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RESEARCH ARTICLE

Comparing MICADAS gas source, direct carbonate, and standard graphite ^{14}C determinations of biogenic carbonate

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Abstract

Northern Arizona University, Flagstaff, Arizona, USA, recently installed a MIni CArbon DAting System (MICADAS) with a gas interface system (GIS) for determining the ^{14}C content of CO_2 gas released by the acid dissolution of biogenic carbonates. We compare 48 paired graphite, GIS, and direct carbonate ^{14}C determinations of individual mollusk shells and echinoid tests. GIS sample sizes ranged between 0.5 and 1.5 mg and span 0.1 to 45.1 ka BP ($n = 42$). A reduced major axis regression shows a strong relationship between GIS and graphite percent Modern Carbon (pMC) values ($m = 1.011$; 95% CI [0.997–1.023], $R^2 = 0.999$) that is superior to the relationship between the direct carbonate and graphite values ($m = 0.978$; 95% CI [0.959-0.999], $R^2 = 0.997$). Sixty percent of GIS pMC values are within ±0.5 pMC of their graphite counterparts, compared to 26% of direct carbonate pMC values. The precision of GIS analyses is approximately ±70 ^{14}C yrs to 6.5 ka BP and decreases to approximately ±130 ^{14}C yrs at 12.5 ka BP. This precision is on par with direct carbonate and is approximately five times larger than for graphite. Six Plio-Pleistocene mollusk and echinoid samples yield finite ages when analyzed as direct carbonate but yield non-finite ages when analyzed as graphite or as GIS. Our results show that GIS ^{14}C dating of biogenic carbonates is preferable to direct carbonate ^{14}C dating and is an efficient alternative to standard graphite ^{14}C dating when the precision of graphite ^{14}C dating is not required.

Introduction

The ability to rapidly measure the ^{14}C content of sub-milligram quantities of biogenic carbonate without conversion to graphite has risen in popularity over the past decade (e.g., Lougheed et al. 2012, 2018; Bush et al. 2013; Longworth et al. 2013; Wacker et al. 2013a, 2013b; Dominguez et al. 2016; Kosnik et al. 2017; Ritter et al. 2017, 2023; Gottschalk et al. 2018; Kowalewski et al. 2018; Tuna et al. 2018; Fagault et al. 2019; Lindauer et al. 2019; New et al. 2019; Parker et al. 2019; Albano et al. 2020, 2023a, 2023b; Missiaen et al. 2020; Dolman et al. 2021; Mollenhauer et al. 2021; Nawrot et al. 2022; Sanchez et al. 2022; Steger et al. 2022). Dating small carbonate samples has become increasingly popular in time averaging or population structure studies (e.g., Kowalewski et al. 2018; Nawrot et al. 2022; Ritter et al. 2023) and in the field of marine geochronology where a few dozen or even single large foraminifera can be dated (e.g., Lougheed et al. 2018; Mollenhauer et al. 2021). Two rapid ^{14}C methods are currently employed: direct carbonate and gas ion source (GIS). The direct carbonate method produces carbon ions (C^-) by directly sputtering powdered carbonate and metal binder (typically iron or niobium) mixtures with cesium atoms (Bush et al. 2013; Longworth et al. 2013; Hua et al. 2019). Alternatively, C- ions are produced by the GIS method through the acid dissolution of carbonate and then sputtering the released CO_2 gas with cesium atoms in the presence of titanium (Middleton 1984; Bronk and Hedges 1987). The GIS method has become increasingly popular with the development of the MIni CArbon DAting System (MICADAS) (Synal et al. 2007) coupled with a carbonate handling system (CHS) inlet to the GIS (Ruff et al. 2007, 2010; Wacker et al. 2013a; Lindauer et al. 2019).

The Arizona Climate and Ecosystems (ACE) Isotope Laboratory at Northern Arizona University (NAU) brought a MICADAS system online in June 2021 (Ebert et al. 2022). The ACE Lab includes elemental analyzers, a GIS, a CHS, and both automated graphitization equipment (AGE) and a manual cryogenic purification line.

This report compares the percent Modern Carbon (pMC) values and analytical precision from 48 samples of biogenic carbonate each analyzed as graphite, GIS, and as direct carbonate. The primary goal of our study is to compare the accuracy and reproducibility of carbonate pMC values from NAU's MICADAS and GIS system against standard graphite and direct carbonate analyses.

