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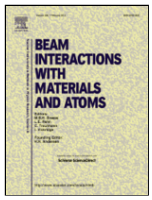

Radiocarbon dating small carbonate samples with the gas ion source of AixMICADAS

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ABSTRACT

Since the beginning of AMS, ^{14}C analyses in foraminifera have been widely used to date deep-sea cores and to estimate reservoir ages of surface and deep ocean layers. Classical AMS requires acid hydrolysis of carbonate samples followed by graphitization of solid targets. For dating very small carbonate samples, an alternative route is to bypass the graphitization step by means of a CO_2 gas ion source coupled to a carbonate hydrolysis system.

We report tests and developments performed over 3 years with a carbonate handling system (CHS) coupled to AixMICADAS. Gas source AMS measurements were performed after different pretreatments applied to various carbonate samples including blanks, reference materials, corals and foraminiferal samples ranging from about 5 μg to 100 μg of carbon. In parallel, the CHS coupled to the automated graphitization system (AGE3, IonPlus AG) was used to develop a similar leaching procedure for carbonates dated with solid targets. The CHS-AGE3 system can be used efficiently and precisely for samples larger than 300 μgC and less precisely down to 100 μgC by applying a constant contamination correction.

The gas method was thoroughly investigated in order to characterize its performances and limitations. Based on measuring numerous IAEA-C1 blank samples pretreated with hydrochloric acid, an equivalent age of about 52,000 yr BP is routinely achieved, though an even lower background close to 55,000 yr BP is reached when the system is flushed to suppress the memory effect from sample to sample. The long-term reproducibility is about 7‰ based on replicated analyses of a modern coral and the accuracy of the gas method was also confirmed by measuring coral and foraminifera samples previously dated by conventional AMS. The background correction is negligible for samples down to 30 μgC and can be effectively corrected for samples down to 10 μgC by applying a constant contamination correction though the recommended samples size is between 30 μgC and 100 μgC to achieve a reasonable precision.

Our methods were applied to date planktonic foraminifera from two deep-sea cores. Several species with different visual aspects were tested for sample sizes ranging from single shells (ca. 10 μgC) to standard size sample (ca. 100 μgC) for the gas source as well as larger samples (ca. 500 μgC) measured as graphite targets. The dataset does not reveal any large age bias, but illustrates how gas CO_2 measurements on small foraminiferal samples could improve the reliability of deep-sea core dating by providing key information on sample heterogeneities due to sediment mixing and diagenesis.

1. Introduction

Radiocarbon analysis of carbonate samples is widely used in paleoceanographic and paleoclimatic studies. For instance, dating planktonic samples is extensively used to establish the chronology of deep-sea sediment cores (e.g. [1]) and ^{14}C age differences between paired benthic-planktonic foraminifera in deep-sea cores can be used to reconstruct surface-deep ocean gradients and provide insight into water mass ventilation (e.g. [2–4]). Reservoir ages can also be reconstructed by comparing planktonic foraminiferal and tephra ages [5–7]. However, this valuable information can only be retrieved from sediment cores where foraminiferal specimens are abundant enough to provide sufficient material (≈1 mg of C) for dating by the conventional method based on the synthesis of graphite targets.

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In addition to the sample mass issue, ^{14}C dating of large samples containing hundreds to thousands of individual specimens can also mask the intra-sample age heterogeneity caused by sediment mixing resulting from physical and biological processes, notably burrowing organisms. This bioturbation has been shown to lead to dating biases when coupled to abundance changes and dissolution of foraminifera [8–13]. Although progress has been made to reduce by an order of magnitude the carbon mass required for graphitization [14–16], it is still a labor-intensive technique, and one which is both prone to contamination effects and which has a limited precision.

An alternative route for dating small carbonate samples is to bypass the graphitization step by using a gas ion source coupled to a hydrolysis unit (e.g. [17–21]). In this paper, we report tests and developments performed over 3 years with the carbonate handling system (CHS, IonPlus AG) coupled to AixMICADAS [22]. More than 1000 AMS measurements were performed with various carbonate samples ranging from ca. 100 μg to 5 μg of C, compared with conventional AMS analyses when enough material was available. This allowed optimizing an analysis protocol including online leaching pretreatment.

2. Method

2.1. Pretreatment and sample hydrolysis

The instrumental set-up for both graphitization and gas measurements have been described elsewhere [19,22]. In short, carbonate samples are weighed and transferred into a 4.5 ml glass vial (Labco Ltd) sealed with a rubber septum and placed in the CHS autosampler. This device is thermostated at 40 °C rather than the 70 °C traditionally used for stable isotope measurements, in order to prevent leaks which can occasionally occur due to the deformation of the polypropylene caps. Each vial is first flushed with helium at 70 ml/min for 3 min by means of a doubled-walled needle, then hydrochloric acid (HCl) is added with concentration and volume adjusted to leach 30% of the initial carbonate mass. Each vial is then gently manually mixed, let to react generally overnight and the CO_2 formed during the leaching step is removed by flushing with helium for 3 min at 70 ml/min. Residual samples are then hydrolyzed with 0.06 ml of phosphoric acid (H_3PO_4 at 85%) and allowed to react for a minimum of 10 min before transferring the first sample of the sequence to the zeolite trap. The released CO_2 is pushed with He at 70 ml/min through a water trap (phosphorus pentoxide) into the zeolite trap of the gas source interface system (GIS) or of the AGE3 graphitization system (transfers to the zeolite trap last 2 and 1 min for the AGE and GIS, respectively).

2.2. Graphitization with the automated system AGE3

The pure CO_2 is released from the zeolite trap at 420 °C into one of the seven reactors of the AGE3 (Ionplus AG), where it is reduced at 580 °C to graphite with hydrogen ($PH_2/PCO_2 = 2.3$) on iron powder (Alfa Aesar, reduced iron 99%, 325 mesh). The reaction time is set to 150 min and the amount of iron is kept constant (3.8–4.2 mg) regardless of the carbon mass. The memory effect from one sample to the next is evaluated at ca. 1% with the AGE3 system connected to the carbonate handling system. In order to minimize this problem, the zeolite trap is first loaded with CO_2 of the same age as the sample (artificial mixture prepared from modern and blank CO_2 or a split of the CO_2 sample to be measured). This so-called PRE-sample is then heated and vented before loading the trap with the real CO_2 sample to be graphitized and measured by AMS.

2.3. Measurements with the gas ion source

The pure CO_2 is released from the zeolite trap at 450 °C and transferred into the syringe of the GIS where it is mixed with He to obtain a final CO_2 concentration of 5% in volume which can be injected into the hybrid ion source of AixMICADAS. The GIS is characterized by a memory effect around 4%, as described in our companion paper (Tuna et al., this issue). The impact of this carry-over can be avoided by loading and purging an aliquot of the CO_2 sample to be measured (so-called PRE-sample) and/or by measuring samples in sequence of increasing ages (e.g. following the stratigraphic pile upward).

