THE CARBONATE ^{14}C BACKGROUND AND ITS COMPONENTS AT THE LEIBNIZ AMS FACILITY

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ABSTRACT. After routine accelerator mass spectrometry (AMS) radiocarbon dating had been established at the Leibniz-Labor with the completion of systems for CO_2 production, graphitization, and target making, a systematic investigation was conducted to find the sources of ^{14}C concentrations observed in background materials. We quantified the contributions of the AMS-system, the reduction, CO_2 production from carbonate, carbonate contamination, and combustion. Carbonate contamination appears to be the dominating factor. Improvements in the pretreatment of foraminifer carbonate have led to the elimination of most of this contamination.

INTRODUCTION

In September 1995, the Leibniz Labor für Altersbestimmung und Isotopenforschung accepted its HVEE Tandetron accelerator mass spectrometry (AMS) system for ^{14}C measurements. Since then, >1500 unknown samples of a wide variety of materials have been measured. Our laboratory and AMS system were described at the Tucson AMS conference (Nadeau *et al.* 1997). Central issues in our laboratory over the past year have been 1) how to simplify our sample processing and increase its output to match the required measuring throughput (see companion paper by Nadeau *et al.*), and 2) how to minimize sample contamination and the ^{14}C processing laboratory blank. A low ^{14}C processing blank is a prerequisite for measuring very old and/or very small samples. Especially, the possibility of dropping the required sample size from the present standard value of 1 mg of carbon to, for example, 0.1 mg, would be a great boon to paleoceanography, atmospheric trace gas studies and the dating of archaeological materials. We therefore systematically investigated the different contributions to our overall background as measured in our AMS system, starting with the AMS system itself, and working back through the different steps such as reduction, CO_2 production, and chemical sample pretreatment. In this we follow procedures similar to Vogel *et al.* (1987) and Beukens (1990). Vogel *et al.* divided their AMS ^{14}C background in three components, *viz.*, 1) *in-situ* sample contamination, 2) contamination during sample preparation, and 3) AMS system background. In addition to our current blank and background values, we will discuss the decrease in reduction system memory that resulted from the shift to metal valves in our new system (Nadeau *et al.* 1998).

Background, Blanks and Contamination

We define *machine background* as ions detected in the ^{14}C window when a target containing no ^{14}C is being sputtered. Since we cannot know for certain if a particular background target is ^{14}C-free, those measurements only produce upper limits for the machine background. *Blank* values describe the ^{14}C added to a sample during the different processing steps in the laboratory. Assuming that the amount of ^{14}C added is a system/process property (that may be influenced by a memory of the previous sample), one can quantify these contributions by varying the amount of sample carbon. *Contamination* covers the admixture to the sample of carbonaceous material with a ^{14}C concentration different from that of the original sample material. This includes *in-situ* production. Careful sample selection and proper procedures of sampling, storage, and mechanical and chemical sample treatment can minimize the contamination problem. Figure 1 shows a breakdown of the ^{14}C concentration measured in a hypothetical "background" sample into different background, blank, and contam-

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ination components. We discuss below tests quantifying a number of these components in our current AMS operation.

