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COMPARING CONTINENTAL CARBONATES WITH OTHER MATERIALS IN DATING A PALEOLAKE

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ABSTRACT. We have studied the application of carbonates and organic matter to the radiocarbon dating of a paleolake. The results show a systematic apparent age shift of these materials with respect to contemporary wood. The apparent age of carbonates is evidently due to the hard-water effect, whereas the apparent age of organic matter, systematically younger than carbonates, is attributed to aquatic plants, which metabolize dissolved CO_2. Terrestrial plants that deposit organic matter also cause apparent age discrepancies between carbonates and organic matter.

INTRODUCTION

In radiocarbon dating, few comparative studies have been made using different kinds of material (Evin 1980). Among these materials, shells and inorganic sedimentary carbonates are the most problematic (Mook 1980; Evin 1980; Chen & Polach 1986). The main difficulty lies in determining initial ^{14}C activity (Krajcar-Bronić *et al.* 1986; Srdoč *et al.* 1986) and in ascertaining whether these systems have been closed with regard to carbon exchange (Buddemeier *et al.* 1972; Grant-Taylor 1972). The initial ^{14}C activity of carbonate sediments depends on several factors, among which the activity of dissolved inorganic carbon (DIC) is most important (Buchardt & Fritz 1980). Initial activity of DIC in continental waters is determined by:

- drainage basin inorganic carbon carried by surface water
- biological productivity
- stream and river discharge and the origin of these waters
- exchange with the atmosphere
- dissolved carbonate rocks

Attempts have been made to determine the initial activity of DIC for different geological environments and climates (Srdoč *et al.* 1986; Srdoč, Horvatinčić & Obelić 1983). Some authors (Pazdur, Pazdur & Szulc 1988; Andrée *et al.* 1986; Pazdur & Pazdur 1986; Pazdur 1988; Chen & Polach 1986) compare carbonate activity with that of contemporary organic matter to determine apparent age (T_{ap}), defined as the difference ($T_{carbonate} - T_{organic\ matter}$). This apparent age reflects the fact that part of the dissolved carbon in groundwater comes from carbonates with low or zero ^{14}C content (the hard water effect). Aquatic plants, which use dissolved CO_2 in photosynthesis, also yield apparent ages modified by this effect (Willkomn & Erlenkensen 1972; Srdoč, Obelić & Horvatinčić 1980).

In this study, we investigate a paleolake from northeastern Spain, dating different types of contemporaneous materials and evaluating the hard water effect in dated samples.

BUBAL PALEOLAKE

Bubal paleolake (0°20'W, 42°37'N, elevation 1115 m) is located in the southern Pyrenees in the Gallego River valley between Biescas and Sabiñanigo, Huesca, Spain (García 1991). The paleolake is a doline developed over Devonian limestones during the last glaciation, when glacially-transported sediment sealed the bottom of the depression. Upon glacial retreat, a small, stagnant lagoon about 25 × 15 m remained (Menéndez & Martí 1973; Martí 1977; Montserrat 1991). Carbonates, organic matter and shells infilled the lake at different levels; wood was found in one level.

SAMPLING & LABORATORY PROCEDURES

A well 4.5 m deep and 1.5 m in diameter was excavated for sampling. We collected carbonate and organic samples from each level, and wood from 264 cm depth. Two samples for radiocarbon dating were collected by drilling in the interval 4.5–6 m. To preclude sampling uncertainty, we established wide-level sampling of 3 cm at each level; this was done because the expected sedimentation rate was approximately 0.5 mm yr^{-1}, according to recent pollen analysis (Montserrat (ms.) 1991). Figure 1 shows the stratigraphy of Bubal paleolake.

