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EVALUATION AND APPLICATION OF THE AMINO ACID RACEMISATION REACTION IN STUDIES OF QUATERNARY COASTAL AND MARINE SEDIMENTS IN AUSTRALIA

by

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To My Parents, who instilled in me
an insatiable desire to learn.

"When the work of the geologist is finished and his final comprehensive report is written, the longest and most important chapter will be upon the latest and shortest of the geological periods."

G.K. Gilbert (1890)

I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

Colin Vincent Murray-Wallace

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C.V. Murray-Wallace

ABSTRACT

The application of the amino acid racemisation reaction is explored in studies of Australian Quaternary marginal marine sediments. A critical appraisal of amino acid D/L ratio variation in stratgraphic studies revealed several error sources that include analytical error (~3%), within-species intra-fossil variation (~8%), within - species interfossil variation (~12%), a genus effect (~30%), and effects or natural variation within a deposit and between site variation. The last two factors are difficult to quantify.

Results of an interlaboratory comparison indicate that amino acid D/L ratios reported by the CSIRO Soils Laboratory (South Australia) compare favourably with American and European laboratories.

The suitability of amino acid techniques for Australian Quaternary marine studies is demonstrated through studies of a range of holostratotypes from several marine and paralic settings. Several regional chronostratigraphies, constructed from disjunct stratigraphic units are presented based on relative and quantitative age assessments using amino acid racemisation data. In addition, the suitability of applying amino acid data in geothermometry is assessed using Holocene and Late-Pleistocene fossils with established diagenetic temperature histories. In addition, the application of amino acid data in studies of sediment reworking is also explored using the Foraminifer Marginopora vertebralis.

In South Australia, the widespread occurrence of Last Interglacial marine sediments is demonstrated by aminostratigraphic correlation. Amino acid data confirms a Penultimate Interglacial age (Oxygen Isotope Stage 7), for marine strata in Spencer Gulf, and assisted in the recognition of Interstadial marine strata (Oxygen Isotope Stage 3) from submarine cores, Gulf St. Vincent.

Aminostratigraphic investigations in the Perth Basin, Western Australia, confirmed the presence of Last Interglacial and Penultimate Interglacial marine strata. In addition, studies of Plio/Pleistocene deposits indicate the probable age range and some of the problems peculiar to amino acid techniques as applied in Australia. Several aminozones are recognised and their intracontinental correlation is demonstrated.

Preliminary aminostratigraphic studies of molluscs from the east coast of Australia have provided a valuable adjunct for assessing temperature effects on diagenetic racemisation. The Australian amino acid data are briefly discussed in a global context and several significant questions regarding the probable upper and lower limits of dating, and nature of molluscan racemisation kinetics are explored in the context of the Australian Quaternary.

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CHAPTER 1 DATING THE AUSTRALIAN QUATERNARY PERIOD AND THE RELEVANCE OF THE AMINO ACID RACEMISATION REACTION

1.1 INTRODUCTION AND BACKGROUND

Stratigraphic studies of the Quaternary involving correlation, earth history, rates of sedimentation and resolution of environmental problems frequently require dating of sediments beyond the range of conventional radiocarbon methods. In Australia, as elsewhere, studies of Quaternary sediments are generally complicated by problems including the short duration of the period, the restricted use of fossils for biostratigraphic age assessments, and the punctuated nature of the depositional record. Moreover, stratigraphic relationships influenced by geomorphic setting, lack of continuous outcrop, irregular facies development and homotaxis have complicated stratigraphic correlation (Charlesworth, 1957; Vita-Finzi, 1973; Ager, 1981; Goudie, 1983; Nilsson, 1983 and Bowen, 1985).

Studies in coastal regions have to deal with the chronostratigraphic correlation of terrestrial and marine deposits which generally display an interfingering relationship. Palaeontological correlations are hampered however, by the lack of fossils in terrestrial sediments, and a complex of environmental controls on the distribution of biota in marine and paralic situations.

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; Playford and Leech, 1977;

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). Such approaches 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).

Subsequent developments in quantitative dating using radiocarbon and uranium-series disequilibrium dating did not always resolve these problems. In many cases the basic assumptions of the techniques in relation to the samples were not upheld in their stratigraphic setting (Faure, 1977).

In this thesis, the application of the amino acid racemisation reaction to studies of Australian Quaternary marine sediments is critically assessed and pursued. The significant advantages of amino acid racemisation dating include speed, small sample size for analysis, a potentially wide age range of the technique in comparison with other techniques (Figure 1.1), and the possibility of dating a wide variety of organic materials. In addition, the technique may also be applied in geothermometry. In view of these advantages, the technique holds considerable promise for dating the Australian Quaternary.

Previous studies have concentrated in the northern hemisphere where several themes emerged in the literature, and some resulted in an unfavourable assessment of the technique by some workers (Davies and Treloar, 1977; Williams and Smith, 1977). These principally included:

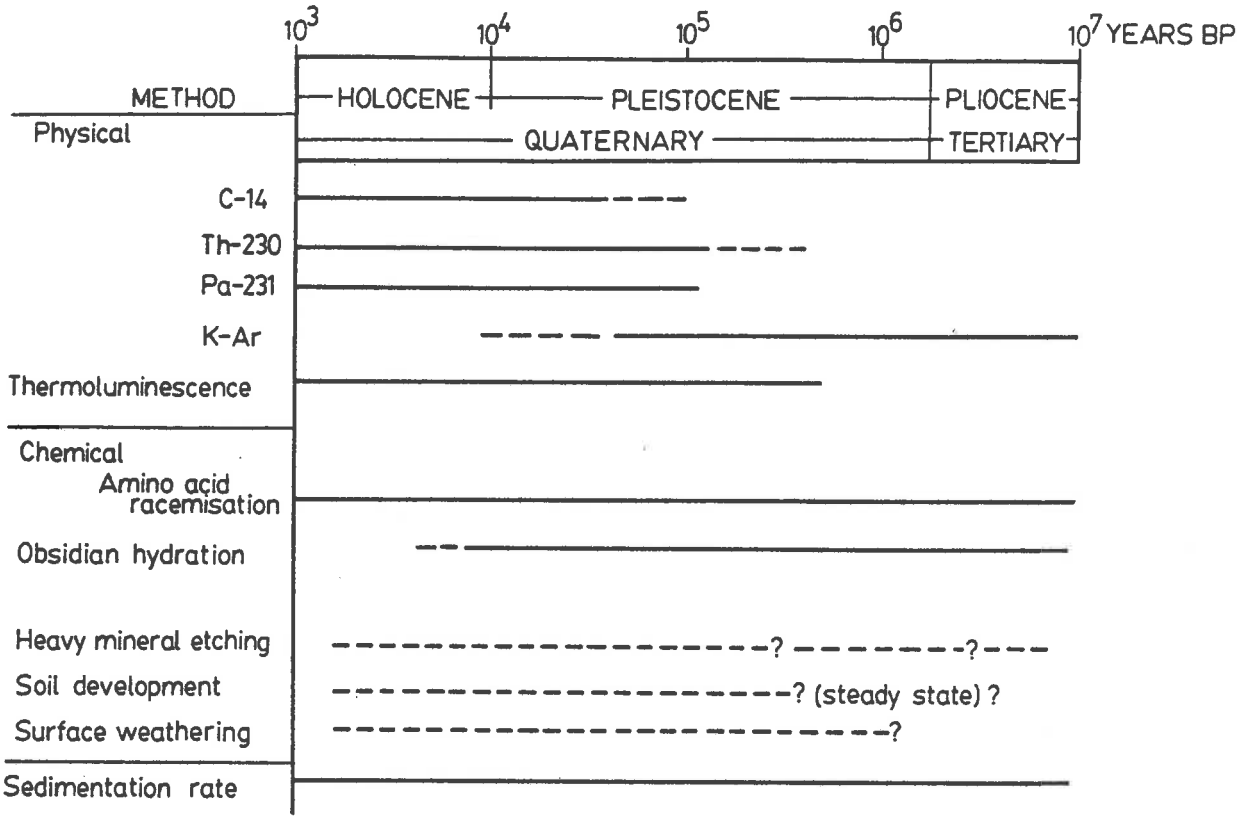


Figure 1.1 Time spans of dating methods that can be applied to Quaternary sediments (modified after Andrews and Miller, 1980 p.265).

(1) In America, the dichotomy between what may be referred to as 'East' and 'West' Schools of thought, regarding the nature of molluscan racemisation kinetics. In particular, the debate centred on whether molluscan racemisation conformed to extended-linear (Kvenvolden et al., 1979,1981) or 'non-linear' kinetics (Wehmiller et al., 1977; Wehmiller and Belknap, 1978 and Wehmiller, 1981).

(2) The over-exuberance of some workers reflected in early publications based on limited data with erroneous interpretations resulting from a disregard for the stratigraphic or archaeological context of fossiliferous materials. The controversy concerning the arrival of man in the Americas is exemplary (Bada, 1972,1974; Stafford et al., 1984).

(3) The general lack of critical assessments of error sources.

1.2 AIMS OF THIS THESIS

Despite a large literature generated principally from the northern hemisphere, the application of amino acid racemisation to the dating of Quaternary strata is still in its infancy, when compared with other Quaternary dating methods. In view of this, several significant areas of research were recognised at the onset of this study.

(1) In view of the complicated nature of molluscan racemisation kinetics, further empirical results for a range of molluscan genera of different ages were required to accurately define the kinetics of the complete reaction. This will only be achieved through extensive calibration using well controlled stratigraphies in conjunction with a variety of independent dating techniques.

(2) A judicious appraisal of the precision (reproducibility of measurements), and accuracy (deviation of determined age from "real" age) of amino acid racemisation dating.

(3) An assessment of the age resolution and the range of the technique including the upper and lower limits of dating.

In view of the above, this study had the following aims:

(1) To critically assess the amino acid racemisation dating technique and quantitatively define its errors.

(2) To assess the usefulness of amino acid racemisation data in Australian Quaternary stratigraphic studies.

(3) To establish a data base for reference in future studies.

The application of an aminostratigraphic approach to age assessments of Quaternary sediments is new in Australia. This investigation presents the first comprehensive assessment of the application of the amino acid racemisation reaction to studies of Australian Quaternary coastal and marine sediments, and provides a valuable adjunct to other geochronological investigations.

In addition to the utilization of established stratigraphic frameworks, amino acid racemisation data were calibrated where possible against other dating techniques including radiocarbon, uranium-series disequilibrium, electron spin resonance and thermoluminescence dating.

Quaternary sediments were sampled from geographically, widely separated localities in Australia in order to fulfil these aims. Sample localities included the gulf region of South Australia (northern Spencer Gulf and Gulf St Vincent), the Perth Basin and the Roe Plains, Western Australia, and from selected localities in eastern Australia, from Princess Charlotte Bay in northern Queensland to Quarantine Bay, New South Wales (Figure 1.2).

This thesis is arranged so that the next chapter presents a summary of the geochronometric utility of the amino acid racemisation reaction, particularly from a stratigraphic viewpoint. With the exception of a few critical, but general review papers (Williams and Smith, 1977; Davies and Treloar, 1977; Pillans, 1982) few studies have systematically assessed the potential sources of error, their magnitudes and the problems they present in Quaternary studies. Furthermore, as the CSIRO Soils Division (Adelaide), is currently the only amino acid racemisation dating laboratory in Australia, several areas of basic research including interlaboratory comparisons were deemed necessary. In view of this, Chapter three summarises a range of errors that may arise in aminostratigraphic studies. Where possible these error sources are quantified and approaches for their reduction are presented.

In Chapter four, South Australian examples are used to demonstrate the suitability of applying the amino acid racemisation reaction to the dating of Australian Quaternary marine strata. In particular the extent of racemisation is used in the chronocorrelation of Last Interglacial marine strata from widely separated localities. These data, in conjunction with

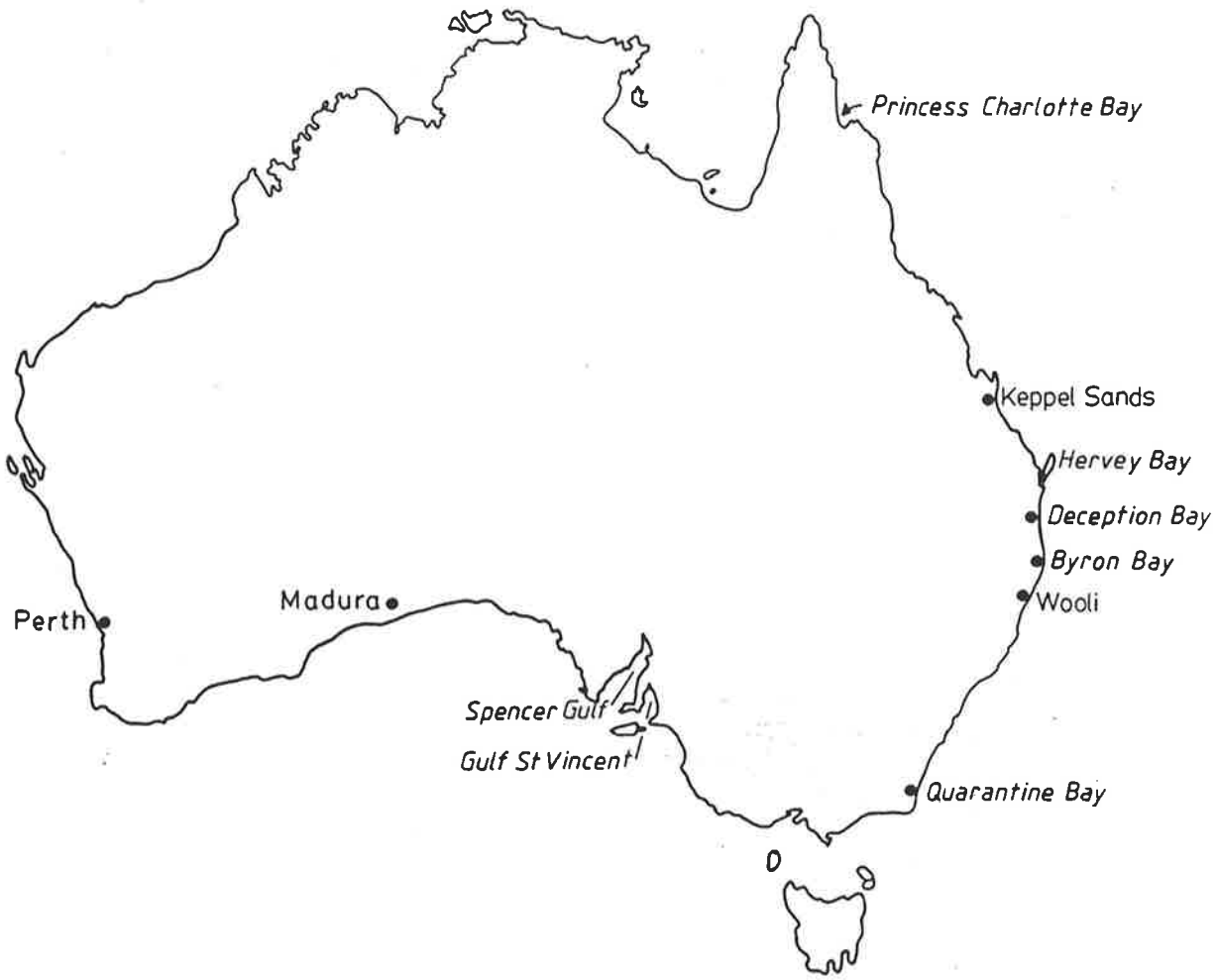


Figure 1.2 Sample localities in this investigation.

results for radiocarbon calibrated Holocene specimens have provided a basis for the construction of a regional chronostratigraphy, and assisted in the recognition of Interstadial marine sediments from submarine cores, Gulf St Vincent (oxygen isotope stage 3) and Penultimate Interglacial marine strata from Redcliff, northern Spencer Gulf (Stage 7). The potential of applying the amino acid racemisation reaction to studies of sediment reworking was also examined using the foraminifer Marginopora vertebralis, a Plio/Pleistocene indicator for South Australian coastal waters. In addition, the suitability of applying amino acid data in geothermometry was also assessed using molluscan fossils of Holocene and latest-Pleistocene age from South Australia.

Data obtained from South Australian Quaternary marine strata provided a framework for comparing results from other Australian coastal settings including the Perth Basin and the east coast of Australia. This approach has facilitated the chronocorrelation of Last Interglacial marine strata, confirmed the presence of Penultimate Interglacial marine strata in the Swan Estuary (Chapter 5), and provided further evidence to highlight the complex nature of molluscan racemisation kinetics (Chapter 6). To minimize cross-referencing, discussions of the established lithostratigraphic frameworks are summarised at the start of the relevant chapters.

Chapter seven presents a summary of the significant conclusions drawn from this study and places the Australian amino acid data into a global context.

CHAPTER 2 THE AMINO ACID RACEMISATION REACTION AND ITS GEOCHRONOMETRIC UTILITY

2.1 INTRODUCTION

Confident age determination of stratigraphic sequences beyond the datable limits of conventional radiocarbon methods has presented a significant problem in Quaternary studies. Although numerous dating techniques have been developed in recent years (Mahaney, 1984; Rutter, 1985), many are restricted to specific time intervals or particular mineralogical components of sediments. Considerable attention has been paid to the application of time dependent protein diagenetic reactions in geochronometry because of several significant advantages including the small sample requirement, rapidity of analyses, the wide range of organic materials that can be analysed and the potential of dating events throughout the entire Quaternary. The most widely used of these reactions are amino acid racemisation and epimerisation. Useful summaries of the application of amino acid racemisation data in Quaternary studies are provided in Bada and Schroeder, (1975); Kvenvolden, (1975); Dungworth, (1976); Schroeder and Bada, (1976); Williams and Smith, (1977); Hare (ed.), (1980); Pillans, (1982); Wehmiller, (1982,1984b) and Rutter et al., (1985). In this chapter the application of amino acid racemisation in marine stratigraphic studies is briefly summarised. In particular, several areas important for stratigraphic studies including the nature of racemisation kinetics, advantages and limitations and the range of organic materials potentially datable by the technique are also discussed. Descriptions of sample preparation and derivatisation procedures are presented in the relevant appendicies.

2.1.1 Amino Acids: Definition

The α-amino carboxylic acids are non-volatile, organic molecules of low molecular mass (ca. 100-200). They are present as building blocks of proteins and as structural components in all living organisms. Amino acids are characterised by a centre of asymmetry at the α-carbon position, to which is attached an amino ($-NH_2$), a carboxyl (-COOH), a hydrogen atom (-H), and a hydrocarbon group (-R) (Figure 2.1). Variation between amino acids results from the presence of different R groups (side chains) (Barrett, 1985, Rutter et al., 1985). Structurally, all amino acids except glycine contain at least one asymmetric "central" tetrahedral carbon atom. In glycine, two hydrogen atoms are attached to the tetrahedral carbon atom (i.e. R=H). Potentially the number of different hydrocarbon groups is limitless, however only 20 different amino acids commonly occur in the protein of organisms (Table 2.1). Amino acids are present in all living organisms as polymers linked together through covalent peptide bonds to form enzymes and structural material (Schroeder and Bada, 1976).

2.1.2 The Amino Acid Racemisation Reaction

Amino acids commonly found in proteins with the exception of glycine, have the potential to exist in two isomeric forms, referred to as L- and D-enantiomers (laevorotatory and dextrorotatory respectively) (Figure 2.1). The physical and chemical properties of enantiomers are identical, except for their ability to rotate plane polarised light in opposite directions. Protein in all living organisms essentially comprises amino acids in the L-configuration, with only a few microbial peptides containing D-amino acids (Salton, 1964).

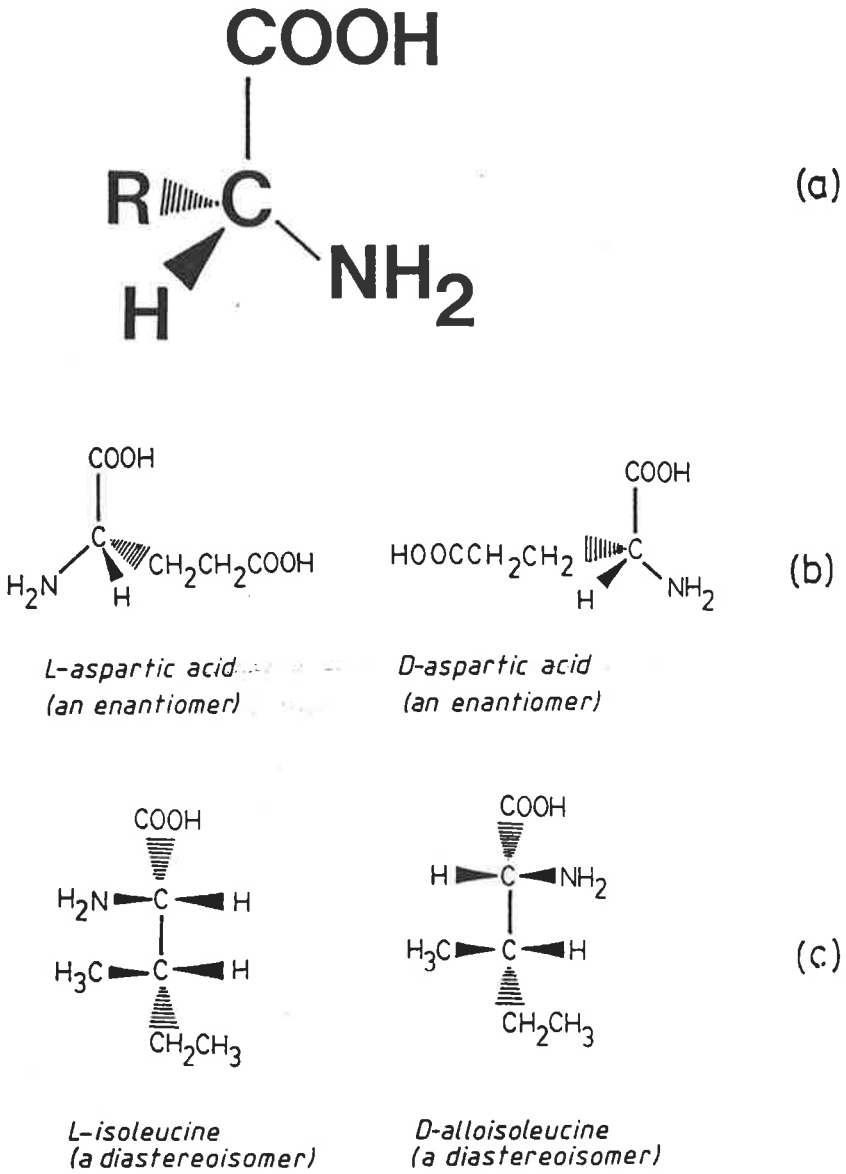


Figure 2.1 (a) A three dimensional representation of the general structure of amino acids. The carboxyl (-COOH) and amino (-NH) groups plot within the plane of the page while the hydrogen atom (-H) and hydrocarbon group(R) fall above and below the plane of the page respectively. (b) L- and D- aspartic acid (enantiomers) and (c) L-isoleucine and D-alloisoleucine (diastereoisomers).

(after Rutter et al., 1985)

Table 2.1 The Protein Amino Acids

alanine (ALA)	histadine (HIS)	threonine (THR)
arginine (ARG)	isoleucine (ALLO/ISO)	tryptophane (TRY)
aspartic acid (ASP)	leucine (LEU)	tryosine (TYR)
asparagine (ASPG)	lysine (LYS)	valine (VAL)
cysteine (CYS)	methionine (MET)	
glutamic acid (GLU)	phenylalanine (PHE)	
glutamine (GLUT)	proline (PRO)	
glycine (GLY)	serine (SER)	

Glycine has no chiral carbon atom; isoleucine and threonine contain two chiral carbon atoms; the others contain only one chiral carbon atom (after Rutter et al., 1985 p.24). Abbreviations for different amino acids referred to in this thesis are indicated above.

Under conditions of chemical equilibrium both enantiomers would be present in equal quantities. A living organism however maintains a disequilibrium state through various enzymatic reactions. After an organism dies however, the metabolic reactions that formerly maintained the disequilibrium condition cease, and a racemisation reaction commences (Bada and Shou, 1980; Bada, 1985). In racemisation, L-amino acids are reversibly converted into corresponding D-amino acids (Figure 2.2). The reaction continues until equal amounts of L- and D- enantiomers are obtained (i.e., D/L ratio = 1), a state referred to as the 'racemic' condition. Although dependent on several parameters, this state has been reported as generally occurring within 10 Ma from the onset of racemisation (Wehmiller and Hare, 1971; Schroeder and Bada, 1976).

Amino acids with one asymmetric carbon atom can exist in two configurations which are mirror images termed enantiomers, optical isomers, or optical antipodes (Schroeder and Bada, 1976). However, four common amino acids contain two chiral carbon atoms and potentially may interconvert at either the α- or β- carbon centres. Such a reaction is termed epimerisation, and the amino acids are termed diastereoisomers. In this reaction the equilibrium constant attains a value greater than unity, and a range of values for isoleucine have been reported between 1.25 to 1.4 (Williams and Smith, 1977). Epimerisation results in a chemically (not just optically) different molecule and is therefore readily distinguished on conventional amino acid analysers. This fact accounts for the popularity of isoleucine in previous studies (Bada et al., 1986). The term racemisation is therefore restricted to a change in configuration only at the α-carbon of an amino acid with only one chiral carbon atom (Schroeder and Bada, 1976; Kvenvolden, 1975; Dungworth, 1976). The four commonly occurring diastereoisomers include isoleucine, threonine, hydroxyproline and hydroxylysine (Kvenvolden, 1975).

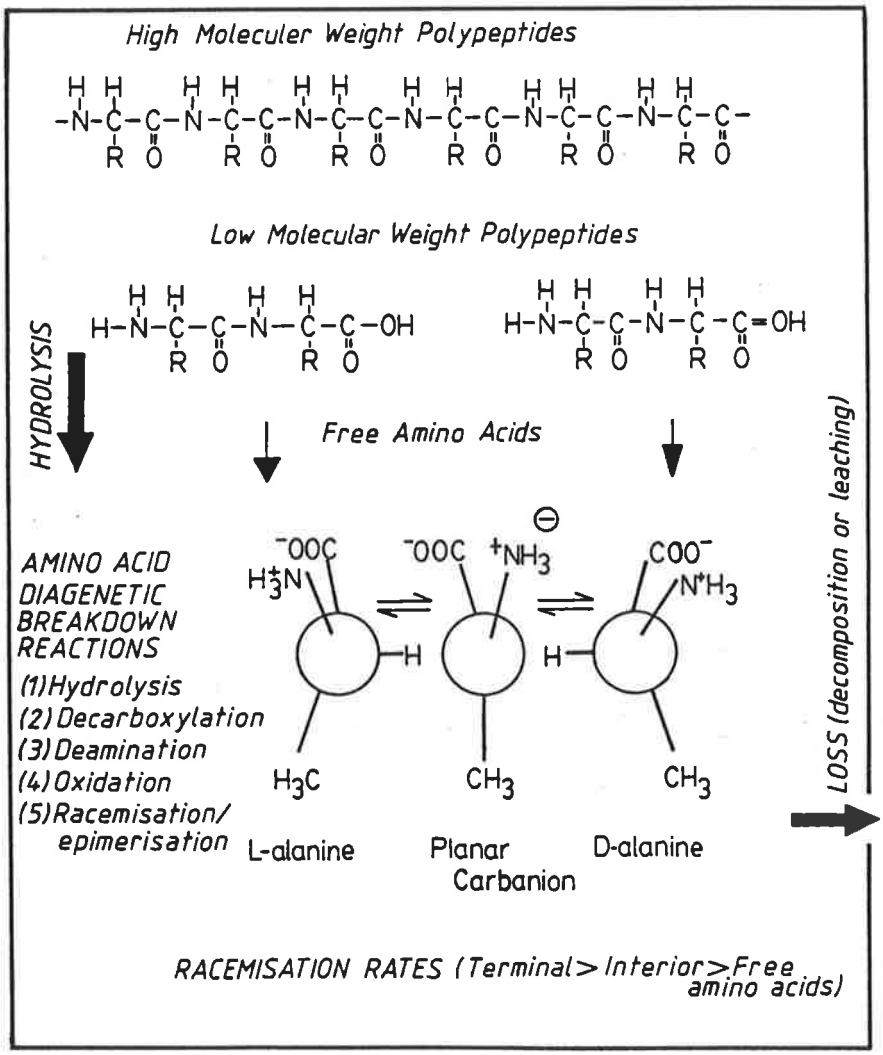


Figure 2.2 Schematic representation of amino acid diagenesis in molluscan fossils. The mechanism of the amino acid racemisation reaction is also depicted, showing the formation of a carbanion intermediate. The hydoxide ion probably abstracts the αC-proton in aqueous solution. This is the rate limiting step in the reaction. Readdition of the proton occurs by reaction of water with the carbanion. Modified after Wehmiller (1984b) and Bada and Schroeder (1975).

The non-protein amino acid D-alloisoleucine, derived from L-isoleucine by interconversion at the α-carbon atom is generally observed in fossils (Hare and Abelson, 1966; Bada et al., 1986). Dungworth (1976) and Bada et al., (1986) attributed the absence of L-alloisoleucine and D-isoleucine to the high activation energies required for the interconversion at the β-carbon atom. Such activation energies are generally not obtained in ambient temperature diagenetic racemisation (Bada et al., 1986).

2.1.3 The Racemisation Reaction: Mechanism

A mechanism for the amino acid racemisation reaction was forwarded by Neuberger (1948), who suggested that the initial rate-limiting step in the reaction involves the removal (ionization) of the proton attached to the α-carbon. This creates a planar carbanion and is rapidly followed by the readdition of a proton from either side (non-stereospecifically) with equal probability of forming either the D- or L-enantiomer. The reaction is general-base catalysed and any nucleophilic species may therefore initiate the reaction through removal of the α-proton. In aqueous solution, the nucleophile is the hydroxide ion (or H_2O) (Schroeder and Bada, 1976; Bada, 1985).

2.1.4 Historical Review

Abelson (1954) pointed out the significance of amino acids in fossil shells and bones as potential age indicators. Subsequent investigations by Erdman et al., (1956) indicated that amino acids were preserved in shallow water marine sediments of Oligocene age (ca. 30 Ma). Using enzymatic techniques, Hare and Abelson (1966) observed the change in relative proportions with geologic time of D- and L-amino acid isomers in the fossil shell Mercenaria. The method used L-amino acid oxidases and

decarboxylases for degradation of the L-enantiomers, enabling quantification of D-enantiomers. The authors convincingly demonstrated that with time L-isoleucine interconverts to D-alloisoleucine with the formation of only trace quantities of D-isoleucine and L-alloisoleucine. From these observations Hare and Abelson concluded that the extent of racemisation (epimerisation) could be used to establish the age of shells. The potential of using the amino acid racemisation reaction in geochronometry was further explored by Hare and Mitterer (1969) who suggested that the method could be applied in geothermometry and stratigraphic correlation.

Interestingly, although the potential of amino acid racemisation in Quaternary studies was anticipated by Abelson (1954) and Erdman et al., (1956), little research followed until the 1970s. Although speculative, developments in radiocarbon dating most likely overshadowed any interest in amino acid racemisation dating. In addition, significant advances have been made since recent developments in gas chromatography technology.

In this study, as with the majority of laboratories, routine analyses were made for the 'total acid hydrolysate' and also free amino acids. The 'total acid hydrolysate' refers to a complex mixture of high molecular weight polypeptides, smaller peptides and free amino acids. As each of these components are characterised by different rates and extents of racemisation, the 'total acid hydrolysate' represents an unweighted average for all these fractions. Generally, the extent of racemisation (epimerisation) evident in the 'total acid hydrolysate' is less than for free amino acids. The more extensively racemised free amino acids were routinely analysed in this study to provide an internal check, on data for the 'total acid hydrolysate'. Details of their preparation are provided in Appendix 1.

2.2 THE KINETICS OF RACEMISATION (EPIMERISATION)

The interconversion (racemisation or epimerisation), of amino acids has been described as a first order reaction (Dungworth, 1976; Schroeder and Bada, 1976; Williams and Smith, 1977; Kvenvolden et al., 1979; and Rutter et al., 1985). In general terms the reaction is represented;

L-amino acid $\rightleftharpoons$ $k_1 k_2$ $\rightleftharpoons$ D-amino acid

where k_1 and k_2 are the first-order rate constants for interconversion of the L- and D-amino acids (Kvenvolden, 1975; Schroeder and Bada, 1976; Williams and Smith, 1977; and Pillans, 1982). For enantiomeric amino acids $k_1=k_2$. For diastereoisomers such as L-isoleucine/D-alloisoleucine, $k_1 \neq k_2$ and the forward rate k_1 is greater than the reverse rate constant k_2. The rate law for interconversion of amino acids is;

$$\frac{-d(L)}{dt} = k_1(L) - k_2(D) \qquad \text{(eqn 2.1)}$$

where (L) is the concentration of the L-amino acid and (D) is the concentration of the D-amino acid. Integration over the age of the sample (t) gives;

$$\ln \frac{[\ 1+(D/L)]}{[\ 1-K'(D/L)\ ]} - \ln \frac{[\ 1+(D/L)\ ]}{[\ 1-K'(D/L)\ ]t=0} = (1+k').KL.t \qquad \text{(eqn 2.2)}$$

where $K'=KD/KL = 1/K_{eq}$ and is the reciprocal of the equilibrium constant (Schroeder and Bada, 1976; Williams and Smith, 1977). Derivation of equation 2.2 is provided by Bada and Schroeder (1972).

The second term on the left hand side of equation 2.2 is a correction for any D-amino acids in the sample at the time of death, and the small amount of racemisation which may occur during sample preparation (e.g., acid hydrolysis). This correction factor is normally evaluated by analysis of modern samples and facilitates greater precision in quantitative age assessments (Pillans, 1982).

Some workers have attempted to define the amino acid racemisation reaction in terms of half-life (τ) (Williams and Smith, 1977). One half-life is obtained when 25% of the L-enantiomer has converted to the D-isomer. The general expression for half-life (τ) derived from equation 2.1 is;

$$\tau = \frac{\ln 2}{k_1 + k_2}$$

or (eqn 2.3)

$$\tau = \frac{\ln 2}{(1+K')k_1}$$

Accordingly, the D/L ratio of an amino acid at the half-life time is given by;

$$(D/L)\tau = \frac{K}{K+2} \qquad \text{(eqn 2.4)}$$

Considerable attention has been paid to the nature of racemisation kinetics in fossils (Bada and Schroeder, 1972; Kvenvolden, 1975; Mitterer, 1975; Schroeder and Bada, 1976; Bada et al., 1978; Kvenvolden et al., 1979,1981; Wehmiller and Belknap, 1978; and Wehmiller, 1981,1982,1984b). These studies were supplemented by numerous investigations that attempted to model the complex nature of racemisation kinetics, through elevated temperature heating studies (Smith et al., 1978; Kriausakul and Mitterer, 1978,1980a,b; Mitterer and Kriausakul, 1984; Steinberg and Bada, 1981,1983). Models that define the nature of racemisation kinetics are of

considerable importance for quantitative age assessments of fossils. Without such models, major errors would arise in quantitative age determinations based on the extent of racemisation in fossils. Kinetic models have been derived from high temperature pyrolysis experiments (Mitterer, 1975; Kvenvolden et al., 1979,1981), and through measurement of enantiomeric ratios in fossils of well defined geological ages (Wehmiller and Belknap, 1978; Wehmiller 1984b). In the latter case, numerous interpretations were based on foraminifera from deep sea cores, which are likely to preserve an uninterrupted depositional record, and therefore a continuous time span of reference. In this context, deep sea cores have played an instrumental role in racemisation kinetic studies.

Two kinetic models have been explored in recent years; a "non-linear" model proposed by Wehmiller (1977,1981,1982,1984b) and Wehmiller and Belknap (1978), and an "extended linear" model (Kvenvolden et al., 1979,1981) (Figure 2.3). In the American literature, much of the controversy concerning molluscan racemisation kinetics concerned the extent of leucine racemisation with age in the molluscs Protothaca and Saxidomus (Wehmiller, 1984b).

In a preliminary assessment of the application of amino acid racemisation in the study of Quaternary sediments at Willapa Bay, Washington, Kvenvolden et al., (1979) invoked an "extended linear" racemisation kinetic model for quantitative age determinations. Based on the extent of racemisation of several amino acids in Saxidomus giganteus and Ostrea lurida, Last Interglacial (120,000±40,000 BP) and Penultimate Interglacial (190,000±40,000 BP) ages were assigned to the sediments studied.

The reliability of these ages was questioned by Wehmiller (1981), who suggested that the extended linear model was inappropriate for age assessments, as it did not account for the complicated nature of molluscan

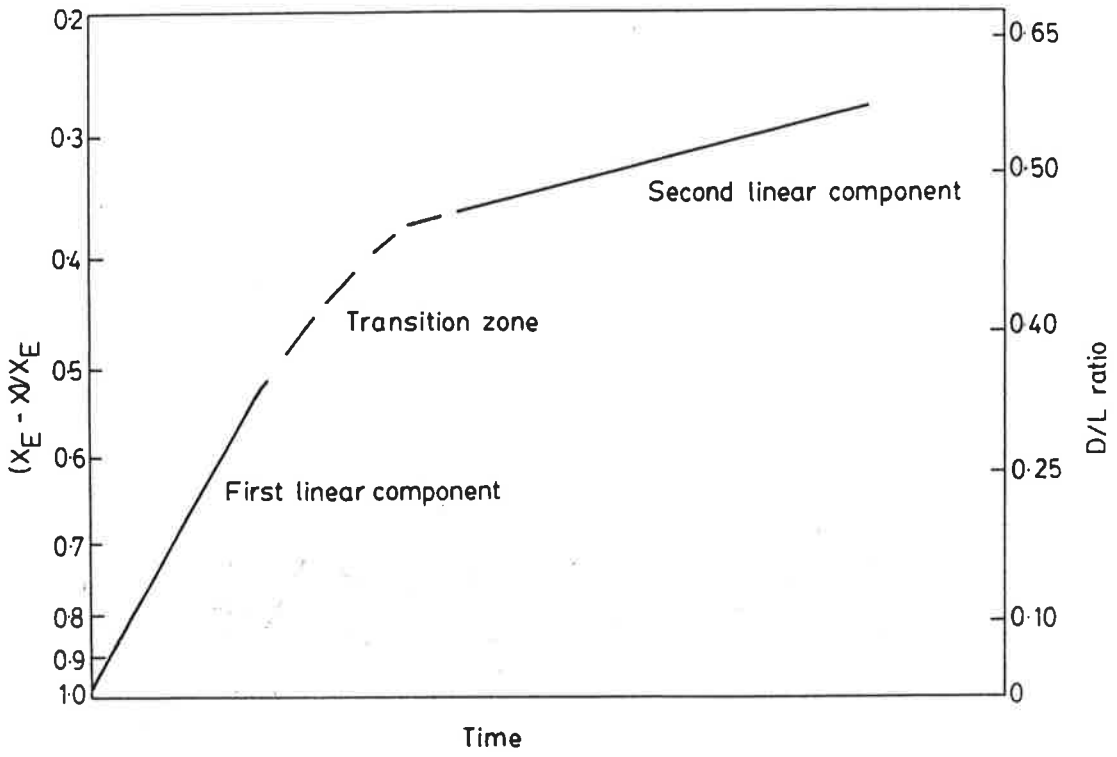


Figure 2.3 "Non-linear" molluscan racemisation kinetic model of Wehmiller (1982,1984b) with two essentially linear kinetic segments separated by a transition zone. The second essentially linear component is approximately 10x slower than the first linear component. The kinetic model is plotted in a logarithmic format after Wehmiller and Hare (1971) and Wehmiller (1982).

racemisation. In particular, enantiomeric ratio data for Holocene molluscs were not included in the model of Kvenvolden et al., (1979), and therefore inconsistencies in palaeotemperatures that would otherwise have arisen from comparisons of Holocene and Pleistocene racemisation rate constants were not considered (Wehmiller, 1981). Further difficulties concerned the inordinately low diagenetic temperature histories required for these age assessments, and the incongruity presented by these data in terms of latitudinal palaeotemperature gradients. To resolve these difficulties, Wehmiller (1981) recommended the use of a "non-linear" kinetic model. Based on enantiomeric ratio data for leucine, the non-linear model is characterised by an early, essentially linear component that spans from D/L leucine 0.0 to 0.25, a transition zone reflecting changes in the relative rates of hydrolysis and racemisation, and a second broadly linear component (Wehmiller, 1981,1982,1984b). This model was derived from observed kinetics in foraminifera from deep sea cores and required extrapolation over a minor temperature range (10-15°C) (Wehmiller and Hare, 1971; Wehmiller, 1984b). However, it was based on the inference that racemisation kinetics in foraminifera are similar to those observed in molluscs. In contrast, the "extended-linear" model of Kvenvolden et al., (1979,1981) was based on results from pyrolysis experiments (140-160°C) and required extrapolation over a large temperature range (ca. 130°C). Results from these experiments however, should be treated with caution, for they may not accurately reflect processes occurring in fossils under geological conditions. In particular, they fail to accurately model the pronounced temperature fluctuations that have characterised the Quaternary. This was highlighted by observations by Mitterer and Kriausakul (1984), who pointed out that reactions other than racemisation (epimerisation) and hydrolysis may occur even in relatively simple systems, making it difficult to obtain accurate kinetic data. Although subsequent

studies (Hearty et al., 1986; Murray-Wallace and Kimber, 1987) have provided data in general support of the "non-linear" model, the ages obtained by Wehmiller (1981) appear to be at variance with the established lithostratigraphy at Willapa Bay. Problems arise concerning the ages of the deposits in the context of Quaternary sea level fluctuations. Invoking the "non-linear" model, Wehmiller (1981) derived ages of 70,000±15,000 BP and 300,000±50,000 BP (oxygen isotope stages 5a and 9 respectively) for the Pleistocene deposits studied by Kvenvolden et al., (1979). If these ages are reliable, then they have important implications concerning the depositional record at Willapa Bay. The apparent absence at Willapa Bay of sediments deposited in response to sea levels associated with isotope stages 5e and 7, two major transgressive phases that had significant global expression, presents a problem. Globally, these transgressive peaks were broadly coincident with contemporary mean sea level. In contrast, sea levels during stage 5a were approximately 15 m below present levels (Bloom et al., 1974; Chappell and Veeh, 1978; Schwebel, 1983; Cronin et al., 1981; Harmon et al., 1981,1983). Therefore, the apparent preservation of evidence for lower sea levels and the absence of evidence for higher sea levels remains unresolved if these ages are accepted.

