

1 **Graphitization of small carbonate samples for palaeoceanographic**
2 **research at the Godwin Radiocarbon Laboratory, University of Cambridge**

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13 **A new radiocarbon preparation facility was set up in 2010 at the Godwin**
14 **Laboratory for Palaeoclimate Research, at the University of Cambridge.**
15 **Samples are graphitized via hydrogen reduction on an iron powder catalyst**
16 **before being sent to the Chrono Centre, Belfast, or the Australian National**
17 **University for accelerator mass spectrometry (AMS) analysis. The**
18 **experimental set-up and procedure have recently been developed to**
19 **investigate the potential for running small samples of foraminiferal**
20 **carbonate. By analysing background values of samples ranging from 0.04-**
21 **0.6mgC along with similar sized secondary standards, the set-up and**
22 **experimental procedures were optimised for small samples. 'Background'**
23 **modern radiocarbon contamination has been minimised through careful**
24 **selection of iron powder, and graphitization has been optimised through**
25 **the use of 'small volume' reactors, allowing samples containing as little as**
26 **0.08mgC to be graphitized and accurately dated. Graphitization**
27 **efficiency/fractionation is found not to be the main limitation on the**
28 **analysis of samples smaller than 0.07mgC, which rather depends primarily**
29 **on AMS machine dependent ion beam optics, suggesting further**
30 **improvements in small sample analysis might yet be achieved with our**
31 **methodology.**

32
33 **Introduction**

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35 Significant advances in the graphitization and AMS-dating of small samples have
36 been made in recent years (e.g. Santos et al., 2007; Delque-Kolic et al., 2013), but

37 only one of these studies have been specifically targeted for small carbonate
38 samples used in palaeoceanographic research (Walter et al., 2015).

39 Carbonate samples, primarily foraminifer shells, are graphitized in the Godwin
40 Radiocarbon laboratory and pressed into cathode targets before being sent for
41 accelerator mass spectrometry (AMS) analysis. The laboratory was initially set-
42 up and developed to run samples containing ~0.6mgC (approximately 6mg of
43 carbonate), but demand for running smaller samples allowing, in particular,
44 dating of foraminifera from deep-sea cores where abundances are low has led us
45 to adapt the process to run smaller samples.

46 In order to do this the background contamination must be accurately determined
47 and reduced. The contamination in our methodology is predominantly modern
48 carbon, with high $^{14}\text{C}/^{12}\text{C}$, such that older and smaller samples are most affected.
49 Fractionation of isotopes during the graphitization process must also be
50 minimised for samples of all sizes and ages, primarily by ensuring the reduction
51 reaction goes to completion.

52 The graphitization process is complex and involves several reactions that are
53 sensitive to temperature, pressure, the initial ratio of $\text{H}_2:\text{CO}_2$, water content, the
54 catalyst and various other factors. Since a high yield of graphite must be
55 produced in order to minimise fractionation of the carbon isotopes, all of these
56 parameters need to be optimised. Here the yield, fractionation (using both $\delta^{13}\text{C}$
57 and $\Delta^{14}\text{C}$ measurements) and contamination are used to optimise the set-up and
58 procedures in order to produce accurate radiocarbon measurement on small
59 samples of carbonate.

60 Both the background contamination and the amount of fractionation during
61 graphitizing were minimised by changing various aspects of the process for both

62 full size and small samples. The new set up was then tested with the secondary
63 standard IAEA-C8 and with a large carbonate sample of approximately 20kyr age
64 that was spilt into small samples.

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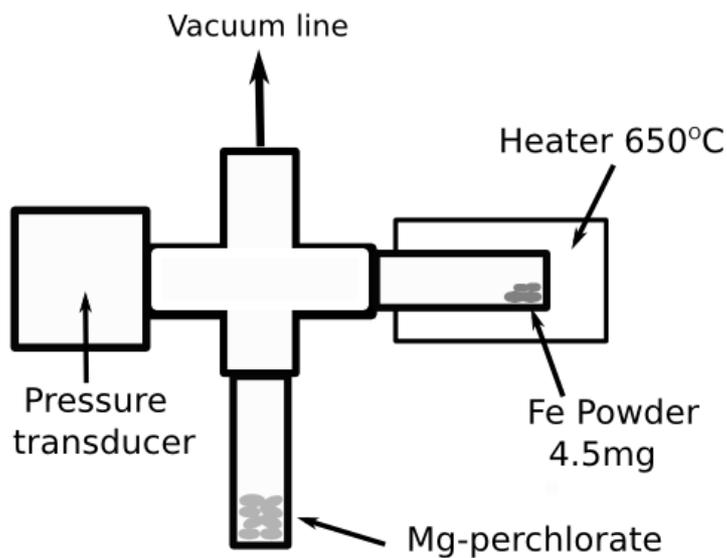
66 **Methods**

