Anomalous radiocarbon ages for foraminifera shells

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[1] The causes for discordant radiocarbon results on multiple species of planktonic foraminifera from high-sedimentation-rate marine sediments are investigated. We have documented two causes for these anomalous results. One is the addition of secondary radiocarbon for which we have, to date, only one firm example. It involves an opal-rich sediment. The other is the incorporation of reworked material. Again, we have, to date, only one firm example. It involves a rapidly deposited ocean margin sediment. However, we have three other examples where reworking is the most likely explanation. On the basis of this study it is our conclusion that, where precise radiocarbon dating of high-deposition-rate marine sediment is required, a prerequisite is to demonstrate that concordant ages can be obtained on pairs of fragile and robust planktic shells. For sediment rich in opal, it is advisable to check for secondary calcite by comparing ages obtained on acid-leached samples with those on unleached samples.

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1. Introduction

[2] Bioturbation and dissolution can cause divergent ^{14}C ages for coexisting species of planktonic foraminifera in marine sediments, depending on the sedimentation rate, extent of dissolution and gradients in faunal abundance [*Peng and Broecker*, 1984; *Manighetti et al.*, 1995]. In an attempt to avoid the loss of fidelity in marine records resulting from these effects, geochemists have turned their attention to high-accumulation-rate sediments (>10 cm/kyr). As such sediments are rare in the open ocean, the targets are, for the most part, sites close to landmasses. Although closed marginal basins such as the South China Sea and Caribbean Sea offer sediments with accumulation rates ranging from 5 to 15 cm/kyr, both have the drawback that the sills separating them from the open ocean lie at only 2 km depth. Hence they provide a record for only the upper half of the adjacent open ocean. In order to obtain rapidly deposited sediments representing deeper waters, targets are generally located along ocean margins. We have shown that in some cases, sediments from this environment yield widely divergent radiocarbon ages for coexisting planktic species [*Broecker et al.*, 1988]. In particular, the ages obtained on *G. sacculifer* (fragile and dissolution prone) are substantially younger than those for *P. obliquiloculata*, (robust and dissolution resistant).

[3] Two explanations exist for these large anomalies. One involves the addition of secondary radiocarbon either through exchange with pore water ΣCO_2 or through the deposition of secondary calcite with a younger ^{14}C age. The other involves downslope transport of pre-aged material. Clearly, it is extremely important to distinguish between these two mechanisms for, were it the first, the radiocarbon measurements yield minimum ages and, were it the second, they yield maximum ages.

[4] We present here five examples of such anomalies. In one case, secondary radiocarbon is certainly the villain. In three cases, there is no way to decide whether to place the blame on secondary calcite or on downslope transport. In the fifth case, we have firm evidence that downslope transport was responsible. As three of these examples have been published, we will only briefly review them here. The other two are based on unpublished results.

2. Example 1: Indian Ocean Diatom-Rich Sediment

[5] Some years ago, as part of a shell weight study on a series of sediment cores from the 90° East Ridge in the Indian Ocean, we stumbled on a core whose pre-Holocene section consisted of 9.6 m of sediment rich in the colonial diatom *Ethmosdiscus rex* [*Broecker et al.*, 2000]. As summarized in Figure 1, while the radiocarbon measurements of the top and base of the 25-cm-thick layer of Holocene calcium carbonate-rich ooze conform to expectation, those on mixed planktic shells from the pre-Holocene *Ethmodiscus rex*–rich sediment were clearly anomalous. The impression is given that initially secondary radiocarbon was added to these shells (in the form of secondary calcite) faster than radiocarbon was lost via radiodecay. Then, as the foraminifera shells aged, the rate of addition of secondary radiocarbon waned to the point where it no longer exceeded that of radiodecay. Below this depth, the radiocarbon age of the shells begins to increase. A sample from the bottom of the core (9.87 m) yielded a radiocarbon age 28,500 years.

