

Alma Mater Studiorum Università di Bologna
Archivio istituzionale della ricerca

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

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Bright J., Ebert C., Kosnik M.A., Southon J.R., Whitacre K., Albano P.G., et al. (2021). COMPARING DIRECT CARBONATE and STANDARD GRAPHITE 14C DETERMINATIONS of BIOGENIC CARBONATES. RADIOCARBON, 63(2), 387-403 [10.1017/RDC.2020.131].

Availability:

This version is available at: <https://hdl.handle.net/11585/845600> since: 2024-05-22

Published:

DOI: <http://doi.org/10.1017/RDC.2020.131>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>).
When citing, please refer to the published version.

(Article begins on next page)

This is the final peer-reviewed accepted manuscript of:

Bright J.; Ebert C.; Kosnik M.A.; Southon J.R.; Whitacre K.; Albano P.G.; Flores C.; Frazer T.K.; Hua Q.; Kowalewski M.; Martinelli J.C.; Oakley D.; Parker W.G.; Retelle M.; Do Nascimento Ritter M.; Rivadeneira M.M.; Scarponi D.; Yanes Y.; Zuschin M.; Kaufman D.S.: *Comparing direct carbonate and standard graphite ^{14}C determinations of biogenic carbonates.*

RADIOCARBON. Vol. 63 ISSN 0033-8222

DOI: 10.1017/RDC.2020.131

The final published version is available online at:

<https://dx.doi.org/10.1017/RDC.2020.131>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

Comparing direct carbonate and standard graphite ^{14}C determinations from an assortment of biogenic carbonates

Jordon Bright^{1*}, Chris Ebert², Matthew A. Kosnik³, Darrell S. Kaufman¹, Katherine Whitacre¹, John R. Southon⁴, Paolo G. Albano⁵, Carola Flores^{6,7}, Thomas K. Frazer⁸, Quan Hua⁹, Michal Kowalewski¹⁰, Julieta C. Martinelli¹¹, David Oakley¹², Wesley G. Parker¹³, Michael Retelle¹⁴, Matias do Nascimento Ritter¹⁵, Marcelo M. Rivadeneira^{6,7,16}, Daniele Scarponi¹⁷, Yurena Yanes¹³, Martin Zuschin⁵

¹ School of Earth and Sustainability, Northern Arizona University, Flagstaff, AZ, 86011, USA

² Center for Ecosystem Sciences and Society, and Department of Biological Sciences, Northern Arizona University, Flagstaff, AZ, 86011, USA

³ Department of Biological Sciences, Macquarie University, New South Wales 2109, Australia

⁴ Keck Carbon Cycle AMS Laboratory, Department of Earth System Science, University of California at Irvine, Irvine, CA 92697, USA

⁵ Department of Paleontology, University of Vienna, Althanstrasse 14, Vienna, Austria

⁶ Centro de Estudios Avanzados en Zonas Áridas (CEAZA), Av. Ossandón 877, C.P. 1781681, Coquimbo, Chile

⁷ Departamento de Biología Marina, Facultad de Ciencias del Mar, Universidad Católica del Norte, Av. Larrondo 1281, Coquimbo, Chile

⁸ School of Natural Resources and Environment, University of Florida, Gainesville, FL, 32611, USA

⁹ Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia

¹⁰ Florida Museum of Natural History, University of Florida, Gainesville, FL, 32611, USA

¹¹ School of Fishery and Aquatic Sciences, University of Washington, Seattle, WA, 98105, USA

¹² Department of Geosciences, Pennsylvania State University, University Park, PA, 16802, USA

¹³ Department of Geology, University of Cincinnati, Cincinnati, OH, 45221, USA

¹⁴ Department of Geology, Bates University, Lewiston, ME, 04240, USA

¹⁵ Centro de Estudos Costeiros, Limnológicos e Marinhos, Campus Litoral Norte, Universidade Federal do Rio Grande do Sul, Imbé, 95625-00, Rio Grande do Sul, Brazil

¹⁶ Departamento de Biología, Universidad de la Serena, Av. Raul Bitrán 1305, La Serena, Chile

¹⁷ Department of Biological, Geological and Environmental Sciences, University of Bologna, Piazza di Porta San Donato, I-40126 Bologna, Italy

* Corresponding author.