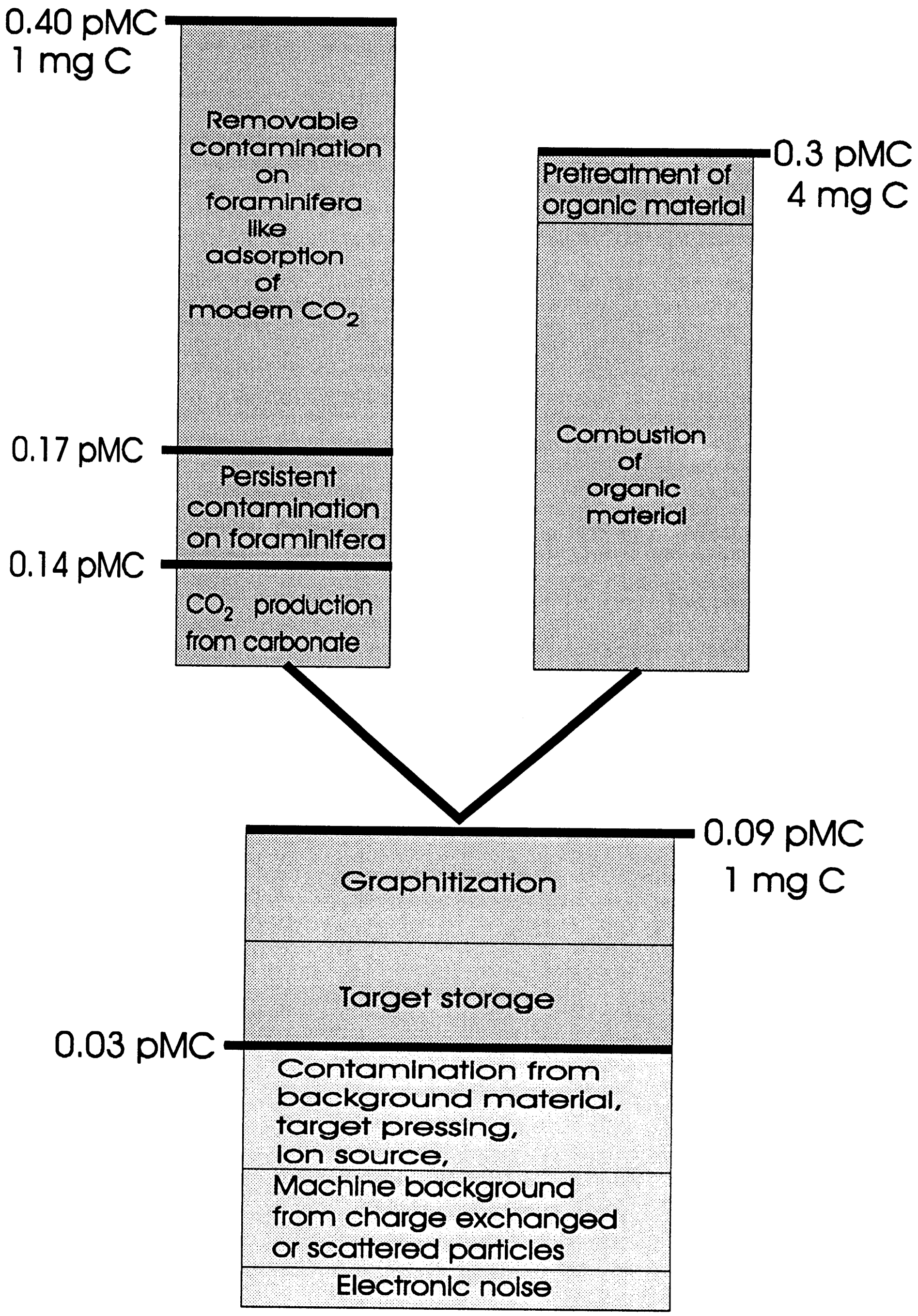

Fig. 1. Breakdown of the background of a ^{14}C measurement in its components, expressed as a percentage of the modern standard ^{14}C concentration

Machine Background

We tested the background of the AMS system using a pure graphite powder with a very low ^{14}C concentration, kindly supplied by our colleagues from the Woods Hole NOSAMS facility (*cf.* Nadeau *et al.* 1997). This powder can be pressed directly into the target holder, which eliminates all but storage and pressing as possible blank contributions. It consistently gives the lowest ^{14}C concentrations we observe in any target, and is measured weekly to check the level and stability of the machine background. These measurements yield a background of 0.03 ± 0.015 pMC, equivalent to 65 ka ^{14}C, similar to machine backgrounds reported for other AMS systems (*e.g.*, Vogel *et al.* 1987; Beukens 1990; van der Borg *et al.* 1997; Kretschmer *et al.* 1997; Kirner *et al.* 1995; Grootes *et al.* 1986; Gillespie and Hedges 1984).

