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Amino acid geochronology of individual foraminifer (*Pulleniatina obliquiloculata*) tests, north Queensland margin, Australia: A new approach to correlating and dating Quaternary tropical marine sediment cores

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[1] In this study, we demonstrate the utility of amino acid geochronology based on single-foraminiferal tests in Quaternary sediment cores from the Queensland margin, Australia. The large planktonic foraminifer *Pulleniatina obliquiloculata* is ubiquitous in shelf, slope, and basin sediments of north Queensland as well as pantropical oceans. Fossil tests are resistant to dissolution, and retain substantial concentrations of amino acids (2–4 nmol mg^{-1} of shell) over hundreds of thousands of years. Amino acid D and L isomers of aspartic acid (Asp) and glutamic acid (Glu) were separated using reverse phase chromatography, which is sensitive enough to analyze individual foraminifera tests. In all, 462 *Pulleniatina* tests from 80 horizons in 11 cores exhibit a systematic increase in D/L ratios down core. D/L ratios were determined in 32 samples whose ages are known from AMS ^{14}C analyses. In all cases, the Asp and Glu D/L ratios are concordant with ^{14}C age. D/L ratios of equal-age samples are slightly lower for cores taken from deeper water sites, reflecting the sensitivity of the rate of racemization to bottom water temperature. Beyond the range of ^{14}C dating, previously identified marine oxygen-isotope stage boundaries provide approximate ages of the sediments up to about 500,000 years. For this longer time frame, D/L ratios also vary systematically with isotope-correlated ages. The rate of racemization for Glu and Asp was modeled using power functions. These equations can be used to estimate ages of samples from the Queensland margin extending back at least 500,000 years. This analytical approach provides new opportunities for geochronological control necessary to understand fundamental sedimentary processes affecting a wide range of marine environments. *INDEX TERMS:* 4267 Oceanography: General: Paleoceanography; 4850 Oceanography: Biological and Chemical: Organic marine chemistry; 3022 Marine Geology and Geophysics: Marine sediments—processes and transport; *KEYWORDS:* Queensland margin, marine sediment, amino acid racemization, geochronology, foraminifera, Quaternary stratigraphy

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1. Introduction

[2] Deep-marine sediment offers the longest continuous record of global climatic and oceanographic change. Only a few techniques are currently available to date these sediments, notably radiocarbon (^{14}C), oxygen isotopes ($\delta^{18}O$), and magnetic reversals. ^{14}C is restricted by its limited temporal range (<40 ka), and by the availability of organic material; ages on bulk sediment are intrinsically less accurate than the analytical precision implies. Over longer time intervals, $\delta^{18}O$ is often used to correlate down core sequences of sediment with the global marine record (SPECMAP [*Imbrie et al.*, 1992]), but is muted by bioturbation, local temperature and taxonomic effects, and the uncertainties generated by "finger matching" of similar curve patterns. Furthermore, the SPECMAP record is dated by only a few independent ages, and aspects of the chronology have been challenged (e.g., in comparison with timing of climatic changes recorded in the well-dated calcite from Devils Hole [*Winograd et al.*, 1992] and of the last interglaciation dated by marine terraces [*Muhs et al.*, 2002]). Despite its shortcomings, the $\delta^{18}O$ record is an essential template in deep-sea cores, and will be used in this study as an independent age and stratigraphic tool. Paleomagnetic reversal stratigraphy provides a few key control points for longer records (e.g., the Brunhes-Matuyama boundary at ~780 ka), but is insufficient to resolve variations in sedimentation rate at time scales shorter than hundreds of thousands of years. In this study, we evaluate the utility of amino acid racemization measured in single tests of foraminifera as a chronostratigraphic tool.

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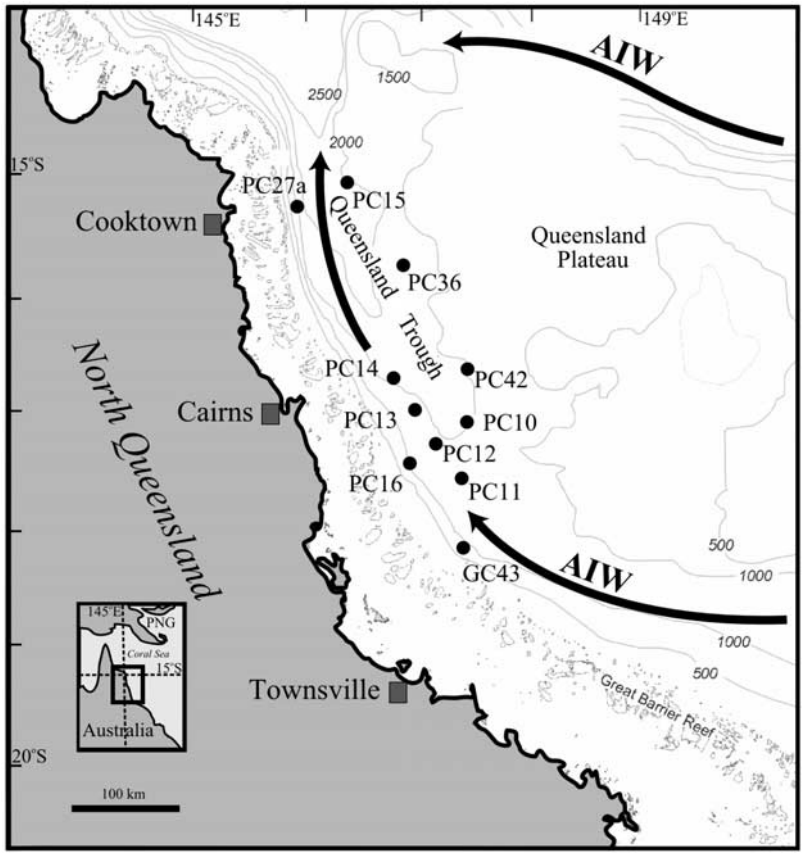

Figure 1. Locality map showing the principal bathymetric features (in meters) of the northeastern Australian continental margin and the position of eleven piston cores used in this study. Arrows indicate flow direction of Antarctic Intermediate Water (AIW).

[3] Some of the earliest research into amino acid geochemistry focused on deep-marine sediment, including foraminifera [e.g., *Wehmiller and Hare*, 1971; *Bada and Schroeder*, 1972; *King and Hare*, 1972; *Kvenvolden et al.*, 1973; *Schroeder and Bada*, 1977; *Bada et al.*, 1978; *Bada and Man*, 1980; *Belknap and Doyle*, 1986; *Stathopolos et al.*, 1987; *Robbins and Brew*, 1990; *Johnson*, 1990]. These studies took advantage of the long-term stability of deep-marine settings to investigate the diagenesis of amino acids over geologic time. Amino acid racemization in fossil foraminifera has been used to estimate the ages of Quaternary marine sediment [*Müller*, 1984; *Sejrup et al.*, 1984; *Macko and Aksu*, 1986; *Sejrup and Haugen*, 1992; *Knudsen and Sejrup*, 1993; *Harada and Handa*, 1995; *Harada et al.*, 1996], and in a few cases, to reconstruct paleotemperature histories [e.g., *Bada and Man*, 1980; *Lehman et al.*, 1988; *Johnson et al.*, 1990].

[4] Foraminifera inhabit a wide range of marine settings and are exceptionally well suited for amino acid geochronology and paleothermometry. Their tests are often well preserved, especially in carbonate-rich deposits; they contain high concentrations of amino acids that are extraordinarily well retained by the test (see section 3.2), and they are held under relatively stable postdepositional hydrochemical and temperature conditions for long intervals. Because they are small, foraminifera are often present in sufficient abundance in sediment cores to allow amino acid geochronology and paleothermometry to be integrated into the study of marine cores. Depositional histories in many marine records are interpreted based upon widely accepted models, such as sequence-stratigraphic concepts [e.g., *Vail et al.*, 1977; *Posamentier and Vail*, 1988], often without sufficient age control to test these inferences. In some cases, Upper Quaternary sediments with well-constrained ages have challenged these conceptual models [e.g., *Goodbred*, 2003; *Page et al.*, 2003; *Walsh and Nittrouer*, 2003; *Larcombe and Carter*, 2004]. Along tropical mixed siliciclastic-carbonate continental margins, for example, the conventional view is that siliciclastic fluxes to basins are greatest during lowstands, when rivers bypass the shelf and discharge along the continental slope, and minimal during transgressions [e.g., *Dolan*, 1989]. However, on the north Queensland margin, the largest modern tropical mixed siliciclastic-carbonate depositional system, *Page et al.* [2003] have demonstrated the opposite pattern and established that maximal siliciclastic flux occurred during the last postglacial transgression between 12 and 7 ka. Unfortunately, this pattern has been demonstrated over only one deglaciation due to the limitations of ^{14}C dating. Also perhaps associated with transgressions are mass wasting deposits identified by GLORIA images along the Queensland continental margin. Many of these mass wasting events may

