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2 Carbonate as Sputter Target Material for Rapid ^{14}C AMS
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14 1. Abstract

15 This paper describes a technique for measuring the ^{14}C content of carbonate samples by
16 producing C^- ions directly in the negative ion sputter source of an accelerator mass
17 spectrometer (AMS) system. This direct analysis of carbonate material eliminates the
18 time and expense of graphite preparation. Powdered carbonate is mixed with titanium
19 powder, loaded into a target cartridge, and compressed. Beam currents for optimally-
20 sized carbonate targets (0.09-0.15 mg C) are typically 10-20% of those produced by
21 optimally-sized graphite targets (0.5-1 mg C). Modern (>0.8 Fm) samples run by this
22 method have standard deviations of 0.009 Fm or less, and near-modern samples run as
23 unknowns agree with values from traditional hydrolysis/graphite to better than 2%.
24 Targets with as little as 0.06 mg carbonate produce useable ion currents and results, albeit
25 with increased error and larger blank. In its current state, direct sputtering is best applied
26 to problems where a large number of analyses with lower precision are required. These
27 applications could include age surveys of deep-sea corals for determination of historic
28 population dynamics, to identify samples that would benefit from high precision analysis,
29 and for growth rate studies of organisms forming carbonate skeletons.

1 1. Introduction

2 Radiocarbon provides a tool for direct dating of carbon-containing materials from
3 the last fifty thousand years and is also used in a wide range of fields to trace the rate and
4 amplitude of processes in which carbon is involved. While the details of sample
5 preparation for solid-source accelerator mass spectrometry (AMS) vary, all methods
6 oxidize samples to CO₂ and then reduce this CO₂ to graphite before analysis [1]. This
7 process is labor-intensive and introduces background contamination through sample
8 handling. These two issues impose limits on the minimum sample size and on sample
9 preparation efficiency. In this study, we investigate the feasibility of using calcium
10 carbonate as a direct carbon source for AMS in order to eliminate some of the problems
11 associated with traditional sample preparation. This method could change the way that
12 carbonate radiocarbon analyses are used in ocean and earth sciences.

13 In the past, most projects have had to select a small subset of samples for AMS
14 analysis due to prohibitively high per-analysis costs. The cost and labor savings with a
15 faster and less expensive method could lead to a new, multi-sample, “survey-mode”
16 analysis strategy. For example, several cruises have collected thousands of fossil deep-
17 sea corals from the North Atlantic and Southern Oceans [2,3], but dating all of these
18 samples to examine the temporal population dynamics, or even to identify samples
19 suitable for paleoclimate studies can be costly and time consuming using either the decay
20 of uranium to thorium, or graphite ¹⁴C hydrolysis methods. Applied to fossil deep-sea
21 corals, rapid, inexpensive analysis of hundreds of samples would add new insights into
22 our understanding of coral population dynamics and their past bio-geography. “Survey-

23 mode” analysis could also be beneficial to studies that seek to produce first-pass
24 chronologies of sediment cores or to survey the age of core-top sediments.
25 A second potential advantage to a direct sputter method is a reduction in required sample
26 mass. At the moment AMS labs typically request samples containing roughly 10 mg of
27 carbonate to make an analysis. Traditional small- or ultra-small sample AMS can
28 analyze graphite targets containing 25 to 100 $\mu\text{g C}$ or 2 to 25 $\mu\text{g C}$, respectively, both at
29 reduced accuracy and precision [4-6]. Assuming 100% yield from a carbonate sample,
30 this would require 16 to 833 μg of carbonate. Reducing the minimum sample size for
31 routine analysis would allow higher resolution studies of continuous records of the
32 history of radiocarbon (e.g. speleothems or coral samples) and may also open up new
33 areas of study, for example dating of single foraminifera in marine sediment cores (figure
34 1b). Dating multiple single foraminifera would put direct constraints on age biases and
35 produce new insights into the rates and depths of smoothing by bioturbation.

