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AMINO ACID RACEMISATION DATING OF THE "OLDER PLEISTOCENE MARINE BEDS", REDCLIFF, NORTHERN SPENCER GULF, SOUTH AUSTRALIA

GEOLOGICAL SURVEY

by

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Summary

Amino acid racemisation reactions are applied in relative and quantitative age assessments of the "Older Pleistocene marine beds" from Redcliff, northern Spencer Gulf. The extent of racemisation (epimerisation) for a range of amino acids in specimens of the fossil bivalve *Anadara trapezia* suggest a Penultimate Interglacial age (oxygen isotope stage 7) of approximately 200,000 yrs B.P., consistent with the geological context of the fossiliferous marine strata.

Key words: Amino Acid Racemisation, Middle Pleistocene, Marine Sediments, Sea Level Change

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Introduction

Until recent years, age assessments of Quaternary marginal marine sediments have been frustrated by complex stratigraphic relationships and the restrictions of some established dating techniques. In response to these difficulties, considerable research undertaken recently has resulted in the development of a variety of dating methods including amino acid racemisation, thermoluminescence and electron spin resonance (Mahaney, 1984; Rutter, 1985). Although the principles on which these techniques are based are long established, their application in Quaternary studies is relatively new.

Some of the difficulties of establishing chronologies in Quaternary marginal marine settings have historically included the interfingering relationship of terrestrial and marine sediments, the lack of fossils in terrestrial sediments, and a complex of environmental controls on the distribution of biota in marine and paralic situations (Murray-Wallace, 1987[1]). Stratigraphic relationships influenced by geomorphic setting, lack of continuous outcrop, irregular facies development and homotaxis have further complicated stratigraphic correlation (Charlesworth, 1957; Vita-Finzi, 1973; Ager, 1981; Bowen, 1985).

Notwithstanding the 'apparent' complexity of stratigraphic relationships in Quaternary sequences, the problems in Australia are further complicated by the need to correlate over large distances. Until recent years, assessments of the age of Quaternary coastal deposits in Australia relied on correlations with European models of Alpine glaciation, which themselves were poorly established (Tindale, 1933,1947; Bauer, 1961; Sprigg, 1952,1959,1979; Ward, 1965; Twidale *et al.*, 1977). The general absence of widespread glaciation during the Australian Quaternary has meant that its indirect expression, glacio-eustatic sea-level fluctuations, have figured prominently in chronostratigraphic classification of marine and paralic sediments. In particular, a range of geomorphological evidence has been cited in this connection and has proved unreliable (Bauer, 1961; Twidale *et al.*, 1977; Buckley *et al.*, 1987). Such approaches

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[1] Murray-Wallace, C.V. (1987) Evaluation and application of the amino acid racemisation reaction in studies of Quaternary coastal and marine sediments in Australia (Unpubl. PhD, Univ. Adelaide) 352 p.

here generally resulted in erroneous age assessments and an incomplete understanding of process rates in coastal evolution. Altitudinal relationships of strandlines and the construction of shoreline relation diagrams formed the basis of these early studies and are still used by some (Ward, 1985).

In this paper, we report results of amino acid racemisation dating of Pleistocene fossiliferous marine strata from Redcliff, northern Spencer Gulf. The results reported serve to illustrate the significant potential of applying amino acid racemisation reactions in the dating of Australian Quaternary sediments.

"Older Pleistocene marine beds"

In a regional investigation of the submarine Quaternary geology of northern Spencer Gulf, Hails *et al.* (1984a,b) described a sedimentary unit they termed the "Older Pleistocene marine beds" (Fig.1). These sediments are represented by poorly sorted sandy clays with low calcium carbonate contents. Although they have similar lithological characteristics to distal alluvial fan sediments, a former marine origin is attested by the presence of foraminifera and the bivalve *Anadara trapezia*. According to Billing (1984) these sediments experienced intense pedogenic modification involving decalcification and clay illuviation. The presence of *Anadara trapezia* suggested a coastal-intertidal depositional environment for these sediments (Hails *et al.*, 1984a,b; Ludbrook, 1984).