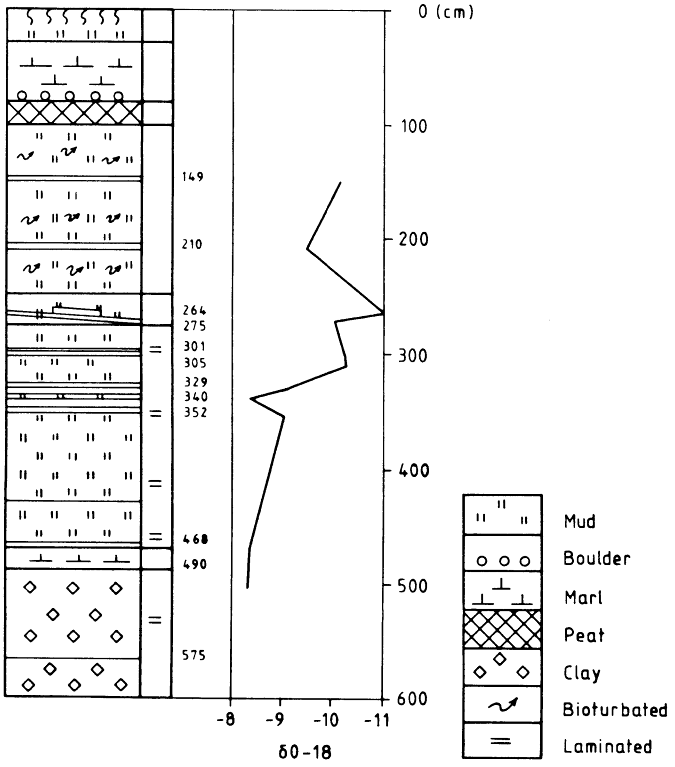

Fig. 1. Bubal paleolake stratigraphy and $\delta^{18}O$ variations

Before analysis, all samples were dried and ground to <1 cm. We homogenized, quartered and ground each sample to <1 mm for determination of organic matter content, carbonate content, X-ray diffraction, stable isotope analysis and ^{14}C dating. Details of each analysis are listed below.

Organic Matter Content: We calcined, at 450°C, *ca.* 0.1 g of sample (previously dried at 110°C) until a constant weight was reached. Relative organic matter content was calculated by mass difference.

Carbonate Content: We suspended in boiling water *ca.* 0.1 g ground sample. We then performed acid-base volumetry using 1 N HCl titrimetric solution with slight stirring and a potentiometric indicator (combined glass pH electrode). The carbonate content was calculated by acid titration to pH 3–4.

X-Ray Diffraction: We performed this analysis on all dated samples using the single-crystal technique.

Stable Isotopes: We performed $\delta^{13}C$ and $\delta^{18}O$ analyses following Gonfiantini (1981) using a V.G. Isogas F.M. SIRA-10 mass spectrometer.

^{14}C dating: 0.05% of shells was separated from sediments in one level, 264 cm. The small proportion found here led us to date both inorganic carbonate and shell fractions together in each level studied. Using the method described in Mestres, García & Rauret (1991), we dated organic matter (MO) and carbonates (C) from 5 levels: 149, 264, 305, 329 and 340 cm, and wood (W) from level 264 cm. This sample, 264-W, is from a pine trunk 20 cm in diameter and 50 cm in length; the outermost 20 rings were dated. At the two deepest levels sampled, we could date only sedimentary carbonates because of the small amount available.

RESULTS AND DISCUSSION

Table 1 shows our results. Along the stratigraphic sequence, ages of organic materials and carbonates increase with depth. At Level 264 cm, the dates for carbonate sample 264-C (9630 ± 100 BP) and organic matter 264-MO (9460 ± 110 BP) are similar, but do not agree with the date for the most reliable material, wood sample 264-W (8830 ± 100 BP).

X-ray diffraction analysis shows that calcite is the main mineral component in all sediment samples. It also reveals that the contribution of dolomite is lower than 2% at any level. Assuming that dolomite monitors the detrital contribution, then this small proportion is unable to produce stratigraphic inversion of dates. Moreover, the high native carbonate content of the sediments minimizes the relative contribution of external carbonate contamination (Siegenthaler & Eicher 1986).

