CARBONATE ^{14}C BACKGROUND: DOES IT HAVE MULTIPLE PERSONALITIES?

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ABSTRACT. Measurements of the radiocarbon concentration of several carbonate background materials, either mineral (IAEA C1 Carrara marble and Icelandic double spar) or biogenic (foraminifera and molluscs), show that the apparent ages of diverse materials can be quite different. Using 0.07 pMC obtained from mineral samples as a processing blank, the results from foraminifera and mollusc background samples, varying from 0.12 to 0.58 pMC (54.0–41.4 ka), show a species-specific contamination that reproduces over several individual shells and foraminifera from several sediment cores. Different cleaning attempts have proven ineffective, and even stronger measures such as progressive hydrolization or leaching of the samples prior to routine preparation, did not give any indication of the source of the contamination. In light of these results, the use of mineral background material in the evaluation of the age of older unknown samples of biogenic carbonate (>30 ka) proves inadequate. The use of background samples of the same species and provenance as the unknown samples is essential, and if such material is unavailable, generic biogenic samples such as mixed foraminifera samples should be used. The description of our new modular carbonate sample preparation system is also introduced.

INTRODUCTION

The desire (and need) for older radiocarbon ages is becoming more pressing with the study of longer and older sediment cores. There is even a stronger need to analyze smaller samples due to low foraminiferal abundance. These factors make the study of the background ^{14}C-level for carbonate samples an urgent matter. This need is important for us, as it has been our experience over the last few years that the scatter of the measurements of a background sample is about one third of its value, an unwelcome uncertainty which is propagated to the final result, increasing its uncertainty (Nadeau et al. 1997; Schleicher et al. 1998). Moreover, as ^{14}C convention requires that no defined age is given when the remaining ^{14}C concentration is less than twice its measured uncertainty (2σ criteria), an unusually large background value lowers the ages at which the undefined "older than", so displeasing to the users of ^{14}C dates, has to be used.

The comparison between the results obtained from mineral and biogenic carbonate background samples leads us to believe that biogenic carbonate samples such as foraminifera tests and mussel shells require an additional cleaning step, their results being consistently younger than those of mineral samples (Schleicher et al. 1998).

After a description of the systems used in the preparation of the samples and their respective processing ^{14}C-blank levels, we will first describe the different species of foraminifera and mussels tested and their respective results under a "standard" treatment. We will then review the results of several variations of the preparation method and describe a few cleaning attempts. All the results reported here have been measured since January 1998 on samples of about 1 mg C.

'STANDARD' SAMPLE PREPARATION METHOD

To minimize the size of our carbonate reaction system and simplify it, we opted for a sealed ampoule reaction system, in analogy with the organic combustion (Nadeau et al 1998). About 10 mg of sample carbonate material is weighed and filled into a 1/4-inch diameter clean glass tube (4 cm in length), which is placed into a short 3/8 inch glass tube for handling. Then 0.2 mL of a 15% hydro-

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gen peroxide solution, previously flushed with nitrogen gas to remove carbon dioxide, is added to the sample and the tube placed in an ultrasonic bath for about 15 min to remove organic surface contaminants and give the carbonate sample material a mild leaching. Thereafter, the solution is siphoned off with a 0.42 mm diameter cannula and the glass tube (with the still-wet sample material) is attached to a pumping manifold where it is evacuated to below 10^{-3} mbar while heated for several hours at 55–60 °C. Meanwhile, a longer 3/8-inch glass ampoule (20 cm in length), already deformed with a flame about 2 cm from the end so that the smaller inner tube will not come in contact with the acid before the tube are turned, is filled with 0.6 mL of concentrated (100%) phosphoric acid, pumped for one hour, then vented with nitrogen.

The 1/4-inch glass tube, also vented with nitrogen, is transferred with tweezers into the longer ampoule, which is then pumped and heated for another 3–4 hr and finally flame sealed. The sealed ampoule is turned upside down, causing the carbonate material to fall into and react with the phosphoric acid. After a reaction time of 2–3 hr in a water bath at 90 °C, the ampoule is slightly scratched and then cracked under vacuum in a B24 ball-joint breaker system. The carbon dioxide is collected in a sample bottle using liquid nitrogen and then reduced as described in Schleicher et al. (1998) and Nadeau et al. (1998).

