

PAIRED AMS ^{14}C DATES ON PLANKTIC FORAMINIFERA FROM A GULF OF MEXICO SEDIMENT CORE: AN ASSESSMENT OF STRATIGRAPHIC CONTINUITY

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ABSTRACT. A series of recent papers has called for multiple radiocarbon dates on planktic foraminifera to assess stratigraphic continuity in deep-sea sediment cores. This recommendation comes from observations of anomalous ^{14}C dates in planktic foraminifera from the same stratigraphic level. Potential reasons include bioturbation, downslope transport, secondary calcification, carbonate dissolution, and differential preservation. In this study, paired ^{14}C dates on dissolution-susceptible *Globigerinoides ruber* and dissolution-resistant *Neogloboquadrina dutertrei* are used to evaluate a Gulf of Mexico sediment core. Fourteen of 15 pairs (between 8815 and 12,995 uncorrected ^{14}C yr BP) yield concordant uncorrected ^{14}C ages (mean difference -2 ± 75 yr), attesting to continuous deposition at high accumulation rates (>35 cm/kyr). For 1 pair, *N. dutertrei* is nearly 1000 yr younger, which is difficult to explain by any combination of dissolution and bioturbation or downslope transport, given the excellent carbonate preservation and persistent laminations. The concordant ages underscore the utility of paired ^{14}C dates in planktic foraminifera as a means of assessing stratigraphic continuity in deep-sea sediment sequences.

INTRODUCTION

Radiocarbon dating of foraminifera from marine sediment cores is widely used as a means of developing age models for paleoceanographic and paleoclimatic reconstructions. Accelerator mass spectrometry (AMS) techniques currently allow measurement of milligram quantities of Holocene foraminifera to ± 30 – 40 yr precision. Application of AMS ^{14}C dating on multiple species of planktic foraminifera, however, has revealed enigmatic offsets between species from the same stratigraphic level (Broecker et al. 1988a,b, 2006). These ^{14}C offsets question the stratigraphic continuity of the sediment cores. Yet, very few studies have analyzed more than 1 species separately to test for stratigraphic problems, with notable exceptions (Broecker et al. 1988b, 1990; Manighetti et al. 1995; Skinner and Shackleton 2004; Hughen et al. 2004, 2006).

Potential reasons for anomalous ^{14}C dates among different species include bioturbation, downslope transport, secondary calcification, carbonate dissolution, and differential preservation. In some cases, ^{14}C differences appear to relate to the susceptibility to dissolution of certain foraminifera species. For example, *Globigerinoides ruber* and *Gs. sacculifera* are considered more dissolution-susceptible than *Pulleniatina obliquiloculata* and *Neogloboquadrina dutertrei* (Berger 1970). Preferential dissolution has been demonstrated to affect foraminiferal assemblages (Le and Thunell 1996). In studies of western equatorial Pacific Ocean sediments, dissolution-susceptible species yielded ^{14}C ages significantly younger than dissolution-resistant species, which implicated differential dissolution and bioturbation (Broecker et al. 1988a, 2006). These observations led to suggestions that multiple planktic foraminiferal species be analyzed separately for ^{14}C in developing age models and in determining planktic-benthic age differences for deep-water residence times (Broecker et al. 1988a, 1999, 2006; Barker et al. 2007). In this study, paired ^{14}C dates on *Gs. ruber* and *N. dutertrei* from a Gulf of Mexico sediment core are used to assess stratigraphic continuity in a deglacial sequence. Uncorrected ^{14}C dates are used throughout to avoid uncertainties related to reservoir correction and calibration to calendar years.

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METHODS

Orca Basin is a small (~400 km²) anoxic intraslope basin on the Louisiana slope 300 km southwest of the Mississippi River delta (McKee and Sidner 1976) that contains a >200-m-thick brine lake, with salinity >250 (Shokes et al. 1977). Brine derives from exposure and dissolution of a salt diapir from the Jurassic Louann evaporite formation on the southeastern flank (Pilcher and Blumstein 2007). The high salinity limits benthic life and results in the preservation of fine laminations. Abundant pteropods and pristine, glassy planktic foraminifera, some with intact spines, attest to minimal carbonate dissolution. These attributes in combination with high accumulation rates make this site a prime archive for proxy reconstruction of Gulf of Mexico climate and Mississippi River history. Orca Basin core MD02-2550 is a Calypso square giant gravity core (25 cm² by 9 m) collected in July 2002 at 26°56.78'N, 91°20.75'W (2248 m water depth) onboard the R/V *Marion Dufresne* PAGE cruise. The core is laminated to 307 cm, faintly laminated from 307–366 cm, and laminated from 366–550 cm except for a homogeneous interval from 442–453 cm. Subsample cores were taken by pressing 9 × 13 cm cross-section D-tubes lengthwise into the sediment. These subcores were sampled at 0.5-cm intervals from top to 466 cm and at 1-cm intervals below.

