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COMPARING DIRECT CARBONATE and STANDARD GRAPHITE 14C DETERMINATIONS of BIOGENIC CARBONATES

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1 **Comparing direct carbonate and standard graphite  $^{14}\text{C}$  determinations from an assortment**  
2 **of biogenic carbonates**

3  
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## 47 ABSTRACT

48

49 The direct carbonate procedure for AMS  $^{14}\text{C}$  dating of sub-milligram samples of biogenic  
50 carbonate without graphitization is becoming widely used in a variety of studies. We compare  
51 the results of 153 paired direct carbonate and standard graphite  $^{14}\text{C}$  determinations on single  
52 specimens of an assortment of biogenic carbonates. An RMA regression shows a strong  
53 relationship between direct carbonate and graphite percent Modern Carbon (pMC) values ( $m =$   
54  $0.996$ ; 95% CI (0.991 to 1.001)). An analysis of differences and a 95% confidence interval using  
55  $\pm 1\sigma$  analytical errors on pMC reveals that there is no significant difference between direct  
56 carbonate and graphite pMC values for 76% of analyzed specimens, although variation in direct  
57 carbonate pMC is underestimated. Offset between the two methods is typically within 2 pMC,  
58 with 61% of the differences being positive. Of the 36 samples that did yield significant  
59 differences, all but three missed the 95% significance threshold by 1.2 pMC or less. The  
60 statistical disagreement in younger samples is driven by low analytical error, not increased  
61 variability or bias. Direct carbonate  $^{14}\text{C}$  dating of biogenic carbonates is a cost-effective and  
62 efficient complement to standard graphite  $^{14}\text{C}$  dating.

63

## 64 INTRODUCTION

65

66 An increasing variety of scientific investigations require a large number of radiocarbon analyses  
67 to address their underlying research questions, as exemplified by recent studies assessing the  
68 degree of time-averaging in natural or anthropological shelly accumulations (Kowalewski et al.,

69 2018; New et al., 2019, Parker et al., 2019; Albano et al., 2020). These studies are generally  
70 constrained by their analytical budget rather than by the number of samples suitable for analysis,  
71 whereas some are limited by the size of the targeted specimens. This is true for a variety of  
72 sample types, including those based on biogenic carbonate. The traditional graphite AMS  $^{14}\text{C}$   
73 technique requires 8 to 10 mg of carbonate, which excludes dating individual small bivalve  
74 shells, for example. In response to this growing need, a direct carbonate AMS  $^{14}\text{C}$  sputter  
75 method was developed by Longworth et al. (2013) that allows sub-milligram samples of  
76 carbonate powder to be analyzed quickly and efficiently. Several publications have highlighted  
77 the utility of direct carbonate  $^{14}\text{C}$  dating where it has been used on its own or in combination  
78 with amino acid racemization to determine time-averaging in taphonomic studies (Dominguez et  
79 al., 2016; Kosnik et al., 2017; Ritter et al., 2017; Parker et al., 2019; Albano et al., 2020) or  
80 coupled with standard precision  $^{14}\text{C}$  and uranium/thorium dating to determine coral age  
81 distributions (Grothe et al., 2016).

82  
83 The direct carbonate AMS  $^{14}\text{C}$  technique uses a cesium sputter source and a metal powder as a  
84 catalyst without the need to convert the carbonate sample to graphite, but yields beam currents  
85 about an order of magnitude lower than the graphite method (Bush et al., 2013; Hua et al., 2019)  
86 which leads to the lower precision. Longworth et al. (2013) analyzed several materials with  
87 percent modern carbon (pMC) between 0.25 and 94.21. Using titanium powder, the method  
88 produced  $1\sigma$  errors that ranged from 0.07 and 0.94 pMC, whereas  $1\sigma$  errors on the same  
89 materials ranged from 0.08 and 0.87 pMC using graphite. Bush et al. (2013) analyzed numerous  
90 coral samples containing 0.10 to 89.06 pMC. Using iron powder, the method produced  $1\sigma$  errors  
91 that ranged from 0.31 and 0.62 pMC, whereas  $1\sigma$  errors on the same materials ranged from 0.03

92 and 0.11 pMC using graphite. Subsequent study by Hua et al. (2019) further established the  
93 utility of the direct carbonate technique, testing iron (Fe), niobium (Nb), and silver (Ag) powders  
94 before concluding that niobium powder was superior because it produced the highest beam  
95 current and lowest background. Smith et al. (2010) showed a strong positive relationship  
96 between carbon/Fe ( $\mu\text{g}/\text{mg}$ ) and beam currents ( $R^2 = 0.84$ ). If the amount of carbonate powder  
97 and Nb or Fe powder in a target are the same, then the number of Nb ion present is about 60%  
98 that of Fe. Therefore, the carbon/metal ion ratio is higher when using Nb, which may explain the  
99 higher beam currents of direct carbonate  $^{14}\text{C}$  determinations that use Nb powder.

100  
101 Several studies have compared small numbers of paired direct carbonate and graphite  $^{14}\text{C}$  results,  
102 showing that the two methods are comparable (Bush et al., 2013; Kosnik et al., 2017;  
103 Kowalewski et al., 2018; Hua et al., 2019, New et al., 2019; Albano et al., 2020). In this paper,  
104 we have compiled a comprehensive dataset ( $n = 153$ ) of published and unpublished direct  
105 carbonate and graphite  $^{14}\text{C}$  determinations from biogenic carbonates belonging to several  
106 taxonomic groups (mollusks, corals, echinoderms, brachiopods) to further quantify any bias in  
107 the results based on the direct carbonate method.