Beam stops inserted at the mid-section of the recombinator (Nadeau *et al.* 1997; Fig. 1) allow the breakdown of this background into counts from the scattering of ions that reach the accelerator *via* the mass-12 or mass-13 path, and ions that follow mass 14 ($^{12}CH_2^-$, $^{13}CH^-$), under otherwise normal operating conditions. No counts were observed in the detector over a 40-min period when the mass 13 and 14 paths were blocked, while a normal $^{12}C^-$ beam was injected into the accelerator. This puts an upper limit of 0.0013 pMC, equivalent to 90.5 ka ^{14}C, if one count had been observed, to the combined background contributions of mass-12 charge exchange/scattering and electronic noise. Blocking only the mass 14 beam, four counts were detected in a 67-min period, resulting in a background of 0.0031 pMC and equivalent age of 83.4 ka. This is similar to the observations of Beukens (1990). The observed 0.03 pMC machine background is thus for *ca.* 90% made up by contributions from mass-14 charge exchange/scattering and true ^{14}C. These contributions appear to be of similar magnitude but will vary with the degree of contamination of the ion source. As stated above, the 0.03 ± 0.015 pMC is an upper limit for the machine background, since the carbon powder may also contain some residual ^{14}C, and additional ^{14}C may have been introduced during storage and target pressing.

Blanks: Reduction System and CO_2 Extraction from Carbonate

To determine the blank contribution of our reduction and carbonate systems (Nadeau *et al.* 1998), we converted varying amounts of Carrara marble (IAEA standard C-1; 8–45 mg) into CO_2. From each extracted CO_2 gas sample, an amount corresponding to *ca.* 1 mg of carbon was graphitized in the reduction system and pressed into a target under identical conditions. From a linear fit of the measured ^{14}C concentrations *versus* the inverse of the carbonate mass (Fig. 2), we obtain a y-axis intercept of (0.091 ± 0.009) pMC, equivalent to the reduction system blank + machine background for an "infinitely large" sample, assuming that the Carrara marble is a true background material. The resulting graphitization contribution to the blank is 0.06 ± 0.02 pMC (equivalent to an age of 60 ka) or 0.6 μg of C, assuming the contamination to be 100 pMC. The measured ^{14}C content of (0.14 ± 0.02) pMC for a Carrara marble sample containing 1 mg carbon, combined with the 0.091 pMC intercept, indicates a blank from the carbonate system of (0.54 ± 0.05) μg (equivalent to 0.054 pMC and 60 ka BP). The analysis shows that, for samples containing at least 1 mg of carbon, contamination during graphitization and during carbonate hydrolysis is normally negligible. System blanks pose a problem for samples containing 0.1 mg or less. Similar observations were made in other laboratories (*e.g.*, Vogel *et al.* 1987; Beukens 1990; Gillespie and Hedges 1984).

Blanks: Organic Combustion

Organic samples are combusted in quartz ampoules with copper oxide and silver wool. Prior to use, the quartz ampoules, copper oxide, and silver are heated in air at 900°C. Combustion of coal background material typically yields values of *ca.* 0.3 pMC (equivalent to *ca.* 47 ka) for a sample con-

