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

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25 April 2024

1   **Comparing direct carbonate and standard graphite ^{14}C determinations from an assortment**

2   **of biogenic carbonates**

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47   ABSTRACT

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49   The direct carbonate procedure for AMS ^{14}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}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   ±1σ 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}C dating of biogenic carbonates is a cost-effective and

62   efficient complement to standard graphite ^{14}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}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}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}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}C and uranium/thorium dating to determine coral age

81   distributions (Grothe et al., 2016).

82

83   The direct carbonate AMS ^{14}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 1σ errors that ranged from 0.07 and 0.94 pMC, whereas 1σ 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 1σ errors

91   that ranged from 0.31 and 0.62 pMC, whereas 1σ errors on the same materials ranged from 0.03

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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 (µg/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}C determinations that use Nb powder.

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101   Several studies have compared small numbers of paired direct carbonate and graphite ^{14}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}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.

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109   MATERIALS AND METHODS

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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),

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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,

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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 ^{14}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_2 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 ^{14}C analysis were graphitized at NAU's

152   Ecoss lab following UCI protocols (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_2 was

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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).

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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 ^{14}C

167 sample, from raw shell to a finished pressed target, typically takes about 25 minutes. In

168 comparison, processing a typical graphite ^{14}C sample, from raw shell to final pressed target,

169 typically takes about 60 minutes. The pressed targets were sent to UCI for AMS ^{14}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 Stuvier and Polach (1977). Sample preparation backgrounds have been subtracted

180 based on measurements of ^{14}C-free calcite (IAEA C1) using an isotope mixing calculation

181 (Donahue et al., 1990). All graphite ^{14}C determinations have been corrected for isotopic

182 fractionation according to conventions of Stuvier and Polach (1977) with δ^{13}C values measured

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183   on prepared graphite using the AMS spectrometer. These can differ from the $\delta^{13}C$ 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

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201   Graphite ^{14}C analysis of NAU's marble blank (IAEA C1) yields 0.44 ± 0.25 pMC (n = 8). Direct

202   carbonate ^{14}C analysis of NAU's C1 blank yields 2.16 ± 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}C contamination in the NAU blank is unclear but likely

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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_2 over several years (Gagnon and Jones, 1993) but it also rapidly adsorbs CO_2

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_2 and then pressed immediately, pressed after four days, and pressed after nine

213 days yields similar pMC (2.5 ± 0.4 (n = 2); 2.3 ± 0.3 (n = 4); 2.1 ± 0.2 (n = 2), respectively). A

214 subsequent test used a ^{14}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_2 yielded similar pMC (1.7 ± 0.1

217 (n = 4); 1.6 ± 0.1 (n = 4); 1.8 ± 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_2 during

221 processing is a significant source of contamination, unless it occurs almost instantaneously upon

222 powdering. As standard practice, all direct carbonate ^{14}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_2, 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_2.

227

228   Graphite ^{14}C analysis of NAU's Holocene carbonate standard (IAEA C2) yields 40.52 ± 0.74

229   pMC (n = 7). The C2 standard is consistent with the consensus value within 1σ error ($41.14 \pm$

230   0.03 pMC; Rozanski et al., 1992). Direct carbonate ^{14}C analysis of NAU's C2 standard yields

231   41.30 ± 0.53 pMC (n = 25) using Fe powder and 40.71 ± 0.60 pMC (n = 114) using Nb powder.

232   Both values are consistent with the consensus value within 1σ error (41.14 ± 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}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}C determination for biominerals

241

242   The traditional graphite ^{14}C processing involves dissolving biominerals in phosphoric acid

243   followed by converting the resultant 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}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" (Fremy, 1855), which is an

254   integral structural component within the biomineral (Galstoff, 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}C processing can liberate carbon from conchiolin.

257   Presumably, conchiolin would be an additional source of carbon present only in direct carbonate

258   ^{14}C determinations. A non-exhaustive literature search suggests that paired shell and conchiolin

259   ^{14}C ages (or ^{14}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}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}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}C technique is less reliable for their oldest coral samples (> 30 ka BP),

272   thus, their samples yielding ≤ 1.3 pMC using graphite are excluded in this comparison. One

273   sample of *Mactra 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}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}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 1σ pMC analytical errors associated with the direct carbonate ^{14}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 1σ 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}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 ± 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}C determinations using Fe and Nb are assessed individually (Figs. 2B and 2C).

302   Variability in the direct carbonate ^{14}C determinations using Fe powder is similar to that of their

303   graphitized counterparts (i.e., RMA slope of 0.999± 0.003; Fig. 2B). In contrast, the lower RMA

304   slope of 0.988 ± 0.006 for the Nb-graphite pairs (Fig. 2C) reveals that the direct carbonate [14]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 2σ errors. Thus, we contend that the differences in pMC values between the direct

308   carbonate and graphite ^{14}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 ± 1.0 pMC, and 94% percent are ± 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}C determinations using Fe yield positive differences

314   whereas the direct carbonate ^{14}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}C technique yields pMC values slightly higher than the graphite technique.