TABLE 1. Results from Bubal Paleolake

Sample no.	UBAR no.	Depth (cm)	^{14}C age (BP)	S age[*]	Act. (dpm g^{-1} C)	S act.[**]	$\delta^{13}C$	$\delta^{18}O$	MO[†] (%)	C[‡] (%)
149-MO	143	149	8580	110	4.061	0.052	-33.88			
149-C	144	149	8870	100	3.918	0.049	-4.78	-10.17	7.3	86.8
210-C		210					-4.89	-9.51	6.3	91.6
264-W	145	264	8830	100	3.937	0.048	-26.53			
264-MO	146	264	9460	110	3.641	0.049	-32.69			
264-C	147	264	9630	100	3.566	0.045	-4.53	-11.05	16.2	78.3
275-C		275					-4.76	-10.09	17.1	78.9
301-C		301					-4.89	-10.24	8.0	87.9
305-MO	148	305	9940	120	3.430	0.050	-35.34			
305-C	149	305	10,630	120	3.147	0.044	-4.63	-10.26	13.5	80.8
329-MO	150	329	10,780	120	3.087	0.044	-28.70			
329-C	151	329	11,390	130	2.864	0.044	-3.31	-9.11	12.9	77.5
340-C		340					-0.61	-8.38	7.2	88.3
352-C		352					-0.49	-9.04	5.7	86.4
468-C	223	468	15,480	180	1.705	0.037	0.72	-8.36	11.3	74.7
490-C	222	490	16,030	130	1.593	0.025	1.75	-8.31	3.3	64.2
575-MO	Gif-8237[§]	575	20,800	400						

[*] Standard deviation of ^{14}C age

[**] Standard deviation of activity

[†] Organic matter content in sample

[‡] Carbonate content in sample

[§] Montserrat (1991)

Using the results from Level 264 cm, we calculated the initial activity A_0 and the apparent age (T_{ap}) for carbonates and organic matter, assuming that they were coeval with the external rings of the pine trunk. The values are:

$$A_0\ (C) = 90.6\%\ A \qquad T_{ap}\ (C) = 800\ yr$$
$$A_0\ (MO) = 92.5\%\ A \qquad T_{ap}\ (MO) = 630\ yr$$

The hard-water effect, which reduces the initial carbonate activity (Srdoč, Obelić & Horvatinčić 1980; Andrée *et al.* 1986), appears to account for the finding that organic matter and carbonates are older than the wood.

Carbonates have fairly high A_0 values and quite low (young) apparent ages. These results agree with those from Sieradowice, Poland (Pazdur, Pazdur & Szulc 1988; Pazdur 1988), a site with similar hydrodynamic conditions, stagnant water and semilimnic deposition of calcareous muds. Here, $A_0 = 89\%$ and $T_{ap} = 910 \pm 120$ yr. Comparable values were also found for the same Preboreal period by Andrée *et al.* (1986), who dated terrestrial plant macrofossils, aquatic plant remains and carbonates from Lake Lobsinger; they measured an apparent age of 800 yr.

These high initial A_0 values may be explained by considerable exchange between dissolved and atmospheric CO_2, which could be related to water residence time in the paleolake (Srdoč, Obelić & Horvatinčić 1980).

In all levels dated, the similarity between the ages of carbonates and organic matter may be explained by the fact that the organic matter comes mainly from aquatic plants (Menéndez & Martí 1973) which used dissolved CO_2 for photosynthesis (Willkomn & Erlenkensen 1972; Srdoč *et al.* 1986). Nevertheless, in all comparisons, carbonates are systematically older than organic matter. This could be explained by the presence of a minor terrestrial plant component in organic matter derived mostly from aquatic plants. Assuming that terrestrial plant activity, A_t, is that of the wood sample 264-C, and that aquatic plant activity, A_{aq}, is that of carbonate samples at 264 cm depth, we calculate the proportion of plants from the two sources

$$A = a\ .\ A_{aq} + (1 - a)\ A_t \tag{1}$$

and obtain 79.8% aquatic plants, and 20.2% terrestrial plants.