Materials and Methods

This study features predominantly mollusk shells and fewer echinoid tests. Several of the standard graphite and direct carbonate analyses were included in an earlier study published prior to the arrival of the MICADAS at NAU (Bright et al. 2021). The compilation featured here comprises pMC values ranging from approximately 99 to 0.4 (radiocarbon ages approximately 0.1 to 45.1 ka BP), based on prior AMS analysis of samples archived at NAU (Bright et al. 2021). To fill in gaps in this dataset, new graphite and direct carbonate powders were processed and analyzed at NAU or at the W.M. Keck Carbon Cycle Accelerator Mass Spectrometer Facility at the University of California – Irvine (UCI), respectively. To obtain equivalent subsamples for the three analyses, each mollusk shell and echinoid test was sampled parallel to growth bands and/or sub-adjacent to each other. This approach minimizes the risk of sampling different aged shell material. For example, some mollusks are slow growing and can live for several hundred years (Moss et al. 2016).

All samples were sonicated briefly to remove loose debris before being exposed to ACS grade 2N hydrochloric acid which removed 30% of their mass. The leaching process was considered complete when effervescence stopped. All samples were rinsed three times with deionized reverse osmosis water (16.7 Mohm*cm) before being dried at 50°C in a convection oven.

Carbonate samples (0.5–1.5 mg; 60–180 µg C) destined for GIS ^{14}C analysis were placed in baked (3 hr at 500° C) glass reaction vials sealed with screw-top caps containing a rubber septum (Exetainer #VW101). The vials were flushed with N_2 gas and sealed until analyzed. The CHS automatically flushes each vial with helium using a double-walled needle, after which 85% phosphoric acid is injected to dissolve the shell material. The evolved CO_2 is carried by helium through a water trap and then to the zeolite trap of the GIS. The CO_2 is released from the zeolite at 450°C and transferred to a syringe where it is mixed with helium to a final CO_2 concentration of 5% by volume, after which it is injected into the ion source. The zeolite trap is optimized for 80–100 µg C (Ruff et al. 2010), which is equivalent to about 0.6–0.8 mg of calcium carbonate. Excess carbon is not analyzed. Detailed description of the MICADAS GIS and CHS analytical method is provided in Synal et al. (2007) and Ruff et al. (2007, 2010).

Ten new samples (0.3–0.5 mg; 36–60 µg C) for direct carbonate AMS analyses at UCI were manually ground to a fine powder with an agate mortar and pestle. The powdered shell was mixed with 6 to 7 mg of niobium powder (Alfa Aesar Puratronic, –325 mesh, 99.99%) in baked (3 hr at 500°C) Kimble borosilicate glass culture tubes (6 mm OD × 50 mm), flushed with nitrogen gas, and capped

Table 1. *Mean pMC values for reference material (IAEA) and laboratory standards analyzed at Northern Arizona University ACE lab. IAEA reference values are from Rozanski et al. (1992)*

Reference material	Reference pMC ± 1 stdev	Measured pMC ± 1 stdev Graphite (n) [outliers]	Measured pMC ± 1 stdev GIS (n) [outliers]
IAEA C1	0.00 ± 0.02	0.18 ± 0.04 (16) [3]	0.67 ± 0.33 (39) [0]
Tridacna	N.A.	0.22 ± 0.07 (9) [0]	0.52 ± 0.28 (33) [0]
IAEA C2	41.14 ± 0.03	40.61 ± 0.70 (20) [0]	41.16 ± 0.64** (89) [5]
CAHI* – graphite	94.44 ± 0.19	94.56 ± 0.34 (9) [0]	N.A.
CAHI* – GIS	93.94 ± 0.61	N.A.	94.42 ± 0.59** (75) [5]

N.A. – not applicable.

*Coral standard provided by UC-Irvine. Graphite reference value as cited in Mollenhauer et al. (2021) from 294 analyses performed at the Keck Carbon Cycle Radiocarbon Laboratory at UC-Irvine. GIS "reference" value is based on 47 analyses reported in Table 3 of Mollenhauer et al. (2021).

**Calibrated values.

with Supelco plastic column caps (1/4" OD) until the carbonate-niobium mixture was manually pressed into pre-drilled (4.1 mm depth) aluminum targets before being sent to UCI.

