CARBONATE SAMPLE PREPARATION FOR ^{14}C DATING USING AN ELEMENTAL ANALYZER

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ABSTRACT. Radiocarbon dating of carbonates is of increasing importance for archaeology and climate research. Like most samples, these usually require pretreatment to remove surface contamination. We studied several pretreatment techniques using snails and shells of different stages of preservation and sensitivity to dissolution during the acid step of the pretreatment. We find that simple acid treatment leads to reliable results, and is applicable especially to very fragile specimens. We also compare conversion of calcite using an elemental analyzer (EA) to the conventional acid dissolution technique.

INTRODUCTION

In radiocarbon dating, organic samples are usually combusted using sealed quartz tubes or, increasingly, by an elemental analyzer (EA). For materials like charcoal, wood, or bone collagen, the advantages of using an EA for conversion to CO_2 are well known (van der Plicht 2000; Yoneda et al. 2004). For carbonates, however, the conversion to CO_2 using acid is still predominately applied. It is attractive to use EA combustion for conversion of carbonates to CO_2 as well because it can be faster and more convenient than the traditional acid dissolution technique. The sample preparation to remove contaminants is still important, and we need to find a pretreatment protocol to remove them before converting the sample to CO_2 gas. We were motivated by a recent publication (Burke et al. 2010) dealing with ^{14}C dating of deep-sea corals after a rather extensive pretreatment and usage of an EA for conversion.

METHODS

We defined 5 sample preparation methods of different strength to be tested, the most elaborate one (C) being the method presented in Burke et al. (2010) and the simplest and mildest method is method D. The methods are summarized in Table 1. Methods A and B represent the fastest way to pretreat the carbonate samples. In method E, we tried to find the ideal pretreatment as a combination of simplicity and speed and hopefully also complete removal of contamination without destroying the sample. Method F, conventional hydrolysis, was done on 2 of the snails in order to obtain an estimate for the comparison to the standard pretreatment and CO_2 production.

Methods A and B consisted of a short etching of the samples in 1% hydrochloric acid (HCl) using an ultrasonic bath (US). The acid concentration was identical in both methods, but we varied the duration because the snails react very sensitively to acid. Method C was the strongest and most destructive method, starting with methanol pretreatment and continuing with a 1:1 mixture of 30% H_2O_2:4% NaOH. The final step involved a 1:1 mixture of 30% H_2O_2:1% $HClO_4$. All steps were carried out using an US and with extensive wash of Milli-Q™ water in between. The easiest way to pretreat the samples was method D with a methanol wash only as adapted from Burke et al. (2010). A combination of methods A and D resulted in our method E. The samples received a methanol wash before being etched in 1% HCl for 1 min, using an US for both steps and thorough washing with Milli-Q water in between as well as afterwards. Details of method F, conventional hydrolysis, can be found in Rethemeyer et al. (2013), who applied this method to some of our samples. As expected,

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Proceedings of the 21st International Radiocarbon Conference edited by A J T Jull & C Hatté
RADIOCARBON, Vol 55, Nr 2–3, 2013, p 364–372

https://doi.org/10.1017/S0033822200057489 Published online by Cambridge University Press

Table 1 Definition of the steps applied to the carbonate samples as explained in the text ("US" = ultrasonic bath; H_2O = Milli-Q™ water).

Reference	Method	Step 1	Step 2	Step 3
This work	A	1 min 1% HCl US; 3 × H_2O US		
This work	B	4 min 1% HCl US; 3 × H_2O US		
Burke et al. 2010	C	20 min methanol US; 2 × 20 min H_2O US	20 min US 1:1 30% H_2O_2:4% NaOH; 3 × H_2O; 2 × 20 min H_2O US	1 min US 1:1 30% H_2O_2:1% $HClO_4$; 3 × H_2O; 2 × 20 min H_2O US
Burke et al. 2010	D	20 min Methanol US; 3 × H_2O US		
This work	E	20 min Methanol US; 3 × H_2O US	1 min 1% HCl US; 3 × H_2O US	
Rethemeyer et al. 2013	F	1M H2SO4; H_2O	99% H_3PO_4 6 hr at 75 °C	

only the well-preserved snails survived nearly all kinds of pretreatment. The thinnest sample, MAMS 13876, only survived method A.