Relative lithostratigraphic relationships indicated these sediments are older than the Mambray Formation (equivalent to the Glanville Formation of the Adelaide region) (Fig.1). In the absence of quantitative data, Hails *et al.* (1984b) invoked a generalised global glacioeustatic sea level curve, to fit an age to the "Older Pleistocene marine beds". Based on altitudinal relationships of the strata, and the suggested heights of former sea levels that were likely to have penetrated northern Spencer Gulf, a Penultimate Interglacial age (220 ka, oxygen isotope Stage 7) was assigned to these sediments (Hails *et al.*, 1984b).

Amino acid racemisation dating

In recent years a large literature has emerged on the principles of amino acid racemisation dating. In particular, useful reviews are provided by Schroeder and Bada (1976), Williams and Smith (1977), Davies and Treloar (1977), Wehmiller (1982,1984) and Rutter *et al.* (1985).

Amino acid racemisation dating is based on the principle that in living organisms, amino acids bound in protein appear essentially in the left-configuration (L-amino acids). With the death of an organism, the enzymic reactions that maintained the former disequilibrium condition cease, and a racemisation reaction commences. This results in the gradual change to right handed (D-amino acids) until an equilibrium condition is attained (i.e., D/L = 1). As amino acid racemisation is a chemical reaction, it is sensitive to a range of environmental factors, particularly prolonged changes in the diagenetic temperature history experienced by fossils (Murray-Wallace and Kimber, 1987). However, with cautious sampling, the technique has considerable potential in establishing relative chronostratigraphies, for stratigraphic correlation and in studies of reworking (Belperio and Murray-Wallace, 1984; Cann and Murray-Wallace, 1986) and in geothermometry.

Sample Collection

Several specimens of the fossil bivalve *Anadara trapezia* (Deshayes) were collected from two vibrocores (Fig.2) from Redcliff, northern Spencer Gulf. The cores were obtained as part of a wider study of carbonate sedimentation (Belperio *et al.*, 1984a).

Only disarticulated *Anadara* were present, and were sampled from cores RED 40 and RED 41 within the depth interval 90-135 cm. Intrashell amino acid D/L ratio variation was avoided by analysing only the hinges.

Analytical Methods

The analytical procedures undertaken in this investigation follow those described more extensively in Kimber and Griffin (1987) and Murray-Wallace and Kimber (1987). Analyses reported are for the 'total acid hydrolysate', a complex mixture of high molecular weight peptides, smaller peptides and free amino acids.

Results and Discussion

Representative results of the extent of amino acid racemisation for the *Anadara trapezia* from the Redcliff Cores are presented in Table 1. These data are compared with Last Interglacial and radiocarbon-calibrated Holocene specimens to provide a framework for comparison.

As *Anadara trapezia* became extinct in South Australian coastal waters after the Last Interglacial, the Holocene specimen was obtained from Hervey Bay in southern Queensland. The radiocarbon age reported was calibrated to sidereal years using the tables of Klein *et al.*, (1982) and has also been corrected for the marine reservoir effect according to Gillespie and Polach (1979). The mean annual temperatures (M.A.T.) of the sample sites are also indicated in Table 1.

Results are reported for aspartic acid (ASP), alanine (ALA), valine (VAL), isoleucine (ALLO/ISO), glutamic acid (GLU) and phenylalanine (PHE). The relative extent of racemisation of the different amino acids in *Anadara trapezia* is in accord with those generally accepted for mollusc fossils of similar age (Lajoie *et al.*, 1980). By analogy with the calibration samples, the *Anadara* from the "Older Pleistocene marine beds" are clearly older than the Last Interglacial, which is most reliably dated at 125,000±10,000 yrs by Uranium series disequilibrium dating (Stearns, 1984).