36 Carbon ions for traditional solid-source AMS are produced by sputtering a
37 mixture of graphite and iron with Cs^+ ions. Ions including C^- are produced and extracted
38 using an electrical potential [7]. Negative ions may also be produced by a Cs sputter
39 source from CO_2 gas introduced onto and retained on a titanium frit at the sputtering
40 location [8,9]. Performance of these hybrid gas ion sources is related to the gettering
41 potential of the metal used for the sputtering surface [10], and the shape of this surface
42 [11,12]. These gas ion sources are assumed to work by adsorption of CO_2 onto the
43 titanium surface followed by breakup and ionization caused by sputtering by the Cs^+
44 beam [13].

45 2. Methods

46 Targets for carbonate sputtering were made by mixing carbonate powder with a
47 metal powder (usually titanium) and loading this mixture into a pre-drilled hole in a front
48 loaded aluminum cartridge. Samples were compressed in the cartridge using a hammer
49 and steel pin. Additional titanium was added on top of samples and again compressed to
50 form a porous sputtering surface. We refer to this additional titanium as a “cap” or a
51 “frit” throughout the paper.

52 2.1. Carbonate samples

53 For developing and testing the carbonate sputtering method, we used a range of
54 carbonate-containing materials (table I). These samples were chosen to span a wide range
55 of Fm, from radiocarbon-dead to -modern. All sample types have been analyzed via AMS
56 using the traditional hydrolysis-graphite technique [14], and several are well quantified as
57 common secondary standards for AMS. Several samples come from a suite of deep-sea
58 corals that have been dated using traditional hydrolysis, combustion via an elemental
59 analyzer [3] and also direct analysis of CO₂ produced by hydrolysis in phosphoric acid
60 *via* a gas ion source [15]. Using these samples has provided an immediate comparison of
61 the accuracy, quality and cost of the direct sputtering method compared to the standard
62 hydrolysis graphite technique as well as allowing comparison with several alternate
63 techniques currently in development.

64 In keeping with rapid, low-cost analysis, the sample preparation was kept as
65 simple as possible. Corals were cut, physically cleaned, and then rinsed with methanol to
66 remove possible organic contamination, while mineral carbonate samples were left

67 untreated. Samples were then ground to a coarse powder (approximately 100 mesh) with
68 a small agate mortar and pestle.

69 2.2. Catalyst / getter powders

70 Initial tests determined that carbonate targets require metal powder mixed with
71 the carbonate sample to produce appreciable currents. Titanium and iron powders in
72 different grain sizes (100 and 325 mesh) were tested. We also measured performance of
73 targets with and without a 0.5 mg titanium “cap” or “frit” (as discussed earlier) added to
74 the front surface of the target. All metal powders were cleaned and activated before
75 preparing each batch of samples by baking in vacuum at 800°C for 4 hours.

76 2.3. Target preparation

77 Three methods were investigated for the weighing, mixing, and pressing of
78 samples into targets. Initially, carbonate and metal powders were weighed into a 6mm x
79 40 mm Pyrex test tube and then combined using a vortex mixer before transferring the
80 mixture to a pre-drilled sputter target. We later found that the sample could be transferred
81 more completely by weighing carbonate and metal powder onto a square of weigh paper,
82 mixing the sample by doubling the paper and rolling the paper to mix the sample in the
83 resulting trough. The sample was then transferred to a weighed target cartridge, allowing
84 a titanium powder “cap” to be weighed directly on top of the sample. Finally, to allow
85 more effective weighing and eliminate transfer losses with extremely small samples, we
86 tried weighing metal powder, carbonate and cap directly into target cartridges. After
87 weighing and transfer to target cartridges, the samples were compressed to a pellet in the

88 cartridge using a hammer and drill blank and loaded into a sample carousel with graphite
89 standards and machine blanks.