The carbonate samples in our laboratory are usually snails or shells. Hence, we focused on these types in our experiments. Our first tests were done on 6 snails, 5 of which were *Scutalus* (Figure 1) collected during excavations in the Palpa region in Peru. From these excavations, snails and other organic material from the same sediment layers had been dated previously (Unkel et al. 2007; Mächtle et al. 2010). These samples had been processed earlier by different colleagues either by using 3N HCl and measured in a gas proportional counter or the subsamples used for AMS were prepared with 4% HCl and then hydrolyzed.

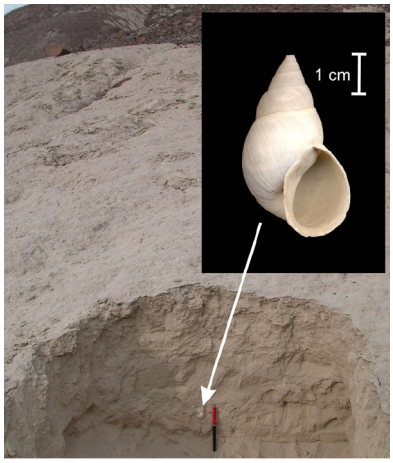


Figure 1 *Scutalus* snail, Pe 111/2, sample MAMS 13877. Photo from Mächtle et al. (2010) with kind permission.

Snail sample MAMS 13876, *Bithynia tentaculata*, was found in a sediment layer in the Kraichgau area, Germany. For this sample, only indirect age control could be provided since the layer below (plant remains and charcoal) had been ^{14}C dated as well (Holzhauer 2012). It should be noted that this Kraichgau sample consisted of several very small snails (<1 cm in size). Details on the snails can be found in Table 2. Where possible, samples were taken close to the foot of the snail as this area should be the youngest and provides a larger amount of material than at the apex. Unfortunately, most of them were not large enough for this choice. However, we received enough snails with a vari-

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ety of thickness and preservation as well an age range from 10,000 BC to modern. Small, fragile specimen are obviously more difficult to handle during pretreatment, as opposed to the ideal, thick samples. In this context, it is essential to find out whether a strong, probably destructive, pretreatment is really necessary.

Table 2 Data for the snails tested. The term "prev. dated" refers to samples that have been ^{14}C dated earlier.

Sample nr	Type	Method	$F^{14}C$	Deviation from mean $F^{14}C$	^{14}C age	Deviation from mean ^{14}C age
13876	*Bithynia tentaculata*	A	0.8028 ± 0.0025	–0.0107	1764 ± 25	105
		F	0.8242 ± 0.0028	0.0107	1553 ± 27	–106
		Mean	*0.8135 ± 0.0151*	—	*1659 ± 149*	—
	Charcoal/plant fragments	Layer below	0.8580 ± 0.0020	—	1228 ± 22	—
13877	*Scutalus chiletensis*	A	0.2859 ± 0.0010	–0.0021	10,059 ± 29	0
		C	0.2909 ± 0.0011	0.0029	9920 ± 31	–139
		D	0.2867 ± 0.0013	–0.0013	10,037 ± 38	–22
		E	0.2883 ± 0.0013	0.0004	9990 ± 36	–69
		Mean	*0.2879 ± 0.0022*	—	*10,059 ± 61*	—
		Prev. dated	0.2922 ± 0.0022	0.0043	9884 ± 62	–175
13878	*Scutalus chiletensis*	A	0.9658 ± 0.0024	–0.0042	280 ± 20	35
		B	0.9803 ± 0.0030	0.0103	160 ± 20	–85
		C	0.9698 ± 0.0023	–0.0002	247 ± 19	2
		D	0.9672 ± 0.0025	–0.0028	268 ± 21	23
		E	0.9671 ± 0.0025	–0.0029	269 ± 21	24
		Mean	*0.9700 ± 0.0059*	—	*245 ± 49*	—
		Prev. dated	0.9316 ± 0.0050	–0.0384	569 ± 43	324
13879	*Scutalus chiletensis*	A	1.3257 ± 0.0030	0.0042	Modern	Modern
		B	1.3352 ± 0.0030	0.0137	Modern	Modern
		D	1.2965 ± 0.0030	–0.0251	Modern	Modern
		E	1.3288 ± 0.0032	0.0072	Modern	Modern
		Mean	*1.3216 ± 0.0172*	—	*Modern*	—
13880	*Scutalus chiletensis*	A	0.9394 ± 0.0026	–0.0065	502 ± 23	55
		B	0.9547 ± 0.0026	0.0088	373 ± 22	–74
		C	0.9506 ± 0.0022	0.0048	407 ± 18	–40
		D	0.9419 ± 0.0018	–0.0039	481 ± 16	34
		E	0.9428 ± 0.0023	–0.0031	473 ± 19	26
		Mean	*0.9459 ± 0.0065*	—	*447 ± 55*	—
		Prev. dated	0.9585 ± 0.0024	0.0126	340 ± 20	–107
13881	*Scutalus chiletensis*	A	1.2030 ± 0.0034	0.0182	Modern	Modern
		E	1.1113 ± 0.0030	–0.0735	Modern	Modern
		F	1.2400 ± 0.0039	0.0552	Modern	Modern
		Mean	*1.1848 ± 0.0663*	—	*Modern*	—