The "non-linear" racemisation kinetic model developed for Protothaca, Saxidomus, Chione and Mercenaria from North America, have been found in the present study to be applicable to Katelysia spp., Anadara trapezia and other mollusca analysed (see Chapters 4 and 5).

The difficulty of applying an "extended-linear" kinetic model to age assessments was also highlighted by Wehmiller and Belknap (1978) in a critique of a study by Mitterer (1975). Mitterer (1975) examined the extent of isoleucine epimerisation in fossil Mercenaria from a variety of Pleistocene marine deposits in Florida, and derived quantitative age

assessments. Using an Arrhenius plot to determine the energy of activation (Ea), Mitterer concluded that there was no significant difference in the temperature dependence of the rate of isoleucine epimerisation as determined from heated samples and natural samples. On this basis Mitterer (1975) concluded that linear epimerisation kinetics applied in fossil Mercenaria to a D/L ratio of 0.9.

However, when the 'extended-linear' kinetic model was applied in age assessments of the fossils, average diagenetic temperatures, some 10°C cooler than inferred from independent sources (e.g. the marine oxygen-isotope record), and full-glacial reductions in the order of 20°C would have to be invoked. In contrast, Wehmiller and Belknap (1978) applied a "non-linear" kinetic model for the dating of the Florida samples, and found that the calculated temperature reductions were consistent with independent evidence.

Clearly then, amino acid racemisation (epimerisation) kinetics are complicated. This complexity has been further highlighted by laboratory heating studies, that have attempted to simulate racemisation that occurs at ambient temperatures over protracted time periods (Smith et al., 1978; Kriausakul and Mitterer, 1978,1980a,b; Mitterer and Kriausakul, 1984; and Steinberg and Bada, 1981,1983). Several of these studies have centred on the relative rates of racemisation of amino acids in different molecular size fractions, and have provided explanations for the complex chemical kinetics evident in the 'total acid hydrolysate'.

Kriausakul and Mitterer (1978) noted that besides temperature and time, isoleucine epimerisation in peptides and proteins is dependent on (1) the position of isoleucine in the peptide chain, (2) the nature of the adjacent amino acids, and (3) the stability of isoleucine peptide bonds. In a subsequent investigation Mitterer and Kriausakul (1984) concluded that the relative rates of racemisation (epimerisation) conformed to the following order;

NH_2-terminal$\geq$diketopiperazine>>COOH-terminal$\cong$interior$\cong$free amino acids.

In contrast, the degree of isoleucine epimerisation were found to be; diketopiperazine>NH_2-terminal>COOH>free>>interior.

Although the relative rates of epimerisation at the (N) NH_2- and (C) COOH-terminal positions have been contested (Steinberg and Bada, 1981; Smith and de Sol, 1980) results reported by Kriausakul and Mitterer, (1978) nevertheless demonstrated the apparently complex racemisation kinetics observed in the 'total acid hydrolysate'. Diketopiperazine forms when free COOH and free alpha NH_2 groups of a dipeptide join to form a cyclic structure.

Mitterer and Kriausakul, (1984) proposed a model for isoleucine and epimerisation applicable to both carbonate fossils and heated aqueous solutions (Figure 2.4). Accordingly, in the 'total acid hydrolysate', isoleucine epimerisation in fossils appears to follow linear first-order kinetics. This occurs once hydrolysis has produced sufficient NH_2-terminal isoleucine and dipeptides. During this early stage of diagenesis, the rate controlling steps are the rates of epimerisation in NH_2-terminal isoleucine and diketopiperazine. Upon further natural hydrolysis, a larger proportion of slow epimerising free isoleucine will be present, and the overall rate of epimerisation will appear to decrease. With high concentrations of free isoleucine in the 'total acid hydrolysate', the rate controlling step will be isoleucine epimerisation of free amino acids (Mitterer and Kriausakul, 1984).

The rate at which isoleucine is transferred from interior to terminal and subsequently to the free amino acid state is dependent on the rate of hydrolysis. In contrast, the rate at which isoleucine epimerises in any specific form is generally independent of the hydrolysis reaction. The overall degree (extent) of isoleucine epimerisation in the 'total acid hydrolysate' is therefore controlled by hydrolysis. Mitterer and Kriausakul (1984) suggested this model may also apply for enantiomeric amino acids.

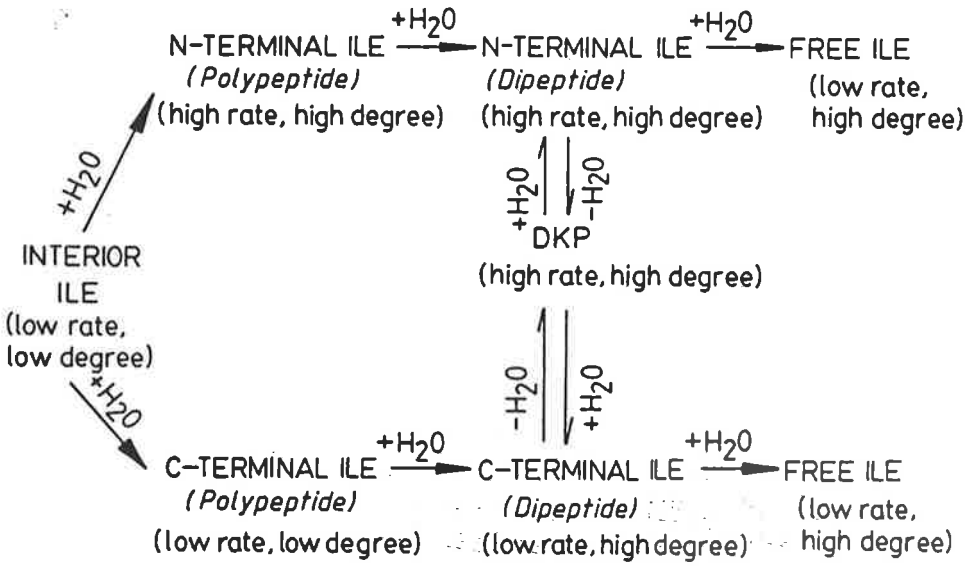


Figure 2.4 Model for the rate and degree of isoleucine epimerisation in various forms. (after Mitterer and Kriausakul, 1984).

As molluscan racemisation (epimerisation) rates are genus specific, the shape of racemisation (epimerisation) rate curves will vary accordingly. As a consequence, racemisation kinetics have to be established independently for different genera for quantitative dating.

Clearly then, a range of parameters, operative at different rates and intensities influence racemisation kinetics in 'non-ideal' systems. At the micro-scale, protein-structure involving the position of amino acids, whether at C- or N-terminal or interior positions and free amino acids have a pronounced influence on the rates of racemisation. Furthermore, initial protein structures in different molluscan genera and different amino acids may exhibit contrasting rates of racemisation. At the meso-scale, factors unique to a particular geological deposit such as pH, temperature and clay mineral catalysis will also influence racemisation rates. Macro-scale factors involving regional differences in diagenetic environments will significantly influence racemisation rates. All these variables were considered in this investigation.

Even at best then, racemisation kinetic models that summarise the kinetics evident in the 'total acid hydrolysate' probably over simplify the complexity of racemisation in 'non-ideal' systems. Some form of simplification is required however, so that age assessments may be obtained using the 'total acid hydrolysate' from natural systems. For these reasons, a cautionary approach was adopted in this study with quantitative age assessments based on the extent of racemisation in fossils.

2.3 AGE DETERMINATION: CALIBRATED AND UNCALIBRATED METHODS

Two methods permit quantitative age assessments using amino acid racemisation data, and are generally referred to as the 'calibrated' and 'uncalibrated' methods (Schroeder and Bada, 1976; Pillans, 1982; and Rutter et al., 1985).

2.3.1 The Calibrated Method

The calibrated method reduces some of the problems and assumptions concerning the temperature history of the dated material (Bada and Protsch, 1973). In the calibrated method D/L ratios obtained for a fossil are compared with an age obtained by independent dating techniques such as radiocarbon or uranium-series dating. An assumption implicit in this approach is that the sample being dated has experienced a similar diagenetic temperature history to the reference sample. From the D/L ratio and the calibrated age (date), an in situ racemisation rate constant is established. This rate constant can then be applied to other fossils from the same site or other closely spaced localities.

2.3.2 The Uncalibrated Method

The uncalibrated method requires a detailed knowledge of the temperature history experienced by the fossil since death and subsequent burial, the racemisation rate constant for the pertinent amino acid (K_L), and the D/L ratio of the amino acid in the fossil. In this method a sample of unknown age is compared with a sample that has been subjected to artificial laboratory induced racemisation at elevated temperatures. Caution

should be exercised with this approach however, as the changes which occur in heating studies may not accurately reflect changes during ambient temperature diagenetic racemisation. An additional complication is that it is unrealistic to assume that a detailed knowledge of the diagenetic temperature history may be obtained in view of the limited evidence preserved in the rock record.

Table 2.2 Parameters influencing racemisation*

(1)	Temperature
(2)	Matrix material
(3)	Hydrolysis state
(4)	Fossil genus
(5)	Clay mineral catalysis
(6)	Hydration (presence of water)
(7)	pH

* parameters listed essentially in order of significance.
(modified after Pillans, 1982 p.230).

Table 2.3 The effect of temperature on the racemisation of aspartate

Temperature (°C)	$kx10^6$ (yr^{-1})	Time (yrs)	D/L
0	1.61	1000	0.0061
25	196	1000	0.195
12.5	19.7	2000	0.0197

after Davies and Treloar (1977 p.81).

2.4 PARAMETERS INFLUENCING RACEMISATION RATES:

Unlike radionuclide decay, racemisation and epimerisation being physico/chemical reactions are sensitive to numerous environmental parameters. These are discussed in the following section. Temperature appears to be the most important rate controlling factor (Table 2.2).

2.4.1 Temperature

Previous studies have suggested that a ±1°C temperature uncertainty results in approximately 15-20% inaccuracy in quantitative age determinations (Schroeder and Bada, 1976; Williams and Smith, 1977; Rutter et al., 1985). According to Schroeder and Bada (1976), rates of racemisation approximately double for every 5°C increase in temperature and highlights the significance of temperature on racemisation. Higher temperatures have a disproportionate effect on racemisation. Based on the extent of racemisation of aspartate, Davies and Treloar (1977) suggested that 1000 years at 25°C results in ten times the extent of racemisation as 2000 years at 12.5°C. These figures were based on calculations using equation 2.2 (Table 2.3).

In view of the reported temperature effect on amino acid diagenesis, important questions arise in stratigraphic studies (Wehmiller et al., 1976). How reliable is the inferred diagenetic temperature history? In addition, how significant have climatic changes been in altering the rate of racemisation (epimerisation)? Could such temperature fluctuations be invoked to explain anomalous results? What constitutes a significant change in the diagenetic temperature history of fossils, and for how long are such changes required before their influence on D/L ratios is realised? In part these difficulties have been overcome by the calculation of an Effective Quaternary Temperature History (Wehmiller, 1982,1984b). This is discussed in Section 2.7.

An additional consideration in the context of mollusca concerns the length of time before their burial. There may potentially be a long delay before a shell is incorporated within a sediment package, and this would become important if the shell material has been subaerially exposed for a significant portion of its diagenetic temperature history.

The minimum depth within a stratigraphic section from which samples should be collected to reduce problems associated with temperature uncertainties is also important. A generally agreed upon depth beyond which surface temperatures assume less importance is approximately 1 m. This could however, be regarded as a limitation for it implies that some parts of subaerially exposed sequences cannot be dated by amino acid racemisation techniques because of temperature uncertainties. Amino acid racemisation data can also be applied in geothermometry, and in this sense can be used to internally assess results. This is further explored in Chapter 4.

2.4.2 Matrix Material

Studies have indicated that rates of racemisation vary according to the nature of the matrix material in which protein is bound (Schroeder and Bada, 1976; Williams and Smith, 1977). Fossil wood has been used in preference to shells as the rate of racemisation is significantly slower and permits older samples to be dated (B. Pillans, pers. comm., 1984). Moreover there appears to be minimal genus effect with wood. Rates of racemisation are fastest respectively in shell and bones with the slowest rates found in wood.

2.4.3 Hydrolysis State

Bada and Schroeder (1972) suggested that racemisation rates also vary according to the state in which amino acids are preserved (i.e., high molecular weight polypeptides, smaller peptides or free amino acids). Racemisation occurs faster respectively in the following order; terminal amino acids, interior amino acids and free amino acids (Mitterer and Kriausakul, 1984; Bada, 1985). This combined with the potential loss or contamination to the "free" fraction of the 'total acid hydrolysate" has led to the suggestion by some workers that racemisation of only the high molecular weight polypeptide bound amino acids be studied (Bada and Schroeder, 1972). However, the question of how long, high molecular weight polypeptides remain in fossils before their ultimate breakdown into smaller molecules by natural hydrolysis should be addressed. In this context, middle molecular weight peptides may potentially represent the most useful size fraction for amino acid dating (Kimber et al., 1986).

2.4.4 Fossil Species

Numerous workers have identified a species effect influencing racemisation rates. In a study of fossil planktonic foraminifera from an equatorial Pacific deep sea core V28-238, King and Neville (1977) noted the strongly species dependent nature of isoleucine epimerisation and suggested that monospecific foraminiferal analyses provided greater precision for quantitative age determinations. Species exhibiting rapid epimerisation rates such as Globorotalia tumida were considered geochronometrically useful as the fast rate of isoleucine epimerisation enabled younger samples to be dated.

The species specific nature of racemisation was also explored by Wehmiller (1980,1984b) who referred to a "chemical taxonomy" which appears to parallel the classical taxonomic organisation of molluscan fauna. Wehmiller suggested that the rates of racemisation in molluscs relates to the relative abundance of stable peptide bonds in various genera. Accordingly, slow-racemising groups contain a greater proportion of stable peptide bonds which hydrolyse more slowly. This results in the production of less of the more extensively racemised free amino acids, and therefore lower D/L ratios for the 'total acid hydrolysate'.

In an examination of inter- and intrageneric trends in apparent racemisation kinetics of amino acids in Quaternary molluscs, Lajoie et al., (1980) noted that differences in apparent racemisation rates were not detectable among species of the same genus. According to Lajoie et al., (1980, p.314) 'apparent racemisation rates' refers to "the relative order of observed enantiomeric ratios either within a single genus or among several genera". These authors noted that apparent racemisation rate differences may be evident among genera in the same subfamily or family, and are generally detected among genera in different families or at higher taxonomic levels. Lajoie et al., (1980) therefore suggested that the species-specific foraminiferal kinetics observed by King and Neville (1977), represent a generic or family effect rather than a species effect.

2.4.5 Clay Mineral Catalysis

Clay mineral catalysis has been invoked by some workers for accelerated rates of racemisation (Pollock et al., 1977; Frenkel and Heller-Kallai, 1977). Accordingly, surface properties of montmorillonite can have a catalytic effect on racemisation.

2.4.6 Hydration (Presence of Water)

The significance of water on amino acid racemisation has been demonstrated by the absence of reaction in heated samples of anhydrous protein (Hare, 1974). This is corroborated by the anomously low extent of racemisation in fossils from the La Brea Tar Pits in California (Kvenvolden and Peterson, 1973).

2.4.7 pH

It has generally been concluded that between pH 5 and 9, racemisation rates are largely independent of pH (Bada and Helfman, 1975; Kvenvolden, 1975; Dungworth, 1976; Schroeder and Bada, 1976; Williams and Smith, 1977). According to Bada (1985) most sedimentary environments including lakes, rivers and oceans have pH values within the range of 6-9.

Given that these parameters influence racemisation, the best settings to obtain samples are those in which the temperature history is known, or at least can be inferred to be similar for all samples. Other variables that influence racemisation should also be held as constant as possible throughout geological time. In this context, samples obtained from deep sea cores, caves, single cores or sections from lake and swamp deposits, or deeply buried materials within a small geographic region are most suited for the technique (Pillans, 1982).

2.5 CONTAMINATION

As with any dating method, contamination presents a significant problem in amino acid studies. Four potential contamination sources are recognised: (1) removal or addition of amino acids by groundwater leaching, (2) diagenetic formation of amino acids, (3) additions from bacteria and other micro-organisms and (4) human induced contamination during sample collection and preparation.

2.5.1 Removal Or Addition Of Amino Acids By Groundwater Leaching

The problem of contamination is greatly magnified when dealing with samples containing low concentrations of indigenous amino acids (Kvenvolden, 1975). A pre-eminent example of the problem of natural contamination is demonstrated in the finding by Schopf et al., (1968) of amino acids in three different samples of chert obtained from the Bitter Springs, Gunflint, and Fig Tree Formations representing points in time of 1, 2 and 3 Ga respectively. Although extreme caution was exercised in the laboratory preparation of these samples, subsequent analyses involving stereochemical techniques demonstrated that the amino acids present were in the L-configuration, and represented contaminants of more recent origin (Abelson and Hare, 1969). Abelson and Hare (1969) suggested that addition of amino acids in the L-configuration by groundwater leaching was the likely source of contamination in this instance.

2.5.2 Diagenetic Formation Of Amino Acids

Bada et al., (1978) have examined the decomposition pathways of two hydroxy amino acids, serine and threonine in foraminiferal tests. Serine and threonine represent two of the more unstable amino acids, as demonstrated by their virtual absence in foraminifera and molluscs with ages exceeding several million years (Schroeder and Bada, 1976). Data obtained in the present study however suggests that these amino acids are lost from molluscs considerably earlier than suggested by Schroeder and Bada (1976).

The diagenetic reactions for serine and threonine are complex (Bada et al., 1978). In basic solutions, serine and threonine undergo rapid decomposition by two pathways: dehydration and reversible aldol cleavage. At neutral pH, decarboxylation may also be a significant decomposition pathway. For serine, the reversible aldol cleavage reaction produces glycine and formaldehyde, the dehydration reaction produces alanine and decarboxylation produces ethanolamine. For threonine, the reversible aldol cleavage reaction yields glycine and acetaldehyde, the dehydration reaction α-amino-n-butyric acid (α-ABA) and decarboxylation yields 2-propanolamine. These reaction pathways are summarised in Figure 2.5. Caution should therefore be exercised in studies that correlate varying concentrations of glycine and another amino acid with fossil age, as a proportion of glycine may be of diagenetic origin.

As serine and threonine are recognised as two of the least stable amino acids, their presence in ancient fossils is indicative of contamination (Bada et al., 1978; Bada and Man, 1980). Interestingly, serine is the most abundant amino acid in fingerprints, and therefore necessitates caution being exercised with sample collection and preparation.

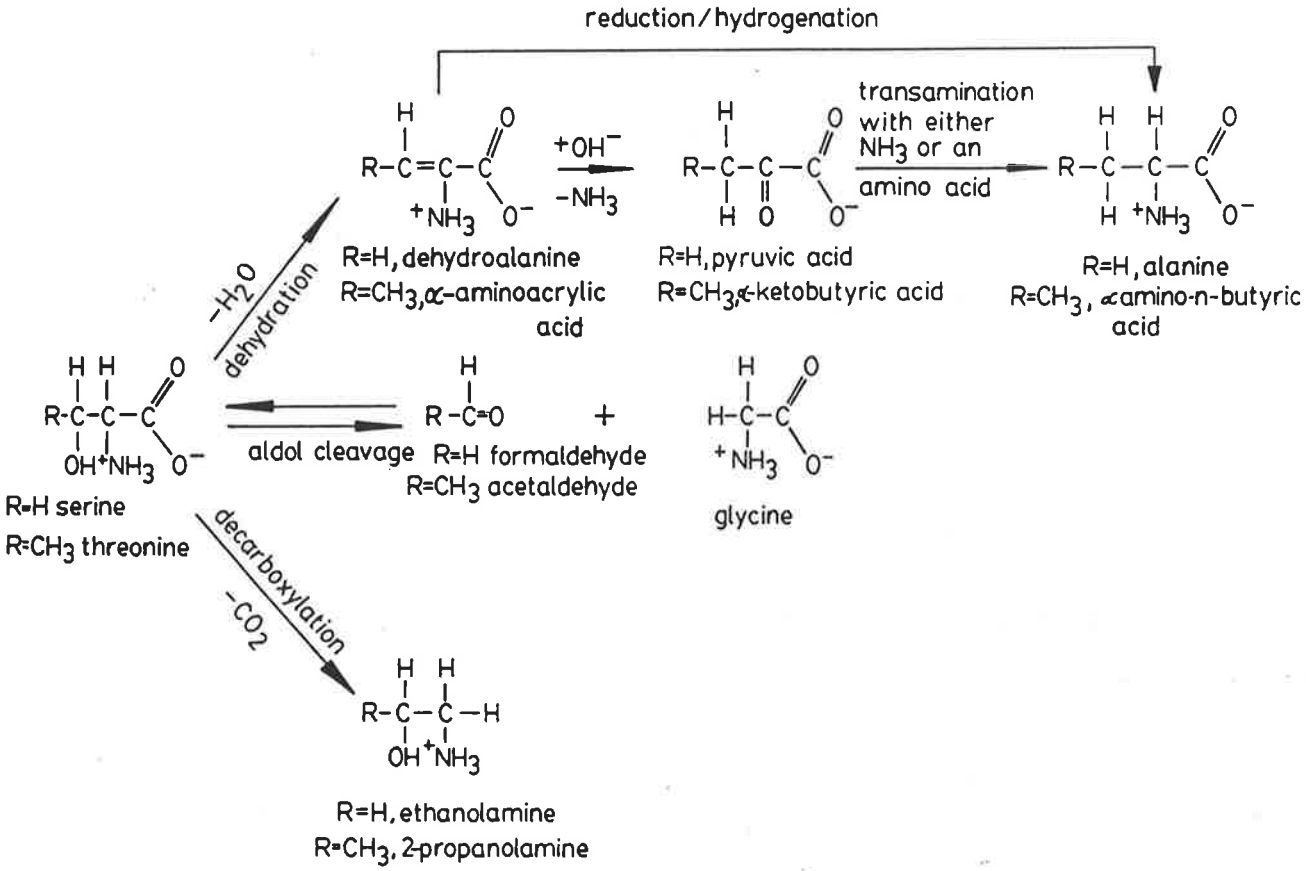


Figure 2.5 Decomposition pathways of serine and threonine. (after Bada et al., 1978)

The origin of the non-protein amino acids β-alanine and γ-amino-n-butyric acid have been attributed to enzymatic decarboxylation of aspartic acid and glutamic acid respectively (Abelson, 1963; Bada, 1971; Schroeder, 1975). However, the diagenetic origin of these amino acids has also been questioned (Wehmiller et al., 1976). The important point concerning the diagenetic origin of amino acids is that they may not be distinguishable from amino acids originally within a fossil (Williams and Smith, 1977).

2.5.3 Additions From Bacteria And Other Sources

The possibility of bacterial induced contamination has also been explored. In a study of the stereochemistry of amino acids in soils, Pollock et al., (1977) demonstrated that the percentages of D-alanine, D-aspartic acid and D-glutamic acid were significantly higher than four other protein amino acids. Pollock et al., (1977) suggested a microbial origin for these amino acids as they represent significant components of bacterial cell walls and metabolites (Table 2.4). These authors suggested that modern surficial marine sediments might be analogous to soils and also contain significant D-amino acids. Pollock and Kvenvolden (1978) subsequently examined two surface samples of marine sediment and observed significantly higher percentages of D-alanine and D-aspartic acid. As these amino acids are observed in bacteria, Pollock and Kvenvolden concluded that the marine sediments had been subject to bacterial contamination. These results however, are based on the assumption that marine bacteria, like terrestrial bacteria contain high percentages of D-alanine and D-aspartic acid. Additional evidence for bacterial contamination include diaminopimelic acid and the presence of amino sugars such as muramic acid and glucosamine (Chichereau and Trichet, 1976).

Table 2.4 Percentage of glutamic acid, aspartic acid and alanine in the D-configuration in bacterial cell walls

	% of total in D-form		
	glutamic acid	aspartic acid	alanine
S.faecalis	85	71	39
L.casei	100	50	61
L.plantarum	100	-	32
L.mesenteroides	73	67	54
L.pentosus	94	-	66
L.citrovorum	89	78	47
L.bulgarious	87	72	40
L.lactis	94	78	61
L.acidophilus	91	67	48

Data from Ikawa and Snell (1960) cited in Salton (1964, p.260)

2.5.4 Human Induced Contamination During Sample Collection And Preparation

The possibility of human induced contamination during sample collection and preparation should not be excluded. Where possible, direct contact of samples with fingers should be avoided. Amino acids in finger-prints of persons handling samples can present a serious source of contamination, particularly for fossils of great antiquity which generally contain low concentrations of indigenous amino acids (Kvenvolden, 1975). Characteristic patterns of fingerprint contamination include high concentrations of both serine and glycine (Rash et al., 1972; Kvenvolden, 1975). The level of contamination of individual amino acids from this source could be as much as 10^{-7} mole. Hence care was taken to avoid fingerprinting laboratory glassware in this study. Rash et al., (1972) reviewed numerous sources of laboratory contamination and demonstrated that nanogram and microgram amounts of amino acids are found in reagents, latex gloves, fingerprints, skin, dandruff, hair, saliva, dust and cigarette smoke. In addition problems associated with amino acid contaminated hydrochloric acid were discussed by Wolman and Miller (1971). This work was carried out for the analysis of lunar samples, where contamination presents a major problem owing to the very low concentrations of indigenous amino acids.

2.6 AMINO ACID RACEMISATION DATING: SAMPLE MATERIALS

A variety of biogenic remains may potentially be dated using amino acid racemisation techniques and have included shells, foraminifera, corals, wood, bones and abiogenic concretions (Schroeder and Bada, 1976; Bada and Helfman, 1975; Dungworth, 1976; Wehmiller et al., 1976; Williams and Smith, 1977; Rutter et al., 1985; Wehmiller, 1982,1984a,b). In this thesis however, fossiliferous materials specifically found only in marine and paralic settings will be discussed.

2.6.1 Molluscs

Molluscs have been extensively used in aminostratigraphic studies (e.g., Mitterer, 1975; Masters and Bada, 1977; Kvenvolden et al., 1979; Karrow and Bada, 1980; von der Borch et al., 1980; Kennedy et al., 1982; McCarton et al., 1982; Wehmiller, 1982,1984a,b; Kimber and Milnes, 1984; Wehmiller and Belknap, 1978; Wehmiller and Emerson, 1980; Hearty et al., 1986; Murray-Wallace and Kimber, 1987). As the optimum sample amount for analysis after cleaning pretreatment approximates one gram small quantities of protein typically in the order of nanomoles/gram are generally involved in amino acid analyses. Shells therefore present a useful and generally readily available material. An added advantage of shells besides confidence in stratigraphic interpretation when using articulated valves, concerns the integrity of the calcium carbonate matrix (Schroeder and Bada, 1976). Laboratory simulation of amino acid diagenesis in mollusc shells heated in a solution containing the non-protein amino acid L-norleucine, revealed that negligible quantities of this tracer were incorporated within the carbonate matrix (Hare and Mitterer, 1969). From this Hare and Mitterer (1969) concluded that simple molecular diffusion of amino acids in the carbonate matrix does not occur to any significant extent.

Amino acids could however, be lost from a shell via small fractures. Microscopic examination of shells that have anomalously low proportions of free amino acids has revealed the presence of pervasive microfractures (Matter and Miller, 1972). This necessitates caution with sample collection. Diagenetic recrystallization of aragonite to the more stable polymorph calcite, has also been suggested as a possible mechanism accounting for the loss of indigenous amino acids from shells (Schroeder and Bada, 1976). However the concomitant loss of amino acids during recrystallization has not been demonstrated.

2.6.2 Foraminifera

Foraminifera have been extensively used in aminostratigraphic investigations. Previous investigations have mainly been performed on planktonic species found in deep sea cores, with less attention paid to benthonic species (King and Neville, 1977; Bada et al., 1978; Bada and Man, 1980; Miller et al., 1983; Sejrup et al., 1984; cf. Belperio and Murray-Wallace, 1984; Cann and Murray-Wallace, 1986). One of the advantages of foraminifera is that they are generally considered to behave as closed systems and therefore experience minor loss of indigenous amino acids with time (Schroeder and Bada, 1976; Williams and Smith, 1977). The requirement of approximately one gram of sample before pre-treatment however, presents a major limitation with the use of foraminifera in aminostratigraphy. In this context D/L ratios reported for foraminifera represent unweighted average values for all tests. This problem is complicated by the genus specific nature of racemisation in foraminifera (King and Neville, 1977; King, 1980).

2.6.3 Corals

Corals have been dated by amino acid racemisation techniques, although with limited success (Wehmiller et al., 1976). In a study of isoleucine epimerisation in fossil corals from a suite of uplifted reef terraces of Mid- to Late Pleistocene age on the island of Barbados, Wehmiller et al., (1976) observed that D/L ratios in many fossil corals did not conform to the concept of increasing racemisation being associated with increasing fossil age. Thirty-eight fossil corals were studied, sixteen of which displayed concordance between increasing age and extent of racemisation. The general lack of concordance was attributed to either extensive leaching of free amino acids from the fossils, or contamination by amino acids in the L-configuration. Wehmiller et al., (1976) concluded that fossil corals are of only modest value as specimens for amino acid geochronological studies.

2.7 EFFECTIVE QUATERNARY TEMPERATURE HISTORY

To ameliorate some of the uncertainties and probable errors likely to arise due to variable diagenetic temperature histories, Wehmiller (1982) proposed a method for establishing more reliable temperature histories experienced by fossils. This approach involves the calculation of the 'Effective Quaternary Temperature' (EQT), a weighted average rate constant (the integrated kinetic effect of all temperatures to which a fossil has been exposed), for a sample of a given age.

According to Wehmiller (1982), EQT values for samples can be determined by reference to the marine oxygen-isotope record as a model for the timing of climatic change, and local palaeoclimatic information as a model for the intensity of climatic change. In this approach, the timing of temperature variations and concomitant influence on the degree of racemisation of amino acids in fossils is taken into account. Temperature reductions during the glacial maxima are first estimated (ΔT_{fg}) (Figure 2.6). Once this has been established, a racemisation rate constant history can be determined. This involves division of the marine oxygen-isotope temperature record into a series of 5000 yr working intervals, and are taken as time intervals that have experienced constant temperatures. From these data, the rate constant history is calculated using the amino acid rate constant expression of Bada and Schroeder (1972);

$$\log k = 15.77-5939/T \qquad \text{(eqn 2.5)}$$

or that of Mitterer (1975);

$$\log k = 17.29-6417/T \qquad \text{(eqn 2.6)}$$

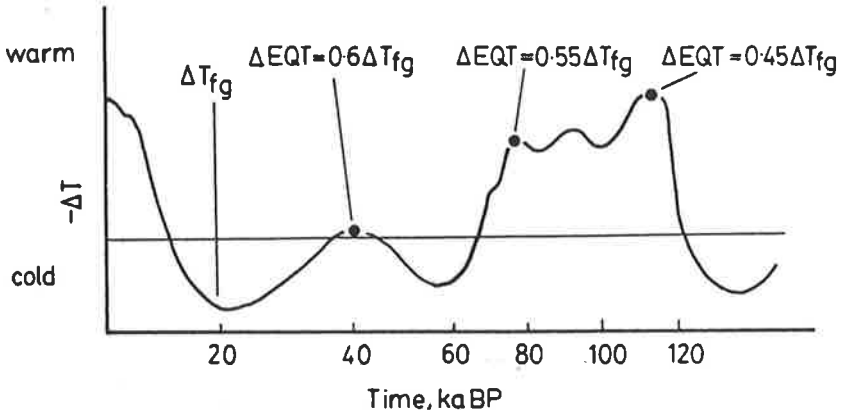


Figure 2.6 Model for the calculation of Effective Quaternary Temperatures (E.Q.T.), from palaeoclimatic data, according to the principles outlined in Wehmiller (1982).

Once this has been established, the average rate constant may be converted to an EQT value using the same temperature dependence equation employed in the calculation of individual rate constants (Wehmiller, 1982).

2.8 ADVANTAGES AND LIMITATIONS OF AMINO ACID RACEMISATION DATING

Clearly, the significant advantages of amino acid racemisation as a geochronometric tool includes the small sample requirement, rapidity of analyses, the wide range of organic materials that can be analysed and the potential of dating geological events beyond the range of conventional radiocarbon methods. Several limitations however, include the requirement of a detailed knowledge of the temperature history experienced by the fossil since death and subsequent burial (if using the uncalibrated method as described in Section 2.3.2), and the requirement of an independent dating technique to serve as a basis for calibration of amino acid data.

As temperature appears to be the most important rate controlling factor influencing racemisation, D/L ratios obtained on fossils from semi-arid regions cannot be directly compared with those from tropical settings. This problem is highlighted in Chapter 6. In some instances this spatial restriction may be regarded as a limitation. Recent studies (Wehmiller and Emerson, 1980; Emerson et al., 1981; and Wehmiller, 1984b), have partly circumvented these difficulties through studies of D/L ratio variation with latitude for isochronous deposits. However, the technique has considerable potential for localised stratigraphic correlation, and in establishing relative chronostratigraphies.

Caution should be exercised with regard to the possibility of a genus effect. Contamination also presents a problem. Another limitation is that sediments must contain fossils that can be dated by the technique. Many Quaternary sequences are barren and therefore cannot be dated using amino acid racemisation techniques.

2.9 CONCLUSIONS

(1) Given the range of chemical reactions protein may potentially undergo during diagenesis, it would appear surprising that protein is preserved for protracted periods.

(2) As a corollary, in view of the complexities of protein diagenesis and amino acid racemisation (epimerisation), it is also surprising how successfully these reactions can be applied in a variety of geological problems.

These include:

- stratigraphic correlation and in establishing relative chronostratigraphies,
- quantitative age assessments,
- geothermometry,
- assessments of reworking, reconnaissance checks for radiocarbon dating as well as other dating techniques, and various other miscellaneous applications.

(3) Amino acid racemisation (epimerisation) involves interconversion of enantiomers (diastereoisomers) from the L to D configuration until an equilibrium ratio (racemic condition) is obtained in the case of enantiomers. Diastereoisomers obtain equilibrium ratios greater than unity, and isoleucine may obtain values approaching 1.4.

(4) Numerous parameters influence racemisation (epimerisation) and include temperature, matrix material, hydrolysis state, fossil genus, clay mineral catalysis, hydration and pH. Temperature generally appears the most important rate controlling factor.

(5) Materials commonly analysed include shells, foraminifera, corals, wood, bones and abiogenic concretions.

(6) The significant advantages amino acid racemisation presents as a geochronometric tool include the small sample requirement, rapidity of analyses, wide range of organic materials that can be analysed and the potential to date events beyond the range of conventional radiocarbon methods.

(7) Limitations include the requirement of a detailed knowledge of the temperature history ('uncalibrated method') or an independent dating technique as a reference in the 'calibrated method'. In addition, the complex nature of racemisation kinetics dictate that large collections of samples of different ages be analysed to avoid imprudent interpretations.

(8) As with any dating technique, contamination presents a significant problem. Contamination sources include (1) removal or addition of amino acids by groundwater leaching, (2) diagenetic formation of amino acids, (3) bacterial contamination and (4) human induced contamination during sample collection and preparation.

CHAPTER 3 AMINO ACID RACEMISATION DATING SYSTEMATICS

3.1 INTRODUCTION

Since the discovery of protein residues in fossils by Abelson (1954,1955) considerable attention has focussed on the application of time-dependent protein diagenesis in geochronometry. Although an extensive literature now exists with useful summaries in Dungworth (1976); Schroeder and Bada (1976); Williams and Smith (1977); Rutter et al. (1985); and Wehmiller (1982,1984b), few studies have critically assessed the reliability of results. In particular, the statistical significance of D/L ratios, and the factors responsible for D/L ratio variation in fossils have generally been neglected or treated inadequately. Moreover, considerations of the age resolving capabilities of amino acid data have frequently been neglected (e.g., do differences in D/L ratios reflect genuine and resolvable age differences or an artefact of analytical or sampling errors). It is partly a result of the lack of such critical assessments that the technique has fallen into some disfavour (Davies and Treloar, 1977; Pillans, 1982). In this chapter, an assessment of potential error sources and D/L ratio variation in fossiliferous sediments based on the extent of racemisation in carbonate fossils is presented. Results are discussed in the context of a scheme that summarises a range of sampling and analytical errors, and will provide a basis for critical evaluation of data presented in subsequent chapters as well as published literature. The age resolving ability of amino acid racemisation techniques is also discussed.

Early studies involving amino acid racemisation techniques were performed on foraminifera from deep sea cores and molluscs from arctic settings, as well as cave deposits. In these early studies, a degree of

temperature control was available based on established palaeoclimatological evidence, and the restriction of dating materials generally within the range of conventional radiocarbon methods. Furthermore, D/L ratio error terms were lower owing to the slower rates of racemisation due to the lower diagenetic temperature histories (Kvenvolden et al., 1970; Wehmiller and Hare, 1971; King and Hare, 1972a,b; Bada and Schroeder, 1976). Subsequent investigations however, branched out to a range of environments and involved age assessments of older materials, where knowledge and the influence of climatic change were less established, and frequently resulted in ambiguous conclusions. Although the application of amino acid racemisation to studies in such settings was not unjustified, it has nevertheless led to a greater appreciation of the complexities such applications present.

3.2 AMINO ACID RACEMISATION DATING: SOURCES OF ERROR

3.2.1 Analytical Error (Gas Chromatography)

An indication of analytical error for the gas chromatographic procedures employed in this study was established by repetitive analysis of a hinge of a late Pleistocene specimen of the mollusc Anadara trapezia. Analyses involving a range of amino acids were made for the 'total acid hydrolysate'. The derivatised sample was repeatedly analysed using a Packard-Becker Model 419 gas chromatograph. Results are documented for six injections (Figure 3.1) with the more complete data presented in Appendix Table 3.1. A further two injections were made 24 hours later, and only proline and aspartic acid were confidently resolved. Amino acid isomers routinely analysed in the CSIRO laboratory include aspartic acid, leucine, alanine, valine, isoleucine, proline, glutamic acid and phenylalanine. Data are not reported for glutamic acid and phenylalanine, as these amino acids did not adequately separate at the time of this study. Average D/L ratios for the six replicate injections were calculated and the standard deviation (1 SD) and percentage standard deviation (coefficient of variation) reported (Figure 3.1). All reported coefficients of variation were less than 5%.