2.4. AixMicadas parameters and data reporting

The tuning procedure and main operation parameters used in gas and solid configurations are fully described in our companion paper (Tuna et al., this issue [23]). The ^{14}C data are reported in terms of conventional ^{14}C age BP and in terms of $F^{14}C$, which is the $^{14}C/^{12}C$ isotope ratio after normalization and blank correction ([24–26]). The $^{13}C/^{12}C$ ratios are reported using the conventional δ notation by using OxA2 NIST standard.

^{14}C blank values are reported without any background or constant contamination while a background correction is applied to standard size samples and an additional correction for the constant contamination is applied to individual foraminifera measurements. Sample masses expressed in this manuscript indicate the residual amount of carbon (μgC) measured from the gas ion source or graphitization system after the pretreatment procedure.

3. Results and discussion

3.1. Pretreatment

Carbonates such as corals and foraminifera are commonly leached with an acid or oxidant prior to ^{14}C measurements in order to remove secondary calcite or exogenous carbon introduced during sample collection or handling in the laboratory [27–30]. Fig. 1 summarizes the results obtained with different pretreatment methods applied to blank and modern samples.

The relatively large scatter of untreated IAEA-C1 samples compared to leached samples with either HCl or HNO_3 suggests that some contamination introduced during sample handling is removed by acid leaching. Although the number of untreated samples is limited, this confirms that acid leaching is useful to get reproducible blanks. The offset for the IAEA-C1 sample treated by the H_2O_2 oxidative step suggests that a carbonaceous contaminant comes either from the glassware or that it is introduced during the sample handling (e.g. grinding step).

Measurements on foraminifera confirm that untreated samples are less reliable than those leached with either HCl or HNO_3. The arithmetic mean of untreated blank foraminiferal samples is $F^{14}C = 0.0027$ with a standard deviation (SD) of 0.0003 for $n = 3$ samples, which is significantly higher than for samples treated either with HNO_3 ($F^{14}C = 0.0017$, SD = 0.0003, $n = 3$) or by HCl ($F^{14}C = 0.0018$, SD = 0.0004, $n = 36$). No clear difference is observed for the pretreatments of the standard IAEA-C2 of intermediate $F^{14}C \approx 0.41$. It is probably easier to detect the cleaning effect on blanks. Overall, the results obtained with HNO_3 are similar to those with HCl and we have retained this latter acid for our standard leaching procedure. No conclusions can be dawn at present regarding the treatment by the oxidative steps with H_2O_2 considering the small number of measurements. In addition, this pretreatment method is prone to caps pop-up issues resulting from the pressure build-up caused by the oxygen released by the decomposition of H_2O_2.

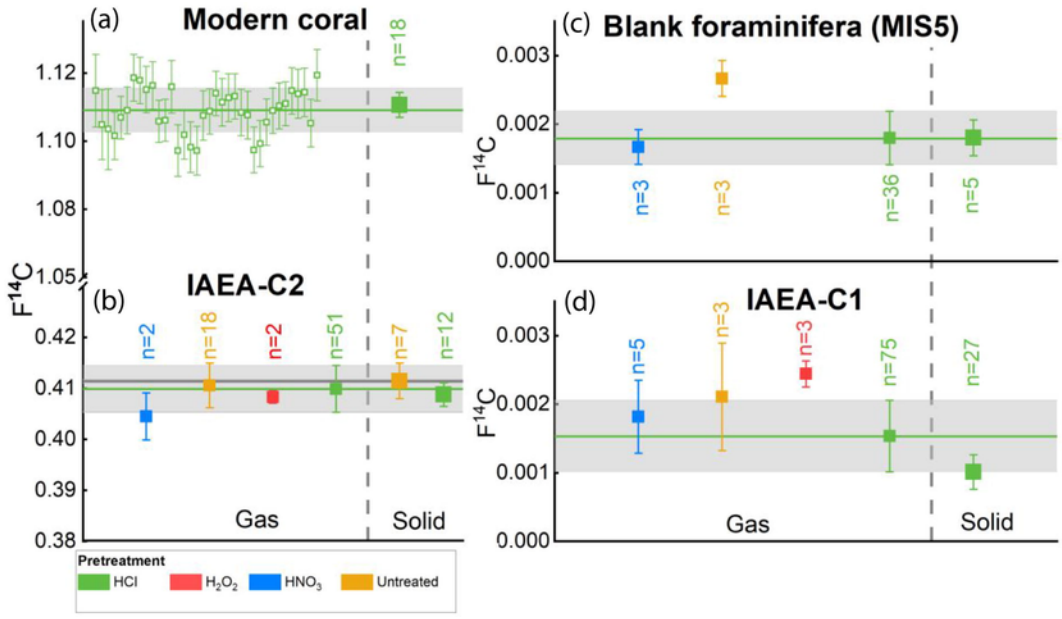

Fig. 1. $F^{14}C$ values of gas and solid measurements of standard and blank samples with standard size (residual mass after leaching of ≈100 µgC and ≈500–1000 µgC for gas and solid measurements respectively). (a) Modern coral (*Porites* from Moorea, Aix-13027), (b) IAEA-C2 reference material, (c) foraminiferal samples picked from a >100 kyr sediment layer (marine isotopic stage 5 from a sediment core raised off Morocco) and (d) IAEA-C1 reference material. Data summarized in this figure were measured over a period of two years.The colors stand for the different pretreatments applied before the final hydrolysis with H_3PO_4 (HCl is used routinely, while HNO_3 and H_2O_2 have also been tested). Empty green symbols show individual gas measurements pretreated with HCl, while solid symbols represent the arithmetic mean with the associated standard deviation for both gas (left) and solid (right) measurements. The horizontal light grey bar indicates the arithmetic mean and associated standard deviation of gas samples leached with HCl, while the darker grey bar (panel b) indicates the consensus value and associated error for the reference material IAEA-C2. The results for the modern coral and IAEA-C2 were corrected for a blank value based on IAEA-C1 samples measured in the same magazine. By contrast, the results for IAEA-C1 and blank foraminifera are reported as raw $F^{14}C$ without background correction. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Background contamination for small samples

The quantification of the background contamination for both gas and solid measurements is based on the assumption that samples are mixed with a contaminant of constant mass (M_c) and activity ($F^{14}C_c$) [e.g. [31–33]]. A modern sample (*Porites* coral from Moorea) and a blank (IAEA-C1 calcite) of various masses were measured with the hybrid ion source as CO_2 gas produced with the CHS and as solid graphite targets prepared with the AGE3. A weighted least squares regression was applied to the results to fit the data (Fig. 2) and determine the constant contaminant parameters (M_c and $F^{14}C_c$).