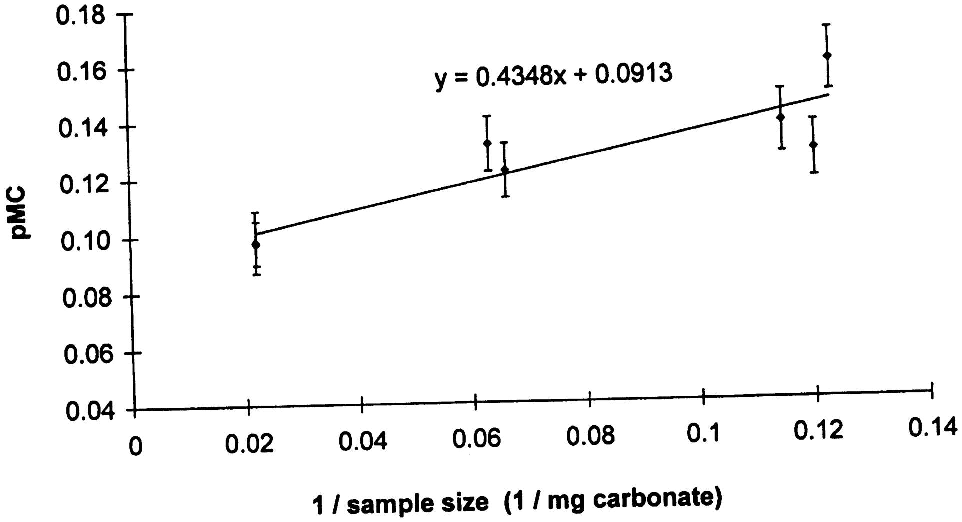

Fig. 2. ^{14}C concentration *versus* the inverse sample size of Carrara marble (IAEA C-1). Sample sizes of *ca.* 8, 15 and 45 mg of carbonate were hydrolyzed into CO_2 and fractions equivalent to 1 mg of carbon were graphitized and pressed. The intercept of the linear fit to the data points with the y-axis defines the background of (0.091 ± 0.009) pMC introduced after hydrolyzation, including a possible contamination in the Carrara marble. The gradient defines the blank ((0.54 ± 0.05) μg modern carbon) introduced during hydrolyzation.

taining 4 mg of carbon. Considering the blank contribution from graphitization, we find that the combustion and the extraction of the CO_2 from the combustion ampoule contribute *ca.* 10 µg of modern carbon. A systematic investigation of the sources of this carbon is currently underway.

Memory Effect

Adsorption of CO_2 on the walls of the reduction system may lead to a memory of the CO_2 sample reduced before, and therefore to a variable blank contribution. The first version of our reduction system (Nadeau *et al.* 1997) showed a significant memory effect (0.6%). Our present reduction system (Nadeau *et al.* 1998) uses metal bellows-sealed valves with Kel-F seat (Nupro BK) to minimize the memory effect. A numerical value for our current memory was obtained in an accidental test where Carrara marble background was prepared in two reduction units immediately after two contaminated samples having a ^{14}C concentration of *ca.* 22 times modern. The observed values of 0.26 and 0.29 pMC compared to our normal Carrara blank result (0.14 pMC) indicate a system memory of (0.006 ± 0.0012)%. A test using modern samples showed no significant memory in agreement with this result.

Contamination of Foraminifera

Most of the carbonate samples measured in our laboratory are mono-specific foraminifera samples. We therefore use Eemian foraminifera (unsorted), which should be >100 ka old and have no measurable ^{14}C concentration, to provide a background material with a similar history and structure as the unknown samples. The mean value of 53 Eemian measurements obtained in the first half of 1997 showed a ^{14}C content of (0.38 ± 0.07) pMC for samples containing 1 mg of carbon (8 mg of carbonate). The difference with the 0.14 pMC obtained for Carrara marble must be due to contamination of the Eemian foraminifera. A similar difference was found by Gulliksen and Thomsen (1992), who measured 0.32 pMC for foraminifera and 0.18 pMC for Icelandic double spar used as background material. Foraminifera shells may contain, in addition to the desired sample carbonate, coccolith carbonate shells and carbonaceous sediment debris, trapped in pores or inside the shell and possibly encrusted by secondary carbonate (Fig. 3B), organic shell material, and adsorbed atmospheric CO_2. A good sample pretreatment should remove all secondary carbonates and CO_2, while leaving the foraminiferal carbonate shells intact. Simultaneous removal of organics prevents trapping of secondary carbonates by organic coatings, and, at the same time, makes the sample carbonate more accessible to the acid used to convert it to CO_2. Scanning electron microscope (SEM) pictures (Fig. 3) of the inner surface of the foraminifer *Globorotalia menardii*, broken before pretreatment (Fig. 3A), illustrate the variety of carbonaceous material trapped inside the foraminifer shell (Fig. 3B). Figure 3C and 3D show that most of the encrusted material is removed by ultrasonic cleaning in dilute HCl and H_2O_2, respectively. Figure 3C indicates that HCl cleaning also damages the foraminifer shell and is therefore less desirable.