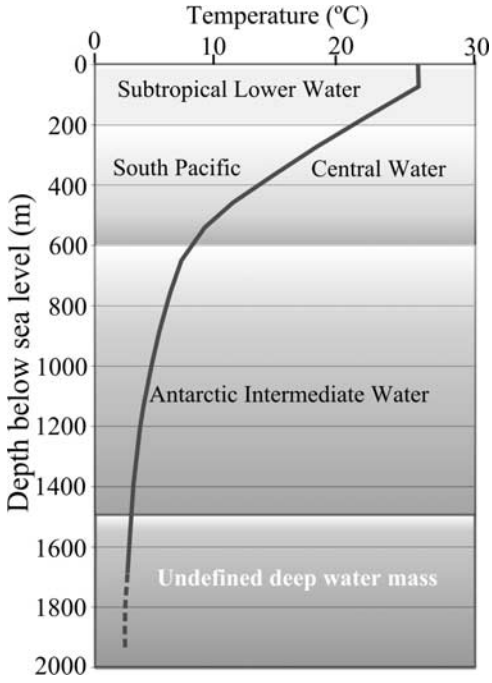

Figure 2. Temperature profile and water mass boundaries in the western Coral Sea [*Corrège*, 1993a] measured from RV *Franklin* cruise FR199006 at 16.226°S latitude and 146.655°E longitude.

have occurred beyond the range of ^{14}C, and intervals bounding slump deposits are often too thin to determine a recognizable pattern from oxygen isotopes. Amino acid geochronology may provide an independent chronostratigraphic tool for investigating and resolving some of these key issues related to mechanisms and timing of sediment fluxes along continental margins relative to multiple glacial-interglacial sea level cycles over the past half million years.

[5] The technique is based on the enantiomeric (D and L) composition of amino acids preserved in foraminifera tests. This new application of amino acid geochronology is feasible because the technology needed for routine enantiomeric separations of amino acids from submilligram quantities of shell has recently become available [*Kaufman and Manley*, 1998]. Reverse phase chromatography (RPC) has improved detection capabilities by at least an order of magnitude compared to conventional ion exchange HPLC (high performance liquid chromatography), which has been used previously for most amino acid geochronological investigations. These small sample sizes afford new opportunities to use microfossils for amino acid geochronology and paleothermometry. In contrast to HPLC analyses of foraminifera, where a few hundred monospecific tests were required for analysis, reliable results can be obtained on a single Pleistocene foraminifera test. This is an order of magnitude less material than is required for AMS ^{14}C dating and presents a new opportunity to date deposits that are organically poor, or are beyond the applicable range of the ^{14}C technique (>40 ka). In addition to reducing sample size requirements, RPC separates enantiomers of multiple amino acids, providing a means of cross checking and identifying aberrant results. Because amino acid D/L ratios among different amino acids tend to be strongly covariant [e.g., *Goodfriend*, 1991], divergence in these trends might be used to diagnose excessive leaching or contamination, both of which undermine the accuracy of the technique and contribute to high intersample variation [e.g., *Müller*, 1984].

[6] The Queensland trough (Figure 1) was selected as the study site for this first systematic application of RPC on foraminifera for several reasons [*O'Leary*, 2001]. Several

Table 1. Location and Other Information on Sediment Cores Used in This Study

Piston Core Identification[a]	Latitude, °S	Longitude, °E	Depth, mbsl	Core Length, m	Bottom Water Temperature,[b] °C
051-GC43	18° 7.97′	147° 28.6′	901	2.55	5.4
FR4/92-PC10	17° 06.3′	147° 23.4′	1334	3.69	3.5
FR4/92-PC11	17° 34.3′	147° 20.9′	1320	3.88	3.5
FR4/92-PC12	17° 16.0′	147° 08.5′	1443	3.48	3.2
FR4/92-PC13	16° 57.1′	146° 55.2′	1507	3.81	3.1
FR4/92-PC14	16° 43.4′	146° 43.9′	1574	4.48	2.9
FR5/90-PC15	15° 04.1′	146° 17.0′	1875	4.95	2.1
FR4/92-PC16	17° 25.9′	146° 53.5′	1043	3.50	4.3
FR5/90-PC27a	15° 17.4′	145° 56.8′	2163	4.56	2.4
FR4/92-PC36	15° 49.5′	146° 49.2′	1824	3.94	2.3
FR4/92-PC42	16° 39.1′	147° 49.6′	1389	3.26	3.3

[a]Cores were collected on the RV *Franklin* cruises 1990/05 and 1992/04.
[b]Bottom water temperatures were measured on cruises 1985/05, 1990/06, 1991/07, 1992/09, and 1997/01 and were taken from the CSIRO marine trawler database (www.marine.csiro.au/datacentre).

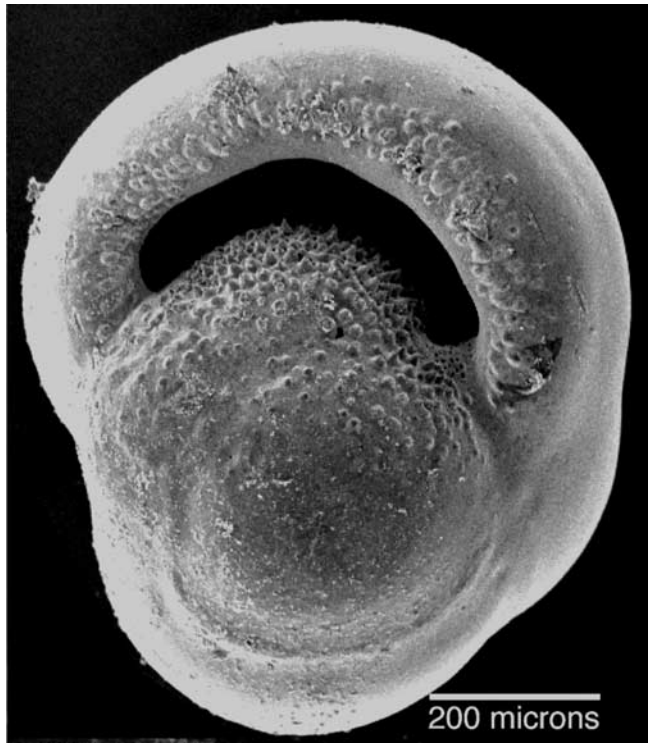

Figure 3. Scanning electron micrograph of the planktonic foraminifer *Pulleniatina obliquiloculata*. *Pulleniatina*'s thick robust shell is resistant to dissolution favoring long-term preservation of amino acids.

Table 2. Various Experimental Pretreatment Methods Tested on Foraminifera[a]

UAL Sample Identification	Duration, hours	Solution	n	Aspartic D/L	Aspartic D/L ± 1σ	Glutamic D/L	Glutamic D/L ± 1σ	Serine D/L	Serine D/L ± 1σ
3590	—	none	8	0.307	0.019	0.125	0.017	0.413	0.035
3954	1	alcohol	9	0.310	0.017	0.122	0.013	0.369	0.078
3598	2	alcohol	9	0.311	0.013	0.123	0.013	0.358	0.038
3593	1	methanol	10	0.318	0.018	0.129	0.013	0.390	0.041
3597	2	methanol	10	0.316	0.032	0.122	0.023	0.366	0.118
3592	1	5% bleach	10	0.312	0.031	0.124	0.020	0.325	0.112
3596	2	5% bleach	9	0.314	0.019	0.124	0.014	0.337	0.094
3591	1	3% perox	10	0.308	0.018	0.120	0.013	0.386	0.084
3595	**2**	**3% perox**	**8**	**0.327**	**0.008**	**0.133**	**0.007**	**0.396**	**0.030**

[a]The 2 hour peroxide method (shown in bold) was determined to be most effective, as indicated by the lowest standard deviation.

hundred piston cores collected in the last 25 years are available from the area. Extensive sedimentological (biostratigraphic and lithostratigraphic), geochronological (^{14}C), and stable isotope analyses were recently completed by *Grace* [1993], *Dunbar* [2000], and *Dunbar et al.* [2000]. Subsequently, *Page et al.* [2003] analyzed an additional 27 AMS ^{14}C ages for which we determined amino acid D/L ratios from equivalent and adjacent core levels. These results provide a solid chronostratigraphic framework against which to evaluate the utility of the amino acid geochronology. Further, the Queensland trough is rich in marine biogenic carbonates and microfauna. Foraminifera of a single taxon are abundant at all sampled depths.

