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1 **Advances in the radiocarbon analysis of carbon dioxide at the NERC Radiocarbon Facility (East**  
2 **Kilbride) using molecular sieve cartridges**

3 Mark H Garnett, Josephine-Anne Newton, Philippa L Ascough

4 **ABSTRACT**

5 Radiocarbon ( $^{14}\text{C}$ ) analysis of carbon dioxide ( $\text{CO}_2$ ) provides unique information on the age, turnover  
6 and source of this important greenhouse gas, raising the prospect of novel scientific investigations  
7 into a range of natural and anthropogenic processes. To achieve these measurements, cartridges  
8 containing zeolite molecular sieves are a reliable and convenient method for collecting  $\text{CO}_2$  samples.  
9 At the NERC Radiocarbon Facility (East Kilbride) we have been refining our molecular sieve methods  
10 for over twenty years to achieve high-quality, reproducible and precise measurements. At the same  
11 time, we have been developing novel field sampling methods to expand the possibilities in collecting  
12 gas from the atmosphere, soil respiration and aquatic environments. Here, we present our latest  
13 improvements to cartridge design and procedures. We provide the results of tests used to verify the  
14 methods using known  $^{14}\text{C}$  content standards, demonstrating reliability for sample volumes of 3 ml  $\text{CO}_2$   
15 (STP; 1.6 mg C) collected in cartridges that had been prepared at least three months earlier. We also  
16 report the results of quality assurance standards processed over the last two years, with results for 22  
17 out of 23 international  $^{14}\text{C}$  standards being within measurement uncertainty of consensus values. We  
18 describe our latest automated procedures for the preparation of cartridges prior to use.

19

20 **INTRODUCTION**

21 Concentrations of the greenhouse gas carbon dioxide ( $\text{CO}_2$ ) continue to increase in the Earth's  
22 atmosphere and most predictions are that this will lead to a rise in global temperature of at least  $1.5^\circ\text{C}$   
23 before the end of the current century (IPCC 2013). Although it is accepted that anthropogenic activities  
24 are driving the increase in  $\text{CO}_2$  levels (IPCC 2013), sources of  $\text{CO}_2$  to the atmosphere are complex and  
25 include both direct (e.g. fossil fuel emissions) and indirect (e.g. land-use change) anthropogenic  
26 emissions, as well as natural emissions of the Earth's carbon cycle. Moreover, the response of the  
27 carbon cycle to climatic warming, and whether this will result in the loss of carbon stores that have  
28 been "locked away" for centuries/millennia, adds further complexity, but is important because it could  
29 lead to a positive feedback to further increase the rate of warming (Walker et al. 2016).

30 Radiocarbon ( $^{14}\text{C}$ ) analysis of  $\text{CO}_2$  provides unique information on the age (since photosynthetic  
31 fixation from the atmosphere) of emissions and rate of carbon turnover, and can help to identify the  
32 contribution of different sources (Levin and Hesshaimer 2000). For example, Campeau et al. (2017)  
33 found that aquatic emissions of carbon dioxide from a boreal fen were predominantly modern (i.e.  
34 with a  $^{14}\text{C}$  concentration  $>100$  pMC) implying that they were substantially composed of carbon that  
35 had been fixed within the last ca. 60 years. In contrast, Newsham et al. (2018) reported that discrete  
36 taxa of fungi respired carbon from Antarctic soil that was over a thousand years old, providing direct  
37 evidence for the release of old organic carbon to the atmosphere.

38 Cartridges containing zeolite molecular sieve (Hardie et al. 2005; Garnett and Murray 2013) are  
39 convenient for collecting  $\text{CO}_2$  samples for  $^{14}\text{C}$  analysis and are particularly useful when the  $\text{CO}_2$  occurs  
40 at less than several thousand ppm. The porous molecular sieve has a crystalline structure, which, when

41 a gas flows through it, precludes large molecules from entering (Breck, 1974). In addition, the  
42 adsorption properties of the zeolite are such that unlike other gases (e.g. nitrogen and oxygen) the  
43 polar molecule CO<sub>2</sub> is rapidly trapped and concentrated into a relatively small and therefore highly  
44 portable volume (Breck, 1974). The sampled CO<sub>2</sub> can be released from the zeolite by heating and  
45 purified using routine cryogenic methods (Hardie et al. 2005; Garnett and Murray 2013).