We tested the effect of mechanical cleaning by ultrasound, alone or in combination with acid leaching and/or the oxidation of organics, by measuring the residual ^{14}C concentration. Table 1 and Figure 4 group nine different pretreatments of Eemian foraminifera and the resulting background ^{14}C concentrations in 3 groups, *viz.* acid leach, dry and wet (H_2O_2) oxidation of organics, and displacement of adsorbed CO_2. "Weak" HCl leaching (*b*) (dissolving 0.4% of the carbonate) produced a scatter similar to that of untreated foraminifera and, if anything, higher ^{14}C. "Strong" HCl leaching (*c*) (10% carbonate dissolution) greatly reduced the scatter and yielded 0.25 pMC. Though this is a very positive result, the treatment severely damaged the foraminifera (Fig. 3c) and resulted in a loss of material. Although organic compounds should not produce CO_2 in phosphoric acid, they might work as a trap for detrital carbonate or CO_2 gas. Removing organic material by only roasting the foraminifera in O_2 at 350°C (*d*) showed no significant reduction of the measured ^{14}C concentration. Ultrasonic treatment in H_2O_2 (*f*) gave a large scatter though a somewhat better average ^{14}C concentration. The combination of roasting with ultrasonic treatment in H_2O_2 and a final HCl rinse (*e*) produced a reduction of ^{14}C but, surprisingly, less than the same treatment without roasting (*g, h* giving (0.25 ± 0.04) pMC and (0.23 ± 0.03) pMC as mean value, respectively). It appears that a reduction in ^{14}C contamination is not obtained by removing organic material but rather by carbonate leaching. As the H_2O_2 solution has a pH = 3, it will also leach some carbonate. It is, however, less destructive to the foraminifer shell (Fig. 3d). All the procedures described above end by drying the foraminifera. This allows readsorption of CO_2 onto the cleaned carbonate surfaces. Following a remark on good background results obtained in Utrecht starting with wet foraminifer samples (Dr. A. F. M. de Jong, personal communication 1997), we tested inserting the pretreated foraminifera wet in the carbonate system ("wet attachment", *i, k*). The ^{14}C results for ultrasound with H_2O show, when compared with ultrasound plus weak leaching (*i*: (0.20 ± 0.02) pMC versus *b*: (0.47 ± 0.09) pMC), that CO_2 adsorption may contribute significantly to the ^{14}C levels observed for background foraminifera. The difference between H_2O and H_2O_2 plus ultrasound (*i, k*) may indicate the presence of some additional carbonate contamination removed by leaching. The ultrasound peroxide treatment with wet attachment produced a background ^{14}C concentration of (0.17 ± 0.01) pMC (equivalent age 51.4 ka), close to the Carrara marble results and a surprisingly small scatter.