[6] A clear demonstration that secondary ^{14}C had been added to these shells was obtained by leaching the shells with acid. By dissolving away 26.5% of the shell carbonate,

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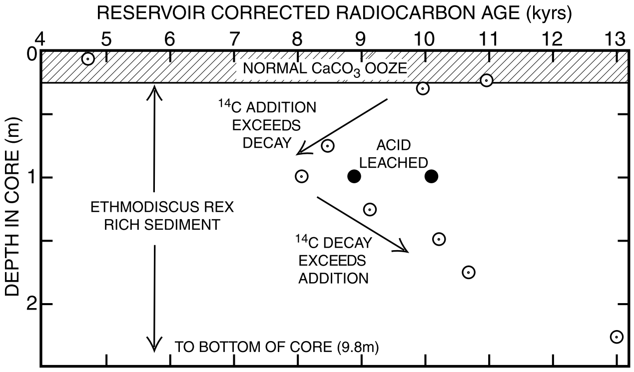

Figure 1. Reservoir-corrected radiocarbon ages for planktic foraminifera shells from Indian Ocean core RC14-31 located at 3.9 km depth and 9°S on the 90°E ridge [*Broecker et al.*, 2000]. While the ages on shells from the Holocene carbonate ooze conform to expectation, those on shells from the diatom section of the core are anomalously young (including a sample from which half the $CaCO_3$ was leached away).

the ^{14}C age of the residue increased by 800 years. By dissolving 48.6%, the age was increased by 2000 years. Of course, it is likely that both primary and secondary calcite would be removed to some degree during the leaching process, so this cannot give an accurate picture of the extent of contamination. To get some impression of how much secondary contamination would be required to obtain the observed ages, even with a zero age, some 20% additional carbonate would need to be added to the sample at 100 cm depth. Attempts to identify secondary calcite growth on these samples were previously inconclusive [*Broecker et al.*, 2000] although further investigation is warranted. A. Engles (University of Washington) is currently measuring ^{14}C on specific organic compounds produced by diatoms. We await, with interest, her results on these samples.

[7] The take-home message from these results is that, at least in opal-rich sediment, secondary radiocarbon addition can occur presumably through diagenetic calcite deposition.

3. Example 2: Eastern Equatorial Pacific Reducing Sediment

[8] Our worst horror story involves core RC11-238 from 2.6 km depth along the continental margin of the eastern equatorial Pacific [*Broecker et al.*, 2004a]. A sample centered at 110 cm depth in this core yielded radiocarbon ages on different planktic species ranging from 16,120 to 20,800 years (see Table 1). After leaching with hydrogen peroxide, *G. tumida* yielded an age 1800 years younger than that on unleached *G. tumida*. In contrast, hydrogen peroxide leaching of *N. dutertrei* yielded no significant age difference.

[9] Shaken by these results, we decided to conduct an intercomparison to be carried out by four AMS laboratories (Kiel, Woods Hole, Lawrence Livermore National Laboratory, and Eidgenossische Technische Hochschule). To this end 7000 *N. dutertrei* were picked from a single sample on which the results listed in Table 1 were obtained. Splits were sent to each lab with the request that two measurements be made, one on the shells as sent and the other after the shells were subjected to extensive leaching by procedures to be chosen by the laboratory. As can be seen in Figure 2, the results spread over nearly as great a range as that for the individual species. For two labs, leaching significantly reduced the age and in one it increased the age. These age differences are certainly not the result of errors in the AMS measurements. Each laboratory has proven its capability of consistently reproducing its results to an extent compatible with the stated measurement error. Interestingly, the samples leached using HCl consistently gave younger ages.