108

## 109 MATERIALS AND METHODS

110

111 The carbonates featured in this study are all biogenic, as opposed to inorganically precipitated  
112 carbonate (e.g., limestone, speleothems). Samples comprise primarily aragonitic valves from the  
113 clams *Arctica islandica* (Linnaeus, 1767), *Chamelea gallina* (Linnaeus, 1758), *Codakia*  
114 *orbicularis* (Linnaeus, 1758), *Corbula gibba* (Olivi, 1792), *Dosinia caerulea* (Reeve, 1850),

115 *Mactra isabelleana* d'Orbigny, 1846, *Mulinia edulis* (King, 1832), *Tawera spissa* (Deshayes,  
116 1835), *Tucetona pectinata* (Gmelin, 1791), from open nomenclature species of the clams  
117 *Timoclea* and *Transennella*, from shells of the terrestrial snails *Actinella nitidiuscula* (Sowerby,  
118 1824) and *Polygyra septemvolva* Say, 1818, and from skeletal material of unidentified corals. As  
119 for the calcite polymorph, samples include valves from the brachiopod *Gryphus vitreus* (Born,  
120 1778) and plates from the sand dollars *Peronella peronii* (Agassiz, 1841) and *Leodia*  
121 *sexiesperforata* (Leske, 1778). Several samples are shells that contain a mixture of aragonite and  
122 calcite polymorphs. These are the gastropods (limpets) *Fissurella maxima* Sowerby, 1834 and  
123 *Patella candei* d'Orbigny 1840, the mussel *Choromytilus chorus* (Molina, 1782), the cockle  
124 *Fulvia tenuicostata* (Lamarck, 1819), the scallop *Argopecten purpuratus* (Lamarck, 1819), and  
125 an open nomenclature species of the mussel *Modiolus*. References pertaining to the  
126 mineralogical composition of the biogenic material used in this study are provided in the  
127 Supplemental Information.

128  
129 Ninety-three paired carbonate samples were processed at Northern Arizona University's (NAU)  
130 Amino Acid Geochronology Lab (AAGL) and NAU's Center for Ecosystem Science and Society  
131 (EcoSS) between 2015 and 2019. Most of the samples processed at NAU have been previously  
132 published (Kosnik et al., 2017; Oakley et al., 2017; Ritter et al., 2017; Kowalewski et al., 2018;  
133 Albano et al., 2020) and are detailed in the Supplemental Information.

134  
135 Sample preparation at NAU followed protocols modified from Bush et al. (2013). Blanks,  
136 standards, and unknowns were sonicated in deionized distilled water (DDI water; 16.7  
137 Mohm\*cm), rinsed three times with DDI water, leached with 2N ACS grade hydrochloric acid,



138 and then finally rinsed three times with DDI to remove surface contaminants before being dried  
139 in a 50° C oven overnight. Samples for direct carbonate <sup>14</sup>C analysis were ground to a fine  
140 powder using an agate mortar and pestle and manually mixed with 6.0 to 7.0 mg of metal powder  
141 in pre-baked (3 hr at 500° C) Kimble borosilicate glass culture tubes (6 mm OD x 50 mm).  
142 Samples processed at NAU before June 2018 were mixed with Fe powder (Alfa Aesar, -325  
143 mesh, reduced, 98%) whereas samples processed after June 2018 were mixed with Nb powder  
144 (Alfa Aesar Puratronic, -325 mesh, 99.99%), following a change from Fe to Nb powders at the  
145 Keck Carbon Cycle AMS facility at the University of California , Irvine (UCI) in 2018.  
146 Powdered carbonate sample masses ranged between 0.30 and 0.50 mg, which equates to 36 to 60  
147 µg of carbon, respectively. The culture tubes were flushed with N<sub>2</sub> gas to reduce contamination  
148 from atmospheric carbon and capped with Supelco plastic column caps (1/4" OD) until the  
149 carbonate-metal powder mixture was pressed into targets.

150  
151 Samples processed at NAU for standard graphite AMS <sup>14</sup>C analysis were graphitized at NAU's  
152 Ecosystem lab following UCI protocols ([sites.uci.edu/keckams/protocols](http://sites.uci.edu/keckams/protocols)). An aliquot of 7 to 8 mg of  
153 carbonate was placed in 13 x 75 mm BD Vacutainer plastic collection tubes and sealed with a  
154 red/grey conventional stopper closure. Ambient atmosphere was removed via vacuum before a  
155 small-bore needle was used to dispense 8 ml of ACS grade 85% phosphoric acid into each tube.  
156 The tubes were placed in a heating block at 70° C until the effervescence stopped. The evolved  
157 gas was removed via vacuum. Water vapor was removed by passing the gas through a mixture of  
158 liquid nitrogen and ethanol at approximately -50° C. Carbon dioxide was condensed to a solid  
159 using a liquid nitrogen bath and the remaining gasses were drawn off. The purified CO<sub>2</sub> was

160 converted to graphite by reaction with Fe powder (Alfa Aesar, -325 mesh, reduced, 98%) in a  
161 hydrogen reducing environment at 550° C for 3 hr (Vogel et al., 1984).

162

163 The carbonate-metal or graphite-metal mixtures were pressed into pre-drilled (4.1 mm depth)  
164 aluminum targets at 400 psi, rotated 90°, and pressed again at 400 psi. Direct carbonate targets  
165 were pressed within 72 hr of powdering the first sample. The IAEA C1 blank and IAEA C2  
166 standard were pressed on the same day they were powdered. Processing a direct carbonate <sup>14</sup>C  
167 sample, from raw shell to a finished pressed target, typically takes about 25 minutes. In  
168 comparison, processing a typical graphite <sup>14</sup>C sample, from raw shell to final pressed target,  
169 typically takes about 60 minutes. The pressed targets were sent to UCI for AMS <sup>14</sup>C analysis  
170 (Southon and Santos, 2007).