318   Much of the offset in contained in the direct carbonate determinations using Fe powder,

14

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}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 CO_2 during the powdering process (e.g., Kosnik et al., 2017). However, adsorption

331   of 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 CO_2 less efficiently than the biomineral powders, which would

334   lead to excess adsorbed atmospheric 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 CO_2 in our blank

338   marble powder or on ^{14}C-dead mollusk shell powder after storage under N_2 for up to 9 days (see

339   previous discussion of blank performance). Thus, adsorption of 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

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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}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}C analyses per individual biomineral specimen. Several of the

359   results complied 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}C values

362   (weighted by 1/variance) and determined the number of biomineral specimens with 1σ 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

16

365   pMC values do (versus the expected 68%). Thus, the reported uncertainty in the direct carbonate

366   ^{14}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}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}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}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

17

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}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}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}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

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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]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}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}C technique. Additional

420 work is needed to better understand the origin of the increased uncertainty in the direct carbonate

421 ^{14}C determinations, but even with this uncertainty, the technique is appropriate for a wide range

422 of applications.

423

424 CONCLUSIONS

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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]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}C technique produces 1σ 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 1σ error differences and a sample's graphite pMC value. Our

433 comparison of 150 paired direct carbonate and graphite ^{14}C determinations reveals a strong RMA

19

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}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}C technique yields pMC values that

442   overwhelmingly are indistinguishable from the standard graphite ^{14}C technique, but with the

443   added benefit of more efficient laboratory preparation and processing.

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445   ACKNOWLEDGEMENTS

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707

708   FIGURE CAPTIONS

709

710   Figure 1. Cross-plots comparing analytical errors for direct carbonate and graphite pMC from the

711   same biogenic carbonates. A - cross-plot of 1σ analytical errors produced by the graphite [14]C

712   method versus the 1σ analytical errors produced by the direct carbonate ^{14}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 1σ

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.

717

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

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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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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
Actinella nitidiuscula	snail	aragonite	10.9	Nb	0.53
Argopecten purpuratus	scallop	mixed	68.9	Fe	0.18
Argopecten purpuratus	scallop	mixed	70.5	Fe	0.10
Arctica islandica	clam	aragonite	50.5	Fe	0.89
Arctica islandica	clam	aragonite	50.9	Fe	0.65
Arctica islandica	clam	aragonite	51.4	Fe	0.13
Arctica islandica	clam	aragonite	55.5	Fe	0.07
Arctica islandica	clam	aragonite	74.0	Fe	1.80
Arctica islandica	clam	aragonite	75.3	Fe	0.11
Codakia orbicularis	clam	aragonite	103.3	Fe	0.70
Codakia orbicularis	clam	aragonite	103.3	Fe	1.72
unidentified coral	coral	aragonite	2.6	Fe	0.25
Corbula gibba	clam	aragonite	94.7	Nb	1.30
Dosinia caerulea	clam	aragonite	66.5	Nb	0.26
Dosinia caerulea	clam	aragonite	77.2	Nb	0.35
Fissurella maxima	limpet	mixed[a]	28.3	Nb	0.08
Fissurella maxima	limpet	mixed[a]	48.8	Nb	0.07
Gryphus vitreus	brachiopod	calcite	76.1	Nb	0.24
Gryphus vitreus	brachiopod	calcite	87.4	Nb	0.29
Gryphus vitreus	brachiopod	calcite	88.9	Nb	0.36
Leodia sexiesperforata	echinoderm	calcite	104.9	Fe	0.30
Modiolus sp.	mussel	aragonite	52.3	Fe	0.14
Modiolus sp.	mussel	aragonite	61.6	Fe	0.04
Modiolus sp.	mussel	aragonite	76.1	Fe	0.45
Modiolus sp.	mussel	aragonite	79.4	Fe	0.32
Mulinia edulis	clam	aragonite	93.2	Fe	0.38
Patella candei	limpet	mixed[a]	77.2	Nb	0.25
Patella candei	limpet	mixed[a]	88.1	Nb	0.19
Peronella peronii	echinoderm	calcite	57.0	Nb	1.01
Peronella peronii	echinoderm	calcite	62.1	Nb	1.17
Peronella peronii	echinoderm	calcite	72.4	Nb	1.17
Peronella peronii	echinoderm	calcite	77.2	Nb	0.83
Peronella peronii	echinoderm	calcite	77.7	Nb	1.15
Polygyra septemvolva	snail	aragonite	33.0	Nb	0.43
Transennella sp.	clam	aragonite	77.2	Fe	0.06
Tucetona pectinata	clam	aragonite	59.0	Fe	0.06