[7] The prevalent deepwater mass in the Queensland trough is Antarctic Intermediate Water (AIW). It is found at depths between 600 and 1600 m [*Pickard et al.*, 1977; *Corrège*, 1993a], and dominates bottom water temperatures at most of the cored sites (3 cores, PC15, PC36 and PC27a

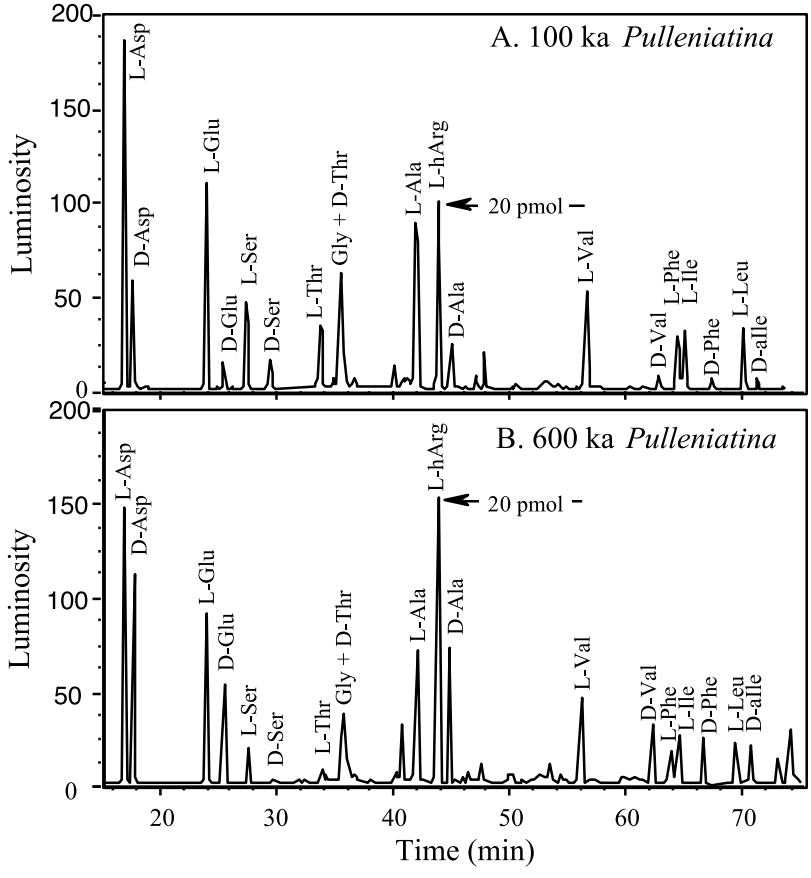

Figure 4. Typical reverse-phase HPLC chromatograms of single-foraminifera (*Pulleniatina*) tests from the Queensland margin (Core PC15). Samples are of two approximate ages: (a) 100 ka and (b) 600 ka. For the 600 ka sample with fewer amino acids the detector was set to a higher gain to amplify the signal. See text for analytical conditions.

Table 3. Derivation of Independent Age Control for Samples Analyzed for Amino Acid Racemization

		Number of Ages			
Core	Number of Samples	Based on ^{14}C	Based on Interpolation/ Extrapolation[a]	Based on $\delta^{18}O$ Correlation[b]	Source[c]
GC43	8	7	1	0	1
PC10	4	0	0	4	2
PC11	7	3	4	0	1
PC12	4	1	0	3	1
PC13	9	4	5	0	1
PC14	8	4	4	0	1
PC15	3	0	0	3	2
PC16	14	5	9	0	3
PC27a	7	6	1	0	1
PC36	11	0	0	11	3
PC42	5	3	0	2	3
Total	80	33	24	23	—

[a]Interpolation and extrapolation of sample ages based on ^{14}C ages (Table 4) and sediment depths (i.e., age models) fit to third-order polynomial trends as follows: GC43, $t = 0.0069x^3 - 2.018x^2 + 213.6x + 1373$; PC11, $t = 0.1413x^3 - 13.361x^2 + 520.0x$ (surface set at t = 0 years B.P.); PC13, $t = 0.0835x^3 - 11.873x^2 + 572.7x - 1327$; PC14: $t = -0.0117x^3 + 2.967x^2 - 43.7x + 1360$; PC16, $t = 0.0020x3 - 0.763x^2 + 130.5x$; PC27a, $t = 0.0007x^3 - 0.304x^2 + 94.3x + 931$. Here t is age in calendar years B.P., and x is depth in meters.

[b]Correlated ages based on $\delta^{18}O$ data and age models were published previously (see footnote c).

[c]Sources are as follows: 1, *Page et al.* [2003]; 2, *Dunbar* [2000]; 3, *Dunbar et al.* [2000].

are below the AIW) (Figure 2). The northward flowing current enters the Queensland trough from the south between the Marion and Queensland plateaus, and passes over a 900 m sill that separates the Queensland and Townsville troughs (Figure 1). Modern AIW water temperatures decrease with depth from 7.5°C at 600 m down to 2.8°C at 1600 m. Below AIW, bottom water temperatures in an undefined deepwater mass decrease down to 2°C at 2000 m. This temperature profile is believed to have remained relatively constant during the Holocene; however, the temperature of AIW in the Queensland trough might have fluctuated from between 1 and 2°C over glacial/interglacial cycles [*Corrège*, 1993b].

2. Materials and Methods

2.1. AAR Method

[8] Amino acid racemization (AAR) geochronology is an effective biogeochemical tool for stratigraphic correlations, and can yield numerical age estimates where the rate of racemization is independently calibrated (for a recent review of the principles of the technique, see *Wehmiller and Miller* [2000]). The AAR method is based on the racemization of amino acids preserved in biominerals. Through time, L-isomer amino acids racemize to their D-isomer form. The ratio of D/L measures the extent of racemization, and increases to an equilibrium ratio of unity with time after death of the organism. Like other chemical reactions, the rate of racemization depends on the ambient temperature of the reaction medium, in this case foraminifera held at ocean bottom water temperature. Thus, for samples of the same age, those from sites under long-term, warmer temperatures are expected to yield incrementally higher D/L ratios.

2.2. Core and Sample Selection

[9] Cores for this study were recovered from the Queensland trough during RV *Franklin* cruises 5/90 (38 piston cores total) and 4/92 (42 piston cores total), and RV *Rig Seismic* cruise 051 (76 gravity cores total). Eleven piston cores were selected because they represent diverse bathymetric settings (slope to basin) and because most have existing ^{14}C age and $\delta^{18}O$ chronologies. Of the 11 sampled cores, five (PC16, PC11, PC12, PC13, PC14, PC27a, and GC43) are from the Queensland shelf slope, and four (PC10, PC42, PC36, and PC15) are from the Queensland trough (Figure 1). The cores were collected from an area of 400 km^2, ranging in water depths between 901 and 2163 m (Table 1).

[10] Initially [*O'Leary*, 2001; *O'Leary and Hearty*, 2002], core sediment samples were collected: (1) adjacent to levels previously analyzed for ^{14}C and $\delta^{18}O$ [*Grace*, 1993; *Dunbar*, 2000; *Dunbar et al.*, 2000]; (2) near core tops and bases; and (3) at intermittent levels in order to strengthen chronostratigraphic correlations and determine differences in sedimentation rates among cores. In this study, samples are coded according to their core identifier and suffix that indicate the depth of the sample in the core barrel (e.g., PC10-250 is from 250 cm depth in core PC10). In light of the positive results from the first batch of samples, the cores were sampled a second time for new ^{14}C ages [*Page et al.*, 2003] and RPC AAR analyses.

2.3. Taxon Selection: *Pulleniatina*

[11] Because the apparent rate of AAR is known to be taxon-dependent [e.g., *King and Neville*, 1977], analyses that are restricted to a single taxon are most easily interpreted. Ideal foraminifera species are ubiquitous and cosmopolitan, well preserved and abundant in marine sediments, large (~500 μm), and easily recognized. In this study, we focus on the genus *Pulleniatina.* It has a single extant species, *P. obliquiloculata* (Figure 3), and therefore cannot be confused with other species of the genus [*Banner and Blow*, 1967]. We refer to it simply as *Pulleniatina*.

[12] Modern populations of *Pulleniatina* inhabit pantropical oceans, but decrease in abundance with increasing latitude to their modern range limit of ~40° north and south. They inhabit the lowermost mixed layer and uppermost thermocline in the water column [*Saito*, 1976]. At these depths (~200 m), *Pulleniatina* experiences significant pressures and strong temperature gradients during life, which may account for its sturdy construction.