171

172 We compiled 60 additional paired determinations generated at UCI or the Australian Nuclear  
173 Science and Technology Organisation (ANSTO) from Bush et al. (2011), New et al. (2019),  
174 Parker et al. (2019), and Hua et al. (2019). The respective publications provide the lab  
175 procedures and methods used for the additional paired determinations. Co-authors contributed all  
176 unpublished ages and previously unreported supporting information from UCI and ANSTO.

177

178 Radiocarbon concentrations are given as percent of the Modern (pMC) standard following the  
179 conventions of Stuiver and Polach (1977). Sample preparation backgrounds have been subtracted  
180 based on measurements of <sup>14</sup>C-free calcite (IAEA C1) using an isotope mixing calculation  
181 (Donahue et al., 1990). All graphite <sup>14</sup>C determinations have been corrected for isotopic  
182 fractionation according to conventions of Stuiver and Polach (1977) with  $\delta^{13}\text{C}$  values measured

183 on prepared graphite using the AMS spectrometer. These can differ from the  $\delta^{13}\text{C}$  values of the  
184 original material and are not provided.

185  
186 Differences were calculated as “direct carbonate – graphite pMC”, with errors calculated in  
187 quadrature. The bivariate relationship between direct carbonate and graphite pMC values was  
188 evaluated using a reduced major axis regression (RMA) analysis. Unlike the classic ordinary  
189 least squares regressions (OLS), the RMA – also known as standardized major axis, geometric  
190 mean regression, or model II regression – minimizes the residual variation across both axes, not  
191 only the Y-axis, and hence accounts for measurement error in both axes (Quinn and Keough  
192 2002, Smith 2009). The RMA regression avoids assumptions about the cause-and-effect between  
193 direct carbonate and graphite pMC values (Smith, 2009). The PAST 4.03 statistical program  
194 (Hammer et al., 2001) was used for the RMA with 95% bootstrapped confidence intervals [N =  
195 1999].

196

## 197 RESULTS AND DISCUSSION

198

199 Blank (IAEA C1) and Holocene standard (IAEA C2) performance

200

201 Graphite  $^{14}\text{C}$  analysis of NAU’s marble blank (IAEA C1) yields  $0.44 \pm 0.25$  pMC ( $n = 8$ ). Direct  
202 carbonate  $^{14}\text{C}$  analysis of NAU’s C1 blank yields  $2.16 \pm 0.42$  pMC ( $n = 22$ ) using Fe and  $1.49 \pm$   
203  $0.67$  pMC ( $n = 115$ ) using Nb powder. Our direct carbonate blank results are similar to Hua et al.  
204 (2019) who demonstrated that Nb powder yields cleaner blanks than either Fe or Ag powders.  
205 The source of the direct carbonate  $^{14}\text{C}$  contamination in the NAU blank is unclear but likely

206 stems from a variety of sources including, but not limited to, contamination during processing,  
207 carbon contamination in both the metal powders and the C1 powder itself, and uptake from  
208 atmospheric sources (Longworth et al., 2013). It is well known that powdered carbonate adsorbs  
209 atmospheric CO<sub>2</sub> over several years (Gagnon and Jones, 1993) but it also rapidly adsorbs CO<sub>2</sub>  
210 after being baked at 500° C to oxidize indigenous and adsorbed carbon (Bush et al., 2013). A  
211 small test conducted at NAU reveals that C1 powder mixed with Nb and stored in capped glass  
212 ampules under N<sub>2</sub> and then pressed immediately, pressed after four days, and pressed after nine  
213 days yields similar pMC ( $2.5 \pm 0.4$  (n = 2);  $2.3 \pm 0.3$  (n = 4);  $2.1 \pm 0.2$  (n = 2), respectively). A  
214 subsequent test used a <sup>14</sup>C-dead *Rangia lecontei* (Conrad, 1853) shell from the Early and Middle  
215 Pleistocene Brawley Formation (Kirby et al., 2007). Targets pressed immediately after  
216 powdering and pressed after four and nine days storage under N<sub>2</sub> yielded similar pMC ( $1.7 \pm 0.1$   
217 (n = 4);  $1.6 \pm 0.1$  (n = 4);  $1.8 \pm 0.1$  (n = 4), respectively). The small difference in pMC between  
218 the C1 blank and the *R. lecontei* blank is within the range of analytical variability of our C1  
219 blank, thus, we contend that the marble and mollusc shell powders do not behave differently  
220 during processing. Neither set of blanks suggest that adsorption of atmospheric CO<sub>2</sub> during  
221 processing is a significant source of contamination, unless it occurs almost instantaneously upon  
222 powdering. As standard practice, all direct carbonate <sup>14</sup>C blanks and standards processed at NAU  
223 are pressed into targets on the same day they are powdered. Unknowns are powdered, stored  
224 under N<sub>2</sub>, and pressed into targets within 72 hours. The metal powder itself is probably a larger  
225 source of carbon contamination (Bush et al., 2013; Hua et al., 2019) than is adsorption of  
226 atmospheric CO<sub>2</sub>.