90 2.4. Sample measurement

91 Samples were analyzed using the compact AMS system at NOSAMS [15]. The
92 ion source was a 134 sample MC-SNICS (NEC) which has been modified for improved
93 performance and better vacuum pumping conductance [16, 17]. Carbonate samples were
94 measured in the same manner as graphite samples. Five to ten measurements were made
95 for each sample. Each measurement continued for three minutes or until 30,000 ^{14}C
96 atoms were counted. Carbon ion beam production from targets is measured as $^{12}\text{C}^-$ ion
97 current at the offset low energy Faraday cup after the 90° injector magnet, and these
98 values are given as beam current averaged over all measurements of a target, unless
99 otherwise specified. The data were normalized to graphite NIST OX-I or OX-II targets
100 following the methods of Stuiver and Polach [18] and represented as Fm. Standards were
101 used at the rate of one standard to every 5 carbonate unknowns. Fm is defined as the ratio
102 of the activity of a sample to the activity of an OX-I standard, both normalized for mass
103 dependent fractionation using the $\delta^{13}\text{C}$ of the sample being analyzed. Raw and corrected
104 ratios for carbonate targets indicate that this correction does account for most of the
105 fractionation inherent in the new method. While normalizing carbonate using graphite
106 OX-I standards worked well for determining the performance of targets and quality of
107 data relative to graphite during method development, we intend to develop carbonate
108 normalizing standards for future work.

109 3. Results / Discussion

110 3.1. Method refinement

111 Initial investigations of carbonate sputtering focused on determining whether
112 repeatable measurements could be made and on increasing the ion current produced by
113 carbonate targets. Increases in ion current are correlated to better precision and accuracy
114 of measurement (figure 2). While this relationship is expected due to reduced numbers of
115 counts for low-current samples, variance and bias beyond that predicted by counting or
116 internal error within runs of a sample is apparent at all currents. The extra variance in
117 ratios is possibly due to a combination of heterogeneity in the samples, variability in the
118 amount and composition of the blank, or variability introduced in sample preparation and
119 pressing. We have not fully investigated the source of this variability and the increased
120 variability at low currents, but will do so in future work.

121 As described in the methods section, the first parameter tested was the presence
122 and type of metal powder mixed with the samples. These tests showed that carbonate
123 samples without metal powder produced unusably low currents ($<0.4 \mu\text{A}$), and that
124 samples with titanium powder produced 6 times more current than samples mixed with
125 iron. This agrees with data from Middleton et al. [8] which shows that performance of an
126 early hybrid solid-gas negative-ion Cs-sputter source was directly related to the gettering
127 potential of the metal frit used as a sputtering substrate, and that titanium was the best
128 material. We suspected that the grain size of carbonate and metal powders controls
129 reaction rates via available surface area and/or controls the movement of gaseous reaction
130 products by the size of interstitial spaces in the target. However, tests of different

131 titanium powders determined that the coarser 100 mesh powder produced the same ion
132 yields as 325 mesh powder within measurement error.

133 Subsequent tests examined the effect of target size and ratio of carbonate to
134 titanium powder. The best ion currents and precision were obtained with 0.5-1.5 mg
135 carbonate powder and ratios of carbonate to titanium from 0.75:1 to 1.5:1 by mass (figure
136 3). Adding a titanium “cap” to the sample to act as a sputtering surface improved ion
137 current and measurement precision in some cases. In keeping with the idea of hybrid gas
138 ion source as an analogue for the carbonate sputtering process, the titanium cap may
139 provide more reactive surface area and increase the production efficiency of C^- from CO_2 .

140 3.2. Performance of carbonate targets

141 We tested the ion production over time and ionization efficiency of carbonate
142 sputtering by running samples to extinction. Compared with graphite targets, current
143 from carbonate samples rises much more slowly, taking roughly 10 min. to reach full
144 output (figure 4). After an initial warm up (~1-2 min.), relatively stable $^{14/12}C$ ratios are
145 maintained until the ion current drops sharply as the target is exhausted. We measured
146 ionization efficiency by comparing the number of ^{12}C atoms in the sample to the number
147 of $^{12}C^+$ ions reaching the final Faraday cup during the period of stable ratios. After
148 correcting for the transmission efficiency of the accelerator and beam transport
149 (previously estimated at 41% and 98%, respectively), we estimate the efficiency of ion
150 extraction as 8%, compared to 25% for graphite samples tested under similar conditions
151 [16].