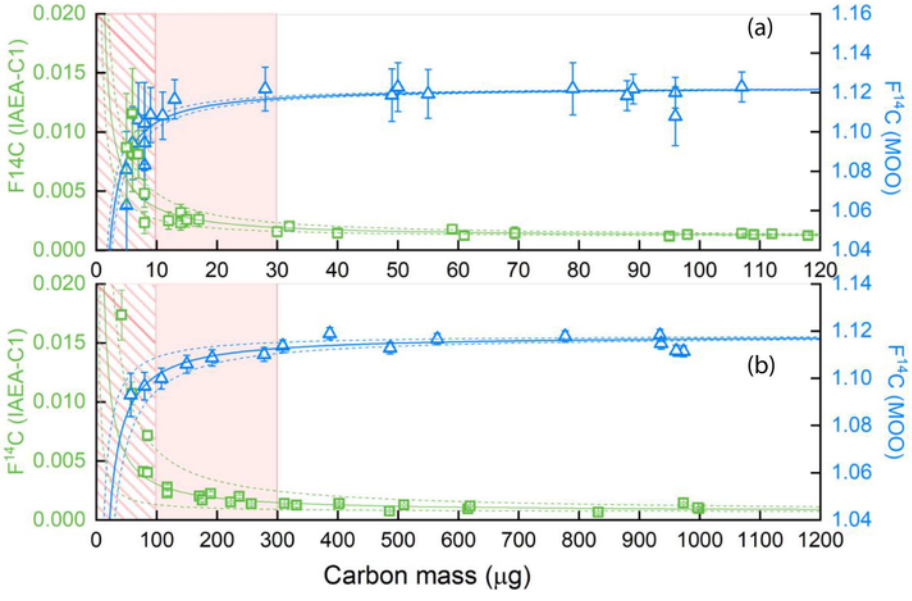

Fig. 2. Constant contamination model for (a) gas measurements and (b) solid measurements. Green and blue symbols show $F^{14}C$ values with their associated uncertainty (1σ) for the blank sample (IAEA-C1) and modern sample (*Porites* coral from Moorea), respectively. The red dashed zones indicate the size-ranges of samples that cannot be accurately measured and the red zones designate the size-ranges where samples can be efficiently corrected for the constant contamination. Nevertheless, the precision is markedly impacted due to low ion currents. The white zones represent the recommended carbon mass ranges for optimal precision and accuracy. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

For carbonates with the gas source, the estimated parameters are $M_c = 0.18 \pm 0.04$ μgC (2σ) and $F^{14}C_c = 0.14 \pm 0.04$ (2σ). It should be noted that the data are very well fitted down to a carbon mass of 10 μg for both modern and blank samples. In addition to the higher influence of the target contamination [34] for samples <10 μgC compared to larger ones, the lower precision and the larger uncertainty for small carbon mass probably explain the scatter for these ultra-small samples. Nonetheless, it is reassuring to see that the background correction is negligible for samples down to 30 μgC. This sample mass also allows the full consumption of a Ti target leading to a reasonable precision equivalent to that for standard size ≈100 μgC samples (see our companion paper by Tuna et al. in this issue).

For solid graphite targets, the estimated parameters are $M_c = 1.74 \pm 0.84$ μgC (2σ) and $F^{14}C_c = 0.14 \pm 0.06$ (2σ). This $F^{14}C_c$ is similar to the CHS-GIS determination and also agree with the recent value determined for the EA-GIS based on the combustion of ultra-small silver cups (see our companion paper by Tuna et al. in this issue).

The $F^{14}C_c$ of the contaminant with the CHS-GIS is thus lower than the one we found ($F^{14}C_c = 0.73 \pm 0.11$ and $M_c = 1.45 \pm 0.26$ μgC) by using the EA-GIS with relatively large silver cups [33] as well as lower than other EA-GIS estimates [31,32]. Higher $F^{14}C_c$ have also been reported in a recent paper [21] focusing on gas ($F^{14}C_c = 0.30 \pm 0.04$ and $M_c = 0.68 \pm 0.10$ μgC) and solid ($F^{14}C_c = 0.49 \pm 0.07$ and $M_c = 0.94 \pm 0.14$ μgC) measurements of carbonates with a MICADAS. One possible interpretation is that the contaminating material, assumed as homogenous in the carbon contamination model, is in fact heterogenous and that the $F^{14}C_c$ of the residual fraction around 0.2 μgC has a different $F^{14}C_c$ than the carbon mix forming higher contamination levels around 1 μgC. Validation of this hypothesis will necessitate further work.

As seen in Fig. 2, the data are well fitted down to a carbon mass around 100 μgC. Although solid samples can be corrected for, it is preferable to graphitize samples larger than 300 μgC for which the background correction is negligible. In addition, the $^{12}C^-$ currents are not optimal and stable for sample masses between 100 and 300 μgC (corresponding to ~20% and ~70% of the typical ion current measured for a 1 mgC sample, respectively). This problem can be reduced by decreasing the amount of Fe catalyst used to produce graphite targets with these small samples.

3.3. Procedural blanks on representative material

Based on 75 measurements of ≈100 μgC aliquots of the reference material IAEA-C1 leached online with HCl, the blank level of the CHS is calculated to be a mean $F^{14}C = 0.0015$, SD = 0.0005 (Fig. 1d and Table 2). This average $F^{14}C$ corresponds to a ^{14}C age of around 52,000 yr BP. This mean $F^{14}C$ value is quite low for a gas source and should be regarded as a conservative estimate because these analyses were mainly performed to purge the CHS before analyzing unknown samples. For instance, an even lower mean value of $F^{14}C = 0.0011$ (≈55,050 yr BP), SD = 0.0003 was obtained from 13 consecutive IAEA-C1 measurements.

Our background is slightly lower than those previously reported [19,21], although a comparison with other MICADAS system is not straightforward due to sample size effects, different pretreatment procedures and improved stripping with He for AixMICADAS compared to the previous system with N_2.

As shown in Fig. 1, the procedural blank obtained from gas measurements (≈90 μgC) of old (>100 kyr BP) foraminifera leached with HCl is an average $F^{14}C = 0.0018$ (≈50,770 yr BP), SD = 0.0004, n = 36 (average sample mass: 89 μgC, SD = 12 μgC). The planktonic foraminifera were hand-picked under the binocular microscope from a sediment layer corresponding to marine isotopic stage 5 in a sediment core off Morocco. Although IAEA-C1 and foraminiferal blanks values are both quite low, a small difference of 0.0003 ± 0.0001 can be calculated with foraminiferal blanks consistently higher than IAEA-C1 values.

The same pattern is observed for solid graphite targets of reference materials and foraminiferal samples. Average $F^{14}C = 0.0010$ (≈55,300 yr BP), SD = 0.0002, n = 27 (average sample mass: 900 μgC, SD = 190 μgC), and 0.0011 (≈54,810 yr BP), SD = 0.0001, n = 2 (average sample mass: 980 μgC, SD = 10 μgC), were measured on IAEA-C1 and SIRI-K samples (sample K, Sixth radiocarbon laboratory intercomparison, 2013), respectively. These blank levels are lower than those measured on old foraminifera samples from the same core as above with a mean $F^{14}C = 0.0018$ (≈50,980 yr BP), SD = 0.0003, n = 5 (average sample mass: 660 μgC, SD = 180 μgC). This offset could indicate that a fraction of the surface or intrinsic contamination of these old foraminifera is not completely removed by the leaching procedure.