67 *Laboratory set-up and experimental procedure*

68 The new Godwin radiocarbon preparation facility was set up based on that used
69 at ANU, which is in turn based on the Irvine lab design (Santos et al., 2007). The
70 laboratory contains one vacuum line with 11 small volume reactors ($\sim 4.0\text{cm}^3$)
71 fitted with 0-15psi pressure transducers and two 50mm quartz tubes (with 4mm
72 internal diameter). Each reactor is preloaded with iron powder and magnesium
73 perchlorate [Figure 1] and flushed with hydrogen several times. One atmosphere
74 of hydrogen is added to the reactors that are then heated for 90mins at 450°C to
75 precondition the line immediately prior to graphitizing. This removes much of
76 the carbon contamination and improves the effectiveness of the iron powder as a
77 catalyst. For carbonate samples, CO_2 is produced by reacting the sample with
78 phosphoric acid in an evacuated double-septum vial at 80°C for a minimum of
79 1hr. The carbonate is loaded into the vial which is then evacuated before
80 phosphoric acid is injected using a single needle. The CO_2 is then introduced into
81 the line via a needle and water vapour is removed using an ethanol cold trap at -
82 80°C . The CO_2 is transferred into a reactor and hydrogen added to give the
83 desired $\text{H}_2:\text{CO}_2$ [see Discussion]. Each reactor is then heated at 650°C for at least
84 2.5 hours, until the reactor pressure reaches a minimum. Finally, the graphite is
85 removed from the line and pressed into cathode targets to be sent to the AMS
86 laboratory along with backgrounds and standards. The carbonate backgrounds

87 and secondary standard IAEA-C2 are graphitized in the same way as the samples.
88 Primary standard OXII and additional secondary standards IAEA-C7 and IAEA-C8
89 are heated with copper oxide and silver at 900°C for 300mins in sealed quartz
90 tubes to produce CO₂ which is then introduced to the line and split into
91 individual samples.

92 **Figure 1:** Schematic diagram of the reactor set-up.



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95 *Isotope Measurements*

96 Once graphitised, samples were either prepared for stable isotope analysis or for
97 radiocarbon dating at an AMS facility. Samples for stable isotope analysis were
98 ground into a fine powder and transferred into tin capsules in the Godwin
99 Laboratory, University of Cambridge. These were then run on a Costech
100 Elemental Analyser attached to a Thermo DELTA V mass spectrometer in
101 continuous flow mode along with IAEA reference standards. The precision of
102 analyses is better than 0.1‰ for ¹³C/¹²C.

103 Samples for radiocarbon analysis were pressed into NEC aluminium cathode
104 targets before being sent to the Chrono Centre, Belfast, or on one occasion the
105 AMS facility at ANU. Each set of samples was run with primary and secondary
106 standards along with calcite blanks (Icelandic Spar) produced in our laboratory
107 via the methods described above.

108 ***Yield***

109 The yield is calculated based on the pressure in each reactor, using the equation:

$$Yield = \frac{(pH_2 + pCO_2)_{initial} - Residual\ pressure}{3 \times pCO_{2,initial}}$$

110 where pH_2 initial and pCO_2 initial are the initial pressures of H₂ and CO₂ respectively,
111 and residual pressure is the final pressure at the end of heating.

112

113 ***Optimising the process***

114 Three different iron powders were tested; Analar Normapur, Alfa Aesar-325
115 mesh and Fisher Fe. For each, the amount was kept constant at 4.5-5mg and the
116 experimental procedure was identical. The amount of hydrogen added to the CO₂
117 was varied to find the optimal H₂:CO₂. The temperature and duration of heating
118 were also investigated to maximise the yield and the rate of reaction. Each of
119 these variables was optimised using the yield, $\delta^{13}C$ and $\Delta^{14}C$ measurements to
120 ensure the reaction was complete, with minimal contamination, and within the
121 shortest time. A standard and a carbonate sample of approximately 20kyr age
122 were then used to test the new set-up for a range of sample sizes.

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124 **Results and Discussion**