The shells of mussels and snails receive an additional pretreatment to remove organic coatings. About 15–20 mg of shell fragments are covered with 30% hydrogen peroxide and cleaned in an ultrasonic bath. The fragments are washed with Milli-Q demineralized water and dried at 60 °C. The dried fragments are then treated as described above.

We built a manifold system with four 10-port lines evacuated independently by mechanical pumps via liquid nitrogen cold traps, allowing the preparation of 20 carbonate ampoules in parallel. The system has consistently given good results. One disadvantage of the procedure is the laborious cleaning of the cracking systems. The ampoules on the other hand are simply discarded. This modular approach also allows a greater flexibility in the preparation of the samples since the carbonate samples can be sealed several days or even weeks before being reacted without degradation of the sample material. Also, since organic samples are combusted in quartz ampoules, which are also 3/8-inch in diameter (Nadeau et al 1998), both types of samples can be cracked in the same ball joint systems.

This ampoule preparation system, which has been used since January 1998, led to a decrease in the blank values of the background sample IAEA C1 Carrara marble by about 0.06 pMC for a 1-mg sample (for background values prior to 1998 see Schleicher et al. 1998).

The sample CO_2 is then reduced to graphite with H_2 at 600 °C over 2 mg of an iron catalyst. The iron/carbon mixture is pressed as a pellet into a target holder for accelerator mass spectrometry (AMS) measurement in a 3 MV Tandetron from High Voltage Engineering Europa (HVEE) with a single caesium sputter ion source and a separator/recombinator for simultaneous injection of the three isotopic carbon beams (Nadeau et al. 1997, 1998).

The ^{14}C concentration of the sample is measured by comparing the simultaneously collected ^{14}C, ^{13}C, and ^{12}C beams of each sample with those of Oxalic Acid standard CO_2 (OX-II). For determination of the measuring uncertainty (standard deviation σ), both the counting statistics of the ^{14}C measurement and the variability of the 8–12 interval results that, together, make up one measurement are observed and the larger of the two is adopted as the measuring uncertainty (Nadeau et al. 1998).

BASIC RESULTS

Before we can look at the results from real carbonate background samples, we have to look into the backgrounds that characterize the different systems influencing a measurement.

1. *Machine background:* As reported by Schleicher et al. (1998), the machine background is small and does not interfere significantly with the results. Since then, some minor modifications to the AMS system have reduced its level further. We tested the background using pure graphite powder (Ultra F purity graphite; 99.9995%; powder (pelletable); CO14145-03/UCP1; 1 oz; LOT: 512-20 supplied by Alfa). A series of 102 measurements between January 1998 and June 2000 leads to an average of 0.019 ± 0.009 pMC (68.7 ka BP). This result includes the machine background proper, i.e. the ions which reach the ^{14}C-detector by charge changing, scatter or other interferences, but also the contamination introduced by target pressing, a "dirty" ion source, and the scarce ^{14}C atoms present in the graphite powder itself.
2. *Reduction and hydrolization blanks:* Two mineral carbonate samples were used to test the process blank, IAEA C1 Carrara Marble (IAEA 1991) and an Icelandic double spar. The samples were processed as described above and included in routine sample sets. They were measured between May 1998 and June 2000, with the following results.

IAEA C1 (75x):	0.080 ± 0.028 pMC (57.2 ka BP)
Icelandic Double Spar (19x):	0.068 ± 0.028 pMC (58.5 ka BP)

The 0.019 ± 0.009 pMC obtained for the machine background is included, which means that the true blank contribution of reduction and hydrolization is about 0.05 pMC.

Biogenic Carbonate Samples

The biogenic carbonate background samples analyzed include the two fossil groups mainly used for dating in paleo-climatological studies, i.e. foraminifera and mollusc shells. All the mussel and snail samples included in this study (see caption of Figure 1 for species names) are from the coring site DA1 (sediment core GIK14350) in north western Germany and of Eemian age (~120 ka), as confirmed by U/Th and ESR dates (K Winn, personal communication 1999). Therefore, the different samples were subjected to similar conditions.