46 Molecular sieves have been used for collecting carbon dioxide for <sup>14</sup>C analysis since at least the 1960's  
47 (Godwin and Willis 1964). At the NERC Radiocarbon Facility (East Kilbride, UK), we have used cartridges  
48 containing zeolite molecular sieves for sample collection for over 20 years, with development of the  
49 technique being documented at various stages (Bol and Harkness 1995; Hardie et al. 2005; Garnett  
50 and Murray 2013). The cartridges have been utilised in novel field sampling methods to enable the <sup>14</sup>C  
51 analysis of soil-respired CO<sub>2</sub> (Hardie et al. 2005), aquatic CO<sub>2</sub> (Garnett et al. 2012) and atmospheric  
52 CO<sub>2</sub> (Garnett and Hartley 2010). Development of our molecular sieve methods continues, most  
53 recently with a focus on further improving the reliability of the method and quality of results, and to  
54 increase capacity and throughput to meet demand from users. Here, we describe the latest  
55 refinements to our methods, present the results of tests used to verify our latest procedures, and  
56 report the results of all known <sup>14</sup>C content quality assurance standards processed alongside samples  
57 over the last two years.

58

## 59 **METHODS**

### 60 **Design of the molecular sieve cartridge**

61 An earlier version of our molecular sieve cartridge was built from quartz glass (Hardie et al. 2005), but  
62 since cartridge temperature does not exceed 500°C we now use tubular borosilicate glass. The  
63 cartridge has a central compartment for containing the molecular sieve material (Figure 1) and is  
64 designed for processing using a tube furnace (MTF 10/15/130, Carbolite, UK). The dimensions of the  
65 three compartments are: centre (14 mm OD, 11 mm ID by 80 mm long), inlet (10 mm OD, 7 mm ID by  
66 95 mm long), exhaust (6 mm OD, 4 mm ID by 95 mm long). At either end of the cartridge, 50 mm  
67 lengths of Iso-versinic<sup>®</sup> tubing (770260-05 and 770360-05, Saint-Gobain, France) are attached into  
68 which couplings (cPMCD22-03 and cPLCD170-06, Colder Products Company, USA) are inserted to  
69 facilitate connection to sample collection and recovery equipment. The couplings have auto-shutoffs  
70 that automatically seal when disconnected. Primary sealing of the cartridge is achieved by placing clips  
71 (PA50, Weloc, Scandinavia Direct, UK) across the Iso-versinic<sup>®</sup> tubing at both ends. The molecular sieve  
72 material (3–4 g, 1.6 mm pellets, Type 13X zeolite, 334340, Sigma-Aldrich, UK) is held within the central  
73 compartment using quartz wool. Prior to cartridge construction, the molecular sieve material is  
74 combusted in a furnace at 500°C for 24 hours.

### 75 **Processing of molecular sieve cartridges**

76 Cartridges are prepared for sample collection by purging with high purity nitrogen (Research Grade  
77 5.0, BOC, UK) and CO<sub>2</sub>-free air while being heated (500°C) over a period of at least 30 minutes. First,  
78 the heated cartridge is purged using nitrogen (150 ml/min) for 8 minutes, which desorbs most of the  
79 CO<sub>2</sub> trapped on the zeolite. The purge gas is then replaced with CO<sub>2</sub>-free air (ca. 400 ml/min; generated  
80 by pumping lab air through soda lime) for 2 minutes to oxidise any contaminants that may be present

81 within the zeolite (Table 1). The purge gas is then switched back to nitrogen for at least another 20  
82 minutes to further desorb CO<sub>2</sub> from the zeolite. At this stage, an infrared gas analyser (PP Systems  
83 EGM-4, Hitchin, UK) is used to ensure that the CO<sub>2</sub> concentration in the exhaust gas is below 50 ppm,  
84 and if so, heating of the molecular sieve is stopped. However, because a small amount of CO<sub>2</sub>  
85 continues to desorb from the zeolite until cooled to ca. 430°C, purging with nitrogen continues for  
86 another 10 minutes by which time the molecular sieve temperature has fallen to less than 400°C and  
87 CO<sub>2</sub> is no longer being desorbed. Valves are then closed to isolate the molecular sieve cartridge, which  
88 is left to cool for a further 20 minutes. Next, the cartridge is tested for leaks by flushing with nitrogen  
89 (150 ml/min) for 0.5 minutes and checking the CO<sub>2</sub> concentration of the purge gas exiting the  
90 molecular sieve (i.e. to determine if ingress of atmospheric CO<sub>2</sub> has occurred). Finally, the cartridge is  
91 filled with nitrogen to ca. 1 bar above atmospheric pressure and the cartridge removed from the  
92 furnace. These stages are all performed using a bespoke automated system (Figure 2) built using  
93 solenoid valves (PU220AR-01, Shako, Taiwan), microcontrollers (Arduino Uno and Mega, Arduino,  
94 Italy; [www.arduino.cc](http://www.arduino.cc)) and PC software written in the Processing 2 programming language  
95 ([www.processing.org](http://www.processing.org)). To maintain positive pressure within the cartridge, a further addition of  
96 nitrogen is performed manually once the cartridge has achieved room temperature. Using these  
97 procedures, we have found that the same molecular sieve cartridge can be recharged and reused for  
98 multiple samples, without any loss in performance.