As only six successive injections permitted the satisfactory resolution of a range of amino acids (because of sample loss after several injections), only data from these injections were incorporated in the calculations. Because of the small sample population, a significant numerical outlier for a single D/L ratio value in a replicate injection could change the calculated average D/L ratio, and therefore increase the apparent error. Alanine

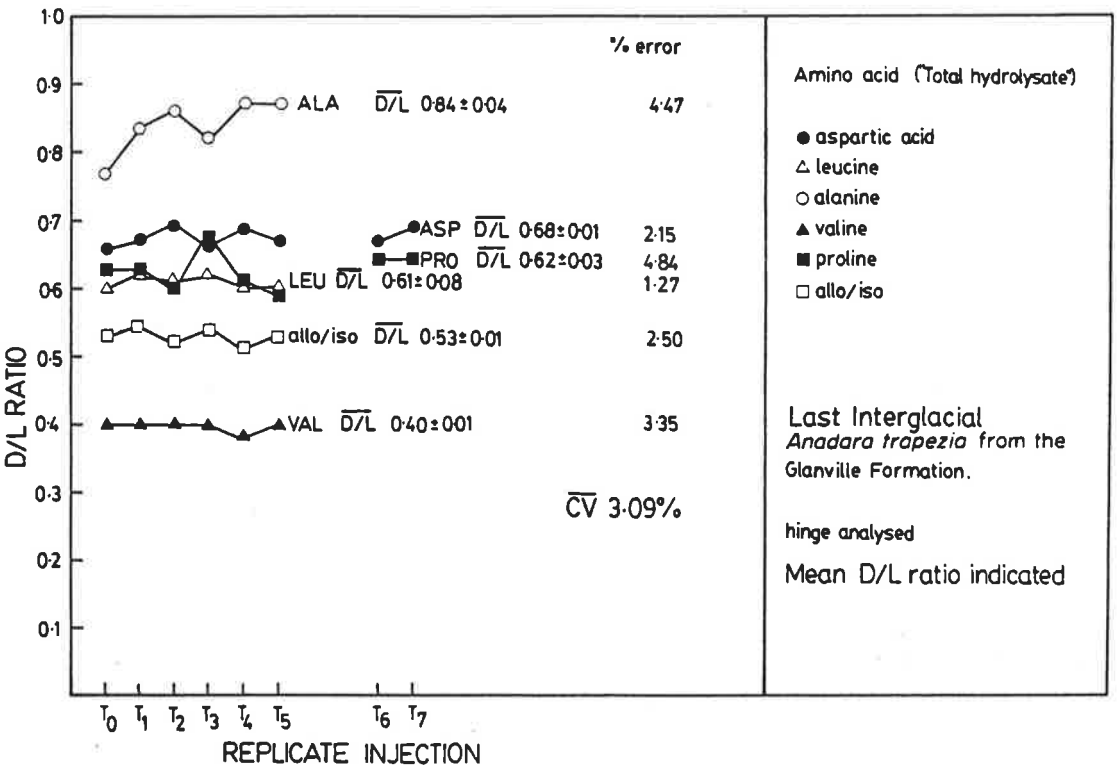


Figure 3.1 D/L ratio variation in a Last Interglacial specimen of Anadara trapezia attributed to analytical precision (% error = coefficient of variation).

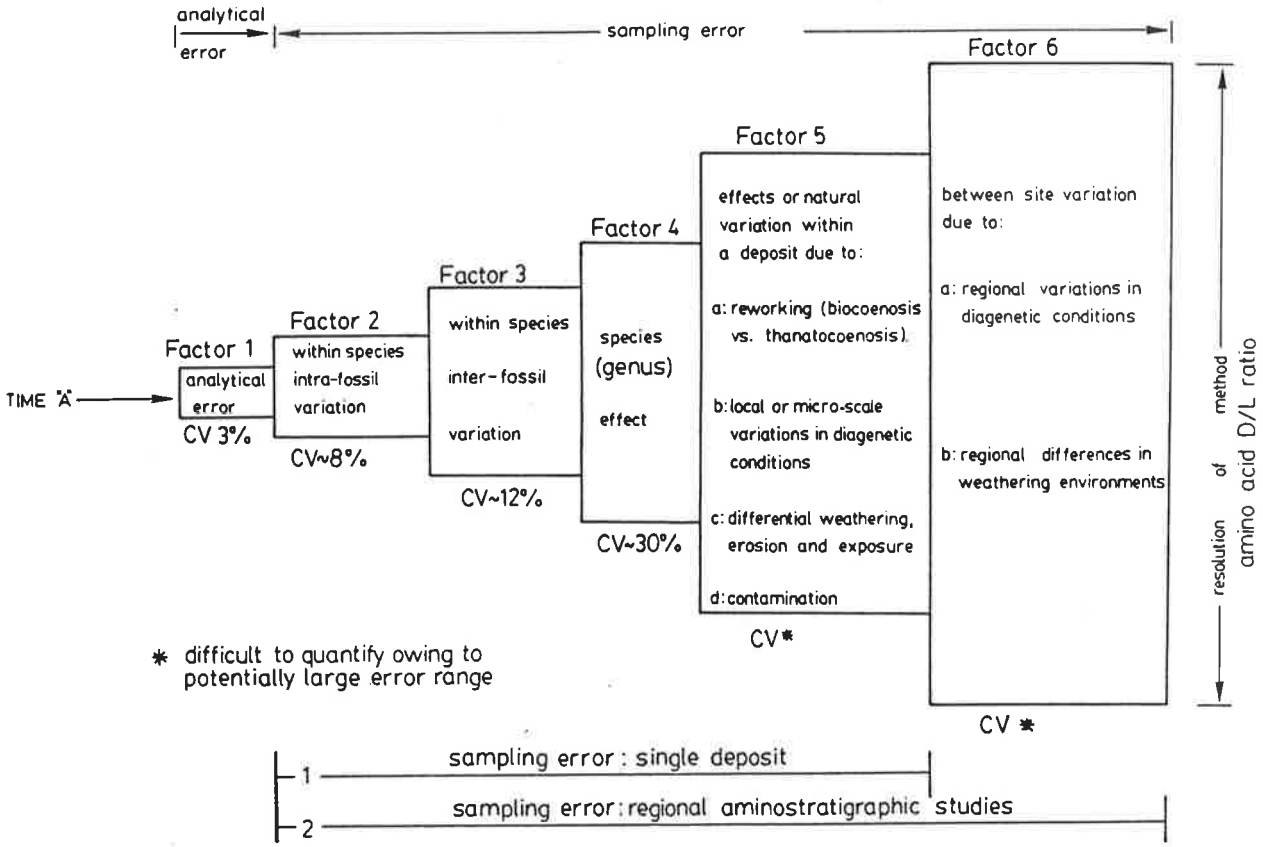


Figure 3.2 An assessment of factors determining D/L ratio variation in fossiliferous geological deposits based on the extent of racemisation in carbonate fossils. Note that the range of coefficients of variation is dependent on the amino acid selected. Coefficients of variation reported above represent averages for several amino acids and are for the 'total acid hydrolysate'.

provides an example of this, where the t_o value falls significantly below the subsequent values (Figure 3.1). Alanine and proline displayed the greatest 'apparent' variation, with coefficients of variation (CV) of 4.47 and 4.84% respectively. However, these higher CV's are the result of a single numerical outlier in each case (Figure 3.1).

An average coefficient of variation of 3% was obtained for the six amino acids analysed (ASP, ALA, LEU, PRO, ALLO/ISO, and VAL), indicating that analytical variation in gas chromatography accounts for only a small margin of error in the final D/L ratio reported by a laboratory. Data obtained from this exercise suggests that amino acid D/L ratios be reported only to two significant figures. Data reported to three significant figures would require considerably larger sample populations. This is further explored in Section 3.2.6.

At a slightly broader scale, analytical error may potentially involve a range of errors that arise within a single analysis including sample preparation, derivatisation procedures as well as gas chromatography. In addition, laboratory induced contamination may occur from a variety of sources, although this can in part be controlled by cautious laboratory practice. These larger margins of variation are incorporated within the error terms discussed in the next section (3.2.2)

Wehmiller (1984b) noted that a fragment representing at least 5% the weight of the original shell should be analysed to ensure representative D/L values are obtained. This reduces the likelihood of variable results, which may potentially arise when small fragments (<0.2 gram) are analysed from large individuals (>30 grams). In the present study, between 5-10% by weight, of Anadara trapezia and 10-20% Katelysia spp. were analysed. A greater relative proportion of the shells of Katelysia spp. were analysed owing to their smaller size and the workable size required for cleaning shell fragments.

Complications also arise with the interpretation of chromatogram traces. Low peak heights/areas for example, are likely to increase the

margin of error in D/L ratio calculations. Additional error is introduced in manual peak height evaluation in the calculation of D/L ratios and problems with coelution and rider peaks introduce a further margin of error.

Errors may also arise in studies specifically concerned with amino acid concentrations in fossils. Variable amino acid concentration data may be influenced by error in the addition of a non-protein amino acid internal standard, as well as problems experienced during sample derivatisation. Factors likely to influence errors in concentration data during derivatisation include sample loss from reacti-vials during esterification and acylation. Furthermore, once volatile derivatives of amino acids have been prepared they should be analysed as soon as possible to ensure reliable concentration data are obtained. This is of particular importance in view of the inherent difficulties of obtaining concentration data by gas chromatography.

The reported relative rates of racemisation in Anadara trapezia for the analytical error exercise are in general accord with those reported in the literature for other carbonate matrices (Dungworth 1976; Bada and Man, 1980; Lajoie et al., 1980) although an exception is alanine which is more extensively racemised than aspartic acid in the Pleistocene Anadara specimens. This is attributed to changes in the relative rates of racemisation with time for these amino acids, and a similar phenomenon has previously been reported (Schroeder and Bada 1976; Lajoie et al., 1980). In Holocene Anadara obtained from Queensland, aspartic acid has generally undergone a greater degree of racemisation than alanine (Table 3.1).

3.2.2 Within-Species Intrafossil D/L Ratio Variation

The possibility of systematic differences in amino acid D/L ratios within fossils has tended to be neglected. Brigham (1983) systematically analysed intrashell variation of amino acid concentrations and isoleucine

Table 3.1 Comparison of the extent of racemisation of alanine with aspartic acid in Holocene and Pleistocene Anadara spp.

	Relative extent of racemisation (D/L)	Number of individuals analysed Free amino acids*	Total acid hydrolysate
Holocene[1]	ASP>ALA	-	4
	ALA>ASP	2	1
Pleistocene[2]	ASP>ALA	2	4
	ALA>ASP	18	36

1 Samples obtained from Princess Charlotte Bay, Queensland.

2 Samples obtained from various Last Interglacial coastal and marine sediments, South Australia

* Less data are available for the free amino acids.

epimerisation ratios in twenty-four valves of the fossil mollusc Hiatella arctica. Although the ratio of D-alloisoleucine/L-isoleucine did not vary significantly between the five anatomically different parts of the shells analysed, higher concentrations of amino acids were recorded for the hinge. On this basis, Brigham (1983) recommended that where possible mollusc hinges should be analysed in amino acid racemisation studies. Using stepwise discriminant analysis Brigham (1983) noted that only 31.5% of the 92 shell fragments of Hiatella arctica could be correctly identified on the basis of free ALLO/ISO and total ALLO/ISO. In contrast, stepwise discriminant analyses of the five shell parts based upon amino acid concentrations indicated that 61% of the shell fragments could be identified. Clearly then, it would appear that amino acid concentrations are more diagnostic than D/L ratios for identifying anatomically different parts of molluscs. As a corollary, Andrews et al., (1985) have noted that several mollusc genera can be identified on the basis of their amino acid chromatograph signatures, involving the relative concentrations of different amino acids.

To assess D/L ratio variation within a single mollusc, a valve of Anadara trapezia was cut into six sections and analysed for the 'total acid hydrolysate' and free amino acids. An assessment of whether systematic variation in D/L ratios or concentration data is evident in different shell fragments, would require the analysis of a large number of shells, and in part such results have already been reported (Brigham, 1983). The purpose of this exercise in contrast, was to obtain a qualitative assessment of the magnitude of D/L ratio variation within a single shell, for a range of amino acids. The sections analysed included the hinge, central region, anterior and posterior growth edges, and two sections of the central growth edge (Figure 3.3 and Appendix Table 3.2). Whereas Brigham (1983) only considered D/L ratio variation for isoleucine, this study

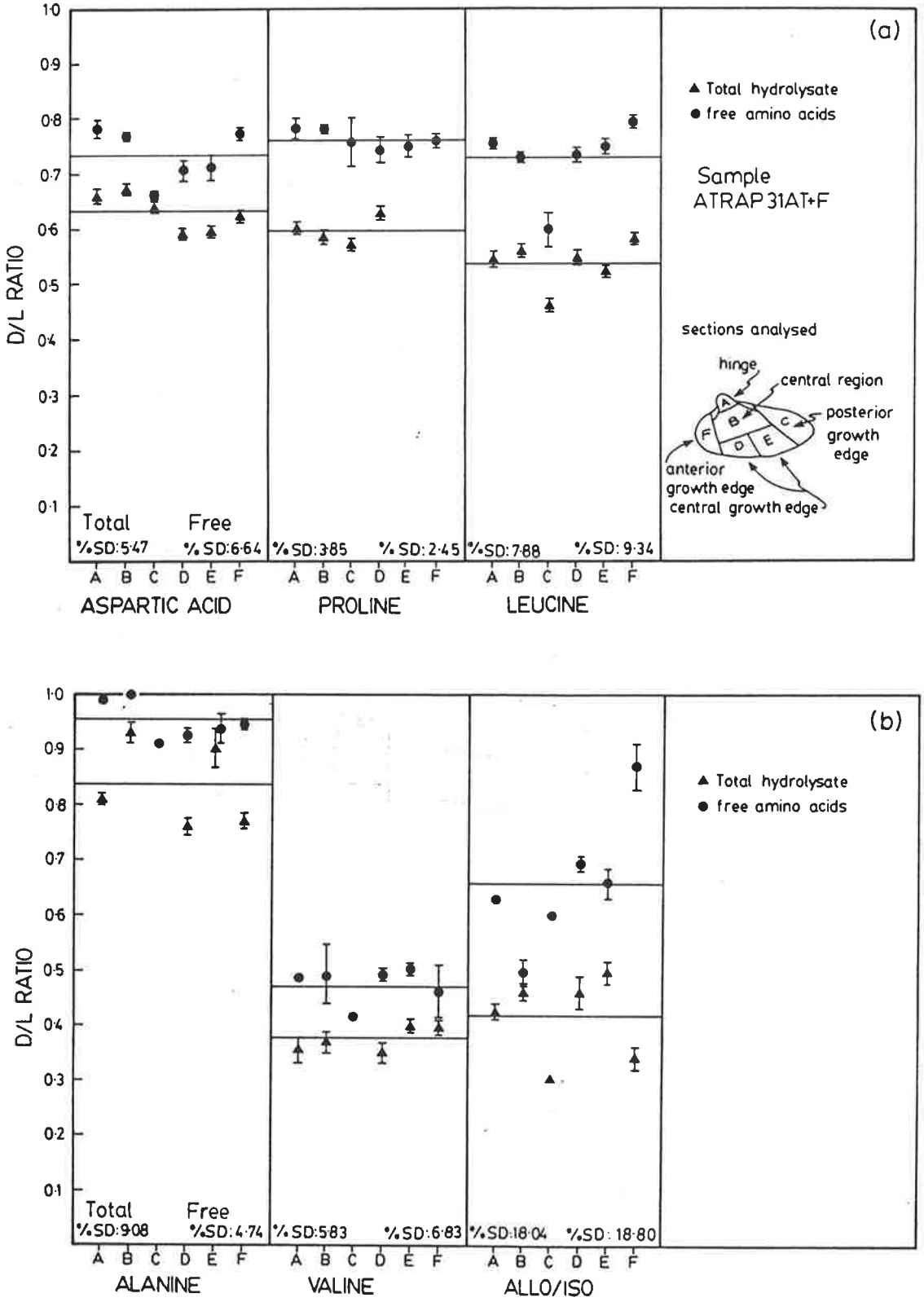


Figure 3.3 Intrashell D/L ratio variation in the bivalve Anadara trapezia obtained from a Last Interglacial marine deposit, Port Wakefield, South Australia (%SD = coefficient of variation).

presents results for aspartic acid, proline, leucine, alanine, valine and isoleucine. The exercise was repeated for the 'total acid hydrolysate'. The data are listed in appendix Table 3.2 and results for the 'total acid hydrolysate' and free amino acids from one of the valves analysed are summarised diagrammatically in Figures 3.3a,b.

Comparison of the coefficients of variation for intrashell D/L ratio variation for the 'total acid hydrolysate' with free amino acids indicated that they were not systematically higher in either fraction. For aspartic acid, leucine and isoleucine the coefficients of variation were greater for free amino acids than the 'total acid hydrolysate'. In contrast, for proline and alanine the coefficients of variation were greater in the 'total acid hydrolysate'. As a chemically similar micro-environment hosts these amino acid fractions, pronounced differences between free and total in terms of coefficients of variation would not be expected.

The greater variability in the results for isoleucine may be due in part to the difficulty of this separation by gas chromatography (Kvenvolden, 1980; Wehmiller, 1984b). Historically, good baseline separation by gas chromatography of D-alloisoleucine and L-isoleucine has been a difficult task. In this study however, broader D-alloisoleucine peaks were occasionally evident, suggesting coelution of an unknown material, and resulted in more variable data. A similar magnitude of variation for isoleucine was noted by Hearty et al., (1986), where ALLO/ISO ratios ranged between 0.47 to 0.65 in a single valve of Glycymeris violescens. Interestingly however, isoleucine represents one of the more extensively studied amino acids, as its analysis on conventional amino acid analysers requires less involved laboratory preparation, than required by gas chromatographic methods.

According to the scheme presented (Figure 3.2), intrashell D/L ratio variation would be expected to be higher than analytical error, although lower than intershell D/L ratio variation (see section 3.2.3).

3.2.3 Within-Species Interfossil D/L Ratio Variation

Interfossil (intershell) variation refers to natural differences in amino acid D/L ratios between fossils of equivalent age. Processes such as reworking and contamination are excluded as mechanisms for D/L ratio variation evident within a single deposit, as these factors give rise to an increased margin of error, and are considered later.

Intershell D/L ratio variation was studied in replicate valves of Anadara trapezia obtained from Last Interglacial stranded beach ridge complex at Port Wakefield (Figure 4.4 for location map). This site was selected as Anadara are particularly abundant, well preserved, and typically buried at depths exceeding 1 metre. For experimental consistency, intrashell D/L ratio variation was avoided by analysing only the hinges. As the majority of shells were disarticulated, the possibility of analysing the same individual twice was avoided by cutting hinges from only right hand valves of Anadara. Analyses were performed for the 'total acid hydrolysate' and free amino acids, with the exception of specimens F, G and H where only the 'total acid hydrolysate' was considered (Figure 3.4 and Appendix Table 3.3). Samples were pretreated and prepared according to the methods outlined in Appendix 1. Analyses of free amino acids and the 'total acid hydrolysate' were performed for each shell. For the sake of greater statistical reliability, approximately two thirds of each dissolved shell was taken up for analysis of free amino acids. Results are depicted with the means, standard deviations and coefficients of variation indicated for each amino acid (Figure 3.4). A tabulated summary of the data is presented in Table 3.2.

In the 'total acid hydrolysate', valine and alanine accounted for the greatest variation in D/L ratios, with coefficients of variation of 18 and 15 percent respectively. The high coefficient of variation for valine in part, is attributed to the apparently high standard deviation in comparison to

Table 3.2 Within-species intershell D/L ratio variation for the estuarine bivalve Anadara trapezia from Last Interglacial marine sediments, Port Wakefield, South Australia.

amino acid	No. of shells analysed (total)	(free)	mean D/L (total)	mean D/L (free)	SD (total)	SD (free)	CV (%) (total)	CV (free)
aspartic acid	11	8	0.60	0.75	±0.06	±0.03	9.32	4.56
leucine	11	8	0.51	0.75	±0.04	±0.06	8.42	7.51
isoleucine	11	7	0.43	0.58	±0.04	±0.06	8.54	11.05
valine	11	6	0.34	0.47	±0.06	±0.04	18.06	8.57
alanine	11	6	0.73	0.92	±0.11	±0.10	14.91	10.47

average coefficients of variation for all amino acids: (total) 11.85%
(free) 8.43%

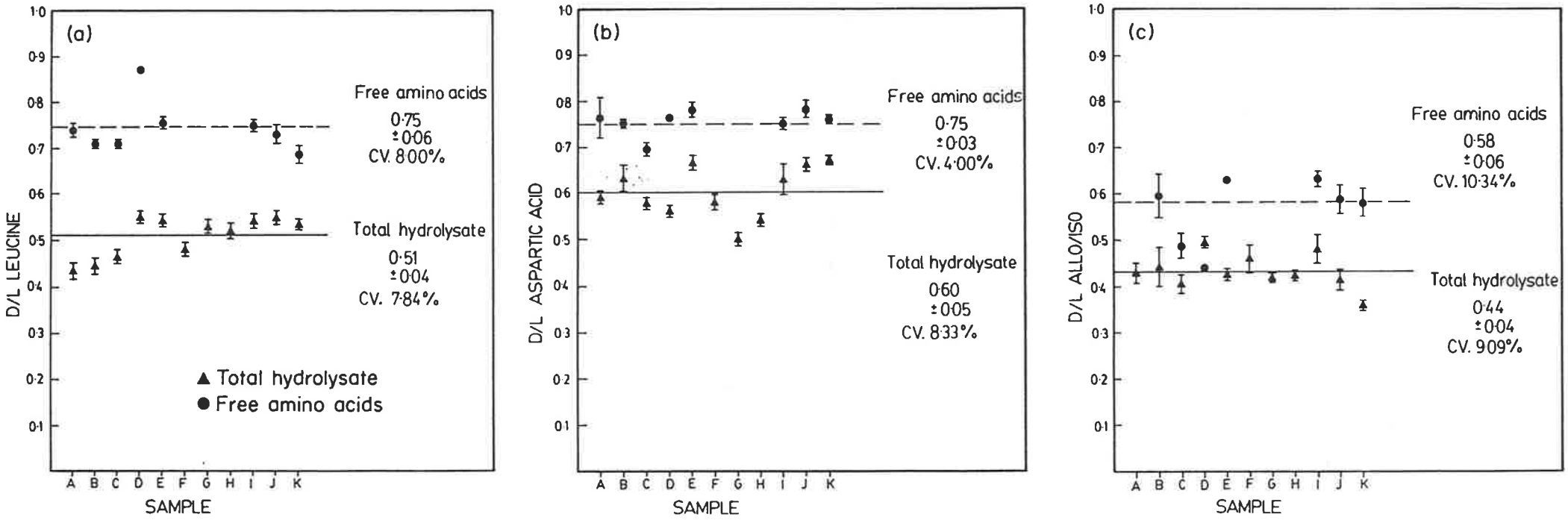


Figure 3.4 Within species Intershell D/L ratio variation in Last Interglacial specimens of Anadara trapezia, Port Wakefield, South Australia (see also Table 3.2).

the observed D/L ratio. The standard deviation for valine however, is not significantly higher than for the other amino acids. Aspartic acid, leucine and isoleucine all had coefficients of variation less than 10%. For free amino acids, isoleucine and alanine displayed the greatest variability in D/L ratios with coefficients of variation of 11 and 10 percent respectively. The coefficients of variation for valine, leucine and aspartic acid were all less than 9%.

Results were not available for proline, glutamic acid or phenylalanine. Proline does not always separate on the capillary column routinely used in the CSIRO Soils laboratory. A further complication was the coelution of D-phenylalanine with L-glutamic acid, preventing the determination of D/L ratios for these amino acids.

The results indicate an average intershell D/L ratio variation in the order of 10 percent. Wehmiller (1982,1984a) cited several criteria for the assessment of the reliability of reported D/L ratio data. The first of these concerned the acceptable precision for multiple analyses of shells of the same genus from the same outcrop. Wehmiller considered this to be between 5-10 percent depending upon the amino acid used. In many respects it is difficult to obtain precision (reproducibility of measurements) greater than 10% for D/L ratios of molluscan fossils, without adequate geological control. Geological control refers to a knowledge of site specific factors likely to introduce variable results. These are generally difficult to quantify but may include reworking, contamination and genuine and resolvable age differences within deposits. Geological control is important in assessing whether the sample is in its true stratigraphic context and whether there is a close relationship between the death of the sample material and the event whose age is sought. In addition to a geological site description of a deposit, several biochemical factors provide a basis

for a further assessment of the reliability of ages based on the extent of racemisation in fossils. Such biochemical factors considered in this study included;

- conformity of individual amino acids to predicted relative rates of racemisation for carbonate fossils.
- conformity to intrageneric and intergeneric trends of racemisation
- indicator compounds suggestive of contamination (e.g. diaminopimelic acid as well as unusually high concentrations of D-ALA, D-ASP and D-GLU derived from bacterial cell walls).
- relative concentration relationships between free amino acids and the 'total acid hydrolysate'.

The general concordance of D/L ratios reported for the Port Wakefield locality, is due in part to the nature of the deposit. The sediments are of Last Interglacial age and were deposited some 120,000 yrs BP in a discrete time interval of approximately 10,000 yrs (or less if only during part of isotope Stage 5e). As a result, resolution of natural age variation within these sediments based on the extent of amino acid racemisation is not yet possible. This phenomenon is further explored in Chapter 4 in the context of Interstadial marine strata.

3.2.4 Species (Genus) Effect

Numerous workers have noted the species specific nature of racemisation. King and Neville (1977) observed the strongly species dependent nature of isoleucine epimerisation in fossil planktonic foraminifera from an equatorial Pacific deep sea core V28-238. These authors suggested that by analysing monospecific samples of foraminifera, greater precision in quantitative age determinations may be obtained. A similar effect has also been noted for molluscan racemisation, although at

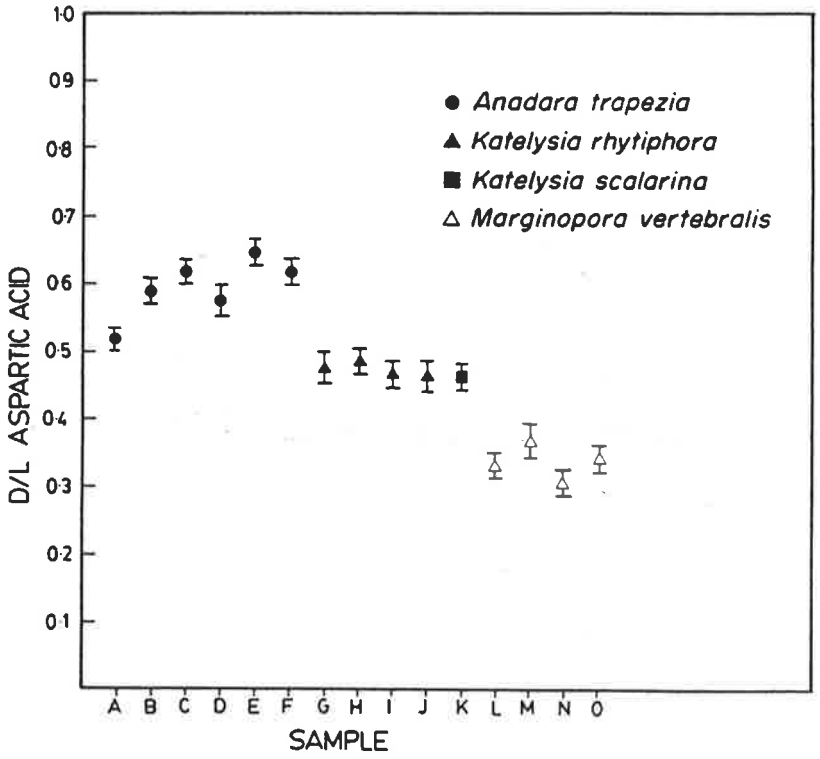


Figure 3.5 Genus-specific nature of amino acid racemisation in fauna from Last Interglacial marine sediments, South Australia.

the genus level (Lajoie et al., 1980). In marked contrast, preliminary results by Kimber and Milnes (1984) suggested that shell hash, representing a mixed-species assemblage could be used to obtain representative age assessments. However, data reported herein dictates a cautionary approach with such suggestions.

The genus specific nature of racemisation for example, is evident in fossils from Last Interglacial marine sediments in South Australia. The degree of racemisation for aspartic acid in fossils of the same age vary consistently from high to low in Anadara trapezia, Katelysia spp. and Marginopora vertebralis respectively (Figure 3.5).

Amino acid D/L ratio variation within a single species is clearly less than between species variation for fossils of equivalent age. These data highlight the importance of analysing several mollusc species from the same deposit, as interpretations based on the analyses of a single species may result in erroneous age assessments. Owing to a variety of palaeoecological factors, some species may be locally absent in geological deposits and therefore several species should be studied from a single deposit. This will increase the chances of correlating with other deposits. An advantage of the genus-specific nature of racemisation, is that any discrepancy in established relative rates of racemisation between fossil species may provide information peculiar to a geological deposit (e.g. reworking of a particular species).

3.2.5 Within-Species Intershell Amino Acid D/L Ratio Variation With Time

The possibility that intershell D/L ratio variation may systematically increase with geological age has previously not been explored in detail. If the margin of variation is higher for older deposits, this would have

significant implications regarding both the precision and accuracy of age assessments using amino acid data. A systematic increase in intershell D/L ratio variation with age for example, would dictate that larger populations be analysed for the confident age characterization of older deposits.

To assess whether a systematic increase in the degree of intershell D/L ratio variation is evident with time, coefficients of variation were calculated for Katelysia spp., obtained from several marine deposits ranging in age from Holocene to Plio/Pleistocene. With the exception of Katelysia spp., from the Roe Calcarenite, samples considered in this exercise were obtained from various localities within the Perth Basin, Western Australia. Descriptions of the stratigraphic context of these fossils are presented in Chapter 5. In this study a species effect was not evident in the genus Katelysia.

The coefficients of variation for intershell D/L ratio variation do not systematically increase with the age of geological deposits on a percentage basis (Table 3.3). This in part increases the degree of confidence that can be placed in the technique for age assessments of fossiliferous materials of great antiquity. It should be noted however, that the number of years represented by the percentage error terms do increase substantially for the older fossiliferous materials (Table 3.3).

The relatively low values for the coefficients of variation for valine, leucine, aspartic acid and isoleucine with time, also indicate that reworking has not been a significant process in these deposits.

3.2.6 Effects Or Natural Variation Within A Deposit

In addition to natural interfossil D/L ratio variation for molluscs of equivalent age, a further and larger margin of error is introduced by natural variation within a single geological deposit. Factors introducing

Table 3.3 Within species intershell amino acid D/L ratio ('total acid hydrolysate') variation with time in Katelysia spp.

Age		Amino acid VAL	ALLO/ISO	LEU	ASP	Number of samples
Herschell Limestone Middle Holocene	D/L	0.11	0.13	0.15	0.37	6
	SD	±0.06	±0.03	±0.03	±0.05	
	CV	54.5%	23.1%	20%	13.5%	
Last Interglacial 125 ka BP Minim Cove Member Tamala Limestone	D/L	0.34	0.38	0.48	0.59	12
	SD	±0.03	±0.05	±0.03	±0.05	
	CV	8.82%	13.16%	6.25%	8.47%	
		(11,000)	(16,500)	(7,800)	(10,600)	
Penultimate Interglacial 225 ka BP Peppermint Grove Member		0.55	0.57	0.61	0.66	7
		±0.05	±0.05	±0.08	±0.09	
		9.09%	8.77%	13.11%	13.64%	
		(20,500)	(20,000)	(29,500)	(30,700)	
Jandakot Beds Plio/Pleistocene		0.81	0.93	0.78	0.97	10
		±0.06	±0.07	±0.04	±0.11	
		7.40%	7.53%	5.13%	11.34%	
		(118,400)	(120,500)	(82,000)	(182,000)	
Roe Calcarenite Plio/Pleistocene		0.83	0.88	0.83	0.83	7
		±0.07	±0.07	±0.09	±0.08	
		8.43%	7.95%	10.84%	9.64%	
		(135,000)	(127,000)	(174,000)	(154,300)	
average CV for all deposits		8.44%	9.35%	8.83%	10.77%	

average CV for all amino acids 9.34%

SD Standard deviation

CV coefficient of variation

( ) Values in parentheses indicate the coefficients of variation expressed in years in relation to geological age. The Plio/Pleistocene Katelysia spp. were considered to have an age of approximately 1.6 Ma, in accordance with palaeontological assessment by Mallett (1982).

such variability include genuine and resolvable age differences within a stratum, reworking of older skeletal detritus or fossils and their incorporation into younger sediments, local or micro-scale variations in diagenetic conditions, a variable diagenetic temperature history resulting from erosion, subaerial, exposure of fossils and reburial and the possibility of contamination. Furthermore, preferential loss of free amino acids from a single fossil resulting in anomalous D/L values for the 'total acid hydrolysate', and differential rates of hydrolysis in different genera will also introduce a margin of variation. Examples of these phenomena are further explored in subsequent Chapters.

As variation in results is potentially high owing to these factors, confident age assessments of deposits based on the extent of racemisation will only be obtained if a number of shells are analysed. Where variable results arise, it is likely that the lowest D/L value will best define the age of the deposit given that leaching and contamination effects have not occurred. However, caution should be exercised when such interpretations are based solely on results of the 'total acid hydrolysate'. Loss of free amino acids from a fossil due to in situ leaching may result in erroneous age assesements based on the 'total acid hydrolysate'. That is, a false impression of age may result from artificially low D/L ratios due to loss of free amino acids so that the 'total acid hydrolysate' is dominated by the less extensively racemised high molecular weight fossil polypeptides. This will be less significant in older fossils however, as the extent of racemisation evident in the 'total acid hydrolysate' will closely approach that of free amino acids. This results from high molecular weight polypeptides breaking down to smaller molecules through natural hydrolysis, which are in turn more rapidly racemised.

Because of the possible range of amino acid D/L values within a collection of molluscs from a single deposit, Miller and Hare (1980) suggested that a minimum of three individuals be analysed for reliable age

assessments. Accordingly, if the racemisation data agree within an error range of (±10%), the mean figure may be taken as reliably characterising the deposit as a whole. The relationship between the number of valves analysed and the precision a stratigraphic unit may be characterised has been summarised mathematically by Miller and Hare (1980, p.429) as:

$$N = \left[\frac{(Z_1 - \frac{1}{2}\alpha)\ \theta}{d} \right]^2 \qquad \text{(eqn 3.1)}$$

where N - the number of individual shell analyses required

$(Z_1 - \frac{1}{2}\alpha)$ - is related to the confidence level. For a 95% confidence level, this is approximately equal to 2.

θ - the standard deviation of the population

and d - is the desired precision of the mean, taken as 0.04 in this thesis.

Clearly, the number of individuals required to characterise a stratigraphic unit based on the above equation, will depend on the amino acid used and the standard deviation associated with its D/L ratio. As a result, some amino acids are particularly useful for confident assessments of geological age. As will be amplified later, excellent concordance of results is evident for valine and leucine. Higher variation however is evident in isoleucine, aspartic acid and alanine. Despite the advantages afforded by a quantitative approach for assessing the reliability of age determinations, difficulties nevertheless arise. In particular, many Pleistocene marine deposits do not contain sufficient fossils to fulfill such quantitative requirements.

3.2.7 Between Site Variation In Amino Acid D/L Ratios

The largest margin of variation of enantiomeric ratio data potentially arises in regional aminostratigraphic investigations. Between site variation

of amino acid D/L ratios may be attributed to a range of factors within the ambit of regional variations in diagenetic conditions and weathering environments (Figure 3.2). As with effects or natural variation within a single deposit (Factor 5 of the scheme outlined in Figure 3.2), the relative contribution of many of the parameters giving rise to amino acid D/L ratio variation at a regional scale are difficult to quantify. However, the temperature dependence of amino acid racemisation should be evident spatially for isochronous deposits.

Systematic variation of amino acid D/L ratios with latitude for sediments of equivalent age has been noted by several workers and provides a basis for regional stratigraphic correlation (Wehmiller et al., 1977; Wehmiller and Belknap, 1978; Wehmiller and Emerson, 1980; and Wehmiller, 1982,1984b). In this approach, amino acid D/L ratios are compared with material independently dated (e.g., radiocarbon or uranium-series disequilibrium dating) from latitudinally widely separated localities. From these data, isochrons are constructed and long distance correlations are facilitated. Previous investigations have centered on regions where mean annual temperature variation conforms to an essentially linear function of latitude (Wehmiller et al., 1977; Wehmiller and Belknap, 1978; Wehmiller, 1982,1984b). A central tenet in this approach is that during the diagenetic history of the fossils, former latitudinal temperature gradients were similar in magnitude to contemporary temperature gradients. A cautious approach should be taken with this inference however as diagenetic temperature histories for some localities may be difficult to establish.

When attempting stratigraphic correlation over widely separated localities, latitudinal as well as the possibility of longitudinal D/L ratio variation for isochronous deposits should be considered. Clearly then, D/L ratios from widely disjunct localities should not be taken at face value. Examples of these sources of variation are discussed in Chapter 4.

3.3 AGE RESOLUTION OF AMINO ACID RACEMISATION DATING

The question of the age resolving ability of amino acid racemisation is complicated when dealing with complex punctuated stratigraphies. The problem of age resolution based on subtle differences in amino acid D/L ratios is highlighted in a study of two, geologically distinct Pleistocene marine terraces at Turtle Bay, northwestern Baja California Sur, in Mexico (Emerson et al., 1981). Based on faunal evidence and the extent of racemisation of several amino acids in the molluscs Saxidomus nutalli, Chione undatella and Chione californiensis, Emerson et al., (1981) assigned ages of 120,000 and 95,000 yrs BP to two marine terraces (Table 3.4).

A critical appraisal of their data however, indicates no significant difference in amino acid D/L ratios for the 120,000 and 95,000 yrs mollusc populations. This is supported by a t-test which indicated no significant difference in these populations at the 95% confidence level. In view of the errors implicit in the data reported by Emerson et al., (1981), including analytical error, different derivatisation procedures, intrashell and intershell D/L ratio variation, the concordance of results is remarkably good.

Average D/L ratios and standard deviations for the mollusc species studied by Emerson et al., (1981) have been calculated and are presented in Table 3.4. Although three species were analysed (including two genera), based on the data reported, the species specific nature of molluscan racemisation is not evident.

A conclusion more consistent with the geomorphological and faunal evidence would therefore be that the terraces are of different ages, however amino acid techniques alone, cannot resolve these age differences. The extent of racemisation in the 'total acid hydrolysate' does not present sufficient resolution to distinguish such subtle age differences. This is

Table 3.4 Amino acid D/L ratios for molluscs obtained from two Pleistocene marine terraces, Turtle Bay, northwestern Baja California Sur, Mexico. Average D/L ratios and standard deviations calculated from data provided in Emerson et al., (1981).

Species	Amino acid							suggested age ka BP
	LEU	GLU	VAL	ALA	PRO	PHE	ASP	
Chione undatella	0.55±0.02	0.54±0.02	0.51±0.03	0.88±0.03	——	0.59±0.08	0.75±0.01	
Saxidomus nuttalli	0.63±0.01	0.59±0.05	0.50±0.03	0.94±0.03	——	0.63±0.03	0.63±0.05	95
Chione californiensis	0.63±0.05	0.59±0.03	0.56±0.04	0.92±0.04	0.71±0.001	0.64±0.06	0.68±0.04	
Saxidomus nuttalli	0.68±0.04	0.59±0.02	0.49±0.03	0.93±0.04	0.81±0.04	0.67±0.06	0.65±0.05	120

Use of an unrelated t-test indicated no significant difference in the age of Saxidomus nuttalli. Using standard statistical tables, a 1-tail test at the 5 per cent level with 10 degrees of freedom indicated a significant difference in age, should $t \geq 1.81$. However the value of 0.18 which fell well below the required value indicated no significant age difference between the two Saxidomus populations.

because the 'total acid hydrolysate' is a complex mixture of high molecular weight polypeptides, smaller polypeptides, peptides and free amino acids. As a result, a greater likelihood for variability of amino acid D/L ratios arises through the loss from the shell of some of these fractions, or diagenetic breakdown reactions which may have an effect on the apparent extent of racemisation.

Age resolution problems of this nature highlight the requirements for extensive data bases that provide a means of critically assessing amino acid enantiomeric ratio data. It was in the light of this that an extensive data base was deemed necessary in the present study. Furthermore, the data reported by Emerson et al., (1981) also demonstrates the necessity for studies involving extensive calibration of amino acid data with a variety of independent dating techniques (e.g., radiocarbon, uranium-series, disequilibrium dating).