ABSTRACT

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

INTRODUCTION

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

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

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

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

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

MATERIALS AND METHODS

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

115 *Macra 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,

and then finally rinsed three times with DDI to remove surface contaminants before being dried in a 50° C oven overnight. Samples for direct carbonate ^{14}C analysis were ground to a fine powder using an agate mortar and pestle and manually mixed with 6.0 to 7.0 mg of metal powder in pre-baked (3 hr at 500° C) Kimble borosilicate glass culture tubes (6 mm OD x 50 mm). Samples processed at NAU before June 2018 were mixed with Fe powder (Alfa Aesar, -325 mesh, reduced, 98%) whereas samples processed after June 2018 were mixed with Nb powder (Alfa Aesar Puratronic, -325 mesh, 99.99%), following a change from Fe to Nb powders at the Keck Carbon Cycle AMS facility at the University of California , Irvine (UCI) in 2018. Powdered carbonate sample masses ranged between 0.30 and 0.50 mg, which equates to 36 to 60 μg of carbon, respectively. The culture tubes were flushed with N_2 gas to reduce contamination from atmospheric carbon and capped with Supelco plastic column caps (1/4" OD) until the carbonate-metal powder mixture was pressed into targets.

Samples processed at NAU for standard graphite AMS ^{14}C analysis were graphitized at NAU's Ecosystem lab following UCI protocols (sites.uci.edu/keckams/protocols). An aliquot of 7 to 8 mg of carbonate was placed in 13 x 75 mm BD Vacutainer plastic collection tubes and sealed with a red/grey conventional stopper closure. Ambient atmosphere was removed via vacuum before a small-bore needle was used to dispense 8 ml of ACS grade 85% phosphoric acid into each tube. The tubes were placed in a heating block at 70° C until the effervescence stopped. The evolved gas was removed via vacuum. Water vapor was removed by passing the gas through a mixture of liquid nitrogen and ethanol at approximately -50° C. Carbon dioxide was condensed to a solid using a liquid nitrogen bath and the remaining gasses were drawn off. The purified CO_2 was

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

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

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

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

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

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

RESULTS AND DISCUSSION

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

Graphite ^{14}C analysis of NAU’s marble blank (IAEA C1) yields 0.44 ± 0.25 pMC ($n = 8$). Direct carbonate ^{14}C analysis of NAU’s C1 blank yields 2.16 ± 0.42 pMC ($n = 22$) using Fe and 1.49 ± 0.67 pMC ($n = 115$) using Nb powder. Our direct carbonate blank results are similar to Hua et al. (2019) who demonstrated that Nb powder yields cleaner blanks than either Fe or Ag powders. The source of the direct carbonate ^{14}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 CO₂ over several years (Gagnon and Jones, 1993) but it also rapidly adsorbs CO₂
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 N₂ 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 ¹⁴C-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 N₂ 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 CO₂ during
221 processing is a significant source of contamination, unless it occurs almost instantaneously upon
222 powdering. As standard practice, all direct carbonate ¹⁴C blanks and standards processed at NAU
223 are pressed into targets on the same day they are powdered. Unknowns are powdered, stored
224 under N₂, 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 CO₂.

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” (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}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; Burlingame, 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

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

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

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

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

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

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

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

The reason for the positively skewed differences (Fig. 2A, Fig. 2B) and for why the two metal powders perform differently is unclear. One potential explanation is the adsorption of young atmospheric CO_2 during the powdering process (e.g., Kosnik et al., 2017). However, adsorption of CO_2 reasonably should affect all of the biomineral powders similarly, and not show a preference for the samples using Fe powder. Kosnik et al. (2017) suggested that perhaps the blank (marble) powder adsorbs CO_2 less efficiently than the biomineral powders, which would lead to excess adsorbed atmospheric CO_2 influence on biomineral pMC after blank subtraction. A blank under-correction of this sort should also affect the carbonate powders mixed with both metals similarly, rather than preferentially affecting the carbonate powders mixed with Fe (Figs. 2B and 2C). Finally, we did not detect any adverse adsorption of atmospheric CO_2 in our blank marble powder or on ^{14}C -dead mollusk shell powder after storage under N_2 for up to 9 days (see previous discussion of blank performance). Thus, adsorption of CO_2 during powdering does not adequately explain the higher tendency for positive differences when using Fe powder (Fig. 2B). It is conceivable that the more equitable differences using Nb powder (Fig. 2C) is related to the

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

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

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

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

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

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

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

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

CONCLUSIONS

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

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

ACKNOWLEDGEMENTS

This study is a collaboration between the Amino Acid Geochronology Laboratory and the Center for Ecosystem Science and Society at Northern Arizona University, the Keck Carbon Cycle AMS Laboratory at the University of California-Irvine, and the Australian Nuclear Science and Technology Organisation.

