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Amino Acid Based Geochronology of Unit 3.1 (Quaternary), CRP-1, Victoria Land Basin, Antarctica

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Abstract - Amino acid-based geochronological analyses were carried out on fossil mollusc shell and foraminifera from Unit 3.1, Cape Roberts Project core CRP-1. Ratios of D-alloIsoleucine to L-Isoleucine (D/L) were measured from 19 fossil samples using cation exchange High Performance Liquid Chromatography (HPLC) methods. Preliminary interpretation of these results suggest that Unit 3.1 contains carbonate fossils having multiple ages. The interpreted ages have a bimodal distribution between ~220 Ka (Quaternary) and ~2.4 Ma (Pliocene). However, these results lack a comprehensive regional and taxonomic context for amino acid studies in Antarctica and therefore should be regarded as preliminary age estimates of fossil shell ages.
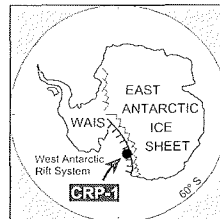
INTRODUCTION

The existing Quaternary marine record of the Ross Sea sector of Antarctica has been assembled from marine cores (Anderson et al., 1992), drilling programmes (Dry Valley Drilling Project, Deep Sea Drilling Project), raised beaches, ice-elevated debris deposits (Stuiver et al., 1981), and cryoturbated sea-floor debris exposed on the surface of the McMurdo Ice Shelf (Kellogg et al., 1990). Most of these records are Holocene in age, although a few exposures may extend back to 50 000 or even 125 000 years before present. Until the recovery of core from CRP-1, older Quaternary marine successions were unknown in this region of Antarctica. In the present investigation we studied the amino acid stereochemistry of macrofossil (bivalve) and microfossil (foraminifera) carbonate from Unit 3.1 (CRP-1). From the results of this preliminary study, we propose age determinations for this stratigraphic unit.

A 148 m-thick upper Cenozoic succession of lower Miocene and Quaternary sediments was recovered from core CRP-1 (Cape Roberts Science Team, 1998). The 43.55 m-thick Quaternary sequence is subdivided into six units and includes poorly consolidated clays, silts, gravels, diamictons, and a highly fossiliferous, very poorly sorted, muddy gravelly sand (Unit 3.1) (Fig. 1). Unit 3.1 has a thickness of 1.93 m and is separated by sharp contacts from the underlying and overlying diamicton units (Cape Roberts Science Team, 1998, p. 146). It is compact but uncemented.
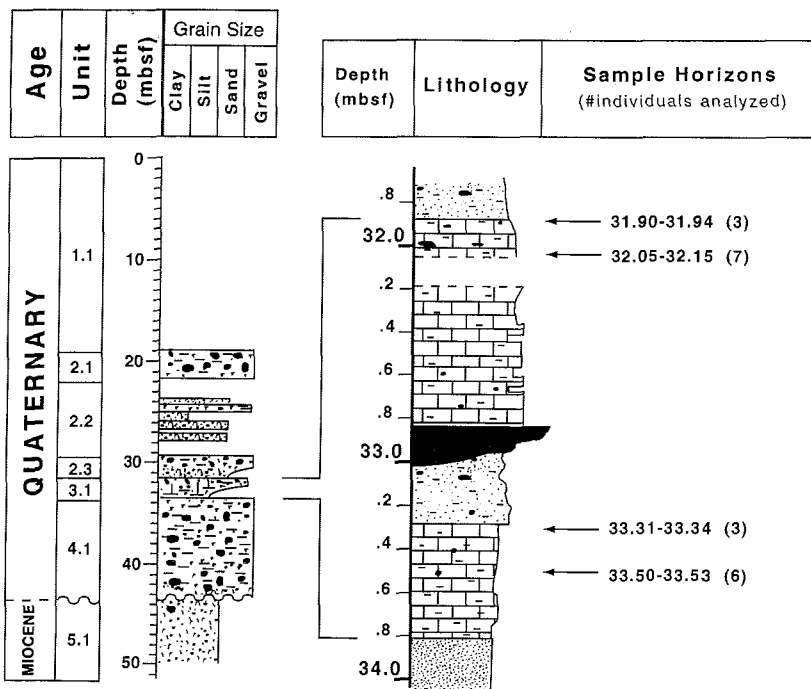

Fig. 1 - Stratigraphic column for CRP-1, illustrating the position of Unit 3.1 within the Quaternary succession. Lithologic descriptions cited from Cape Roberts Science Team (1998). The stratigraphic position for samples used in this investigation are noted on the enlarged section at right. The numbers in parentheses indicate the number of individual shell samples analyzed from that level.