3.4 INTERLABORATORY COMPARISON STUDY

Kvenvolden (1980) carried out the first systematic interlaboratory comparison of amino acid D/L ratios in the fossil mollusc, Saxidomus giganteus. The results of this study however, were highly variable because of the different methods and analytical procedures undertaken. In a more extensive study, Wehmiller (1984a) conducted an interlaboratory comparison of amino acid D/L ratios obtained in Pleistocene molluscs. Three homogeneous powdered samples of contrasting ages were sent to the participating laboratories. The samples included the genus Saxidomus with an approximate age of 50,000 yrs (sample ILC-A), and two samples of the genus Mercenaria, with approximate ages of 100,000-250,000 yrs and 1 million years respectively (ILC-B, ILC-C).

These homogeneous powdered fossil samples were used in the present study. Details of sample preparation are provided in Wehmiller (1984a).

Wehmiller concluded from the interlaboratory comparison that the coefficients of variation (C.V.) were lowest for alanine, glutamic acid and aspartic acid D/L ratios (3-8%). Leucine and phenylalanine had C.V.'s falling within the range of 5-10%. The C.V.'s ranged from 10-18% for isoleucine, proline and valine. Wehmiller (1984a) also noted that individual laboratories generally reported analytical precision between 2-5%. In contrast, significant differences were recorded between laboratories, and would introduce a large margin of error in quantitative age assessments. The powder samples were proposed as reference standards and Wehmiller suggested that the results for these samples as well as a description of the derivatisation procedures used, be reported in all future publications reporting amino acid enantiomeric results.

3.4.1 Interlaboratory Comparison: CSIRO Soils Results

To assess the reliability of D/L ratios reported in this investigation in relation to other laboratories, samples previously analysed in an interlaboratory comparison (Wehmiller, 1984a) were analysed in this study. In this investigation a Packard-Becker model 419 gas chromatograph with a Chrompack 50 m length column coated with the liquid stationary phase XE-60-s-Val-s-x-pea was used for analyses. Detection of the amino acid derivatives was achieved using a flame ionization detector (F.I.D.), which ionizes and detects all eluted carbon containing molecules. Individual amino acid peak heights or areas were recorded using an SP4100 Spectra Physics Computing Integrator. Derivatisation procedures used at the CSIRO Soils laboratory are summarised in Appendix 1. Results obtained for the interlaboratory comparison samples in this study are summarised in Table 3.5 with the more complete data presented in Appendix Table 3.4. Four replicate injections were made for each specimen. A comparison of the CSIRO results with the grand mean of the interlaboratory comparison for all laboratories, and results from the University of Delaware are depicted in Figure 3.6. Results are for the 'total acid hydrolysate'. Tables 3.6 and 3.7 compare the CSIRO Soils results with those of the published interlaboratory comparison. The range of the published interlaboratory comparison results are presented in Tables 3.8 and 3.9, and the relationship of the CSIRO data to the published interlaboratory comparison results are presented in Tables 3.10 and 3.11.

In this thesis results are reported for alanine, valine, isoleucine, leucine and aspartic acid. A significant limitation of the study involved the use of different analytical procedures and equipment by different laboratories that participated in the interlaboratory comparison. In particular, the use of different derivatisation techniques and gas

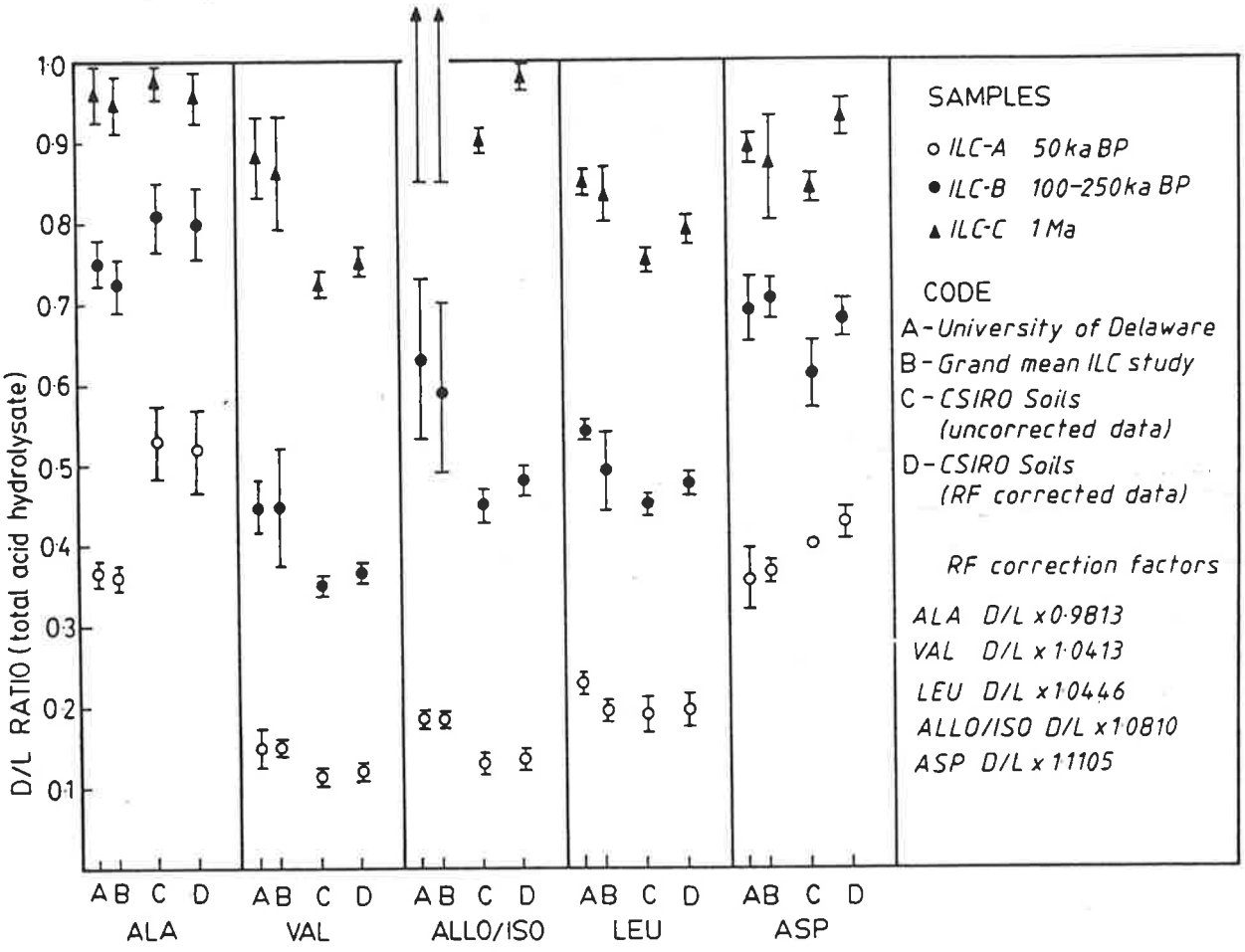


Figure 3.6 Interlaboratory comparison of amino acid D/L ratios in fossil Pleistocene molluscs.

Table 3.5 Summary of results (uncorrected data) of interlaboratory comparison samples analysed in the CSIRO Soils laboratory. D/L ratios are for the 'total acid hydrolysate'.

Sample	Age		Amino acid				
			ALA	VAL	ALLO/ISO	LEU	ASP
ILC-A *Saxidomus*	~50 ka BP	D/L	0.5342 (0.364)	0.1133 (0.159)	0.1274 (0.212)	0.1897 (0.196)	0.4036 (0.378)
		S.D.	0.0636 (0.017)	0.0020 (0.030)	0.0017 (0.036)	0.0142 (0.021)	— (0.028)
		C.V.	11.91 (4.7)	1.77 (18.9)	1.33 (16.8)	7.49 (10.7)	— (7.4)
ILC-B *Mercenaria*	100-250 ka BP	D/L	0.8162 (0.725)	0.3507 (0.449)	0.4457 (0.54)	0.4548 (0.497)	0.6112 (0.705)
		S.D.	0.0479 (0.034)	0.0046 (0.068)	0.0156 (0.081)	0.0115 (0.049)	0.0379 (0.028)
		C.V.	5.87 (4.7)	1.31 (15.2)	3.50 (15.0)	2.53 (9.8)	6.20 (4.0)
ILC-C *Mercenaria*	1 Ma	D/L	0.9754 (0.946)	0.7241 (0.868)	0.9029 (1.215)	0.7628 (0.833)	0.8368 (0.894)
		S.D.	0.0238 (0.029)	0.0063 (0.084)	0.0167 (0.015)	0.0048 (0.043)	0.0124 (0.079)
		C.V.	2.44 (3.1)	0.87 (9.7)	1.85 (1.2)	0.63 (5.2)	1.48 (8.8)

S.D. - Standard deviation (1 σ)

C.V. - Coefficient of variation ($CV = \frac{\theta}{\bar{x}} \times 100$)

Data based on four replicate injections.

Grand means, standard deviations (1θ) and coefficients of variation from the published results of the Interlaboratory Comparison Study (Wehmiller, 1984a) are depicted in parentheses.

Table 3.6 Difference between the grand mean of D/L ratios from the Interlaboratory Comparison Study (ILC) (Wehmiller, 1984a) and CSIRO Soils results (uncorrected data). The prefix signs indicate whether the CSIRO Soils data fall above or below the grand mean of the ILC study.

Sample	Amino acid				
	ALA	VAL	ALLO/ISO	LEU	ASP
ILC-A	+0.1702	-0.0457	-0.0846	-0.0063	+0.0256
ILC-B	+0.0912	-0.0983	-0.0943	-0.0422	-0.0938
ILC-C	+0.0294	-0.1439	-0.3121	-0.0702	-0.0572

Table 3.7 Difference between the grand mean of D/L ratios from the ILC study and the CSIRO Soils data, corrected for variable Gas Chromatography Detector Response Factors (RF) introduced by Flame Ionization Detection.

Sample	Amino acid				
	ALA	VAL	ALLO/ISO	LEU	ASP
ILC-A	+0.1602	-0.0410	-0.0743	+0.0022	+0.0702
ILC-B	+0.0759	-0.0838	-0.0582	-0.0219	-0.0263
ILC-C	+0.0112	-0.1140	-0.2390	-0.0362	+0.0925

Response Factor correction values

ALA	D/L	×	0.9813
VAL	D/L	×	1.0413
LEU	D/L	×	1.0446
ALLO/ISO	D/L	×	1.0810
ASP	D/L	×	1.1105

Table 3.8 Lowest D/L ratios obtained in the published interlaboratory comparison study of Wehmiller (1984a)

	Amino acid				
	ALA	VAL	ALLO/ISO	LEU	ASP
ILC-A	0.339 ±0.007	0.12	0.14	0.141 ±0.014	0.33 ±0.023
ILC-B	0.668 ±0.086	0.38 ±0.021	0.45 ±0.02	0.423 ±0.006	0.689 ±0.006
ILC-C	0.878 ±0.129	0.80	0.87	0.749 ±0.001	0.808 ±0.039

Table 3.9 Highest D/L ratios obtained in the published interlaboratory comparison study of Wehmiller (1984a)

	Amino acid				
	ALA	VAL	ALLO/ISO	LEU	ASP
ILC-A	0.395 ±0.035	0.208 ±0.009	0.254 ±0.021	0.218 ±0.008	0.43
ILC-B	0.770 ±0.023	0.597 ±0.022	0.630 ±0.031	0.582 ±0.028	0.747 ±0.009
ILC-C	0.981 ±0.017	1.01 ±0.12	1.27 ±0.02	0.89 ±0.011	1.033 ±0.021

Table 3.10 Relationship of CSIRO Soils interlaboratory comparison data (uncorrected data), to the range of the published results of Wehmiller (1984a), where (√) indicates that the result falls between the highest and lowest D/L ratio, (-) CSIRO result is below the lowest value and (+) CSIRO result is above the highest score.

	Amino acid				
Sample	ALA	VAL	ALLO/ISO	LEU	ASP
ILC-A	+	-	-	√	√
ILC-B	+	-	-	√	-
ILC-C	√	-	√	√	√

Table 3.11 Relationship of CSIRO Soils interlaboratory comparison data (corrected for variable Response Factors), to the range of the published results of Wehmiller (1984a).

	Amino acid				
Sample	ALA	VAL	ALLO/ISO	LEU	ASP
ILC-A	+	√	√	√	+
ILC-B	+	√	√	√	-
ILC-C	√	-	√	√	√

chromatograph capillary columns introduced an additional margin of error in the interlaboratory comparison study of Wehmiller (1984a). Results reported as preliminary by Wehmiller (1984a) were not included in the statistical comparisons made in this investigation. Based on the analysis of racemic external standards it was noted that using the Flame Ionization Detector, the Response Factors for the D-isomers were systematically slightly lower than for the L-isomer in the CSIRO laboratory. In view of this, correction factors were calculated to compensate for this in sample unknowns (Footnote, Table 3.7). For brevity, the results presented below are summarised separately for each amino acid.

3.4.1.1 Alanine

Alanine D/L ratios for ILC-A were significantly higher than those obtained at the University of Delaware as well as the grand mean of the interlaboratory comparison (Figure 3.6). In addition the value for alanine exceeded the highest value in the published results of Wehmiller (1984a). In contrast, closer agreement in alanine D/L ratios were obtained with samples ILC-B and ILC-C, although the CSIRO values were still higher than the grand mean of the interlaboratory comparison.

The CSIRO corrected values for ILC-A and ILC-B were higher than the range of values obtained in the interlaboratory comparison study, although ILC-C was within the range of values (Tables 3.5-3.11). The artificially high alanine D/L ratios reported in this study resulted from the coelution of an unknown substance with D-alanine. The unknown was observed as a rider peak on D-alanine.

3.4.1.2 Valine

Although valine D/L ratios obtained at CSIRO Soils for ILC-A fall slightly below those obtained at Delaware and the grand mean of the interlaboratory comparison, close agreement is nevertheless observed (Figure 3.6). Both the corrected values for ILC-A and ILC-B fall within the range of values of the published interlaboratory comparison. In contrast ILC-C falls significantly below the range of published results of Wehmiller (1984a).

3.4.1.3 Isoleucine

Uncorrected data for isoleucine indicated that ILC-A and ILC-B plotted below the lowest values recorded in the interlaboratory comparison, whilst the uncorrected values for ILC-C fell within the range of values of the interlaboratory comparison (Figure 3.6). In contrast, the corrected values for all specimens fall within the range of published interlaboratory comparison results (Tables 3.5-3.11).

3.4.1.4 Leucine

The best concordance of results between the CSIRO laboratory and the grand mean of the interlaboratory comparison and Delaware values were obtained for leucine (Figure 3.6). This applied for all three specimens. Although the CSIRO leucine values fell slightly below the grand mean of the published interlaboratory comparison, both the uncorrected and corrected values fell within the range of values reported by Wehmiller (1984a) (Tables 3.5-3.11). The lower leucine D/L ratio observed in ILC-C in this study was subsequently demonstrated to have resulted from the coelution of β-alanine with L-leucine. This appears to be a problem characterisitic of the capillary column used at the time of this study,

due to reduced resolving power. At the time this problem was experienced in this study it was noted that β-alanine was only observed in old specimens. The origin of this non-protein amino acid was briefly outlined in Chapter 2. As this amino acid was found to coelute with L-leucine, external standards of a range of amino acids were routinely analysed to check retention times, and additional checks were made using a different gas chromatograph fitted with a Chirasil-Val capillary column. A significant advantage with gas chromatography is the potential of analysing a range of amino acids. As different amino acids have characteristic racemisation rates, anomalously low leucine D/L values were confidently recognised.

3.4.1.5 Aspartic Acid

In ILC-A, the aspartic acid D/L value obtained at CSIRO was slightly higher than that of the interlaboratory comparison or the Delaware value, although within the range of values, of the interlaboratory comparison (Figure 3.6). The uncorrected aspartic acid D/L ratio for ILC-B fell significantly below the grand mean as well as below the range of the interlaboratory comparison. Although ILC-C fell below the grand mean of the interlaboratory comparison, the uncorrected values plotted within the range of the published interlaboratory comparison results (Tables 3.5-3.11).

3.4.1.6 Glutamic Acid And Phenylalanine

When the interlaboratory comparison samples were analysed at the CSIRO Soils laboratory, L-glutamic acid coeluted with D-phenylalanine. In consequence, results are not available for these amino acids.

The significant question arising from this study concerns what the D/L ratio variation between laboratories represents in the context of quantitative age uncertainties. Although dependent on the absolute value of the D/L ratio and its relation to kinetic models, Wehmiller (1984a) suggested that for linear kinetics a 10% uncertainty of enantiomeric ratios would represent an age uncertainty of approximately 13.5% for aspartic acid. A similar margin of variation would be expected for other amino acids. However for non-linear racemisation kinetics, a larger margin of uncertainty may be expected. According to Wehmiller (1984a) in the early portion of the non-linear model (D/L <0.25) the relationship between analytical and age uncertainties is the same as cited above. However in the latter portion of the racemisation pathway (D/L >0.45) a 10% analytical uncertainty will represent an age uncertainty of approximately 25% (Wehmiller, 1984a). In view of the difficulties of accurately defining the nature of the transition zone, Wehmiller (1984a) did not provide details of the relationship of analytical uncertainty to age uncertainty for this portion of the non-linear kinetic model.

From the analysis of the interlaboratory comparison specimens, the following conclusions were made.

(1) The response factor (RF) corrected CSIRO data generally fell within the range of the published interlaboratory comparison results.

(2) Both the corrected and uncorrected CSIRO data consistently fell below the grand mean of the interlaboratory comparison, although these differences were generally not statistically significant.

(3) For the uncorrected data alanine tended to fall above the range of the interlaboratory comparison. In contrast, uncorrected valine D/L ratios consistently fell marginally below the range of the interlaboratory comparison. A similar trend was evident for isoleucine. The uncorrected D/L ratios for both leucine and aspartic acid fell within the range of values reported by Wehmiller (1984a).

(4) Wehmiller (1984a) noted that the closest agreement between laboratories were for aspartic acid, alanine and glutamic acid. Data from the present study for isoleucine, leucine and aspartic acid most closely agreed with the published interlaboratory comparison results.

3.4.2 Interlaboratory Comparison Of Leucine D/L Ratios In The Bivalve Anadara trapezia

To supplement the interlaboratory comparison study, specimens of Anadara trapezia previously analysed by E. Keenan at the University of Delaware (U.S.A.) and reported in Belperio et al., (1984), were analysed in the CSIRO Soils laboratory. As Anadara trapezia commonly occurs in Pleistocene marine sediments in Australia, and were extensively analysed in the present study, an additional qualitative assessment of the CSIRO Soils laboratory results was considered a useful adjunct to the Interlaboratory comparison of Wehmiller (1984a). It should be emphasised however, that this does not represent an interlaboratory comparison sensu stricto, as different parts of the same shells were analysed. As a result, intrashell D/L ratio variation, a feature noted by Brigham (1983) was introduced in this exercise. Sample preparation and derivatisation procedures used at the CSIRO Soils laboratory are reported in Appendix 1. Laboratory procedures used at Delaware followed those outlined in Wehmiller and Emerson (1980) and Atwater et al., (1981). Results of this study are summarised in Tables 3.12 and 3.13. More extensive data including results for free amino acids are documented in Appendix 3.5.

Clearly, the results from the CSIRO laboratory compares favourably with those obtained in the Delaware laboratory. The variation in leucine D/L ratios can be attributed to intrashell D/L ratio variation. In this context, the differences in leucine D/L ratios obtained between the two laboratories are not large enough to be otherwise interpreted as genuine and resolvable age differences.

Table 3.12 Comparison of leucine D/L ratios for Anadara trapezia analysed at the University of Delaware and CSIRO Soils. Values reported are for the 'total acid hydrolysate'.

Sample CSIRO lab code	Location	Univ. Delaware Leu D/L	CSIRO Soils Leu D/L	C.V.*
(1) ATRAP73ATI	SG#182-220 cm	0.48	0.52±0.020	3.85
(2) ATRAP73ATI	SG#171-100 cm	0.54	0.48±0.001	0.21
(3) ATRAP74ATI	Cultana Beach ridge	0.63	0.58±0.008	1.34
(4) ATRAP71ATI	Glanville Formation	0.42	0.46±0.003	0.65
(5) ATRAP70ATI	Queensland (Modern)	0.05	0.04±0.006	15.00
Average of 1,2 and 4**		0.48	0.49	

* Coefficient of variation for CSIRO data.
** Average of three specimens of Last Interglacial age.

TABLE 3.13 Difference between University of Delaware and CSIRO Soils, leucine D/L values for Anadara trapezia, and the difference expressed as coefficients of variation for the CSIRO data.

Sample (CSIRO lab code)	ΔD/L* (D/L ratio difference)	ΔD/L** C.V.
(1) ATRAP72ATI	(+) 0.04	7.69
(2) ATRAP73ATI	(-) 0.06	12.50
(3) ATRAP74ATI	(-) 0.05	8.62
(4) ATRAP71ATI	(+) 0.04	8.69
(5) ATRAP70ATI	(-) 0.01	25.00
	$\bar{x}$ΔD/L (-) 0.008	

* Indicates whether CSIRO leucine D/L value was above (+) or below(-) University of Delaware values.

** Difference in leucine D/L values (ΔD/L) expressed as coefficient of variation of the CSIRO values.

Analytical error appears significantly higher for modern specimens as reflected in the high coefficient of variation in the modern Anadara trapezia (Table 3.12). However, this is illusory because error terms in modern shells are not as 'diluted' by the observed D/L ratios, as in older shells, where amino acids are more extensively racemised. Coefficients of variation compare favourably with those reported for leucine by Wehmiller (1984a).

The differences in D/L leucine values between the Delaware and CSIRO laboratories exceed one standard deviation (66% confidence level). However, as different sections of the same shell were analysed the percentage difference can be explained in the context of natural intrashell variation.

3.5 SAMPLE COLLECTION

Knowledge of the degree of D/L ratio variation within fossiliferous geological deposits has important implications regarding the ultimate reliability and resolution of the method for quantitative and relative age determinations. Without a knowledge of natural D/L ratio variation within and between deposits, erroneous age assessments could be made.

As with any dating technique, a detailed site description was considered to be of pre-eminent importance, for the evaluation of D/L ratios and for age assessments. The following factors were considered:

(1) the stratigraphic context of the fossiliferous material and the relationship between the death of the sample material and the geological event whose age was sought (time-event relationships),

(2) sample contamination, particularly the likelihood of recrystallization or diagenetic introduction of organic compounds including amino acids in either the L- or D- configuration or bacterial contamination,

(3) loss of indigenous amino acids, especially free amino acids resulting from in situ leaching,

(4) knowledge of the temperature history experienced by the fossil since death.

Specimens studied were from the subsurface and were collected from cores or recent quarry exposures at depths generally in excess of 1 metre. Because of the reported temperature effect on racemisation rates, selection of samples in this manner reduces the degree of uncertainty in ages by lowering the chances of variable Effective Quaternary Temperature histories since burial, a feature reported to characterise surface samples. This is particularly important if the duration of subaerial exposure is long in proportion to the 'absolute' age of the fossil. This is highlighted with Holocene samples, archaeological samples and all samples subaerially exposed in arid climates for protracted periods (Wehmiller, 1984b).

Where possible articulated bivalves wer collected for amino acid analyses. Articulated specimens are more likely to provide a closer approximation of the time of sedimentation than single mollusc valves or fragments, which may display a history of reworking. In addition, as articulated shells are likely to have experienced minimal post-mortem transport, their valve surfaces are less likely to be abraded. As a result near surface contamination by exogenous amino acids along abrasion micro-fractures, a contamination mechanism suggested by Williams and Smith (1977) may be excluded.

3.6 MODERN SAMPLES

Because of the slight amount of racemisation that results from laboratory sample preparation (acid hydrolysis), as well as any amino acids in the D-configuration present at the time of death, analyses of modern samples are required. Amino acid D/L ratios obtained from modern specimens are then subtracted from the D/L ratio obtained for the fossil mollusc as indicated by the rate expression for molluscan racemisation (eqn 2.2). This procedure ensures greater reliability with quantitative age assessments (Schroeder and Bada, 1976; Williams and Smith, 1977).

Representative D/L ratio values for modern mollusc specimens are presented in Table 3.14, with the raw data presented in Appendix Table 3.6. All the bivalves, with the exception of Anadara trapezia were collected from Semaphore Beach, Adelaide. As Anadara trapezia is now no longer living in South Australian coastal waters (Belperio and Murray-Wallace, 1984) a modern specimen was obtained from Quarantine Bay, southern New South Wales. All individuals analysed were articulated and extremely well preserved. Only the hinges of these molluscs were analysed, to avoid variation due to intrashell D/L ratio variation.

Table 3.14 Amino acid D/L ratios ('total acid hydrolysate') for modern molluscs

Species	Amino acid				
	VAL	ALLO/ISO	LEU	ASP	GLU
Fulvia tenuicostata	0.02	0.03	0.05	0.05	0.03
Glycymeris (Tucetilla) striatularis	0.03	0.02	0.07	-	-
Katelysia scalarina	0.03	0.04	0.04	0.05	0.06
Katelysia rhytiphora	0.02	0.02	0.03	0.07	0.02
Mactra australis	0.02	0.03	0.05	0.06	0.03
Anadara trapezia	0.02	0.02	0.03	0.11	0.08

3.7 DISCUSSION

Clearly, numerous factors should be considered when establishing relative or quantitative ages of geological deposits based on the extent of amino acid racemisation. Errors may arise due to the mis-association of true sample age with the geological event being dated, diagenetic contamination and species (genus) misidentification. Moreover, errors resulting from analytical variation should not be excluded. When correlating stratigraphic units and establishing relative chronostratigraphies, effects within and between deposits should also be addressed. These may result from reworking, local or micro-scale variations in diagenetic conditions, differential weathering, erosion, and subaerial exposure of fossils and reburial, contamination and regional variations in diagenetic and weathering conditions, both spatially and temporally. Many of these factors, the earth scientist has little or no control over, and their relative contribution to the overall extent of racemisation observed in fossils may be difficult to quantify.

The scheme presented summarises these variables (Figure 3.2). The ultimate precision (reproducibility of measurements) and accuracy (deviation of determined age from "real" age) of the technique, will in part be determined by the degree of control that can be placed on these factors. Variation due to analytical error, intra-fossil variation, within species inter-fossil variation and a genus effect can all be quantified with confidence. In contrast, variation within sediments due to contamination or reworking, and between site variation of factors that influence racemisation are more difficult to assess. For example, the effect of a varying degree of contamination on ages determined by amino acid racemisation methods is a factor still not entirely clear, and awaits quantification in a manner similar to radiocarbon methods (Gupta and Polach, 1985) whereby a knowledge of the relative contribution of a contaminant to the outcome of the reported age is understood.

3.8 CONCLUSIONS

(1) A scheme has been presented that summarises a range of factors that influence amino acid D/L ratio variation in fossiliferous geological deposits. In increasing order of significance these include analytical error; within species intra-fossil variation; within species inter-fossil variation, a genus effect; effects or natural variation within a deposit and between site variation.

(2) Based on coefficients of variation the following margins of variation were recognised:

- analytical error ~3%
- within species intra-fossil variation ~8%
- within species inter-fossil variation ~12%

(3) At a higher level, a genus effect accounted for a maximum observed variation of approximately 30%. Effects or natural variation within a deposit and between site variation could not be quantified, because of their environmentally specific nature.

CHAPTER 4 SOUTH AUSTRALIAN QUATERNARY COASTAL AND MARINE AMINOSTRATIGRAPHY

4.1 INTRODUCTION

In this chapter the application of the amino acid racemisation reaction is explored in terms of providing time frameworks for Quaternary coastal processes. Data obtained from this study will also provide a valuable adjunct in understanding process rates of calcretisation, Quaternary neotectonics and in the relative dating of paralic and terrestrial sediments. The latter generally cannot be directly dated because of the absence of fossiliferous materials suitable for dating. In addition, the South Australian amino acid data will provide an important data base from which other Australian marine settings may be compared, and as a step towards correlating Australian Quaternary oceanic and terrestrial stratal sequences.

Molluscs were obtained from several marine units of differing ages. As the lithostratigraphic relationships of these stratal sequences are relatively well understood in small geographic settings near their holostratotypes, they provided a basis for calibrating amino acid racemisation data for Australian conditions. In addition, independent dating techniques also provided calibration. At large distances from the holostratotypes however, problems of correlation arise and amino acid data are instrumental in this regard for establishing age equivalence.

4.2 ESTABLISHED QUATERNARY LITHOSTRATIGRAPHIC NOMENCLATURE

The South Australian Quaternary lithostratigraphy relevant to this thesis is summarised in Figure 4.1. The stratigraphic nomenclature is after Firman (1969), and Hails et al., (1984a). Samples for amino acid racemisation analyses were collected only from marine units. The following discussion summarises the original stratigraphic definitions of these units, but more critical appraisals of aspects of the established stratigraphic nomenclature are presented later in this chapter in the relevant sections.

It is difficult to summarise the lithostratigraphy as many of the stratigraphic units were originally poorly defined and their current informal usage may differ from original definitions. Several facies (Firman, 1969) were assigned formation status and are not mappable lithostratigraphic units in the sense of Staines (1985). This resulted largely from the failure to recognise the discontinuous nature of deposition and Walther's Law of Facies (1894). In addition, some of the lithostratigraphic nomenclature (Hails et al., 1984a) has not been formally recorded and holostratotypes have not been proposed. Furthermore some redefined stratigraphic units have been ignored.

4.2.1 Gulf St Vincent.

4.2.1.1 Hindmarsh Clay

The Hindmarsh Clay was described by Firman (1969) in reference to a thick sequence of terrestrial clays and sands with channel lag gravel lenses. Firman (1969) suggested an Early Pleistocene age for these sediments but provided no quantitative evidence to support this contention.

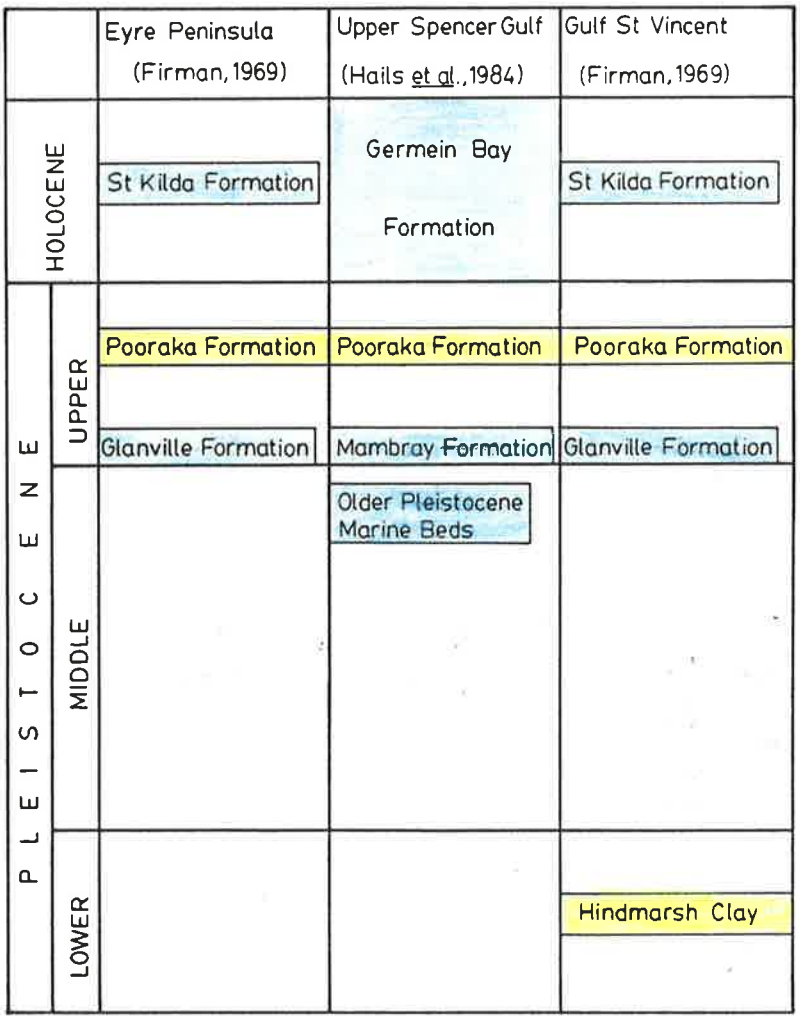


Figure 4.1 Summary of established lithostratigraphic nomenclature discussed in this study. After (Firman, 1969; Hails et al., 1984a). Marine and terrestrial sediments are represented by blue and yellow shading respectively. Gaps do not necessarily indicate lacunae.

4.2.1.2 Glanville Formation

Marine carbonate rich sediments containing abundant molluscan fossils and generally capped by an indurated carbonate crust were referred to by Firman (1966,1967,1969) as the Glanville Formation. Although a variety of ages have been assigned to these sediments a Late Pleistocene age is favoured. These sediments have a complex interfingering relationship with Pleistocene terrestrial sediments. However, they generally unconformably overlie terrestrial sediments referred as the Hindmarsh Clay, and are overlain either by the Late Pleistocene Pooraka Formation or the Holocene St Kilda Formation. Equivalents of the Glanville Formation occur in marine embayments on Eyre Peninsula (Firman, 1969). These sediments contain the Pleistocene indicator fossils for southern Australia Anadara trapezia, Marginopora vertebralis, and Pinctada carchariarum (Cann, 1978; Ludbrook, 1984).

4.2.1.3 Pooraka Formation

Sediments described by Firman (1967) in reference to a widespread sheet drape of fluviatile sands and clays of Late Pleistocene age were termed the Pooraka Formation. The age of these sediments is difficult to establish in the absence of materials suitable for dating. However, on the basis of radiocarbon dating of wood fragments from the holostratotype, Williams (1969) suggested a last glacial age for these sediments. Sediments displaying similar lithological characteristics have been recognised in northern Spencer Gulf (Firman, 1967,1969; Hails et al., 1984a,b) and on Eyre Peninsula (Firman, 1967,1969).

4.2.1.4 St Kilda Formation

Shallow marine and paralic sediments of Middle Holocene age were referred to by Firman (1966,1967) as the St Kilda Formation. According to Firman (1969) shells from the top of this unit were dated at about 1,100 yrs and shells from the base were dated at approximately 4,000 yrs. However, no discussion was made of whether these were marine environmentally corrected ages in radiocarbon years or sidereal ages. These sediments are overlain by aeolian sands. Time equivalents of the St Kilda Formation were recognised along the coastline of Eyre Peninsula and in northern Spencer Gulf (Firman, 1969).

4.2.2 Upper Spencer Gulf

In a study of the Quaternary submarine lithostratigraphy of upper Spencer Gulf, Hails et al., (1984a,b) invoked several new stratigraphic names to avoid homotaxial correlations with sediments displaying similar lithological and palaeontological aspects in the Adelaide region. The sediments specifically referred to in this thesis are indicated in Figure 4.1. Given that chronostratigraphic correlation of these units is possible, then the original stratigraphic names from the Adelaide region take precedence.

4.2.2.1 "Older Pleistocene marine beds"

The oldest sediments studied by Hails et al., (1984a,b) were the "Older Pleistocene marine beds". These are tenacious sandy-clay rich sediments with low calcium carbonate contents. Hails et al., (1984a,b)

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suggested a Penultimate Interglacial age for these sediments (Marine Oxygen Isotope Stage 7). These sediments were suggested by Hails et al., (1984a) to interfinger with the Hindmarsh Clay. If this interpretation is correct then the Hindmarsh Clay represents a longer time interval than suggested by Firman (1969).

4.2.2.2 Mambray Formation

Richly fossiliferous marine sediments with high calcium carbonate contents that have a complex interfingering relationship with terrestrial sediments were referred to as the Mambray Formation by Hails et al., (1984a). These sediments have similar lithological and palaeontological characteristics to the Late Pleistocene Glanville Formation of the Adelaide region, and a preliminary chronostratigraphic correlation was made by Belperio et al., (1984). These sediments contain the Pleistocene indicator fossils for southern Australia Anadara trapezia, Marginopora vertebralis and Pinctada carchariarum (Cann, 1978; Ludbrook, 1984; Belperio and Murray-Wallace, 1984).

4.2.2.3 Germein Bay Formation

The Germein Bay Formation refers to all subtidal, intertidal and supratidal sediments in upper Spencer Gulf of Holocene age (Hails et al., 1984a). These sediments in part, correlate with the Middle Holocene St Kilda Formation of the Adelaide region (Firman, 1969).

4.3 AMINOSTRATIGRAPHY

4.3.1 Glanville Formation

In view of the importance of the Glanville Formation for the calibration of Last Interglacial amino acid data, a lengthy discussion of the sedimentary characteristics and geological setting of this formation are presented. Although sediments now ascribed to the Glanville Formation have been extensively documented from numerous coastal sections in South Australia (Tate, 1879a,1882,1890,1898; Howchin, 1888,1909,1912,1924,1935; Greenway and Phillips, 1902; Verco, 1910; Tindale, 1933; Crocker, 1946a,b; Sprigg, 1952; Miles, 1952; Aitchison et al., 1954; Cotton, 1957; Firman, 1965,1966,1967; Ward, 1966; Ludbrook, 1976; Cann, 1978; Belperio et al., 1984a; Belperio, 1985), few geochronometric studies of the formation have been undertaken.

The name Glanville Formation was given to the holostratotype section of "Pleistocene (marine) ... Older raised sea bed, with many shells locally extinct" of Howchin (1935, p.87), the name being "derived from the suburb of Glanville where the original section described by Howchin (1888, p.31) at "Fletcher's New Graving Dock" is located (Firman, 1966). No surface exposures of the Glanville Formation are known to occur in this area, although its occurrence was demonstrated in several bore holes (Firman, 1963; Lindsay, 1969; Ludbrook, 1976). Cann (1978) briefly described a neostratotype for the Glanville Formation (Figure 4.2) at Dry Creek and proposed a reference section located in the northeastern corner of a salt crystallization pan, owing to the burial of the holostratotype during engineering construction.

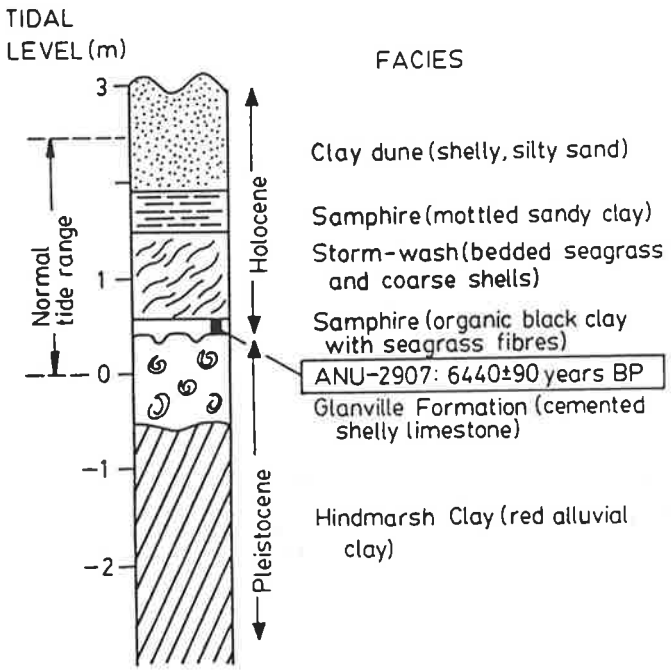


Figure 4.2 Glanville Formation neostratotype, Globe Derby Park. After Cann (1978) and Belperio et al.,(1983). See Figure 4.4 for location.

4.3.1.1 Sedimentary Characteristics

A variety of marine and paralic lithofacies are preserved within the Glanville Formation including subtidal, estuarine, intertidal and supratidal flat sediments and beach ridge complexes. The presence of the latter depended on the energy conditions of the coastline during the Last Interglacial. Sediments of the Glanville Formation are represented by poorly consolidated muddy skeletal grainstones, and in places are locally pedogenically modified. The sediments host an abundant molluscan fossil assemblage, and include the estuarine bivalve Anadara trapezia and the foraminifer Marginopora vertebralis, both species now no longer living in South Australian coastal waters (Ludbrook, 1984; Belperio and Murray-Wallace, 1984). These species generally favour warmer climatic conditions and appear to have become locally extinct in southern Australian coastal waters following the Last Interglacial. Their presence in Holocene sediments is the result of reworking.