This agrees with previous observations [35], justifying the measurement of blank levels in samples representative of the same archive (e.g. old foraminifera found in deeper layers of the same deep-sea core). For example, we have re-measured mono-specimen blanks of three foraminifera species from the deeper layers of core MD04-2873 from the Pakistan Margin, which gave a mean $F^{14}C = 0.0018$ (≈50,600 yr BP), SD = 0.0003, n = 3 (*Orbulina*, *G.sacculifer* and *G.ruber,* average sample mass: 570 μgC, SD = 220 μgC) with solid graphite targets and a mean $F^{14}C = 0.0019$ (≈50,170 yr BP), SD = 0.0005, n = 11 (*Orbulina* and *G.ruber*, average sample mass : 82 μgC, SD = 7 μgC) for gas measurements. Both values agree with our previous estimation by conventional AMS [36]. Nevertheless, more work is still needed on sediment cores from different locations and depths in order to characterize the source of the residual contamination in foraminifera.

3.4. Precision and accuracy

The accuracy of the gas method was tested by re-measuring two coral samples previously dated by conventional AMS (Table 1). These well-preserved samples collected offshore Tahiti were used in the frame of the IntCal calibration curve [30]. Both sets of gas replicates measured on ≈100 μgC aliquots are in good agreement for the two corals and the results between the two methods are fully compatible.

More systematic work was performed with gas and solid measurements of a modern coral (MOO, a Porites from Moorea) and the IAEA-

Table 1
Coral samples from IODP #310 cores offshore Tahiti [28]. Gas measurements are compared with ^{14}C measurements by conventional AMS (French ARTEMIS facility). Samples were corrected with the mean of three IAEA-C1 obtained during the measurement ($F^{14}C = 0.0019$) and a conservative error of ±30% of this value, based on the long-term variability of IAEA-C1 standard size blanks.

Sample	Gas samples		Conventional method	
	Aix n°	^{14}C Age yr BP ± 1σ	Artemis n°	^{14}C Age BP ± 2
310-M0023B-12R-2W 113-127	Aix-10510.1.1	12720 ± 130	SacA-8601	12810
	Aix-10511.1.1	12840 ± 130	SacA-10227	12790
	Weighted mean	12780 ± 80		
310-M0024A-10R-1W 98-116	Aix-10519.1.1	12790 ± 120	SacA-18555	12920
	Aix-10520.1.1	12810 ± 120		
	Weighted mean	12800 ± 80		

C2 standard. The results are summarized and compared in Fig. 1 (panels a & b) and Table 2.

The precision for gas and solid measurements can be evaluated from the modern coral. A total of 36 gas samples (over 13 different day-sessions) and 18 solid samples (over 5 different day-sessions) have been measured over a period of two years. Both averages are close to each other, within 2‰. As expected, the scatter of the solid measurements (SD ≈ 4‰) is smaller than that observed for gas measurements (SD ≈ 7‰).

A total of 73 IAEA-C2 gas samples (51 leached with HCl, 2 leached with HNO_3, 2 oxidized with H_2O_2 and 18 untreated) have been measured with the gas ion source over a period of 2 years (over 19 different day-sessions). The data show reproducible results with standard deviations on the order of 10‰ and 11‰ of the mean value (leached with HCl and untreated samples, respectively) for this 7 kyr-old sample. This value is in the same order of magnitude than recently reported by the University of Bern (12‰ and 10‰ for leached and untreated samples, respectively) [21]. As expected, the scatter for solid measurements is lower than gas measurements, though leached samples seem to be more reproducible (SD ≈ 6‰ of the mean value, n = 12) than untreated samples (SD ≈ 8‰ of the mean value, n = 7).

Leached and untreated samples mean values for both solid and gas samples are consistent within one standard deviation with the consensus value (0.4114). However, looking at face values, it seems that untreated samples lead to $F^{14}C$ values higher on average than leached samples (6‰ and 2‰ for solid and gas, respectively). Although the observed differences are small, they could be linked to a residual contamination of the IAEA-C2 material introduced during the sample handling, as already hypothesized for untreated blanks (see Section 3.1). The fact that similar offsets are observed for solid and gas measurements would exclude a specific effect linked to the gas source.

The mean $\delta^{13}C$ value of solid IAEA-C2 samples (−8.0‰, SD = 1.9‰ and −9.1‰, SD = 0.9‰ for leached and untreated samples, respectively) and IAEA-C1 samples (3.5‰, SD = 2.2‰) are compatible within one sigma uncertainty with the consensus value (−8.25 ± 0.31‰ and 2.42 ± 0.33‰ for IAEA-C2 and IAEA-C1, respectively) [35,36]. Gas samples are more reproducible (SD ≈ 1‰) than solid samples but the mean values are systematically shifted toward negative values when compared to solid samples (about −2‰ and −3.5‰ for IAEA-C1 and IAEA-C2 samples, respectively, and −4‰ for the modern coral). Similarly, the $\delta^{13}C$ values measured for the different blank samples through the EA + GIS, exhibit also a negative shift of around −2‰ when compared to precise and accurate results on solid graphite targets (see our companion paper by Tuna et al. in this issue). By contrast OxA2 samples considered as unknown measured directly from the CO_2 standard bottles lead to a mean $\delta^{13}C$ of 18.0‰ with an SD of 1.8‰ (n = 132) in agreement with the provided IRMS value (−17.2‰).

The observed $\delta^{13}C$ offset is probably due to isotopic fractionation linked to the zeolite trap system of the GIS which are not corrected with our normalization procedure based on the measurement of OxA2 samples from a CO_2 bottle. It must be stressed that with the gas ion source, the fate of the CO_2 gas is quite different between the OxA2 standard (bottle-CO_2 injected directly into the GIS syringe) and the samples (CO_2 production with the CHS, drying, adsorption in and desorption from the zeolite trap, mixing of CO_2 with He in the GIS syringe).

Normalization with IAEA-C2 carbonate samples has been tested occasionally in order to use the very same procedure for standard and unknown samples. This procedure seems to be efficient to produce less negative $\delta^{13}C$ values in better agreement with consensus values for IAEA-C1 and IAEA-C2 samples. However, because of ^{14}C counting statistics, it would be better to normalize the data with a modern carbonate standard rather than with IAEA-C2 ($F^{14}C \approx 0.4$). Unfortunately, such a modern carbonate standard is currently not available. This issue was also raised by Gottschalk et al [21]. In our companion paper by Tuna et al., we propose to use OxA2 samples introduced with the EA in order to normalize data of samples measured through the EA, instead of normalizing with measurements from the OxA2 bottle, which bypass the zeolite trap. Further work will be pursued to develop a similar procedure for carbonates.

In any case, the normalization procedure used so far does not affect $^{14}C/^{12}C$ ratios as natural and procedural isotopic fractionations are corrected for in the $F^{14}C$ normalization procedure with measured $^{13}C/^{12}C$ ratios.