Samples were freeze-dried, washed over a 63- μ m sieve, and oven-dried at <50 °C. Between 1–9 mg of *Gs. ruber* and *N. dutertrei* were picked separately from the >150- μ m size fraction in 15 washed sediment samples from core MD02-2550, sonicated, oven-dried at <50 °C, and analyzed in the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory (LLNL). At LLNL, samples were evacuated in individual vacutainers, heated and acidified with orthophosphoric acid at 90 °C, graphitized with Fe as a catalyst, and pressed into aluminum target holders for AMS analysis using standard procedures (Vogel et al. 1987; Guilderson et al. 2003). Raw ¹⁴C dates are corrected for background and δ^{13} C (Stuiver and Polach 1977). Results are given in Table 1 and shown versus depth in the core (Figure 1).

Table 1 AMS ¹⁴C dates on *Gs. ruber* and *N. dutertrei* from core MD02-2550.

CAMS ^a #	Depth (cm)	C (mg)	<i>Gs. ruber</i> ¹⁴ C yr BP	±	<i>N. dutertrei</i> ¹⁴ C yr BP	±	Difference	± ^b
100674 ^c	270	0.67	8815	40				
137078	270	0.47			8915	35	100	53
100675 ^c	290	0.59	9285	40				
137079	290	0.29			9365	45	80	60
130344	318	0.73	9965	35				
137082	318	0.48			9970	35	5	49
130345	329.5	0.54	10,215	35				
137083	329.5	0.38			10,260	50	45	61
130346	337.5	0.52	10,500	45				
137084	337.5	0.25			10,550	60	50	75
137085	342	0.49	10,470	40				
137086	342	0.22			10,540	70	70	81
130349	367	0.77	10,925	40				
137087	367	0.08			11,040	160	115	165
137088	389.5	0.32	11,575	50				
137089	389.5	0.18			11,650	90	75	103
130352	407	1.06	12,085	40				
130353	407	0.51			12,090	35	5	53
130354	418.5	0.54	12,515	40				
137090	418.5	0.43			12,345	45	-170	60

Table 1 AMS ¹⁴C dates on *Gs. ruber* and *N. dutertrei* from core MD02-2550. (Continued)

CAMS ^a #	Depth (cm)	C (mg)	<i>Gs. ruber</i> ¹⁴ C yr BP	±	<i>N. dutertrei</i> ¹⁴ C yr BP	±	Difference	± ^b
130355	427.5	0.99	12,590	40				
130356	427.5	0.24			12,550	70	-40	81
130357	441	0.47	12,785	45				
130358	441	0.41			12,675	45	-110	64
130360	466	0.98	12,980	40				
130361	466	0.24			12,810	70	-170	81
130362	475	0.59	12,805	40				
130363	475	0.27			11,850	60	-955	72
147644	479	0.28	12,995	35				
147643	479	0.52			12,910	60	-85	69
137091	485	0.36	13,100	60				
137092	495	0.41	13,145	50				
137093	505	0.35	13,330	60				
137094	515	0.26	13,610	80				

^aCAMS is Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory. All ages are uncorrected AMS ¹⁴C dates in years before 1950.

^bDifference error is compounded from individual age error estimates.

^cAges for *Gs. ruber* previously reported (LoDico et al. 2006).