The foraminiferal samples consisted of the benthic species *Pyrgo murrhina* (sediment core GIK23068 at 338.5 cm depth with an approximate age of 110 ka; Vogelsang 1990) and of planktic foraminifera. As general foraminiferal background material we use a foraminiferal sand (>315 μm) from sediment core GIK16458 in the tropical Atlantic off NW-Africa (KIA 2718) consisting of >99% of planktic foraminifera, mainly the species *Globigerinoides trilobus* and *Globorotalia menardii*, and very few benthic foraminifera or ostracode shells. The age of this foraminiferal sand from a core depth of 647–650 cm is estimated to be 455 ka based on the oxygen isotope stratigraphy of Winn et al. (1991). Mono-specific samples of *Globigerinoides trilobus*, *Globorotalia menardii*, *Pulleniatina obliquiloculata*, and *Neogloboquadrina dutertrei* selected from the sand were measured separately for this study. Previous results for background samples (older than 80 ka) of the planktic foraminifera *Neogloboquadrina pachyderma* (sinistral) from sediment cores in the northern North Atlantic and the North Pacific were also included in the study (Voelker 1999). All the results reported here were obtained from samples of about 1 mg carbon.

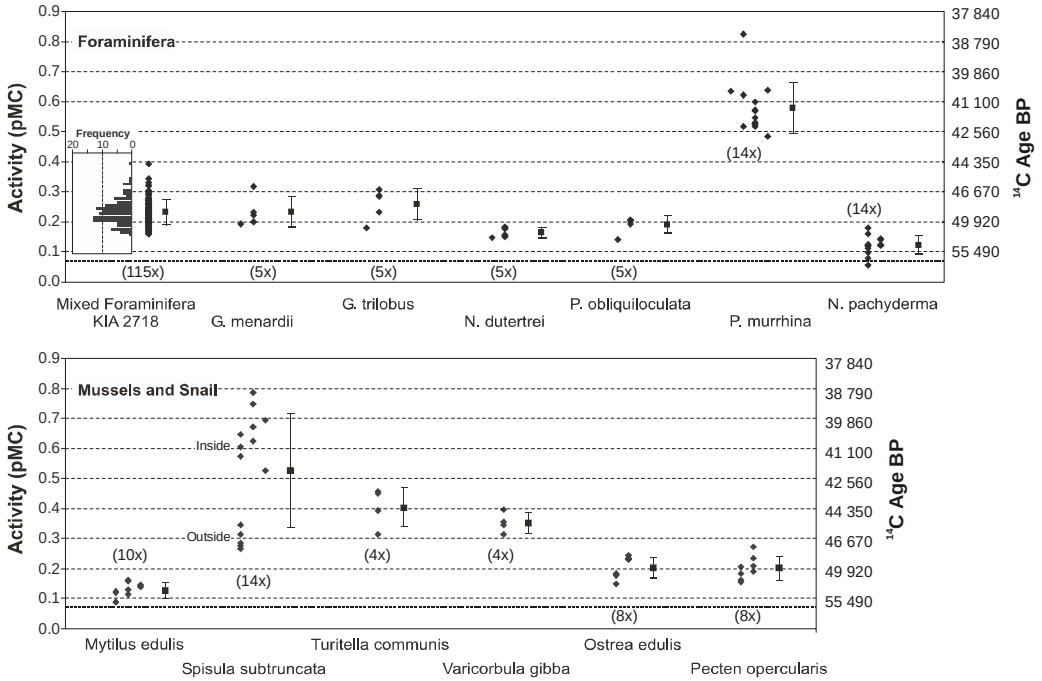

Figure 1 ^{14}C activities measured on various carbonate background materials. The numbers in brackets indicate the number of repetitions for a particular sample. The diamonds represent individual measurements while squares indicate averages with their standard deviation as uncertainty. The insert shows a histogram of the distribution of the results of the mixed foraminifera sample KIA 2718. The thicker dashed lines indicate the corresponding mineral background level. Different horizontal positioning for a certain species indicates different test series. The results of *N. Pachyderma* samples shown on the left were left coiling (sinistral) while the fewer results on the right were from a mixture of left and right coiling (sinistral and dextral).

