

Towards radiocarbon dating of single foraminifera with a gas ion source

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ABSTRACT

Carbonate shells from foraminifera are often analysed for radiocarbon to determine the age of deep-sea sediments or to assess radiocarbon reservoir ages. However, a single foraminiferal test typically contains only a few micrograms of carbon, while most laboratories require more than 100 µg for radiocarbon dating with an accelerator mass spectrometry (AMS) system. The collection of the required amount of foraminifera for a single analyses is therefore time consuming and not always possible. Here, we present a convenient method to measure the radiocarbon content of foraminifera using an AMS system fitted with a gas ion source. CO₂ is liberated from 150 to 1150 µg of carbonate in septum sealed vials by acid decomposition of the carbonate. The CO₂ is collected on a zeolite trap and subsequently transferred to a syringe from where it is delivered to the ion source. A sample of 400 µg (50 µg C) typically gives a ¹²C⁻ ion source current of 10–15 µA over 20 min, yielding a measurement precision of less than 7 per mil for a modern sample. Using this method, we were able to date a single 560 µg *Cibicides pseudoungerianus* test at 14,030 ± 160 radiocarbon years. Only a minor modification to our existing gas handling system was required and the system is fully automatable to further reduce the effort involved for sample preparation.

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1. Introduction

The preparation of graphite targets for ¹⁴C accelerator mass spectrometry measurements is time-consuming and labor-intensive. In the case of carbonate samples, CO₂ formed after decomposition with acid, has to be quantitatively trapped and converted to graphite [1–4]. Carbonate shells from foraminifera are often analysed for radiocarbon to determine the age of deep-sea sediments [5] or to assess radiocarbon reservoir ages [6–8]. However, a single foraminifera test contains typically only a few micrograms of carbon, while most laboratories require more than 100 µg carbon for radiocarbon analysis with an AMS system. The collection of the number of foraminifera required is therefore time-consuming and not always possible due to a low abundance in the sediment. In many cases, sections of sediment cores of high paleoceanographic interest cannot be ¹⁴C dated.

Gas ion sources have been developed by the AMS community to measure CO₂ directly and circumvent the graphitization process. They have been used to measure CO₂ liberated from carbonate samples containing as little as 10 µg of carbonate [9]. While this is considered a very small sample by radiocarbon standards, the technique has received relatively little attention when compared

with conventional sources. Here, we will present a new and simple approach where CO₂ is efficiently fed into the gas ion source of an AMS system for radiocarbon analyses.

2. Methods

Planktonic and benthic foraminifera with a size >250 µm were used as samples. SO90-93KL was collected from NE Arabian Sea (Indian Ocean), KK-410MO from the Mozambique Strait (Indian Ocean) and M51/3-SL110 from the Levantine Sea (Eastern Mediterranean). Mixed planktonic foraminifera with an age of >100 ky were used as a blank. Oxalic acid I (OX-1) [10] in helium (4%) was used as a standard for normalisation. For quality control, we also measured OX-1 as barium carbonate. CO₂ from combusted OX-1 was bubbled through a solution of Ba(NO₃)₂ in 10% ammonia and the resulting precipitate of BaCO₃ collected and dried. IAEA-C1 was used as a blank and FIRI-C and IAEA-C2 were used as internal standards. Foraminiferal samples were analysed by conventional AMS via graphite for comparison.

Between 150 and 1150 µg of carbonate sample (18–130 µg C) were weighed for the analysis and, where necessary, cleaned to remove organic contaminants. Foraminiferal samples were oxidised with 15% H₂O₂ in an ultrasonic bath for 5–15 min and then rinsed with Milli-Q water and dried. For small samples of less than 200 µg carbonate (24 µg C), careful handling of the sample was required.

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Preparation of the CO₂ gas from the samples was performed in a similar fashion to that for stable-isotope measurements with a Gas-Bench (Thermo Fisher [11], Fig. 1). The carbonates were put in 4 ml septum sealed vials (Labco, UK) where they were first flushed with helium (50 ml/min) for 15 min by means of a double-walled needle (Thermo Fisher, Gasbench). 0.5 ml H₃PO₄ (85% or 103%) was added with a syringe to decompose the carbonate. This was done one at a time while samples were being measured but could also be done as a batch prior to analysis. The vials were heated at 75 °C for at least 30 min and the product CO₂ flushed with helium (50 ml/min) via a water trap of phosphorus pentoxide to a trap containing 80 mg of X13 zeolite within 2 min [12] (see Fig. 2). The trap was heated to 500 °C to release the CO₂, which was then transferred using a lower flow of helium to a gas tight syringe so a final concentration of 3% CO₂/He v/v was obtained. Because the syringe is dimensioned for samples <60 µg carbon, the concentration for larger samples was increased (more than 6% CO₂/He v/v for 130 µg carbon). Slightly lower ionization efficiency had then to be accepted.