[13] Inspection of Pleistocene *Pulleniatina* tests by scanning electron microscopy (SEM) (Figure 3) found little evidence of dissolution [*O'Leary*, 2001]. Samples taken from one of the deepest and oldest sampled cores (PC15) yielded the largest and most abundant specimens of *Pulleniatina*. SEM also reveals that the foraminifer tests have an outer layer of a finely crystalline calcite, which appears smooth and pristine; this is underlain by a thick, coarsely crystalline calcite structural layer. Mineralogical purity of the calcite test was verified for a representative suite of samples from PC36 with X-ray diffraction. The results

Table 4. The ^{14}C Ages Used to Calculate Age Models and to Calibrate the Rate of Racemization in Cores Analyzed in This Study[a]

Sample	Depth, cm bsl	Laborator Code	^{14}C Age, years B.P.	^{14}C Age ±1σ	Calibrated Age,[b] years B.P.	Calibrated Age Half 1σ Range	Source[c]
GC43-005	5	OZF296	2,760	40	2,460	80	1
GC43-031	31	OZG452	5,570	50	5,930	40	1
GC43-051	51	OZG453	7,810	60	8,290	80	1
GC43-071	77	OZE893	8,600	50	9,010	160	1
GC43-153	153	OZE894	10,370	50	11,120	370	1
GC43-171	171	OZG454	12,680	80	14,130	420	1
GC43-209	209	OZF297	18,230	140	21,080	360	1
PC11-036	26	OZF724	6,490	50	6,980	60	1
PC11-060	50	OZE875	9,530	50	10,280	90	1
PC11-079	69	OZF725	16,180	90	18,720	300	1
PC12-059	59	OZE876	9,750	50	10,460	150	1
PC13-005	5	OZG455	1,680	40	1,250	30	1
PC13-055	55	OZF299	7,690	50	8,150	40	1
PC13-079	79	OZE874	10,300	50	10,990	380	1
PC13-104	104	OZF722	20,550	140	23,750	440	1
PC14-025	25	OZF298	2,330	40	1,940	50	1
PC14-075	75	OZE808	9,180	60	9,820	150	1
PC14-088	88	OZE809	10,980	60	12,490	330	1
PC14-109	109	OZE810	14,370	80	16,640	250	1
PC16-034	21	OZC967	2,160	50	1,740	60	2
PC16-100	80	OZC968	6,280	70	6,720	70	2
PC16-185	165	OZC969	9,370	110	10,060	230	2
PC16-253	230	OZC970	11,550	150	13,020	130	2
PC16-282	259	OZD811	15,050	150	17,420	300	2
PC16-287	264	OZD812	40,400	3500	NA[d]	—	2
PC16-367	344	OZD813	36,800	2000	NA[d]	—	2
PC27a-007	7	OZG450	1,960	40	1,520	40	1
PC27a-052	52	OZG451	4,760	50	4,990	70	1
PC27a-084	84	OZD814	7,160	90	7,620	60	2
PC27a-151	151	OZD815	9,320	90	9,910	230	2
PC27a-193	193	OZD816	11,250	160	12,870	170	2
PC27a-218	218	OZD817	12,900	150	14,340	580	2
PC27a-318	318	OZG449	22,100	140	NA[d]	—	1
PC42-010	2	WK2724	4,440	220	4,580	270	3
PC42-050	42	WK2725	15,420	340	17,840	500	3
PC42-100	92	WK2726	32,000	1200	NA[d]	—	3

[a]All analyses are on foraminifera (*Globigerinoides ruber* and *G. sacculifer*), except PC42, which are on bulk carbonate.
[b]Ages were calibrated using CALIB [*Stuvier et al.*, 1998]; midpoint and one-half of 1σ range are reported.
[c]Sources for ^{14}C ages are as follows: 1, *Page et al.* [2003]; 2, *Dunbar et al.* [2000]; 3, *Grace* [1993].
[d]NA indicates calibrated age is beyond the range of calibration by CALIB and not used in age models.

confirm the tests are composed of pure calcite, and after standard cleaning procedures, appear to be free of exotic minerals. Despite the great water depth (>1500 m), their tests maintain a consistent mass, resist breakage when pressure is applied with a probe, and show no evidence of etching even on the oldest *Pulleniatina* tests. In general, the above and other qualities noted below, make *Pulleniatina* ideal for AAR studies.

2.4. Sample Preparation

[14] Approximately 4 cm^3 of sediment was collected from 80 core horizons. Sediment samples were wet sieved to 125 μm with tap water. The >125 μm fraction was rinsed in deionized water and dried at low temperature (40°C) for 3 hr. Between 10 and 100 of the largest and most pristine individuals of *Pulleniatina* were picked from each horizon and placed in plastic vials for pretreatment prior to AAR analysis.

[15] Because the surface-to-mass ratio of foraminifera is high, contamination by modern amino-acid-bearing molecules is a concern. A few studies have evaluated the effectiveness of pretreatment procedures for foraminifera and other samples analyzed for amino acid geochronology [e.g., *Katz and Man*, 1980; *Johnson*, 1990]. The primary objective of the pretreatment procedures is to remove foreign particles and organic molecules without destroying the test itself, or inducing racemization. Ultrasonic cleaning has proven to be an effective means of removing adhering particles. Oxidizing agents such as hydrogen peroxide are typically used to oxidize organic matter adsorbed to the carbonate tests. In this study, we cleaned all tests in a 60 W ultrasonic bath for 2 min, and rinsed thoroughly with deionized water. To remove secondary organic molecules adsorbed to the test, we evaluated the effectiveness of two oxidizing reagents: 3% H_2O_2 and 5% NaOCl, and two organic solvents: isopropyl alcohol and methanol. Following ultrasonic cleaning, groups of 8-10 foraminifera, all from sample PC42-250, were soaked for 1 and 2 hr in each of the four chemicals, then rinsed thoroughly with deionized water and dried under laminar airflow.

[16] We assume that lowest intershell variation in D/L ratios is an effective measure of the best cleaning procedure.

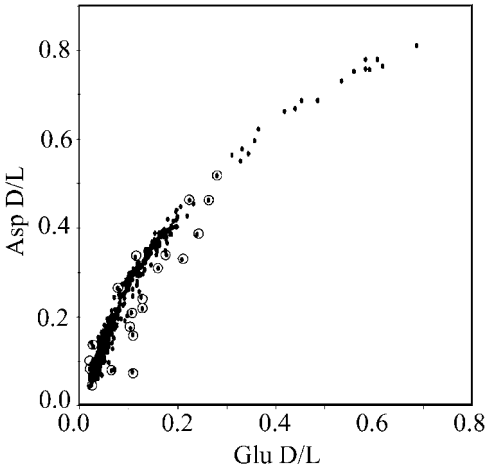

Figure 5. Covariance of aspartic acid (Asp) and glutamic acid (Glu) D/L ratios for 526 individual *Pulleniatina* tests. Circled data points were rejected because they fall outside of ± 2σ of other samples taken from the same sedimentary horizon. The cohesive relationship between Asp and Glu D/L for the entire age range supports the integrity of the amino acid system.

The coefficient of variation (CV = mean/standard deviation) was calculated for the D/L ratios of three amino acids for each group of tests (Table 2). The results are somewhat variable, but overall, only the 2 hr, H_2O_2 treatment significantly reduced the intershell variation in D/L for all three amino acids. The 2 hr peroxide treatment was also determined to be the most effective for ostracode shells [*Kaufman*, 2000] and we applied it to all samples in this study. The extended effects of soaking times on concentration and degradation of amino acids were beyond the scope of this study.

[17] Cleaned tests were hydrolyzed individually in separate microreaction vials by dissolving in 10 μl of 6 M HCl, sealing under N_2, and heating at 110°C for 6 hr. Because the forams we used were all of similar mass (∼0.1 mg), the influence of carbonate on hydrolysis was essentially constant among preparations. The hydrolysates are then evaporated to dryness in vacuum and rehydrated in 4 μl of 10 μM HCl before injection into an integrated Hewlett-Packard HP1100 liquid chromatograph. Each sample was generally injected only once. Multiple injections of the same sample solution show internal reproducibility of 2–5%, depending on the amino acid [*Kaufman and Manley*, 1998]. The synthetic amino acid L-*h*Arg served as an internal standard for quantifying the concentration of amino acids of a small subset of tests. This required longer-duration analyses on the HPLC and an estimate of the individual foraminifer test mass. We estimated the test mass by weighing groups of tests and determining the average, assuming that each test had the same mass. On the basis of 39 samples from six different cores (average of 31 tests per sample), the average test mass is 100 ± 24 μg.

2.5. Analytical Procedures

[18] Samples were analyzed according to methods presented previously (*Kaufman and Manley* [1998], with modifications by *Kaufman* [2000]). Briefly, the method employed precolumn derivatization with *O*-phthaldialdehyde (OPA) together with the chiral thiol, N-isobutyryl-L-cysteine (IBLC), to yield fluorescent diastereomeric derivatives of chiral primary amino acids. The derivatization was performed online prior to each injection using an autoinjector. Separation was by a reverse phase column packed with a C_{18} stationary phase (Hypersil BDS, 5 μm) using a linear gradient of aqueous sodium acetate, methanol, and acetonitrile. Detection was by fluorescence. HP Chemstation computer software integrated the fluorescence signal and controlled the eluent gradient and automated sample derivatization and injection program. Two chromatograms from RPC analysis of individual foraminifera illustrate the typical analytical performance of the technique (Figure 4).