The unit is characterized by both weak and strong, and thin to medium bedding. Locally, bedding is defined by shell beds. Fossil material present includes palynomorphs, diatoms, foraminifera, ostracodes, sponge spicules, bryozoans, gastropods, bivalves, brachiopods, barnacles, echinoderm spines and worm tubes (Figs. 6 & 14, Cape Roberts Science Team, 1998). These sediments also include an ice-rafted clastic terrigenous component.

Unit 3.1 is interpreted as an open water shell bank formed in water depths of up to 150 m, with the depositional site well removed from glacier grounding lines. Diatom biostratigraphy suggested that Unit 3.1 falls within the lower Quaternary *Fragilariopsis kerguelensis* Zone (1.25 to 1.8 Ma) of Harwood and Maruyama (1992) (Cape Roberts Science Team, 1998). More recently, the diatom-based age has been revised to 700 ka to 1.35 Ma (Harwood et al., this volume).

Webb & Strong (this volume) report large and diverse (>70 species) assemblages of calcareous benthic foraminifera and high numbers of the planktic foraminiferan *Neogloboquadrina pachyderma* in eleven samples from Unit 3.1. Relative species abundances within individual assemblages are maintained within the limits of natural variability throughout the unit and assemblages are interpreted as representing *in situ* biocoenoses. A small but persistent element of recycled Pliocene foraminifera, including the large trochospiral *Ammoelphidiella antarctica* Conato and Segre (=*Trochoelphidiella onyxi* Webb), is present in Unit 3.1 and was probably introduced by ice-rafting from near-shore facies of the Victoria Land Basin or from the Taylor, Wright and/or ?Mackay paleofjords (Ishman & Webb, 1988; Ishman & Rieck, 1992; Webb, 1974; Webb & Strong, this volume, 473-478). No Miocene or older foraminifera were recovered from Unit 3.1. Preservation states for intact bivalve and gastropod shells, fragmented macrofossil shells, foraminifera and ostrascodes, suggests that palaeontological material of two or more ages is present in Unit 3.1.

Amino acid geochronology is based upon the preservation of proteins within the matrix of carbonate fossils (Miller & Brigham-Grette, 1989). This technique has been widely employed as a geochronologic tool in Quaternary sequences from many locations throughout the world (*e.g.*, Miller, 1985; Wehmiller et al., 1995), yet prior to this pilot study it has received limited application in Antarctica. The presence of substantial quantities of biogenic carbonate in the Quaternary section of the Cape Roberts Core provides an excellent opportunity to test the utility of this technique in a stratigraphic context from Antarctic marine sediments.

UNIT 3.1 MATERIAL ANALYSED

Macrofossils and foraminifera occur in abundance throughout the unit (Cape Roberts Science Team, 1998), although all macrofossil material available to the authors was highly fragmented. Preservation is generally excellent and shell samples exhibit little evidence of corrosion or dissolution. Bivalve shell fragments were recovered from four samples and foraminifera from one sample between 31.90 and 33.53 mbsf CRP-1 (Fig. 1). Shell identifications were tentative since available material was so thoroughly fragmented, and several fragments were completely unidentifiable. Identifiable bivalve genera analyzed included *Philobrya, Limatula, Cyclocardia* (Tab. 1). Webb & Strong (this volume, 455-472) conclude that the dominant youngest foraminiferal assemblages recovered from Unit 3.1 represent essentially *in situ* biocoenoses, therefore age projections derived from these taxa are likely to represent the depositional age of the host sediment. The macrofossil assemblage has not been subjected to population census examination, and prior to amino acid analysis these were assumed to be the same age as the foraminifera, or perhaps older.

Sedimentologic, stratigraphic and micropalaeontologic studies indicate that Unit 3.1 may be subdivided into two

Tab. 1 - Table of analytical results for 19 amino acid analyses from Unit 3.1 CRP-1.