Thirteen new samples for graphite analysis (8-10 mg; 960–1200 µg C) at NAU were placed in baked (3 hr at 500°C) acid-washed glass vials sealed with rubber septa from BD Vacutainer® plastic collection tubes (No. 366704). Ambient atmosphere was removed via vacuum before a small-bore needle added approximately 0.8 mL of ACS grade 85% phosphoric acid to each vial. Vials were warmed in a heating block set to 70°C until the shell material entirely dissolved. The evolved gas was removed via vacuum on a manual cryogenic purification line. Water vapor was removed by passing the gas through a mixture of ethanol and liquid nitrogen at approximately –80°C. Carbon dioxide was condensed to a solid using a liquid nitrogen bath and the remaining gases were drawn off. The purified CO_2 was converted to graphite by reaction with iron powder (Alfa Aesar, -325 mesh, reduced 98%) in a hydrogen reducing environment at 550°C for 3 hr (Vogel et al. 1984). The graphite-iron mixture was packed into targets using an automated press before being loaded onto the MICADAS.

Radiocarbon (^{14}C) concentrations are reported as pMC following the conventions of Stuvier and Polach (1977). Sample preparation backgrounds have been subtracted based on measurements of ^{14}C-free calcite processed in the same fashion as the unknowns. All ^{14}C determinations have been corrected for isotopic fractionation according to the conventions of Stuvier and Polach (1977) with $\delta^{13}C$ values being measured on the AMS. These $\delta^{13}C$ values are superior when used to correct for fractionation but can differ from the actual value of the original material and are thus not reported. Machine performance was monitored by repeat analysis of the IAEA standards C1 (^{14}C-dead marble; consensus pMC = 0.00 ± 0.02; Rozanski et al. 1992) and C2 (travertine; consensus pMC = 41.14 ± 0.03; Rozanski et al. 1992), the CAHI coral standard provided by UCI (pMC = 94.44 ± 0.19; Mollenhauer et al. 2021), and a Pliocene ^{14}C-dead *Tridacna* shell provided by the Florida Museum of Natural History (specimen UF 143174) which accounts for possible matrix effects that the marble C1 blank might not. All GIS ^{14}C determinations of unknowns have been calibrated by assigning a blank pMC value of 0 and forcing the IAEA C2 travertine standard and the CAHI coral standard runs in the same batch through their consensus values (e.g., Gottschalk et al. 2018). The blank and standard compilations were analyzed using boxplot and whisker diagrams to identify outliers, which were removed, without iteration, from the mean and standard deviation calculations. The number of outliers is included in Table 1. Data from the MICADAS was processed using BATS software (version 4.0; Wacker et al. 2010). When reported, radiocarbon ages are uncalibrated years BP, without consideration of the marine reservoir effect, with BP meaning conventional radiocarbon years before AD 1950 (Stuvier and Polach 1977).

The relationship between GIS and graphite or direct carbonate and graphite pMC values was evaluated using a reduced major axis regression (RMA) analysis, which minimizes the residual variation across both the X- and Y-axes (Quinn and Keough 2002; Smith 2009). An RMA regression avoids assumptions about the dependent and independent variables between GIS and graphite or direct carbonate and graphite pMC values (Smith 2009). The PAST 4.13 statistical program (Hammer et al. 2001) was used for the RMA with 95% bootstrapped confidence intervals [n = 1999 replications]. The Akaike Information Criterion (AIC) (Akaike 1973; Cavanaugh and Neath 2019) using the R language version 4.3.1 (R Core Team 2023) and R package "rcompanion" version 2.4.30 (Mangiafico 2023) was used to compare the performance of the GIS versus graphite and direct carbonate versus graphite models. Scores were calculated by AIC = 2K – 2ln(L), where K is the number of model parameters and ln(L) is the log-likelihood of the model. The lowest AIC score is considered the better fit.

Results and Discussion

ACE Laboratory Blank (IAEA C1 and Pliocene **Tridacna** *Shell) and Holocene Standard (IAEA C2 and CAHI) Performance*

The quality of our carbonate ^{14}C determinations is monitored by repeat analysis of certified and internal reference blanks and standards (Table 1). The pMC values overlap published values at one standard deviation (Rozanski et al. 1992; Mollenhauer et al. 2021). At the ACE Lab, the C1 procedural blank yields graphite and GIS ages of 50.6 ± 1.9 and 40.2 ± 3.9 ka BP, respectively. The *Tridacna* procedural blank yields graphite and GIS ages of 49.2 ± 2.4 and 42.2 ± 4.3 ka BP, respectively.