The next step was to apply the most promising 3 methods—A, C, and E (see Results and Discussion)—to the shell samples. For this purpose, we used 4 shell samples that had not been dated before, but 2 had an indirect age control provided by ^{14}C ages from the same context, although on organic material. These samples were rather well preserved and of different types, e.g. *Terebralia* and *Anadara uropigimelana* (see Figure 2). All had been found during excavations in the United Arab Emirates (UAE). None of them was complete, and one consisted of only a few broken bits (MAMS 14398). From these samples, due to the limited amount of material, only MAMS 14396 and 14397 were also analyzed by the conventional hydrolysis method F for comparison. Details on the shells can be found in Table 3.

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Figure 2 *Anadara uropigimelana* shell (MAMS 14397)

Table 3 Data for the shells used. The mean values are given in italic to distinguish them more easily.

Sample	Type	Method	$F^{14}C$	Deviation from mean $F^{14}C$	^{14}C age	Deviation from mean ^{14}C age
14396	*Anadara uropigi-melana*?	A	0.3804 ± 0.0011	0.0019	7764 ± 24	–41
		C	0.3814 ± 0.0015	0.0029	7743 ± 32	–62
		E	0.3669 ± 0.0016	–0.0116	8053 ± 34	248
		F	0.3853 ± 0.0017	0.0068	7660 ± 34	–145
		Mean	*0.3785 ± 0.0080*	—	*7805 ± 171*	—
14397	*Anadara uropigi-melana*	A	0.3676 ± 0.0013	–0.0021	8038 ± 27	44
		C	0.3784 ± 0.0014	0.0087	7807 ± 30	–187
		E	0.3670 ± 0.0014	–0.0027	8052 ± 31	58
		F	0.3658 ± 0.0016	–0.0039	8080 ± 35	86
		Mean	*0.3697 ± 0.0058*	—	*7994 ± 126*	—
14398	Unidentified fragments	A	0.5687 ± 0.0014	0.0010	4534 ± 19	–11
		E	0.5672 ± 0.0014	–0.0007	4555 ± 20	11
		Mean	*0.5679 ± 0.0010*	—	*4545 ± 15*	—
14399	*Tere-bralia*	A	0.6669 ± 0.0015	–0.0003	3254 ± 18	3
		C	0.6746 ± 0.0020	0.0074	3162 ± 23	–89
		E	0.6601 ± 0.0019	–0.0071	3337 ± 23	86
		Mean	*0.6672 ± 0.0073*	—	*3251 ± 88*	—

After precleaning of the sample, the remaining material was dried. Between 10 and 15 mg of carbonates were wrapped in tin foil and converted to CO_2 in an elemental analyzer (EA; Elementar Vario Micro), where the resulting gases CO_2, N_2, and H_2O are separated. The CO_2 was collected in a cryogenic trap cooled by liquid nitrogen (see Figure 3). This trap links the EA to the graphitization, where the samples are reduced using hydrogen gas with iron as a catalyst. Using an EA is a convenient way of combusting a sample. The EA does not induce fractionation when combustion is complete (Burke et al. 2010) and it can be used to check whether the sample is completely converted to CO_2. To check for complete conversion, a second run (empty position) was done after each sample, and no remaining carbon was detected (lower detection limit <100 ppm as given by Elementar; we managed to detect <20 µg according to our pressure gauge).