152 A low-energy magnet scan shows the range of negative ions produced by
153 carbonate samples as compared to graphite. We increased the magnet field from 3 kG to

154 8.5 kG while measuring currents at the off-axis Faraday cup at the accelerator entrance
155 (figure 5). The most notable differences of carbonate samples relative to graphite are
156 reduced $^{12}\text{C}^-$ production, a large $^{16}\text{O}^-$ beam, lack of $^{12}\text{C}_2^-$, and presence of a peak possibly
157 corresponding to CaH_3^- . We examined targets with an optical microscope before and after
158 exposure. After a typical ~30 min. run, targets were partially eroded with mottled grey
159 and black deposits. Titanium “capped” samples did not typically appear to have been
160 sputtered through the cap.

161 The carbonate sputtering method currently has an important drawback. Depending
162 on running conditions, a coating forms on surfaces in the ion source which limits the
163 number of carbonate sample which may be run before the source must be serviced. We
164 have not found reports of similar problems with titanium frit hybrid gas ion sources built
165 around similar sputtering geometry. We hope the problem can be solved by reducing
166 erosion of the titanium front surface of the target during sputtering by replacing the
167 powdered titanium “cap” with a pre-formed frit or solid titanium disk with channels to
168 allow gas transfer to the target surface.

169 3.3. Measurement quality

170 To assess carbonate sputtering as a measurement technique, we chose a subset of
171 data meeting the following criteria: 0.4-1.5 mg carbonate mixed with titanium, having a
172 titanium powder “cap” and producing more than 6 μA of $^{12}\text{C}^-$ current. Except as noted,
173 the following sections all use this selected dataset. Where means are compared, we used
174 Welch’s two-sample t-test assuming unequal variances, with results reported as “t(N) =
175 T, p = p”, where N is the degrees of freedom, T is the T statistic, and p is the probability
176 that the null hypothesis (means are equal) is false.

177 3.3.1. Blank correction

178 Radiocarbon-dead carbonates run by the carbonate sputtering method show that
179 there is a significant contaminant blank present in this method and that this blank is larger
180 than that of the same samples measured as graphite (Figure 6). The blank has a number of
181 potential sources, including the titanium powder, atmospheric CO₂ adsorbed into the
182 carbonate, and carbon contaminant in the carbonate powders. Tests of targets containing
183 only titanium powder produce ¹²C⁻ ion currents of 0.35 μA (SD = 0.26 μA, n = 11),
184 which is 2% of the mean current of carbonate targets but higher than currents from
185 aluminum or iron. The elevated current from titanium could be due to adsorption of CO₂
186 from air. Comparison of Carrera marble (C1) and a radiocarbon-dead coral (zap-04) show
187 a much larger blank in the coral, similar to the results of Eltgroth et al [19], which used
188 the same coral in a study using graphite. This variable blank complicates the application
189 of a single blank correction based on radiocarbon dead mineral with a low blank because
190 blank corrections must assume that blank is added equally to unknowns and to the
191 standards used in blank correction.

192 We tested two methods for evaluating and correcting the contaminant blank in
193 carbonate samples. The first method compares Fm values from carbonate sputtering to
194 Fm of (previously) blank-corrected data from the same sample suite run as graphite and
195 uses the linear Fm dependence of this shift to extract the mass and Fm of a blank
196 contribution common to any sample being sputtered as carbonate. The Fm dependence of
197 the shift in Fm error can be seen in Fig. 7a. The negative slope implies a blank addition
198 which adds positive bias at low Fm. When samples have the same Fm as the blank, there
199 should be no bias, assuming no bias inherent in the method. Based on these observations,

200 the size of the blank is related to the slope of the regression, and the Fm of the blank
201 should be the intercept with the x-axis. This method estimates the mass of the blank as
202 0.6 $\mu\text{g C}$ (SD = 0.3), with a Fm of 1.30 (SD = 0.8). This method is derived from Bland
203 and Altman's work [20] showing the bias of a new method by showing the difference in
204 methods being compared as a function of the dependent variable.