4.3.1.2 Occurrence

The approximate distribution of the Glanville Formation is outlined in Figure 4.3. Knowledge of the extent of the formation is incomplete, and investigations are still in progress (Belperio, 1985). Accurate delineation of the transgressive, feather-edge of the Glanville Formation is difficult to establish, as in places it is unconformably overlain by younger alluvial sediments of the Pooraka Formation (Firman, 1967) and marine sediments deposited in response to the Holocene transgression (St Kilda Formation of Cann and Gostin, 1985).

The Glanville Formation occurs extensively along the South Australian coastline. In the Adelaide region, where it was first described (Tate,

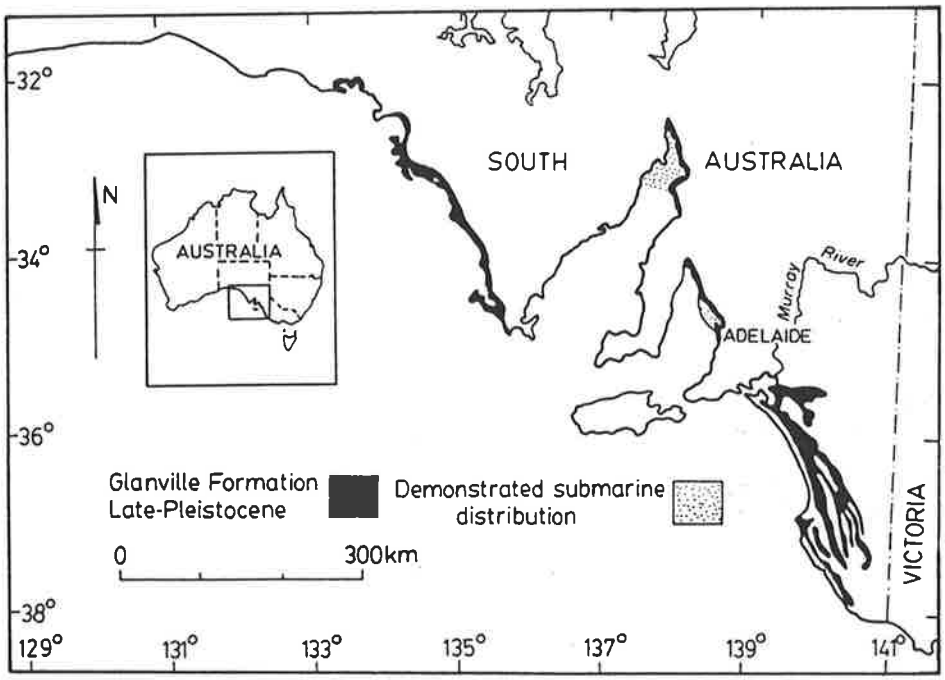


Figure 4.3 Geographical extent of the Late Pleistocene Glanville Formation in South Australia (modified after Ludbrook, 1984).

1879a), the formation has no surface expression. In northern Gulf St Vincent a pedogenically modified, calcreted and karstified crust of the Glanville Formation extensively outcrops on the surface of contemporary supratidal flats (Belperio, 1985). These are former intertidal flat sediments of the Glanville Formation. Equivalents of the Glanville Formation have also been identified in submarine cores from upper Spencer Gulf (Hails et al., 1984a,b) and in the Gulf St Vincent in shallow water subtidal vibrocores (Belperio, 1985). On Eyre Peninsula, the Glanville Formation crops out in numerous coastal embayments, that acted as localised depocentres during the Last Interglacial.

Thickness variation and differences in elevation of the Glanville Formation are evident in South Australia. In northern Spencer Gulf, the formation commonly attains thicknesses of approximately 1.5-2 m. In the Gulf St Vincent however, it is more thinly developed and seldom exceeds 50 cm (Belperio, 1985). Channel fill facies however give rise to notable thickness variation, and the formation may attain thicknesses of 10 m in such settings. At a broad scale the regional thickness variations and altitudinal differences in the Glanville Formation may have neotectonic implications, and reflect hydroisostatic responses to eustatic change.

4.3.1.3 Age And Origin

Surprisingly few quantiative age assessments have been attempted on the Glanville Formation. This is the result of several factors including (1) inherent difficulties in dating molluscan fossils whose ages are in excess of conventional radiocarbon dating capabilities, (2) the lack of fossiliferous material suitable for dating by other techniques (e.g., corals using Uranium-Series dating), (3) the unsuitability of other long-established techniques such as K/Ar dating or Obsidian Hydration (4) and historically, a subordinate interest in Quaternary stratigraphy.

Early studies of the Glanville Formation designated a variety of ages ranging from Sub-Recent to Pleistocene. Although some researchers anticipated a Pleistocene age, no quantitative data were available to support their contentions (Tate, 1879a; Howchin, 1888,1909; Tindale, 1933). Early suggestions of a Pleistocene age for the Glanville Formation were based on attempted correlations with the Quaternary of Europe and North America, and inferences based on faunal evidence. Tindale (1933) summarised the distribution of Anadara beds ('Arca Zone') on a 6.1 m terrace in the south east of South Australia and compared this with the Pamlico (Mid-Wisconsin) terrace in the eastern United States, and the 20-foot London terrace. Ward (1966) subsequently suggested that the Anadara beds at Dry Creek were of Late Pleistocene age, and equated them with the Epimonastirian high sea level (Zeuner, 1953) of the Last Interglacial. Firman (1966) granted formation status to these sediments and termed them the Glanville Formation.

Schwebel (1978) using Th^{230}/U^{234} dating of molluscs reported an age of 125,000±20,000 yrs BP for the Woakwine Range (WI) sediments, ascribed as Glanville Formation equivalents in the south east of South Australia.

Based on thermoluminescence dating of quartz sands from equivalents of the Glanville Formation from submarine vibrocores in northern Spencer Gulf, Smith (1983) reported ages of 90,000±15,000 and 96,000±24,000 yrs BP (Table 4.1). The age reported by Smith (1983), although in general agreement with the expected geological age in terms of order of magnitude, nevertheless has significant implications concerning the resolution of thermoluminescence dating and the potential of dating interstadials younger than the Last Interglacial. The reported age of 96,000±24,000 BP for example, implies that the sediments dated can be expected to have an age falling between 72,000-120,000 yrs. It could therefore be argued that in the absence of geological control, the sediments may conceivably be

Table 4.1 Quantitative age assessments of the Glanville Formation and equivalents.

Location	reference	sample	dating technique	Calculated age kaBP
Northern Spencer Gulf	Smith (1983) Belperio et al., (1984)	Submarine core SG#182 2.20 m	Thermoluminescence (fine grained quartz) (coarse grained quartz)	90±15 96±24
Northern Spencer Gulf	Belperio et al., (1984)	Submarine core SG#182 2.20 m	Amino Acid Racemisation	110^{+19}_{-17}
South East of South Australia	von der Borch et al., (1980)	Lake Hawdon Borehole 2.80 m	Amino Acid Racemisation	120±10
South East of South Australia	Schwebel (1978)	Woakwine Range (WI) molluscs	Th^{230}/U^{234}	125±20
South Eastern Australia	Gill (1974)	Shelly limestones Victorian coastline	Th^{230}/U^{234}	>100

equated with stages 5a (82,000 yrs BP), 5c (105,000 yrs BP) or 5e (125,000 yrs BP) of the marine oxygen isotope record. As this problem concerns the resolution of thermoluminescence dating, numerous replicate age assessments would be required before a high confidence level could be assigned to ages derived by this method.

Another important point to consider is that the dating techniques described, may be dating different events. Amino acid racemisation, uranium-series and radiocarbon dating methods all date the death of organic material, which generally predates the time of sedimentation by a period that cannot be uniquely defined (Belperio et al., 1984). In contrast, thermoluminescence in principle, dates the time of sedimentation, based on when a sample was last exposed to sunlight.

Radiocarbon dating of molluscs from the Glanville Formation suggested an age in excess of 45,000 yrs BP (Daily et al., 1976). Preliminary uranium-series analyses on shells obtained from shelly limestones along the Victorian coastline, having similar lithostratigraphic and palaeontological aspects to the Glanville Formation provided ages of 100,000 yrs BP and older (Gill, 1974), and these sediments were compared with the Glanville Formation by later workers (Daily et al., 1976). Since these studies, there has been an uncritical acceptance of the Last Interglacial age for the Glanville Formation.

Despite some variability in age assessments due to a combination of precision (the reproducibility of measurements) and accuracy (deviation of determined age from "real" age), all the available evidence points to a Last Interglacial age for the Glanville Formation. This equates with stage 5e of the marine oxygen isotope record, which globally has been variously bracketed between 100-140 kaBP (Bloom et al., 1974; Marshall and Thom, 1976; Chappell and Veeh, 1978; Szabo, 1979; Stearns, 1984) although the generally most accepted age is 125±10 kaBP by uranium-series measurements (Stearns, 1984).

4.3.2 Amino Acid Racemisation Age Assessments Of The Glanville Formation

In recent years several age assessments have been made of the Glanville Formation, a number of which were based on the application of the amino acid racemisation reaction (von der Borch et al., 1980; Belperio et al., 1984; and Kimber and Milnes, 1984). These preliminary studies highlighted some of the difficulties faced with these techniques, and of the necessity of establishing a large data base for Australian fossils of Quaternary age. In particular, these early studies relied on the comparison of results with American data, a practice which involved the extrapolation of amino acid data over unacceptably large distances, with a disregard for the genus-specific nature of molluscan racemisation. In addition differences in the timing and intensity of climatic change were also neglected with quantitative age assessments.

In an examination of various strandlines of late-Quaternary age in the south east of South Australia, von der Borch et al., (1980) assigned a Last Interglacial age to the uppermost component of the Woakwine Range barrier-estuarine sequence, an equivalent of the Glanville Formation of the Adelaide region. Based on the extent of racemisation of alanine, glutamic acid and leucine, and isoleucine epimerisation in Katelysia scalarina an age of 120±10 kaBP was assigned to these sediments. An age of 92 kaBP was also assigned to interstadial marine strata (von der Borch et al., 1980). However, caution was not exercised by these authors, and several important points were neglected.

The Holocene calibration sample (sample A of von der Borch et al., 1980) was a surface sample and was inferred to be the same age as shells dated using radiocarbon methods by Blackburn (1966). Comparison of the data reported by von der Borch et al., (1980) with radiocarbon calibrated

D/L ratios in the present study, illustrates the unsuitability of their calibration sample (Table 4.2). Although the two localities have different Mean Annual Temperatures (MAT's), these differences would not account for the anomalously high extent of racemisation in the sample of von der Borch et al., (1980) from the south east of South Australia. Indeed, higher D/L ratios would be expected for the west coast samples, consistent with the higher mean annual temperatures. This has important implications concerning the validity of the results reported by von der Borch et al., (1980), as an in situ racemisation rate constant (k) was calculated on the basis of their calibration sample, and therefore suggests the ages they obtained were fortuitous.

In addition, von der Borch et al., (1980) compared the extent of racemisation in Chione, an extensively studied genus from the Californian coast with Katelysia spp. in Australia. Accordingly, the similarity in shell morphology suggested the possibility of comparable rates of molluscan racemisation. Shell morphology however, is not a satisfactory criterion for an assessment of the genus-specific nature of racemisation. Only through the analysis of large sample populations can such suggestions be validated.

A more fundamental criticism of the study by von der Borch et al., (1980) however, was their use of an 'extended-linear' racemisation kinetic model, which involved the comparison of two species of Pleistocene age from widely separated localities. The complex nature of molluscan racemisation kinetics and the general unsuitability of the 'extended-linear' kinetic model for age assessments of fossils of late-Pleistocene age were discussed in Chapter 2.

In a preliminary investigation, Belperio et al., (1984) using amino acid racemisation and thermoluminescence dating methods proposed a Last Interglacial age for the Glanville Formation. Based on the extent of leucine racemisation in the bivalve Anadara trapezia, an age of $110,000 \pm^{19,000}_{17,000}$ yrs BP was assigned to the Glanville Formation (Belperio

Table 4.2 Comparison of the extent of amino acid racemisation in Holocene Katelysia spp. illustrating artificially high D/L ratios for 'total acid hydrolysate' in surface samples(1).

Species	Locality	MAT (°C)	Calendric age(2) BP	Amino acid			
				ALA	GLU	LEU	ALLO/ISO
Katelysia scalarina(a)	Lake St Clair surface sample	14.5	4330±100	0.29	0.17	0.28	0.11
Katelysia peronii(b)	Smoky Bay West Coast South Australia 1.35-1.45 m	16.9	4580±150	0.20	0.08	0.16	0.11
Katelysia scalarina(b)	Smoky Bay West Coast South Australia 4.88-4.96 m	16.9	7200±300	0.22	0.14	0.24	0.09

(a) data reported by von der Borch et al., (1980)
(b) data obtained in the present study
(1) Data obtained in the present study indicates that a species effect is not evident in the genus Katelysia
(2) Ages reported in sidereal years (BP), converted from environmentally corrected radiocarbon years (bp) using tables by Klein et al., (1982).

et al., 1984). In addition, a preliminary correlation of the Mambray Formation (Hails et al., 1984a), of northern Spencer Gulf with the Glanville Formation neostratotype of the Adelaide region was made based on leucine D/L ratio equivalence in Anadara (Belperio et al., 1984). Although a cautious approach was adopted by these authors, their age assessment also relied on comparisons with North American data. However, they rightly allowed for a large margin of error in their age assessment because of the uncertainty in the calculation of an Effective Quaternary Temperature history (E.Q.T.).

Kimber and Milnes (1984) examined the extent of amino acid racemisation in Holocene and Pleistocene molluscs from two marine units within the Hindmarsh River Valley, South Australia (Figure 4.4). They correctly noted the complex nature of molluscan racemisation kinetics, and for these reasons did not attempt quantitative age assessments.

4.4 GLANVILLE FORMATION: AMINO ACID RACEMISATION ANALYSES

Representative results from this study of D/L ratio data for molluscan fossils from the Glanville Formation are summarised in Table 4.3. Relative intrageneric rates of racemisation were in accord with those for other carbonate fossils and aqueous solution in laboratory studies (Dungworth, 1976; Schroeder and Bada, 1976; Lajoie et al., 1980) and compare favourably with results of Kimber and Milnes (1984) for fauna from the Glanville Formation.

4.4.1 Aminostratigraphic Correlation Of The Glanville Formation

Previous studies (Firman, 1965,1966,1967,1969; Daily et al., 1976; Ludbrook, 1984) have uncritically assumed the widespread nature of marginal marine sediments of Last Interglacial age, without quantitative age control. Correlations of the Glanville Formation of the Adelaide region with other localities in southern Australia traditionally relied on lithological and palaeontological evidence. The presence of the Pleistocene indicator species including Anadara trapezia, Marginopora vertebralis and Pinctada carchariarum were previously used to establish biostratigraphic correlations. However, these fauna also occur in older sediments (Gill, 1977) as well as reworked into Holocene sediments, and therefore preclude their use for correlation of solely Last Interglacial sediments. Furthermore, both Anadara and Marginopora are examples of 'facies-fossils' and their absence in some sections is of palaeoecological rather than chronostratigraphic significance.

An indurated carbonate crust present on the Glanville Formation at the holostratotype (Cann, 1978) was previously used (Firman, 1967,1969) as a basis for regional lithostratigraphic correlation. However, the presence in some stratal sequences of several calcrete profiles intercalated

Table 4.3 Representative amino acid D/L ratios for 'total acid hydrolysates' from molluscan fauna from the Last Interglacial Glanville Formation, South Australia

Species	Locality	Depth of burial (m)	Amino acid						
			ALA	VAL	ALLO /ISO	LEU	ASP	PHE	GLU
Anadara trapezia	Port Wakefield	3	0.67 ±0.02	0.32 ±0.06	0.43 ±0.02	0.51 ±0.02	0.54 ±0.03	0.73 ±0.06	0.43 ±0.01
Katelysia rhytiphora	Port Wakefield	3	0.72 ±0.03	0.32 ±0.04	0.41 ±0.04	0.45 ±0.01	0.46 ±0.01	0.67 ±0.04	0.38 ±0.04
Katelysia scalarina	Wardang Island	1	0.79 ±0.008	0.40 ±0.004	0.43 ±0.02	0.32 ±0.02	0.66 ±0.01	—	0.54 ±0.04
Fulvia tenuicostata	Tourville Bay	3	0.61 ±0.01	0.41 ±0.01	0.74 ±0.06	0.83 ±0.04	0.41 ±0.02	0.68 ±0.04	0.45 ±0.01

with marine sediments precludes the use of calcretes as reliable litho- and chronostratigraphic markers. Correlation of the Glanville Formation over widely separated localities in South Australia therefore highlights the use of amino acid racemisation for avoiding homotaxial interpretations. Homotaxis refers to,

> "... the similarity in separate regions of the serial arrangement or succession of strata of comparable compositions or of included fossils. The term ... (was) ..., proposed by Huxley (1862, p.xlvi) to emphasize that similarity in succession does not prove age equivalence of comparable units"
> (North American Stratigraphic Code, 1983 p.851).

In a preliminary investigation, Belperio et al., (1984) suggested a chronostratigraphic correlation of the Glanville Formation neostratotype of the Adelaide region (Cann, 1978) with the Mambray Formation of northern Spencer Gulf (Hails et al., 1984a). This chronocorrelation was based on leucine D/L ratio equivalence in Anadara trapezia and involved only a few specimens. In this study Anadara trapezia and Katelysia spp., were collected from a range of coastal settings in South Australia (Figure 4.4). The thick shells of these species render them particularly suitable for amino acid studies, for they are less likely to develop microfractures permitting contamination by non-indigenous amino acids. Intrashell D/L ratio variation was avoided by analysing only hinges. Where disarticulated specimens were used, only left hand valves were analysed to prevent the same individual being analysed twice. The D/L ratio data for Anadara trapezia and Katelysia spp., are presented in Tables 4.4 and 4.5 respectively and in Appendix Table 4.1. Results for Anadara are also depicted in Figure 4.5.

The integrity of these data can be assessed in a comparison with the results presented in Chapter 3. There it was outlined that analytical error accounted for an average D/L ratio variation of approximately 3%. Larger margins of variation were represented by within-species intrashell

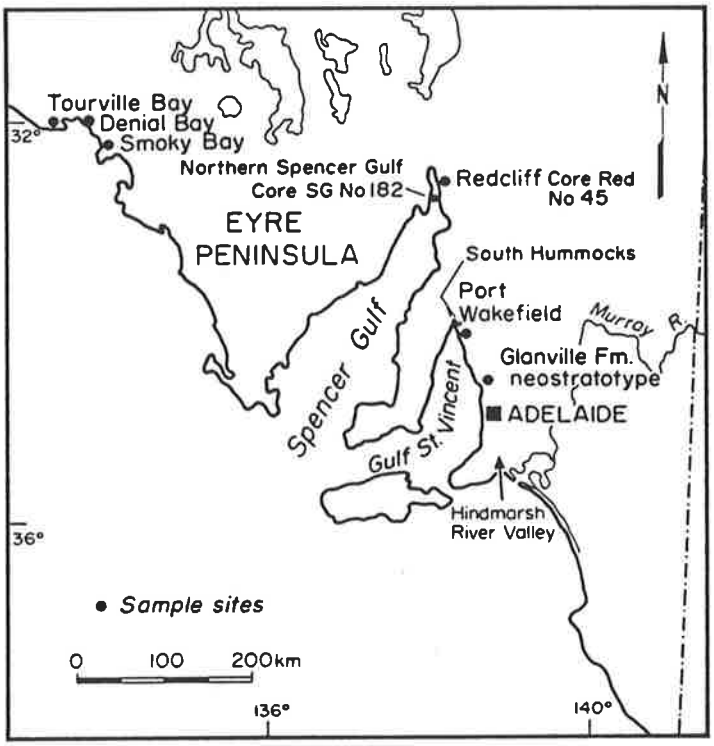


Figure 4.4 Location of sample sites from which Last Interglacial specimens of Anadara trapezia were collected.

Table 4.4 Aminostratigraphic correlation of the Late Pleistocene Glanville Formation based on the extent of racemisation (epimerisation) in the bivalve Anadara trapezia

Locality	No of specimens	MAT °C	Amino acid D/L ratios ('total acid hydrolysate') ALA	VAL	ALLO /ISO	LEU	ASP	GLU
(A) Tourville Bay	4	16.9	0.66 ±0.06	0.36 ±0.05	0.47 ±0.02	0.45 ±0.02	0.66 ±0.03	0.38 ±0.06
(B) Denial Bay	3	16.9	0.64 ±0.07	0.33 ±0.02	0.44 ±0.03	0.44 ±0.01	0.64 ±0.02	0.47 ±0.01
(C) Port Wakefield	11	17.0	0.73 ±0.11	0.34 ±0.06	0.43 ±0.04	0.51 ±0.04	0.60 ±0.06	
(D) Redcliff, Core RED#45	1	19.0			0.50 ±0.04	0.52 ±0.01	0.60 ±0.02	0.40 ±0.03
(E) Northern Spencer Gulf	1	18.0		0.46 ±0.05	0.38 ±0.02	0.44 ±0.01	0.52 ±0.01	0.46 ±0.02
(F) South Hummocks north west of Port Wakefield	1	17.0	0.83 ±0.03	0.40 ±0.01	0.48 ±0.01	0.59 ±0.01	0.64 ±0.01	
(G) South Hummocks north of Port Wakefield	3	17.0	0.78 ±0.04	0.29 ±0.02	0.35 ±0.03	0.42 ±0.02		0.40 ±0.02
(H) Glanville Formation neostratotype, Dry Creek	2	16.9		0.31 ±0.01	0.39 ±0.01		0.61 ±0.01	0.54 ±0.14
(I) Hindmarsh River, Victor Harbor	1	15.7	0.58 ±0.07	0.28 ±0.04	0.35 ±0.05	0.45 ±0.05		0.42 ±0.01
Average D/L ratios, SD and CV's		D/L	0.70	0.35	0.42	0.48	0.61	0.44
		SD	±0.09	±0.06	±0.06	±0.06	±0.05	±0.05
		CV	12.9%	17.1%	14.3%	12.5%	8.2%	11.4%

Average coefficient of variation (CV) for all amino acids - 12.7%

Table 4.5 Aminostratigraphic correlation of the Late Pleistocene Glanville Formation based on the extent of racemisation (epimerisation) in Katelysia spp.

Locality	Species	No. of specimens	MAT °C	Depth of burial (m)	Amino acid D/L ratios ('total acid hydrolysate') ALA	VAL	ALLO /ISO	LEU	ASP	PHE	GLU
Glanville Formation neostratotype Gulf St Vincent	Katelysia spp.	2	16.2	2	—	0.46 ±0.02	0.54 ±0.02	0.54 ±0.008	—	0.73 ±0.05	0.54 ±0.04
Tourville Bay Eyre Peninsula	Katelysia rhytiphora	4	16.9	1.5	0.78 ±0.02	0.38 ±0.03	0.51 ±0.04	0.57 ±0.07	0.49 ±0.04	0.73 ±0.05	0.45 ±0.03
Port Wakefield 'Anadara beds'	Katelysia scalarina	1	~17.0	3	0.52 ±0.01	0.42 ±0.004	0.50 ±0.01	0.58 ±0.02	0.49 ±0.001	0.70 ±0.01	0.43 ±0.01
Port Wakefield 'Anadara beds'	Katelysia rhytiphora	4	~17.0	3	0.73 ±0.03	0.32 ±0.04	0.45 ±0.07	0.51 ±0.07	0.46 ±0.02	0.67 ±0.05	0.38 ±0.04

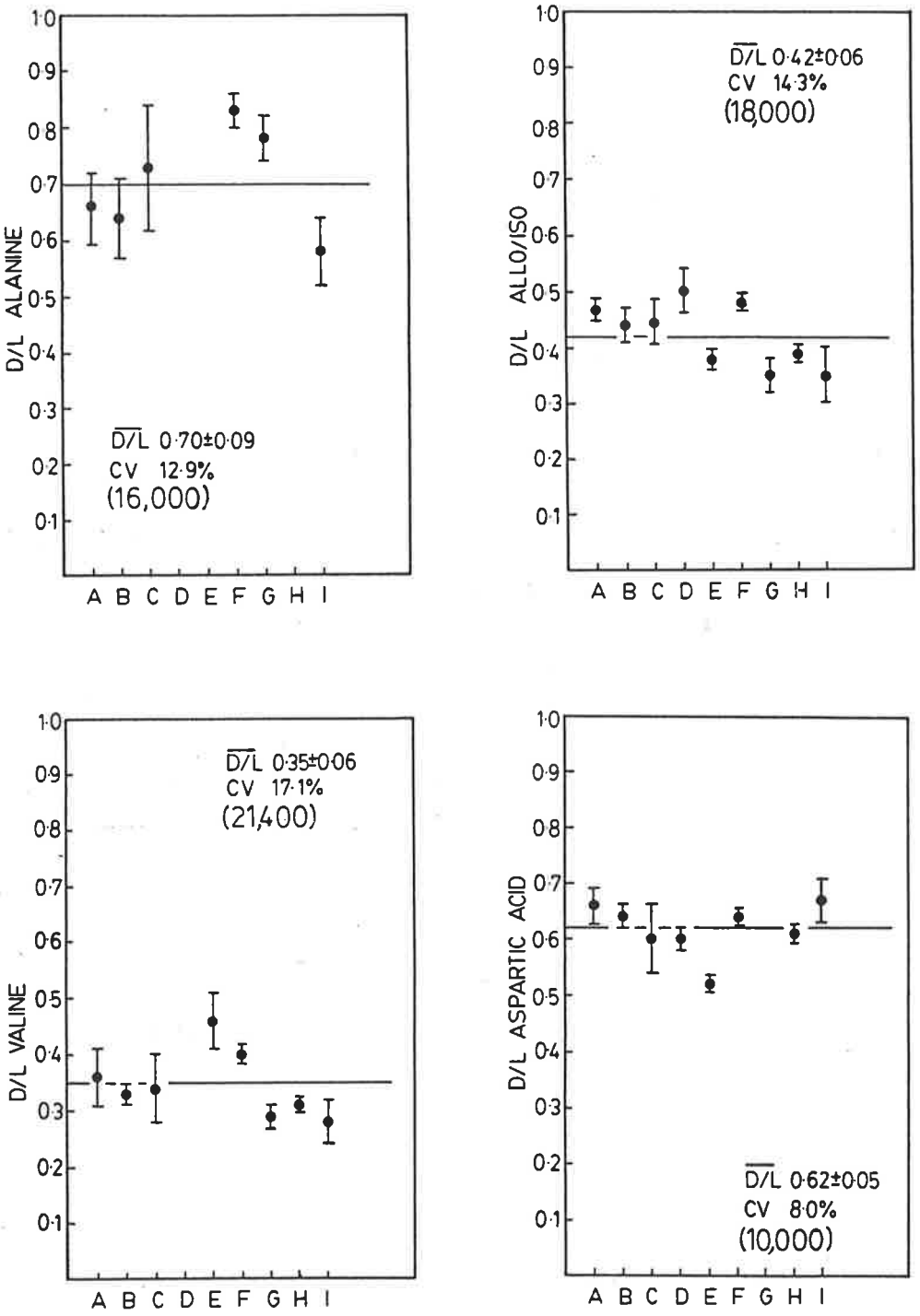


Figure 4.5 Correlation of the Late Pleistocene Glanville Formation based on the extent of racemisation in the bivalve Anadara trapezia. Sample localities indicated in Table 4.4.

The absolute values in years that the coefficients of variation represent in relation to 125 ka (age of the Glanville Formation), are presented in parentheses.

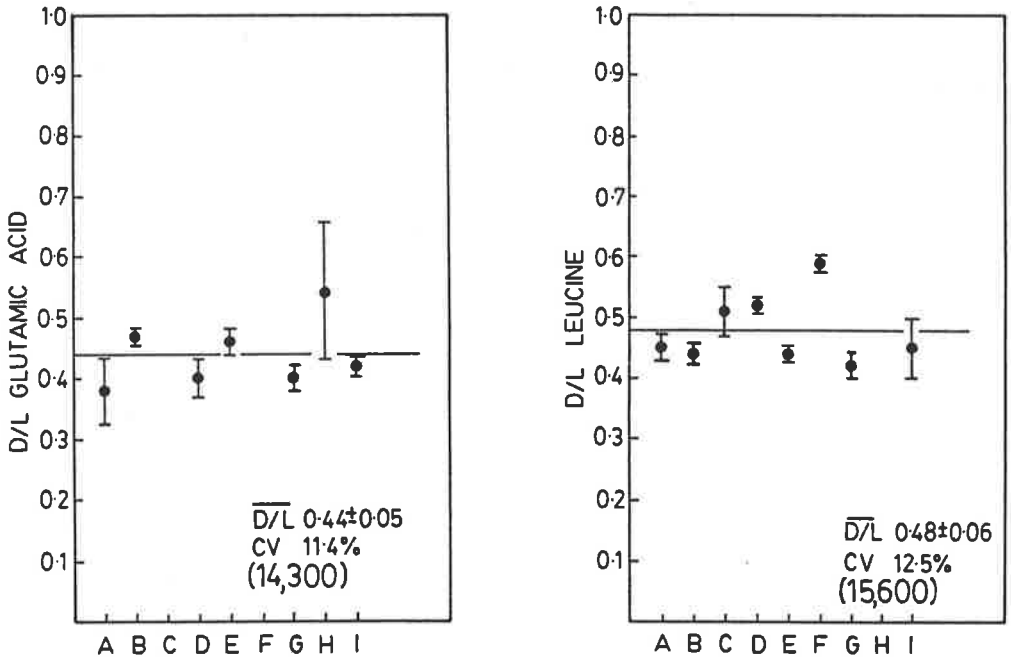


Figure 4.5 (continued)

D/L ratio variation (6-8% depending on whether results for isoleucine are considered), and between 11-20% for within-species intershell D/L ratio variation for a single deposit.

The results for Anadara trapezia indicate an average coefficient of variation of 13% for all amino acids for the range of South Australian coastal settings from which the samples were obtained. This compares favourably with the results for the Port Wakefield 'Anadara beds', and confirms that all the sediments sampled are of Last Interglacial age. The marginally higher average coefficient of variation for Anadara from a wide range of coastal settings is most probably due to latitudinal variation in amino acid D/L ratios. The chronocorrelation afforded by Anadara trapezia is also evident in the genus Katelysia (Table 4.5).

Because contemporary mean annual air temperatures are in general a smooth function of latitude, systematic differences in amino acid D/L ratios should be evident for isochronous deposits (Wehmiller, 1984b). This is based on the assumption however, that former latitudinal temperature gradients followed a similar trend to contemporary patterns. This situation is complicated however with coastlines characterised by large marine re-entrants such as South Australia with Spencer Gulf and Gulf St Vincent. In such circumstances, mean annual temperatures (MAT) will not strictly be a function of latitude and may reflect local climates.

To assess whether a systematic variation in D/L ratios with latitude is evident in South Australia, Anadara trapezia from the Last Interglacial Glanville Formation were studied. Samples were obtained from several settings ranging from Tourville Bay (lat 32°8'; long 133°42') on the west coast to the Hindmarsh River (lat 35°33'; long 138°37') at Victor Harbor (Table 4.4). Intrashell D/L ratio variation was avoided by analysing only the hinges. Where disarticulated specimens were used, only the left hand valves were analysed to avoid analysing the same individual twice. Amino acid D/L ratios are for the 'total acid hydrolysate'.

As samples were collected from over a latitudinal range of only 3°, difficulties were anticipated in the detection of a latitudinal effect. The 3° of latitude corresponded to a difference of approximately 2.4°C from the highest to the lowest MAT. In contrast, Wehmiller (1984b) reported results of North American data spanning a latitudinal range of approximately 11° and noted significant differences in leucine D/L ratios for Last Interglacial Protothaca.

A latitudinal temperature effect on the extent of racemisation in Anadara was clearly evident for isoleucine and valine (Figure 4.6). Systematic variation was less apparent however for leucine. Aspartic acid and glutamic acid displayed no systematic relationship. Nevertheless the data indicate that for chronocorrelations over widely separated localities, a latitudinal effect on amino acid D/L ratios for isochronous deposits should be considered. Two significant questions however arose from these data. Firstly, how pronounced statistically is the observed latitudinal effect in view of other sources of D/L ratio variation (e.g., analytical error, intershell variation)? Secondly, are the data an expression of D/L ratio variation with latitude (temperature) or are the data in part an expression of diachronism?

Results for isoleucine and valine would appear to be significant. In Chapter 3 it was outlined that analytical error accounted for only a small margin of variation (approximately 3%). At a higher level within-species intershell D/L ratio variation for a single deposit accounted for an average variation of 12% for all amino acids. In contrast, coefficients of variation for Anadara from the range of Last Interglacial deposits for valine and isoleucine were 17 and 14% respectively. These higher coefficients of variation are therefore attributed to a latitudinal (temperature) effect for these deposits.

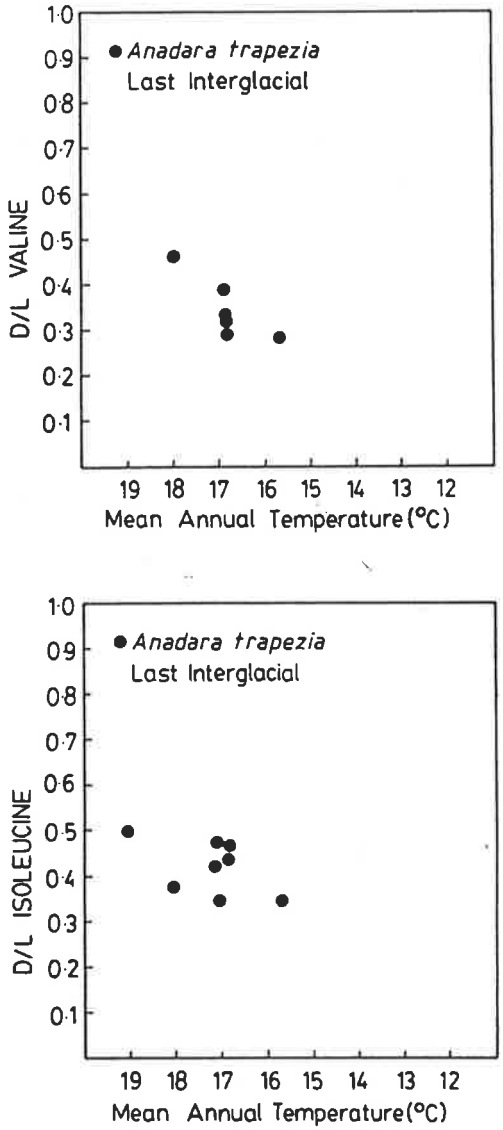


Figure 4.6 Plot of amino acid D/L ratio variation in Last Interglacial specimens of Anadara trapezia against mean annual air temperatures. As contemporary mean annual air temperatures are essentially a smooth function of latitude, the systematic variation reflects a latitudinal temperature effect, evident since the Last Interglacial.

Deposition of the Glanville Formation occurred during the Last Interglacial which is represented by sub-stage 5e of the marine oxygen isotope record. Previous workers (Bloom et al., 1974; Marshall and Thom, 1976; Chappell and Veeh, 1978; Szabo, 1979) have variously bracketted this transgressive event between 100,000 to 140,000 yrs BP. The sea level maximum of 5e is now widely accepted as 125,000±10,000 yrs (Stearns, 1984) and the time interval represented by this event is now more strictly defined as approximately 10,000 yrs with interstadials following this event. Although the suggestion of a double transgressive peak has been forwarded by several investigators (Veeh et al., 1979; Szabo, 1979; Stearns, 1984), few coastal sections record this event, and the complex stratigraphic relationships seriously test the resolution of uranium-series dating. If a double peak represents 5e then the length of time representing the "Last Interglacial" would be greater than stated above. Despite this complication however, amino acid racemisation dating does not have sufficient resolution to distinguish systematic age variation within this depositional package based on the 'total acid hydrolysate'. Therefore, although the bounding surfaces of the Glanville Formation are diachronous, the time intervals represented by these surfaces can not be distinguished using amino acid data. In this context the widespread occurrence of the Glanville Formation may be treated as isochronous. An additional complication arises in that the Glanville Formation may not represent all of 5e.

4.5 "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". These sediments are represented by poorly sorted sandy clays with low calcium carbonate contents. Although they have similar 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). The "Older Pleistocene marine beds" occur at the base of the Spencer Gulf Group and may represent a marine to paralic time-equivalent of the terrestrial Hindmarsh Clay (Hails et al., 1984a,b). Relative lithostratigraphic relationships suggest these sediments are older than the Mambray Formation (equivalent to the Glanville Formation of the Adelaide region). 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 preliminary age of 220 kaBP was assigned to these sediments (Hails et al., 1984b).

4.5.1 "Older Pleistocene Marine Beds": Amino Acid Racemisation Age Assessments

In the absence of quantitative data, Hails et al., (1984b) used circular reasoning to assess the age of sediments they termed "Older

Pleistocene marine beds". Although relative stratigraphic relationships indicated these sediments were older than the Last Interglacial, quantitative evidence was not available to support their contention.

To independently establish the age of these sediments, and the transgressive sea-level event they were related to, the extent of racemisation for a range of amino acids was examined in Anadara trapezia. The results obtained for Anadara from the "Older Pleistocene marine beds" were then compared with D/L ratios for this species from the Glanville Formation of Last Interglacial age (Table 4.6). Analyses were made for the 'total acid hydrolysate' and free amino acids (Appendix Table 4.2). Samples analysed were obtained from shallow vibrocores taken at Redcliff, upper Spencer Gulf (cores RED#40 and 41) (Figure 4.7). Intrashell D/L ratio variation was avoided by analysing only the hinges. All the bivalves were disarticulated, and their undisturbed core depths ranged from 90 cm to 135 cm.

Based on the extent of racemisation in Anadara trapezia an age older than Last Interglacial may be assigned to these sediments (Tables 4.6 and 4.7), and is consistent with the lithostratigraphic relationships of these sediments. Leucine D/L ratios were not reported as β-ALA coeluted with L-leucine resulting in artificially low D/L values. Interestingly, this problem was only experienced in molluscs whose ages were older than the Last Interglacial, and in part its presence is attributed to the diagenetic breakdown of aspartic acid.

Quantitative age assessment of the "Older Pleistocene marine beds" was made using the integrated rate expression for the amino acid racemisation reaction (eqn 2.2). Although this relationship is inappropriate for accurately defining the overall nature of molluscan racemisation kinetics, as the D/L ratio data fall within the second

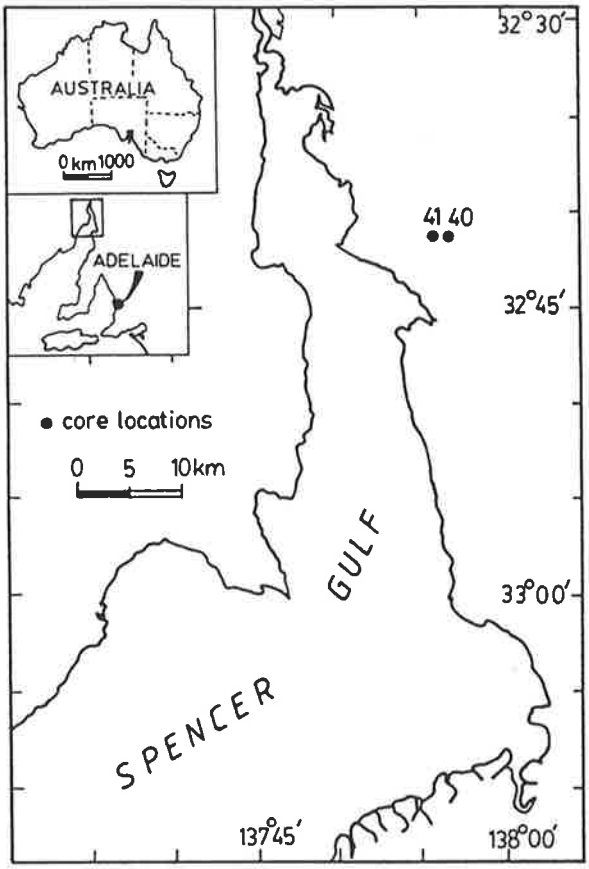


Figure 4.7 Location map of Redcliff Cores RED#40 and RED#41.

Table 4.6 Amino acid D/L ratios ('total acid hydrolysate') for Anadara trapezia from the Glanville Formation equivalent and "Older Pleistocene Marine Beds", northern Spencer Gulf.