This work is supported by grants NSF-1855381 (DSK), EAR-1559196 (DS), FONDECYT 3170913 (CF), FONDECYT 3160342 (JCM), FONDECYT 1140841, 1181300 and 1191452 (MMR), IODP/CAPES-091727/2014, and CNPq/MCTI-422766/2018-6 (MNR), EAR-1559196 (MK), NSF-1802153 (YY), and NSF-GRFP-1610397 (WGP). We thank Dan Cameron, Kathryn Geyer, and Aibhlin Ryan (NAU) for assisting with the direct carbonate ^{14}C samples. We thank

Jenny E. Ross for providing the *R. lecontei* shell from the Brawley Formation, and both Austin Hendy (Natural History Museum of Los Angeles County) and Charles L. Powell, II, for assistance with the taxonomic references. Thoughtful comments from the Associate Editor Pieter Grootes and two anonymous reviewers greatly improved this manuscript.

REFERENCES

Agassiz L. 1841. Monographies d'Echinodermes vivans et fossiles. Échinites. Famille des Clypeasteroides. 2 (Seconde Monographie). Des Scutelles. Neuchâtel, Switzerland, i-iv, 1-151, pls 1-27.

Albano PG, Hua Q, Kaufman DS, Tomašových A, Zuschin M, Agiadi K. 2020. Radiocarbon dating supports bivalve-fish age coupling along a bathymetric gradient in high-resolution paleoenvironmental studies. *Geology* 48:589-593, doi:10.1130/G47210.1.

Berger R, Fergusson GJ, Libby WF, 1965. UCLA radiocarbon dates IV*. *Radiocarbon* 7:336-371, doi:10.1017/S0033822200037310.

Born I. 1778. Index rerum naturalium Musei Cæsarei Vindobonensis. Pars I.ma. Testacea. Verzeichniß der natürlichen Seltenheiten des k. k. Naturalien Cabinets zu Wien. Erster Theil. Schalthiere. [1-40], 1-458, [1-82]. Vindobonae; (Kraus).

- 479 Burleigh R. 1983. Two radiocarbon dates for freshwater shells from Hierakonpolis:
480 Archaeological and geological implications. *Journal of Archaeological Science* 10:361-367,
481 doi:10.1016/0305-4403(83)90074-2.
- 482
- 483 Bush SL, Santos GM, Xu X, Southon JR, Thiagarajan N, Hines SK, Adkins JF. 2013. Simple,
484 rapid, and cost effective: a screening method for ^{14}C analysis of small carbonate samples.
485 *Radiocarbon* 55:631-640, doi:10.1017/S0033822200057787.
- 486
- 487 Conrad TA. 1853. Descriptions of new fossils shells of the United States. *Journal of the*
488 *Academy of Natural Sciences of Philadelphia* 2:273-276.
- 489
- 490 Cuif J-P, Dauphin Y, Berthet P, Jegoudez J. 2004. Associated water and organic compounds in
491 coral skeletons: Quantitative thermogravimetry coupled to infrared absorption spectrometry.
492 *Geochemistry, Geophysics, Geosystems* 5, Q11011, doi:10.1029/2004GC000783.
- 493
- 494 Cusack M, Parkinson D, Freer A, Perez-Huerta A, Fallick AE, Curry BB. 2008. Oxygen isotope
495 composition of *Modiolus modiolus* aragonite in the context of biological and crystallographic
496 control. *Mineralogical Magazine* 72:569-577.
- 497
- 498 d'Orbigny AD. 1834-1847. Voyage dans l'Amérique méridionale (le Brésil, la République
499 orientale de l'Uruguay, la République Argentine, la Patagonie, la République du Chili, la
500 République de Bolivia, la République du Pérou), exécuté pendant les années 1826, 1827, 1828,
501 1829, 1830, 1831, 1832 et 1833, 5(3):Mollusques: i-xliii, 1-758, lám 1-85. Paris/Estrasburgo.