205 The second blank correction method is a simple mass balance method using
206 measurements of radiocarbon-dead samples to establish the blank [14]. If the contaminant
207 blank is assumed to be modern and present in all samples equally and all samples are
208 similar in mass, the average Fm of the dead carbonate may be subtracted from unknowns
209 and then scaled such that the full blank is subtracted from dead samples, giving them a
210 corrected Fm of 0, and nothing is subtracted from modern samples, giving them an Fm of
211 1 (equation 1).

$$212 \quad (1) \text{ Fm}_c = (\text{Fm}_u - \text{Fm}_b) / (1 - \text{Fm}_b)$$

213 Carbonate data corrected using this method are shown in figure 7b. We chose to use this
214 method for our estimates of the precision and accuracy of carbonate sputtering because it
215 may be easily applied to any suite of unknowns, so long as dead carbonate blanks are
216 included with the samples, while the regression-based method requires a minimum of two
217 standards of differing Fm.

218 3.3.2. Precision and accuracy

219 Precision and accuracy of the method were assessed using data from a suite of
220 corals and carbonate standards, selected as described previously. We examined these data
221 before and after applying blank corrections using the second method discussed above.
222 Number of samples, weighted mean and standard deviation for each sample type are

223 listed in table I, before and after applying the blank correction, and in comparison with
224 the same sample types analyzed as graphite at NOSAMS. In general, carbonate sputtering
225 is less precise than the hydrolysis method. Standard deviations by sample type for
226 corrected data range from 0.0020 Fm for C1 to 0.0094 Fm for the zap-01 coral. The range
227 of deviations for samples run as graphite was 0.0008 Fm for C1 to 0.0087 for zap-01.
228 Standard deviation for the UCI coral standard (CSTD) was 0.0007 when run as
229 carbonate, but this is likely not a reliable statistic. No carbonate sample from this dataset
230 deviated by more than 0.018 Fm from the mean of samples run as graphite.

231 Examining the distribution of individual sample types provides further insight into
232 the behavior of carbonate sputtering with differing sample composition. Certain sample
233 types (zap-02, zap-04, C2) group with samples of the same type, but have a positive bias
234 relative to graphite. This result implies that all samples do not share a single blank
235 addition of set mass and Fm, or that sample composition affects the sputtering process.
236 The additional blank present in these sample types may be due to organic contamination
237 which is removed by traditional cleaning and hydrolysis, but which remains in the sample
238 and contributes carbon during sputtering of the carbonate. This effect may be mitigated
239 by better cleaning procedures prior to target preparation, or could be controlled for by
240 careful assessment of the organic material present in a suite of samples.

241 Any systematic bias with the carbonate method is made apparent by examining
242 difference of samples when run as carbonate and graphite as a function of Fm. The slope
243 of a linear regression through these data shows bias related to Fm, while the y-intercept is
244 related to constant bias for all samples. Figure 7 shows that there is little overall bias to
245 the method, and the blank correction accounts for all of the proportional bias and much of

246 the constant bias. Before blank correction, the weighted mean difference of all selected
247 data from values when run as graphite is 0.005 Fm (SD = 0.007, n = 38). After blank
248 correction, this mean decreased to 0.002 Fm (SD = 0.006, n = 38), not significantly
249 different from zero constant bias (one-sample $t(37) = 1.9$, $p = 0.07$).

250 We compared agreement of carbonate data with graphite data for each sample
251 type using a two-sample t-test assuming unequal variances as an estimate of agreement
252 between the hydrolysis-graphite and carbonate sputtering methods. With the exception of
253 the zap-02 coral (two-sample $t = 3.5$, $p = 0.01$), the means of samples run using the direct
254 carbonate sputtering method did not differ significantly (p values > 0.05 , see table 2)
255 from means of the same sample type when analyzed as graphite.

256 Observed scatter between samples of a type is often larger than within-sample
257 measurement error. This can be accounted for by heterogeneity in sample composition;
258 since samples are mixtures of powders, performance may be affected by distribution and
259 size of Ti and carbonate grains within the sample. This is seen to a lesser extent with
260 graphite targets. Estimates of the precision of an individual measurement will only be a
261 predictor of repeatability across multiple samples of the same material if samples and
262 preparation are perfectly homogenous.