Results from Biogenic Carbonate Samples

Results (115x) from the mixed foraminifera sample (KIA 2718), processed as described above, range from 0.16 to 0.4 pMC with an average of 0.23 ± 0.04 pMC (48.7 ka BP), which is significantly higher than the results obtained from the mineral carbonate samples (Figure 1 and insert).

The four different planktic foraminifera species picked from the mixed sample (KIA 2718) reveal apparent ages within a two-sigma range of the mixed sample result (Figure 1). However, it is interesting to note that the species present in larger abundances in the mixed sample, *G. menardii* and *G. trilobus*, show slightly more contamination and a larger scatter than the two other species picked from the mixed sample and could be responsible for the larger scatter of the bulk sample. The results obtained from *N. pachyderma* samples have been better and more consistent than those of other foraminifera species throughout this study with an average of 0.12 ± 0.03 pMC (53.9 ka BP). This is noteworthy considering that the samples were obtained from different cores and different basins. The results from the benthic species *Pyrgo murrhina* were consistently disappointing with an average of 0.58 ± 0.09 pMC (41.4 ka BP) considering that this species had been selected because of its thick shell and smooth surface in the hope of a lower contamination.

The results obtained from mussel and snail samples were more diversified. The species *Ostrea edulis* (0.20 ± 0.04 pMC, 49.9 ka BP), *Pecten opercularis* (0.20 ± 0.04 pMC, 49.9 ka BP), *Varicorbula*

gibba (0.35 ± 0.03 pMC, 45.4 ka BP), and *Turitella communis* (snail) (0.40 ± 0.07 pMC, 44.4 ka BP) gave reasonable and consistent results from material obtained from different individuals of each species. The samples taken from *Mytilus edulis* gave even older and more consistent results (0.13 ± 0.03 pMC, 53.4 ka BP) although they were also taken from various individuals. The results of the different samples of *Spisula subtruncata* varied more than the uncertainty of the measurements and depended on where the sample was taken from a single shell. The data points labeled "inside" and "outside" (Figure 1) were taken from the respective surfaces of a single individual. Although it does not lead to any firm conclusion, it is interesting to note that most species have shells made of aragonite and calcite except *Ostrea edulis*, which has a pure calcite shell. This difference is not seen in the result, neither in age nor in the size of the scatter.

Variations of the Preparation Method

In an attempt to reduce the consistent difference between the results of biogenic and mineral carbonate background materials, several variations of our "standard" preparation method were tested. These modifications are quite moderate and could be incorporated into daily routine work if need be. The results, shown in Figure 2, were obtained for the mixed foraminifera sample, KIA 2718. The problem is two-fold: one needs to have the necessary steps to clean a "regular" sample adequately but, since each preparation step adds contamination, these should be kept to a minimum. Also, the routine preparation should be mild enough not to destroy a significant part of the sample material in the process.