A quantitative age assessment of the "Older Pleistocene marine beds" was undertaken by applying the integrated rate expression for the amino acid racemisation reaction (Mitterer, 1975), and using the Last Interglacial *Anadara trapezia* as a basis for calibration. This approach takes into account the non-linear nature of molluscan racemisation kinetics and therefore integrates the kinetic complexities of the transition zone in the non-linear model of Wehmiller (1984). The racemisation rate constant (k) used was 1.89×10^{-6}. In view of the slight amount of racemisation that occurs during sample preparation (acid hydrolysis), the extent of racemisation evident in modern *Anadara* was subtracted from the *Anadara* obtained from the "Older Pleistocene marine beds".

A mean age of 200,000±50,000 yrs BP was calculated based on the extent of racemisation in aspartic acid, valine, glutamic acid and phenylalanine. The error term allows for a diagenetic temperature history uncertainty of approximately 3°C.

These data therefore indicate the "Older Pleistocene marine beds" were deposited during the Penultimate Interglacial (Stage 7 of the marine oxygen-isotope record), and supports the preliminary age assessment made by Hails *et al.* (1984b). A global glacio-eustatic sea level event of about this age is also known from coastal deposits in New Guinea, Barbados, Bermuda, New Zealand, Western Australia and various localities in southern Australia (Chappell, 1974; Gill, 1977; Fairbanks and Matthews, 1978; Harmon *et al.*, 1983; Pillans, 1983; Hewgill *et al.*, 1983, Belperio *et al.*, 1984b).

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Table 1 Extent of amino acid racemisation in *Anadara trapezia* obtained from the "Older Pleistocene marine beds", Redcliff, northern Spencer Gulf, compared with Holocene and Last Interglacial results.

Lithostratigraphic unit	No. of specimens	Age	M.A.T.* (°C)	Amino acid D/L ratio+ ASP	ALA	VAL	ALLO /ISO	GLU	PHE
Quarantine Bay New South Wales	2	modern	14.7	0.05	-	0.02	0.02	0.08	-
Holocene sediments Hervey Bay Queensland	2	6400±140	21.5	0.44 ±0.005	0.52 ±0.02	0.15 ±0.01	0.17 ±0.002	-	-
Glanville Formation Port Wakefield, Gulf St Vincent South Australia	8	125,000	17	0.54 ±0.03	0.68 ±0.02	0.32 ±0.06	0.43 ±0.04	0.42 ±0.01	0.73 ±0.06
"Older Pleistocene marine beds" Redcliff	4	-	19	0.76 ±0.02	0.83 ±0.03	0.48 ±0.01	0.55 0.02	0.62 ±0.02	0.89 ±0.03

* Mean annual temperature

\+ ASP = Aspartic acid, ALA = Alanine, VAL = Valine, ALLO/ISO = Alloisoleucine/ Isoleucine, GLU = glutamic acid, PHE = Phenylalanine

Figure Captions

FIGURE 1 Summary of local lithostratigraphic nomenclature of Quaternary marginal marine strata, after Firman (1969) and Hails *et al.* (1984a), showing the relative stratigraphic position of the "Older Pleistocene marine beds".

FIGURE 2 Location map of Redciff cores RED 40 and RED 41.

		UPPER SPENCER GULF (HAILS et. al. 1984a)	GULF ST VINCENT (FIRMAN, 1969)
HOLOCENE		GERMEIN BAY FORMATION	ST KILDA FORMATION
PLEISTOCENE	UPPER		
	UPPER	POORAKA FORMATION	POORAKA FORMATION
	UPPER		
	UPPER	MAMBRAY FORMATION	GLANVILLE FORMATION
	MIDDLE		↑ ?
	MIDDLE	OLDER PLEISTOCENE MARINE BEDS	
	MIDDLE	↑ ?	
	LOWER	HINDMARSH CLAY	HINDMARSH CLAY

Fig. 1 SUMMARY OF ESTABLISHED LITHOSTRATIGRAPHIC NOMENCLATURE OF QUATERNARY MARGINAL MARINE STRATA, AFTER FIRMAN (1969) AND HAILS et. al. (1984a), SHOWING THE RELATIVE STRATIGRAPHIC POSITION OF THE "OLDER PLEISTOCENE MARINE BEDS".