GIS versus Graphite and Direct Carbonate versus Graphite FMC Determinations

There is considerable time savings when using the GIS method. Processing samples for the direct carbonate method requires manual powdering of the samples, followed by manual subsampling, weighing, and manipulation of that powder plus a metal binder into small borosilicate tubes. The powder and metal mixture is then carefully poured into manually drilled aluminum cathodes before being manually pressed into targets. In contrast, the GIS preparation method is more streamlined and only requires weighing the cleaned carbonate samples into glass reaction vials. Processing a shell for GIS analysis takes roughly half as much time as processing a shell for direct carbonate analysis. For example, an undergraduate worker typically produces a batch of 51 unknowns for direct carbonate analysis in approximately 12 hours. That same worker can produce a batch of 48 unknowns for GIS analysis in approximately five to six hours. Converting carbonate to graphite is more time consuming. It typically takes approximately three hours to process eight unknowns to where the purified CO_2 is converted to graphite.

Forty-one blank-corrected pMC values range from 98.68 to 20.51 (Supple. Info.), or spanning ^{14}C ages of approximately 0.1 to 12.6 ka BP. One mid-Pleistocene *Rangia* shell that yields measurable carbon was analyzed in triplicate using each of the three AMS methods. The triplicates were averaged into a single value for each method to provide a lower limit to the compilation at a pMC value of approximately 0.36 (Supple. Info.), or approximately 45.1 ka BP. Six additional ^{14}C-dead mollusk and echinoid samples were analyzed using each AMS method to determine and compare the limits of detection (Supple. Info.).

The RMA regression of the graphite versus GIS pMC values yields a slope with a 95% confidence interval that includes 1.000 (Figure 1; Table 2), which outperforms the RMA regression of the graphite versus direct carbonate values (Figure 1; Table 2). The RMA regression of graphite versus GIS and graphite versus direct carbonate yield slopes that are statistically indistinguishable from each other (p-value same slope = 0.003). Analyzing the graphite versus GIS and graphite versus direct carbonate data as linear regressions using AIC, where graphite pMC values are the dependent variable, yields a lower AIC score for graphite versus GIS (102.5) than for graphite versus direct carbonate (147.2). The lower AIC score indicates that graphite values are better explained by a model in which GIS values are the predictor than a model in which direct carbonate values are the predictor (Akaike 1973; Cavanaugh and Neath 2019).