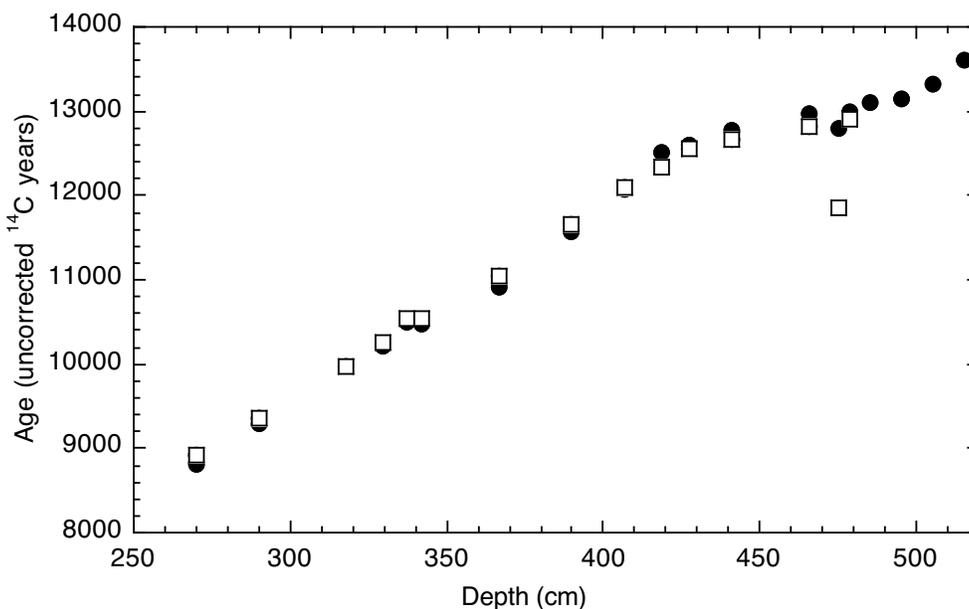


Figure 1 Uncorrected AMS ¹⁴C ages BP of *Gs. ruber* (filled circles) and *N. dutertrei* (open squares) vs. depth in core MD02-2550 (Table 1). Uncertainties in AMS ¹⁴C ages are smaller than plot symbols.

RESULTS

Fourteen of 15 pairs of *Gs. ruber* and *N. dutertrei* ¹⁴C dates (between 8815 and 12,995 uncorrected ¹⁴C yr BP) yield similar ¹⁴C ages (mean difference -2 ± 75 yr; Table 1). Age differences for 8 pairs are not significantly different from zero. Among the 14 pairs, maximum age differences reach $170 \pm$

80 yr. In the 1 exception at 475 cm (discussed below), the *N. dutertrei* ^{14}C age is 955 ± 72 yr younger than *Gs. ruber*. Age plateaus appear to be recorded by both species at about 337–342 cm ($\sim 10,400$ ^{14}C yr) and about 418–466 cm ($\sim 12,500$ ^{14}C yr) (Figure 1). These appear to correlate with well-known ^{14}C age plateaus (Stuiver et al. 1998) that assist in age model development (Guilderson et al. 2005). The concordant ^{14}C ages attest to continuous deposition in Orca Basin at high accumulation rates (>35 cm/kyr; calibration in Williams et al. 2010). This data set represents a positive step toward “best practices” in ^{14}C age control, which should include multiple ^{14}C ages to assess stratigraphic continuity (Broecker et al. 1988a, 1999, 2006; Barker et al. 2007).

When age differences are plotted versus depth (Figure 2), a downcore trend is apparent in which *N. dutertrei* ^{14}C ages become younger than *Gs. ruber*. Below 407 cm, age differences change sign (Table 1). Five of the 6 lowermost pairs yield age differences significantly different from zero. However, given the compounded error in ^{14}C age differences, the downcore trend is not significant without the anomalous results at 475 cm.