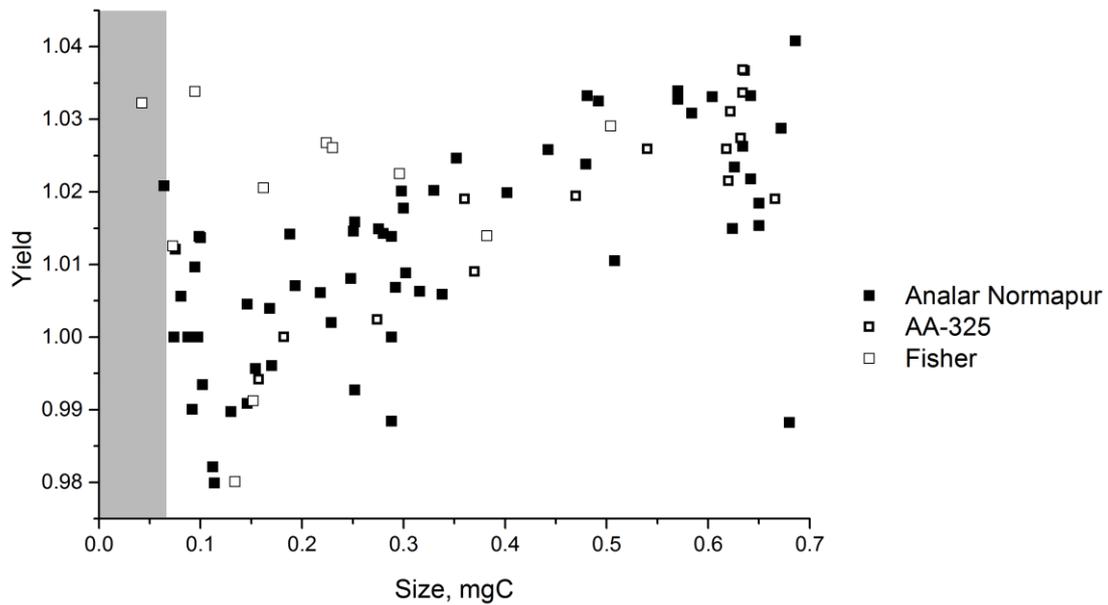
125 ***Iron Powder***

126 Samples of radiocarbon 'free' Icelandic Spar calcite were graphitised using three
127 different iron powders as the catalyst. For each, a range of sample sizes were
128 graphitized and the yield determined to assess the completeness of the reaction
129 and hence the potential for fractionation. The samples were then sent to the AMS
130 laboratory to be dated in order to determine the background contamination
131 levels. Figure 2 shows the variation in yield for the different iron powders over a
132 range of sample sizes. The yield was high, over 98%, for all of the iron powders
133 for samples ranging from 0.04mgC to 0.7mgC and often greater than 100% (see
134 section: H₂:CO₂). There is a fair amount of scatter in the yields, especially for the
135 smaller samples, but none of the iron powders had a significantly better yield
136 than the others. Figure 3 shows the background ¹⁴C/¹²C data for a range of
137 sample sizes using each of the three iron powders. This clearly shows that the
138 background varies significantly depending on the iron powder used, with Alfa
139 Aesar-325 leading to the highest background values and Analar Normapur being
140 associated with the lowest background values. A lower background means that
141 samples can be smaller and/or older before they are significantly affected by the
142 contamination. Background (i.e. 'radiocarbon-dead') samples smaller than
143 0.3mgC start to be significantly affected by the contamination when Alfa Aesar-
144 325 is used, whereas only those smaller than around 0.07mgC are affected when
145 Analar Normapur is used. For this reason, Analar Normapur is now used as the
146 catalyst for all samples.

147 The amount of catalyst is kept constant regardless of the size of the sample. This
148 has the advantage of keeping the contamination constant and the current beam
149 as high as possible for the small samples (Turnbull et al., 2010).

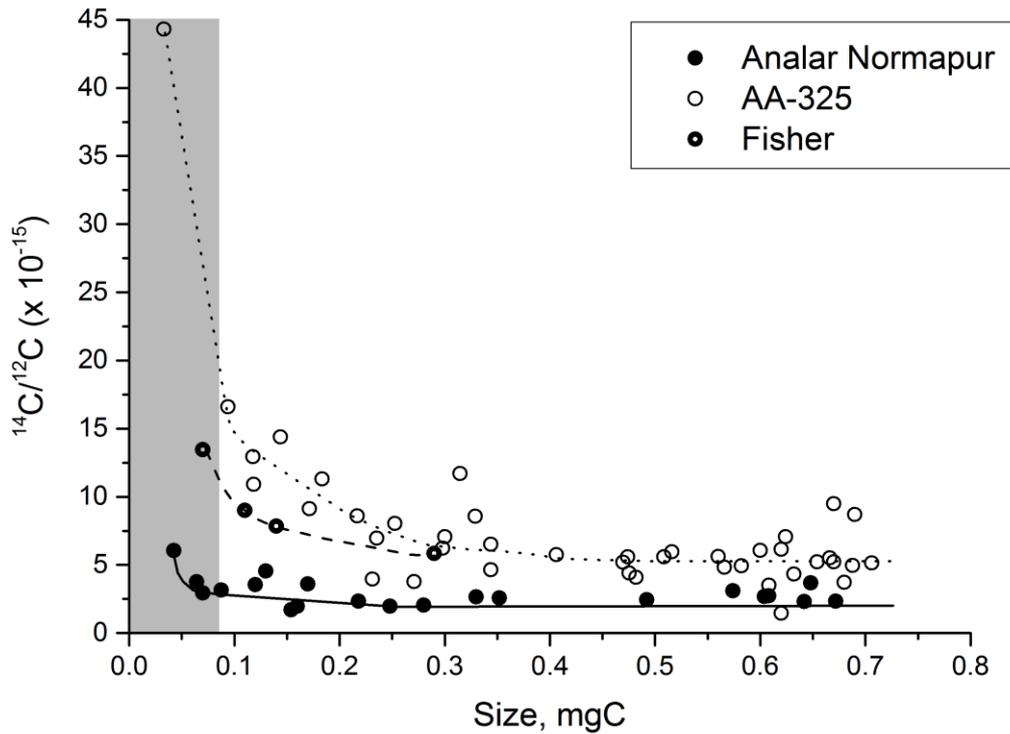
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151 **Figure 2:** Yields resulting from using different iron powders to catalyse the
152 graphitising reaction, for a range of sample sizes. The grey bar indicates the
153 region where samples cannot be accurately dated.