Core Depth (m)	Taxa	AAL	SID	D/L	Std. Dev.	n	Projected Age (ka)
31.90-31.93	*Philobrya ?*	8840	A	0.264	0.002	2	378
31.90-31.93	*Philobrya ?*	8840	B	0.268	0.001	2	385
31.90-31.93	indeterminate	8840	C	0.175	0.001	2	244
32.05-32.15	foraminifera	8839	A	0.204	0.025	2	288
32.05-32.15	*Limatula ?*	8852	A	0.773	0.028	2	2740
32.05-32.15	*Cyclocardia ?*	8852	B-1	0.271	0.014	2	390
32.05-32.15	*Cyclocardia ?*	8852	B-2	0.178	0.003	2	250
32.05-32.15	indeterminate	8852	C-1	0.770	0.022	2	2715
32.05-32.15	indeterminate	8852	C-2	0.732	--	1	2452
32.05-32.15	indeterminate	8852	C-3	0.217	0.005	2	307
33.31-33.34	*Limatula ?*	8841	A	0.196	0.001	2	277
33.31-33.34	*Limatula ?*	8841	B	0.157	--	1	218
33.31-33.34	*Limatula ?*	8841	C	0.190	0.004	2	267
33.50-33.53	*Limatula ?*	8842	A	0.215	0.004	2	304
33.50-33.53	*Limatula ?*	8842	B	0.223	--	1	317
33.50-33.53	pecten ?	8842	C	0.292	0.001	2	421
33.50-33.53	*Cyclocardia ?*	8843	A	0.190	--	1	268
33.50-33.53	*Cyclocardia ?*	8843	B	0.172	--	1	241
33.50-33.53	*Cyclocardia ?*	8843	C	0.176	--	1	247

Note: AAL = Amino Acid Lab number, SID = sample designation, D/L = D-alloIsoleucine/L-Isoleucine, n = number of replicate analyses per sample.

broad subunits that might be slightly or significantly different in age. To test this possibility two samples were selected for analysis from both the lower and upper carbonate sediments (Fig. 1). Foraminifera from the upper subunit were regarded as the best example for *in situ* biogenic carbonate from Unit 3.1. Therefore analysis of these fossils might provide the true age of the unit. The following four foraminiferal taxa (Family Miliolidae) from sample 32.05-32.15 mbsf were used to provide a bulk sample for analysis: *Planispirinoides bucculentus* (Brady), *Cruciloculina triangularis* d'Orbigny, *Pyrgo patagonica* (d'Orbigny), and *Pyrgo depressa* (d'Orbigny). These taxa are large, heavily calcified, and very well preserved.

Bivalve shell fragments used in this study were quite small, all pieces being smaller than 4.0 mm. Although the shell samples used were sufficient for amino acid analysis, sample size constraints substantially limited the quality of pre-analysis cleaning that could be performed. Shells were assigned Amino Acid Laboratory (AAL) numbers and are logged in the database at the Center for Geochronological Research (Tab. 1). Macrofossils are present, but relatively rare, in the other Quaternary units of the CRP-1 succession. Their suitability for amino acid analysis remains to be evaluated.

ANALYTICAL RESULTS

Mollusc shell and foraminifera samples were prepared and analyzed using cation exchange methods of High Performance Liquid Chromatography (HPLC) described by Miller (1985) and Miller & Brigham-Grette (1989). This technique measures the extent of epimerization of the naturally occurring amino acid L-Isoleucine to D-alloIsoleucine. The results are reported as the ratio of D-alloIsoleucine to L-Isoleucine (D/L). Higher D/L ratios reflect greater amounts of Isoleucine epimerization and hence longer amounts of time since fossil deposition. Because the conversion of L-Isoleucine to D-alloIsoleucine is a reversible reaction, eventually equilibrium between the two diastereomers is achieved producing a D/L ratio of approximately 1.3 (Hare & Mitterer, 1969). The rate of Isoleucine epimerization is also influenced by the temperature carbonate fossils experience during burial and diagenesis. Lower temperatures slow the reaction rate, increase the interval of time until equilibrium is achieved and consequently decrease the age resolution possible with this method. Therefore amino acid age estimates must consider the depositional context of the fossil and its thermal history.