Meanwhile, a titanium target was pre-sputtered for 2 min for cleaning. The final CO₂/He mixture contained in the syringe was then injected at a 2 µg C/min into the ion of the MICADAS system [13,14] over a period of 5–25 min, depending on sample size. During the measurement of a sample, the trap was cleaned by heating to 500 °C for 2 min and cooled down to 200 °C for 2 min. During the cleaning and cooling procedure, the trap was continuously flushed with helium.

3. Results and discussion

The radiocarbon concentration of the carbonate samples are given in Table 1. Sample sizes of the foraminifera ranged from 300 to 1150 µg and two of these samples were single foraminifera. These were a relatively large benthic species and it should be noted that much smaller (>10 µg carbon) samples have been successfully analysed elsewhere [15]. Values for individual measurements were repeatable and generally in good agreement with accepted values [16,17] or those derived from graphite measurements [18]. Thirteen of the 15 sample measurements agreed within the 95% confidence limit (2-σ) and 11 agreed within 1-σ. There was no systematic offset in radiocarbon concentration nor was there any significant difference in the radiocarbon concentration for samples that were pre-treated with H₂O₂ or not.

Blank foraminifera samples (>100 ky) were measured to contain 0.001 ± 0.002 F¹⁴C, the same value as we measured for ¹⁴C-free CO₂ gas. This indicated that the gas transport from the septum vials via the trap did not add a significant amount of contamination. When OX-I as barium carbonate was measured, we obtained the same radiocarbon result as for OX-I measured directly from a gas bottle (not including the decomposition in septum sealed vials and the transfer over the zeolite trap). However, in the formation of the BaCO₃ we observed a fractionation of 3% in δ¹³C (by AMS) but this was corrected for during data processing.

Normally between 10 and 40 foraminifera of >250 µm diameter were used for a single analysis. For these samples, a 400 µg sample would comprise 3–30 planktonic foraminifera or single heavier benthic foraminifera. We were able to analyse a single 560 µg *Cibicides pseudoungerianus* foraminifera with a 1 mm diameter giving a value of 14,030 ± 160 radiocarbon years from 6090 ¹⁴C counts (Table 1; ETH label-41212.1.2). The progress of the measurement over time for this sample is shown in Fig. 3. It represents a typical measurement of a sample that contains about 50 µg C. The first 2 min show the pre-sputtering of the Ti target to clean it and reduce the ¹²C⁻ current to less than 0.1 µA. A quick rise in current is visible when the CO₂ is let into the source. A sample of 50 µg C (400 µg

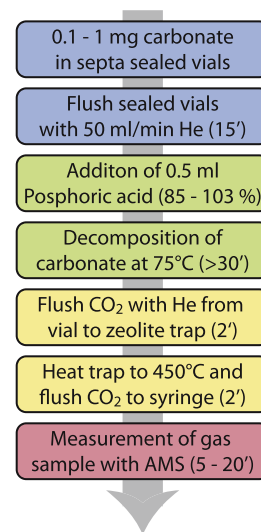


Fig. 1. Flowchart of the method used to measure the radiocarbon content of foraminifera.

carbonate) typically produces a ¹²C⁻ current of 10–15 µA over 20 min, which results in a measurement precision of approximately 7‰ for a modern sample including standard normalisation (5‰ on pure counting statistics).

Because the measurement of small samples is in general prone to contamination [19], we tested the contribution of the phosphoric acid used for decomposing the carbonate. While concentrated phosphoric acid contained no observable amount of carbon, we found a small amount modern carbon in blank samples when we increased the amount of 85% phosphoric acid from 0.5 to 2 ml. We calculated from the measurements, that the 85% phosphoric acid contains 0.21 ± 0.05 µg/ml modern carbon. This can be explained by dissolved CO₂ in the water contained in the acid (according to the Henry law of gases). Concentrated phosphoric acid (103%) does not show this contamination, however the handling of this material is significantly more difficult as it has to be kept above at 75 °C to remain a liquid.

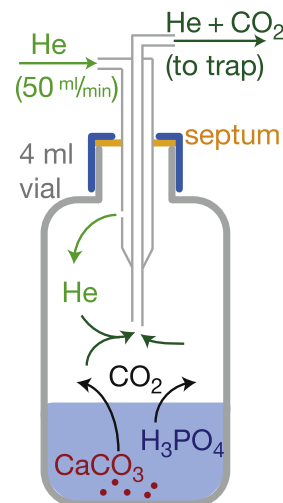


Fig. 2. Diagram of the sample preparation procedure. CO₂ is liberated from a carbonate sample by decomposition with phosphoric acid in septum sealed vial. The CO₂ is then flushed out with helium to a zeolite trap from where it is transferred to a gas tight syringe for delivery to the gas ion source AMS.

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