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155 **Figure 3:** Background measurements using different iron powders, for a range of
156 sample sizes. The grey bar indicates the region where samples cannot be
157 accurately dated.



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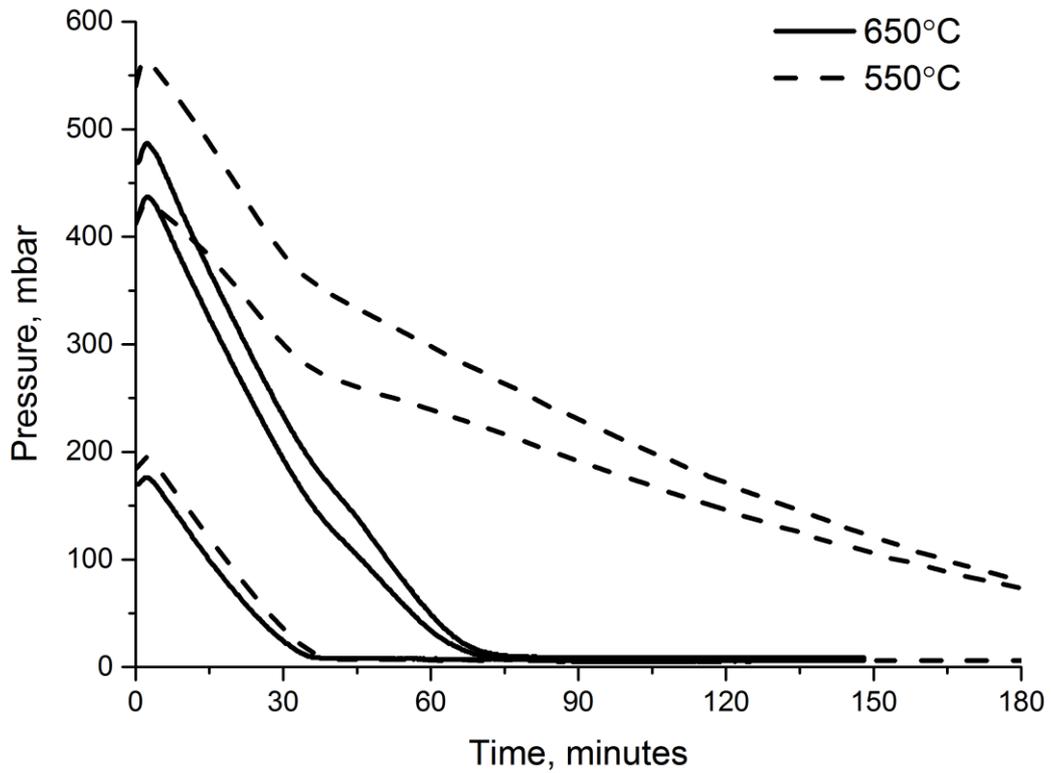
162 ***Temperature and Duration of Heating***

163 The graphitization reaction is highly sensitive to temperature, with the yield and
 164 the reaction time both being affected. The optimal temperature will allow the
 165 reaction to have a high yield in a short amount of time. The reactor pressure can
 166 be used as an indicator of the reaction completeness as the reaction involves two
 167 gases, CO_2 and H_2 , being converted into a solid, graphite. Water vapour is also
 168 produced but is removed by the magnesium perchlorate. Figure 4 shows the
 169 reactor pressure for a series of reactors containing different initial amounts of
 170 CO_2 over the course of the graphitization at both 550°C and 650°C . The pressure
 171 initially increases as the heaters are switched on, but quickly decreases as the
 172 reaction starts to occur. For samples heated at 550°C , the decrease is much
 173 slower than for those heated at 650°C and, for the larger samples, the reaction at

174 550°C is still not complete after 3hrs. For samples heated at 650°C the reaction
175 is complete within 1.5hrs for all sample sizes. Figure 5 shows the effect of
176 increasing the temperature during the reaction. Samples were heated at 550°C
177 for just over 3hrs before the temperature was increased to 650°C. On increasing
178 the temperature, the rate of reaction immediately increases and the reaction was
179 completed after a further 40mins, for the largest sample. Graphitizing at higher
180 temperatures can cause the graphite to sinter and whilst this does start to occur
181 in our reactors at 650°C, it is insufficient to prevent samples from being pressed
182 effectively and does not affect the AMS results.