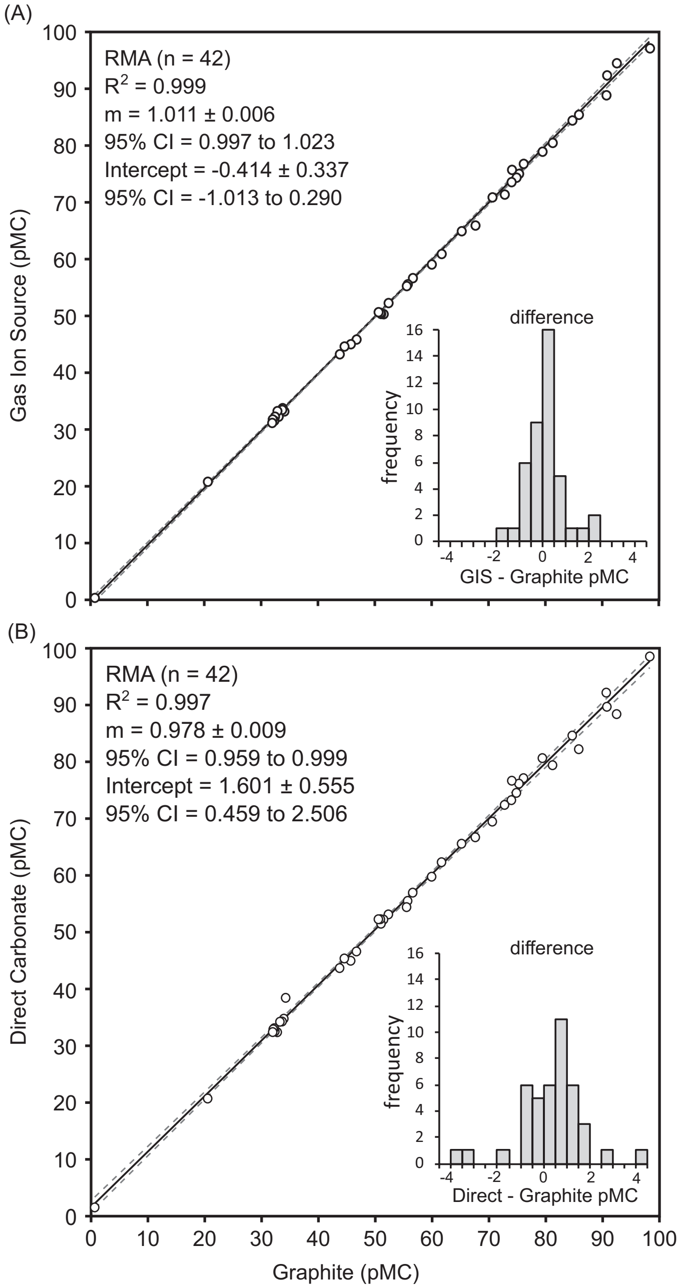

Figure 1. Reduced major axis (RMA) regression of paired rapid and graphite pMC determinations of biogenic carbonate. A – relationship between gas ion source (GIS) and graphite. B – relationship between direct carbonate and graphite. Analysis performed using PAST 4.13 statistical software (Hammer et al. 2001). Fine dashed lines are 95% bootstrapped confidence intervals (n = 1999). Inset diagrams are frequency histograms of pMC differences, calculated as “GIS – graphite pMC” in A and “direct – graphite pMC” in B.

Table 2. *Comparison of reduced major axis regression (RMA) of paired graphite and gas interface (GIS) or graphite and direct carbonate pMC determinations*

Comparison (n)	RMA slope ± 1 stdev [95% CI]	RMA y-intercept ± 1 stdev [95% CI]	R^2
Graphite-GIS (42)[*]	1.011 ± 0.006 [0.997 to 1.023]	–0.415 ± 0.337 [–1.016 to 0.290]	0.999
Graphite-GIS (42)[*,**]	1.005 ± 0.006 [0.990 to 1.018]	–0.431 ± 0.337 [–1.038 to 0.257]	0.999
Graphite-Direct (42)[*]	0.978 ± 0.009 [0.959 to 0.999]	1.601 ± 0.555 [0.459 to 2.506]	0.997
Graphite-Direct (150)[†]	0.996 ± 0.003 [0.991 to 1.001]	0.42 ± 0.18 [0.15 to 0.0.67]	0.999
Graphite-GIS (30)[‡]	1.023 ± 0.021 [0.988 to 1.057]	–1.282 ± 0.944 [–2.294 to 0.101]	0.988
Graphite-GIS (9)[§]	0.955 ± 0.022 [0.852 to 0.989]	0.790 ± 0.582 [0.188 to 3.857]	0.996

[*] This study.

[**] Uncalibrated. Not normalized using a blank pMC value of 0.00 and IAEA C2 and UCI CAHI consensus values.

[†] Bright et al. (2021).

[‡] Missiaen et al. (2020). Radiocarbon ages converted to pMC using the equation $\mathrm{pMC} = (e^{^{14}\mathrm{C\ yr}/-8033}) \times 100$.

[§] Wacker et al. (2013b).

An alternative method of data reduction that does not calibrate the unknown pMC values by forcing the IAEA C2 and CAHI standards in each batch through their consensus values does not appreciably change the outcome of the RMA comparison (Table 2). We conclude that GIS outperforms direct carbonate ^{14}C determinations, acknowledging the relatively small number of paired analyses ($n = 42$) used in this comparison.

A larger study of 150 graphite versus direct carbonate pairs of mollusk, echinoid, and brachiopod carbonate yielded results that are more comparable to the graphite versus GIS comparison presented here (Table 2) (Bright et al. 2021). The RMA regression slope of graphite versus direct carbonate data in Bright et al. (2021) and the graphite versus GIS regression slope in this study are not statistically distinguishable ($p\text{-value} = 0.167$). Additional comparisons using foraminifera have shown that graphite and GIS analyses also yield comparable results (Table 2) (Wacker et al. 2013b; Gottschalk et al. 2018; Missiaen et al. 2020). Our mollusk and echinoid graphite versus GIS comparison yields slightly better results than the foraminifera comparisons, which we suspect reflects true age heterogeneity within the collections of analyzed foraminifera tests, which can be prone to mixing and reworking in some environments (Fagault et al. 2019; Dolman et al. 2021). Mollusk shells and echinoid tests have the advantage of being large enough to routinely date single specimens (e.g., Scarponi et al. 2013; Harnik et al. 2017; Kowalewski et al. 2018; Nawrot et al. 2022; Ritter et al. 2023) or individual growth lines (e.g., Lindauer et al. 2019; Towers 2022).