Stratigraphic unit	Geologically expected age kaBP	AAR derived age kaBP	Amino acid ASP	ALA	VAL	ALLO /ISO	GLU	PHE
Glanville Formation	125	110[1]	0.54	0.68	0.32	0.43	0.42	0.73
"Older Pleistocene Marine Beds"	225	200[2]	0.76	0.83	0.48	0.55	0.62	0.89

[1] Amino acid racemisation derived age reported in Belperio et al. (1984)
[2] Age obtained in the present study

Table 4.7 Amino acid racemisation derived ages for the "Older Pleistocene marine beds" Redcliff, northern Spencer Gulf, based on the extent of racemisation in Anadara trapezia.

Amino acid	derived age kaBP
aspartic acid	233
valine	184
glutamic acid	206
phenylalanine	177
average age	200±50*

* The error term allows for an 'Effective Quaternary Temperature' history (EQT) uncertainty of approximately 3°C.

essentially linear component of the "non-linear" racemisation kinetic model, it is valid to use this equation for quantitative age assessments for these sediments. The value of k was calculated using the expression derived by Mitterer (1975) (eqn 2.6). Last Interglacial D/L values for Anadara trapezia were used as a basis of calibration. This approach takes into account the non-linear nature of racemisation kinetics and therefore integrates the kinetic complexities of the transition zone. According to Wehmiller (1984b) the slope of the second essentially linear component in the "non-linear" racemisation kinetic model is approximately 10% of the initial slope, and on this basis the value of k was found to be 1.8892×10^{-6}.

Individual age assessments using aspartic acid, valine, glutamic acid and phenylalanine were calculated, and from these data a mean age of 200,000±50,000 BP was determined representing the minimum age of these sediments. The error term in the final reported age allows for diagenetic temperature history uncertainty of approximately 3°C.

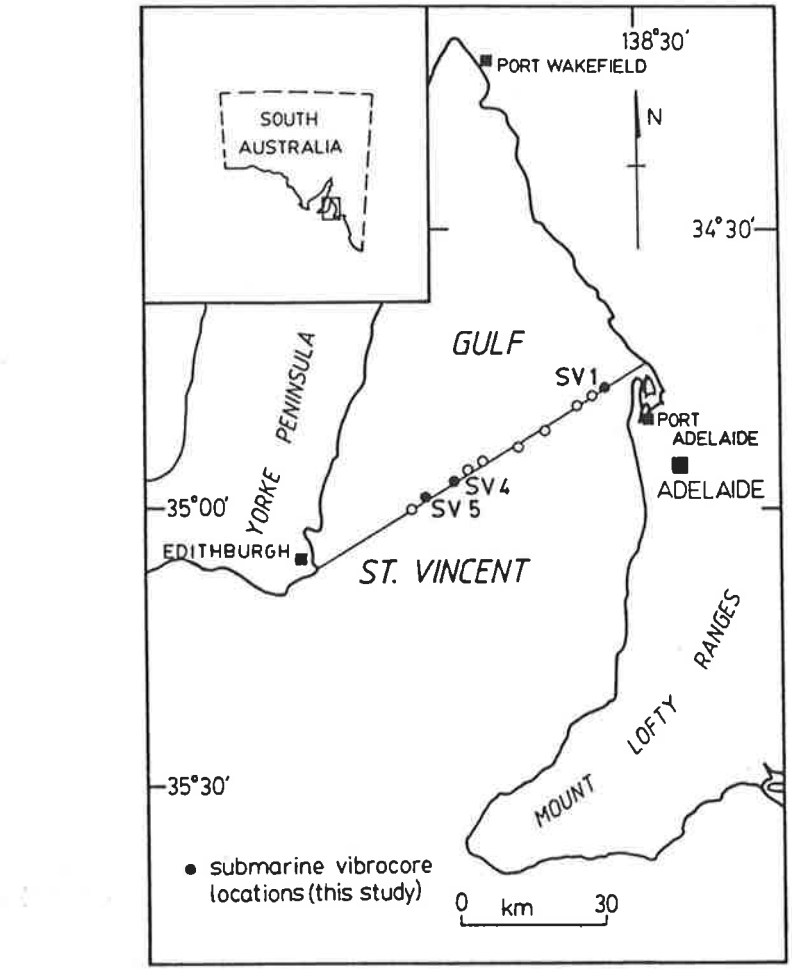
These data therefore indicate the "Older Pleistocene marine beds" were deposited during the Penultimate Interglacial (Stage 7 of the marine oxygen-isotope record), and supports the preliminary age assessment made by Hails et al., (1984b). This global glacio-eustatic sea level event is also expressed in 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).

4.6 INTERSTADIAL MARINE STRATA: GULF ST VINCENT

As part of ongoing studies of the Quaternary marine geology of South Australia directed by Drs V.A. Gostin and A.P. Belperio, a series of submarine vibrocores were taken in 1985, along a transect from Outer Harbour, Adelaide, across the Gulf St Vincent to Edithburgh (Figure 4.8). Detailed sampling of molluscs for amino acid racemisation analyses from cores SV-4 and SV-5 were made, as they had the greatest core recovery, represented by 2.77 m and 3.90 m respectively. Sedimentological logs of these cores are provided in Figure 4.9. In relation to contemporary mean sea level, the tops of these cores were -40 m and -36.4 m respectively (Figure 4.8). Additional samples for amino acid racemisation analyses were also obtained from core SV-1, located near Outer Harbour, Port Adelaide (Figure 4.8). Radiocarbon dating was also performed on molluscs from several of these cores, with the results for cores SV-4 and SV-5 reported in Table 4.8. Radiocarbon dating was undertaken to serve as a basis of comparison with the amino acid racemisation results.

Species sampled for amino acid racemisation analyses included Katelysia rhytiphora, Katelysia scalarina, Fulvia tenuicostata, Callucina lacteola, Anapella cycladea, Brachidontes erosus, Circumphalus disjecta and Ostrea angasi (Ludbrook, 1984). These species frequent subtidal to lower intertidal habitats. The molluscan fauna were generally well preserved, unabraded, with both articulated and disarticulated individuals represented. These species were studied, as they could be compared with results obtained from other Australian Quaternary sequences examined in the present study.

The host sediments were characterised by light grey (N7) shelly and very fine sandy carbonate muds, and occur beneath a thin veneer (0.5 m) of Holocene light greenish grey (5GY7/1) poorly sorted sediments, rich in skeletal detritus (Figure 4.9a,b).



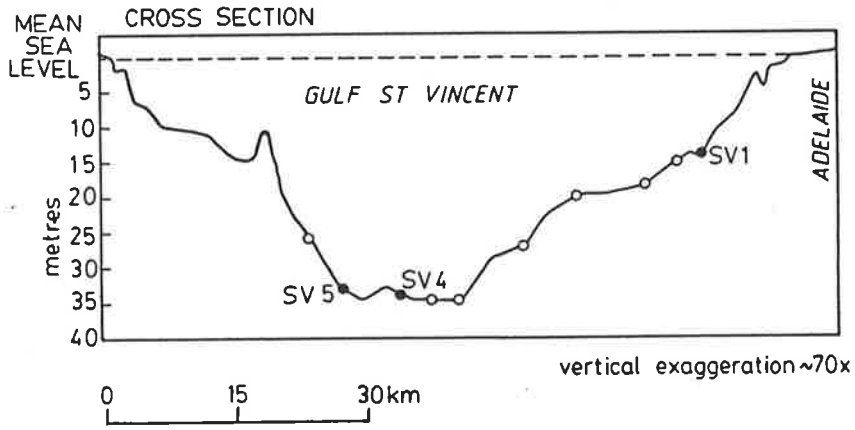


Figure 4.8 Gulf St Vincent submarine vibrocore transect showing the location of cores sampled from in this study.

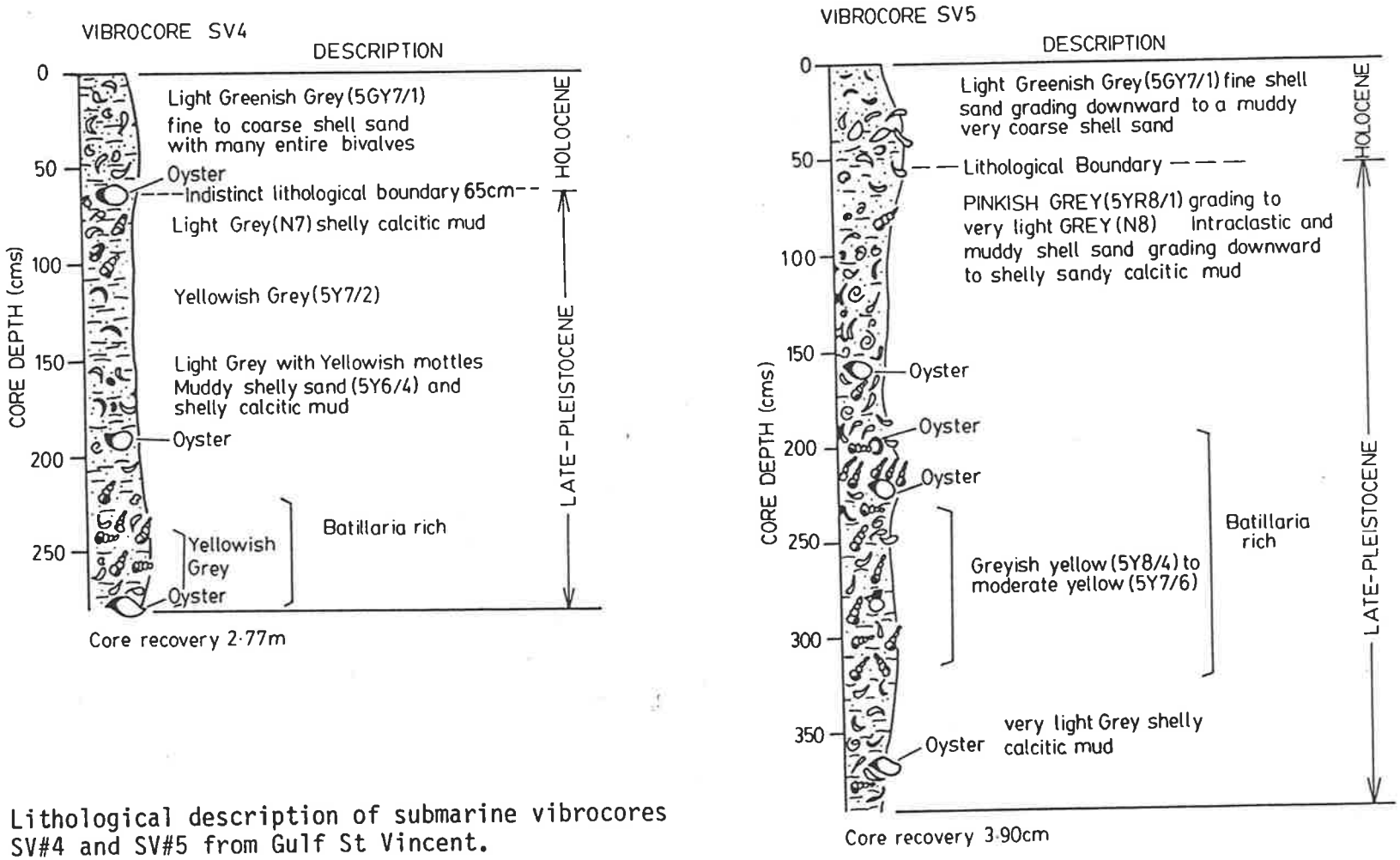


Figure 4.9 Lithological description of submarine vibrocores SV#4 and SV#5 from Gulf St Vincent.

Table 4.8 Carbon Isotope Measurements and C-14 Ages, for Gulf St Vincent Submarine Cores SV-4 and SV-5

Core	Depth (cm)	Material	$\Delta^{13}C$	d-C14	D-C14	Conventional Age yrs bp	Geologically expected age
SV-4	58-60	Single Oyster	+0.83	-976.4±1.9	-977.7±1.8	$30,500^{+650}_{-600}$	Late-Pleistocene
SV-4	280	Large Oyster fragments	+1.4	-988.5±1.9	-989.1±1.8	$36,300^{+1450}_{-1250}$	Late-Pleistocene
SV-5	23-27	Scallop fragments	+1.36	-170.9=8.9	-214.7±8.5	1940±90	Holocene
SV-5	138-142	Katelysia rhytiphora	+1.36	-990.2±1.8	-990.7±1.7	$37,600^{+1700}_{-1400}$	Late-Pleistocene
SV-5	160-165	Ostrea angasi	+0.91	-	-	<40,000	Late-Pleistocene
SV-5	368-372	Ostrea angasi	+0.99	-996.2±1.8	996.4±1.7	$45,100^{+5100}_{-3100}$	Late-Pleistocene

Two of the mollusc specimens were initially suspected as having an early Holocene age, occurring within what were considered, basal Holocene sediments deposited during the onset of the Holocene transgression. Both these specimens are Fulvia tenuicostata, obtained from core SV-4 at a depth of 0.64 m. This interval occurs directly above an indistinct lithological boundary within the core sample. Although the boundary is subtle, it was considered to represent a depositional hiatus, separating late Pleistocene sediments (interstadial sediments younger than the Last Interglacial), from Holocene sediments. Based on the extent of racemisation in these specimens (FTCOS23AT1 and FTCOS24AT1), a younger age is inferred for they consistently plot below the other values, suggested to represent a late Pleistocene age (Figures 4.10a-e). Furthermore t-tests performed on the results for aspartic acid, leucine, isoleucine, valine and alanine indicated a significant difference between D/L ratios for these specimens and those ascribed as late Pleistocene in age. In addition an age assessment using the integrated rate expression for molluscan racemisation derived a mean age of 10,000±1,500 yrs BP for these specimens based on D/L ratios for leucine, valine and isoleucine.

The presence of Fulvia tenuicostata at a depth of 0.64 m in core SV-4 with an age of approximately 10 kaBP, and the lithological boundary at 0.65 m suggests that the oyster and Katelysia valve, which occurred at a depth of 0.58-0.60 m, and dated at $30,500\pm^{650}_{600}$ yrs BP by conventional radiocarbon methods were reworked into basal Holocene sediments during the post-glacial transgression. This is important for it suggests that the interstadial marine strata are thinner than would otherwise be assumed if only the radiocarbon results were considered. More importantly, the results indicate that approximately 10 kaBP, sea-level had attained a level greater than or equal to -41 m in relation to contemporary mean sea level.

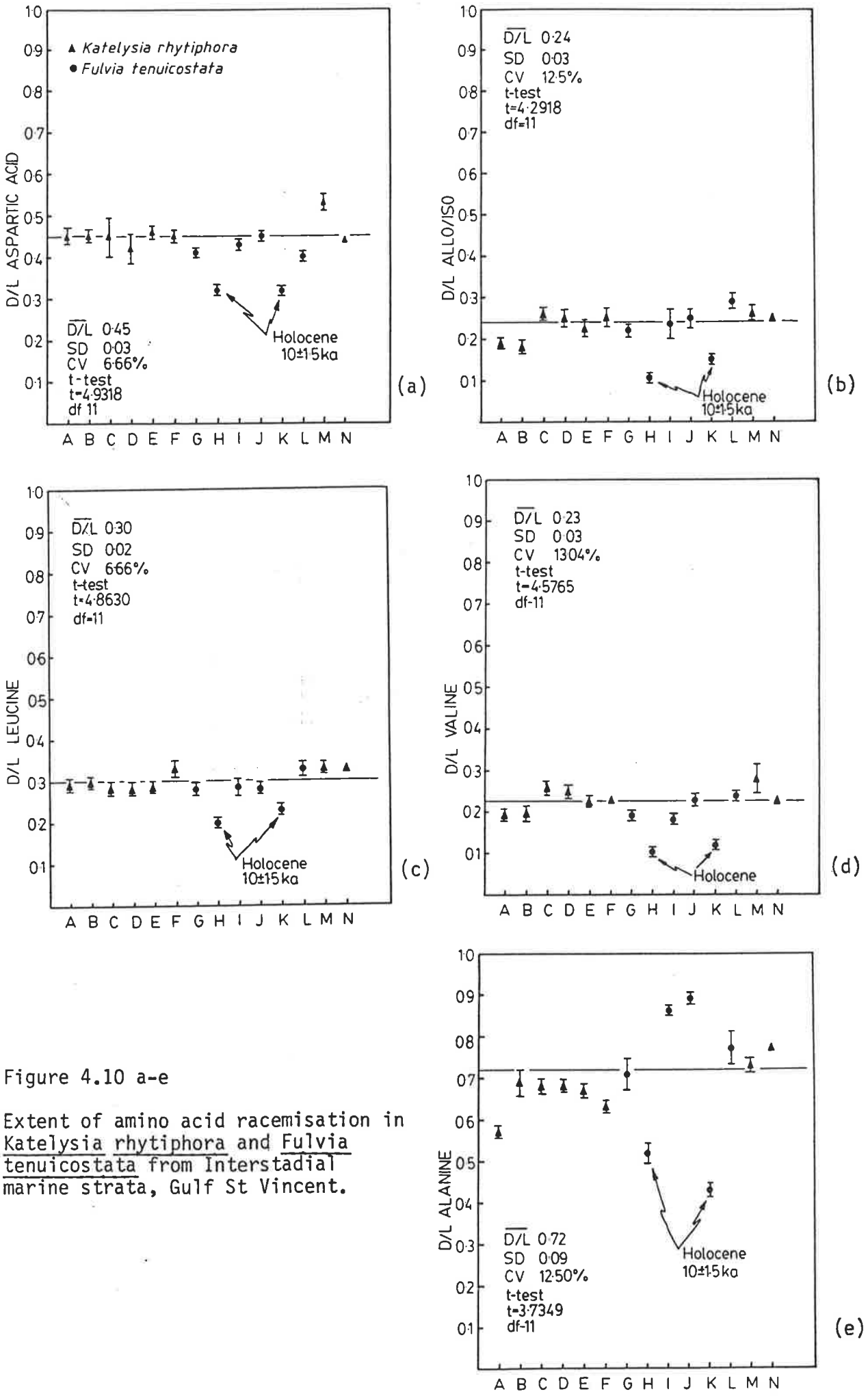


Figure 4.10 a-e

Extent of amino acid racemisation in Katelysia rhytiphora and Fulvia tenuicostata from Interstadial marine strata, Gulf St Vincent.

The majority of the sediments however, in cores SV-4 and SV-5 are of Pleistocene age as demonstrated by results of radiocarbon and amino acid racemisation dating.

Results are reported for the amino acids, alanine (ALA), isoleucine (ALLO/ISO), leucine (LEU) and valine (VAL) (see also Appendix Table 4.3). Analyses were made predominantly, for the 'total acid hydrolysate', although results for free amino acids are presented in Table 4.11. The relative extent of racemisation of these amino acids is in accord with those previously reported for carbonate matrices (Dungworth, 1976). Coefficients of variation for amino acid D/L ratios in specimens of Katelysia rhytiphora are provided in Table 4.10. Molluscs of Last Interglacial age and a radiocarbon calibrated Holocene specimen are also included in order to serve as a basis for calibration of the racemisation data (Table 4.9). Results from these cores suggest little intergeneric differences in racemisation rates for the molluscs Katelysia rhytiphora and Fulvia tenuicostata (Tables 4.12a, 4.13 and Figures 4.10a-e). The only exception is alanine, where there is a tendency for D/L values to be greater in Fulvia tenuicostata.

Clearly by analogy with the calibration samples, the sediments representing the majority of cores SV-4 and SV-5 are younger than Last Interglacial but older than Holocene (Table 4.9). Based on these data, a relative age of latest Pleistocene was inferred for these sediments, for the D/L ratios tend to be closer to Holocene than Last Interglacial values. In accordance with equation 3.1 a minimum of 3 molluscs were required to adequately characterise the age of these sediments. This applied for all amino acids studied with the exception of alanine which required 20 specimens because of the higher standard deviation (Figure 4.10e).

Systematic downcore increase in amino acid D/L ratios, consistent with increasing age was not evident within the Pleistocene sediments in cores SV-4 and SV-5 (Tables 4.12a and 4.13). Although a preliminary

Table 4.9 Extent of amino acid racemisation in Katelysia rhytiphora from marine sediments of late Quaternary age, South Australia

Age kaBP	Number of specimens analysed	Amino acid D/L ratio ('total acid hydrolysate') LEU	VAL	ALLO/ISO	ALA
7* (Holocene)	(1)	0.16	0.08	0.12	0.23
SV-5 interstadial marine strata isotope stage 3	(8)	0.29	0.24	0.23	0.67
120 Last Interglacial	(4)	0.51	0.32	0.47	0.73

* Calendric age calculated from an environmentally corrected C-14 age (bp)

Table 4.10 Intershell D/L ratio variation in Katelysia rhytiphora from interstadial marine strata, Gulf St Vincent

Amino acid	Number of individuals analysed	Mean D/L ratio and standard deviation (±1σ) ('total acid hydrolysate')	Coefficient of variation
aspartic acid	8	0.46±0.03	6.52%
leucine	8	0.29±0.03	10.34%
isoleucine	8	0.23±0.03	13.04%
valine	8	0.24±0.03	12.50%
alanine	8	0.67±0.05	7.46%

Table 4.11 Comparison of the extent of racemisation evident in the 'total acid hydrolysate' with free amino acids in Katelysia and Ostrea from Gulf St Vincent Core SV#4

Species/core location	Fraction total (T) free (F)	Amino acid D/L ratio			
		ALA	VAL	ALLO/ISO	LEU
Katelysia rhytiphora	(T)	0.74	0.28	0.26	0.33
Core SV#4 0.58 - 0.60 m	(F)	1.04	0.42	0.43	0.60
Ostrea angasi	(T)	0.78	0.34	0.49	0.49
Core SV#4 0.58 - 0.60 m	(F)	0.86	0.62	1.02	0.74

Table 4.12a Representative data of the extent of amino acid racemisation (epimerisation) in molluscs obtained from Gulf St Vincent Core SV-4

Species	Depth core (m)	Amino acid D/L ratio ('total acid hydrolysate') LEU	VAL	ALLO/ISO	Age
Katelysia rhytiphora	0.58-0.60	0.29 ±0.006	0.19 ±0.003	0.19 ±0.002	~30-40 ka
Fulvia tenuicostata	0.64	0.22 ±0.002	0.12 ±0.004	0.15 ±0.005	~30-40 ka
Ostrea angasi	0.58-0.60	0.49 ±0.003	0.34 ±0.002	0.49 ±0.009	C-14, $30,500^{+650}_{-600}$ yrs bp
Fulvia tenuicostata	2.47	0.28 ±0.003	0.19 ±0.003	0.22 ±0.005	~30-40 ka
Fulvia tenuicostata	2.77	0.33 ±0.01	0.24 ±0.005	0.30 ±0.004	~30-40 ka

Table 4.12b Extent of amino acid racemisation in Callucina lacteola in Gulf St Vincent Core SV-1

Species	Depth core (m)	amino acid D/L ratio ('total acid hydrolysate') ALA	VAL	ALLO/ISO	LEU	ASP	Age
Callucina lacteola	0.34	0.24 ±0.002	0.11 ±0.005	0.15 ±0.002	0.24 ±0.003	0.36 ±0.004	~40 kaBP

Table 4.13 Extent of amino acid racemisation in molluscs obtained from Gulf St Vincent Core SV-5

Species	Depth in core (m)	Amino acid D/L ratio ('total acid hydrolysate') LEU	VAL	ALLO/ISO	Age
Circomphalus disjecta	0.25-0.27	0.11	0.05	0.05	4 ka BP Holocene
Katelysia rhytiphora	0.54	0.28	0.23	0.23	30-40 kaBP Late Pleistocene
K. rhytiphora	1.38-1.40	0.29	0.25	0.25	-----
Fulvia tenuicostata	2.00	0.28	0.23	0.26	-----
F. tenuicostata	2.19	0.28	0.18	0.24	-----
K. rhytiphora	3.50	0.28	0.26	0.26	-----
K. rhytiphora	3.69	0.29	0.20	0.18	-----

quantitative age may be assigned to these sediments, discrimination of age variation based on amino acid racemisation data alone is not yet possible within the late Pleistocene marine unit. The general concordance of D/L ratios for the interstadial marine strata however, is very good with coefficients of variation for intershell D/L ratio variation ranging from 6.5 to 13.0%. These values are low considering that analytical variation is generally in the order of 3% and that intrashell D/L ratio variation frequently attains values slightly higher.

In contrast radiocarbon dating of these sediments suggested that two chronostratigraphic units may be identified within the late Pleistocene sequence. These include sediments deposited between 45 ka (the limit of conventional radiocarbon), to 40 ka and 35 to 30 ka. The significance of these dates is amplified later.

Despite earlier suggestions to the contrary (Thom, 1973) recent investigations (Aharon, 1983; Chappell, 1983) have provided stratigraphic evidence supporting the validity of radiocarbon ages for interstadial marine sequences. Thom (1973) however, listed several criteria to be considered when assessing the reliability of radiocarbon dates falling within the age range of 25-40 kaBP. These included:

(1) geochemical analyses to demonstrate that little or no sample contamination has occurred (e.g. contamination induced by recrystallization from metastable aragonite to calcite, with the incorporation of carbonate from external sources);

(2) corroboration of single dates with sample replicates;

(3) clear identification of the stratigraphic context of the fossiliferous materials and an assessment of former depositional environments.

These considerations were made in the present study for the Gulf St Vincent materials. X-ray diffraction analyses of the radiocarbon and amino acid dated Katelysia shells indicated little recrystallization had occurred

(i.e. <3%). In contrast, the oysters consisted of primary calcite (Ludbrook, 1984).

That the interstadial marine strata overall, have a reduced rather than oxidised character also suggested pedogenesis had not significantly affected these sediments when subaerially exposured during the last glacial maxima. The general lack of cementation of the calcite muds and the dC-13 values indicated minimal alteration by fresh water. As a surrogate test for this, dC-13 values reported for the radiocarbon dates were compared with the predicted range for marine carbonate (Gupta and Polach, 1985). None of the radiocarbon dates reported had anomalous dC-13 values, and these results did not deviate significantly from the suggested average dC-13 values for marine carbonates (Gupta and Polach, 1985).

By rearranging the integrated rate expression for the amino acid racemisation reaction (eqn 2.2), with time as the subject, it is possible to establish quantitative ages of fossils (Schroeder and Bada, 1976; Williams and Smith, 1977). The value of k was calculated using the expression derived by Mitterer (1975) (eqn 2.6). Quantitative age assessments were made based on the extent of leucine and valine racemisation and isoleucine epimerisation in Katelysia rhytiphora.

The calibrated method was used to calculate the age of the interstadial marine strata using amino acid data. Using an average radiocarbon age of approximately 40 kaBP for the interstadial marine strata in cores SV-4 and SV-5, an 'Effective Quaternary Temperature' (EQT) (Wehmiller, 1982) of 13.95°C was derived from the oxygen isotope record (Prell et al., 1980). In this approach, the marine oxygen isotope record of Shackleton and Opdyke (1973) was used to establish the timing of climatic change, but the intensity of climatic change was established, based on data from southern Australia (Prell et al., 1980). Amino acid D/L

ratios for leucine, valine and isoleucine, indicated a mean age of 27,000±4,000 yrs BP for the interstadial marine strata. The error term allows for a temperature uncertainty of 1°C in the calculated Effective Quaternary Temperature History. A greater uncertainty would result in a larger error term.

As this age assessment used the integrated rate expression, which is based on linear racemisation kinetics, the age reported represents a minimum age. The non-linear nature of racemisation kinetics however, was outlined in Chapter 2. Wehmiller (1982,1984b) noted the "non-linear" nature of racemisation kinetics in the mollusc genera Protothaca and Saxidomus. Accordingly, the early portion of the racemisation rate curve is defined by an essentially linear component to a leucine D/L value of approximately 0.2. This is followed by a progressive decrease in slope, a section of the curve referred to as the transition zone (Figure 2.3), which continues to a D/L ratio of approximately 0.35 for leucine. After this, the reaction is represented by a second broadly linear component with the slope approximately 10x less than the first linear component (Wehmiller, 1984b). Wehmiller discussed the difficulty of obtaining amino acid racemisation derived ages for fossils occurring within the transition zone.

The under estimation in age for the interstadial marine strata based on the racemisation data is attributed to the D/L ratios falling within the early portion of the transition zone (i.e. divergence of racemisation from essentially-linear reversible first order kinetics) (Figure 4.11). That the D/L ratios are generally closer to 0.2, the approximate onset of the transition zone, than 0.35, the approximate termination of the transition zone, suggests the results reported herein, fall within the early portion of the transition zone. This is in part supported by the fact that the amino acid estimated age does not fall below the radiocarbon derived age by a larger order of magnitude.

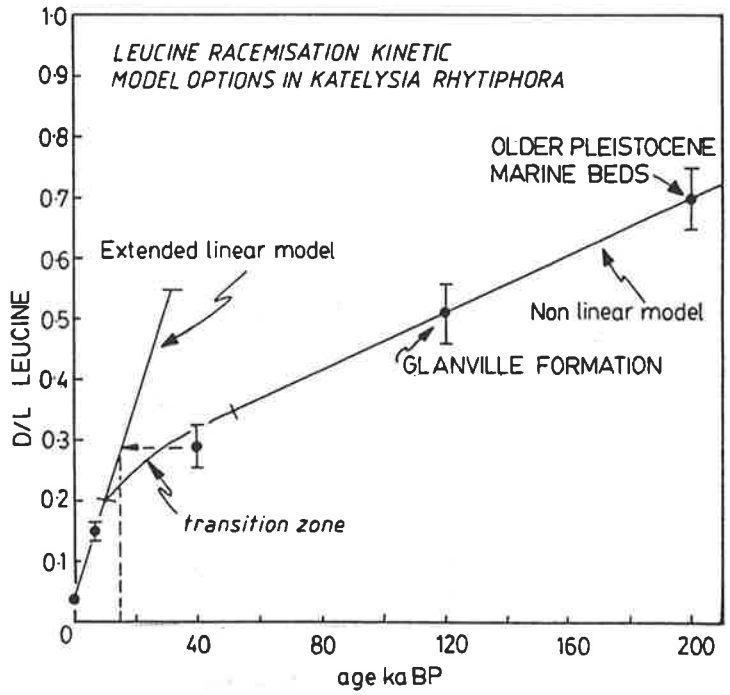


Figure 4.11 Schematic representation of amino acid D/L ratio data for leucine ('total acid hydrolysate') for a range of marine sediments from South Australia, demonstrating the departure of D/L ratios from extended linear kinetics in Katelysia rhytiphora of interstadial age (40 ka BP; oxygen isotope stage 3).

Indirect evidence in support of latest Pleistocene age for the strata is based on the absence of the Late Pleistocene (Last Interglacial) indicator species for South Australian coastal sediments, Marginopora vertebralis, Anadara trapezia and Pinctada. Evidence from northern Spencer gulf points to their localised extinction following the Last Interglacial, for they do not appear in younger sediments unless reworked (Gostin et al., 1981; Belperio and Murray-Wallace, 1984). Although subsequent interstadials penetrated northern Spencer Gulf (Belperio et al., 1984; Hails et al., 1984a,b), these fauna which favour warmer climatic conditions did not return during these cooler interstadials. However, some caution should be exercised with this inference, as species absence can provide an unreliable means of age assessment.

4.6.1 Interstadial Marine Strata: Geothermometry

A mean ambient diagenetic temperature history was calculated from the amino acid racemisation data, by rearranging the integrated rate expression (eqn 2.2) with temperature as the subject. Based on the extent of racemisation of the amino acids reported, a mean ambient diagenetic temperature history of 12°C was derived, representing the mean temperature the molluscs in the interstadial marine strata have experienced during the last 40 kaBP. This temperature agrees favourably with that extrapolated from oxygen-isotope data of 14°C (Schackleton and Opdyke, 1973; Prell et al., 1980).

4.6.2 Gulf St Vincent: Interstadial Marine Strata: Discussion

The combination of lithostratigraphic relationships and results from radiocarbon and amino acid racemisation dating, provides incontrovertible

evidence that the majority of sediments in cores SV-4 and SV-5 were deposited during the latest Pleistocene (Stage 3 of the marine oxygen isotope record). Few studies of sediments of this age have been made in Australian coastal settings.

Results from radiocarbon and amino acid racemisation dating support the following sea level history for the central part of Gulf St Vincent. Before 45 kaBP sea level was in excess of 40 m below contemporary mean sea level and was in excess of 37 m some 35 kaBP. By 30 kaBP sea level in Gulf St Vincent had reached -41 m but had not reached -38 m as indicated by age-depth relationships of the sediments in cores SV-4 and SV-5. The radiocarbon and lithological evidence suggests continuous sedimentation from 30 to 45 kaBP, with the exception of a possible break between 40-45 kaBP, reflected by the partially oxidised character of the sediments in the interval between the latter dates. Subsequently, the post-glacial rise in sea level resulted in the deposition of sediments that preserve a thin albeit more complete Holocene chronostratigraphy, than previously found in other South Australian neritic settings. This is attested by an amino acid racemisation derived age of 10 kaBP for Fulvia tenuicostata from core SV-4. This age fortuitously coincides with the Pleistocene/Holocene boundary. Allowing for variation due to tectonics and hydroisostasy, these sea levels were broadly coincident with levels reported from other coastal settings (Aharon, 1983; Chappell, 1983) (Figure 4.12).

The combination of geothermometry and relative and quantitative age assessments provides a better understanding of the nature and timing of the onset of the transition zone in the "non-linear" racemisation kinetic model. Historically, the modelling and more quantitative discussions of the transition zone has been a neglected area of research. This is unfortunate in view of the critical importance of this feature for quantitative age assessments of fossils younger than the Last Interglacial.

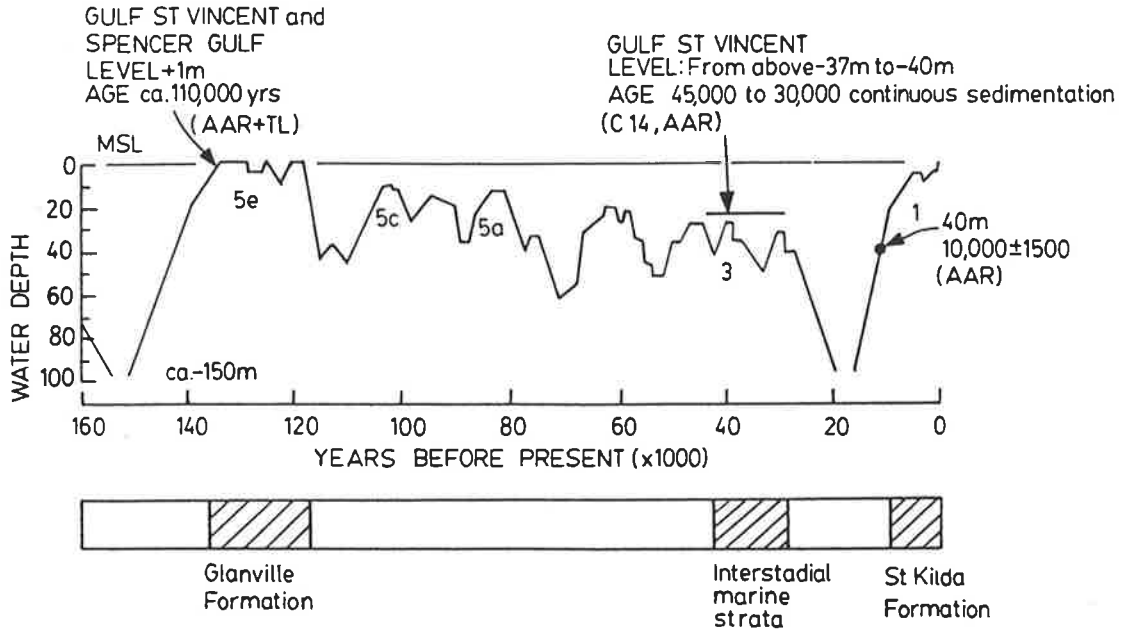


Figure 4.12 Sea level change over the last 160 ka. Results from Gulf St Vincent and Spencer Gulf are compared with results of Chappell (1983) for the Huon Peninsula.

4.7 HOLOCENE STUDIES

4.7.1 The St Kilda Formation: Description

The St Kilda Formation was described by Firman (1966,1967) in reference to shelly sands deposited in response to a reported 1.5 m higher stand of Holocene sea level (Daily et al., 1976). However, Belperio et al., (1983) critically reviewed the evidence for reported higher Holocene sea levels in South Australia, and concluded that there was little evidence in support of higher Holocene sea levels in the Adelaide region. In recent years the term St Kilda Formation has been loosely used in reference to unconsolidated marginal marine sediments of Holocene age. Daily et al., (1976) reported radiocarbon ages on shells from the St Kilda Formation of 3800±500 yrs BP and 1120±75 yrs BP, for the base and top of the unit respectively. However, no details were provided concerning the stratigraphic context of the dated materials, except that the younger date was from a beach ridge. Caution should be exercised however with the dating and interpretation of data from beach ridges as they rate poorly as palaeosea-level indicators. On this basis, Firman (1966,1967) had previously suggested that sediments younger than 1120±75 yrs BP were excluded from the St Kilda Formation.

Cann and Gostin (1985) redefined the St Kilda Formation as all subtidal, intertidal and supratidal sediments of Holocene age. As contemporary sedimentary processes could not readily be distinguished from those operative during the Middle-Holocene, they considered that upper surfaces of the formation are not confined, but rather surfaces of active sedimentation (Cann and Gostin, 1985). The St Kilda Formation represents a time-equivalent to the Germein Bay Formation of northern Spencer Gulf (Hails et al., 1984a). However it is likely that the term St Kilda Formation will take precedence in future investigations.

Equivalents of the St Kilda Formation occur extensively around the South Australian coastline (Figure 4.13). In the South Australian gulfs region, the St Kilda Formation and equivalents are best developed along the eastern coastline of the gulfs. Here they are represented by a complex association of intertidal and supratidal sediments that display a well defined sediment-organism zonation (Belperio et al., 1986). In contrast, along the open ocean coastline of Eyre Peninsula, the St Kilda Formation is restricted to numerous coastal embayments, created by postglacial drowning of an undulating, calcreted Pleistocene topography.

4.7.2 St Kilda Formation: Amino Acid Racemisation Analyses

As part of an assessment of the extent of racemisation in Holocene molluscan fauna, samples were obtained from the St Kilda Formation from Smoky Bay and Tourville Bay on the west coast of South Australia (Figure 4.4). This study is significant, for it presents a larger number of radiocarbon calibrated Holocene samples than previously reported in the literature. The sample localities both have mean annual air temperatures of approximately 16.9°C. Shell specimens were obtained mainly from cores although a few near-surface samples were collected from the crests of beach ridges (Table 4.14). The latter were obtained to assess the influence an elevated diagenetic temperature history has on age assessments using amino acid racemisation. The shells were radiocarbon dated and a small amount of each sample was retained for amino acid racemisation analyses. Although different shells were analysed by radiocarbon and amino acid racemisation it is assumed that the specimens from the same sample are of equivalent age. This is generally a safe assumption for shells collected in close proximity from the same horizon away from unconformities.

Mollusc species analysed included Fulvia tenuicostata, Ostrea angasi, Katelysia peronii, Katelysia rhytiphora, Katelysia scalarina and Anapella

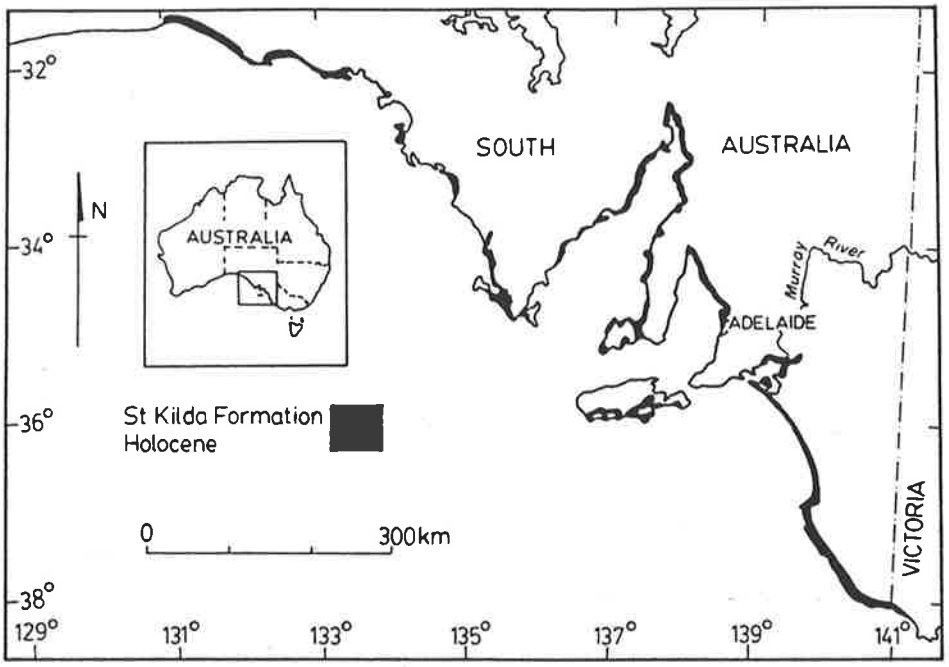


Figure 4.13 Demonstrated geographical extent of the Holocene St Kilda Formation in the sense of Cann and Gostin (1985). (modified after Ludbrook, 1984).

cycladea. All specimens were very well preserved, and were either articulated or disarticulated whole shells. The shells did not have surface encrustations, a feature often present on Pleistocene material. Where possible hinges were analysed.