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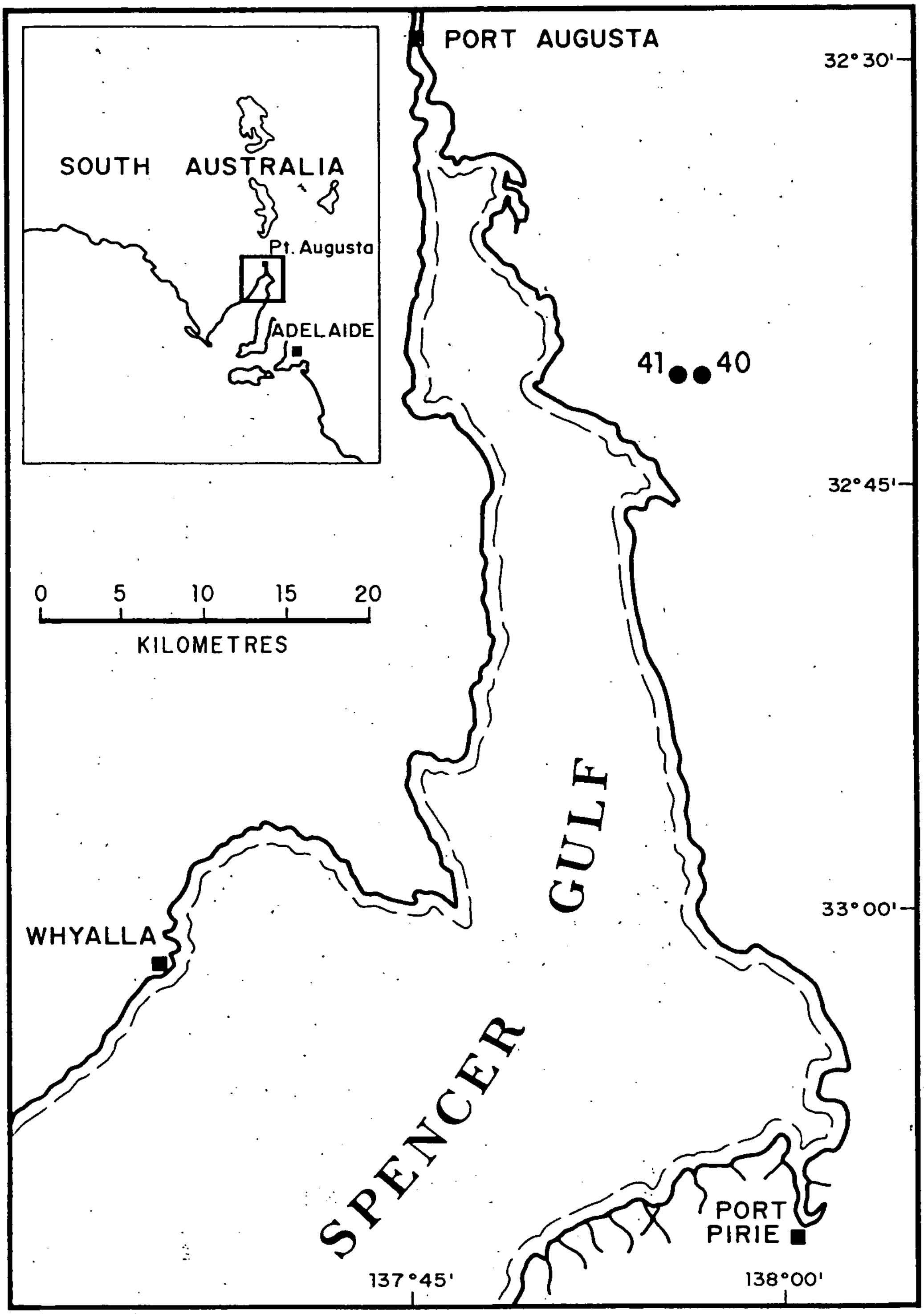

Fig. 2 LOCATION MAP OF REDCLIFF CORES RED 40 and RED 41.

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