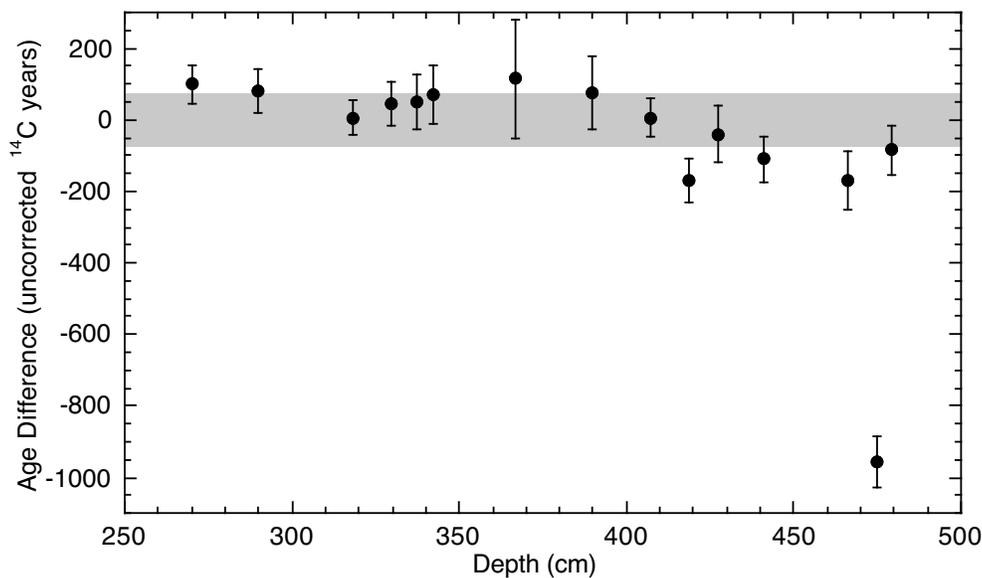


Figure 2 Uncorrected AMS ^{14}C age differences between paired *Gs. ruber* and *N. dutertrei* vs. depth in core MD02-2550. Uncertainties are based on propagation of errors in differencing AMS ^{14}C age determinations (Table 1). Mean uncertainty (75 yr) is shaded.

DISCUSSION

The *Gs. ruber* and *N. dutertrei* dates ($12,805 \pm 40$; $11,850 \pm 60$ yr BP, respectively) at 475 cm is the only pair with a large offset (-955 ± 72 yr; Table 1). Four of the 5 lowest *Gs. ruber*/*N. dutertrei* pairs were analyzed on the same day, including the dates at 475 cm, arguing against instrumental problems between runs. Although *N. dutertrei* is known to prefer deeper waters than *Gs. ruber* in the Gulf of Mexico (Bé 1982), the lower $^{14}\text{C}/^{12}\text{C}$ ratio in modern thermocline waters can only explain a difference of a few hundred years at most. We also have no ready explanation for the downcore trend in which *N. dutertrei* ^{14}C ages become younger than *Gs. ruber* below 407 cm (12.09 ka BP). Even if surface waters were indeed more stratified with respect to $^{14}\text{C}/^{12}\text{C}$, it is difficult to explain higher $^{14}\text{C}/^{12}\text{C}$ ratios in the thermocline necessary for younger *N. dutertrei* ^{14}C ages.