263 3.4. Small Samples

264 It is worth noting that optimally-sized carbonate targets (750 μg carbonate or 90
265 μg C) are within the realm of small-sample AMS run at NOSAMS and elsewhere.
266 Preliminary tests of the performance of ultra-small carbonate samples showed promising
267 results. Samples containing as little as 60 μg carbonate (7 μg C) produced better than 4
268 μA of $^{12}\text{C}^-$ current. The currents from samples containing 7-15 μg C were also relatively

269 stable over the course of 10 runs lasting 3 minutes each, starting at a mean current of 6
270 μA rising to a mean peak current of 10 μA before falling to a mean final current of 5 μA .
271 These smallest samples tested had increased internal error due to reduced count rates and
272 increased between-sample error possibly due to variability of blank contribution or
273 increased effect of any heterogeneity of the source materials. Coral standard samples in
274 this size range had a mean F_m of 0.9267 and SD of 0.0109 ($n = 3$), and a two-sample t-
275 test shows that the mean small sample F_m is in agreement with the mean for this standard
276 run as graphite ($t(2) = 2.3$, $p = 0.14$). Two small C1 samples show that blank is elevated
277 for extremely small samples ($F_m = 0.0549$, compared to 0.0075 for large carbonate
278 C1's).

279 4. Conclusion

280 We developed a method for the rapid analysis of carbonate samples via AMS by
281 producing carbon ions directly from carbonate in a cesium sputter source. The best results
282 were obtained from 0.4-1.5 mg carbonate powder mixed with 0.5-2.5 mg titanium
283 powder and with an additional 0.5 mg titanium powder "cap" at the front of the target.
284 Samples with this composition generally produced 10-20% of the current of optimally
285 sized (0.5-1.0 mg) graphite targets. Disregarding samples with low current, modern (>0.8
286 F_m) samples have a between sample standard deviation of 0.009 F_m or less. Means of
287 sample types tested are not significantly different than means when samples are run as
288 graphite, with the exception of one sample type. Given the potential for sample
289 dependent bias, limited number of samples in this study, and ongoing development of the
290 method, we conservatively estimate that near-modern samples run using the carbonate
291 sputtering method should agree with values from traditional analysis to within 2%. The

292 technique also holds promise for ultra-small carbonate samples, producing current from
293 samples containing as little as 7 μg C.

1 5. Acknowledgements

2 The authors would like to thank Lloyd Keigwin for initial discussion leading to
3 this project, Joshua Burton for preparing initial tests, Maureen Auro for sample
4 preparation, and the staff of NOSAMS. This work was funded by a WHOI Mellon
5 Interdisciplinary award, NSF NOSAMS cooperative agreement, and NSF OPP #s
6 0944474 and 0902957.

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1 7. Tables

2 Table I. Summary statistics for sample types used in this study.

3
4

Sample type	Description	Graphite			Carbonate				
		n	Fm	sd	Uncorrected			Blank corrected	
					n	Fm	sd	Fm	sd
CSTD	UCI coral standard	29	0.9413	0.0024	3	0.9421	0.0007	0.9418	0.0007
zap-01	Deepwater coral	12	0.8816	0.0087	8	0.8782	0.0094	0.8775	0.0095
C2	C2 travertine	29	0.4116	0.0027	3	0.4212	0.0034	0.4180	0.0034
zap-02	Deepwater coral	4	0.2000	0.0031	5	0.2156	0.0062	0.2112	0.0062
zap-03	Deepwater coral	2	0.1535	0.0030	4	0.1640	0.0032	0.1594	0.0032
C1	C1 marble	44	0.0025	0.0008	11	0.0055	0.0020		
zap-04	Deepwater coral	5	0.0038	0.0017	4	0.0165	0.0030		

5

6 Table II. Summary of two-sample t-tests for agreement of mean Fm between sample
7 types analyzed as graphite or carbonate.