A total of 19 samples from Unit 3.1 were analyzed as total acid hydrolysates. Where possible, replicate analyses were performed to evaluate between run reproducibility (Tab. 1). A bimodal distribution of D/L ratios was found among samples collected from the 32.05 m level of the CRP-1 core (Figs. 2 & 3). Three samples, representing at least two different fossil taxa, 32.05 mbsf yielded ratios in the 0.732 - 0.773 range. All other samples, representing at least six fossil taxa, produced D/L ratios clustered between
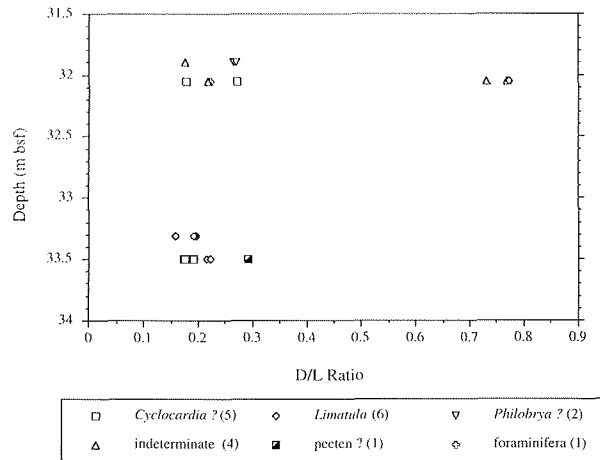

Fig. 2 - Stratigraphic-D/L ratio plot for 19 analyses from CRP-1 (Unit 3.1). Note that there is no significant increase in the lower cluster of ratios (left side of plot) throughout the thickness of Unit 3.1. This distribution of ratios is interpreted as evidence strongly suggesting deposition of this unit over a relatively short interval of time. Numbers in parentheses in figure legend indicate the number of specimens analyzed.

0.153 and 0.292 (Figs. 2 & 3). This difference in D/L ratios within a single stratigraphic level is greater than differences in rates of Isoleucine epimerization that would be observed between different fossil genera. The low standard deviations on nearly all analyses (Tab. 1) clearly show that the two D/L ratio groups represent fossils of decidedly different ages.

Interpreting numerical ages from amino acid data requires knowledge of the temperature experienced by the fossil during burial and diagenesis. The thermodynamics of the Isoleucine to alloIsoleucine conversion has been well-studied with particular regard to the interpretation of numerical ages from D/L ratios (Mitterer & Kriausakul, 1989). This present study used a model developed by Miller (1985) and employed by Kaufman & Brigham-Grette (1993) to translate amino acid data into numerical age estimates using a model of Isoleucine epimerization kinetics developed from experimental heating of shell
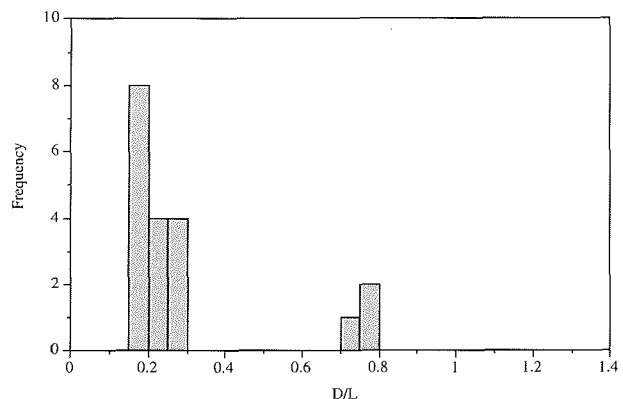

Fig. 3 -Histogram plot of amino acid ratio-frequency for the 19 amino acid analyses from CRP-1 (Unit 3.1). Note the bimodal grouping of amino acid ratios.

samples. These experiments substituted heat for time to drive the epimerization reaction. Fossil samples analyzed for model development were calibrated against numerical dating techniques. Therefore the age determination model requires some estimate of the average temperature a sample has experienced during diagenesis. Isoleucine epimerization kinetics in this model were developed from data collected from two mollusc genera, *Mya* and *Hiatella*.

The mean diagenetic temperature experienced by CRP samples is assumed to be that of the present day bottom temperature found in the Ross Sea, about -1.8°C (Jacobs et al., 1985). Modern day Ross Sea bottom water temperature estimates are used in order to make preliminary numerical age assignments for the CRP amino acid samples. The lower group of amino acid ratios suggest an age range of 218-421 ka for those samples (Tab. 1). The three samples with higher ratios from the 32.05 m-depth sample are compatible with an age of approximately 2.4-2.7 million years.