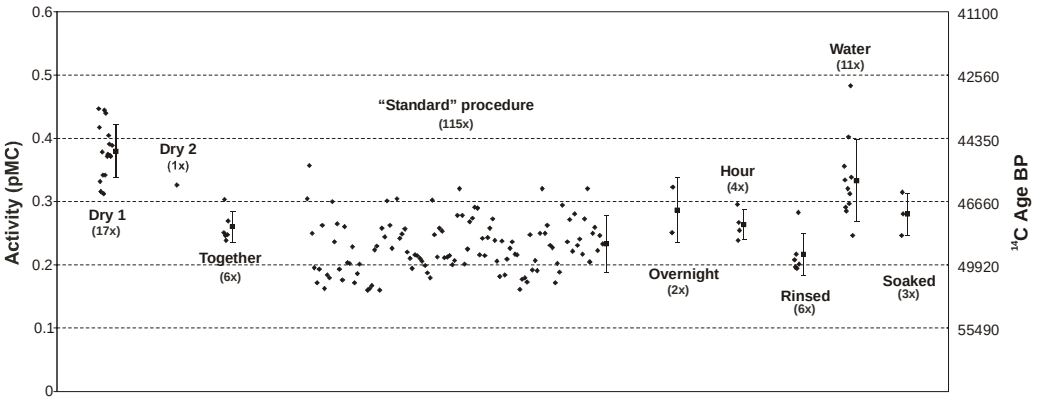

Figure 2 ^{14}C activities measured on the mixed foraminifera sample KIA 2718 after different variations of the preparation method. The numbers in brackets indicate the number of repetitions for a preparation method. The procedures used and their labels are described in the text.

Although one can see from the results of the mineral samples that the "standard" preparation does not introduce much contamination, the first trials were done using simpler preparations:

- The samples were not treated with hydrogen peroxide or any other chemical, the tubes were not evacuated separately first and were not heated during pumping. This led to younger results: (17x) 0.38 ± 0.04 pMC ("dry 1" on Figure 2).
- Again, the sample was not treated with peroxide or any other chemical, but the tubes were evacuated separately first and heated during pumping. This led to a younger result as well: (1x) 0.33 ± 0.03 pMC, showing that degassing alone is not sufficient to eliminate the younger biogenic carbonate background levels ("dry 2" on Figure 2). The samples were treated with H_2O_2 but the tubes were not pumped separately, (6x) 0.26 ± 0.02 pMC ("together" on Figure 2).

Several preparations with additional steps were also performed:

- The samples were left longer in H_2O_2:

1 hour (4 x)	0.26 ± 0.02 pMC	("Hour" on Figure 2)
Overnight (2 x)	0.29 ± 0.05 pMC	("Overnight" on Figure 2)

- The samples were treated with water in addition or instead of the H_2O_2 treatment:

Rinsed with H_2O after H_2O_2 (6 x)	0.22 ± 0.03 pMC	("Rinsed" on Figure 2)
In water (1.5 hour) before H_2O_2 (3 x)	0.28 ± 0.03 pMC	("Soaked" on Figure 2)
Water instead of H_2O_2 (11 x)	0.33 ± 0.06 pMC	("Water" on Figure 2)

The use of hydrogen peroxide instead of water, providing a mild leaching of the samples as well as the removal of some organic contaminants, was established previously by Schleicher et al. (1998). These results were verified in the present study. None of the results shown above warrant the making of an additional preparation step.

Extra Cleaning Procedures

Since small variations to the preparation method did not provide any indication as to how to remove the apparent contamination of the biogenic carbonate samples, a few drastic cleaning methods were tested. These could not be used as routine sample preparation because they require too much material or are too complex.

To determine if the higher biogenic carbonate background levels are due to surface contamination not removed by the mild H_2O_2 leaching, we carried out a progressive hydrolization of four mussel and foraminifera samples, IAEA C1 Carrara marble and Icelandic double spar (Figure 3A). The gas from the sample hydrolization was collected in four fractions. The first fraction consisted of the gas produced during the first 4 min of the reactions. The other fractions were collected then from 4 to 15 min, 15–35 min, and from 35 min to the end of the reaction, about 50 min. The samples were not treated with H_2O_2 prior to the hydrolization. This method required about 50 mg of sample material instead of the 4–10 mg used for routine preparation.

All materials showed some surface contamination, the early fraction being significantly younger than the subsequent gas fractions in most cases. Some, such as Icelandic double spar or the mussel *Mytilus edulis*, revealed very little difference between the various gas fractions while other sample materials such as *Pyrgo murrhina* exhibited a much larger surface contamination. In all cases, however, the last and cleaner gas fraction had a ^{14}C content similar to that of the complete samples prepared by our "standard" method, indicating that the existing surface contamination does not play a big role in the final result or that this contaminated surface is leached by H_2O_2 during "standard" preparation. The results of Icelandic double spar and IAEA C1 reflect well the different nature of the sample surface, the cleaner double spar—a larger crystal—being less likely to retain atmospheric gases.