3.5. Demonstration of the method on foraminiferal samples

3.5.1. Single foraminifera measurements

In order to test the gas method on small carbonate samples and to study sediment mixing, we have started a measurement program on individual specimens of foraminifera. Fig. 3 shows the individual measurements of 32 single foraminiferal shells (*G.truncatulinoides* with masses ranging between 3 and 15 μg C) compared with standard size (≈100 μgC) multi-specimen samples of two species (*G. truncatulinoides* and *G. inflata*). All samples were sieved and picked under the binocular from the same depth in a sediment core raised off Morocco. A parallel objective of the study was the detection of the contamination by rare modern shells (only two) artificially mixed with the old ones representative of the core depth (see Skinner et al. 2010 [37] also reporting a contamination problem).

Overall, the 30 single foraminifera leached with HCl lead to an average ^{14}C age of 27,790 yr BP with a standard deviation of 1680 yr (represented on Fig. 3 as the green solid square method a). This is larger than the average uncertainty of individual measurements (970 yr). Bioturbation may have contributed to the age heterogeneity. Indeed, this particular deep-sea core has an average sedimentation rate of 14 cm/kyr, which implies that foraminifera over a millennium are mixed in the bioturbation zone (typically on the order of 10 cm).

In addition, the constant contamination model is not ideal for samples smaller than 10 μgC, which also contributed to this large scatter. This non-ideal contamination correction could also be responsible for

Table 2
$F^{14}C$ and $\delta^{13}C$ values obtained with AixMICADAS for gas and solid measurements of the reference materials IAEA-C1 and IAEA-C2, and the modern coral (MOO, *Porites* sample from Moorea). The $F^{14}C$ and $\delta^{13}C$ consensus values are 0.4114 ± 0.0003 and −8.25 ± 0.31‰ respectively [39,40].

Sample description	$F^{14}C$	Standard deviation $F^{14}C$	Standard error ($SD/\sqrt{n}$)	$\delta^{13}C$ (% VPDB)	Standard deviation $\delta^{13}C$	N analyses
Gas, leached, IAEA-C2	0.4098	0.0042	0.0006	−10.4	1.1	51
Gas, untreated, IAEA-C2	0.4106	0.0044	0.0010	−10.5	0.9	18
Solid, leached, IAEA-C2	0.4088	0.0023	0.0007	−8.0	1.9	12
Solid, untreated, IAEA-C2	0.4114	0.0035	0.0013	−9.1	0.9	7
Gas, leached, modern coral	1.1114	0.0078	0.0013	−3.7	1.3	36
Solid, leached, modern coral	1.1133	0.0046	0.0010	0.2	2.0	19
Gas, leached, IAEA-C1	0.0015	0.0005	0.0001	0.0	1.0	75
Solid, leached, IAEA-C1	0.0010	0.0002	0.0001	3.5	2.0	27

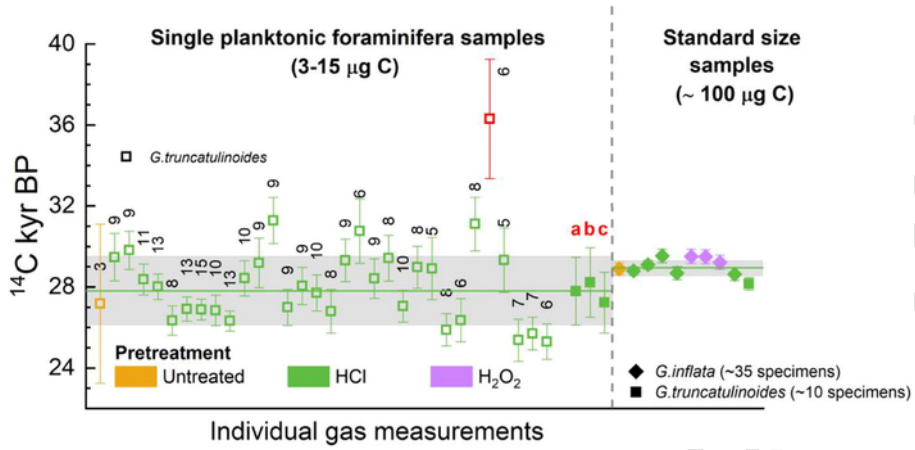

Fig. 3. $F^{14}C$ values corrected for the constant contamination model of 32 single foraminifera samples (the sample represented in red was considered as an outlier) compared to 10 standard size samples from the same depth in deep-sea core raised off Morocco. Numbers above data points indicate the sample weight in µgC (the mean is 8.3 µg). Letters in red stand for the mean and standard deviation of the 30 single samples leached with HCl (a) corrected for the constant contamination correction, (b) an alternative correction based on two blank foraminifera of similar size (7 and 10 µgC) and, for the sake of comparison, (c) the simple correction based only on standard size blanks. Conservative blank errors are propagated to calculate errors bars: ± 40% for blank single foraminifera and ±25% for standard size samples (based on numerous measurements of MIS-5 foraminiferal samples from this particular core). The horizontal grey bars show the mean and standard deviation for both single and standard size foraminiferal samples pretreated with HCl. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the residual offset observed between the mean result on single foraminifera (27,790 yr BP, SD = 1,680 yr, n = 30) and the mean on standard size (≈100 µgC) foraminifera samples (28,150 ± 305 yr BP for *G. truncatulinoides* and 28,950 yr BP, SD = 380 yr, n = 5, for *G. inflata*).

An alternative correction with blanks of the same size as the single foraminifera samples, measured during the same sessions, lead to a mean ^{14}C age of 28,220 yr BP, SD = 1710 yr, (Fig. 3, method b) similar to the value calculated with the constant contamination model on single foraminifera and in full agreement with the standard size gas samples. For comparison, the raw data without contamination correction (Fig. 3, method c) give a younger ^{14}C age (27,230 yr BP, SD = 1500 yr).

The gas measurements of standard size samples of foraminifera were also used to test the different chemical pretreatment methods (no treatment, HCl, H_2O_2), but no significant difference was detected with these individual measurements (Fig. 3).

Although this dataset is limited to a specific sediment layer from a single deep-sea core, the data already highlight the advantage of the gas ion source compared to conventional AMS. Indeed, it would have been impossible to study the heterogeneity of this sediment without gas measurement on small CO_2 aliquots (see also [13] for further demonstration). More work is ongoing to compare results of different foraminifera species and size fractions in cores from various locations and depths.

3.5.2. Age models of deep-sea sediments

Constructing an age-depth model requires the dating of numerous discrete core depth intervals. Although valuable age-depth models are routinely based on conventional AMS dating (with ≈1 mgC samples) this technique suffers from three main drawbacks. First, it is only applicable when enough foraminifera shells are available, thereby restricting studied locations in the global ocean. Second, many complications such as mixing of the upper sediment layer by burrowing organisms may disturb recorded signals and lead to erroneous interpretation. Third, the diagenesis is often poorly constrained, which may also lead to incorrect age with large samples [9,38].