2.6. Independent Age Control

[19] The chronology for each core is based on previously published ^{14}C ages or $\delta^{18}O$ stratigraphy, or both (Table 3). ^{14}C ages for 36 core levels were calibrated using CALIB version 4.3 [*Stuvier et al.*, 1998], to correct for both variable atmospheric ^{14}C levels and marine reservoir effects (Table 4). Included in the ^{14}C calibration is a correction for the marine reservoir effect of approximately 400 to 500 years, depending on age. All ^{14}C analyses were on mixed populations (∼20 mg) of the planktonic foraminifera *Globigerinoides ruber* and *G. sacculifer*, except those from PC42, which were on bulk carbonate [*Grace* 1993; *reported in Dunbar et al.*, 2000]. Four samples yielded ages near the limit of delectability for ^{14}C dating, and were excluded from the age models. The remaining 32 ^{14}C ages from eight cores were used to directly date AAR samples from the same layers and to constrain age models for the cores. Age models for samples younger than ∼30 ka were based on least squares polynomial fits to down core trends (listed in Table 3). Third-order polynomials correctly model the shift toward higher sedimentation rate during the Pleistocene-Holocene transition, which has been documented previously for the northeast Australian margin [*Page et al.*, 2003]. Ages of 24 undated samples from six cores were interpolated or extrapolated from these models. Ages from the remaining 23 AAR samples were based on $\delta^{18}O$ stratigraphy in five cores correlated previously with the SPECMAP global marine record [*Dunbar*, 2000; *Dunbar et al.*, 2000].

3. Results

3.1. Data Screening and Intershell Variability

[20] Between 5 and 16 (average 6–7 per level) tests were analyzed for each of the 80 core levels totaling 526 analyses. In some cases, samples contained tests with D/L ratios that were much different than the others of the group. Higher than expected D/L ratios might indicate reworking of older tests into younger sediment, whereas the lower than expected ratios might indicate contamination by secondary amino acids. The results from individual tests were rejected when their D/L ratios fell beyond ±2σ of the mean of the rest of the sample. The strong covariance between the D/L ratios in aspartic acid (Asp) and glutamic acid (Glu) provides an additional screening criterion, although no mechanism is immediately evident to explain the deviation

Table 5. Amino Acid Data and Independent Age Control for Samples Analyzed in This Study[a]

UAL Laboratory Identification	Sample	Age,[b] calendar years B.P.	Depth, cm bsl	n	ex	Aspartic Acid D/L	Aspartic Acid D/L ± 1σ	Glutamic Acid D/L	Glutamic Acid D/L ± 1σ	Serine D/L	Serine D/L ± 1σ
3936	GC43-005	**2,460**	5	3	2	0.115	0.010	0.044	0.000	0.186	0.020
3935	GC43-031	**5,930**	31	5	0	0.139	0.010	0.048	0.007	0.220	0.019
3949	GC43-051	**8,290**	51	5	0	0.149	0.010	0.053	0.007	0.255	0.018
3934	GC43-071	**9,010**	77	3	1	0.171	0.010	0.062	0.010	0.288	0.030
3933	GC43-153	**11,120**	153	5	0	0.178	0.014	0.059	0.010	0.235	0.074
3937	GC43-171	**14,130**	171	4	1	0.181	0.000	0.068	0.000	2.660	0.040
3950	GC43-189	16,250	189	5	0	0.191	0.010	0.066	0.008	0.298	0.041
3932	GC43-209	**21,080**	209	4	1	0.222	0.030	0.085	0.010	0.300	0.030
3942	PC27a-007	**1,520**	7	5	0	0.079	0.008	0.035	0.006	0.143	0.028
3943	PC27a-052	**4,990**	52	5	0	0.112	0.009	0.045	0.008	0.212	0.019
3944	PC27a-084	**7,620**	84	5	0	0.132	0.004	0.047	0.006	0.240	0.018
3945	PC27a-151	**9,910**	151	4	1	0.131	0.006	0.045	0.004	0.222	0.025
3946	PC27a-193	**12,870**	193	5	0	0.140	0.006	0.049	0.003	0.243	0.033
3947	PC27a-218	**14,340**	218	5	0	0.148	0.013	0.056	0.008	0.262	0.045
3948	PC27a-318	22,646	318	5	0	0.184	0.009	0.063	0.006	0.293	0.031
3614	PC14-025	**1,940**	25	8	3	0.078	0.009	0.031	0.009	0.115	0.031
3938	PC14-047	**4,648**	47	5	0	0.114	0.014	0.040	0.012	0.189	0.074
3939	PC14-061	**7,082**	61	5	0	0.166	0.015	0.057	0.005	0.259	0.023
3616	PC14-075	**9,820**	75	6	0	0.131	0.010	0.045	0.007	0.231	0.036
3615	PC14-088	**12,490**	88	6	0	0.150	0.013	0.053	0.007	0.260	0.040
3940	PC14-099	**14,767**	99	5	0	0.185	0.021	0.069	0.011	0.313	0.058
3613	PC14-109	**16,640**	109	5	1	0.179	0.018	0.063	0.012	0.285	0.052
3941	PC14-130	**20,125**	130	5	0	0.214	0.009	0.077	0.009	0.375	0.025
3733	PC16-015	258	2	4	1	0.054	0.011	0.027	0.007	0.052	0.021
3627	PC16-034	**1,740**	21	6	0	0.076	0.006	0.028	0.003	0.136	0.008
3979	PC16-056	4,361	43	4	1	0.097	0.003	0.038	0.003	0.166	0.003
3977	PC16-078	5,392	58	3	2	0.129	0.008	0.058	0.010	0.199	0.017
3621	PC16-100	**6,720**	80	5	1	0.134	0.010	0.046	0.013	0.206	0.046
3978	PC16-118	7,331	98	3	2	0.153	0.004	0.062	0.009	0.257	0.026
3625	PC16-185	**10,060**	165	5	1	0.162	0.022	0.061	0.013	0.245	0.043
3628	PC16-253	**13,020**	230	4	1	0.172	0.009	0.053	0.005	0.271	0.016
3975	PC16-263	14,767	240	4	1	0.174	0.014	0.064	0.004	0.271	0.045
3976	PC16-272	15,781	249	5	0	0.200	0.013	0.075	0.009	0.317	0.032
3624	PC16-282	**17,420**	259	3	3	0.207	0.010	0.072	0.100	0.251	0.040
3622	PC16-287	17,733[c]	264	5	1	0.296	0.023	0.104	0.013	0.329	0.096
3984	PC16-307	20,907[c]	284	4	1	0.280	0.038	0.122	0.027	0.357	0.041
3626	PC16-367	35,246[c]	344	6	0	0.282	0.015	0.112	0.012	0.345	0.057
3971	PC13-005	**1,250**	5	3	2	0.101	0.006	0.047	0.004	0.139	0.028
3967	PC13-020	6,046	20	4	1	0.103	0.002	0.043	0.007	0.176	0.025
3974	PC13-040	7,929	40	4	1	0.115	0.005	0.042	0.004	0.207	0.024
3969	PC13-055	**8,150**	55	4	1	0.131	0.011	0.044	0.005	0.230	0.017
3968	PC13-079	**10,990**	79	5	0	0.150	0.012	0.054	0.005	0.275	0.022
3970	PC13-086	13,225	86	5	0	0.149	0.007	0.051	0.007	0.256	0.049
3966	PC13-095	17,519	95	5	0	0.189	0.007	0.068	0.006	0.304	0.015
3972	PC13-104	**23,750**	104	4	1	0.206	0.013	0.074	0.008	0.327	0.046
3973	PC13-121	42,066	121	5	0	0.204	0.008	0.071	0.005	0.307	0.04
3987	PC11-023	4,816	13	3	2	0.101	0.005	0.043	0.007	0.172	0.028
3990	PC11-036	**6,980**	26	5	0	0.125	0.009	0.041	0.004	0.249	0.031
3988	PC11-048	8,232	38	5	0	0.141	0.020	0.049	0.005	0.261	0.039
3986	PC11-060	**10,280**	50	3	2	0.160	0.010	0.058	0.004	0.243	0.012
3991	PC11-070	13,639	60	4	0	0.173	0.009	0.064	0.005	0.278	0.007
3983	PC11-079	**18,720**	69	5	0	0.190	0.008	0.069	0.008	0.322	0.024
3989	PC11-090	28,459	80	5	0	0.197	0.019	0.067	0.009	0.322	0.031
3602	PC42-010	**4,580**	2	8	5	0.097	0.012	0.031	0.004	0.162	0.026
3604	PC42-050	**17,840**	42	14	2	0.151	0.012	0.051	0.007	0.263	0.037
3603	PC42-100	32,000	92	5	1	0.214	0.020	0.078	0.011	0.313	0.059
3595	PC42-250	*175,000*	242	8	0	0.327	0.008	0.133	0.007	0.396	0.030
3646	PC42-335	*209,000*	327	9	2	0.367	0.020	0.157	0.016	0.383	0.058
3605	PC10-060	*18,300*	45	6	0	0.166	0.007	0.052	0.007	0.279	0.031
3607	PC10-250	*156,000*	235	6	0	0.321	0.017	0.135	0.015	0.413	0.041
3606	PC10-345	*216,000*	330	6	0	0.366	0.030	0.159	0.021	0.402	0.055
3608	PC10-380	*238,000*	365	6	0	0.388	0.004	0.169	0.004	0.414	0.033
3735	PC12 005	*1,400*	5	5	3	0.072	0.011	0.033	0.009	0.103	0.030
3609	PC12-059	**10,460**	59	5	0	0.151	0.007	0.052	0.011	0.256	0.020
3611	PC12-250	*74,000*	250	5	0	0.278	0.018	0.104	0.016	0.321	0.075
3610	PC12-345	*101,000*	345	6	0	0.294	0.016	0.111	0.009	0.361	0.046
3623	PC15-005	*6,250*	0	9	3	0.101	0.016	0.034	0.005	0.198	0.042
3631	PC15-100	*200,000*	93	6	0	0.359	0.017	0.164	0.016	0.423	0.028
3633	PC15-200	*380,000*	193	5	1	0.441	0.011	0.206	0.015	0.386	0.038