Results of amino acid analyses for the 'total acid hydrolysate' are listed in Table 4.14. Results are reported for the amino acids alanine, valine, isoleucine, leucine, proline, aspartic acid, glutamic acid and phenylalanine and graphical plots for each amino acid are provided (Figure 4.14a-g). The relative intrageneric rates of racemisation are in accord with those reported for carbonate fossils and aqueous solution (Dungworth, 1976; Schroeder and Bada, 1976; Lajoie et al., 1980) (Table 4.15).

In broad view, the data suggest three groups of amino acids may be recognised in Holocene fossils, based on their racemisation rates (Figure 4.15). These include a slow group represented by valine, isoleucine and glutamic acid, an intermediate group represented by proline and leucine, and a fast racemising group that includes aspartic acid and alanine. Given reliable data, aspartic acid and alanine may provide the greatest precision (age resolving ability) in Holocene studies because of their relatively fast racemisation rates.

In Figures 4.14a-g, D/L ratios were plotted against sidereal years to assess how systematically, D/L ratios increase with increasing fossil age. Because of the reported divergence of radiocarbon years (bp) from calendar years (BP), marine environmentally corrected radiocarbon years were converted to calendar years using tables of Klein et al., (1982). This is especially important for samples in the order of 6,000 radiocarbon years, where a departure of approximately 800 years from the calendar age of 6800 yrs (BP) is evident. Linear regression analyses were made for each amino acid, and involved regression of samples ranging from 8,000 yrs BP to modern (zero-age).

Table 4.14 Extent of amino acid racemisation in Holocene radiocarbon calibrated mollusc samples, West Coast of South Australia

Sample	Depth (m)	$\delta^{13}C$	dC14	DC14	CSIRO Lab Code	mollusc species	Env. corrected age (bp)	Calendric age (BP)	amino acid D/L ratio ('total acid hydrolysate') ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
Core 64	3.38-3.48	+0.22	-449.9 ±8.3	-477.7 ±7.9	FTCOS64A1	Fulvia tenuicostata	4770 ±140	5470 ±175	0.09 ±0.007	0.08 ±0.01	0.10 ±0.01	0.15 ±0.002	0.26 ±0.002	0.22 ±0.008	0.28 ±0.06	0.13 ±0.01
Core 77	1.76-1.80	+0.14	-434.1 ±6.9	-462.5 ±6.5	OST77A1	Ostrea angasi	4540 ±100	5200 ±140	0.43 ±0.01	0.24 ±0.01	0.48 ±0.001	0.38 ±0.005	0.47 ±0.01	0.28 ±0.01	-	-
Sample 69	near surface	+1.20	-310.8 ±7.4	-346.8 ±7.0	KPER01F1	Katelysia peronii	2970 ±90	3100 ±140	0.14 ±0.01	0.07 ±0.01	0.09 ±0.002	0.13 ±0.01	0.11 ±0.01	0.24	-	0.13 ±0.02
Core 70	1.20-1.30	+0.38	-349.8 ±9.1	-382.8 ±8.6	FTCOS01F1	Fulvia tenuicostata	3430 ±120	3740 ±180	0.15 ±0.01	0.03 ±0.01	0.05 ±0.01	0.11 ±0.01	0.16 ±0.01	0.17	0.14 ±0.01	0.09 ±0.001
Core 81	1.35-1.45	+0.48	-436.2 ±7.4	-464.9 ±7.0	KPER03H1	Katelysia peronii	4580 ±150	5295 ±210	0.20 ±0.002	0.08 ±0.002	0.11 ±0.004	0.16 ±0.004	0.12	0.24	0.33	0.08 ±0.006
Core 81	1.82-1.88	+0.86	-555.5 ±9.0	-578.5 ±8.5	KRHY03H1	Katelysia rhytiphora	6490 ±170	7370 ±180	0.23 ±0.009	0.08 ±0.002	0.12 ±0.002	0.16 ±0.02	0.16 ±0.06	0.23	0.27	0.10 ±0.004
Sample 72	near surface	+1.59	-46.6 ±9.7	-97.3 ±9.2	KSCAL04H1	Katelysia scalarina	370 ±80	422 ±80	0.07 ±0.0006	0.05 ±0.001	0.07 ±0.008	0.12 ±0.003	0.10 ±0.009	0.11 ±0.002		0.06 ±0.005
Core 69	4.74-4.80	-12.35	-494.9 ±10.8	-507.6 ±10.5	FTCOS01F2	Fulvia tenuicostata	5240 ±180	6000 ±200	0.24	0.08	0.11	0.13				
Sample 70	surface sample	-0.56	-55.1 ±9.6	-101.3 ±9.1	KSCAL05H1	Katelysia scalarina	410 ±80	450 ±80	0.18 ±0.007	0.09 ±0.004	0.12 ±0.006	0.14 ±0.01	0.11			0.13 ±0.002
Core 70	1.20-1.30	+0.38	-349.8 ±9.1	-382.8 ±8.6	KPER03H2	Katelysia peronii	3430 ±120	3740 ±180	0.20 ±0.004	0.08 ±0.001	0.12 ±0.001	0.16 ±0.004	0.10			0.09 ±0.003
Sample 69	surface sample	+1.20	-310.8 ±7.4	-346.8 ±7.0	KSCAL01F1	Katelysia scalarina	2970 ±90	3100 ±140	0.19 ±0.001	0.08 ±0.001	0.09 ±0.001	0.22 ±0.001	0.14 ±0.05	0.26		0.13 ±0.005
Sample 70	Surface sample	-0.56	-55.1 ±9.6	-101.3 ±9.1	KPER03H3	Katelysia peronii	410 ±80	450 ±80	0.22 ±0.002	0.10 ±0.01	0.09 ±0.002	0.26 ±0.003	0.14 ±0.01	0.31 ±0.01		0.15 ±0.005
Core 81	4.88-4.96	-15.27	-566.0 ±16.2	-574.5 ±15.9	KSCAL08A1	Katelysia scalarina	6410 ±310	7240 ±310	0.22 ±0.003	0.07 ±0.005	0.09 ±0.001	0.24 ±0.01	0.18 ±0.001	0.25 ±0.003		0.14 ±0.001
Sample 83	near surface	+0.85	-209.9 ±10.1	-250.8 ±9.6	ACYCL01A1	Anapella cycladea	1870 ±110	1650 ±110	0.19 ±0.008	0.09 ±0.002	0.12 ±0.004	0.17 ±0.03	0.19 ±0.03	0.23	0.27 ±0.02	0.14 ±0.00

Table 4.15 Intrageneric apparent relative rates of racemisation in various molluscan fauna from Quaternary marine sediments, South Australia

Katelysia scalarina (Holocene)	ASP>ALA>LEU>PRO>GLU>ALLO/ISO>VAL
Katelysia rhytiphora (Holocene)	ASP>ALA>PRO>LEU>ALLO/ISO>GLU>VAL
Katelysia peronii (Holocene)	ASP>ALA>LEU>PRO>ALLO/ISO>GLU>VAL
Fulvia tenuicostata (Holocene)	ASP>ALA≧PRO>LEU>GLU>ALLO/ISO>VAL
Anapella cycladea (Holocene)	ASP>ALA≧PRO>LEU>GLU>ALLO/ISO>VAL
Anadara trapezia (Pleistocene)	ALA>ASP>PHE>LEU>ALLO/ISO>GLU>VAL
Marginopora vertebralis (Pleistocene)	ASP>ALA>PRO>GLU>LEU>ALLO/ISO>VAL
Katelysia rhytiphora (Pleistocene)	ALA>ASP>LEU>ALLO/ISO>GLU>VAL

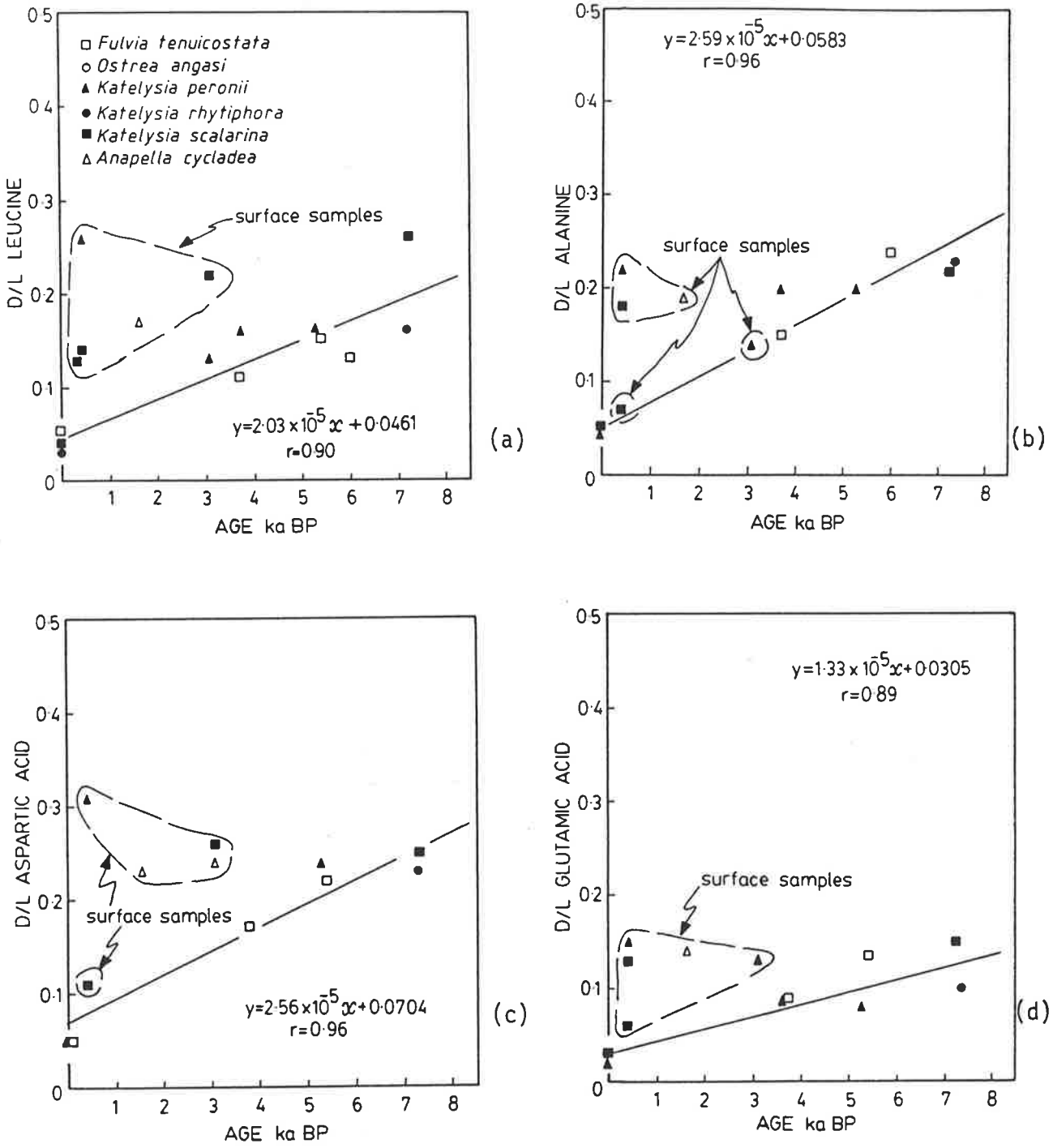
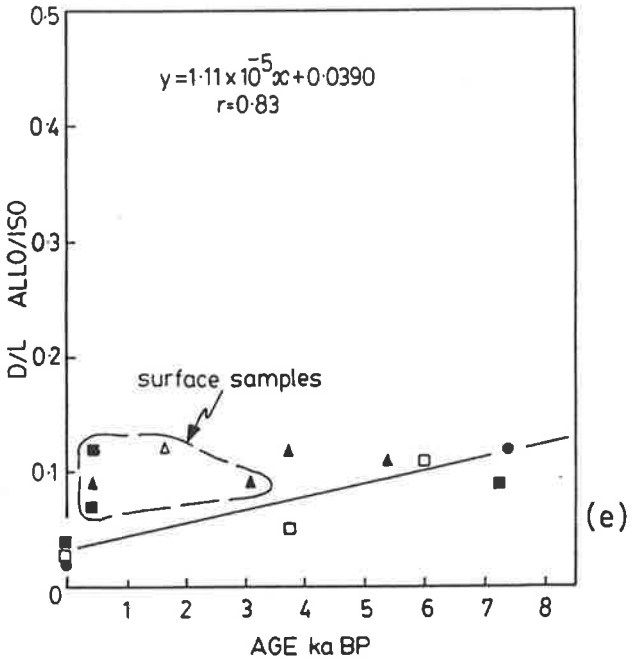
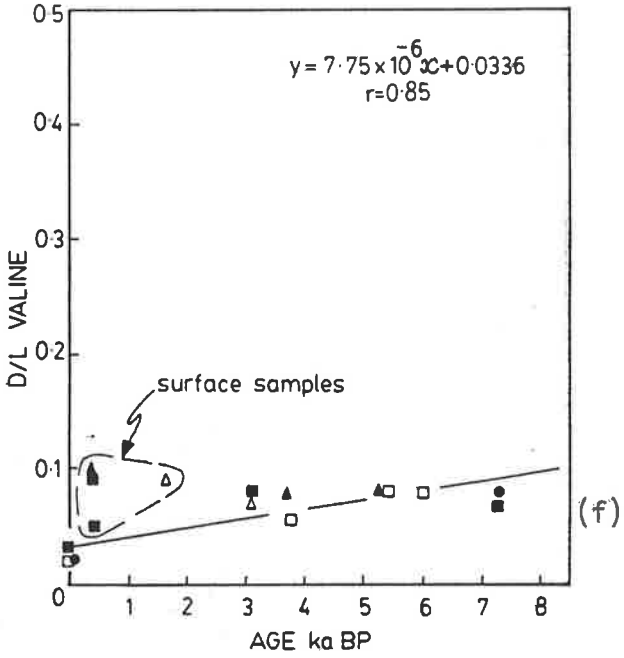


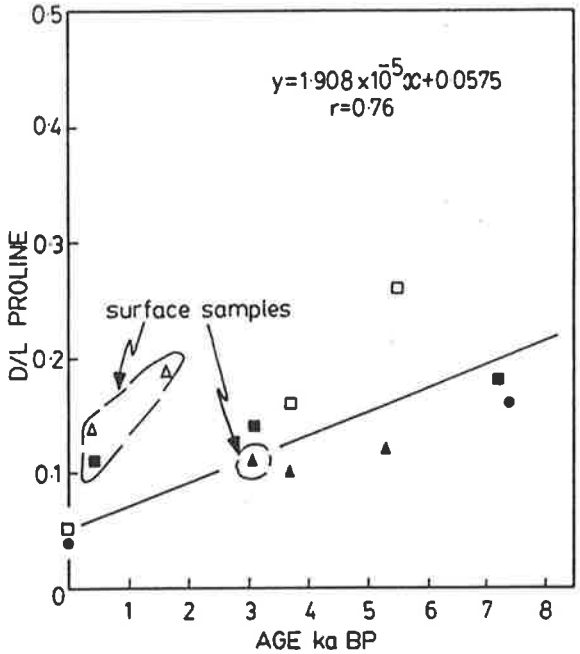
Figure 4.14 a-g Summary plots of the extent of racemisation in Holocene molluscan fossils from the St Kilda Formation. Artificially high D/L ratios are evident for the surface samples.



(e)



(f)



(g)

Figure 4.14 (continued)

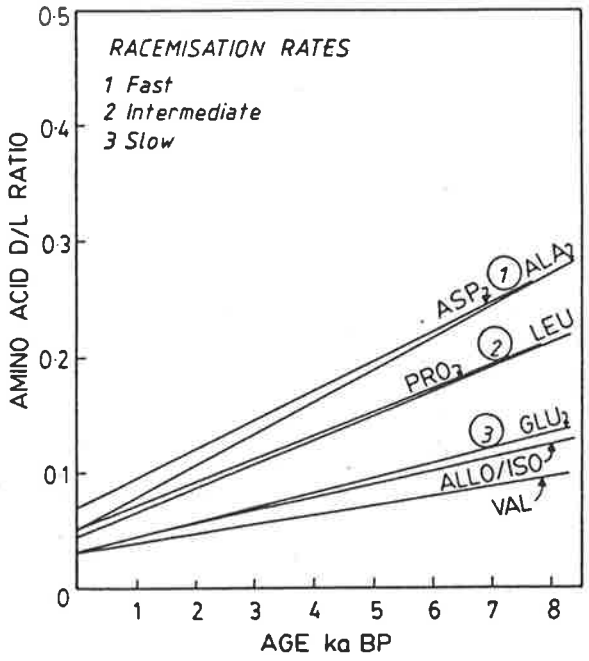


Figure 4.15 Summary plot illustrating different relative racemisation rates in Holocene molluscan fossils.

Surface samples were not incorporated in the regression analyses as the influence of higher diagenetic temperature histories on racemisation rates is clearly evident (Figures 4.14a-g). The correlation coefficient is indicated in each graph. The relatively high correlation coefficients are due to the inclusion of modern values in the regression analyses.

Several factors may be responsible for the observed scatter in the regressed data. These include analytical variation, the genus specific nature of molluscan racemisation, intrashell D/L ratio variation and the possibility that the samples analysed by amino acid racemisation are of a different age to the radiocarbon dated specimens. Nevertheless, the data consistently show a slight, but progressive increase in D/L ratios with increasing fossil age. Although these differences appear small, they are statistically significant when their ages are considered. For example, aspartic acid D/L ratios for modern and 7,400 yr mollusc specimens are approximately 0.05 and 0.25 respectively. These differences are consistent with the rapid initial rate of racemisation predicted by the non-linear racemisation kinetic model (Wehmiller, 1984b). In contrast, D/L ratio data presented earlier in this Chapter, for molluscs of Penultimate Interglacial (Older Pleistocene marine beds), and Last Interglacial age (Glanville Formation), indicate comparable differences in D/L ratios for aspartic acid but for a time interval of some 100 ka.

The surface samples consistently plot above the regression lines. In particular, the surface samples plot significantly above the regression lines for leucine, proline, alanine, glutamic acid and aspartic acid. In contrast, the results for valine and isoleucine, two of the slower racemising (epimerising) amino acids, plot closer to their regression lines, suggesting these amino acids may be less sensitive to surface temperature effects during diagenesis than other amino acids.

Clearly the scatter in the regressed data indicate that amino acid racemisation results for the 'total acid hydrolysate' will only obtain approximate ages for radiocarbon calibrated Holocene specimens for some amino acids. In particular, this would apply to some of the slower racemising amino acids. This is illustrated for example in the leucine D/L ratios for Fulvia tenuicostata. The leucine D/L ratio in the 5,400 yr specimen is actually higher (by 0.02) than for the 6,000 yr specimen. This standard deviation exceeds that for analytical variation for Holocene samples.

Based on the radiocarbon calibrated D/L ratio data for a Katelysia scalarina specimen with a calendric age of 7,400 yrs BP, an error term of ±0.01 for amino acid D/L ratios (which represents a high level of analytical error for a Holocene specimen), is equivalent to approximately 600 yrs. This in association with other sources of variation outlined in Chapter 3 indicate that a large margin of error should be taken into account for when applying amino acid racemisation in quantitative age assessments.

The composite plot of the racemisation rate curves (Figure 4.15) suggests the possibility that the rates of racemisation for aspartic acid and alanine cross-over with time and that alanine begins to racemise faster than aspartic acid. This phenomenon was also evident with proline and leucine. Similar changes in relative racemisation rates were noted both at the intra- and intergeneric level by Lajoie et al., (1980). This issue is further explored in Chapter 6.

4.8 HOLOCENE GEOTHERMOMETRY

Previous studies (Schroeder and Bada, 1973; Miller and Hopkins, 1980) have applied amino acid D/L ratio data in assessments of palaeotemperature histories. In addition, palaeogeothermal gradients based on the extent of racemisation in deep sea sediments have also been established (Bada and Man, 1980; Katz et al., 1979). However in a critical review Williams and Smith (1977) outlined the large errors implicit in these studies and suggested a cautionary approach. The majority of these studies have been undertaken in the northern hemisphere on fossiliferous materials older than the last glacial which have experienced pronounced fluctuations in their diagenetic temperature histories. The assumption held in these studies however was that the fauna analysed had experienced glacial and postglacial temperatures for equivalent lengths of time, and because of this a palaeotemperautre history could be easily defined (Bada, 1972; Bada and Helfman, 1975; Bada and Schroeder, 1976; and Bada, 1981).

In this thesis the potential of amino acid geothermometry as a method of assessing the reliability of amino acid derived ages is presented. Few studies have explored Holocene materials where climatic change has been minimal. The rationale behind this approach suggests that as minor long-term temperature fluctuations have characterised the Holocene for southern Australia, the mean diagenetic temperature history calculated from the radiocarbon calibrated molluscs should closely agree with contemporary mean annual temperatures. If these results do closely agree, then they increase the validity of palaeotemperature assessments for older materials, provided kinetic and analytical complications can be accounted for.

To test this hypothesis molluscs were obtained from cores from Smoky Bay, situated on the west coast of South Australia. In addition, two surface samples from beach ridges from the same locality were also

analysed to assess the influence an elevated diagenetic temperature history has on amino acid racemisation geothermometry. The contemporary mean annual air temperature at Smoky Bay is approximately 16.9°C.

Molluscs analysed included Katelysia peronii, Katelysia rhytiphora, Katelysia scalarina, and Fulvia tenuicostata. Analyses were made for the 'total acid hydrolysate', and D/L ratios were compared with calendric ages (BP) that had been converted from marine environmentally corrected radiocarbon years (bp) (Klein et al., 1982). By rearranging the integrated rate expression for racemisation (eqn 2.2) with temperature as the subject, it is possible to determine an average diagenetic temperature, fauna have experienced since death (Williams and Smith, 1977). The following equation was used in this study to calculate palaeotemperatures:

$$\text{Temp} = \frac{6417}{17.29 - \log\left[\dfrac{\text{Ln}\left(\frac{1+D/L}{1-D/L}\right) - \text{Ln}\left(\frac{1+D/L}{1-D/L}\right)_{t=0}}{2 \times \text{age}}\right]} \qquad \text{eqn 4.1}$$

where Temp is the absolute temperature (°K) and the constants were derived from the empirical rate constant expression of Mitterer (1975) (eqn 2.6).

Results of palaeotemperature calculations are provided in Table 4.16. Several assumptions were implicit in these palaeotemperature estimations. These included:

- essentially linear racemisation kinetics applied for the Holocene specimens as demonstrated in section 4.7.2
- based on the marine oxygen isotope record, little temperature change has occurred during the Holocene in southern Australia (Prell et al., 1980)
- the age of the shells studied by amino acid racemisation were the same as the calibration samples.

Table 4.16 Amino acid racemisation geothermometry on radiocarbon calibrated Holocene molluscs, Smoky Bay, west coast of South Australia

Species	Calendric age BP	Depth of burial (m)	Contemporary M.A.T. (°C)	amino acid inferred mean diagenetic temperature (°C)					average diagenetic temperature based on all amino acids (°C)
				VAL	ALLO /ISO	LEU	ASP	GLU	
Katelysia peronii (KPER03H3)	450±80	surface sample	16.9	31.5	30.8	38.4	39.9	34.7	35.1
Katelysia scalarina (KSCAL01F1)	3100±140	surface sample	16.9	18.3	18.1	25.1	26.1	21.7	21.8
Katelysia rhytiphora (KRHY03H1)	7370±180	Core 81 1.82-1.88	16.9	14.0	15.6	17.7	20.1	14.4	16.4
Katelysia peronii (KPER03H1)	5295±210	Core 81 1.35-1.45	16.9	15.2	17.1	19.6	22.1	15.3	17.8
Fulvia tenuicostata (FTCOS64A1)	5470±175	Core 64 3.38-3.48	16.9	15.3	16.3	19.0	21.3	18.0	18.0

D/L ratio data for these molluscs are listed in Table 4.14

In addition there is the question of how representative contemporary mean annual air temperature records are for sample localities. Generally such records represent only a small time interval since the incorporation of fossils in sediments as noted in archaeological studies by Bada and Helfman (1975).

Clearly the two Katelysia surface samples have experienced elevated diagenetic temperature histories. If age assessments were attempted based on the extent of racemisation in these fossils, the ages obtained would over estimate their 'true' age. In contrast, the amino acid determined diagenetic temperatures closely agreed with contemporary mean annual temperatures for the well buried core samples (Table 4.16). These data suggest that a change in mean annual temperature for the Smoky Bay region is not evident for the last 7,000 calendar years, an interpretation consistent with conventional wisdom (Prell et al., 1980).

4.9 THE PROBLEM OF REWORKING AND ITS SIGNIFICANCE IN QUATERNARY GEOCHRONOMETRY

Reworking of older fossiliferous material into younger sediments represents a significant problem in Quaternary studies. This is especially significant in investigations that require a high degree of precision and accuracy in quantitative age assessments. Frequently, assessments of the stratigraphic context of fossiliferous material to be dated are complicated by reworking. In the following discussion, the problem of reworking is highlighted by a recent controversy concerning the significance of the foraminifer Marginopora vertebralis as a Pliocene/Pleistocene indicator in South Australian coastal sediments (Bone, 1984; Belperio and Murray-Wallace, 1984). This case study demonstrates the usefulness of amino acid data in assessments of reworking.

Bone (1984) suggested that tests of Marginopora vertebralis found on an intertidal flat between Wardang Island and Goose Island (Figure 4.16) were of recent origin, and that this species may be extant within the adjacent waters. This hypothesis was based on the fresh and uncemented appearance of individual specimens, the $MgCO_3$ content of various samples, and on the apparent absence of outcropping (erosional) sources of older material. Several studies in northern Spencer Gulf (Belperio et al., 1984; Burne, 1982; Gostin et al., 1981; Hails et al., 1983) have demonstrated that reworking of older material is a significant process which must be considered, particularly where isotopic dating of the carbonate fraction of sediments is contemplated. One verified indicator of reworking is the presence of the bivalve Anadara trapezia in Holocene coastal sediments of South Australia, and a similar conclusion was assumed in the case of M. vertebralis (Belperio et al., 1984). Results from the present study indicate that the specimens of M. vertebralis found on the tidal flat between Wardang Island and Goose Island were derived from erosion of

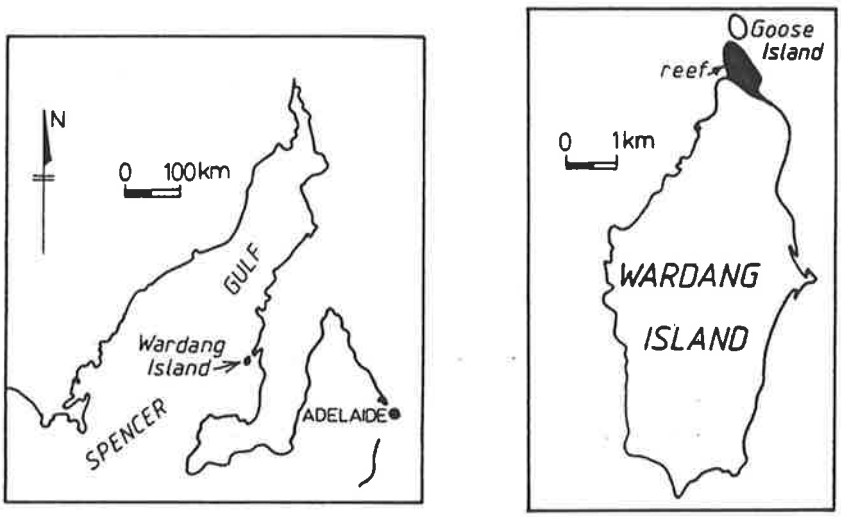


Figure 4.16 Wardang Island, location map.

underlying weakly cemented Pleistocene marine sediments. Field evidence and results from radiocarbon and amino acid racemisation dating are consistent with the interpretation that M. vertebralis represents a Pliocene/Pleistocene index fossil for South Australian coastal sediments.

The tidal flat connecting Goose Island with Wardang Island, erroneously referred by Bone (1984) as a reef, is developed on sediments having similar lithological and palaeontological aspects to the Glanville Formation neostratotype of the Adelaide region (Cann, 1978) as well as equivalents in northern Spencer Gulf and along the west coast of South Australia. These sediments are represented by semi-consolidated muddy skeletal grainstones and are partially karstified. They are exposed at high tide. Resting above these sediments is a thin 'modern' veneer (mostly <10 cm) of unconsolidated skeletal detritus. The origin of this veneer is due in part, to marine planation on the seaward-edge of the tidal flat. Carbonate detritus derived from the crumbling seaward 'reef' edge, including M. vertebralis is swept over the 'reef' surface and represents the predominant source of the sediment of the intertidal veneer. Thus the "modern" intertidal veneer is largely composed of reworked Pleistocene skeletal detritus (lithoskels). Additional evidence for reworking of Last Interglacial fauna and their incorporation into 'Holocene' tidal flat sediments is highlighted by the D/L ratios for a specimen of Katelysia scalarina obtained from these sediments (Table 4.17). Clearly these D/L values represent a Last Interglacial age by analogy with the values reported in Table 4.5 and contrast with the Holocene specimen also collected from the intertidal veneer.

To avoid problems due to homotaxis, age assessments of the sediments providing the source of M. vertebralis were undertaken. Radiocarbon dates were obtained for the 'reef' rock, and the intertidal sand (Table 4.18).

Table 4.17 Extent of amino acid racemisation in specimens of Katelysia scalarina found loose on the tidal flat between Goose Island and Wardang Island

Amino acid D/L ratios ('total acid hydrolysate')							Geological Age
ALA	VAL	ALLO/ISO	LEU	PRO	ASP	GLU	
0.09 ±0.02	0.06	—	0.09 ±0.01	0.14	0.24	0.09 ±0.02	Holocene
0.79 ±0.008	0.40 ±0.02	0.43 ±0.004	0.32 ±0.02	0.57 ±0.01	0.66 ±0.01	0.54 ±0.04	Late-Pleistocene (reworked)

Lithostratigraphic and biostratigraphic evidence, supported a preliminary correlation of the 'reef' rock with the Last Interglacial Glanville Formation. It was therefore anticipated that this sample would be well beyond the range of conventional radiocarbon methods, resulting in 'dead carbon' being reported. However, a finite, albeit 'apparent' age of $30,800^{+750}_{-700}$ yrs BP was obtained (Table 4.18). This age was attributed to the incorporation of younger carbon. In contrast, the 'modern' intertidal sand, based on radiocarbon was dated at 6290±90 yrs. However, this also represents an 'apparent' age resulting from the physical intermixing of Late Pleistocene lithoskels with modern skeletal detritus.

Individual fragments of the crumbling reef rock are visibly calcreted. Evidence however, of cementation and calcretisation enveloping individual grains is reduced and eventually eliminated by continual abrasion in the intertidal environment. In particular, specimens of M. vertebralis have secondary carbonate infillings progressively removed with distance landwards from the reef edge, explaining the "fresh" and "uncemented" appearance of the specimens observed by Bone (1984).

Resolution of the controversy regarding the age of Marginopora required direct dating of the fossils themselves. This was not possible however by conventional radiocarbon methods, because of the problem of sample size. Radiocarbon dating of marine carbonate requires approximately 20-50 grams of fossiliferous material after preliminary laboratory cleaning (Worsley, 1981; Gillespie, 1982; Gupta and Polach, 1985) and would require counting unacceptably large numbers of foraminiferal tests.

Because of the small sample requirement and the ability of establishing relative ages beyond the range of conventional radiocarbon methods, amino acid racemisation analyses were performed on Marginopora vertebralis from Wardang Island. Specimens obtained from sediments of

Table 4.18 Radiocarbon measurements on samples from Wardang Island

Sample	Fraction Dated	Radiocarbon Age	Geological Age
Reef rock	Bulk carbonate	$30,800^{+750}_{-700}$ yrs[1]	Late Pleistocene
Intertidal sand	Bulk sediment	6,290±90 yrs[2]	Holocene

[1] An "apparent age" resulting from the incorporation of some modern carbon into Late Pleistocene (Glanville Fm) sediment.

[2] An "average age" resulting from the physical intermixing of Late Pleistocene lithoskels with modern skeletal detritus.

confirmed Last Interglacial age (Belperio et al., 1984) from other South Australian localities, as well as Recent specimens from the Great Barrier Reef, Queensland, were also analysed as a basis for comparison. The large test size of M. vertebralis (up to 8 mm in diameter) renders it suitable for amino acid racemisation techniques. To fulfil the requirements of sample weight, each analysis was made on approximately 50 individuals. Reported D/L ratios therefore represent unweighted averages for all these individuals. As Marginopora has a porous open-framework structure providing a microenvironment for algae and bacteria, an ultrasonic cleaning procedure involving dilute HCl (1M) was used. Because of the reported disturbed amino acid signature resulting from protracted ultrasonication (Katz and Man, 1979), this technique did not exceed 10 minutes. Marginopora from the 'reef' rock and the intertidal veneer were analysed, and the results for the 'total acid hydrolysate' and free amino acids, for these two populations were compared (Table 4.19 and Appendix Table 4.4).

Clearly, the foraminifera extracted from the Wardang Island 'reef' rock are of Late Pleistocene age (ca. 120,000 yrs BP), by analogy with the northern Spencer Gulf samples (Table 4.19). Analyses of the foraminifera found loose on the tidal flat however, led to what were initially considered ambiguous results. Amino acid D/L ratios for these samples, consistently resulted in anomalously low values for the 'total acid hydrolysate'. Because the Marginopora found loose on the tidal flat were also observed weathering out of the reef rock, the lower D/L values for these samples do not reflect a genuine and resolvable age difference. Therefore, the significantly lower D/L values suggested the following possibilities. Firstly, the loose tidal flat specimens were contaminated by amino acids in the L-configuration, resulting in younger 'apparent' ages (e.g. algal contamination). The possibility of bacterial contamination was excluded however, as anomalously high concentrations of D-aspartic acid, D-alanine

Table 4.19 Summary of the extent of amino acid racemisation in Marginopora vertebralis ('total acid hydrolysate' and free amino acids).

Locality	No. of analyses	total/ free	Amino acid D/L ratios							Geological Age
			ALA	VAL	ALLO /ISO	LEU	PRO	ASP	GLU	
Wardang Island 'Reef Rock'	6	total	0.30 ±0.05	0.10 ±0.02	0.14 ±0.02	0.15 ±0.01	0.27 ±0.02	0.36 ±0.03	0.23 ±0.01	Late-Pleistocene 125 ka
Northern Spencer Gulf	2	total	0.25			0.16	0.28 ±0.01	0.36 ±0.01	0.18	125 ka
Wardang Island 'loose on tidal flat'	9	total	0.11 ±0.02	0.03 ±0.009	0.05 ±0.01	0.05 ±0.01	0.09 ±0.05	0.18 ±0.03	0.13 ±0.04	125 ka
Wardang Island 'Reef Rock'	2	free	0.34	0.20	0.19	0.31 ±0.07		0.51 ±0.06	0.18	125 ka
Wardang Island 'loose on tidal rock'	1	free	0.35	0.22	0.33	0.33		0.46 ±0.07		125 ka
Great Barrier Reef Pipon Reef	3	total	0.06 ±0.01	0.04 ±0.02	0.03 ±0.005	0.05 ±0.02	0.07 ±0.02	0.11 ±0.03	0.06	Holocene (<2 ka)

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and D-glutamic acid, three significant components of bacterial cell walls (Salton, 1964), were not detected. Moreover, diamino-pimelic acid was not present.

A second possibility was the loss of 'free' amino acids as well as a proportion of the more labile peptides. As these fractions are more extensively racemised, their loss from a fossil would result in lower D/L ratios for the 'total acid hydrolysate'. This is because the D/L ratio would be weighted towards the less racemised, higher molecular weight polypeptides that remain in the fossil. A third possibility is that both these factors affected the foraminifera loose on the tidal flat.

Free amino acid analyses for Marginopora extracted from the 'reef' rock as well as those loose on the tidal flat were also undertaken. The results indicated no significant difference in the extent of racemisation of free amino acids for these two populations (Table 4.19). In this case, D/L ratio similarity does indicate age equivalence as free amino acids are not subject to the complex chemical dynamics that characterise the 'total acid hydrolysate' (Mitterer and Kriausakul, 1984).

Although obtaining accurate concentration data is difficult by gas chromatography, a comparison of relative concentrations was made to assess whether free amino acids had leached from the foraminifera loose on the tidal flat. The results indicated that concentrations of both D- and L-isomers together, were lower in these specimens than the reef rock specimens, consistent with the second hypothesis previously discussed (Table 4.20). These results challenge conventional wisdom, as foraminifera have generally been regarded as closed systems, that experience minor loss of indigenous amino acids with time (Schroeder and Bada, 1976; King and Neville, 1977; Sejrup et al., 1984).

Amino acid D/L ratios for the unleached specimens of Marginopora vertebralis both for the 'total acid hydrolysate' and free amino acids were consistently lower than any of the Last Interglacial molluscan fossils

Table 4.20 Amino acid concentrations (nanomoles/gram) for Pleistocene Marginopora vertebralis from Wardang Island. Values for modern specimens were obtained on Marginopora from the Great Barrier Reef, Queensland. Because of the inherent difficulties of obtaining accurate concentration data by gas chromatography, these values are approximate only.

Sample	Amino acid concentration (D + L isomers) ALA	VAL	ALLO /ISO	LEU	ASP
'total acid hydrolysate' ('Reef Rock')	980	370	170	250	366
'total acid hydrolysate' (loose on tidal flat)	215	119	74	78	284
free amino acids ('Reef Rock')	17	-	12	26	179
free amino acids (loose on tidal flat)	-	16	5	12	56
modern Marginopora Great Barrier Reef, Queensland ('total acid hydrolysate')	2183	764	543	570	632

studied. The general concordance of the data for the unleached specimens supports the suggestion that the D/L ratios represent values for indigenous amino acids. From these data it was concluded that racemisation (epimerisation) rates are slower for this species than other carbonate fossils analysed in this study. This is consistent with observations for some North American mollusc species, and the 'apparently' slow racemisation rates were attributed to slow rates of natural hydrolysis (Wehmiller, 1984b). Accordingly, high molecular weight polypeptides are less readily broken down so that D/L ratios for the 'total acid hydrolysate' are primarily represented by this less racemised fraction. This well displays the potential for Marginopora vertebralis to be used in aminostratigraphic studies to date sediments of greater antiquity owing to the apparently slow rates of racemisation. This point is further discussed in Chapter 5 for Marginopora obtained from the Plio/Pleistocene Roe Calcarenite.

This study is significant for it highlights, that through a combination of amino acid D/L ratios for the 'total acid hydrolysate' and 'free' amino acids, as well as concentration data, an assessment of apparently anomalous D/L ratio data can be made. In addition, amino acid racemisation provides a powerful tool for assessments of reworking and for studies of population dynamics.

4.10 AMINOSTRATIGRAPHIC RESULTS: DISCUSSION

4.10.1 Aminostratigraphy: Definition

The term 'aminostratigraphy' was introduced by Nelson (1978) and further discussed by Miller and Hare (1980). Although the term now has wide usage (Wehmiller, 1982,1984b; Bowen 1985), a satisfactory definition has not been provided. In this thesis aminostratigraphy is defined as a branch of chemostratigraphy which seeks to divide the stratigraphic record into chronostratigraphic units termed aminozones. Aminozones are here defined as chronostratigraphic (time stratigraphic) units, which represent discrete time intervals and are characterised by the grouping (clustering) of amino acid D/L ratios. Designation of aminozones is supported by lithostratigraphic and biostratigraphic evidence. According to Hedberg (1976) chronostratigraphic units are bounded by isochronous surfaces. In the context of the Quaternary stratigraphy examined in this thesis however, although the bounding surfaces of the various marine lithostratigraphic units are transgressive or regressive (diachronous), the time intervals represented by these bounding surfaces are insignificant compared with the length of time represented by the intervening depositional hiatuses. Furthermore, age variation along these diachronous surfaces is not readily resolvable by amino acid racemisation techniques for Pleistocene sequences.