502
503 d' Orbigny AD. 1839-1842. Mollusques, Echinodermes, Foraminifères et Polypiers recueillis
504 aux Iles Canaries par MM. Webb et Berthelot et décrits par Alcide d'Orbigny. Mollusques. 117
505 p., pl. 1-7, 7B (p. 1-24 [Aug. 1839], 25-48 [Sept. 1839], 49-72 [Oct-1839], 73-104 [Jan. 1840],
506 105-136 [Mar. 1840], 137-143 [Apr. 1840], 145-152 [Aug. 1842] pl. 1 [Jul. 1836], 2 [Dec. 1836],
507 3 [May 1842], 4-5 [June 1840], 7 [May 1842], 6, 7B [Aug. 1842]. Béthune, Paris.

508
509 Deshayes, GP, Milne-Edwards H. 1835. Histoire Naturelle des Animaux sans Vertèbres,
510 présentant les caractères généraux et particuliers de ces animaux, leur distribution, leurs classes,
511 leurs familles, leurs genres, et la citation des principales espèces qui s'y rapportent, par J.B.P.A.
512 de Lamarck. Deuxième édition, Tome sixième. Histoire des Mollusques. iv + 600 pp. J. B.
513 Baillièrre: Paris.

514
515 Dominguez JG, Kosnik MA, Allen AP, Hua Q, Jacob DE, Kaufman DS, Whitacre K. 2016.
516 Time-averaging and stratigraphic resolution in death assemblages and Holocene deposits:
517 Sydney Harbour's molluscan record. *Palaios* 31:564-575, doi:10.2110/palo.2015.087.

518
519 Donahue DJ, Linick TW, Jull AJ. 1990. Isotope-ratio and background corrections for accelerator
520 mass spectrometry radiocarbon measurements. *Radiocarbon* 32:135-142,
521 doi:10.1017/S00338222000040121.

522
523 Dubois, P. 2014. Calcification in echinoderms. In: Jangoux M, Lawrence JM, editors.
524 Echinoderm Studies 3. Rotterdam: Balkema. p. 109-178.

- 525
- 526 Fenger T, Surge D, Schone B, Milner N. 2007. Sclerochronology and geochemical variation in
527 limpet shells (*Patella vulgate*): A new archive to reconstruct coastal sea surface temperature.
528 Geochemistry Geophysics GeoSystems 8, Q07001, doi:10.1029/2006GC001488.
- 529
- 530 Flores, C., Gayo, E.M., Salazar, D., Broitman, B.R. 2018. $\delta^{18}\text{O}$ of *Fissurella maxima* as a proxy
531 for reconstructing Early Holocene sea surface temperatures in the coastal Atacama desert (25°S).
532 Palaeogeography, Palaeoclimatology, Palaeoecology 499:22-34,
533 doi:10.1016/j.palaeo.2018.03.031.
- 534
- 535 Fremy ME. 1855. Recherches chimiques sure les os. Annales de Chimie et de Physique 43:47-
536 107.
- 537
- 538 Gagnon AR, Jones GA. 1993. AMS-graphite target production methods at the Woods Hole
539 Oceanographic Institution during 1986-1991. Radiocarbon 35:301-310,
540 doi:10.1017/S0033822200064985.
- 541
- 542 Galstoff PS. 1964. The American Oyster *Crassostrea virginica* Gmelin. Fishery Bulletin of the
543 U.S. Fish and Wildlife Service 64, 480 p.
- 544
- 545 Gmelin JF. 1791. Vermes. In: Gmelin JF. (Ed.) Caroli a Linnaei Systema Naturae per Regna Tria
546 Naturae, Ed. 13. Tome 1(6). G.E. Beer, Lipsiae [Leipzig]. pp. 3021-3910.
- 547