Table 5. (continued)

UAL Laboratory Identification	Sample	Age,[b] calendar years B.P.	Depth, cm bsl	n	ex	Aspartic Acid D/L	Aspartic Acid D/L ± 1σ	Glutamic Acid D/L	Glutamic Acid D/L ± 1σ	Serine D/L	Serine D/L ± 1σ
3722	PC36-020	*3,260*	5	8	2	0.098	0.017	0.037	0.009	0.176	0.032
3723	PC36-050	*19,680*	35	11	2	0.192	0.015	0.066	0.010	0.313	0.059
3724	PC36-106	*64,810*	91	11	1	0.269	0.023	0.096	0.011	0.388	0.040
3725	PC36-126	*82,240*	111	11	1	0.262	0.015	0.099	0.011	0.393	0.029
3726	PC36-194	*125,880*	176	13	0	0.306	0.015	0.118	0.012	0.416	0.056
3727	PC36-204	*129,580*	182	10	2	0.324	0.017	0.131	0.017	0.385	0.051
3728	PC36-234	*163,110*	216	8	1	0.339	0.016	0.142	0.014	0.364	0.059
3729	PC36-302	*230,130*	302	10	1	0.360	0.019	0.157	0.014	0.433	0.091
3730	PC36-333	*238,460*	323	10	1	0.379	0.021	0.162	0.017	0.395	0.090
3731	PC36-351	*246,000*	333	7	1	0.363	0.017	0.162	0.016	0.394	0.032
3732	PC36-409	*294,000*	391	11	0	0.401	0.015	0.189	0.014	0.459	0.025

[a]Here n is the number of subsamples used to calculate the mean D/L and standard deviation, where each subsample comprised a single foraminifera test, and ex is the number of excluded analyses as discussed in text.

[b]Ages in bold are based on direct ^{14}C ages (Table 4); ages in plain type (neither bold nor italic) are interpolated based on sedimentation rate models (Table 3); ages in italic are based on correlation with marine oxygen-isotope stages published previously.

[c]These ages (PC16) were not included in the calibration model (Figure 10) for reasons discussed in the text.

from the covariance. Results were rejected when D/L ratios fell outside the trend exhibited by the other subsamples (Figure 5). In all, results from 64 individual tests (12% of the total) were rejected, of which 18 clearly deviated from the expected covariance between Asp and Glu D/L. These aberrant results reflect poorly understood processes that affect the diagenetic pathway of organic molecules in complex biogeochemical systems.

[21] Most of the remaining 48 rejected ratios were higher than the mean of the remainder of the group, and it is reasonable to assume that these represent tests that were reworked from older stratigraphic levels by bioturbation. Small percentages of foraminifera may be progressively moved up through stratigraphic levels beyond the normal range of mixing. Through the analysis of individual foraminifera with RPC, we reveal what we consider to be inherent variability in the composition and level of diagenesis of foraminifera, combined with the end effects of changing sedimentation rates and reworking. Such inherent variability is masked when aggregate samples are analyzed. Furthermore, by excluding only the conspicuously aberrant ratios (22 values or 4% of total) does not significantly affect the relation between D/L and age (see section 4.2; r^2 is reduced from 0.95 to 0.93 in Asp and from 0.91 to 0.88 in Glu). Thus, whether minimal or maximal exclusions are made, neither approach significantly alters the average values or conclusions drawn in this study. Moreover, the outlying values may hold the key to understanding processes of bioturbation and sediment transport along the shelf margin. We reserve this line of investigation for future papers.

[22] Following data screening, the intershell variability in D/L from core levels was relatively low (Table 5). The coefficient of variance (CV) for Asp, Glu, and Ser D/L averaged 7, 14, and 14%, respectively, for the 80 core levels. This is similar to the intershell variation reported for single-age populations of ostracodes and land snails [*Kaufman*, 2003a; *Hearty et al.*, 2004]. The uppermost sample for each of the 11 cores typically produced the highest intershell variation (Table 5). For example, the CV for Asp D/L in the upper samples was twice as high as the average CV for all of the samples, and these samples contained twice the frequency (21%) of aberrant tests. This may be a result of sediment dislocation during piston coring, combined with the rapid rate of racemization in these youngest samples, which would tend to amplify small age differences. In addition, CVs are typically higher for samples with lower absolute D/L in which small differences in D/L have a disproportionately large effect on CV.

3.2. Amino Acid Composition and Concentration of *Pulleniatina*

[23] The concentrations of amino acids in fossil foraminifera are intermediate between those of ostracodes and gastropods (Figure 6). The combined concentration of seven common amino acids (Asp, Glu, Ser, Gly, Ala, Val, and Ile) in the total acid hydrolsate, are typically 2–4 nmol mg^{-1} of shell. In contrast to the other two fossil types, foraminifera that are hundreds of thousands of years old show only

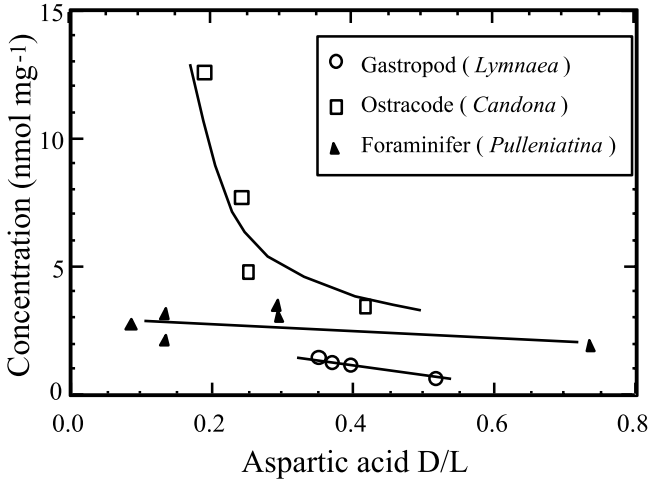

Figure 6. Examples of amino acid concentrations in foraminifer compared with gastropods and ostracodes, each related to the extent of racemization (D/L) in aspartic acid (Asp). Concentrations are the sum of seven amino acids in the total acid hydrolsate (Asp, Glu, Ser, Gly, Ala, Val, and Ile) per milligram of shell. Values (low to high Asp D/L) are from core levels PC14-024, PC14-075, PC12-059, PC12-345, PC14-450, and PC15-400.