99 Collection of samples and quality assurance standards on cartridges is usually undertaken by active  
100 sampling (at a flow rate of ca. 500 ml/min) using a molecular sieve CO<sub>2</sub> sampling system originally  
101 described by Hardie et al. (2005), but with the following improvements. First, all Tygon E-3603 tubing  
102 has been replaced with Iso-versinic<sup>®</sup> tubing (due to its greater rigidity and lower CO<sub>2</sub> permeability).  
103 Second, instead of calcium sulphate, we now use cartridges containing magnesium perchlorate (0.7–  
104 1.2 mm grains, Elemental Microanalysis, UK), which we believe to be superior for drying the sample  
105 gas before collection on the molecular sieve. Third, for processing quality assurance standards (CO<sub>2</sub> in  
106 sealed 6 mm OD glass tubes) a strong 750 ml glass bottle (an empty standard wine bottle cleaned  
107 using carbon-free detergent; Decon90<sup>®</sup>, Decon Laboratories Limited, UK) fitted with a rubber bung  
108 and two stainless steel sampling ports is used to provide an air-tight chamber into which the gas  
109 standards can be released. This is achieved by firstly removing atmospheric CO<sub>2</sub> from the bottle by  
110 circulating the headspace through soda lime (Hardie et al. 2005), and then by shaking the bottle to  
111 break the scored glass tube against the bottle wall, thus releasing the standard gas.

112 Recovery of CO<sub>2</sub> from molecular sieve cartridges is performed by purging (150 ml/min) the molecular  
113 sieve with high purity nitrogen while heating the cartridge inside a tube furnace, followed by cryogenic  
114 collection. The method is similar to that described by Garnett and Murray (2013), except for the  
115 following changes. First, prior to heating, the cartridge is connected to the vacuum rig and evacuated  
116 ( $1 \times 10^{-1}$  mbar) at both ends up to the clips, and then flooded with N<sub>2</sub> (Table 1). Second, the CO<sub>2</sub>  
117 concentration is no longer monitored using an infrared gas analyser during desorption, and instead,  
118 all cartridges are simply desorbed for a set time of 15 minutes. Third, cartridges are now desorbed at  
119 425°C and not 500°C as in the earlier method.

## 120 **Tests of current cartridge design and procedures**

121 The current molecular sieve cartridge and procedures were tested using ca. 3 ml (STP; standard  
122 temperature and pressure) CO<sub>2</sub> standards of known carbon isotope concentration produced from

123 reference materials (Iceland Spar Calcite (ISC), background; TIRI Barley Mash (TBM),  $116.35 \pm 0.0084$   
124 pMC; Gulliksen and Scott 1995; FIRI Belfast Cellulose (FBC),  $57.22 \pm 0.04$  pMC; Boaretto et al. 2002).  
125 The first tests were performed on freshly prepared cartridges where the charging, gas collection, and  
126 gas recovery were undertaken within one week (i.e. storage time = 0 months). To assess the cartridges  
127 after a period of storage, tests were also performed on cartridges that had been charged at least three  
128 months before being used to trap CO<sub>2</sub> standards (storage time = 3 months; i.e. the cartridges were  
129 charged, left three months, used to trap CO<sub>2</sub> standards that were then recovered within the following  
130 week). To test for sample carry-over, we ensured that some of the previous CO<sub>2</sub> stored on the  
131 molecular sieve cartridge had a <sup>14</sup>C or <sup>13</sup>C concentration that contrasted with the chosen standard. We  
132 also performed tests using CO<sub>2</sub> produced from the abovementioned standard materials with each  
133 batch of molecular sieve samples submitted for analysis. For these tests, the volume of the standard  
134 used was selected to be similar to the samples and where possible undertaken using molecular sieve  
135 cartridges that had been prepared at the same time as those used for the samples, and often had  
136 accompanied the submitter to the field site.