As a first test, we analyzed small and large samples from a deep-sea core from the Pakistan Margin in the Arabian Sea (MD04-2876), which is characterized by a high sediment rate (~50 cm/kyr, Bard et al., 2013). The data are shown in Fig. 4, with panels 4a, 4b and 4c showing the details for three particular core depths illustrating how gas measurements on small samples can be used to improve our understanding of sediment mixing and diagenesis.

Several planktonic foraminifera species (*G. ruber, G. sacculifer, N. dutertrei, G. bulloides* and *Orbulina*) were picked under the binocular to provide suitable samples for optimal gas source measurements (≈100 µgC representing between 10 and 35 specimens depending on the species). We also distinguished the shells by their visual aspect under the binocular (white, black, opaque, translucent), which may reflect different preservation states or contamination levels by extraneous material. Indeed, the carbonate fraction calculated from the CO_2 pressure in the GIS varies significantly between 25 and 95% of the raw material introduced in the CHS vials. Translucent foraminifera are often considered as particularly well preserved but in this core they may be linked to dissolution as they contain less calcite (69%, SD = 5% n = 4) than opaque or white specimens (80%, SD = 7%, n = 56 and 82%, SD = 7%, n = 4 respectively). Black shells probably contain some pyrite formed in anoxic conditions as the core is located with the Oxygen Minimum Zone. As expected, the calcite content was even lower for these samples (47%, SD = 25%, n = 3).

As can be seen in Fig. 4 (panels a, b and c), the dataset does not reveal any clear age bias between the different species of foraminifera, nor their different aspects. For each of the three depths, the individual gas measurements for one particular species are compatible according to the chi-square test (p = 0.05) and the different species are also in good agreement within one sigma uncertainty of their weighted means. When shell abundance was sufficient, graphite targets were also produced and measured for much larger samples (≈350 to 550 µgC). The available solid data (yellow symbols in Fig. 4) confirm the agreement between species and are compatible within one sigma uncertainty with the gas measurements (n = 5). The weighted averages based on the various gas replicates (red symbols in Fig. 4 (panels a, b and c)) show that the final weighted error is similar to typical errors for solid measurements (e.g. 25,940 ± 140 yr BP and 25,830 ± 140 yr BP, for gas and solid measurements of *Orbulina* from 1450 cm core depth).

The absence of strong discrepancies may seem surprising in the light of the abundant literature on the subject (e.g. [9,13,38]). This may be due to the very high sedimentation rate (50 cm/kyr) and limited bioturbation in these sections of the studied core from the Arabian Sea OMZ. In any case, this preliminary dataset is reassuring concerning

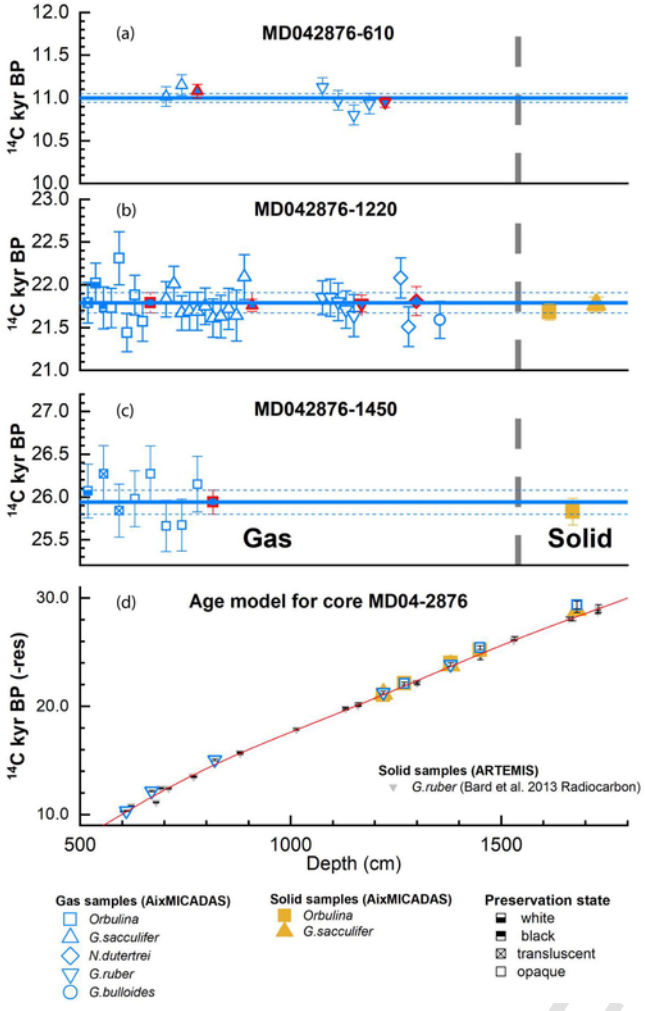

Fig. 4. Measurements of solid and gas planktonic foraminiferal samples in core MD04-2876 from the Pakistan Margin. (a)(b)(c) comparison between ^{14}C ages of samples made from different planktonic foraminifera species with different visual aspects (for *Orbulina*). Solid and dashed lines (in blue) show the weighted mean and weighted error based on the gas measurements of opaque individuals (only 5 Orbulina samples for 1220 & 1450 cm depths and 6 G.ruber & G.sacculifer samples for 610 cm depth). Symbols with a red outline show the weighted mean and associated weighted error based on individual measurements (opaque specimens only) of the same species. (d) new measurements of small planktonic samples compared to the age-depth model based on large samples by conventional AMS (Bard et al. 2013). Gas sample symbols in blue show the weighted mean and associated error based on three gas measurements. New solid samples measured with AixMICADAS were prepared with masses ranging between 350 and 550 μgC. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the efficiency of our pretreatment and the reproducibility of the dating protocol.

Fig. 4d provides the age-depth profile for the new ^{14}C ages measured on planktonic foraminifera with AixMICADAS (both gas and solid measurements). It is compared with the previous age model based on conventional AMS measured at the French ARTEMIS facility [36]. Gas measurements correspond to the weighted mean and associated error from 3 gas measurements. Although more were available for some depths, 3 gas measurements are enough to reach a weighted error comparable to uncertainties of solid graphite analyses.

In general, the new ^{14}C ages are compatible with the previous ones, except for the 1680 cm core depth for which the new results for gas (29360 ± 340 yr BP) and solid (28880 ± 210 yr BP) are about 1000 yr and 540 yr older than the former age. However, this offset is not much larger than typical error bars in that time range. In addition, the available new measurements were performed on different foraminifera species (*G. sacculifer and Orbulina*) than the previous ones (*G. ruber*). More data will be produced on this particular level to check the reality, size and source of this apparent offset.

4. Conclusion

We pursued technical developments with a carbonate handling system (CHS) coupled to both the gas ion source of AixMICADAS and the automated graphitization system (AGE3) producing solid AMS targets. After testing chemical pretreatments, our preferred method is based on leaching 30% of the sample with HCl, followed by complete hydrolysis of the residual carbonate with phosphoric acid.