- 548 Goetz AJ, Steinmetz DR, Griesshaber E, Zaefferer S, Raabe D, Kelm K, Irsen S, Sehrbrock A,
549 Schmahl WW. 2011. Interdigitating biocalcite dendrites for a 3-D jigsaw structure in brachiopod
550 shells. *Acta Biomaterialia* 7:2237-2243, doi:10.1016/j.actbio.2011.01.035.
551
- 552 Grothe PR, Cobb KM, Bush SL, Cheng H, Santos G.M, Southon JR, Edwards RL, Deocampo
553 DM, Sayani HR. 2016. A comparison of U/Th and rapid-screen ^{14}C dates from Line Island fossil
554 corals. *Geochemistry, Geophysics, Geosystems* 17:833-845, doi:10.1002/2015GC005893.
555
- 556 Hadden CS, Loftis KM, Cherkinsky A. 2018. Carbon isotopes ($\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$) in shell
557 carbonate, conchiolin, and soft tissues in eastern oyster (*Crassostrea virginica*). *Radiocarbon*
558 60:1125-1137, doi:10.1017/RDC.2018.27.
559
- 560 Hadden, CS, Loftis KM, Cherinsky A, Ritchison BT, Lulewicz IH, Thompson, VD. 2019.
561 Radiocarbon in the marsh periwinkle (*Littorina irrorata*) conchiolin: applications for
562 archaeology. *Radiocarbon* 61:1489-1500, doi:10.1077/RDC.2019.53.
563
- 564 Hammer Ø, Harper DAT, Ryan PD. 2001. PAST: Paleontological statistics software package for
565 education and data analysis. *Palaeontologia Electronica* v. 4, no. 1, 9 pp.
566 http://palaeo-electronica.org/2001_1/past/issue1_01.htm. Accessed version 4.03, June 30, 2020.
567
- 568 Haynes CV, Jr, Mead AR. 1987. Radiocarbon dating and paleoclimatic significance of subfossil
569 Limicolaria in northwestern Sudan. *Quaternary Research* 28:86-99,
570 doi:10.1016/0033-5894(87)90035-4.

- 571
572 Hua Q, Lavchenko VA, Kosnik MA. 2019. Direct AMS ^{14}C analysis of carbonate. Radiocarbon
573 61:1431-1440, doi:10.1017/RDC.2019.24.
574
575 Jones CA. 2010. Mineralogy and seasonal growth of south Pacific mussel valves [MS thesis].
576 The University of Alabama, Tuscaloosa, Alabama, 73 pp.
577
578 Keith J, Stockwell S, Ball D, Remillard K, Kaplan D, Thannhauser T, Sherwood R. 1993.
579 Comparative analysis of macromolecules in mollusc shells. Comparative Biochemistry and
580 Physiology B 105:578-496, doi:10.1016/0305-0491(93)90078-J.
581
582 Kennedy WJ, Taylor JD, Hall A. 1969. Environmental and biological controls on bivalve shell
583 mineralogy. Biological Review 44:499-530.
584
585 King PP. 1832. Description of the Cirrhipeda, Conchifera and Mollusca, in a collection formed
586 by the officers of H.M.S. Adventure and Beagle employed between the years 1826 and 1830 in
587 surveying the southern coasts of South America, including the Straits of Magalhaens and the
588 coast of Tierra del Fuego. Zoological Journal 5: 332-349.
589
590 Kirby SM, Janecke SU, Dorsey RJ, Housen BA, Langenheim VE, McDougall KA, Steely AN.
591 2007. Pleistocene Brawley and Ocotillo Formations: Evidence for initial strike-slip deformation
592 along the San Felipe and San Jacinto Fault Zone, southern California. The Journal of Geology
593 115:43-62, doi:10.1086/509248.

- 594
- 595 Kosnik MA, Hua Q, Kaufman DS, Kowalewski M, Whitacre K. 2017. Radiocarbon-calibrated
596 amino acid racemization ages from Holocene sand dollars (*Peronella peronii*). Quaternary
597 Geochronology 39:174-188, doi:10.1016/j.quageo.2016.12.001.
- 598
- 599 Kowalewski M, Casebolt S, Hua Q, Whitacre KE, Kaufman DS, Kosnik MA. 2018. One fossil
600 record, multiple time resolutions: Disparate time-averaging of echinoids and mollusks in a
601 Holocene carbonate platform. Geology 46:51-54, doi:10.1130/G39789.1.
- 602
- 603 Lamarck J-BM de. 1819. Histoire naturelle des animaux sans vertèbres. Tome sixième, 1re
604 partie. Paris: published by the Author, vi + 343 pp.
- 605
- 606 Leske NG. 1778. Additamenta ad Jacobi Theodori Klein Naturalem Dispositionem
607 Echinodermatum et Lucubrationum de Aculeis Echinorum Marinorum. 216p.
- 608
- 609 Linnaeus C. 1758. Systema Naturae per regna tria naturae, secundum classes, ordines, genera,
610 species, cum characteribus, differentiis, synonymis, locis. Editio decima, reformata [10th revised
611 edition], vol. 1: 824 pp. Laurentius Salvius: Holmiae.
- 612
- 613 Linnaeus C. 1767. Systema naturae per regna tria naturae: secundum classes, ordines, genera,
614 species, cum characteribus, differentiis, synonymis, locis. Ed. 12. 1., Regnum Animale. 1 & 2.