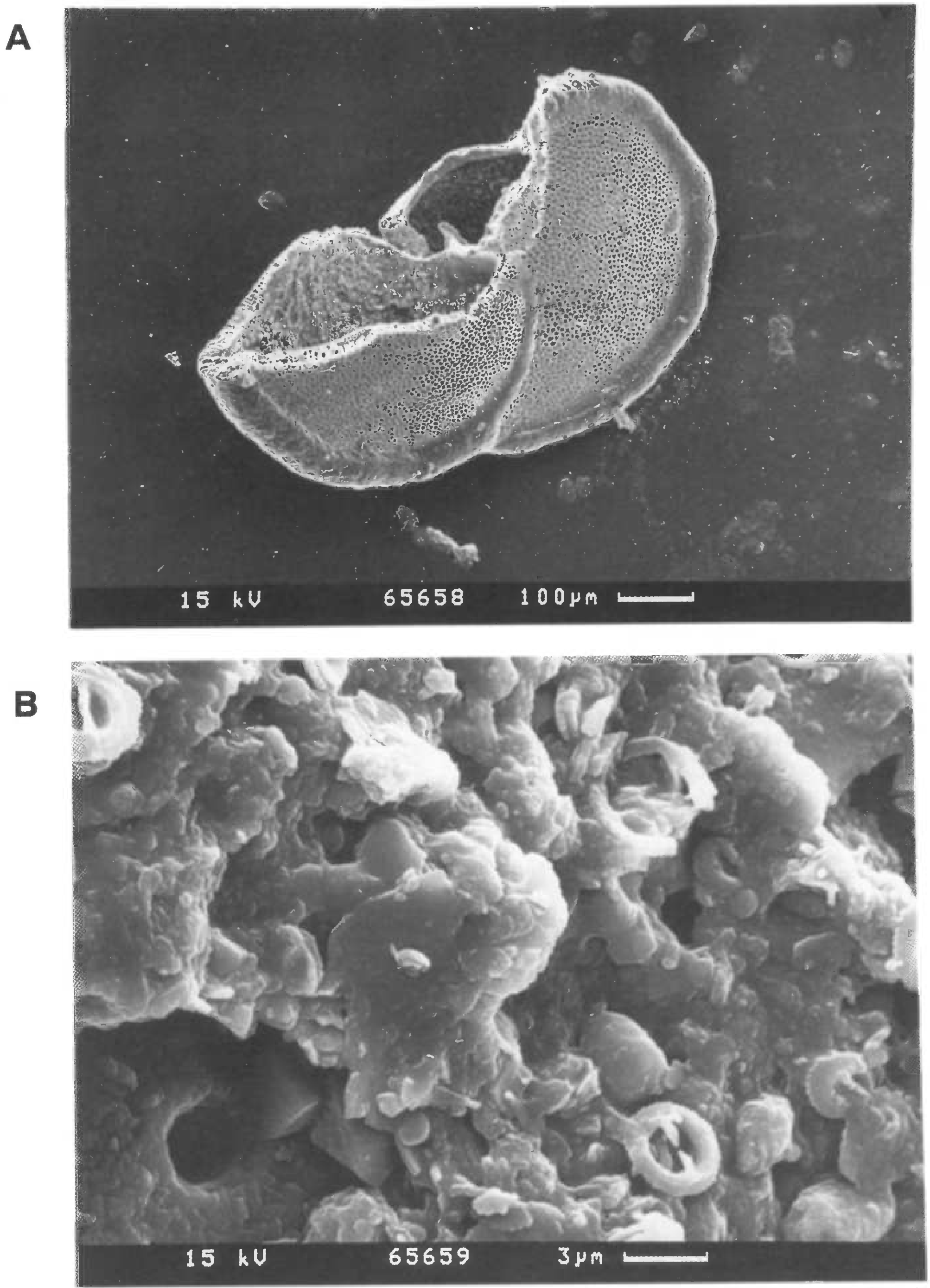

Fig. 3A,B. Scanning electron microscope (SEM) pictures of the foraminifer *Globorotalia menardii*. This species is part of the unsorted Eemian foraminifera used in the pretreatment test and distinguishes itself by a very small shell aperture. A. and B. are unpretreated foraminifera, outer and inner surface (covered with debris).