Sample type	Description	Degrees of freedom	t-statistic	p
CSTD	UCI coral standard	8	0.5	0.65
zap-01	Deepwater coral	14	1.0	0.35
C2	C2 travertine	2	3.0	0.08
zap-02	Deepwater coral	6	3.5	0.01
zap-03	Deepwater coral	2	2.2	0.14

8

1 8. Figure captions

2

3 Figure 1. (a) Stylasterid coral from West Antarctic Peninsula showing numbered samples
4 for traditional methods that required 4-12 mg of carbonate. Direct sputtering methods
5 may allow dating of individual bands that are highlighted by dotted lines. (b)
6 Foraminiferal tests weighing ~20 µg each.

7

8 Figure 2. The relationship of ion current to sample Fm precision and accuracy. The y-axis
9 is the difference of carbonate samples from accepted values for graphite targets
10 producing ~100 µA of $^{12}\text{C}^-$ current, with a value of zero indicating perfect agreement.

11 Triangles and circles are samples with and without a Ti powder “cap,” respectively. Error
12 bars show the greater of error due to counting statistics or one standard deviation of all
13 runs of a target. Lines indicate expected counting error for Fm 0.8 at these currents.

14 Figure 3. Current produced by carbonate targets compared to (a) the mass of carbonate
15 powder used and (b) the ratio of carbonate to Ti powder by mass. Currents are
16 normalized to current from graphite samples for each run to eliminate differences in
17 AMS system performance between runs. Triangles and circles are samples with and
18 without a Ti powder “cap,” respectively.

19 Figure 4. Performance of a carbonate target over time. Circles indicate average $^{12}\text{C}^-$
20 current for each 210 s measurement of a single carbonate target. Squares are raw $^{14}/^{12}\text{C}$
21 ratio for these measurements, with errors due to counting statistics indicated by error
22 bars. The horizontal line indicates the mean of all measurements.

23

24 Figure 5. Mass scans of graphite (a) and carbonate (b) targets, produced by measuring ion
25 current at the offset Faraday cup while increasing magnet current.

26

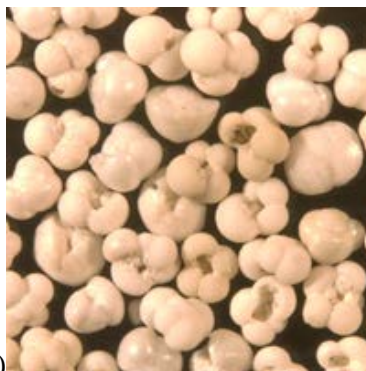
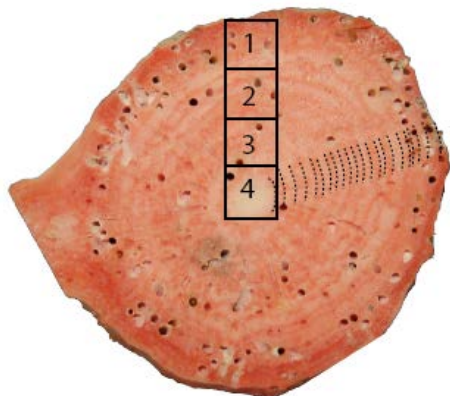
27 Figure 6. Comparison of blank carbon for carbonate sputtering and hydrolysis-graphite,
28 grouped by sample type. Boxes and whiskers represent the distribution of the data where
29 the central line is the median, edges of the box are the 1st and 3rd quartiles, whiskers are
30 1.5 times the inner quartile range, and lone points are outliers. C1 is radiocarbon-dead
31 carrera marble representing 11 and 44 measurements of carbonate and graphite,
32 respectively, and zap-04 is a radiocarbon-dead deep-sea coral with 4 measurements as
33 carbonate and 5 as graphite.

34

35 Figure 7. (a) Difference of carbonate samples from accepted values for graphite vs
36 carbonate Fm. Error bars show the greater of error due to counting statistics or one
37 standard deviation of all runs of a target. The grey line with negative slope is a linear fit
38 to the data, and the horizontal line is the mean of all data. The same data with a blank
39 correction applied as described in the text are shown in (b). The horizontal grey lines
40 represent the weighted mean and one weighted standard deviation of these data.

1 9. Figures

2



3 a)

b)

4

5 1.

6

7 Remaining Figures submitted as EPS or PDF files