137 After recovery, the volume of CO<sub>2</sub> was determined using a pressure transducer and a calibrated  
138 volume, and split into aliquots. One aliquot was used for measurement of  $\delta^{13}\text{C}$  using isotope ratio  
139 mass spectrometry (Thermo-Fisher Delta V, Germany) with results expressed in per mil relative to  
140 VPDB. A second aliquot was transformed to graphite using Fe-Zn reduction (Slota et al. 1987) and  
141 analysed by accelerator mass spectrometry (AMS) at the Scottish Universities Environmental Research  
142 Centre. Following convention, <sup>14</sup>C measurements were corrected for isotopic fractionation by  
143 normalising to a  $\delta^{13}\text{C}$  of -25 ‰ using the measured  $\delta^{13}\text{C}$  values and reported as both pMC and  
144 conventional <sup>14</sup>C ages (in BP = years before AD1950; Stuiver and Polach 1977).

145

## 146 **RESULTS**

### 147 **Tests of the current cartridge design and procedures**

148 The <sup>14</sup>C concentration of the background standards (CO<sub>2</sub> derived from Iceland Spar Calcite) used to  
149 test the latest cartridge design and procedures ranged from 0.41 to 0.77 pMC and are below the long-  
150 term background for molecular sieve cartridges at the NERC Radiocarbon Facility ( $1.0 \pm 0.5$  (SD) pMC  
151 based on  $n = 15$  measurements between 2010 and 2015; Table 2). The <sup>14</sup>C results for the non-  
152 background standards were all within 1  $\sigma$  measurement uncertainty of consensus values, for both  
153 freshly-prepared and stored cartridges (Table 2). The  $\delta^{13}\text{C}$  values for all standards were also within  
154 measurement uncertainty ( $<1 \sigma$ ) of the accepted values derived from measurements of bulk gas at  
155 NERC Radiocarbon Facility (TBM  $-26.9 \pm 0.3$  ‰; FBC  $-23.7 \pm 0.3$  ‰; ISC  $2.4 \pm 0.3$  ‰).

156 The results for CO<sub>2</sub> derived from Iceland Spar Calcite showed that during 2016–2017 the <sup>14</sup>C  
157 background of the method was  $1.08 \pm 0.51$  pMC ( $n = 10$ ), which is similar to the long-term background  
158 for molecular sieve cartridges at the NERC Radiocarbon Facility ( $1.0 \pm 0.5$  pMC). During the same  
159 period a total of 14 TBM CO<sub>2</sub> and 9 FBC CO<sub>2</sub> standards were processed alongside samples. For TBM,  
160 all results except one differed from the consensus value (116.35 pMC) by  $<2 \sigma$  and the mean ( $116.13$   
161  $\pm 0.61$  SD pMC) was not significantly different ( $p=0.20$ ; 1-sample T-test, Minitab 18; Figure 3). For FBC,  
162 the mean ( $56.99 \pm 0.24$  SD pMC) was slightly lower than the consensus value (57.22 pMC;  $p=0.02$ ), but  
163 with measurement uncertainty all results overlapped with the consensus value at  $<2 \sigma$  (Figure 3).  $\delta^{13}\text{C}$

164 values for all quality assurance standards (mean  $\pm$  SD; TBM  $-26.8 \pm 0.2$  ‰; FBC  $-23.6 \pm 0.1$  ‰) agreed  
165 with accepted values.

166

## 167 **DISCUSSION**

168 The benefit of cartridges containing zeolite molecular sieve for collecting carbon dioxide samples for  
169  $^{14}\text{C}$  analysis is being increasingly recognised, with new systems having been recently reported from  
170 several other labs (Hämäläinen et al. 2010; Palonen 2015; Walker et al. 2015; Wotte et al. 2017b). At  
171 the NERC Radiocarbon Facility, development of our molecular sieve method has continued with a  
172 focus on improving the reliability of the method and quality of results, and to increase capacity and  
173 throughput to meet demand from users. The analyses performed to test our latest cartridge design  
174 and procedures demonstrate that, within the operating parameters that we currently recommend  
175 ( $\text{CO}_2$  sample volume  $>3$  ml, storage time  $< 3$  months), our molecular sieve system is reliable. From a  
176 total of 29 measurements on international  $^{14}\text{C}$  standards over two years (6 new cartridge test  
177 standards plus 23 known  $^{14}\text{C}$  content standards accompanying samples), only one provided a  $^{14}\text{C}$  value  
178 that was  $>2 \sigma$  of the consensus value. Moreover, for the 6 test standards (Table 2) the agreement of  
179  $\delta^{13}\text{C}$  values with consensus values show the absence of fractionation effects. Reliable  $^{14}\text{C}$   
180 measurements from standards of disparate  $^{14}\text{C}$  concentrations demonstrate the absence of  
181 contamination and sample carry-over effects in both newly charged cartridges and cartridges that  
182 have been in storage for 3 months.

