 2), except for the data obtained for layer 0 where the result is strongly influenced by the heterogeneity of the material.

The differences between the consensus values of the experiments presented here and the ones published earlier (table 2) as well as the differences between the radiocarbon activity of the entire sample (F) (table 3) are in most cases significant but small (figure 8). If we take into account that the entire lime burial is only 40 cm thick and, as suggested by this study as well as by the previous analysis, covers a period of about 700-1000 radiocarbon years, each individual layer of ca. 5 to 10 cm thickness represents an accumulation of lime and bones during a period of roughly 140-200 radiocarbon years. Furthermore, the deposition at the burial site of the remains of the incineration ritual (the cremated bones and the slacked lime) is done un-orderly, so bones and lime from different cremations are mixed (see figures 7 & 8). This implies that there is no real fine vertical stratigraphy and that small inversions in the depositions are possible. As a result of this radiocarbon age differences in the order of 100-200 years of the consensus of different samples from one and the same layer may be expected. With the exception of layer 2, the observed differences between the data fall all within this range.

The inhomogeneity of the depositions in the lime burial is also demonstrated by the important difference in the fossil limestone carbon content present in the various samples sampled from layer 3. Here the total activity of both samples from layer 3 was ca. 60pMC, while in the previous study the ^{14}C activity of the sample of the same layer was ca. 76pMC (see table 3). In contrast, the total activity of the three samples from layer -1, which is considered containing the least amount of fossil carbonates, hardly varied.

Figure 7: profile of the Cova de Na Dent lime burial

Figure 8: sample from layer 3

Sample	-1	0	1	2	3
4 fractions	69.61±0.27	70.44±0.25	66.46±0.25	2a: 65.37±0.26 2b: 61.47±0.24	76.52±0.27
7 fractions BIS	69.19±0.30	69.61±0.29	68.53±0.28	70.05±0.28	59.59±0.25
7 fractions TRIS	68.96±0.30	70.31±0.28	68.80±0.29	70.28±0.28	60.16±0.26

Table 3:% ^{14}C activity (F) of each sample calculated from the activity (f) of the individual fractions (n)

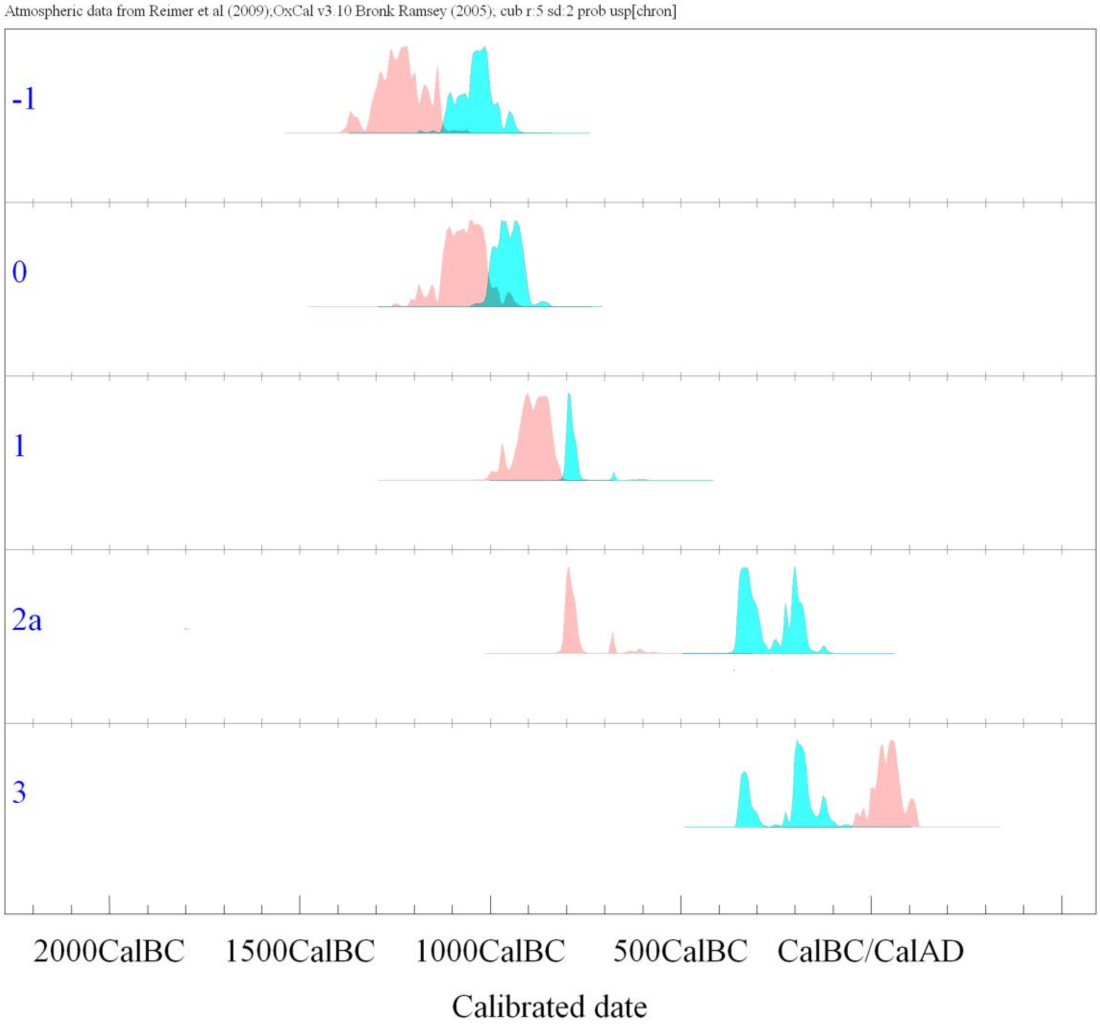
Atmospheric data from Reimer et al (2009);OxCal v3.10 Bronk Ramsey (2005); cub r:5 sd:2 prob usp[chron]