227

228 Graphite  $^{14}\text{C}$  analysis of NAU's Holocene carbonate standard (IAEA C2) yields  $40.52 \pm 0.74$   
229 pMC ( $n = 7$ ). The C2 standard is consistent with the consensus value within  $1\sigma$  error ( $41.14 \pm$   
230  $0.03$  pMC; Rozanski et al., 1992). Direct carbonate  $^{14}\text{C}$  analysis of NAU's C2 standard yields  
231  $41.30 \pm 0.53$  pMC ( $n = 25$ ) using Fe powder and  $40.71 \pm 0.60$  pMC ( $n = 114$ ) using Nb powder.  
232 Both values are consistent with the consensus value within  $1\sigma$  error ( $41.14 \pm 0.03$  pMC;  
233 Rozanski et al., 1992). The difference in mean pMC is likely due to the smaller number of C2  
234 standards analyzed with Fe powder. Thus, there is evidence for extraneous young carbon  
235 contamination for the C1 and *R. lecontei* blanks (see previous section), but not for the C2  
236 standard. Recently, Hua et al. (2019) demonstrated that the  $^{14}\text{C}$  level of carbon contamination at  
237 ANSTO is similar to the C2 standard pMC. Thus, extraneous carbon contamination would be  
238 detectible in the C1 blank, but not in the C2 standard.

239  
240 Key differences between direct carbonate and graphite  $^{14}\text{C}$  determination for biominerals  
241  
242 The traditional graphite  $^{14}\text{C}$  processing involves dissolving biominerals in phosphoric acid  
243 followed by converting the resultant  $\text{CO}_2$  to graphite. Negatively charged carbon ions are  
244 produced by sputtering a mixture of graphite and iron powder with cesium ions and then  
245 extracting the negatively charged carbon ions using an electric potential (Longworth et al.,  
246 2013). The direct carbonate  $^{14}\text{C}$  method bypasses the graphitization process and uses cesium ions  
247 and an electrical potential to extract negatively charged carbon ions directly from powdered  
248 carbonate mixed with a metal powder.

249

250 The presence/absence of the acid dissolution step is a key difference between two methods, and  
251 might have interesting implications regarding the sources of carbon measured by the two  
252 methods. Various studies suggest that mollusk shells (and other biominerals) contain a few tenths  
253 of a percent up to 5% by mass organic material, or “conchiolin” (Freymy, 1855), which is an  
254 integral structural component within the biomineral (Galstorf, 1964; Keith et al., 1993; Cuif et  
255 al., 2004; Zhang and Zhang, 2006; Hadden et al., 2019). It is unclear if the acid dissolution of a  
256 biomineral during traditional graphite  $^{14}\text{C}$  processing can liberate carbon from conchiolin.  
257 Presumably, conchiolin would be an additional source of carbon present only in direct carbonate  
258  $^{14}\text{C}$  determinations. A non-exhaustive literature search suggests that paired shell and conchiolin  
259  $^{14}\text{C}$  ages (or  $^{14}\text{C}$  activities) are similar (Berger et al., 1965; Burliegh, 1983; Haynes and Mead,  
260 1987; Hadden et al., 2019). In some environments, however, organisms may preferentially  
261 incorporate significant amounts of  $^{14}\text{C}$ -dead carbon in their conchiolin that is not present in their  
262 soft tissues or shell carbonate (Masters and Bada, 1977; Hadden et al., 2018). We cautiously  
263 assume that small amounts of conchiolin in the biominerals featured in this study do not  
264 significantly influence the direct carbonate pMC values, but the topic deserves additional study.

265

266 Direct carbonate versus graphite pMC determinations

267

268 We compiled pMC values from 153 individual carbonate specimens analyzed using both the  
269 direct carbonate and graphite  $^{14}\text{C}$  techniques. Seventy-eight and 75 direct carbonate targets used  
270 Fe and Nb powder, respectively (Supplemental Information). Bush et al. (2013) concluded that  
271 the direct carbonate  $^{14}\text{C}$  technique is less reliable for their oldest coral samples ( $> 30$  ka BP),  
272 thus, their samples yielding  $\leq 1.3$  pMC using graphite are excluded in this comparison. One

273 sample of *Maetra isabelleana* powder yielded strongly dissimilar graphite (78.5 pMC) and direct  
274 carbonate (105.7 pMC) results when analyzed seven months apart. Two samples of *Actinella*  
275 *nitidiuscula* material also produced strongly dissimilar graphite (0.91 and 0.36 pMC) and direct  
276 carbonate (2.0 and 2.5 pMC) results, respectively. The reason for the discrepancies is unclear.  
277 All three samples used Fe powder in the direct carbonate  $^{14}\text{C}$  determinations. Two of the samples  
278 yield pMC values close to background and are therefore sensitive to contamination, and the third  
279 sample yielded pMC showing bomb  $^{14}\text{C}$  contamination when analyzed with the direct carbonate  
280 technique whereas it did not when analyzed as graphite, thus, these three samples were excluded  
281 from further discussion. The remaining 150 specimens yield graphite and direct carbonate pMC  
282 values between 2.2 and 106.0 (Supplemental Information).

283  
284 Notably, the  $1\sigma$  pMC analytical errors associated with the direct carbonate  $^{14}\text{C}$  technique are  
285 typically two to eight times higher than for their graphite counterpart (Fig. 1A). There is a  
286 moderately weak negative relationships between the magnitude of the relative  $1\sigma$  analytical  
287 errors and a sample's graphite pMC when using Fe ( $r = -0.62$ ) and Nb ( $r = -0.17$ ) in direct  
288 carbonate  $^{14}\text{C}$  analyses (Fig. 1B). With better counting statistics and less proportional  
289 background interference, direct carbonate pMC measurements on young samples tend to be  
290 indistinguishable from their graphite counterpart measurements as compared to older samples.