Table 1. Radiocarbon Ages of Handpicked Shells From a Depth of 105–115 cm in East Equatorial Pacific Core RC11-238[a]

Species	Age
G. ruber	18,460 ± 140
G. sacculifer	16,410 ± 130
N. dutertrei	17,130 ± 120
N. dutertrei[b]	17,100 ± 110
P. obliquiloculata	16,120 ± 110
G. tumida	19,050 ± 130
G. tumida[b]	17,240 ± 110
O. universa	20,800 ± 150
O. universa	20,400 ± 140
Benthics	20,160 ± 150

[a]See *Broecker et al.* [2004a].
[b]Residue after ~50% of the $CaCO_3$ was removed by leaching in hydrogen peroxide.

[10] In the *Broecker et al.* [2004a] paper, we leaned toward the addition of secondary radiocarbon rather than reworking as the explanation. The reason was that exceptionally large amounts of reworked forams were required. However, it now appears more likely that the forams in this sample are largely reworked. The difference among species would then be explained by differences in species make up of the reworked material. The decrease in age induced by leaching perhaps reflects the greater fragility of the reworked shells as the result of partial dissolution at their previous site of burial.

[11] Explaining the 1500-year range of results on unleached *N. dutertrei* is more difficult. This age spread likely involves self sorting during our splitting of 7000

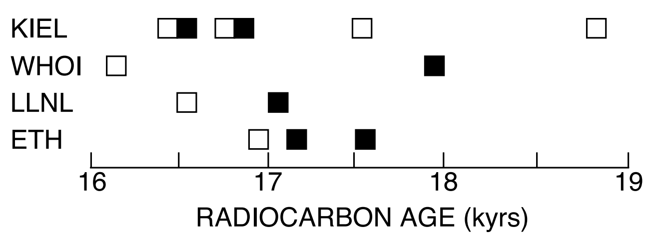

Figure 2. Results of laboratory intercomparisons on *N. dutertrei* from 105 to 115 cm depth in eastern equatorial Pacific piston core RC11-238. The solid squares are the ages of unleached samples, and the open squares are those of leached samples. The leaching procedures employed by Eidgenossische Technische Hochschule (ETH), Lawrence Livermore National Laboratory (LLNL) and Woods Hole Oceanographic Institution (WHOI) involved etching with HCl; up to 50–66% by weight was removed in these cases. Leaching in the Kiel lab was performed using 15% H_2O_2.

Table 2. Comparison of the Radiocarbon Ages on Pairs of Robust and Fragile Planktic Foraminifera From Three South China Sea Cores[a]

	Robust Species *P. obliquiloculata*		Fragile Species *G. sacculifer*			
Depth in Core, cm	^{14}C Age, years	Error, years	^{14}C Age, years	Error, years	Δ Age, years	Combined Error, years
V35-5, 7.2°N, 112.1°E, 1953 M						
65	6500	130	5750	120	750	170
65	6190	110	5830	110	360	160
72	6870	150	5990	150	880	210
82	8350	150	7670	140	680	210
87	7910	150	7500	150	416	210
95	9000	130	8250	140	750	190
95	8820	150	8130	140	690	210
102	9520	130	9050	130	470	180
107	9880	140	8930	150	950	210
112	9800	180	9050	160	750	210
117	10400	220	9610	200	790	300
155	12210	190	11580	200	630	280
177	13170	210	11860	190	1310	280
177	13600	170	12980	210	620	270
187	15160	220	13240	190	1920	290
187	14780	210	13220	190	1560	280
215	14340	200	13740	190	600	280
247	16010	440	14570	600	1440	740
277[b]	17530	330	16170	290	1360	440
309	17300	500	16380	590	920	770
309	18440	270	17540	260	900	380
				average	890 (21)[c]	
V35-6, 7.2°N, 112.2°E, 2030 M						
10	5140	90	4860	90	280	130
20	6060	100	6040	100	20	140
28	6810	100	6420	100	370	140
41	8030	110	7890	110	140	160
49	9020	120	8780	120	240	170
61	9630	120	9550	120	80	170
				average	190 (6)[c]	
Sonne50-37KL, 18.9°N, 115.8°E, 2695 M						
162	15300	150	15140	150	160	210
177	15890	120	15910	110	−20	160
197	17270	150	17460	160	−190	220
207	17225	190	17660	180	−435	260
				average	−120 (4)[c]	

[a]See *Broecker et al.* [1988 and 1990].
[b]Value represents *G. sacculifer* plus *G. ruber*.
[c]Values in parentheses indicate total number of pairs.

forams and/or during the further splitting carried out in the measurement labs.