183 Whilst many radiocarbon laboratories use lower temperatures for smaller
184 samples, (e.g. Santos et al., 2007; Delque-Kolic et al., 2013), high yields and low
185 fractionation have been achieved during these experiments for samples as small
186 as 0.04mgC at 650°C thus demonstrating no need to lower the temperature. This
187 could be a result of very effective water removal (Turnbull et al., 2010).

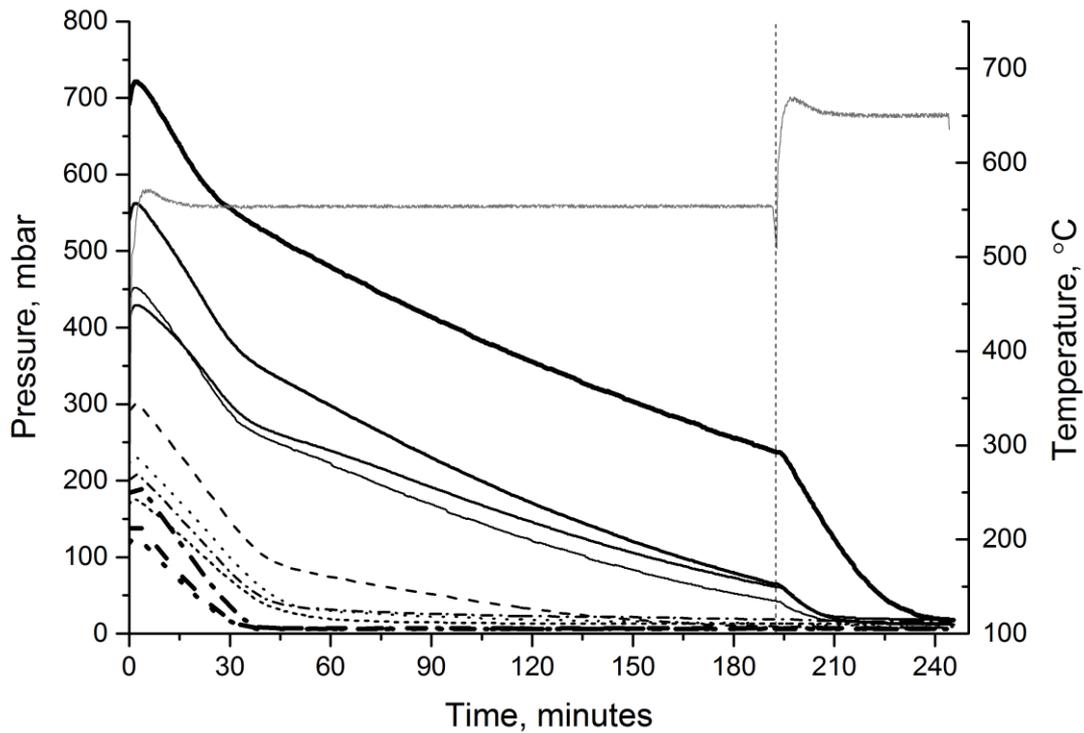
188 **Figure 4:** Reactor pressure over the course of graphitizing at either 550°C
189 (dashed) or 650°C (solid), for various sample sizes.



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192 **Figure 5:** Reactor pressure (black lines) over time when heated initially at
193 550°C, then at 650°C. Each line represents a different reactor. The reactor
194 temperature (grey line) is also shown.



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197 **Water removal**

198 Magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$) flakes are used to chemically remove any
 199 water, following Santos et al. (2004). Around 40mg of magnesium perchlorate
 200 flakes are preloaded in the reactors prior to preconditioning. These remove
 201 water during both the preconditioning and during the graphitization reaction.
 202 The water removal appears to be highly effective, so this part of the set-up
 203 remained unaltered.