183 The performance of our molecular sieve sampling method compares well with similar systems  
184 developed in other laboratories. Radiocarbon concentrations of our background  $^{14}\text{C}$  standards are  
185 similar to those reported by Wotte et al. (2017a), and lower than those of Walker et al. (2015;  
186 calculated by Wotte et al. 2017a). While our developments have enabled a reduction in the  
187 recommended sample size from ca. 10 ml (Hardie et al. 2005) to  $> 3$  ml for the current system, the  
188 results of Wotte et al. (2017a) suggest that a further reduction in sample size may be possible  
189 (although they acknowledge that smaller samples are vulnerable to contamination and carry-over  
190 effects).

191 We have previously demonstrated that our molecular sieve methods are reliable for stable-carbon  
192 and  $^{14}\text{C}$  measurement of  $\text{CO}_2$  (Garnett and Murray 2013). To construct more cartridges to meet higher  
193 demand from users, it has been necessary for us to source new supplies of Type 13X zeolite. Although  
194 molecular sieve traps can be reused, we had limited quantities of the BDH (British Drug Houses) 13X  
195 used in earlier cartridges (Hardie et al. 2005; Garnett and Murray 2013) and were unable to obtain  
196 new supplies. We found that the performance characteristics of new Type 13X zeolite from several  
197 suppliers differed slightly, and that they did not completely desorb all the  $\text{CO}_2$  that they had trapped  
198 when processed using the earlier reported methods (Garnett and Murray 2013), leading to significant  
199 sample carry-over (typically ca. 0.1 to 0.3 mg C). We found that we could overcome this problem when  
200 using Sigma-Aldrich Type 13X molecular sieve (used for all results presented here) by preparing the  
201 cartridges at  $500^\circ\text{C}$  but recovering the sample  $\text{CO}_2$  at a lower temperature of  $425^\circ\text{C}$ . Although this  
202 results in a slightly lower yield (by ca. 5%, presumably due to incomplete desorption at the lower  
203 temperature), it prevents significant sample carry-over and as shown in the results reported here,  
204 enables reliable  $^{14}\text{C}$  and  $^{13}\text{C}$  measurement (Table 2, Figure 3).

205 A considerable improvement to our molecular sieve method has been the construction of an  
206 automated charging rig for preparing the molecular sieve cartridges before use. This system ensures  
207 that all cartridges are prepared consistently, incorporates several different charging steps (purging  
208 with nitrogen and CO<sub>2</sub>-free air, slightly over-pressurising cartridges with nitrogen) and performs a leak  
209 test to check the integrity of the cartridges. Moreover, after a minimal set up, the rig can be left to  
210 process three cartridges with no further operator input required until the charging processes is  
211 completed. Thus, up to 9 molecular sieve cartridges can be prepared in a standard working day, with  
212 a total operator time of less than one hour. An automated rig for recovering sample CO<sub>2</sub> from  
213 molecular sieve cartridges is currently in the final phase of development and testing. This rig will be  
214 solely for CO<sub>2</sub> recovery for analysis, with used cartridges being recharged on the existing automated  
215 charging rig as required.

216 Presently, we are undertaking tests to make cartridges more robust since even though they are  
217 provided to users in protective housing (polyethylene foam pipe insulation), they occasionally break  
218 in transit. Metal cartridges offer one solution (e.g. Wotte et al. 2017b), though we have often found it  
219 useful to observe inside the cartridge to check for the presence of water (particularly when using the  
220 cartridges for passive sampling aquatic CO<sub>2</sub>; Garnett et al. 2012) or contamination. For example, on at  
221 least one occasion a carbon-rich black deposit has formed on the 13X zeolite during sample recovery,  
222 which we suspect was due to the reduction of hydrocarbons (likely present on the molecular sieve  
223 due to the sample type). Since this was a potential contaminant for future samples processed using  
224 the cartridge we incorporated the CO<sub>2</sub>-free air purge in the automated charging process (during the  
225 air-purge ca. 1 ml CO<sub>2</sub> was observed in the exhaust gases and the black deposits were removed). Other  
226 modifications currently under trial include the replacement of quartz wool in the cartridges with  
227 stainless steel wool, which reduces back pressure during sampling, and should enable the cartridges  
228 to perform more consistently during sample collection.