For the CHS coupled to the gas source, the average blank on the IAEA-C1 calcite standard corresponds to a $F^{14}C = 0.0015$, SD = 0.0005, n = 75. This mean value is equivalent to a ^{14}C age of around 52,000 yr BP. An even lower background age of ca. 55,000 yr BP, can be achieved by flushing the CHS to further minimize the sample-to-sample memory.

The procedural blank obtained from gas measurements for foraminifera based on analyzing old (>100 kyr BP) foraminifera in two deep-sea sediment cores is determined to be an average of $F^{14}C = 0.0018$, SD = 0.0005, n = 47. Foraminiferal blanks are thus slightly, but consistently, higher than IAEA-C1 values. A similar residual difference is observed for solid graphite targets. These observations illustrate the need to measure realistic blanks in order to correct ^{14}C measurements in a particular sediment core.

The long-term reproducibility of the gas method is about 7‰ based on replicated analyses of a modern coral and the accuracy was confirmed by dating coral and foraminifera samples previously dated by conventional AMS.

Although the gas source handles samples between ca. 5 μg to 100 μgC, it is better to measure samples larger than 30 μgC to optimize precision and reduce the impact of the blank correction uncertainty. Nevertheless, our detailed study of the contamination showed that a correction may be applied for samples down to 10 μgC by assuming a constant contaminant.

Our methods were applied to date planktonic foraminifera from two deep-sea cores. The dataset does not reveal any large age bias between species nor visual aspects of the foraminifera. Measurements on single foraminifera specimens are used to assess the scatter linked to sediment mixing and/or alteration. Although this preliminary study is promising, we plan further tests on foraminifera samples from other sediment cores characterized by different sedimentation rates and dissolution conditions.

Uncited reference

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References

[1] E. Bard, M. Arnold, P. Maurice, J. Duprat, J. Moyes, J.-C. Duplessy, Retreat velocity of the North Atlantic polar front during the last deglaciation determined by ^{14}C accelerator mass spectrometry, Nature 328 (1987) 791.
[2] W. Broecker, A. Mix, M. Andree, Hans Oeschger, Radiocarbon measurements on coexisting benthic and planktic foraminifera shells: potential for reconstructing ocean ventilation times over the past 20 000 years, Nucl. Instrum. Methods B 5 (1984) 331–339, https://doi.org/10.1016/0168-583X(84)90538-X.
[3] L.D. Keigwin, Radiocarbon and stable isotope constraints on Last Glacial Maximum and Younger Dryas ventilation in the western North Atlantic, Paleoceanography 19 (2004) PA4012, https://doi.org/10.1029/2004PA001029.

[4] T.M. Marchitto, S.J. Lehman, J.D. Ortiz, J. Flückiger, A. van Geen, Marine radiocarbon evidence for the mechanism of deglacial atmospheric CO_2 Rise, Science (2007) https://doi.org/10.1126/science.1138679.

[5] E. Bard, M. Arnold, J. Mangerud, M. Paterne, L. Labeyrie, J. Duprat, M.-A. Mélières, E. Sønstegaard, J.-C. Duplessy, The North Atlantic atmosphere-sea surface ^{14}C gradient during the Younger Dryas climatic event, Earth Planet. Sci. Lett. 126 (1994) 275–287, https://doi.org/10.1016/0012-821X(94)90112-0.

[6] E.L. Sikes, C.R. Samson, T.P. Guilderson, W.R. Howard, Old radiocarbon ages in the southwest Pacific Ocean during the last glacial period and deglaciation, Nature 405 (2000) 555.

[7] D.J.R. Thornalley, I.N. McCave, H. Elderfield, Tephra in deglacial ocean sediments south of Iceland: Stratigraphy, geochemistry and oceanic reservoir ages, J. Quaternary Sci. 26 (2011) 190–198, https://doi.org/10.1002/jqs.1442.

[8] E. Bard, M. Arnold, J. Duprat, J. Moyes, J.-C. Duplessy, Reconstruction of the last deglaciation: deconvolved records of $\delta^{18}O$ profiles, micropaleontological variations and accelerator mass spectrometric ^{14}C dating, Clim. Dyn. 1 (1987) 101–112, https://doi.org/10.1007/BF01054479.

[9] W. Broecker, S. Barker, E. Clark, I. Hajdas, G. Bonani, Anomalous radiocarbon ages for foraminifera shells, Paleoceanography 21 (2006) PA2008, https://doi.org/10.1029/2005PA001212.

[10] S. Barker, W. Broecker, E. Clark, I. Hajdas, Radiocarbon age offsets of foraminifera resulting from differential dissolution and fragmentation within the sedimentary bioturbated zone, Paleoceanography 22 (2007) PA2205, https://doi.org/10.1029/2006PA001354.

[11] L. Löwemark, K.I. Konstantinou, S. Steinke, Bias in foraminiferal multispecies reconstructions of paleohydrographic conditions caused by foraminiferal abundance variations and bioturbational mixing: a model approach, Mar. Geol. 256 (2008) 101–106, https://doi.org/10.1016/j.margeo.2008.10.005.

[12] L.D. Keigwin, T.P. Guilderson, Bioturbation artifacts in zero-age sediments, Paleoceanography 24 (2009) PA4212, https://doi.org/10.1029/2008PA001727.

[13] B.C. Lougheed, B. Metcalfe, U.S. Ninnemann, L. Wacker, Moving beyond the age–depth model paradigm in deep-sea palaeoclimate archives: dual radiocarbon and stable isotope analysis on single foraminifera, Clim. Past 14 (2018) 515–526, https://doi.org/10.5194/cp-14-515-2018.

[14] G. Santos, J. Southon, S. Griffin, S. Beaupre, E. Druffel, Ultra small-mass AMS ^{14}C sample preparation and analyses at KCCAMS/UCI Facility, Nucl. Instrum. Methods B. 259 (2007) 293–302, https://doi.org/10.1016/j.nimb.2007.01.172.

[15] S. Shah Walter, A. Gagnon, M. Roberts, A. McNichol, M. Lardie Gaylord, E. Klein, Ultra-small graphitization reactors for ultra-microscale ^{14}C analysis at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility, Radiocarbon. 57 (2015) 109–122, https://doi.org/10.2458/azu_rc.57.18118.

[16] E. Freeman, L.C. Skinner, R. Reimer, A. Scrivner, S. Fallon, Graphitization of small carbonate samples for paleoceanographic research at the Godwin Radiocarbon Laboratory, University of Cambridge, Radiocarbon 58 (2016) 89, https://doi.org/10.1017/RDC.2015.8.

[17] C.P. McIntyre, M.L. Roberts, J.R. Burton, A.P. McNichol, A. Burke, L.F. Robinson, K.F. von Reden, W.J. Jenkins, Rapid radiocarbon (14 C) analysis of coral and carbonate samples using a continuous-flow accelerator mass spectrometry (CFAMS) system, Paleoceanography 26 (2011) https://doi.org/10.1029/2011PA002174.