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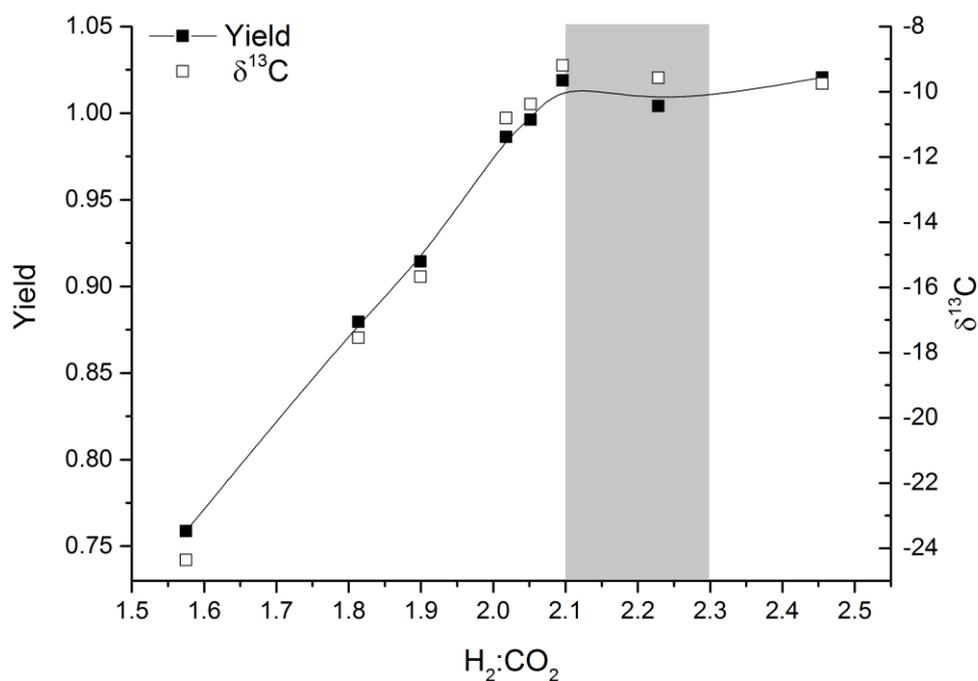
205 **$\text{H}_2:\text{CO}_2$**

206 For each reactor, the pressure of hydrogen added to the line is twice the
 207 pressure of CO_2 in the reactor. The CO_2 is frozen down and the reactor opened to
 208 allow H_2 in (this is done as rapidly as possible in order to minimise excess
 209 condensation and over-pressurization of H_2 in the reactors). This results in a
 210 ratio of $\text{H}_2:\text{CO}_2$ in the reactor of 2.1:1 to 2.3:1, depending on the size of the CO_2

211 sample frozen down. For larger samples, the ratio is at the higher end and the
212 yield is typically greater than one, indicating that more H₂ is used in the reaction
213 than expected from the stoichiometry of the reaction. This could be attributed to
214 the formation of a small amount of CH₄ or CO (Rinyu et al., 2007), however the
215 lack of any deviation from the expected $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ values for the larger
216 samples indicate that no significant fractionation takes place (Figure 6). If
217 additional carbon bearing products were produced fractionation would be
218 expected. Alternatively, hydrogen molecules may be adsorbed onto the graphite.
219 Lower H₂:CO₂ ratios were also tested but the yield dropped off rapidly and
220 fractionation was observed (Figure 6).

221

222 **Figure 6** : Yield (solid squares) and $\delta^{13}\text{C}$ (open squares) for various H₂:CO₂
223 ratios. The shaded region represents the typical range of H₂:CO₂ values used.



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226 ***Size corrections***

227 Background values for the new set up were determined using both Spar calcite
228 and 'radiocarbon-dead' planktonic foraminifera (from Marine Isotope Stage 6;
229 >130 ka). The small samples of 'radiocarbon-dead' planktonic foraminifera were
230 individually weighed out and processed rather than being split on the line so that
231 the background represents that of our sample process as closely as possible.

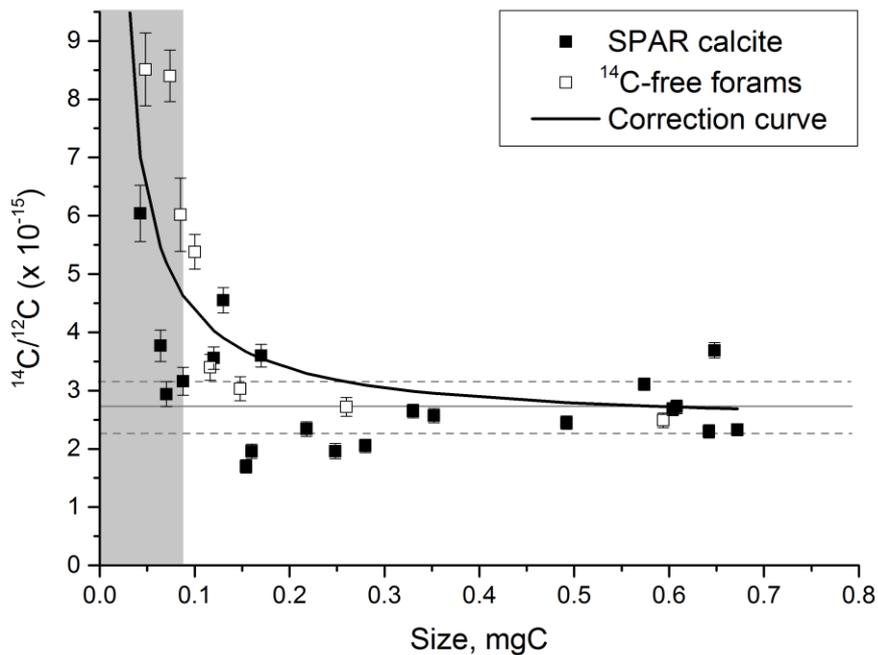
232 The constant background contamination has an inverse mass relationship that
233 becomes significant for background samples smaller than around 0.3mgC and
234 particularly important for those less than 0.07mgC. A correction is therefore
235 applied of the form $y(x_i) = a \frac{1}{x_i} + b$, where x is the mass of the sample (Figure 7).