Oxalic acid (OxII) is combusted in the same way as the samples (Skrzypek and Paul 2006; Kromer et al. 2013) apart from other IAEA standards like cellulose (IAEA C3), travertine (IAEA C2), marble (IAEA C1), and sucrose (IAEA C6, Figure 4). Not all standard measurements are shown here, but marble is a carbonate blank and sucrose (IAEA C6) is a secondary standard for quality control. We included all data points on sucrose acquired during our test measurements here to make Figure 4 really representative. The IAEA standards are not pretreated because they serve only as a combus-

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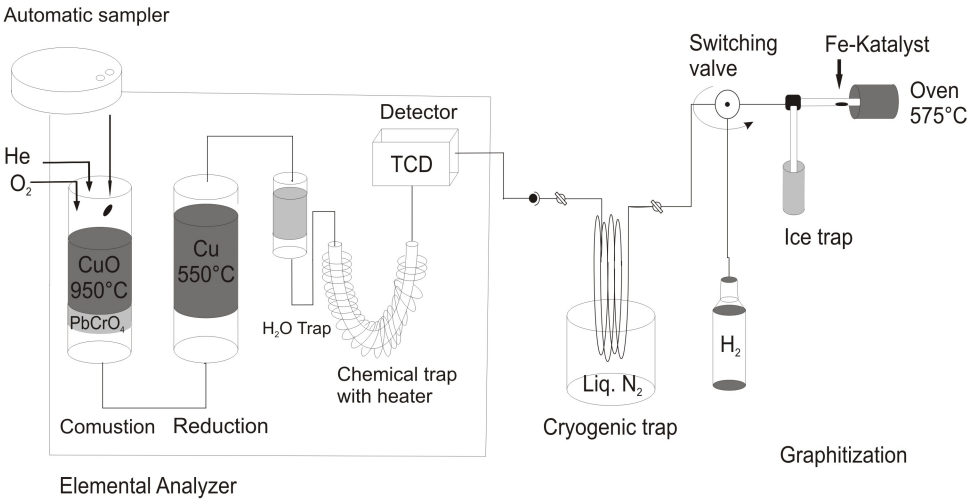


Figure 3 Schematic illustration of the EA graphitization system at the KTL Mannheim. It should be mentioned that using tin foil for the samples to be combusted increases the reaction temperature to 1800 °C (see EA Manual or Elementar Vario Micro Homepage for reference).

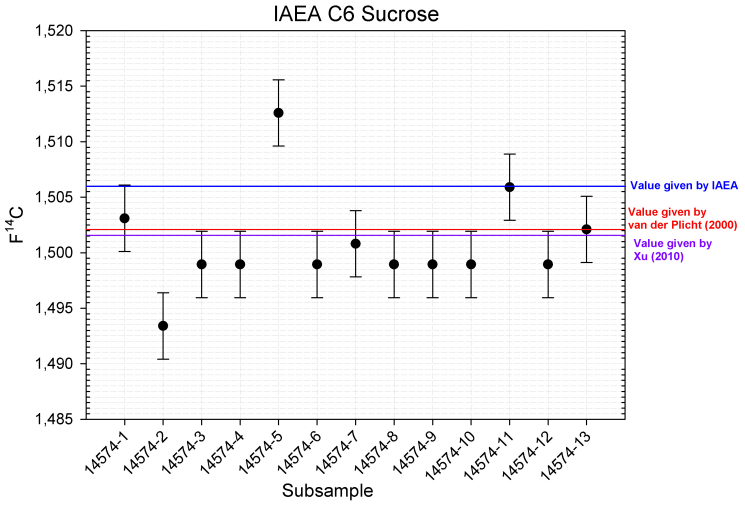


Figure 4 IAEA C6 proceeded with the EA graphitization system of Figure 3, as mentioned in the text.

tion and graphitization quality control. The 3 measurements of IAEA C1–marble resulted in an uncorrected mean value of $F^{14}C = 0.2333 \pm 0.0379$ (theoretical value = 0). Our second carbonate graphitization standard IAEA C2 (travertine) gave a mean value of $F^{14}C = 0.4147 \pm 0.0022$ (theoretical value 0.4114). This implies a minor modern contamination during our combustion and graphitization process for older samples without organic carbon.