615 Holmiae, Laurentii Salvii. Holmiae [Stockholm], Laurentii Salvii. pp. 1-532 [1766] pp. 533-1327
616 [1767].

617

618 Longworth BE, Robinson LF, Roberts ML, Beaupre SR, Burke A, Jenkins WJ. 2013. Carbonate
619 as a sputter target material for rapid ^{14}C AMS. Nuclear Instruments and Methods in Physics
620 Research B 294:328-334, doi:10.1016/j.nimb.2012.05.014.

621

622 Masters PM, Bada JL. 1977. Racemization of isoleucine in fossil molluscs from Indian middens
623 and interglacial terraces in southern California. Earth and Planetary Science Letters 37:173-183,
624 doi:10.1016/0012-821X(77)90162-5.

625

626 Molina DJI. 1782. Compendio de la historia geografica natural y civil del Reyno de Chile.
627 Primera parte. Madrid. 418 pp.

628

629 New E, Yanes Y, Cameron RAD, Miller JH, Teixeira D, Kaufman DS. 2019. Aminochronology
630 and time averaging of Quaternary land snail assemblages from colluvial deposits in the Madeira
631 Archipelago, Portugal. Quaternary Research 92:483-496, doi:10.1017/qua.2019.1.

632

633 Nielsen JK, Helama S, Rodland D, Nielsen JK. 2007. Eemian marine mollusks and barnacles
634 from Ristinge Klint, Denmark: hydrodynamics and deficiency. Netherlands Journal of
635 Geoscience 86:95-115.

636

- 637 Oakley DOS, Kaufman DS, Gardner TW, Fisher DM, VanderLeest RA. 2017. Quaternary
638 marine terrace chronology, North Canterbury, New Zealand, using amino acid racemization and
639 infrared-stimulated luminescence. *Quaternary Research* 87:151-167, doi:10.1017/qua.2016.9.
640
- 641 Olivi G. 1792. *Zoologia Adriatica, ossia catalogo ragionato degli animali del golfo e della lagune*
642 *di Venezia*. Bassano [G. Remondini e fl.]. [ix] + 334 + xxxii pp., 9 pls.
643
- 644 Parker WG, Yanes Y, Hernández EM, Hernández Marreno JC, Paris J, Surge D. 2019. Scale of
645 time-averaging in archaeological shell middens from the Canary Islands. *The Holocene* 1-14,
646 doi:10.1177/0959683619883020.
647
- 648 Paul D, Mauldin R. 2013. Implications for Late Holocene climate from stable carbon and oxygen
649 isotopic variability in soil and land snail shells from archaeological site 41KM69 in Texas, USA.
650 *Quaternary International* 308-309:242-252, doi:10.1016/j.quaint.2012.08.006.
651
- 652 Quinn GP, Keough MJ. 2002. *Experimental design and data analysis for biologists*. Cambridge
653 University Press, Cambridge, UK. 537 pp.
654
- 655 Reeve LA. 1850. Monograph of the genus *Artemis* . pp. pls 1-10 in Reeve LA. *Conchologia*
656 *Iconica*. London : L. Reeve & Co. Vol.6.
657