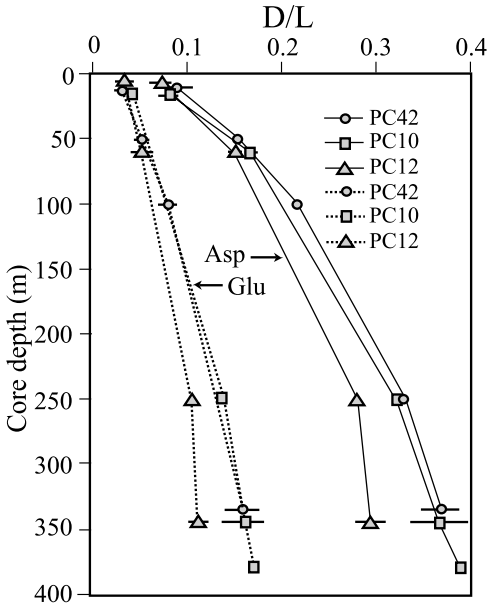

Figure 7. Down core trend of D/L in aspartic acid (Asp) and glutamic acid (Glu) in *Pulleniatina* from cores PC42, PC10, and PC12. The cores are located within 100 km of each other in water depths of 1389, 1344, and 1443 m, respectively (Figure 1). PC42 and PC10 exhibit sedimentation rates of ~1.6 cm ka^{-1}, while PC12, owing to its proximity to the shelf slope, has a higher sedimentation rate of ~3.4 cm ka^{-1}. The respective aminostratigraphies of PC10 and PC42 confirm similar thermal and sedimentation conditions, while comparatively lower D/L ratios in PC12 result from higher sedimentation and cooler bottom water temperatures.

nominal loss in concentrations of amino acids. This suggests that amino acids in Quaternary *Pulleniatina* tests from marine sediment degrade more slowly or are retained more completely than in ostracodes or gastropods from terrestrial deposits. As such, foraminifer tests come closer to approximating a closed system, such as that in emu eggshell [e.g., *Miller et al.*, 1997], which simplifies and adds confidence to models of racemization kinetics.

3.3. Initial D/L Ratios

[24] Attempts to isolate modern or submodern *Pulleniatina* from core tops were unsuccessful, probably due to well-known problems with piston coring. Extrapolating the D/L trend in cores PC14, PC16, and PC42 to the surface results in initial D/L ratios of ~0.07 for Asp and ~0.02 for Glu (Figure 7). *Harada and Handa* [1995] report a higher initial Asp D/L ratio of 0.14 at their core top using gas chromatography on large numbers of *Pulleniatina* individuals comprising bulk samples. Three foraminifera from PC16-015 returned Asp D/L values of 0.042, 0.048, and 0.058. This core has the best chance of preserving near-modern tests because it is from a site with rapid sedimentation rate and apparently minimal bioturbation. On the basis of extrapolation of these ratios from 15 cm depth, we estimate an initial Asp D/L ratio of 0.03–0.04. These ratios are similar to those measured in living ostracodes from nonmarine settings [*Kaufman*, 2000, 2003b], but ongoing analyses of surface grab samples from 1000 m depth from the Queensland trough will determine initial ratios from living and recently dead *Pulleniatina*.

4. Discussion

4.1. Evaluating the Integrity of AAR in Single-Foraminifera Tests

[25] To assess the utility and reliability of this application of amino acid geochronology using RPC on single *Pulleniatina*, we subjected the results to five fundamental tests. We evaluate the results vis-à-vis stratigraphic superposition, concordance with independent ages, detection of stratigraphic discontinuities, similarity of environments of deposition, and sensitivity to different water masses.

4.1.1. Do D/L Ratios Increase Consistently Down Core?

[26] A fundamental test of the technique is based on stratigraphic superposition. Assuming that depositional ages of sediments and foraminifera increase down core, then so should their D/L ratios. Of the 83 samples from 11 cores, 76 exhibit mean Asp values in correct stratigraphic order (Table 5). Of the seven reversed mean Asp D/L values, five are not statistically significant (i.e., they overlap within errors), with differences of <3% of the mean. Their statistical overlap likely reflects mixing and rapid sedimentation rather than a shortcoming of the method. The down core progression of D/L ratios in PC10, PC12, and PC42 is shown in Figure 7. Another example of the quality of the data set is provided from core PC36. This is the most densely sampled core, with 122 foraminifera analyzed from 11 horizons (Table 5).

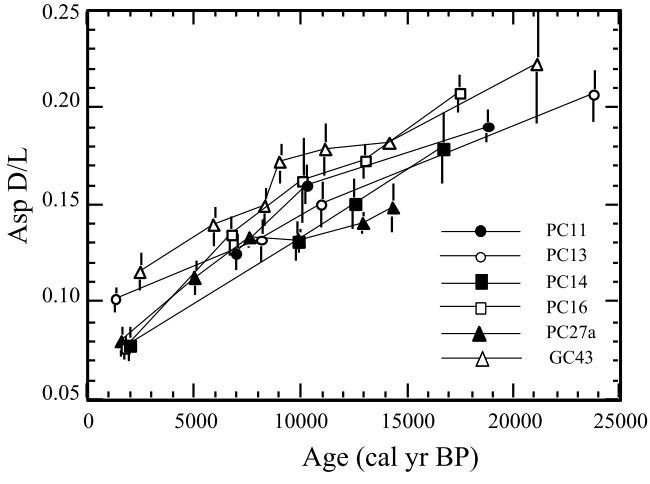

Figure 8. Extent of racemization (D/L) versus age in aspartic acid (Asp) from all ^{14}C dated levels in six cores from the Queensland slope and trough. Ages are based on AMS ^{14}C on planktonic foraminifera [*Dunbar et al.*, 2000; *Page et al.*, 2003] calibrated in this study using CALIB [*Stuvier et al.*, 1998]. Errors are ±1σ of multiple single-test analyses (calibrated age errors are not shown but are listed in Table 4).

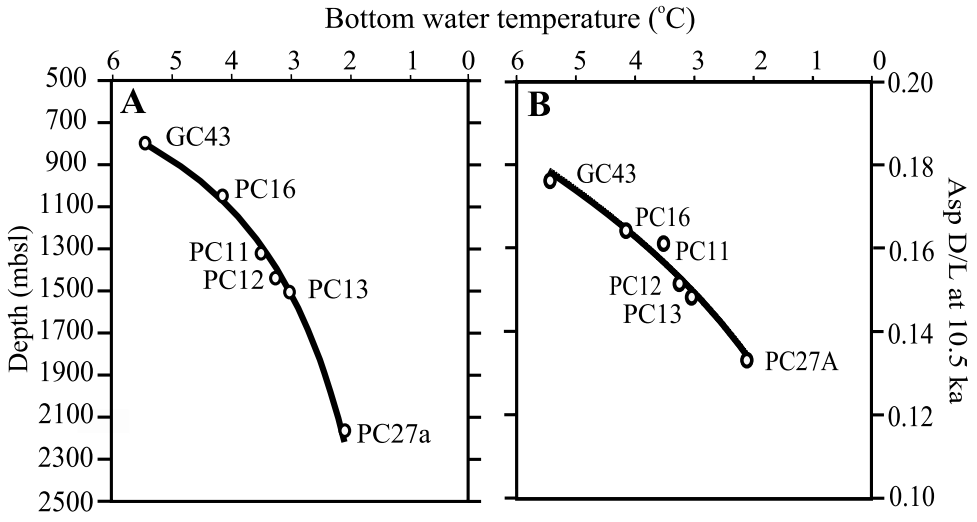

Figure 9. Water temperatures at six core sites and their relation to the extent of racemization in *Pulleniatina*. (a) Mean annual bottom water temperature versus depth of selected cores from the Queensland margin. (b) Interpolated aspartic acid (Asp) D/L ratios from selected cores at age levels equivalent to 10,500 calendar years B.P. D/L decreases with decreasing site temperature for similar-aged samples demonstrating the long-term effect of temperature on the rate of racemization. Temperature data are from the CSIRO marine trawler database (www.marine.csiro.au/datacentre).

4.1.2. Do D/L Ratios Vary in Accordance With Independent ^{14}C Ages?

[27] D/L ratios in *Pulleniatina* were determined from six cores with finite ^{14}C ages (Table 4), and show a systematic increase with increasing radiometric age in nearly all cases (Figure 8). Differences in D/L among cores are largely attributable to differences in temperature histories at the core sites (see section 4.1.5).

4.1.3. Are Known Stratigraphic Discontinuities Discernible?

[28] Between 282 and 287 cm depth in PC16, ^{14}C ages increase from 17 to 40 ka (Table 4). This abrupt increase in age, along with bio/lithostratigraphic evidence, suggests that at least 20000 years of sediment has been eroded. Asp D/L ratios support this inference, with an abrupt increase from 0.207 to 0.296 between 282 and 287 cm (Table 5). The AAR data also suggest that the 40400 ^{14}C years age at 287 cm should be considered a minimum age, rather than finite. First, based on the trends in all other cores, an Asp D/L ratio of ~0.296 should equate to about 80 to 100 ka. Second, δ^{18}O values from this horizon are too depleted to be ascribed to the marine isotope stage 3, and instead suggest an interglacial age of around 80 to 100 ka [*O'Leary*, 2001].

[29] Core PC14 exhibits the most dramatic down core variation in Asp D/L values (>30%), changing from 0.114, to 0.166, to 0.131 in only 28 cm depth (47–75 cm). The reversal coincides with the early stages of racemization when the reaction rates are highest. When combined with rapid sedimentation in PC14 (6.5 cm ka^{-1}), minor discontinuities are accentuated. The stratigraphically reversed D/L ratios are not apparent in the ^{14}C chronology (Table 5), and may be the result of localized transport and deposition of older individuals by scour in this relatively high-energy slope environment.