[12] The take home message from this example is that when dealing with high-deposition-rate cores from ocean margins, it is important to carry out ^{14}C measurements on more than one planktic species. Where possible, one of these should be a species with a fragile shell (for example, *G. sacculifer*) and another, a robust shell (for example, *N. dutertrei*).

4. Example 3: South China Sea

[13] In a paper published long ago [*Broecker et al.*, 1988], it was shown for two closely spaced South China Sea cores VM30-5 and VM30-6 (7°N, 112°E, ~2 km) that the radiocarbon ages of *G. sacculifer* were consistently younger than those of coexisting *P. obliquiloculata*. The puzzle was that despite the fact that the cores were only a few miles apart and at water depths differing by only 80 m in one (VM30-5), the average age difference for six *P. obliquiloculata–G. sacculifer* pairs was 190 years; in the other (VM30-6), the average age difference for 21 *P. obliquiloculata–G. sacculifer* pairs was 890 years (see Table 2). For a third South China Sea core (SM50-37, 19°N, 116°E, 2.7 km), in four pairs, as shown by *Broecker et al.* [1990], the *P. obliquiloculata* averaged 120 years younger than the coexisting *G. sacculifer* (see Table 2). While again there is no way to demonstrate why so large an age difference characterized the pairs from VM30-5, it is easier for us to accept that the cause was addition of reworked material than to believe that two cores in the same setting with similar accumulation rates could have undergone such different extents of secondary radiocarbon addition. It should be noted that while the robust species live deeper in the water column than the fragile species, the difference in ^{14}C to C ratio in the DIC of the water in which they formed can give rise to, at most, a few hundred years age difference.

[14] Again, the take home message is that when dealing with rapidly accumulating sediment crosschecks involving

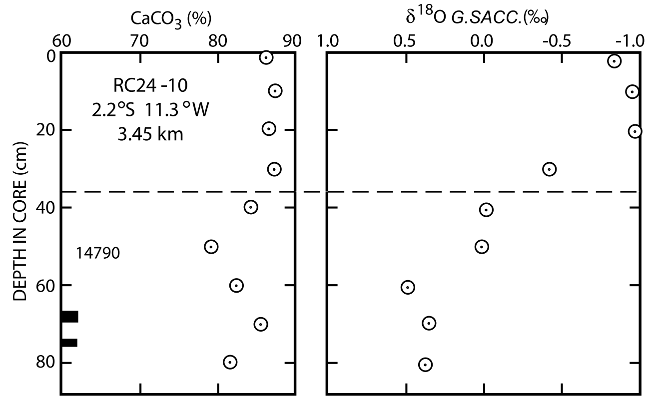

Figure 3. $CaCO_3$ and planktic ^{18}O for Mid-Atlantic Ridge core RC24-10. The dashed line marks the mid-depth of the deglacial transition (~12 ^{14}C kyr). The radiocarbon date at 52 cm is on bulk coarse fraction $CaCO_3$. The two bars mark the depths of the samples on which detailed radiocarbon analyses were conducted (see Table 3).

Table 3. Radiocarbon Results on Handpicked Shells From Piston Core RC24-10 From the Western Flank of the Mid-Atlantic Ridge (2.2°S, 11.3°W, 3.45 km)

Species	Radiocarbon Age, years
Depth 67–70 cm	
G. sacculifer	22,490 ± 170
N. dutertrei	27,600 ± 240
Mixed benthics	21,440 ± 200
Depth 74–76 cm	
G. sacculifer	20,430 ± 160
N. dutertrei	26,180 ± 280
Mixed benthics	NA[a]

[a]These are to be run.