236 The constant coefficient a is $0.1958e^{-15}$, determined using a least squares
237 minimisation and b is calculated using a full size background sample for each
238 wheel run at the AMS facility. Typically b is around $2.5e^{-15}$, with an error of 25%,
239 corresponding to 0.3-1.3 μ g of modern carbon contamination.

240

241 **Figure 7:** Background values for Spar calcite (solid squares) and 'radiocarbon-
242 dead' planktonic foraminifer samples (open squares) graphitized using Analar
243 Normapur iron powder. The solid line represents the size dependent background
244 correction. The grey bar indicates the region where samples cannot be

245 accurately dated.



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248 **Testing the new set-up**

249 Once the graphitization process had been refined, a series of samples were run in

250 order to assess the size range over which accurate radiocarbon dates could be

251 measured. A secondary standard was used, IAEA-C8, which has a known age of

252 15,224±91yrs, and a $\delta^{13}\text{C}$ value of -18.31‰ (Le Clercq et al., 1998). Figure 8

253 shows the $\delta^{13}\text{C}$ and radiocarbon ages obtained on samples from 0.04 to 0.7mgC.

254 The current beams were >40µA for the largest samples but dropped to 6-10 µA

255 for the smallest samples. Samples <0.07mgC could not be measured accurately

256 on the AMS, as indicated by the large deviations in $\delta^{13}\text{C}$ measured by AMS that

257 are not present in the graphite $\delta^{13}\text{C}$ values measured 'off-line' in the Godwin

258 laboratory. The large deviations in radiocarbon activity and $\delta^{13}\text{C}$ are therefore

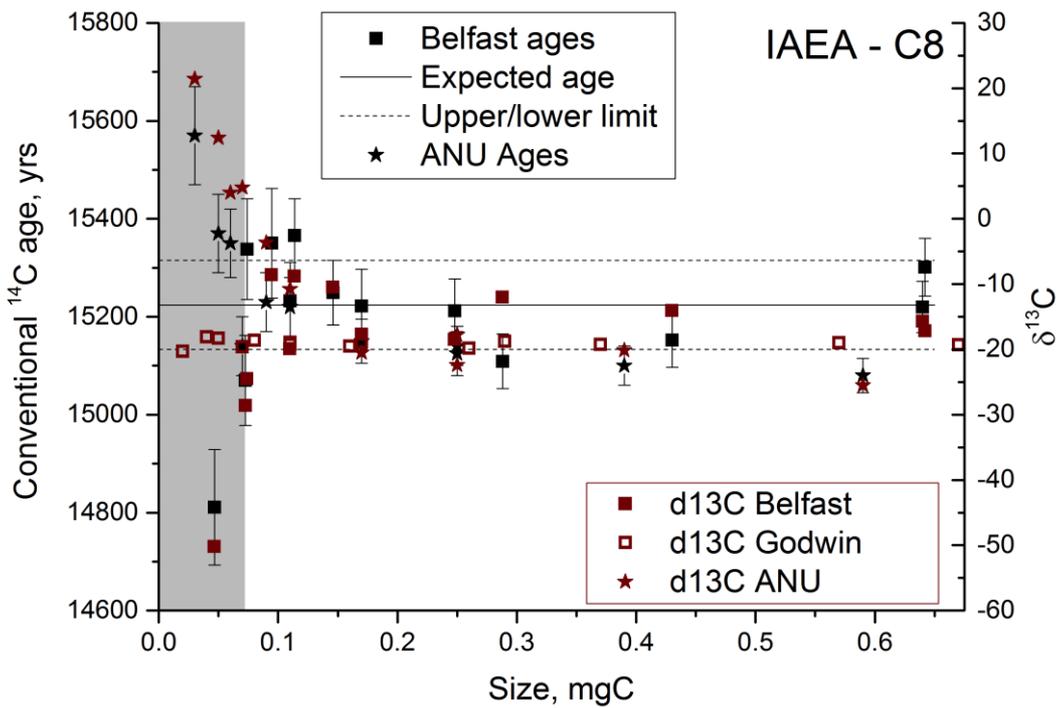
259 not due to fractionation during graphitization, and instead are most likely due to

260 the ion optics that become particularly important when the beam current is low.
261 Deviations were found to be roughly of the same magnitude but in the opposite
262 direction for similar sized samples run at the Chrono Centre versus at the ANU
263 radiocarbon facility.