754 [a] "mixed" refers to shells that contain both calcite and aragonite polymorphs.
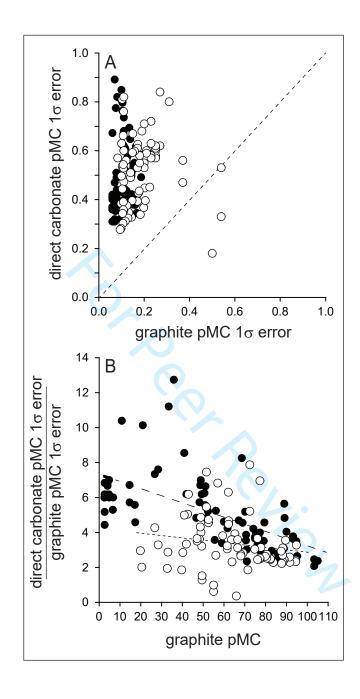
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756

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
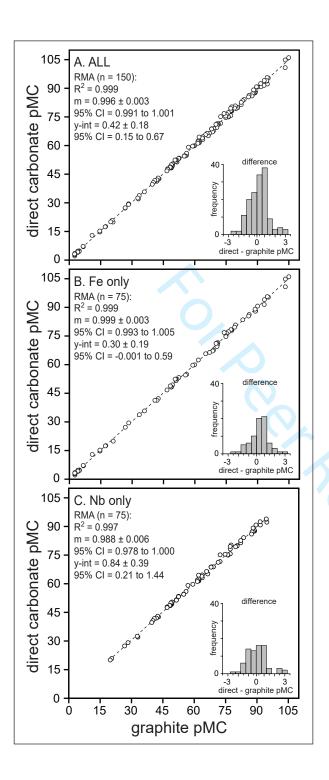759 samples featured in this study.
760

Taxon	n	Group	Polymorph	Residuals include 0	Reference
Actinella nitidiuscula	6[a]	snail	aragonite	3/4	New et al. (2019)
Argopecten purpuratus	5	scallop	mixed	3/5	this study
Arctica islandica	6	clam	aragonite	0/6	this study
Chamelea gallina	1	clam	aragonite	1/1	this study
Choromytilus chorus	12	mussel	mixed[b]	12/12	this study
Codakia orbicularis	6	clam	aragonite	4/6	this study
unidentified coral	20	coral	aragonite	19/20	Bush et al. (2011)
Corbula gibba	3	clam	aragonite	2/3	Albano et al. (2020)
Corbula gibba	2	clam	aragonite	2/2	this study
Dosinia caerulea	24	clam	aragonite	22/24	this study
Fissurella maxima	10	limpet	mixed[b]	8/10	this study
Fulvia tenuicostata	8	cockle	mixed[b]	8/8	Hua et al. (2019)
Gryphus vitreus	6	brachiopod	calcite	3/6	this study
Leodia sexiesperforata	1	echinoderm	calcite	0/1	Kowalewski et al. (2018)
Mactra isabelleana	1[a]	clam	aragonite	0/1	Ritter et al. (2017)
Modiolus sp.	10	mussel	aragonite	6/10	this study
Mulinia edulis	5	clam	aragonite	4/5	this study
Patella candei	5	limpet	mixed[b]	3/5	Parker et al. (2019)
Peronella peronii	11	echinoderm	calcite	6/11	Kosnik et al. (2017)
Polygyra septemvolva	2	snail	aragonite	1/2	this study
Tawera spissa	1	clam	aragonite	1/1	Oakley et al. (2017)
Timoclea sp.	1	clam	aragonite	1/1	this study
Transennella sp.	4	clam	aragonite	3/4	this study
Tucetona pectinata	3	clam	aragonite	2/3	Kowalewski et al. (2018)

761 [a] 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 [b] "mixed" refers to shells that contain both calcite and aragonite polymorphs.

A. ALL
RMA (n = 150):
$R^2 = 0.999$
m = 0.996 ± 0.003
95% CI = 0.991 to 1.001
y-int = 0.42 ± 0.18
95% CI = 0.15 to 0.67

B. Fe only
RMA (n = 75):
$R^2 = 0.999$
m = 0.999 ± 0.003
95% CI = 0.993 to 1.005
y-int = 0.30 ± 0.19
95% CI = -0.001 to 0.59

C. Nb only
RMA (n = 75):
$R^2 = 0.997$
m = 0.988 ± 0.006
95% CI = 0.978 to 1.000
y-int = 0.84 ± 0.39
95% CI = 0.21 to 1.44

direct carbonate -
graphite pMC