Figure 9: consensus values calibrated by OxCal (Bronk Ramsey 2005) (red previous study, blue this study)

6. CONCLUSIONS

The new analysis strategy of subdividing the CO_2 release in a larger number of fractions, evidences a complex system of anthropogenic and fossil carbonate sources with varying and interfering acid reaction activities. A variable influence of the presence of fossil carbonates is observed certainly from the second fraction onward. If the first fraction is entirely free of the influence of fossil carbonates could not be attested and should therefore not be assumed. Consensus dates, obtained on duplicate samples through extrapolation of the age profiles to determine the acid reaction onset, fall generally within a statistically margin of error, implying that the applied titration method yields reproducible results. Individual age profiles are in some cases however influenced by outliers, which are the result of the natural heterogeneity of the lime burial. This heterogeneity is also held responsible for the observed age differences of separately sampled material from each individual layer.

Although from a methodological point of view the new sample preparation strategy showed some important improvements, the general archaeological interpretation of the site has not changed. The onset of the lime burial must be situated at the end of Bronze Age and lasted till the Roman period. So far the Cova de Na Dent lime burial is the only lime burial that gives such old starting dates. It must however be mentioned that the Cova de Na Dent lime burial is the only one besides the lime burial at Son Matge that has been dated extensively. According to an older study, based on charcoal dates, the Son Matge lime burial goes back to 800 BC. The stratigraphic origin of that charcoal is however unclear (Van Strydonck and Waldren 1995). A recent study on the pottery found at Son Matge proved that the burial site was in use until the Roman period (De Mulder and Van Strydonck 2012). This is in agreement with the presented studies on Cova de Na Dent.

7. REFERENCES

M. Boudin, T. Van den Brande, H.-A. Synal, L. Wacker, M. Van Strydonck. RICH – a new AMS facility at the Royal Institute for Cultural Heritage, Brussels Belgium. In prep.

Bronk Ramsey C. 2005. http://c14.arch.ox.ac.uk/oxcal3/oxcal.htm

Castro Martnínez PV, GiliSuriñach S, González Marcén P, Lull V, Micó Perez R, Rihuete Herrada C. 1997. Radiocarbon dating and the Prehistory of the Balearic Islands. *Proceedings of the Prehistoric Society* 63: 55-86.

De Mulder G, Van Strydonck M. 2012. Un descubrimiento imprevisto nueveos hallazgos de cerámica en Son Matge. *BSAL (Bolletí de la Societat Arqueològica Lulbliana)* 68 :15-26.

De Mulder G, Hayen R, Boudin M, van den Brande T, Decq L, Salas Burguera M, Ramis D, Borms H, Van Strydonck M. 2014. ^{14}C Dating and material analysis of the lime burial of Cova de Na Dent (Mallorca, Spain). *Radiocarbon* 56(2): 387-398.

Lindroos A, Heinemeier J, Ringbom Å, Braskén M, Sveinbjörnsdóttir Á. 2007. Mortar dating using AMS ^{14}C and sequential dissolution: examples from medieval, non-hydraulic lime mortars from the Åland islands, SW Finland. *Radiocarbon* 49(1): 47-67

Micó Pérez R. 2005. *CronologiàAbsoluta y periodización de la prehistoria de las IslasBaleares*. BAR International Series 1373. Oxford: Tempus Reparatum: 621.

Micó Pérez R. 2006. Radiocarbon dating and Balearic Prehistory : reviewing the periodization of the prehistoric Sequence. *Radiocarbon* 48(3): 421 – 434.

Van Strydonck M, Dupas M, Dauchot-Dehon M, Pachiaudi C, Maréchal J. 1982/1983. A further step in the radiocarbon dating of old mortars. *Bulletin van het Koninklijk Instituut voor het Kunstpatrimonium* 19: 155-171.

Van Strydonck M, van der Borg K. 1990/1991. The construction of a preparation line for AMS-targets at the Royal Institute for Cultural Heritage Brussels.*Bulletin van het Koninklijk Instituut voor het Kunstpatrimonium* 23: 228-234.

Van Strydonck M, Waldren WH. 1995. Radiocarbon dating of the Son Matge rock shelter. In Waldren WH, Ensenyat JA, Kennard RC, editors. *Ritual, Rites and Religion in Prehistory. IIIrd Deya International Conference of Prehistory*. BAR International series 611(1): 164-182.

Van Strydonck M, Boudin M, Decq L, Van Den Brande T, Borms H, Ramis D, De Mulder G. 2011. AMS ^{14}C dating of Balearic Lime-Burials. *Radiocarbon* 53 (4): 563–574.

Van Strydonck M, Decq L, Van den Brande T, Boudin M, Ramis D, Borms H, De Mulder G. 2013. The Protohistoric “Quicklime Burials” from the Balearic islands: cremation or inhumation. *Osteoarchaeology*: in press.

Van Strydonck M, Aramburu J, Fernández Martínez A, De Mulder G. Radiocarbon dating of the Cova de s’Estora (Can Pellicer) lime burial (Calvià, Mallorca). In prep.