291  
292 An RMA regression shows a strong relationship between direct carbonate and graphite pMC ( $n =$   
293 150) (Fig. 2A). The slope of an RMA regression line is defined as the standard deviation of the  
294 y-axis values (direct carbonate pMC) divided by the standard deviation of the x-axis values  
295 (graphite pMC). The y-intercept is defined by the regression line passing through the bivariate

296 centroid, or the point  $(\bar{x}, \bar{y})$ , which here would be the mean of the graphite pMC values and the  
297 mean of the direct carbonate pMC values, respectively. The RMA regression using our entire  
298 compilation (Fig. 2A) yields a slope near 1.000 ( $0.996 \pm 0.003$ ; 95% bootstrapped CI [N = 1999]  
299 of 0.991 to 1.001), and a y-intercept slightly above 0.00 (0.42; 95% bootstrapped CI [N = 1999]  
300 of 0.15 to 0.67) (Fig. 1A). We observe slight differences in the RMA regression results when the  
301 direct carbonate  $^{14}\text{C}$  determinations using Fe and Nb are assessed individually (Figs. 2B and 2C).  
302 Variability in the direct carbonate  $^{14}\text{C}$  determinations using Fe powder is similar to that of their  
303 graphitized counterparts (i.e., RMA slope of  $0.999 \pm 0.003$ ; Fig. 2B). In contrast, the lower RMA  
304 slope of  $0.988 \pm 0.006$  for the Nb-graphite pairs (Fig. 2C) reveals that the direct carbonate  $^{14}\text{C}$   
305 determinations using Nb powder yield pMC values that are slightly less variable than their  
306 graphite counterparts. The difference in the Fe-only and Nb-only RMA regression slopes is small  
307 and overlap at  $2\sigma$  errors. Thus, we contend that the differences in pMC values between the direct  
308 carbonate and graphite  $^{14}\text{C}$  techniques is insignificant for most analytical goals.

309  
310 The vast majority of direct carbonate pMC values are comparable to their graphite counterparts.  
311 Seventy-seven percent of differences are  $\pm 1.0$  pMC, and 94% percent are  $\pm 2.0$  pMC. Overall,  
312 we observe that 61% of differences are positive (Fig. 2A). When considered individually,  
313 however, 69% of the direct carbonate  $^{14}\text{C}$  determinations using Fe yield positive differences  
314 whereas the direct carbonate  $^{14}\text{C}$  determinations using Nb yield differences that are more equally  
315 distributed, but still with a slight positive skew (53%) (Figs. 2B and 2C). The mean value of the  
316 differences is 0.19 pMC (95% CI: 0.04 to 0.34 pMC) for the entire compilation, indicating that  
317 the direct carbonate  $^{14}\text{C}$  technique yields pMC values slightly higher than the graphite technique.  
318 Much of the offset is contained in the direct carbonate determinations using Fe powder,



319 however. When considered individually, the mean value of the Fe-graphite differences is 0.26  
320 pMC (95% CI: 0.06 to 0.46 pMC), whereas the mean of the Nb-graphite differences is roughly  
321 half that, at 0.11 pMC (95% CI: -0.23 to 0.34 pMC). Dividing the differences by the direct  
322 carbonate pMC value yields a coefficient of variation of 0.9% (95% CI: -0.65% to 1.58%) for the  
323 entire compilation. When considered individually, the coefficient of variation for the Fe and Nb  
324 differences are 1.6% (95% CI: 0.3% to 2.8%) and 0.3% (95% CI: -0.3% to 0.6%) respectively.  
325 Collectively, this reveals a slight positive bias in direct carbonate  $^{14}\text{C}$  measurements relative to  
326 the graphite technique, with a more pronounced bias when using Fe powder.

327  
328 The reason for the positively skewed differences (Fig. 2A, Fig. 2B) and for why the two metal  
329 powders perform differently is unclear. One potential explanation is the adsorption of young  
330 atmospheric  $\text{CO}_2$  during the powdering process (e.g., Kosnik et al., 2017). However, adsorption  
331 of  $\text{CO}_2$  reasonably should affect all of the biomineral powders similarly, and not show a  
332 preference for the samples using Fe powder. Kosnik et al. (2017) suggested that perhaps the  
333 blank (marble) powder adsorbs  $\text{CO}_2$  less efficiently than the biomineral powders, which would  
334 lead to excess adsorbed atmospheric  $\text{CO}_2$  influence on biomineral pMC after blank subtraction.  
335 A blank under-correction of this sort should also affect the carbonate powders mixed with both  
336 metals similarly, rather than preferentially affecting the carbonate powders mixed with Fe (Figs.  
337 2B and 2C). Finally, we did not detect any adverse adsorption of atmospheric  $\text{CO}_2$  in our blank  
338 marble powder or on  $^{14}\text{C}$ -dead mollusk shell powder after storage under  $\text{N}_2$  for up to 9 days (see  
339 previous discussion of blank performance). Thus, adsorption of  $\text{CO}_2$  during powdering does not  
340 adequately explain the higher tendency for positive differences when using Fe powder (Fig. 2B).  
341 It is conceivable that the more equitable differences using Nb powder (Fig. 2C) is related to the

342 improved beam current and reduced uncertainties when using Nb powder (Hua et al., 2019). We  
343 believe that our compilation is the largest of its kind, but it may still be too small to determine  
344 the reason for the positive skew in differences when using Fe powder (Fig. 2B).