- 658 Ritter MN, Erthal F, Kosnik MA, Coimbra JC, Kaufman DS. 2017. Spatial variation in the
659 temporal resolution of subtropical shallow-water molluscan death assemblages. *Palaaios* 32:572-
660 583, doi:10.2110/palo.2017.003.
- 661
- 662 Roger LM, George, AD, Shaw J, Hart, RD, Roberts M, Becker T, McDonald BJ, Evans, NJ.
663 2017. Geochemical and microstructural characterization of two species of cool-water bivalves
664 (*Fulvia tenuicostata* and *Soletellina biradiata*) from Western Australia. *Biogeosciences* 14:1721-
665 1737, doi:10.5194/bg-14-1721-2017.
- 666
- 667 Rozanski K, Stichler W, Gofiantini R, Scott EM, Beukens RP, Kromer B, Van Der Plicht J.
668 1992. The IAEA ^{14}C Intercomparison Exercise 1990. *Radiocarbon* 34:506-519,
669 doi:10.17/S0033822200063761.
- 670
- 671 Say T. 1818. Account of two new genera, and several new species, of fresh water and land
672 snails. *Journal of the Academy of Natural Sciences of Philadelphia* 1: 276-284.
- 673
- 674 Smith RJ. 2009. Use and misuse of the reduced major axis for line-fitting. *American Journal of*
675 *Physical Anthropology* 140:476-486, doi:10.1002/ajpa.21090.
- 676
- 677 Smith AM, Hua Q, Williams A, Levchenko V, Yang B. 2010. Developments in micro-sample
678 ^{14}C AMS at the ANTARES AMS facility. *Nuclear Instruments and Methods in Physics Research*
679 *B* 238:919-912, doi:10.1016/j.nimb.2009.10.064.
- 680

- 681 Southon J, Santos GM. 2007. Life with MC-SNICS. Part II: Further ion source development at
682 the Keck Carbon Cycle AMS Facility. *Nuclear Instruments and Methods in Physics Research B*
683 259:88-93, doi:10.1016/j.nimb.2007.01.147.
- 684
- 685 Sowerby, GB, I. 1824. Descriptions, accompanied by figures, of several Helices, discovered by
686 T. E. Bowdich, Esq. at Porto Santo. *Zoological Journal* 1: 56-58 [March].
- 687
- 688 Sowerby GB., I; Sowerby, GB, II. 1832-1841. The conchological illustrations or, Coloured
689 figures of all the hitherto unfigured recent shells. London, privately published.
- 690
- 691 Stuvier M, Polach HA. 1977. Discussion reporting of ^{14}C data. *Radiocarbon* 19:355-363,
692 doi:10.1017/S0033822200003672.
- 693
- 694 Tschudin P. 2001. Shell morphology, shell texture and species discrimination of Caribbean
695 *Tucetona* (Bivalvia, Gylcymeridae). *Journal of Paleontology* 75:658-679.
- 696
- 697 Vogel, JS, Southon, JR, Nelson, DE, Brown, TA. 1984. Performance of catalytically condensed
698 carbon for use in accelerator mass spectrometry. *Nuclear Instruments and Methods in Physics*
699 *Research* 223:289-293.
- 700
- 701 Yanes Y, Al-Qattan NM, Rech JA, Pigati JS, Dodd JP, Nedila JC. 2019. Overview of the oxygen
702 isotope systematics of land snails from North America. *Quaternary Research* 91:329-344,
703 doi:10.1017/qua.2018.79.

704

705 Zhang C, Zhang R. 2006. Matrix proteins in the outer shells of Molluscs. *Marine Biotechnology*
706 8:572-586, doi:10.1007/s10126-005-6029-6.

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”.

723

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

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

For Peer Review

Table 1 Detailed breakdown of the taxa, generalized biological group, carbonate polymorph, standard graphite pMC values, direct carbonate metal powder, and absolute pMC value of individual differences that exclude 0 at 95% CI.

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 ^a	28.3	Nb	0.08
<i>Fissurella maxima</i>	limpet	mixed ^a	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 ^a	77.2	Nb	0.25
<i>Patella candei</i>	limpet	mixed ^a	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

^a “mixed” refers to shells that contain both calcite and aragonite polymorphs.

Table 2 Summary of the taxa, sample size (n), generalized biological group, carbonate polymorph, number of differences that include 0 at 95% CI, and publication information for samples featured in this study.

Taxon	n	Group	Polymorph	Residuals include 0	Reference
<i>Actinella nitidiuscula</i>	6 ^a	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 ^b	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 ^b	8/10	this study
<i>Fulvia tenuicostata</i>	8	cockle	mixed ^b	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 ^a	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 ^b	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)

^a Two analyses of *Actinella nitidiuscula* and one analysis of *Mactra isabelleana* yield widely different direct carbonate and graphite pMC values and are excluded from discussion and statistical analysis. See Supplemental Information.

^b “mixed” refers to shells that contain both calcite and aragonite polymorphs.