229 Finally, the results presented here demonstrate the reliability of our methods under currently  
230 recommended operating parameters (>3 ml CO<sub>2</sub>, and <3 months storage time), future investigations  
231 will seek to more accurately resolve the limitations of the current methods, and to find improvements  
232 that will enable reliable <sup>14</sup>C measurement of smaller sample volumes (Walker et al. 2015; Wotte et al.  
233 2017a).

234

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239

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292 **Table 1** Summary of molecular sieve charging and sample recovery procedures.

293

Procedure	Temperature (°C)	Flow rate (ml/min) / carrier gas	Time (min)	Comment
Charging	500	150 / N <sub>2</sub>	8	First flush step
	500	ca. 400 / CO <sub>2</sub> -free air	2	Combustion step
	500	150 / N <sub>2</sub>	20/>20 if required for CO <sub>2</sub> concentration to be <50 ppm	Second flush step
	Cooling to <400	150 / N <sub>2</sub>	10	Cooling flush
	Cooling <250	No flow (isolated)	20	Cooling
		150 / N <sub>2</sub>	1	Leak test and refilling cartridge with 1 bar N <sub>2</sub> . Cartridge then removed from furnace
	<25	N <sub>2</sub>	1	Refilled to 1 bar N <sub>2</sub>
Sample recovery	425	150 / N <sub>2</sub>	15	Cryogenic collection

294

295 **Table 2** Results for aliquots of CO<sub>2</sub> derived from <sup>14</sup>C standard material trapped on molecular sieve  
 296 cartridges and recovered using the latest procedures described in the text and Table 1. Consensus  
 297 values for reference materials are: ISC = Iceland Spar Calcite, background; TBM = TIRI Barley Mash,  
 298 116.35 ± 0.0084 pMC (Gulliksen and Scott 1995); FBC = FIRI Belfast Cellulose, 57.22 ± 0.04 pMC  
 299 (Boaretto et al. 2002). \*Superscripts indicate previous gas stored on the molecular sieve cartridge:  
 300 <sup>a</sup>atmospheric CO<sub>2</sub>, <sup>b</sup>TBM CO<sub>2</sub>, <sup>c</sup>ISC CO<sub>2</sub>, <sup>d</sup>FBC CO<sub>2</sub>, <sup>e</sup>unknown.

301

Publication code (SUERC-)	Source of CO <sub>2</sub> standard*	Storage time (months)	CO <sub>2</sub> recovered (ml)	Yield (%)	δ <sup>13</sup> C <sub>V</sub> PDB (‰ ± 0.3 ‰)	<sup>14</sup> C content (pMC ± 1 σ)	Conventional <sup>14</sup> C age (BP ± 1 σ)
74589	TBM <sup>a</sup>	0	3.01	95	-26.8	116.03 ± 0.54	Modern
74586	ISC <sup>b</sup>	0	2.86	90	+2.6	0.66 ± 0.01	40356 ± 138
74590	ISC <sup>a</sup>	0	3.03	92	+2.7	0.41 ± 0.01	44195 ± 150
76518	TBM <sup>c</sup>	3.4	3.18	95	-26.8	116.06 ± 0.54	Modern
76519	ISC <sup>d</sup>	3.4	2.82	90	+2.7	0.77 ± 0.01	39135 ± 131
76520	FBC <sup>e</sup>	3.4	2.93	96	-23.4	57.47 ± 0.33	4449 ± 46

302

303 **Figure captions**

304 **Figure 1** Molecular sieve cartridges used at the NERC Radiocarbon Facility (East Kilbride) for routine  
305 samples.

306 **Figure 2** a) Photograph and b) schematic of the automated rig for charging molecular sieve cartridges  
307 at the NERC Radiocarbon Facility (East Kilbride). MSC = molecular sieve cartridge. IRGA = infrared gas  
308 analyser.

309 **Figure 3** Radiocarbon concentration of known <sup>14</sup>C content quality assurance standards collected on,  
310 and recovered from, molecular sieve cartridges during 2016–2017. CO<sub>2</sub> derived from TIRI Barley Mash  
311 (TBM; top) and FIRI Belfast Cellulose (FBC; bottom). Error bars are  $\pm 1 \sigma$ . Full lines represent the  
312 international consensus value for each standard and dashed line the mean for measured standards.