345

346 The majority of the individual differences in our compilation (76%) include 0 at 95% CI,  
347 indicating there is no significant difference between the majority of paired direct carbonate and  
348 graphite pMC values (Supplemental Information). However, 36 of the differences (24%) do not  
349 meet this criterion. These differences are evenly split between direct carbonate  $^{14}\text{C}$   
350 determinations using Fe powder ( $n = 19$ ) and Nb powder ( $n = 17$ ) (Table 1). Thirty-one of the 36  
351 differences that do not include 0 are from samples that yield  $> 50$  pMC as graphite, and the  
352 remaining five come from samples that yield  $< 50$  pMC as graphite (Table 1). All five of the  
353 older samples yield differences that miss the 95% CI threshold by 0.5 pMC or less (Table 1). For  
354 the younger samples, 28/31 of the differences miss the 95% CI threshold by less than 1.2 pMC.  
355 The remaining three differences miss the 95% CI threshold by 1.3, 1.7, and 1.8 pMC (Table 1).

356

357 We acknowledge and caution that our study is limited to comparing the results of one direct  
358 carbonate and one graphite  $^{14}\text{C}$  analyses per individual biomineral specimen. Several of the  
359 results compiled from Bush et al. (2013) comprise multiple analyses per coral specimen, but the  
360 overwhelming majority of our comparisons are based on single paired results (Supplemental  
361 Information). We calculated the weighted mean of the graphite and direct carbonate  $^{14}\text{C}$  values  
362 (weighted by  $1/\text{variance}$ ) and determined the number of biomineral specimens with  $1\sigma$  analytical  
363 errors that overlapped the weighted mean. Ninety-three percent of the graphite pMC values  
364 overlap the weighted mean (versus the expected 68%), but only 45% of the direct carbonate

365 pMC values do (versus the expected 68%). Thus, the reported uncertainty in the direct carbonate  
366  $^{14}\text{C}$  determinations underestimates the actual variance. We also suspect that some of the  
367 differences noted in this study may reflect slight variability between subsamples of a single  
368 biomineral specimen. Future comparative studies would benefit from analyzing each specimen  
369 multiple times with each AMS  $^{14}\text{C}$  technique to more fully assess if there are statistically  
370 significant differences between the two techniques. Researchers typically only date a biomineral  
371 specimen once rather than multiple times, thus our study is more directly analogous to that  
372 approach. Keeping in mind that the direct carbonate pMC variance is underestimated and that we  
373 are using a single paired graphite and direct carbonate comparison per specimen, we contend that  
374 our study shows that the differences between the direct carbonate and graphite  $^{14}\text{C}$  techniques is  
375 insignificant for most analytical goals.

376  
377 We also observe a potentially interesting association between particular taxa and the differences  
378 that do not include 0 at a 95% CI. For example, the clams *Arctica islandica* (6/6 analyses) and  
379 *Modiolus* sp. (4/10 analyses), the sand dollar *Peronella peronii* (5/12 analyses), and the  
380 brachiopod *Gryphus vitreus* (3/6 analyses) appear to be disproportionately affected (Tables 1 and  
381 2). The cause of this pattern is unclear. Carbonate mineralogy can be excluded because both  
382 aragonitic samples and calcitic samples populate the group (Table 1). Furthermore, some  
383 differences from the same taxon do include 0 at a 95% CI, for example, the remaining 3/6  
384 *Gryphus vitreus* shells (Table 2). Thus, neither the organism (in a broader taxonomic sense) nor  
385 the carbonate mineralogy of the various skeletal materials is a satisfactory explanation. Using Fe  
386 or Nb powder for direct carbonate  $^{14}\text{C}$  analysis does not explain why some taxa seem more  
387 affected than others (Table 1). The apparent patterns in Tables 1 and 2 may be an artifact of the

388 small sample sizes per taxon, but it may hint that taxonomy or perhaps environmental variables  
389 specific to the habitat or life cycle of each taxon requires further consideration (e.g., Kosnik et  
390 al., 2017; Hadden et al., 2018). Larger sample sizes and additional tests are needed to better  
391 understand what may be causing differences between direct carbonate and graphite pMC  
392 determinations.

393  
394 To further explore the relationship between the direct carbonate and graphite  $^{14}\text{C}$  methods, the  
395 pMC differences shown in Figure 2A are plotted with respect to their respective taxonomic  
396 classifications in Figure 3. As noted previously in our discussion, the direct carbonate pMC  
397 values are more consistently higher than their graphite equivalents (Fig. 3). There are hints in  
398 Figure 3 that some biogenic carbonates might be prone to producing direct carbonate pMC  
399 values that are systematically offset from their graphite counterpart, although again, the sample  
400 sizes per taxon are admittedly small (1 to 24 individuals). The metal powder used in the direct  
401 carbonate  $^{14}\text{C}$  technique again does not appear to be a controlling factor at the taxonomic level  
402 (Fig. 3). Note that the brachiopod *Gryphus vitreus* yields exclusively negative differences using  
403 Nb powder, the clams *Tucetona pectinata* and *Transennella* sp. yield exclusively positive  
404 differences using Fe powder, and the echinoderm *Peronella peronii* yields positive differences in  
405 nine of 11 analyses using Nb powder (Fig. 3). Additional work is need to determine whether the  
406 perceived taxonomic differences are real, for example if different taxa or perhaps different shells  
407 from different environments contain consistently different amounts of conchiolin with different  
408  $^{14}\text{C}$  activities than the surrounding shell carbonate (Hadden et al., 2018), or whether the  
409 perceived differences are merely an artefact of small sample sizes.