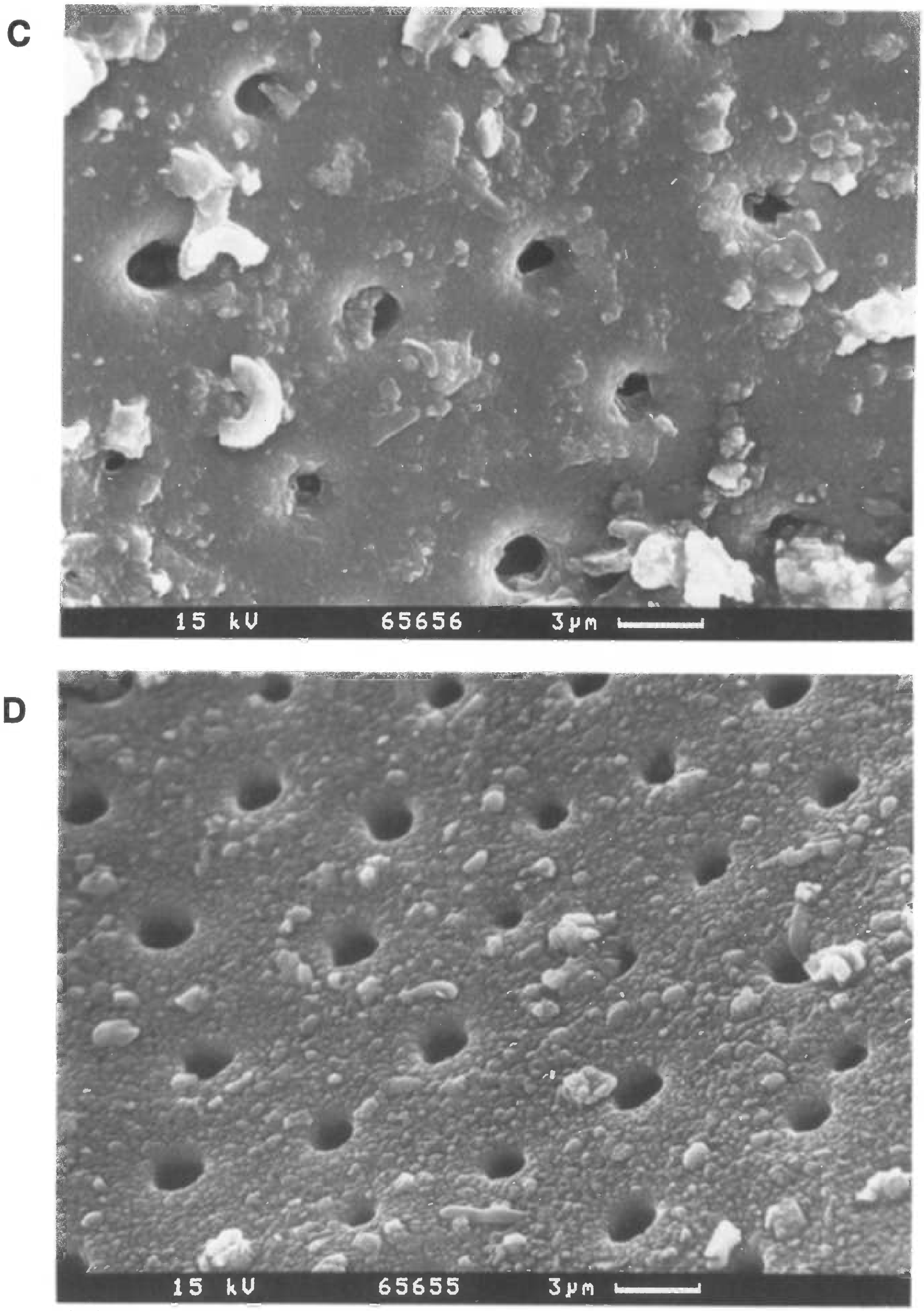

Fig. 3C. The inner surface after leaching with HCl, and 3D. after H_2O_2 treatment, both with ultrasound. The debris can be removed by these procedures; leaching also damages the surface of the foraminifer.

TABLE 1. Summary of Pretreatments Used for Removing the Contamination on Foraminifera

Pretreatment procedure	^{14}C concen. (pMC)	σ* (pMC)	Eqv. age (yr BP)	σ age (yr BP)	No. of targets
a) None	0.401	0.084	44,330	+1870 −1520	10
b) Weak HCl leaching (0.1% dissolution) with 1h ultrasonic and final HCl rinse (0.3% dissolution)	0.470	0.086	43,060	+1630 −1350	10
c) Strong HCl leaching (10% dissolution) with 15 min ultrasonic and final HCl rinse	0.251	0.014	48,100	+450 −420	6
d) Roasting in O_2 at 350°C	0.400	0.014	44,350	+290 −280	2
e) Roasting in O_2 at 350°C plus 30% H_2O_2, 1h ultrasonic, with final HCl rinse	0.330	0.014	45,900	+340 −330	2
f) 30% H_2O_2, 1h ultrasonic, no final HCl rinse	0.346	0.065	45,530	+1680 −1390	3
g) 30% H_2O_2, 1h ultrasonic, with final HCl rinse†	0.247	0.043	48,220	+1550 −1300	10
h) Combined weak HCl (0.1% dissolution) and 30% H_2O_2 treatment	0.226	0.029	48,940	+1110 −980	10
i) Dist. H_2O, 15 min ultrasonic, (wet attachment to the carbonate system)	0.202	0.023	49,830	+980 −870	5
k) 30% H_2O_2, 15 min ultrasonic, (wet attachment to the carbonate system)	0.166	0.008	51,420	+380 −370	6