[18] L. Wacker, S.M. Fahrni, I. Hajdas, M. Molnar, H.-A. Synal, S. Szidat, Y.L. Zhang, A versatile gas interface for routine radiocarbon analysis with a gas ion source, Nucl. Instrum. Methods B. 294 (2013) 315–319, https://doi.org/10.1016/j.nimb.2012.02.009.

[19] L. Wacker, J. Lippold, M. Molnár, H. Schulz, Towards radiocarbon dating of single foraminifera with a gas ion source, Nucl. Instrum. Methods B. 294 (2013) 307–310, https://doi.org/10.1016/j.nimb.2012.08.038.

[20] M. Roberts, A. High-Throughput, Low-cost method for analysis of carbonate samples for ^{14}C, Radiocarbon 55 (2013) 585–592, https://doi.org/10.2458/azu_js_rc.55.16190.

[21] J. Gottschalk, S. Szidat, E. Michel, A. Mazaud, G. Salazar, M. Battaglia, J. Lippold, S.L. Jaccard, Radiocarbon measurements of small-size foraminiferal samples with the mini carbon dating system (MICADAS) at the University of Bern: implications for paleoclimate reconstructions, Radiocarbon 60 (2018) 469–491, https://doi.org/10.1017/RDC.2018.3.

[22] E. Bard, T. Tuna, Y. Fagault, L. Bonvalot, L. Wacker, S. Fahrni, H.-A. Synal, AixMICADAS, the accelerator mass spectrometer dedicated to ^{14}C recently installed in Aix-en-Provence, France, Nucl. Instrum. Methods B. 361 (2015) 80–86, https://doi.org/10.1016/j.nimb.2015.01.075.

[23] T. Tuna, Y. Fagault, L. Bonvalot, M. Capano, E. Bard, Development of small CO_2 gas measurements with AixMICADAS, Nucl. Instrum. Methods Phys. Res., Sect. B (2018) https://doi.org/10.1016/j.nimb.2018.09.012.

[24] M. Stuiver, H.A. Polach, Discussion reporting of ^{14}C data, Radiocarbon 19 (1977) 355–363.

[25] J. Vanderplicht, A. Hogg, A note on reporting radiocarbon, Quat. Geochronol. 1 (2006) 237–240, https://doi.org/10.1016/j.quageo.2006.07.001.

[26] P.J. Reimer, T.A. Brown, R.W. Reimer, Discussion: reporting and calibration of post-bomb ^{14}C data, Radiocarbon 46 (2004) 1299–1304, https://doi.org/10.1017/S0033822200033154.

[27] E. Bard, B. Hamelin, R.G. Fairbanks, A. Zindler, G. Mathieu, M. Arnold, U/Th and ^{14}C ages of corals from Barbados and their use for calibrating the ^{14}C time scale beyond 9000 years B.P., Nucl. Instrum. Methods B 52 (1990) 461–468, https://doi.org/10.1016/0168-583X(90)90458-7.

[28] G.S. Burr, R.L. Edwards, D.J. Donahue, E.R.M. Druffel, F.W. Taylor, Mass spectrometric ^{14}C and U-Th measurements in coral, Radiocarbon 34 (1992) 611–618, https://doi.org/10.1017/S003382220006389X.

[29] Y. Yokoyama, K. Lambeck, P. De Deckker, P. Johnston, L.K. Fifield, Timing of the Last Glacial Maximum from observed sea-level minima, Nature 406 (2000) 713.

[30] N. Durand, Comparison of ^{14}C and U-Th ages in corals from IODP #310 Cores offshore Tahiti, Radiocarbon 55 (2013) 1947–1974, https://doi.org/10.2458/azu_js_rc.v55i2.16134.

[31] M. Ruff, S. Fahrni, H.W. Gaggeler, I. Hajdas, M. Suter, H.-A. Synal, S. Szidat, L. Wacker, On-line radiocarbon measurements of small samples using elemental analyzer and MICADAS gas ion source, Radiocarbon 52 (2010) 1645–1656.

[32] G. Salazar, Y.L. Zhang, K. Agrios, S. Szidat, Development of a method for fast and automatic radiocarbon measurement of aerosol samples by online coupling of an elemental analyzer with a MICADAS AMS, Nucl. Instrum. Methods B. (2015) https://doi.org/10.1016/j.nimb.2015.03.051.

[33] L. Bonvalot, T. Tuna, Y. Fagault, J.-L. Jaffrezo, V. Jacob, F. Chevrier, E. Bard, Estimating contributions from biomass burning, fossil fuel combustion, and biogenic carbon to carbonaceous aerosols in the Valley of Chamonix: a dual approach based on radiocarbon and levoglucosan, Atmos. Chem. Phys. 16 (2016) 13753–13772, https://doi.org/10.5194/acp-16-13753-2016.

[34] S.M. Fahrni, L. Wacker, H.-A. Synal, S. Szidat, Improving a gas ion source for 14C AMS, Nucl. Instrum. Methods B. 294 (2013) 320–327, https://doi.org/10.1016/j.nimb.2012.03.037.

[35] M. Schleicher, P.M. Grootes, M.-J. Nadeau, A. Schoon, The carbonate ^{14}C background and its components at the Leibniz AMS facility, Radiocarbon 40 (1997) 85–93, https://doi.org/10.1017/S0033822200017926.

[36] E. Bard, G. Ménot, F. Rostek, L. Licari, P. Böning, R.L. Edwards, H. Cheng, Y. Wang, T.J. Heaton, Radiocarbon calibration/comparison records based on marine sediments from the Pakistan and Iberian margins, Radiocarbon 55 (2013) 1999–2019.

[37] L.C. Skinner, S. Fallon, C. Waelbroeck, E. Michel, S. Barker, Ventilation of the deep southern ocean and deglacial CO_2 Rise, Science 328 (2010) 1147–1151, https://doi.org/10.1126/science.1183627.

[38] J. Wycech, D.C. Kelly, S. Marcott, Effects of seafloor diagenesis on planktic foraminiferal radiocarbon ages, Geology 44 (2016) 551–554, https://doi.org/10.1130/G37864.1.

[39] K. Rozanski, In: Consultants' group meeting on 14C reference materials for radiocarbon laboratories. February 18-20, 1991, Internal Report, IAEA, Vienna, Vienna, Austria, 1991, p. 1991.

[40] K. Rozanski, W. Stichler, R. Gonfiantini, E.M. Scott, R. Beukens, B. Kromer, J. Van der Plicht, The IAEA ^{14}C Intercomparison exercise 1990, Radiocarbon 34 (1992) 506–519.

[41] S. Shah, A. Pearson, Ultra-microscale (5–25 μg C) analysis of individual lipids by ^{14}C AMS : Assessment and correction for sample processing blanks, Radiocarbon 49 (2007) 69–82.