Regarding the measurements of IAEA C6, which we use quite often and thus have a better statistical basis, and taking into account the different consensus values for IAEA C6 found to be 1.5022 ± 0.0007 (van der Plicht 2000) and 1.5016 ± 0.0005 (Xu et al. 2010), our measurements are consis-

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tently lower (mean value 1.5008 ± 0.0046) but quite close to Xu et al. (2010). Therefore, for modern samples containing organic carbon, at some step in the system there seems to be a dead carbon contamination or an incomplete processing of organic carbon involved. This needs to be checked thoroughly. This represents our standard procedure. The samples were measured with our Mini Carbon Dating System (MICADAS; Kromer et al. 2013). The $\delta^{13}C$ values are also measured by the MICADAS for isotope fractionation correction purposes.

RESULTS AND DISCUSSION

We will discuss our results as if any difference could be related to the sample preparation only, but we are aware that carbonate dates are difficult to interpret due to many possibilities of incorporating carbon. These possibilities include seasonal variations depending on the lifespan of the snails or the shells as well as diagenetic effects (Culleton et al. 2006; Collins 2012). In our case, *Scutalus* snails live for about 2 yr whereas *Terebralia* reach adult size only after 4 yr. However, we cannot measure to what extent these effects influence our data compared to the contribution by sample preparation and measurement error. As mentioned above, the snails used were not whole samples as used for the original dating, but snails from the same sediment layer.

For each sample, we calculated mean values of $F^{14}C$ and ^{14}C age from all methods tested (apart from previously determined data). One criterion applied was how much a method would differ from the mean value. The deviation from mean $F^{14}C$ and ^{14}C age (pre-bomb samples only) is displayed in Figures 5 and 6, respectively. No ^{14}C age for modern samples was reported. Following the recommendation of Reimer et al. (2004), post-bomb data were only reported using $F^{14}C$. The measured results of each method and each sample can be found together with mean values and deviations in Table 2 (for snails) and Table 3 (for shells).

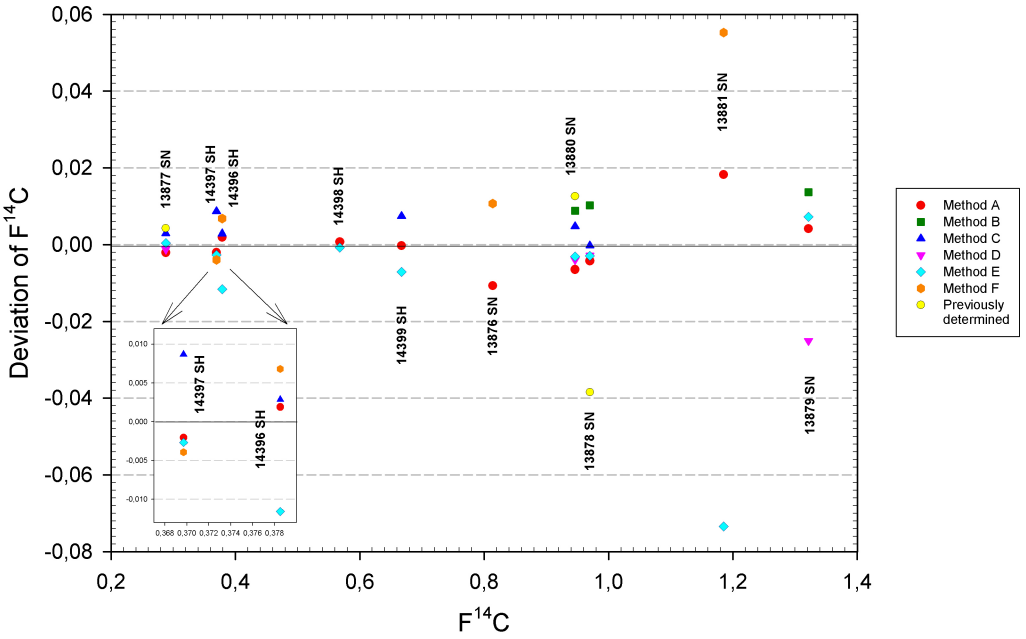


Figure 5 Deviations from mean $F^{14}C$ for all samples tested in all methods that produced results. The inset shows a close-up of the data for samples MAMS 14396 and 14397. The labels "SH" and "SN" indicate whether the sample number refers to a shell or a snail. Negative deviation means getting older.