Table 4. Radiocarbon Ages on Wood and Foraminifera Shells From Morotai Basin Core MD98-2181

Species/Type	Radiocarbon Age,[a] years
Depth 1046–1048 cm	
G. sacculifer	12990 ± 95
P. obliquiloculata	16180 ± 110
Mixed benthics	13700 ± 95
Depth 1048–1050 cm	
Wood	9540 ± 80
Wood	9625 ± 75
G. sacculifer	14210 ± 100
P. obliquiloculata	17820 ± 120
Mixed benthics	14,870 ± 100
Depth 1050–1052 cm	
G. sacculifer	14280 ± 100
P. obliquiloculata	17540 ± 120
Mixed benthics	14740 ± 95
Depth 1098–1100 cm	
G. sacculifer	12990 ± 140
P. obliquiloculata	13270 ± 110
Pteropod	14490 ± 150
Mixed benthics	14240 ± 220
Depth 1262–1268 cm[b]	
G. sacculifer	16650 ± 110
N. dutertrei	16800 ± 95
Mixed benthics	18050 ± 130
Depth 1270–1276 cm[b]	
Wood	15950 ± 120
Wood	15970 ± 120
G. sacculifer	16480 ± 120
P. obliquiloculata	16330 ± 100
P. obliquiloculata	16760 ± 110
N. dutertrei	16740 ± 110
G. tumida	16290 ± 110
>63 μm $CaCO_3$	17150 ± 120
Mixed benthics	17690 ± 130
Depth 1279–1285 cm[b]	
P. obliquiloculata	16900 ± 130
N. dutertrei	17150 ± 130
Mixed benthics	18350 ± 120
Depth 1767–1783 cm	
Wood	25070 ± 200
Wood	24430 ± 190
P. obliquiloculata	24400 ± 370
N. dutertrei	25100 ± 260
Mixed benthics	26180 ± 340

[a]As can be seen, only the ages on samples from 1046 to 1052 cm are anomalous. The ages on planktics and wood from deeper samples are nicely concordant.
[b]See *Broecker et al.* [2004b].

radiocarbon measurements on coexisting fragile and robust planktic shells should be conducted.

5. Example 4: Mid-Atlantic Ridge Oxidized Sediment

[15] As part of a study of a series of sediment cores from the entire length of the western flank of the Mid Atlantic Ridge, we attempted to obtain a valid benthic-planktic age difference for the glacial section of piston core RC24-10 (2.2°S, 11.3°W, 3.45 km, Figure 3). The results for two such samples are listed in Table 3. The radiocarbon ages for the *G. sacculifer* are respectively 5150 and 5750 years younger than those for the coexisting *N. dutertrei.* In the shallower sample, the benthics are 1050 years younger than the coexisting *G. sacculifer* and 6160 years younger than the coexisting *P. obliquiloculata.* Although in this case the low accumulation rate (~3 cm/10^3 years based on the ^{18}O transition from glacial to Holocene) invites anomalies resulting from both the couple between bioturbation and differential dissolution and that between bioturbation and differential abundance gradients, these anomalies should not exceed the ratio of mixed layer depth (~9 cm) and accumulation rate (3 cm/10^3 years) or 3000 years. So, once again, it appears that downslope transport of reworked material is involved.