The accuracy of the GIS ^{14}C determinations outperforms the direct carbonate method when compared to graphite. Sixty percent (25/42) of the GIS determinations are within ±0.5 pMC of their graphite counterparts, compared to 26% (11/42) of the direct carbonate determinations (Figure 1). Furthermore, 86% (36/42) of the GIS determinations are within ±1.0 pMC of their graphite counterparts, compared to 67% (28/42) of the direct carbonate determinations (Figure 1). A larger study found that 39% (59/150) and 77% (116/150) of direct carbonate determinations were within ±0.5 pMC and ±1.0 pMC, respectively, of their graphite counterparts (Bright et al. 2021), indicating that GIS accuracy outperforms the direct carbonate method regardless of the number of samples analyzed. We suspect that part of the difference in performance is due to the smaller carbon content of the direct carbonate samples (36–60 μg C) compared to the GIS samples featured in this study (60–100 μg C), which may render the direct carbonate ^{14}C determinations more vulnerable to any contamination introduced during the powdering process or with the addition of the metal binder. In addition, the direct carbonate ^{14}C determinations were conducted over a roughly 5 yr span whereas most (38/42) of the GIS ^{14}C determinations were run in a single day (Supple. Info.), thus, direct carbonate ^{14}C measurements might have captured additional long-term variability in AMS performance. However, the average

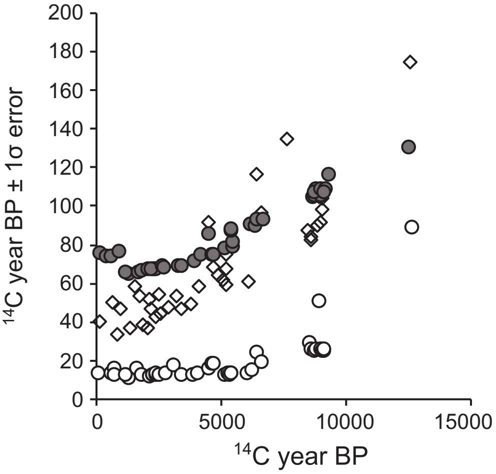

Figure 2. *Cross-plot comparing analytical precision as a function of ^{14}C age to 12.7 ka BP for gas ion source, direct carbonate, and graphite. White circles – graphite. Dark gray circles – gas ion source. White diamonds – direct carbonate.*

graphite and GIS pMC values over roughly two years of analysis for the IAEA C2 standard and the CAHI coral standard differ by 0.55 and 0.14 pMC, respectively (Table 1), suggesting the typically small differences between graphite and GIS pMC values measured in this study are robust and are not necessarily a function of the short analytical timeframe for the GIS samples.

Graphite ^{14}C determinations have comparatively small, typically decadal-scale precision due in part to the long sputter times (approximately 75 minutes) and large number of carbon counts per analysis, which can be on the order of one million counts. In contrast, the GIS method analyzes a sample in roughly 15 minutes and generates a few thousand to a few tens of thousands of carbon counts, thus the lower precision is based on counting statistics. In our compilation, the GIS ages have precision on the order of ±60 to ±80 ^{14}C yrs back to about 6.5 ka BP. At around 9 ka BP, the precision decreases to about ±110 ^{14}C yrs, and decreases further to about ±130 ^{14}C yrs at 12.5 ka BP (Figure 2). The precision of the GIS is on par with that of the direct carbonate method and averages four to five times worse than graphite precision (Figure 2). Although the precision for the GIS and direct carbonate method both increase with age (Figure 2), the variation in the GIS precision (stdev = 17 ^{14}C years) is similar to that of graphite (stdev = 13 ^{14}C years), and both are better than for direct carbonate errors (stdev = 30 ^{14}C years). This is likely because the GIS and graphite methods spall C- ions from comparatively pure CO_2 gas and graphite sources, respectively, which promotes more homogenous ion formation conditions (e.g., Middleton 1984; Bronk and Hedges 1987), whereas the direct carbonate method spalls C- ions from a mixture of powdered calcium carbonate and metal binder.