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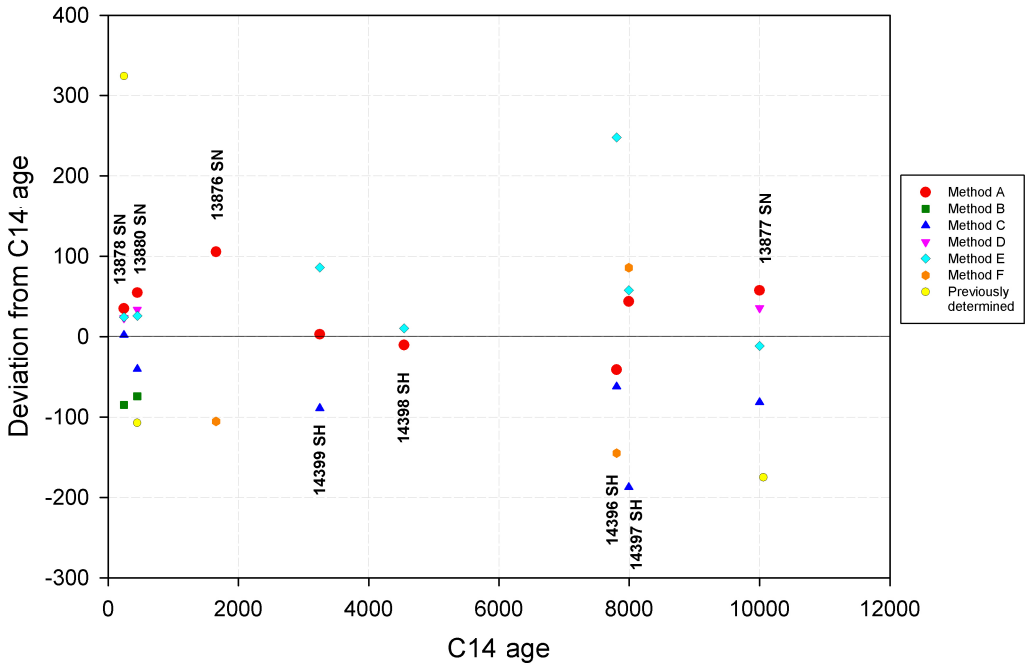


Figure 6 Deviations from mean ^{14}C ages for pre-bomb samples tested in all methods that produced results. As in Figure 5, labels "SH" and "SN" indicate whether the sample number refers to a shell or a snail.

Snails

Beginning sample sizes ranged from 50 to 100 mg. For the conversion to CO_2 via EA, we used around 10–15 mg. Only sample MAMS 13876 yielded <5 mg per method, which may indicate a lower carbon content of the sample. For MAMS 13877, the $F^{14}C$ values of the different methods agree within 2σ. Method C shows a tendency towards a younger age, but agrees better with the previously dated sample. The previously determined age for a snail of the same layer as MAMS 13878 was significantly lower than the subsamples pretreated with methods A–E. Nevertheless, methods A, C, D, and E agreed well.

The modern samples MAMS 13879 and 13881 showed significantly larger spreads between the methods, and hence quite a large offset from the mean $F^{14}C$ value. The sample pretreatment and following conversion to CO_2 using an EA needs to be investigated further for samples containing bomb ^{14}C including duplicate samples using conventional methods to rule out sample inhomogeneity.

Unfortunately, the 2 fragile snails, MAMS 13881 and 13876, barely survived the pretreatment and produced only few results. MAMS 13881 was a modern sample without previous measurements or a comparable sample. The results differed significantly, with method E producing the oldest age and method F yielding the youngest.