6. Example 5: Morotai Basin Margin Sediment

[16] Firm evidence for the presence of reworked material was found for a single level in core MD98-2181 from the Morotai Basin south of the Philippine Island of Mindanao. While samples from several levels deeper in this core yielded beautifully concordant results [*Broecker et al.*, 2004b], those from an interval deposited close to the time of the onset of the Bolling-Allerod yielded highly anomalous results (see Table 4 and Figure 4). The *P. obliquiloculata* from this interval were 3000 to 5000 years older than expected from the upward extrapolation of the age versus

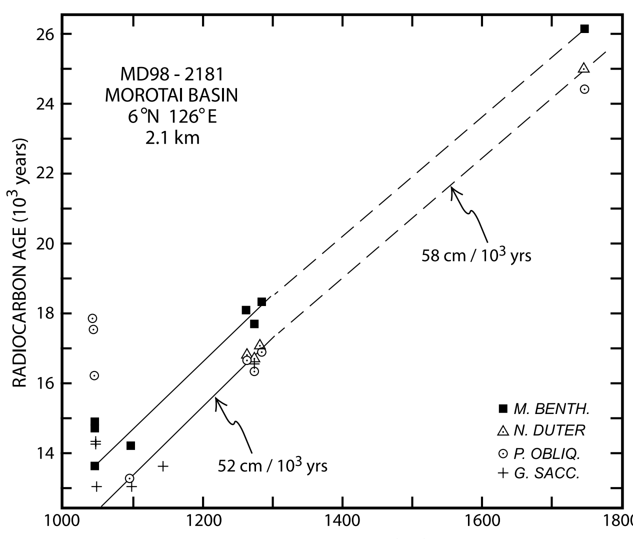

Figure 4. Radiocarbon ages as a function of depth in core MD98-2181 from 2.1 km depth in the Morotai Basin south of the Philippines. As can be seen, except for the results on the samples from 1046 to 1052 cm, the agreement between coexisting planktonics is excellent. The older than expected ages for foraminifera shells from the 1046- to 1052-cm interval require that reworked material has been incorporated in this sample. Clearly the ratio reworked to normal shells is much higher for *P. obliquiloculata* than for *G. sacculifer* or mixed benthics.

depth trend for the deeper concordant samples. The *G. sacculifer* from this interval, although closer to the expected age, were 1000 to 2000 years too old. One mixed benthic age fell close to the expected trend; the other two were about 1000 years too old.

[17] The ages of two pieces of wood found in this interval add to the confusion for they are more than 2000 years younger than expected from the age-depth trend. If the wood ages are reliable, it would demand some sort of slump event to emplace such young material. However, it is possible that is that a single piece of wood was caught in the core cutter and dragged down a meter or so before being broken up and pushed into the adjacent sediment.

[18] The pattern of foraminifera ages fits our idea that robust species like *P. obliquiloculata* are more likely to survive reworking and transport than fragile species like *G. sacculifer*. Whether or not this is the correct explanation, it is clear that the signature of reworking is a discordance between the ages of robust species (older) and fragile species (younger).

7. Summary

[19] If sediments from high-accumulation-rate environments are to be used for paleoceanographic studies, it is obligatory that assurance be given that the sediment is free of reworked material. Not only will the presence of such material lead to excessive radiocarbon ages but also it will bias isotopic and chemical measurements made on foraminifera. The best way to detect reworked material is through a comparison of radiocarbon ages on fragile foraminifera shells (i.e., *G. sacculifer* or *G. ruber*) and robust foraminifera shells (i.e., *P. obliquiloculata* or *N. dutertrei*). If the latter are significantly older than the former, then reworked material is likely present.

[20] For sediments rich in opal, there is a danger of the incorporation of secondary calcite. In order to check whether or not this is the case, the radiocarbon age of acid-leached samples should be compared with those of unleached samples.

[21] Surprisingly few measurements of paired planktic shells have been published. One reason is the sizable cost of a radiocarbon analysis (~$300). Another has to do with the fact that as most of the results fell in stratigraphic order, there appeared to be no necessity for cross checks. However, as the field of paleoceanography matures, more attention will be focused on chronologic precision and proxy reliability. Hence the extra expense associated with paired radiocarbon analyses will be viewed as a requirement rather than a luxury.

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