Six Plio-Pleistocene carbonate samples, determined to be ^{14}C-dead by graphite analysis, yielded finite pMC values and 29.4 to 36.7 ka BP ages when analyzed using the direct carbonate method but yielded non-finite pMC values when analyzed by GIS (Supple. Info). Bush et al. (2013) also reported a direct carbonate result from an old coral sample that was approximately 6 ^{14}C kyr younger than the paired graphite result. They attributed the difference to a variety of issues, including extended storage (five years) of their carbonate materials between the graphite and direct carbonate analyses, modern contamination of the carbonate powder during processing, and heterogeneity in the carbonate sample. They concluded that lower beam currents and lower count rates, coupled with modern contamination of the carbonate powders during processing led to less favorable results on samples with ages over 30 ka BP. In our study, there is a six-year difference between the direct carbonate analyses of the six ^{14}C-dead samples and their graphite counterparts, whereas the GIS counterparts were processed five months after the graphite analyses. Thus, the more similar GIS and graphite pMC results on the ^{14}C-dead shells could also be a function of reduced sampling time between the two analyses, as proposed by Bush et al. (2013). The IAEA C1 blank yielded a pMC value of 0.67 ± 0.33 ($n = 39$) when run by GIS at ACE, whereas 188 direct carbonate analyses of IAEA C1 processed at ACE and analyzed at UCI between 2017 and 2021 yielded a pMC value of 1.67 ± 0.69. We suspect that the poorer performance of the direct carbonate analyses results from carbon contamination during powdering and the addition of a metal binder that is known to contain some carbon (Bush et al. 2013; Hua et al. 2019). Similarly, 142 direct carbonate analyses of the IAEA C2 standard processed at ACE and analyzed at UCI between 2017 and 2021 yielded a pMC value of 40.81 ± 0.63, whereas 89 GIS analyses of C2 analyzed at ACE over the past two years yielded a pMC value of 41.16 ± 0.64 (Table 2). The two mean values are statistically distinguishable at a 95% confidence interval ($p\text{-value} = 6 \times 10^{-5}$) and the GIS average falls closer to the consensus value of 41.14 ± 0.03 (Rozanski et al. 1992).

Thus, collectively, we conclude that the GIS method is superior to the direct carbonate method, especially when it comes to older samples (e.g., > 20 ka BP).

Conclusions

This study compared 42 samples of biogenic carbonate (mollusk shells and echinoid tests) that were dated using a MICADAS plus gas interface system (GIS) at Northern Arizona University's Arizona Climate and Ecosystems Lab, by direct carbonate methods, and by standard graphite.

- Preparing carbonate samples for GIS analysis is roughly 50% less time-consuming than required for the direct carbonate method.
- The GIS method yields pMC values that are virtually indistinguishable from graphite ($\text{slope} = 1.011 \pm 0.006$, 95% CI [0.997–1.023]; $R^2 = 0.999$) and outperforms the direct carbonate method ($\text{slope} = 0.978 \pm 0.009$, 95% CI [0.959 – 0.999]; $R^2 = 0.997$).
- Sixty percent (25/42) and 86% (36/42) of the GIS determinations are within ±0.5 and ±1.0 pMC of their graphite counterparts, respectively, compared to 26% (11/42) and 67% (28/42) of the direct carbonate determinations, respectively.
- Errors on the GIS determinations are on par with those generated by the direct carbonate method and are roughly four to five times worse than errors derived from standard graphite determinations.
- Six Plio-Pleistocene shells, ^{14}C-dead as determined by graphite analysis, yielded finite direct carbonate ages but yielded expected non-finite GIS ages.
- Our evaluation of graphite, GIS, and direct carbonate ^{14}C determinations reveals that GIS outperforms direct carbonate, especially for older samples (e.g., > 20 ka BP) and at smaller sample sizes.
- MICADAS + GIS ^{14}C determinations of small biogenic carbonate samples are an effective alternative to graphite ^{14}C determinations, especially when the precision of graphite is not required. This rapid and reliable dating method is useful for a broad range of applications, including the dating of minute specimens (e.g., small mollusks, foraminifera tests, ostracode valves, fish otoliths, etc.), determining degrees of time averaging across environments and taxa, and inferring temporal changes in population dynamics from post-mortem age distributions.

Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1017/RDC.2024.45

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