A similar pattern was found for MAMS 13876. Although here the difference might originate from the fact that the snails were rather small, as mentioned before, and therefore different snails may have been used for each method. However, both results received for MAMS 13876 were reasonable compared to the age determined for the organic sample of the sediment layer below. One sample, MAMS 13880, produced a result for all methods A–E. Methods B and C were closest to the result

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of the previous measurement on a sample from the same layer, but methods A, D, and E also agreed within 2σ, yielding a lower $F^{14}C$ value and hence resulting in an older age.

Surprisingly, the simplest method, A, proves to be a very reliable method with the smallest deviations from mean values. This is important for samples that would not survive a strong pretreatment and therefore normally are precluded from dating. Method B tends to result in younger ages, with Method D showing a tendency to older ages. Although the deviations are close to the mean values, this gives the impression that the organic solvent is not completely removed.

Shells

The shells were better preserved than the snails and hence larger sample amounts could be used for testing. In general, the sample size at the beginning varied between 200–800 mg; for conversion via the EA we used around 15 mg for each sample in each method. The snail results gave similar indications as the pretreatment of the shells. We dropped 2 methods: method D did not seem appropriate and method B did not improve the results. One of the shells (MAMS 14398) was not used for method C because there were only a few broken bits. Methods A, C, and F produced the same $F^{14}C$ value for MAMS 14396 within 2σ, and only method E was significantly older. For the shell MAMS 14397, again method A and F agreed, but this time with method E, whereas method C resulted in a younger age. It would have been interesting to have more material from MAMS 14398 to test methods C and F also, but methods A and E agreed very well.

The tendency in deviations from mean values confirms the results of the snail samples. Unfortunately, for the shells no real age control was available. This will be included in the next test with more shells including modern ones. But the first 2 shells, MAMS 14396 and 14397, are in accordance with the other ^{14}C data of the same locality (H-P Uerpmann, personal communication).

The additional methanol step of method E seems to remove some organic carbon contamination that is more soluble in organic solvent than in acid. On the other hand, some of the methanol possibly remains in the sample. This is an important point for us to investigate in the near future. In contrast to the snail results, here method F (hydrolysis) showed no explicit tendency towards lower or higher $F^{14}C$ values. Modern shell samples were not available, but need to be tested as well, as it turns out that modern samples are more sensitive to pretreatment than older ones. This may be due to more organic carbon preserved in the younger samples. When converting the $F^{14}C$ values to ^{14}C ages, the differences between each method become more obvious. Positive values represent ages that are older than the average.

In general, it can be said that the standard deviation of the samples is in most cases more than twice the measurement error. This is quite worrying as it implies inconsistent results of the methods or inhomogeneous material. Methods A and E\, although only tried for some samples, seemed to give the most reliable results. Nevertheless, the differences between the methods are larger than expected, especially for modern samples. This might be due to our precleaning methods not being ideal for the insoluble organic contents of the samples.

CONCLUSION

We studied several pretreatment methods of calcite samples for ^{14}C dating. We see some differences between the methods and we find that a simple acid wash leads to reliable results, and is applicable even to very fragile specimen. It is obvious that snail samples containing bomb ^{14}C are more sensitive to different pretreatment methods than the older samples. Conversion of organic C-free calcite to CO_2 using an elemental analyzer (EA) is a simple and flexible alternative to the acid dissolution

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method. For carbonate samples still containing organic carbon, the preparation methods need to be adjusted and complete combustion using an EA needs to be verified in a second test.

ACKNOWLEDGMENTS

The authors would like to thank Bertil Mächtle and Ingmar Holzhauer, Geographical Institute of Heidelberg University, for providing the snails. Ingmar Unkel was helpful in discussing the results on the snails, which he had also worked on previously. Hans-Peter Uerpmann and Johannes Kutterer, Tübingen University, kindly provided us with the shell samples and information about them, including a reservoir effect discussion. We are indebted to Janet Rethemeyer, University of Cologne, who performed the hydrolysis (method F) on the 4 samples including measurement in the Cologne AMS system. We also thank Jens Fohlmeister, Institute for Environmental Physics, Heidelberg University, for helpful discussions.

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