*σ calculated from the scatter of the measurements of each test
†Measurements on different samples of old foraminifera yielded similar results

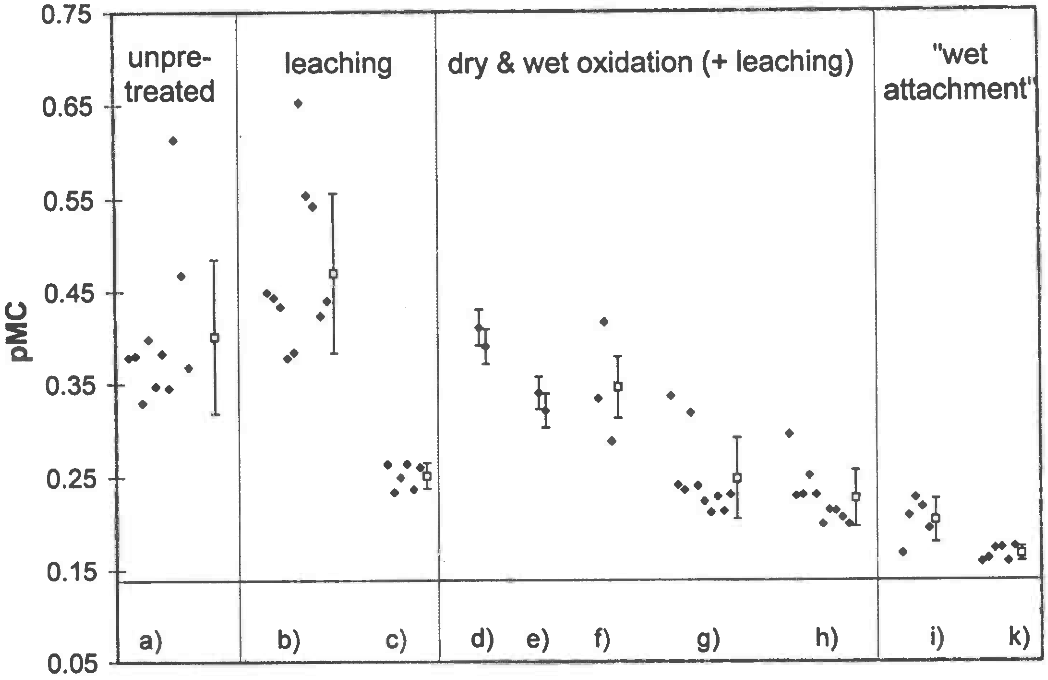

Fig. 4. ^{14}C concentrations of Eemian foraminifera pretreated with methods described in Table 1. The lowest ^{14}C concentrations, almost down to the value of the system blank (Carrara marble, graphed as bottom line), are obtained by H_2O_2 pretreatment with "wet attachment" (k).

CONCLUSION

Tests with the IAEA standard C-1, Carrara marble, show that the CO_2 production from carbonate and the reduction to graphite presently contribute about equally (*ca.* 0.05 pMC and 0.06 pMC, respectively, for a 1 mg carbon sample) to the (0.14 ± 0.02) pMC (equivalent to 52.6 ka) observed as background. This allows age determinations up to 59.6 ka, using the 2-σ convention and assuming a measurement on the same sample material (marble) and thus the same error. The machine background is about half as much (0.03 pMC). The main contribution to the ^{14}C concentrations of *ca.* 0.40 pMC observed in Eemian foraminifera used as carbonate background was made by contamination of the foraminifera themselves. This contamination appears to be mainly adsorbed modern CO_2, which can be greatly reduced by placing the foraminifer samples wet in the carbonate-CO_2 system, immediately after ultrasound cleaning. Use of H_2O_2 provides an additional lowering of the ^{14}C level to 0.17 pMC (equivalent age 51.2 ka), without significantly damaging the foraminifer shells. The initial large difference between the Carrara marble and Eem foraminifera backgrounds demonstrates the importance of using a background material closely similar to the samples being measured. For organic materials, the combustion is presently our main source of contamination (*ca.* 10 µg of modern carbon, giving an apparent background age of *ca.* 47 ka for a 4 mg sample). The origin of this contamination still needs to be resolved.

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