Since the foraminifera *Pyrgo murrhina* gave such young apparent ages, we also tried to leach the tests (in HCl 0.003N, 2 hr, 20 °C) (Figure 3B) or crack them mechanically to remove secondary carbonates from inside the shells (Figure 3C) before preparation. The results, shown in Figure 3, did not give any encouragement, being similar to the apparent ages of the "standard" preparation. The same leaching was applied to the mixed foraminifera samples KIA 2718 and to *N. pachyderma* for the sake of completeness with similar results.

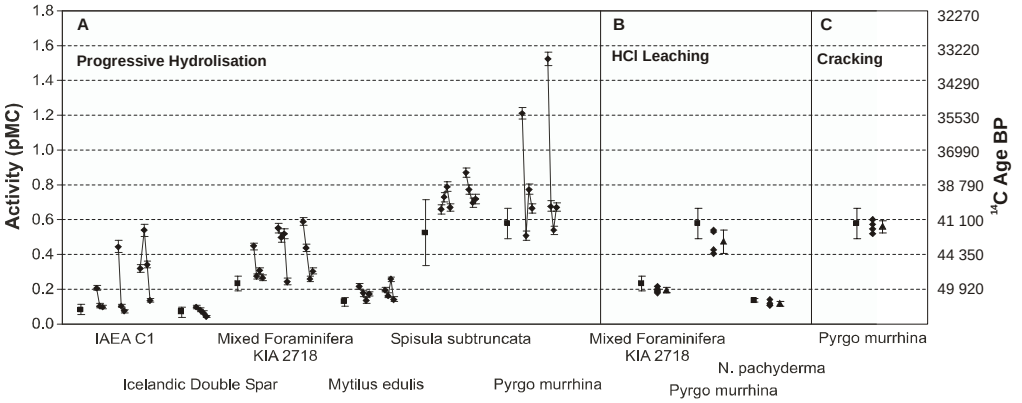

Figure 3 ^{14}C activities measured from different samples after different cleaning procedures described in the text. The squares represent the average of the "standard" procedure as shown in figure 1, the diamonds show the single measurements, the triangles display their averages. A) The progressive hydrolization results are shown from left to right, the lines link the 3 or 4 measurements made of a single hydrolization. B) Pre-leaching with HCl: each sample was treated 4 times. C) Cracking: four samples were prepared and analyzed.

CONCLUSIONS

Repeated tests on different biogenic and mineral carbonate background samples have shown the apparent ages of biogenic samples to be younger than their mineral counterpart. The ^{14}C concentration differences between biogenic and mineral carbonate background samples varied from 0.05 pMC (*Mytilus edulis*) to 0.5 pMC (*Pyrgo murrhina*). Furthermore, the apparent ages of biogenic samples seem species related and can be reproduced measuring different individuals for larger shells or even different sediment cores for foraminifera. Although tests showed some surface contamination, it was not possible to reach lower ^{14}C levels through cleaning, indicating the contamination to be intrinsic to the sample.

So far, no theory explaining the results has survived all the tests. No connection between surface structure and apparent ages could be established. The smoother surface belonging to the species giving the younger results, *Pyrgo murrhina* (0.58 pMC, 41.4 ka BP) while foraminifera with rougher surfaces lead to older results, *N. pachyderma* or *N. dutertrei*. It has been suggested that the carbonate crystal structure of the shells and the defects in them could be responsible for the younger apparent background ages, as the crystals may incorporate atoms, at some later stage, from its surrounding for the curing process (S Weiner, personal communication 2000; Lowenstam and Weiner 1989). Unfortunately, we do not have enough evidence at this point to validate or disprove this theory.

Although it has proven so far impossible to fully remove the contamination of biogenic carbonate samples, it is clear from the results that a certain amount of cleaning is effective and thus required (Schleicher et al. 1998). Since the degree of contamination is specific to the foraminifera or mussel species used, the only course of action to estimate accurately the age of older samples (>30 ka) is to use background material (>80 ka) of the same species and from the same provenance as the unknown samples. If such material is not available, generic biogenic background material (>80 ka) such as mixed foraminifera should be used since mineral carbonate samples cannot represent adequately the contamination of unknown biogenic samples.

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