410

411 To summarize, we find that 114/150 (76%) of the direct carbonate pMC values in this  
412 compilation are statistically indistinguishable from their paired graphite pMC values (i.e.,  
413 differences include 0) at the 95% confidence interval, and of the 36 samples that are not, all but  
414 three are less than 1.2 pMC beyond the 95% confidence threshold. All direct carbonate  $^{14}\text{C}$   
415 determinations, even the three with the largest differences exceeding the 95% CI threshold, show  
416 offsets from their graphite pMC values that are insignificant for most analytical goals. We can  
417 confidently demonstrate that in the large majority of cases the direct carbonate  $^{14}\text{C}$  technique  
418 yields pMC values from a variety of biogenic carbonates that are indistinguishable to pMC  
419 values produced using the more costly and time-intensive graphite  $^{14}\text{C}$  technique. Additional  
420 work is needed to better understand the origin of the increased uncertainty in the direct carbonate  
421  $^{14}\text{C}$  determinations, but even with this uncertainty, the technique is appropriate for a wide range  
422 of applications.

423

## 424 CONCLUSIONS

425

426 This study compared 153 individual biogenic carbonate samples from echinoderms, mollusks,  
427 brachiopods and corals that have been dated using both direct carbonate and graphite  $^{14}\text{C}$   
428 techniques. Three samples were excluded from discussion because their direct carbonate and  
429 graphite pMC values were strongly discordant. The remaining 150 samples range from 2.2 to  
430 106.0 pMC. The direct carbonate  $^{14}\text{C}$  technique produces  $1\sigma$  pMC errors that are primarily two  
431 to 8 times higher than the associated graphite errors, and there is a weak negative correlation  
432 between the magnitude of the  $1\sigma$  error differences and a sample's graphite pMC value. Our  
433 comparison of 150 paired direct carbonate and graphite  $^{14}\text{C}$  determinations reveals a strong RMA

434 regression relationship between the two techniques ( $m = 0.996$ ; 95% CI (0.991 to 1.001)), and  
435 pMC values that are statistically indistinguishable from each other in 76% of the samples (at  
436 95% CI). The variance in direct carbonate pMC values is underestimated, however. All but three  
437 of the direct carbonate  $^{14}\text{C}$  determinations in this study were within 1.2 pMC of the 95% CI  
438 threshold of being statistically indistinguishable from their graphite equivalent. Some types of  
439 biogenic carbonates appear to produce direct carbonate pMC values that are consistently offset  
440 from their graphite values, but sample sizes are small and the paired pMC values still statistically  
441 overlap in the vast majority of cases. The direct carbonate  $^{14}\text{C}$  technique yields pMC values that  
442 overwhelmingly are indistinguishable from the standard graphite  $^{14}\text{C}$  technique, but with the  
443 added benefit of more efficient laboratory preparation and processing.

444

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461

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## 708 FIGURE CAPTIONS

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710 Figure 1. Cross-plots comparing analytical errors for direct carbonate and graphite pMC from the  
711 same biogenic carbonates. A - cross-plot of  $1\sigma$  analytical errors produced by the graphite  $^{14}\text{C}$   
712 method versus the  $1\sigma$  analytical errors produced by the direct carbonate  $^{14}\text{C}$  method. Dashed line  
713 is a 1-to-1 line. B - cross-plot of graphite pMC versus the ratio of direct carbonate to graphite  $1\sigma$   
714 pMC analytical errors. Moderate negative correlations are defined by the coarse (Fe;  $r = -0.62$ )  
715 and fine (Nb;  $r = -0.17$ ) dashed lines. Solid black circles in both panels – Fe powder. Solid white  
716 circles in both panels – Nb powder.

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718 Figure 2. Reduced Major Axis (RMA) regression of paired direct carbonate and graphite pMC  
719 determinations. A –relationship using all data. B – relationship using iron (Fe) powder. C –  
720 relationship using niobium (Nb) powder. Analysis performed using PAST 4.03 statistical  
721 software (Hammer et al., 2001). Inset diagrams are frequency histograms of pMC differences,  
722 calculated as “direct – graphite pMC”.

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724 Figure 3. Differences in pMC (direct carbonate – graphite) from an assortment of biogenic  
725 carbonates. Bp -brachiopod, G – gastropod, E – echinoderm, B – bivalve mollusk. Note that most  
726 differences are positive and that some biogenic carbonates more consistently yield either

727 negative (e.g., *Gryphus vitreus*) or positive (e.g., *Transennella* sp.) differences, while others are  
728 more evenly distributed (e.g., *Dosinia caerulea*, coral skeletons). See Supplemental Information  
729 for additional information on taxonomy and carbonate polymorphs. Solid black circles– Fe  
730 powder. Solid white circles – Nb powder.