DISCUSSION

Miller & Brigham-Grette (1989) noted that L-Isoleucine epimerization rates vary among different mollusc species. Differences in shell microstructure and mineralogy between different molluscan families and orders can contribute significantly to the overall quantity of amino acid preserved in fossilized shells. Careful sampling and analysis has also shown that D/L ratios may vary significantly on a single shell specimen depending upon where that shell was sampled for amino acid analysis (Brigham, 1983). Evaluation of Isoleucine epimerization data from Antarctic molluscs is in an early stage of development. No Antarctic mollusc genera have been systematically evaluated for intrashell variability of amino acid content nor have epimerization rates been evaluated with heating experiments. The D/L ratios obtained from *Cyclocardia*, *Limatula* and *Philobrya* samples (Tab. 1) fall within a relatively narrow range among samples included in the cluster of lower D/L values (Fig. 3). This could be broadly interpreted as evidence that these genera exhibit fairly similar rates of isoleucine epimerization. However, because of the preliminary nature of the data from this pilot study, the numerical ages assigned to D/L ratios reported in table 1 should be regarded as projections.

The results from sixteen analyses on material selected from the four stratigraphic levels, and including both the lower and upper carbonate beds of Unit 3.1, suggest that entire unit is the same age and deposited between 210 and 430 ka. The similarity of D/L ratios obtained from macrofossil (bivalves) and microfossil (foraminifera) carbonate, suggesting that these groups were contemporaneous in bioclast-enriched sediments deposited near the crest of Roberts Ridge. The variability found among D/L ratios from these sixteen samples may be attributable to taxonomic variability of Isoleucine epimerization rates. More extensive use of amino acid analysis on Antarctic Quaternary fossils is necessary to assess this taxonomic factor.

The age projected for Unit 3.1 based upon amino acid analysis is significantly younger than dates proposed from Strontium analysis (Lavelle, this volume) and diatom biostratigraphy (Bohaty et al., this volume). Our amino acid age projections assume a mean temperature of -1.8°C since burial of these fossils and Isoleucine epimerization rates identical to that of the bivalve genus *Mya*. The presence of grounded ice on Roberts Ridge during the Pleistocene would have lowered sediment temperatures some unknown amount for thousands of years. This period of cooling would depress the rate of Isoleucine epimerization, effectively making the projections presented here too young.

Three analytical results obtained from mollusc shell fragments at 32.05-32.15 mbsf suggest the presence of possible recycled Pliocene (~2.4 Ma) biogenic carbonate. This interpretation is compatible with the palaeontologic observation of recycled Pliocene foraminifera that are common in Unit 3.1 and also in other units of the CRP-1 succession.

The lack of samples with high (>0.7) D/L ratios at levels in other than the 32.05 mbsf sample is puzzling but may reflect a sampling artifact of the limited amount of material available for this study. More thorough sampling and analysis of bivalve shells from throughout Unit 3.1 should provide an answer to this question and possibly reveal the identity of older fossil shells in Unit 3.1. Further analytical work, incorporating a larger population of individual shells or fragments, should reveal the extent of mixed ages of shell carbonate in the Quaternary section of CRP-1. Amino acid studies of shell carbonate recovered from Ross Sea continental shelf piston cores also revealed the presence of Pleistocene and Neogene fossils at the same stratigraphic levels as Holocene age shells (Hart et al., 1996; Hart, unpublished data). This result suggests that there is considerable potential for recycling shell carbonate in Ross Sea continental shelf sediments.

Further analytical work is in order to make more precise numerical age estimates from amino acid data from the Antarctic. This will include amino acid experimental kinetics studies on common Antarctic shell species plus paired analyses for amino acids and other numerical dating methods, such as radiocarbon and strontium, from a single shell sample. This would enable amino acid data to be calibrated and enable calculation of diagenetic temperatures for these sediments. The completion of bore hole geophysical studies, including sediment temperature measurements, in future Cape Roberts Project holes will considerably aid the calibration of amino acid based geochronology for obtaining well constrained numerical ages.

This study offers a preliminary examination of the ages of carbonate fossils in the Quaternary section of the CRP-1 core. It has examined shell material representing possibly eighteen different individual molluscs. While this represents a very small population from the total recovery of biogenic carbonate from this interval of CRP-1, it is a much larger sample population compared with other dating techniques applied to this core. Amino acid analysis has clearly demonstrated the mixed ages of fossil biogenic

carbonate present in Unit 3.1. The age interpretations developed from this study, while not completely compatible with biostratigraphic and absolute age studies of CRP-1, do suggest avenues for further study in order to refine amino acid geochronology methods in Antarctica.

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