264 In order to assess the performance of the graphitization procedure for typical
265 samples that would be analysed (i.e. relatively old carbonate), tests were run on
266 a mix of IAEA-C2 and Icelandic Spar calcite, combined to give an age of around
267 20,300yrs. These tests indicated similar trends in radiocarbon and $\delta^{13}\text{C}$, with
268 significant deviations in the AMS occurring for samples $<0.07\text{mgC}$ (Figure 9). The
269 smallest samples were up to 400yrs offset from the expected age of 15,224yrs
270 for IAEA-C8 and 500yrs offset from the average age of 20,295yrs observed for
271 the Spar-C2 mix. For this reason, samples smaller than 0.08mgC are not run at
272 present. Having said this, the fractionation trends do initially look to be
273 consistent at the different AMS facilities. If this is the case, by size matching
274 samples of similar age, for example co-existing benthic and planktonic
275 foraminifera, the age difference between the two samples could be determined
276 accurately so long as they are measured at the same facility. This remains to be
277 tested however.

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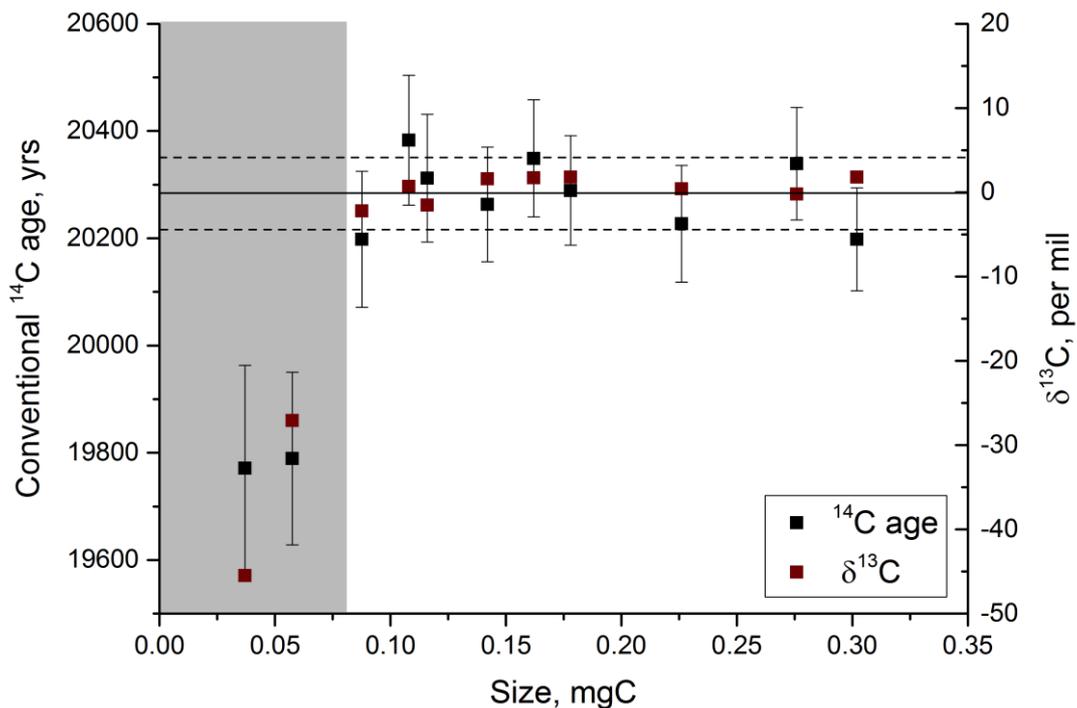
279 **Figure 8:** Radiocarbon and stable carbon measurements for a range of sizes of
280 IAEA-C8 samples analysed at various different locations. The grey bar indicates
281 the region where samples cannot be accurately dated.



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284 **Figure 9:** Radiocarbon and stable carbon measurements for a range of sizes of
285 an approximately 20,300yr old sample, measured at the Chrono Centre, Belfast.
286 The grey bar indicates the region where samples cannot be accurately dated.

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288

289 **Conclusions**

290 The Godwin Radiocarbon laboratory has been set up at the University of
291 Cambridge allowing the graphitization of carbonate and organic carbon samples,
292 and the preparation of standards. The experimental procedure has been
293 streamlined for small and relatively old carbonate samples (>20,000 years), and
294 refined to maximise the yield, ensuring no fractionation occurs, while minimising
295 the background radiocarbon levels. The reaction time has also been reduced.
296 Standards have been used to show that samples containing 0.08-0.7mg of
297 carbon, with a fraction modern radiocarbon >0.08, can be graphitized
298 successfully. Samples smaller than 0.08mgC can be graphitized without any
299 fractionation occurring, but radiocarbon measurements will not be accurate
300 unless the AMS analysis of these samples can be optimised for such small current
301 beams, which remains to be demonstrated.

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303 **Acknowledgements**

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305 measurements, as well as the Royal Society and NERC grant NE/L006421/1 for
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307

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