[30] These examples highlight the benefit of the RPC analyses of individual foraminifera in its ability to detect stratigraphic discontinuities, such as sedimentary lacunae, scour, and overturned beds. Traditional AMS ^{14}C analyses require a considerable number of individuals, and may have the effect of obscuring such discontinuities.

4.1.4. Do Foraminifera in Cores From Similar Depths Yield Similar D/L Ratios Down Core?

[31] Cores PC10, PC12 and PC42 were taken from similar depths and oceanographic settings within 100 km of each other (Figure 1). The stratigraphy and sedimentation rates for PC10 and PC42 are similar [*Dunbar et al.*, 2000], and the D/L ratios from these cores exhibit nearly identical down core progressions (Figure 7). For example, samples taken at equivalent core depths of 250 cm return overlapping mean Asp D/L ratios of 0.321 ± 0.017 (PC10) and 0.327 ± 0.008 (PC42) (Table 5). In PC12, the sample from 250 cm returns a somewhat lower D/L ratio of 0.278 ± 0.018. This can be explained by a higher sedimentation rate in PC12 due to its proximity to the Queensland shelf. Thus the rate of change of D/L ratios down core can be used to evaluate the rate of sedimentation, regardless of absolute age.

4.1.5. Does the Racemization Rate Vary With Differences in Water Temperature With Depth?

[32] The rate of racemization varies systematically among the cores, as implied by their ^{14}C ages. The difference in reaction rate can largely be ascribed to differences in bottom water temperatures at depth. The shallow water depths of cores used in this study eliminate any role that dissolution might play in the diagenesis of foraminifera samples. To assess the relation between site temperature and racemization rate, we interpolated the Asp D/L ratios for the 10,500 calendar years B.P. level of each core (Figure 9). Cores from shallower water depths have incrementally higher D/L

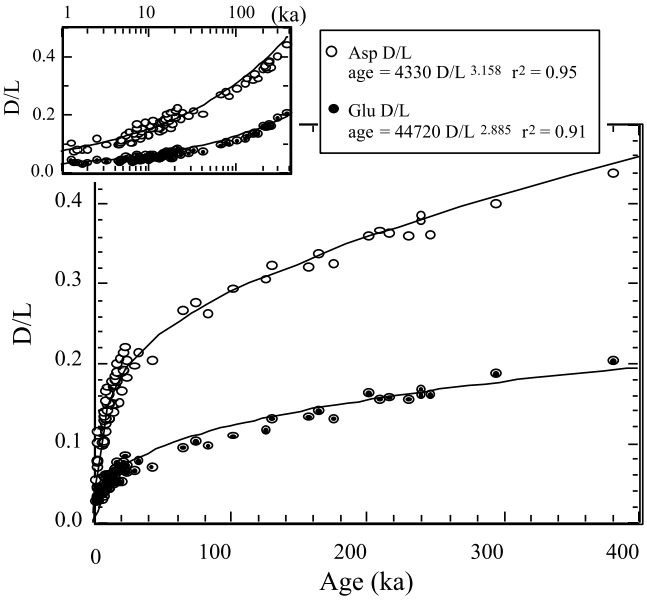

Figure 10. A linear plot of the extent of racemization (D/L) versus age (large graph) for aspartic acid (Asp) and glutamic acid (Glu) in *Pulleniatina* from the Queensland margin. The long-normal graph (inset) better demonstrates the D/L versus age in the ^{14}C range. Ages are either determined directly by ^{14}C analysis (Table 4) or are estimated based on previously published $\delta^{18}O$ analysis and correlation with the global marine oxygen-isotope record [*Dunbar et al.*, 2000; *Page et al.*, 2003]. Curves (inset) are power functions fit by regression. The scatter about the models can be attributed to differences in temperature histories among core sites. No attempt was made to adjust D/L ratios according to these temperature differences, resulting in some moderate uncertainty. The power functions provide generalized calibrated age equations that can be applied to Quaternary *Pulleniatina* elsewhere in the region.

ratios. Shallower cores are also bathed by warmer water (www.marine.csiro.au/datacentre). Oceanographic surveys indicate that water temperature increases from 2.0°C at the greatest sample depth (2163 m) in the Queensland trough, to 5.5°C at 901 m (Figure 9a). On the basis of the modern bottom temperatures, a 1°C increase is associated with a 0.02 increase in Asp D/L for 10.5 ka *Pulleniatina.* This illustrates the effect of temperature on D/L and implies that AAR can be used to resolve paleotemperatures within 1°C for samples of known age and known thermal history.

4.2. Long-Term Racemization Rates

[33] Asp and Glu D/L increase systematically with sample age (Figure 10). The rate is higher during the earlier stages of the reaction, especially for Asp. The decrease in the rate of racemization as the reaction approaches equilibrium is expected. As discussed previously, racemization rates vary with water temperature, as demonstrated for the ^{14}C dated samples. When considering the full body of the data set, however, including samples hundreds of thousands of years old, the variation due to differences in water temperature are secondary to the effect of sample age. To evaluate the overall, long-term rate of racemization, data from all 11 cores were aggregated to develop a calibrated age equation that relates the extent of racemization in *Pulleniatina* to sample age.

[34] We evaluated the goodness of fit for two models. The decreasing rate with increasing sample age (Figure 10) is consistent with a parabolic trend that has been used previously to model the rate of racemization [e.g., *Mitterer and Kriausakul*, 1989; *Harada et al.*, 1996; *Kaufman*, 2003b]. For this model, the square root of sample age is assumed to vary linearly with D/L. Least squares regression shows that this model provides an excellent fit to the data for Glu D/L ($R^2 = 0.95$), but not for Asp D/L ($R^2 = 0.76$). The rate of Asp racemization during the initial stages of the reaction is too rapid to conform to a parabolic model. Instead, we fit the data to power functions, which provide good fits to both Asp and Glu D/L (Figure 10). Least squares regressions fit to the power-transformed D/L ratios yield the calibrated age equations for *Pulleniatina,* which can be applied to other cores from the north Queensland margin over the middle and late Quaternary.

The age equation for Asp is

$$t = 4330\ \mathrm{D/L}^{3.158} \quad \left(R^2 = 0.95, P < 0.001\right) \qquad (1)$$

and for Glu it is

$$t = 44720\ \mathrm{D/L}^{2.885} \quad \left(R^2 = 0.91; P < 0.001\right) \qquad (2)$$

where t is age in ka. Although the rate of racemization in the two amino acids are affected by the same systematic errors and are therefore not strictly independent, samples that yield similar ages for the two amino acids can be viewed with greater confidence. A minor element of uncertainty is inherent in the model due to the effects of variable bottom water temperature histories of the samples.

5. Conclusions

[35] *Pulleniatina* is a large, ubiquitous, conspicuous, and well-preserved planktonic foraminifera that is well suited for amino acid geochronology in the north Queensland continental margin, as well as pantropical oceans up to 40° latitude. *Pulleniatina* tests are well preserved and retain high concentrations of amino acids for hundreds of thousands of years. Asp and Glu D/L ratios from 462 individual foraminifera tests from 80 levels in 11 cores exhibit a systematic increase of D/L ratios down core. Asp and Glu D/L ratios covary systematically. Cores that are proximal to one another show similar D/L ratios at similar core depths. Differences in D/L ratios from age equivalent levels can be attributed to bottom water temperature differences among the core sites. These results support the integrity of individual foraminifera tests for amino acid geochronology.

[36] The results of this study provide a foundation for future studies of deep-marine sediments of middle

to late Quaternary age. Potential applications might include: (1) Stratigraphic correlations among cores within similar oceanographic settings. (2) Numerical dating of core samples following calibration with independent ages (^{14}C in younger core intervals), and modeling of racemization rates. (3) Detection of stratigraphic discontinuities including lacunae, reworked or scoured zones, slumped intervals or overturned beds in cores. (4) Direct assessment and quantification of the degree of mixing of foraminifera in core intervals [*O'Leary et al.*, 2004]. (5) Approximation of the temperature history for samples of known age over glacial-interglacial cycles. (6) Determination of relative and absolute sedimentation rates in a spatial context, and processes related to sediment flux using an independent chronometer effective over 500 ka. (7) Assessment of the spatial-temporal pattern of sedimentation over broad time ranges of multiple sediment cores, compatible with the rapid and inexpensive analysis of sediment intervals that contain even sparse foraminifers. As the RPC database expands with additional studies, the approach will offer solutions for a variety of oceanographic questions. In the interim, however, we are seeking to further understand factors that may complicate these clear benefits.

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