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For Peer Review

750 Table 1 Detailed breakdown of the taxa, generalized biological group, carbonate polymorph,  
 751 standard graphite pMC values, direct carbonate metal powder, and absolute pMC value of  
 752 individual differences that exclude 0 at 95% CI.  
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Taxon	Group	Polymorph	Graphite pMC	Direct carbonate powder	Absolute pMC beyond 95% CI
<i>Actinella nitidiuscula</i>	snail	aragonite	10.9	Nb	0.53
<i>Argopecten purpuratus</i>	scallop	mixed	68.9	Fe	0.18
<i>Argopecten purpuratus</i>	scallop	mixed	70.5	Fe	0.10
<i>Arctica islandica</i>	clam	aragonite	50.5	Fe	0.89
<i>Arctica islandica</i>	clam	aragonite	50.9	Fe	0.65
<i>Arctica islandica</i>	clam	aragonite	51.4	Fe	0.13
<i>Arctica islandica</i>	clam	aragonite	55.5	Fe	0.07
<i>Arctica islandica</i>	clam	aragonite	74.0	Fe	1.80
<i>Arctica islandica</i>	clam	aragonite	75.3	Fe	0.11
<i>Codakia orbicularis</i>	clam	aragonite	103.3	Fe	0.70
<i>Codakia orbicularis</i>	clam	aragonite	103.3	Fe	1.72
unidentified coral	coral	aragonite	2.6	Fe	0.25
<i>Corbula gibba</i>	clam	aragonite	94.7	Nb	1.30
<i>Dosinia caerulea</i>	clam	aragonite	66.5	Nb	0.26
<i>Dosinia caerulea</i>	clam	aragonite	77.2	Nb	0.35
<i>Fissurella maxima</i>	limpet	mixed <sup>a</sup>	28.3	Nb	0.08
<i>Fissurella maxima</i>	limpet	mixed <sup>a</sup>	48.8	Nb	0.07
<i>Gryphus vitreus</i>	brachiopod	calcite	76.1	Nb	0.24
<i>Gryphus vitreus</i>	brachiopod	calcite	87.4	Nb	0.29
<i>Gryphus vitreus</i>	brachiopod	calcite	88.9	Nb	0.36
<i>Leodia sexiesperforata</i>	echinoderm	calcite	104.9	Fe	0.30
<i>Modiolus</i> sp.	mussel	aragonite	52.3	Fe	0.14
<i>Modiolus</i> sp.	mussel	aragonite	61.6	Fe	0.04
<i>Modiolus</i> sp.	mussel	aragonite	76.1	Fe	0.45
<i>Modiolus</i> sp.	mussel	aragonite	79.4	Fe	0.32
<i>Mulinia edulis</i>	clam	aragonite	93.2	Fe	0.38
<i>Patella candei</i>	limpet	mixed <sup>a</sup>	77.2	Nb	0.25
<i>Patella candei</i>	limpet	mixed <sup>a</sup>	88.1	Nb	0.19
<i>Peronella peronii</i>	echinoderm	calcite	57.0	Nb	1.01
<i>Peronella peronii</i>	echinoderm	calcite	62.1	Nb	1.17
<i>Peronella peronii</i>	echinoderm	calcite	72.4	Nb	1.17
<i>Peronella peronii</i>	echinoderm	calcite	77.2	Nb	0.83
<i>Peronella peronii</i>	echinoderm	calcite	77.7	Nb	1.15
<i>Polygyra septemvolva</i>	snail	aragonite	33.0	Nb	0.43
<i>Transennella</i> sp.	clam	aragonite	77.2	Fe	0.06
<i>Tucetona pectinata</i>	clam	aragonite	59.0	Fe	0.06

754 <sup>a</sup> “mixed” refers to shells that contain both calcite and aragonite polymorphs.

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757 Table 2 Summary of the taxa, sample size (n), generalized biological group, carbonate  
 758 polymorph, number of differences that include 0 at 95% CI, and publication information for  
 759 samples featured in this study.  
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Taxon	n	Group	Polymorph	Residuals include 0	Reference
<i>Actinella nitidiuscula</i>	6 <sup>a</sup>	snail	aragonite	3/4	New et al. (2019)
<i>Argopecten purpuratus</i>	5	scallop	mixed	3/5	this study
<i>Arctica islandica</i>	6	clam	aragonite	0/6	this study
<i>Chamelea gallina</i>	1	clam	aragonite	1/1	this study
<i>Choromytilus chorus</i>	12	mussel	mixed <sup>b</sup>	12/12	this study
<i>Codakia orbicularis</i>	6	clam	aragonite	4/6	this study
unidentified coral	20	coral	aragonite	19/20	Bush et al. (2011)
<i>Corbula gibba</i>	3	clam	aragonite	2/3	Albano et al. (2020)
<i>Corbula gibba</i>	2	clam	aragonite	2/2	this study
<i>Dosinia caerulea</i>	24	clam	aragonite	22/24	this study
<i>Fissurella maxima</i>	10	limpet	mixed <sup>b</sup>	8/10	this study
<i>Fulvia tenuicostata</i>	8	cockle	mixed <sup>b</sup>	8/8	Hua et al. (2019)
<i>Gryphus vitreus</i>	6	brachiopod	calcite	3/6	this study
<i>Leodia sexiesperforata</i>	1	echinoderm	calcite	0/1	Kowalewski et al. (2018)
<i>Mactra isabelleana</i>	1 <sup>a</sup>	clam	aragonite	0/1	Ritter et al. (2017)
<i>Modiolus</i> sp.	10	mussel	aragonite	6/10	this study
<i>Mulinia edulis</i>	5	clam	aragonite	4/5	this study
<i>Patella candei</i>	5	limpet	mixed <sup>b</sup>	3/5	Parker et al. (2019)
<i>Peronella peronii</i>	11	echinoderm	calcite	6/11	Kosnik et al. (2017)
<i>Polygyra septemvolva</i>	2	snail	aragonite	1/2	this study
<i>Tawera spissa</i>	1	clam	aragonite	1/1	Oakley et al. (2017)
<i>Timoclea</i> sp.	1	clam	aragonite	1/1	this study
<i>Transennella</i> sp.	4	clam	aragonite	3/4	this study
<i>Tucetona pectinata</i>	3	clam	aragonite	2/3	Kowalewski et al. (2018)

761 <sup>a</sup> Two analyses of *Actinella nitidiuscula* and one analysis of *Mactra isabelleana* yield widely  
 762 different direct carbonate and graphite pMC values and are excluded from discussion and  
 763 statistical analysis. See Supplemental Information.

764 <sup>b</sup> “mixed” refers to shells that contain both calcite and aragonite polymorphs.