For the other levels dated, we calculated the difference between carbonate age, T_c, and organic matter age, T_{mo}, which from its similarity with T_{ap}, may be called $T_{ap'}$

$$T_{ap'} = T_c - T_{mo} \tag{2}$$

Table 2 shows the values of $T_{ap'}$ for each level dated. A discontinuity is seen between levels 264 and 305 cm; the $T_{ap'}$ values below 305 cm are around 600–700 yr BP, while the values are 200–300 yr BP toward the top of the section. This discontinuity also appears in pollen data for the drier and colder Younger Dryas period, between 354 and 305 cm depth in the Bubal section. Montserrat (1991) found, by principal component analysis, 8 different pollen zones corresponding to distinct pollen assemblages. He concluded that the Younger Dryas appeared in zone BUB-5 (394–354 cm) with the appearance of steppe *Artemisia*, and disappeared in BUB-3 (321–305 cm) with the presence of *Quercus*.

The relation between environmental changes and $\delta^{18}O$ values of lake carbonates is complex (Siegenthaler & Eicher 1986). $\delta^{18}O$ values (Fig. 1) show a change between 264 and 340 cm depth,

TABLE 2. Difference between Carbonate Age (T_C) and Organic Matter Age (T_{mo})

Level	$T_{ap'}$*
146–149	290 ± 150**
261–264	170 ± 150**
304–305	690 ± 170**
326–329	610 ± 170**

*$T_{ap'} = T_c - T_{mo}$

**$\sigma T_{ap'} = [(\sigma_{mo})^2 + (\sigma_c)^2]^{1/2}$

similar to that obtained by Duplessy *et al.* (1981) through correlation of deep-sea cores from the Bay of Biscay with six continental sites in France and Spain. In this study, the Younger Dryas is dated at *ca.* 10,400 BP; its end is related to the disappearance of *Artemisia* and the increase of *Quercus*, as found at Bubal.

Sedimentation rates were calculated from the ^{14}C results (Table 3). The sedimentation rate above 264 cm is higher than below 304 cm, and intermediate between the two layers. This change occurs at the same depth as the change in the $T_{ap'}$ values, and corresponds to X-ray results showing only dolomite at 275 cm depth. These data support the occurrence of a change with the variation of $T_{ap'}$.

TABLE 3. Sedimentation Rates

Depth (cm)	Sedimentation rate organic matter (mm yr^{-1})	Sedimentation rate carbonates (mm yr^{-1})
149–264	1.31	1.52
264–305	0.85	0.41
305–329	0.28	0.31
468–490	—	0.40
329–575	0.25	—

For contemporary samples, the difference between T_{mo} and T_c is given by

$$T_{ap'} = T_c - T_{mo} = \frac{t_{1/2}}{\ln 2} \ln \left(a + \frac{(1 - a)}{f_c}\right) \qquad (3)$$

where: a = fraction of aquatic plants

f_c = the factor establishing the relationship between the ^{14}C activity in the atmosphere and the initial ^{14}C activity of carbonates.

$t_{1/2}$ = ^{14}C half-life.

Some studies suggest that the apparent age of carbonates (T_{ap}) for a given site remains constant, especially in stagnant water (Pazdur & Pazdur 1986; Pazdur, Pazdur & Szulc 1988), which means f_c is constant. If we assume this, the increase in $T_{ap'}$ values should relate to a change in the proportion, a, between the aquatic and terrestrial plant components of the organic matter dated. This hypothesis has been corroborated by pollen analysis which shows a substantial change from terrestrial plant pollen to aquatic plant pollen from 270 cm depth downward (Montserrat 1991). Thus, from 304 cm depth, the initial activity of the organic matter should be closer to atmospheric values than in the upper levels, and T_{ap}, would be higher. This explanation seems more reasonable than to expect a sudden change in the component that provides the ^{14}C to the system. Another hypothesis is that organic matter and carbonates were not deposited at the same time, and thus may have different real ages.

CONCLUSIONS

The results obtained in the Bubal Paleolake study confirm those found at other locations with similar hydrodynamic and lithological conditions. The values of initial carbonate activity and T_{ap} depend on several factors that do not permit generalization. Nevertheless, the results from Bubal should establish a chronology for climatic change in this area; specific studies of the geochemical conditions at similar Pyrenean lakes could yield ^{14}C results where carbonates are the only materials available.

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