313

314 Fig. 1

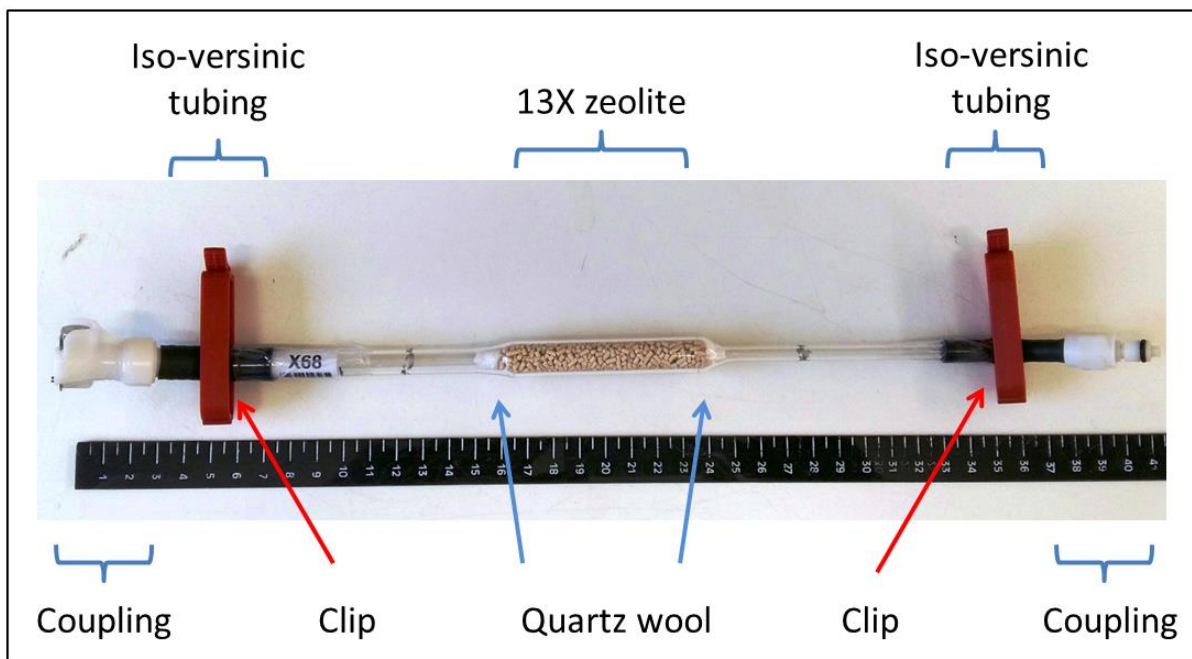
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321

322 Fig. 2

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324

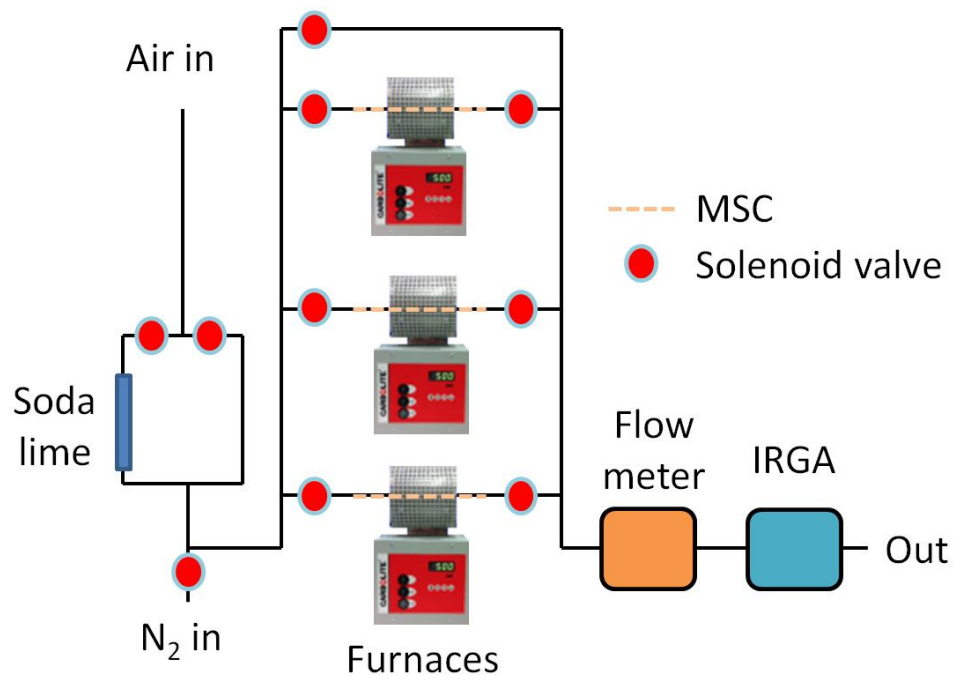
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326

a)