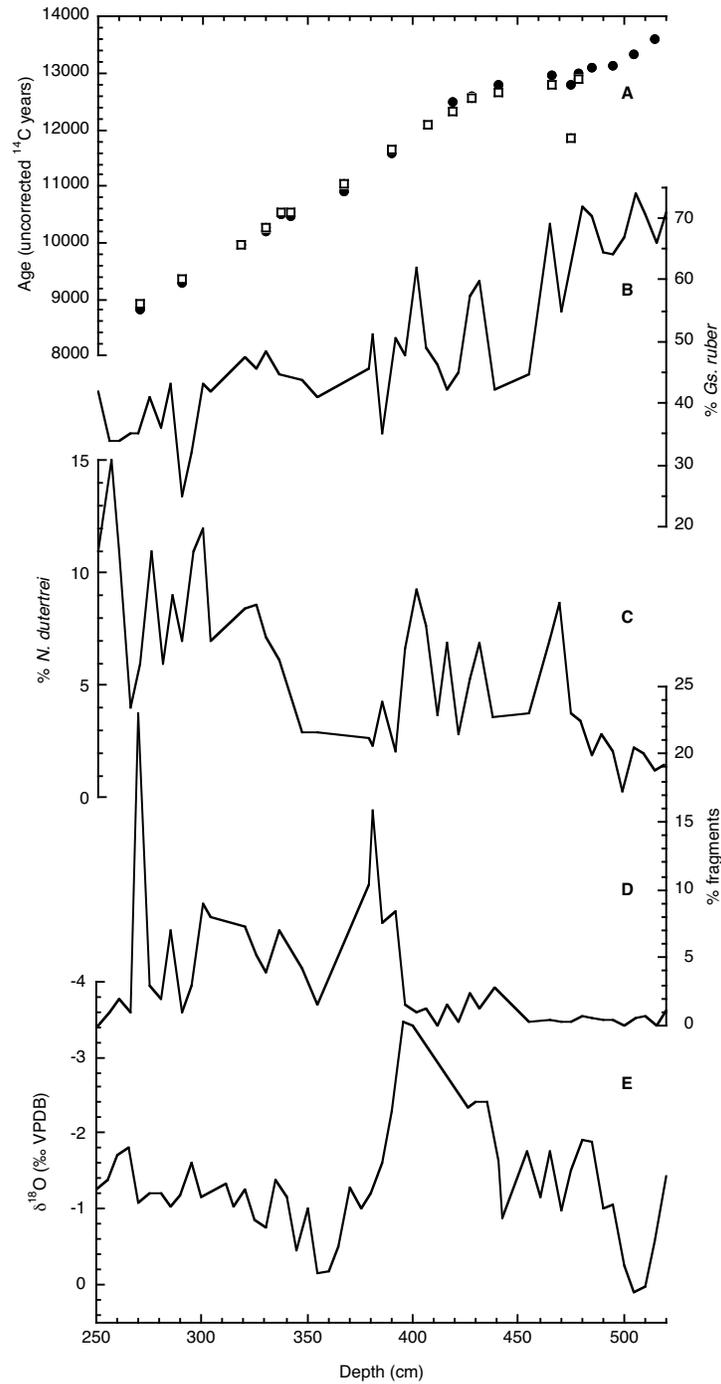


Figure 3 Comparison of AMS ^{14}C ages BP of *Gs. ruber* (filled circles) and *N. dutertrei* (open squares) (panel A), percent *Gs. ruber* (panel B), percent *N. dutertrei* (panel C), percent foraminiferal fragments (panel D), and $\delta^{18}\text{O}$ of *Gs. ruber* (Williams et al. 2010; panel E) vs. depth in core MD02-2550. The $\delta^{18}\text{O}$ record (panel E) demonstrates that the anomalous ^{14}C ages bear no relation to inferred meltwater input.

Anomalously young dates are sometimes found near the regional reappearance of a given species, e.g. *Globorotalia menardii* in the lower Holocene in the western equatorial Atlantic (Broecker et al. 1999). In our core, downward mixing of young *N. dutertrei* into late glacial sediments where its abundances are low (Kennett et al. 1985; Flower and Kennett 1990) might contribute to young ^{14}C ages. Figure 3 demonstrates substantial changes in percent frequency of *N. dutertrei* in the studied interval, including low abundances (<3%) and concentrations (not shown) below 480 cm. For that reason, there were insufficient *N. dutertrei* for paired ^{14}C dates below this depth. In contrast, *Gs. ruber* averages about 50% of the planktic foraminiferal assemblage, while exhibiting a long-term increase toward the glacial section. Accordingly, bioturbational mixing of younger *N. dutertrei* might have decreased the mean ^{14}C age at 475 cm. However, we note that specimens would have had to mix down at least 75 cm to explain the ~1000 yr younger age, which seems unlikely given persistent laminations in this interval (Meckler et al. 2008).

A second possibility is that dissolution may preferentially break up older tests because of their greater residence time in the sedimentary mixed layer (Broecker and Clark 2001; Barker et al. 2007). Younger ages are determined because of fewer whole tests of greater ages, and this is indeed a problem in low-accumulation rate cores. In our core, young *N. dutertrei* would again have had to mix down at least 75 cm. Furthermore, there is no evidence for substantial changes in dissolution near 475 cm, based on either percent foraminiferal fragment data (Figure 3) or weight/foram data (Williams et al. 2010).

Anomalously old ^{14}C ages have been observed in dissolution-resistant species from Ontong Java Plateau sediment cores (e.g. Broecker et al. 1988a). In this case, a systematic mean age difference of 890 yr was observed between *Gs. sacculifera* and *Pulleniatina obliquiloculata*, with the latter dissolution-resistant species yielding older ages. This finding was interpreted to reflect preferential dissolution of the dissolution-susceptible species *Gs. sacculifera* (Broecker et al. 1988a). In part because a nearby core yielded a much smaller offset of 190 yr, the possibility of reworked older *P. obliquiloculata* was considered (Broecker et al. 2006). The idea is that more robust species such as *P. obliquiloculata* might better survive reworking processes. However, in our core it is the dissolution-resistant species that yields a younger age, which is difficult to explain by either preferential dissolution or downslope transport. Furthermore, the *Gs. ruber* date also seems anomalously young (by ~100 yr instead of ~1000 yr) (Figure 1), so perhaps related processes are responsible for young dates in both species.