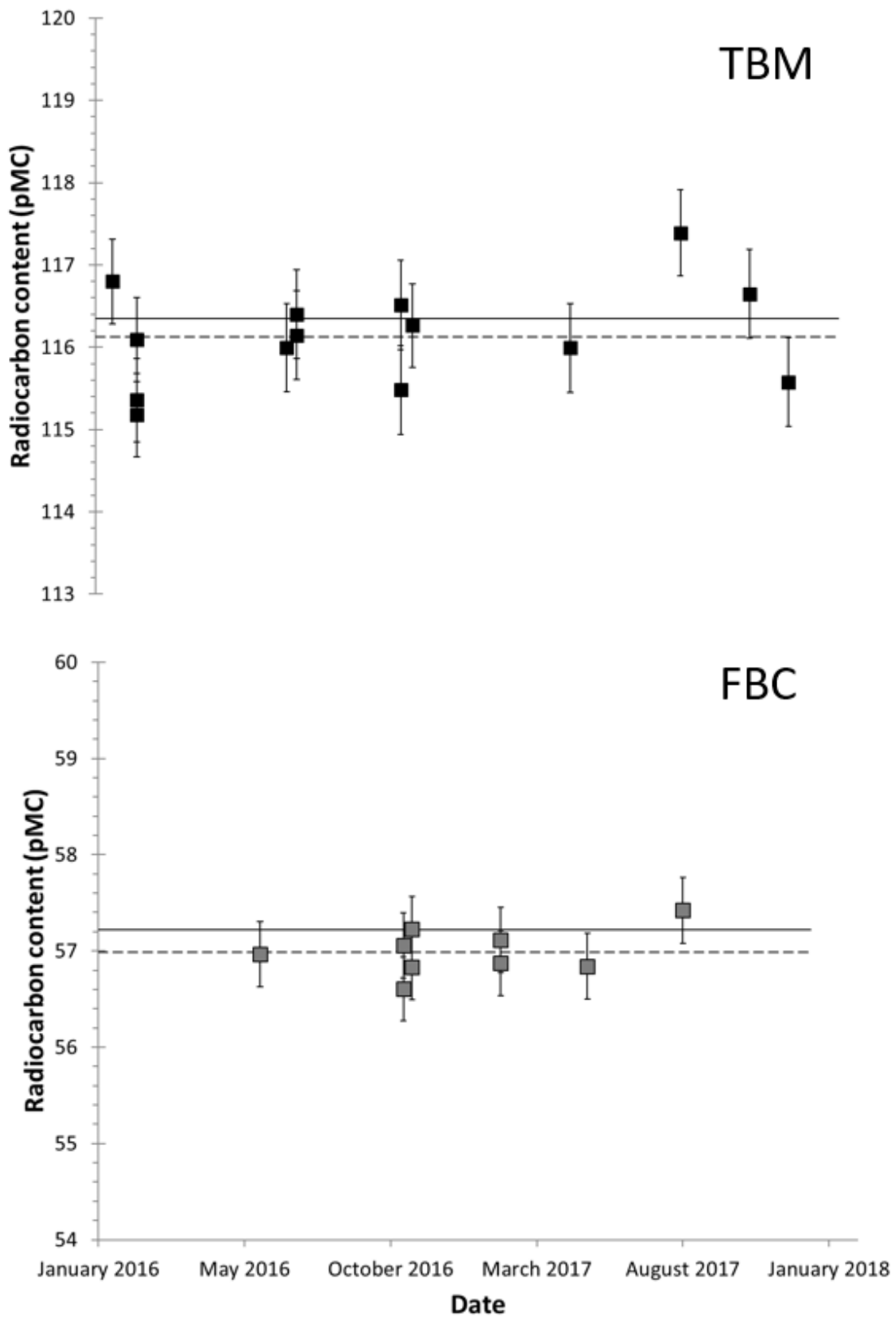
b)



327

328

329 Fig. 3



330

331