Equilibration with modern atmospheric CO_2 may produce anomalously young ages, if isotopic exchange occurs after core collection. It has been suggested that diagenetic calcite may form during core curation and incorporate modern ^{14}C (Barker et al. 2007). If this process were to increase test mass, both *Gs. ruber* and *N. dutertrei* weights per specimen should be elevated, yet they are not (Williams et al. 2010). Furthermore, this process might be expected to affect thinner-walled *Gs. ruber* more than *N. dutertrei* because secondary calcite should form a greater fraction of shell mass, yet it is *N. dutertrei* that yields a ~1000 yr younger age. Accordingly, there is no clear evidence for modern equilibration, but we cannot rule it out.

Overall, it is difficult to imagine how stratigraphic problems at 475 cm might yield ages that are substantially younger relative to the surrounding *Gs. ruber* dates. Well-defined laminations persist during this interval (Meckler et al. 2008), and there is no geochemical evidence for anomalous sedimentation or diagenesis. For example, neither magnetic susceptibility data (Labeyrie and Shipboard Scientific Party 2005), weight/foram data, nor Mn/Ca in *Gs. ruber* (Williams et al. 2010) show anomalous excursions. Finally, a comparison to *Gs. ruber* $\delta^{18}\text{O}$ (Figure 3) indicates no obvious rela-

tion to inferred meltwater input. There are several positive and negative $\delta^{18}\text{O}$ excursions between 520 and 350 cm, with lowest values at 395 cm, but none coincide with the anomalous ^{14}C dates at 475 cm. Furthermore, the calibrated age for this sample (14.4 cal ka BP) does not appear to coincide with known climatic events that might affect ^{14}C age. Accordingly, we find no evidence for an environmental cause. Nevertheless, the anomalous *Gs. ruber* and *N. dutertrei* ^{14}C dates may indicate potential stratigraphic problems at least with this sample, and related data are treated with caution in our paleoceanographic records (e.g. Williams et al. 2010).

IMPLICATIONS

In addition to the stratigraphic integrity of the MD02-2550 core, the concordance observed between *Gs. ruber* and *N. dutertrei* ^{14}C dates indicates that paired proxy data can be compared with confidence that the signals are coeval within compounded ^{14}C error. For example, $\delta^{18}\text{O}$ data on surface-dwelling *Gs. ruber* and deeper-dwelling *N. dutertrei* can be used to assess the thickness of the deglacial meltwater layer in the Gulf of Mexico (Leventer et al. 1982; Flower and Kennett 1990). The $\delta^{18}\text{O}$ gradient represents some combination of temperature and salinity difference across the depth habitats of the 2 species. Furthermore, comparison of Mg/Ca data on paired *Gs. ruber* and *N. dutertrei* can assess the Mg/Ca temperature and $\delta^{18}\text{O}$ seawater gradients in the upper water column. These comparisons would not be robust without concordant ^{14}C ages.

CONCLUSION

Fourteen of 15 pairs of *Gs. ruber* and *N. dutertrei* ^{14}C dates (between 8815 and 12,995 ^{14}C yr BP) yield concordant uncorrected ^{14}C ages (mean difference -2 ± 75 yr; $n = 14$), attesting to continuous deposition in Orca Basin at high accumulation rates (>35 cm/kyr). For 1 pair at 475 cm, *N. dutertrei* is nearly 1000 yr younger, which is difficult to explain by any combination of dissolution and bioturbation or downslope transport, given the excellent carbonate preservation and persistent laminations, but could potentially reflect equilibration with modern atmospheric CO_2 . These results underscore the utility of paired ^{14}C dates in planktic foraminifera as a means of assessing stratigraphic continuity deep-sea sediment sequences, and highlight the value of high accumulation rate cores in paleoceanographic reconstructions. In particular, paired *Gs. ruber* and *N. dutertrei* proxy data such as $\delta^{18}\text{O}$ and Mg/Ca can be compared with confidence that the signals are coeval within compounded ^{14}C error.

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