The merit of an aminostratigraphic approach in Quaternary studies centres on its non-genetic character. In the absence of well defined lithostratigraphies, relative chronostratigraphic classifications can be undertaken in localised regions. At a larger scale, regional chronostratigraphies can be established provided the 'Effective Quaternary Temperature' history is known or independent dating techniques are

available to serve as a basis for calibration. A significant advantage with this approach is the avoidance of homotaxial correlations, a problem implicit in lithostratigraphic studies.

4.10.2 South Australian Quaternary Marine Aminostratigraphy

Several aminozones were identified within the South Australian Quaternary marine sediments studied (Figure 4.17a-d). These are here referred to as the St Kilda aminozone, Gulf St Vincent aminozone, Glanville aminozone and the Redcliff aminozone. These are equated with oxygen isotope stages 1,3,5e and 7 respectively, and are in accord with conventional geological interpretations. Scatter diagrams were used to depict these aminozones for they conveniently demonstrate the increase in D/L ratios for two amino acids with increasing fossil age. In each case, for a range of specimens in the scatter diagrams (Figure 4.17a-d) amino acid pairs have clustered distributions within each aminozone, consistent with age equivalence. The broad range of values evident in the Glanville aminozone (Figure 4.19a) resulted from the wide geographic range of sample localities which have experienced different 'Effective Quaternary Temperature' histories. In addition a genus-effect is evident, for aspartic acid is more extensively racemised in Anadara trapezia than Katelysia spp.

The linear trend evident within the St Kilda aminozone (Figure 4.17 a,c,d) is most likely an expression of racemisation kinetics, and represents the first essentially linear component of the "non-linear" kinetic model of Wehmiller (1984b) (Figure 2.3). This trend was not evident in Figure 4.19b as less data were available for leucine.

The Holocene specimens in the St Kilda aminozone span ages from 7,400 to 450 calendar years. Significant differences were not evident for the extent of racemisation in 450 yrs compared with modern molluscs for

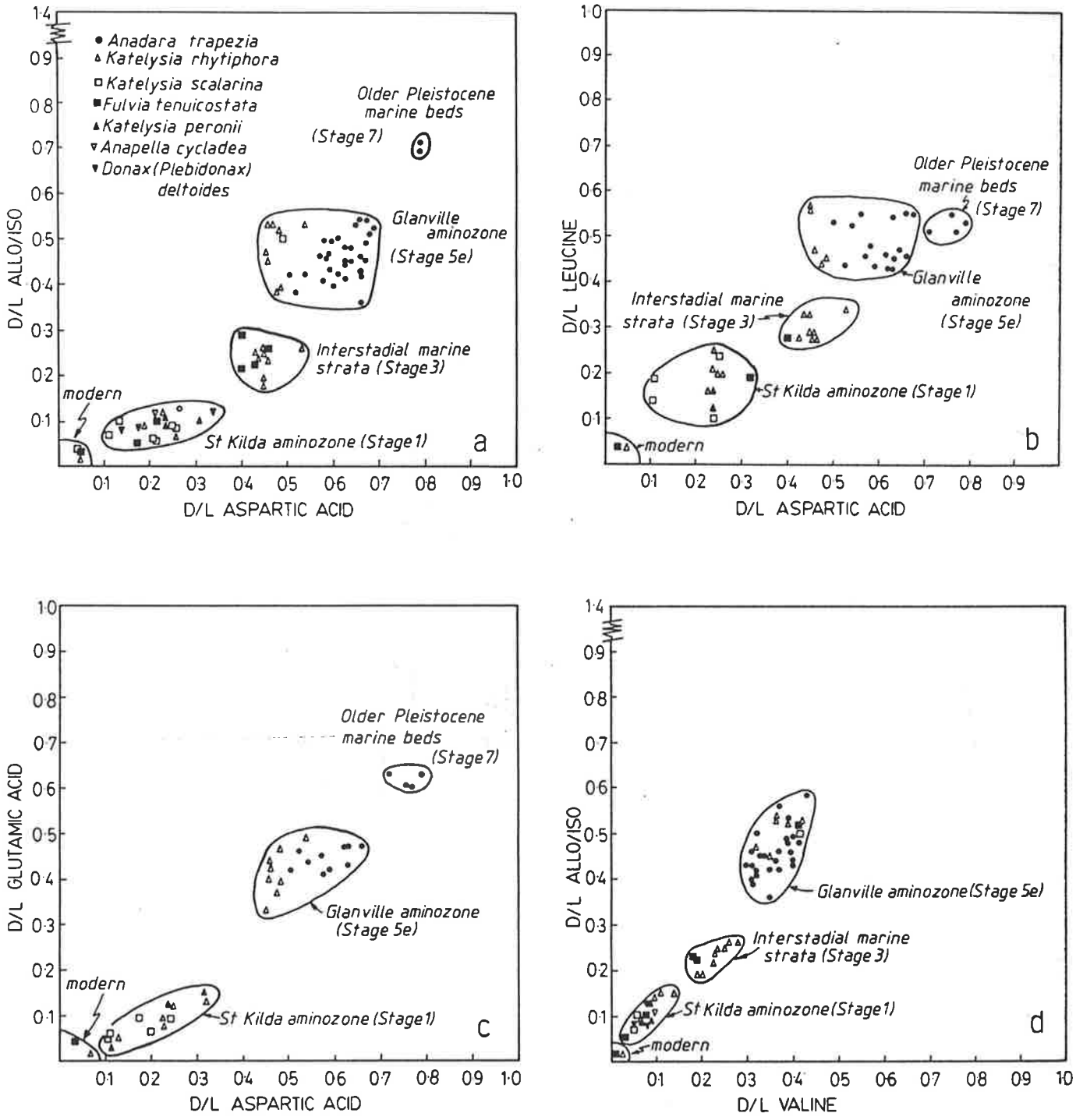


Figure 4.17 Summary plots of D/L ratio data for molluscan fossils obtained from Late Quaternary coastal and marine sediments in South Australia. Results depicted are for the 'total acid hydrolysate'.

glutamic acid, isoleucine and valine. In contrast, aspartic acid and leucine did differ significantly and may relate to the faster rates of racemisation evident in these amino acids.

Unfortunately, changes in conditions of gas chromatograph capillary columns sometimes prevent particular compounds from being resolved with confidence. In particular, at the time of analyses β-alanine co-eluted with L-leucine resulting in artificially low leucine D/L ratios for the specimens from the "Older Pleistocene marine beds" (Figure 4.17b). This was confirmed by routine analysis of amino acid standards. In addition L-glutamic acid co-eluted with D-phenylalanine preventing glutamic acid and phenylalanine values from being reported.

4.11 CONCLUSIONS

The significant conclusions from this study include:

(1) Confirmation of a Penultimate Interglacial age (oxygen-isotope stage 7) for the "Older Pleistocene marine beds" at Redcliff, northern Spencer Gulf.

(2) Recognition of Interstadial marine strata (stage 3) from submarine cores, Gulf St Vincent.

(3) Confirmation that the foraminifera Marginopora vertebralis is a Plio/Pleistocene indicator species for southern Australian coastal waters.

(4) Demonstration of the application of amino acid racemisation in studies of reworking.

(5) The widespread occurrence of the Last Interglacial Glanville Formation was demonstrated by aminostratigraphic correlation and has circumvented problems of homotaxis.

(6) Latitudinal amino acid D/L ratio variation within the Glanville aminozone was demonstrated.

(7) Although a cautionary approach is desirable, the application of amino acid racemisation in geothermometry provides a useful method of internally assessing the reliability of amino acid derived ages.

(8) The extent of racemisation evident in a range of molluscan fauna of different ages supported the 'non-linear' racemisation kinetic model.

(9) In the context of a punctuated event stratigraphy, the product of Quaternary sea level fluctuations, several aminozones were recognised. These included the St Kilda aminozone (oxygen isotope stage 1), Gulf St Vincent aminozone (stage 3), Glanville aminozone (stage 5e) and the Redcliff aminozone (stage 7).

CHAPTER 5 WESTERN AUSTRALIAN QUATERNARY COASTAL AND MARINE AMINOSTRATIGRAPHY

5.1 INTRODUCTION

The aminostratigraphic study of Quaternary molluscs from Western Australia was initially prompted by the observed latitudinal variation of amino acid D/L ratios in Anadara trapezia from sediments of Last Interglacial age in southern Australia. Comparison with similar fauna from the same latitude, although longitudinally widely separated may provide valuable palaeoclimatic information, and would greatly assist intracontinental chronostratigraphic correlation. Mollusc specimens were obtained from various deposits in the Perth Basin and from the Roe Plains, Western Australia.

A further aim was to apply the amino acid racemisation reaction to resolve some of the complex Quaternary lithostratigraphic relationships within the Perth Basin. In addition, direct chronostratigraphic correlation of Plio/Pleistocene deposits have previously not been possible in Australia, and therefore a preliminary correlation of the Jandakot Member of the Yoganup Formation with the Roe Calcarenite was attempted.

A number of samples analysed in this study were obtained from museum collections, and so were not specifically collected to avoid problems of surface temperature exposure. However, every effort was made to assess the original stratigraphic context of the fossiliferous material, and on this basis numerous fossils were excluded from analysis.

5.2 THE PERTH BASIN: PHYSIOGRAPHY AND CLIMATE

The Perth Basin is a narrow, elongate structure with an area of approximately 55,000 km^2 (Palfreyman, 1984) (Figure 5.1). The basin straddles the Western Australian coastline for some 900 kms starting near Northcliffe in the south, and terminating inland from Shark Bay. The Darling Range defines the eastern boundary of the basin. The sedimentary fill ranges in age from Silurian to Modern. Quaternary sediments within the basin attain a maximum thickness of 150 m, although in most areas they are less than 20 m (Playford et al., 1976).

The climate is mediterranean in character, and experiences hot, dry summers and cool wet winters. Summer months (December - February) experience average maximum and minimum temperatures of 28.8°C and 17.1°C respectively (Playford et al., 1976). Average maximum and minimum temperatures for the winter months (June - August) attain 17.7°C and 9.3°C respectively (Playford et al., 1976). The mean annual air temperature for the Perth region is approximately 18.5°C (Australian Climatic Averages). Average annual rainfall for the Perth area is in the order of 883 mm.

In this study, mollusc specimens were obtained from the Swan Coastal Plain, a gently undulating area of low relief. Holocene and Pleistocene dune complexes are extensively developed along the Swan Coastal Plain, and have a complex interfingering relationship with marine and paralic sediments. To the east, sheet drapes of alluvial and colluvial sediments flank the Darling Scarp.

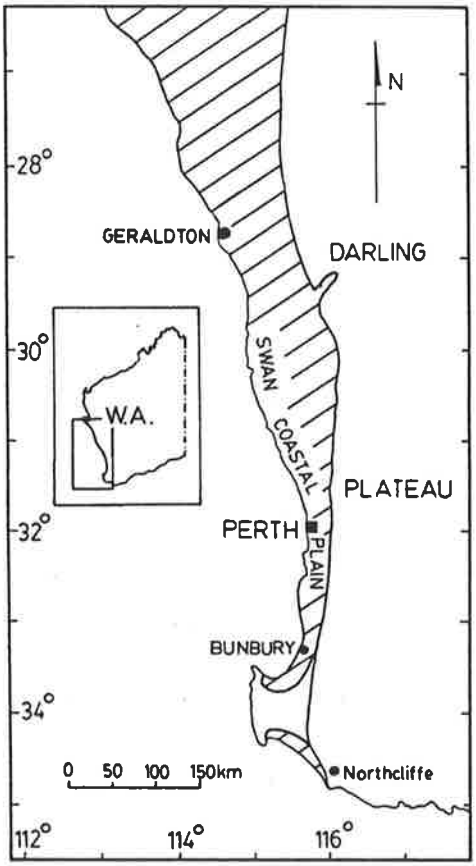


Figure 5.1 The Perth Basin, Western Australia

5.3 SUMMARY OF ESTABLISHED QUATERNARY LITHOSTRATIGRAPHIC NOMENCLATURE

5.3.1 Perth Basin

The established Late Neogene-Quaternary lithostratigraphic nomenclature for the Perth Basin is summarised in Figure 5.2, and has been discussed by Allen (1976,1981), Fairbridge (1953,1954), Playford et al., (1976), Playford and Leech (1977), and Somerville (1920). The units specifically referred to in this study are part of the Kwinana Group (Figure 5.2). The Kwinana Group refers to Late Tertiary to Holocene coastal-dune, littoral and neritic sediments exposed on the Swan and Scott Coastal Plains (Playford et al., 1976).

Several complications arose in summarising the established lithostratigraphic nomenclature. Firstly, some of the Neogene and Quaternary sediments have been given formation status without consideration of the facies concept of stratigraphy. Lithostratigraphic subdivisions gave age significance to lithofacies in the absence of chronostratigraphic evidence or principles of superposition. The application of the conventional approach to stratigraphic subdivision that is used for subdividing ancient rock sequences resulted in a poor appreciation of the complex stratigraphic relationships of Neogene-Quaternary sediments in the Perth Basin. The widespread occurrence of Holocene and Pleistocene aeolian dunes which blanket the marine horizons has also hampered studies of the latter for they are generally only observed through core sampling, limited natural exposures and man-made excavations. However, since the marine sequences contain fossils, the dating of these can provide the time-framework in studies of the evolution of the Quaternary basin fill.

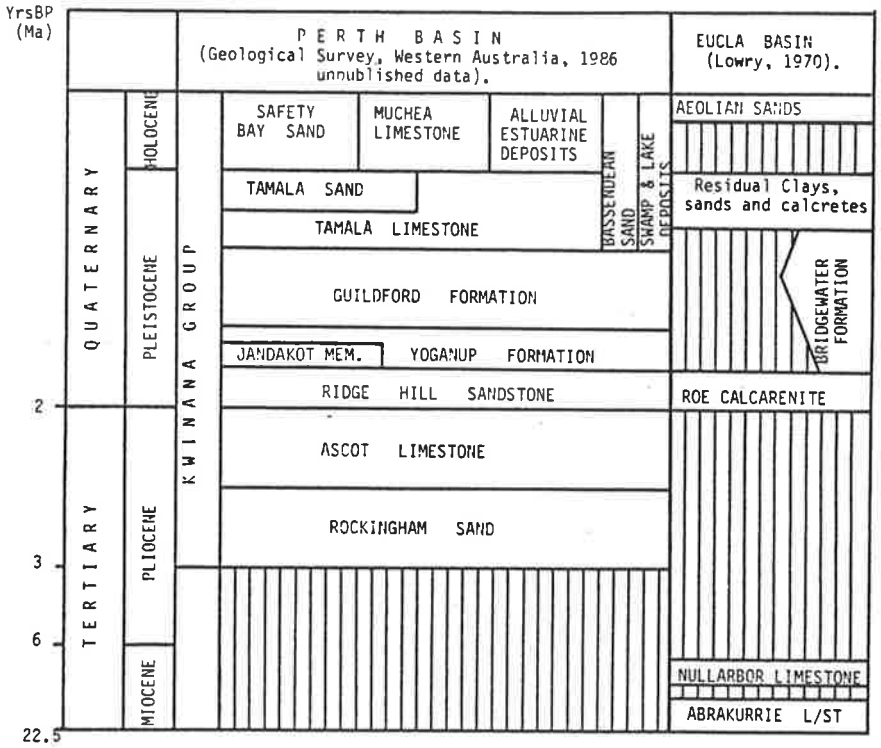


Figure 5.2 Modified summary of the Late Neogene-Quaternary lithostratigraphic nomenclature for the Perth and Eucla Basins, Western Australia. Details of the Eucla Basin lithostratigraphy are summarised in Lowry (1970). The summary of the Perth Basin lithostratigraphy is based on unpublished data of the Geological Survey of Western Australia. (B. Gozzard, pers. comm., 1986).

A further reason for the poorly defined Late Neogene-Quaternary lithostratigraphy has been the subordinate interest in studies of these sediments.

5.3.1.1 Jandakot Member

The oldest unit examined in this study is the Jandakot Member of the Yoganup Formation (Figure 5.2). These sediments were previously informally referred to as the 'Jandakot Beds' by Allen (1976,1981) in reference to richly fossiliferous shelly sands of Early-Middle Pleistocene age. Member status has been informally assigned to these sediments by the Geological Survey of Western Australia. The Yoganup Formation refers to a sequence of littoral and aeolian sands and clays with basal conglomerate channel lags (Playford et al., 1976). The holostratotype is situated near Yoganup, south of Perth.

5.3.1.2 Tamala Limestone

The term 'Tamala Limestone' was applied to a succession of Mid- to Late Pleistocene aeolian calcarenites within the Perth Basin (Playford et al., 1976; Allen, 1981). This represented a modification of the original nomenclature of Logan (1968) for the "Tamala Eolianite" in the Shark Bay area of the Carnarvon Basin (Playford et al., 1976). These authors proposed the amendment as the term aeolianite has a genetic connotation.

5.3.1.3 Tamala Sand

Tamala Sand is an informal term of the Geological Survey of Western Australia in reference to reworked surficial material such as aeolian dunes, derived principally from the Tamala Limestone (B. Gozzard, Western Australian Geological Survey, pers. comm., 1986).

5.3.1.4 Safety Bay Sand

Holocene coastal sand dunes and shallow marine to littoral sands in the Rockingham-Safety Bay area were described by Passmore (1967,1970) as the Safety Bay Sand. Playford and Low (1972) extended the usage of this term to describe similar sediments within the Perth Basin of Holocene age.

5.3.2 Eucla Basin

The Eucla Basin occupies an area of some 225,000 km^2 and flanks the Great Australian Bight (Palfreyman, 1984). The basin fill is dominated by Cretaceous to Tertiary sediments, although a fragmentary record of Quaternary sediments is also represented. Molluscs analysed in this study were obtained from the Roe Calcarenite.

5.3.2.1 Roe Calcarenite

The term Roe Calcarenite refers to richly fossiliferous, semi-indurated, medium to coarse grained calcarenites of Early Pleistocene age (Lowry, 1970; Ludbrook, 1958,1978).

5.4 AMINOSTRATIGRAPHY

In the following discussion the aminostratigraphic approach is used as an aid to understanding the complex lithostratigraphic relationships within the Perth Basin. Several dating techniques have provided some age control to the lithographic framework. These have included uranium-series dating (Veeh, 1966; Veeh et al., 1979; Szabo, 1979), radiocarbon dating (Playford and Leech, 1977 and G.W. Kendrick, unpubl. data) and electron spin resonance dating (Hewgill et al., 1983). However, because of some of the limitations presented by these methods, amino acid racemisation was applied in this study to integrate the existing information. An additional aim was to revise some aspects of the stratigraphic nomenclature and relate the results to established models of Quaternary sea level fluctuations.

5.4.1 Jandakot Member

The Jandakot Member of the Yoganup Formation is an entirely subsurface marine unit, located south of Perth. The unit represents one of the main aquifers within the Perth Basin and its top is commonly intercepted in water bore-holes at depths of 20 m. The Jandakot Member unconformably overlies the Cretaceous Osborne Formation and underlies the Late Pleistocene Bassendean Sand. The sediments contain abundant shallow water molluscs, but their endemic nature has precluded stratigraphic correlation at an international scale (Darragh and Kendrick, 1971; Mallett, 1982).

5.4.1.1 Jandakot Member: Age

Darragh and Kendrick (1971) favoured a Pleistocene age for this unit. Allen (1976,1981) briefly referred to these sediments and assigned an Early-Middle Pleistocene age. In a more detailed study of the planktonic foraminiferal content of the sediments from the Jandakot Bore, Mallett (1982) suggested a Plio/Pleistocene age. Mallett recovered less than 300 identifiable planktonic foraminifers from 6 kg of sediment, and his age designation was based on the first appearance of Globorotalia truncatulinoides. The First Appearance Datum (F.A.D.) of G. truncatulinoides has been well established from extensive studies of deep sea cores and occurs just below the base of the Olduvai at 1.8 Ma (Haq et al., 1977; Berggren et al., 1980). The specimens occurring in the Jandakot Member represent transitional forms from Globorotalia tosaensis to the phylogenetically more developed Globorotalia truncatulinoides. According to Haq et al., (1977) the Plio/Pleistocene boundary at La Castella in Italy postdates the calcareous nannoplankton Gephyrocapsa, especially Gephyrocapsa caribbeanica (F.A.D. 1.62 Ma) and Gephyrocapsa oceanica (F.A.D. 1.57 Ma). As these nannofossils are documented as appearing after Globorotalia truncatulinoides in deep sea cores, the absence of G. truncatulinoides below and around the marker horizon at La Castella has been assumed to be unrelated to the first evolutionary appearance of this species (Mallett, 1982).

The presence of phylogenetically primitive forms of G. truncatulinoides at Jandakot suggests that the unit may lie in the earliest part of the species range, equivalent to the section below the boundary marker at La Castella. Caution however should be exercised with this interpretation. The Jandakot sediments are transgressive (diachronous), and as a continuous depositional record from the Tertiary is not evident,

the first appearance of Globorotalia truncatulinoides is most likely migratory rather than an evolutionary appearance. An additional difficulty arises in the correlation of pelagic and neritic sediments. To what extent the presence or absence of foraminiferal species is an expression of biofacies (e.g., sedimentary environment, water depth, temperature, lighting conditions and salinity) rather than a function of time (age) should be questioned.

However, Mallett (1982) cited a number of criteria suggesting the phylogenetically primitive nature of Globorotalia truncatulinoides from the Jandakot Bore. These included the presence of a very thin carina (keel), small and narrow umbilicus, the ventral side is less conical than later forms and the chambers are more laterally compressed. On this basis a level close to the First Appearance Datum of Globorotalia truncatulinoides was suggested for the Jandakot fauna (Mallett, 1982).

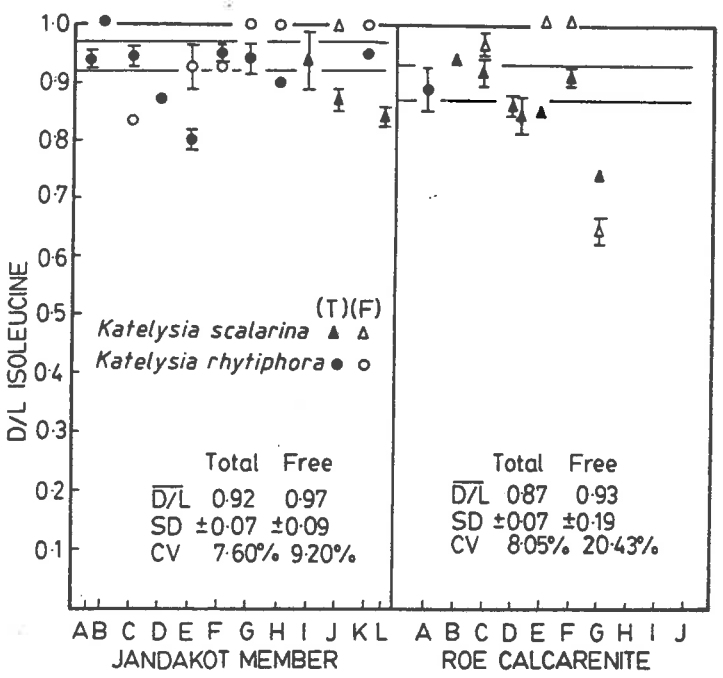
The Jandakot Member also contains a rich mollsucan fossil assemblage with numerous articulated and disarticulated Katelysia spp., represented. The pelagic janthinid gastropod, Hartungia dennati chavani, a species diagnostic of the Early Pleistocene (Ludbrook, 1984) is absent in the Jandakot Member. It does occur in the Ascot Limestone, which according to the Geological Survey of Western Australia is of Pliocene age. The species is common in the Roe Calcarenite and in the Point Ellen Formation (Ludbrook, 1983; Milnes et al., 1983) at Point Ellen, South Australia and less common at Cape Jervis, South Australia.

In summary, although it is difficult to delineate the precise age of the Jandakot Member, at present the sediments are best considered as Plio/Pleistocene. This interpretation antedates the age assigned by Allen (1976, 1981).

5.4.1.2 Jandakot Member: Amino Acid Racemisation Analyses

Samples for amino acid racemisation analyses were obtained from collections of the Western Australian museum. Mollusc specimens analysed included Katelysia rhytiphora and Katelysia scalarina from Paulik's Bore (38.8-41.8 m) at Jandakot, some 18 km south of Perth and an adjacent, supplementary bore (29.0-45.6 m). The molluscs analysed from Paulik's Bore appeared immediately above the interval studied by Mallett (1982). Mollusc specimens were very well preserved with articulated and disarticulated individuals represented. Recrystallisation of the shell matrices from metastable aragonite to calcite was not evident and only trace amounts of calcite were detected by X-ray diffraction (<3%). Where possible the hinge region of the bivalves was analysed. As lower concentrations of indigenous amino acids were anticipated because of their age, larger sample amounts were prepared ranging between 1.0 to 2.5 grams. Analyses were made for the 'total acid hydrolysate' and free amino acids. Results of these analyses are presented in Table 5.1 and graphically represented in Figures 5.3a-d (see also Appendix Table 5.1). A representative chromatogram for a Katelysia specimen ('total acid hydrolysate') from the Jandakot Member is presented in Figure 5.4.

The extent of racemisation evident in the 'total acid hydrolysate' is marginally less than the free amino acid fraction and suggests that the extent and rates of racemisation evident in the Jandakot fauna had for some time in their late diagenetic history been largely controlled by the rate of racemisation of free amino acids. This suggestion is consistent with the work of Mitterer and Kriausakul (1984) and Wehmiller (1984b). Coefficients of variation for D/L ratios of the 'total acid hydrolysate' ranged between 6-17%. The lower coefficients of variation for phenylalanine and glutamic acid are unrepresentative, as these values are



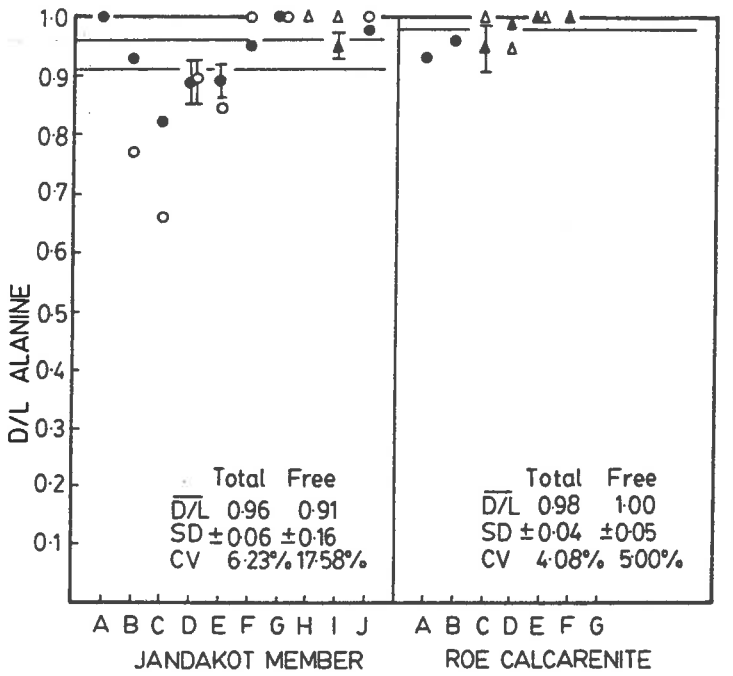
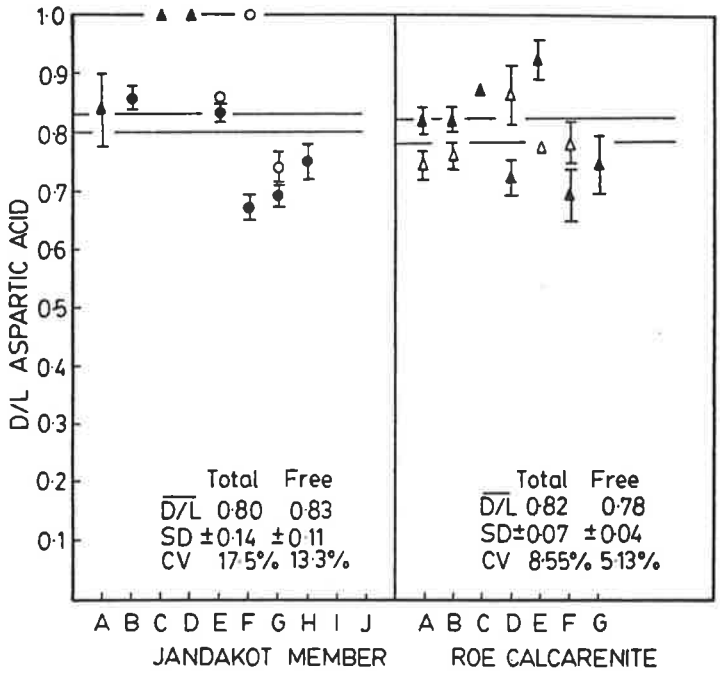
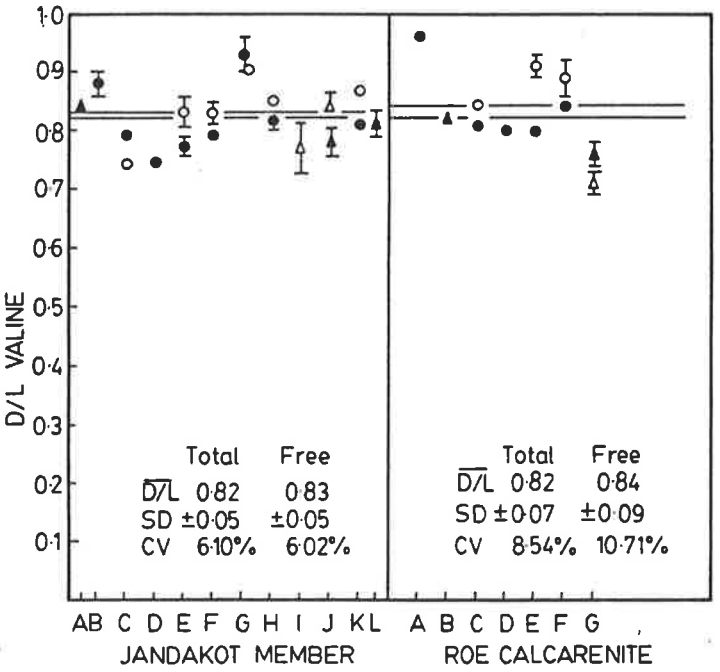


Figure 5.3 a-d Extent of amino acid racemisation in Katelysia spp., from the Plio/Pleistocene Jandakot Member of the Yoganup Formation, Perth Basin, and the Plio/Pleistocene Roe Calcarenite, Roe Plains, Western Australia.



(c)



(d)

Figure 5.3 (continued)

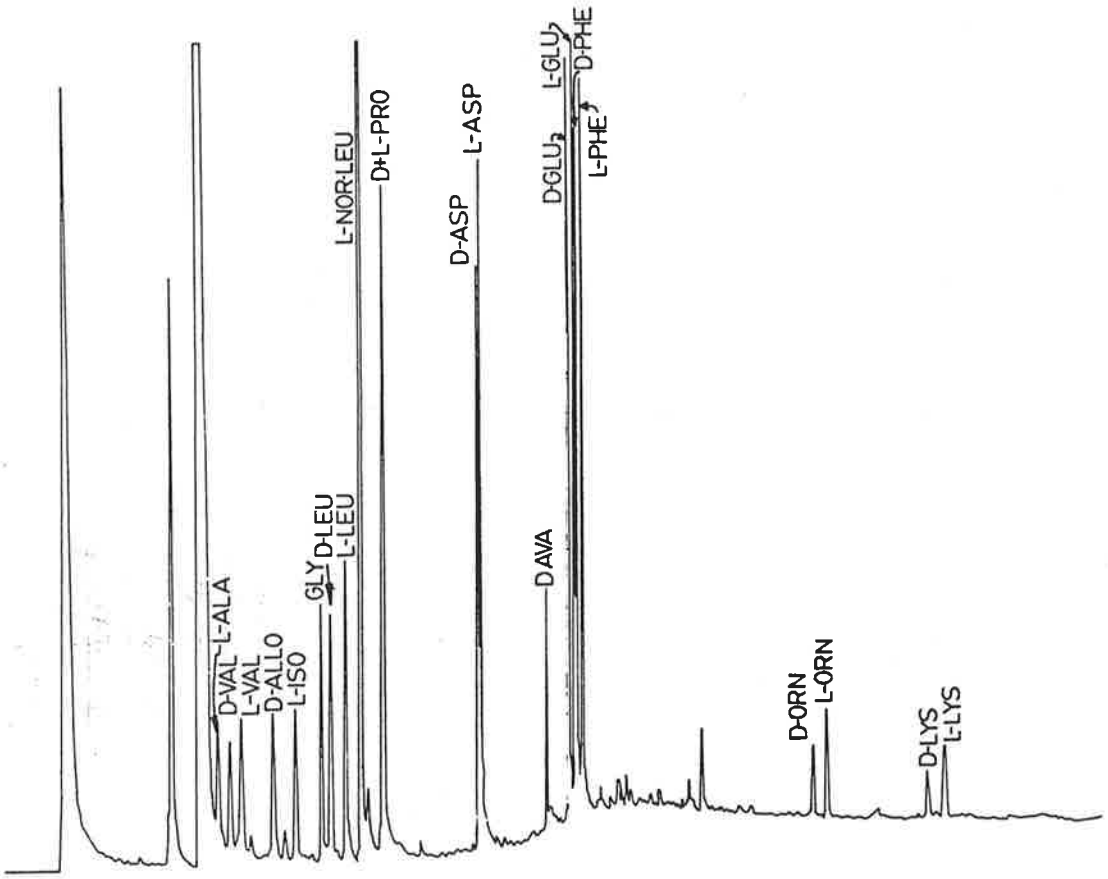


Figure 5.4 Gas chromatogram ('total acid hydrolysate') of amino acids contained in a specimen of Katelysia rhytiphora from the Plio/Pleistocene Jandakot Member of the Yoganup Formation. Details of the gas chromatograph, capillary column and computing integrator are provided in Section 3.4.1 and Appendix 1.

Table 5.1 Aminostratigraphic correlation of the Plio/Pleistocene Jandakot Member, Yoganup Formation with the Roe Calcarenite based on the extent of racemisation (epimerisation) in Katelysia spp. ('total acid hydrolysate' and free amino acids).

Stratigraphic unit; locality	Contemporary M.A.T. °C	No. of individuals analysed	Total/ Free	Amino acid D/L ratios						
				ALA	VAL	ALLO/ ISO	LEU	ASP	PHE	GLU
Jandakot Member, Yoganup Formation, Perth Basin	18.0	12	T	0.96 ±0.06 (6.25%)	0.82 ±0.05 (6.10%)	0.92 ±0.07 (7.60%)	0.64* ±0.11 (17.19%)	0.80 ±0.14 (17.5%)	0.95 ±0.02 (2.10%)	0.78 ±0.01 (1.28%)
		6	F	0.91 ±0.16 (17.58%)	0.83 ±0.05 (6.02%)	0.97 ±0.09 (9.28%)	0.85 ±0.12 (14.12%)	0.83 ±0.11 (13.25%)		
Roe Calcarenite, Madura, Roe Plains	18.2	7	T	0.98 ±0.04 (4.08%)	0.82 ±0.07 (8.54%)	0.87 ±0.07 (8.05%)	0.77* ±0.11 (14.28%)	0.82 ±0.07 (8.53%)		
		4	F	1.00 ±0.05 (5.00%)	0.84 ±0.09 (10.71%)	0.93 ±0.19 (20.43%)	0.91 ±0.08 (8.79%)	0.78 ±0.04 (5.13%)		

* D/L leucine values are artificially low resulting from coelution of β-ALA with L-leucine

() Values in parentheses indicate the coefficient of variation for each amino acid.

for only a single mollusc. Enantiomeric ratios were not reported for glutamic acid and phenylalanine for the majority of analyses of the 'total acid hydrolysate' and free amino acids due to the coelution of L-phenylalanine with D-glutamic acid. The low D/L ratio evident for leucine resulted from the coelution of β-alanine and L-leucine producing artificially low values. This was confirmed by routine analysis of amino acid standards, in conjunction with additional analyses made on a Hewlett-Packard model 5890 gas chromatograph using a Chirasil-Val fused silica column.

Coefficients of variation for the free amino acid fraction ranged between 6 to 17%, an equivalent range to the 'total acid hydrolysate'. In view of the antiquity of these fossils, the coefficients of variation compare favourably with significantly younger materials. This issue was discussed in section 3.2.5 in the context of intershell amino acid D/L ratio variation with time.

Several significant questions arose from the Jandakot amino acid data. The first concerns whether the enantiomeric ratios reflect results for purely indigenous amino acids. Secondly, if the amino acid D/L ratios are not the result of contamination or other external diagenetic effects, then the question arises of whether they statistically represent a racemic condition, and if not, at what time the racemic state is obtained. These questions are further explored in Chapter 7.

5.4.2 Tamala Limestone

The Tamala Limestone fringes the western margin of the Swan Coastal Plain, a long narrow region of low relief extending from the Whicher Scarp south of Bunbury to Geraldton, some 550 km to the north (Figure 5.1). Playford et al., (1976) and Playford and Leech (1977) described the Tamala Limestone strictly as an aeolian calcarenite with palaeosols and well indurated calcrete horizons.

Although some lithological variation is evident, the sediments are characterised by medium to coarse grained skeletal detritus including comminuted molluscs and foraminifera. Several marine units interfinger with the aeolian calcarenites, and their contribution to the total sediment volume is minor in comparison with the aeolian facies (Wyrwoll, 1984).

5.4.2.1 Tamala Limestone: Age

Although no detailed chronostratigraphic study has previously been undertaken, lithostratigraphic, morphostratigraphic and indirect biostratigraphic evidence suggest an age of 500 ka for the lower limit of the base of the Tamala Limestone (McNamara, 1983). The Tamala Limestone is strongly diachronous (Wyrwoll and King, 1984), and caution should be exercised in its correlation between different localities.

Debate continues however concerning the top of the unit. According to Playford et al., (1976) the Tamala Limestone is of Late Pleistocene age. Wyrwoll (1984) and Wyrwoll and King (1984) briefly discussed aspects of the stratigraphy of the unit but did not refer to its age. The Geological Survey of Western Australia have designated the Late-Middle Pleistocene to basal Holocene age for the Tamala Limestone (B. Gozzard, pers. comm., 1986) (Figure 5.2). In contrast, Playford and Leech (1977) and McNamara (1983) suggested that the top of the formation is unconfined and represents an active surface of sedimentation, as former depositional processes could not be distinguished from contemporary patterns of sedimentation.

Previous workers (Playford et al., 1976; Playford and Leech, 1977), have confined their descriptions of the Tamala Limestone to the aeolian component. However, several transgressive marine intercalations have a complex interfingering relationship with the aeolian calcarenites. Although these units have been examined at various sites (Fairbridge, 1953,1954),

no integrated study of the chronostratigraphic relationships of these facies or their stratigraphic significance has been carried out. This study presents results of amino acid racemisation analyses from two marine units within the Tamala Limestone. These units crop out at Minim Cove and at Peppermint Grove in the Swan Estuary (Figure 5.5) and preliminary age assessments suggest Last Interglacial and Penultimate Interglacial ages, respectively for these sediments (Hewgill et al., 1983).

5.4.2.2 Peppermint Grove

Fossiliferous marine strata at Peppermint Grove (Figure 5.5) were first described by Somerville (1920), who invoked uplift in explanation of their elevated position. The sediments at Peppermint Grove were originally granted formation status by Fairbridge (1954) who referred to these beds as the Peppermint Grove Formation. The holostratotype is situated at the bank of the Swan River near Scotch College boatshed (lat. 31°59'30"S, long., 115°46'10"E). The marine component of these sediments consists of a richly fossiliferous bioclastic limestone mantled by aeolian calcarenites and well indurated calcreted gravels. The total thickness of the section is 5 m. The shell bed ranges in elevation from 1.0 to 7.3 m above mean sea level (Playford et al., 1976).

According to Reath (1925) the Peppermint Grove sediments contain molluscan fauna suggestive of warmer temperatures during the period of deposition than prevail today. However, this was disputed by Kendrick (1960) who demonstrated that the molluscan fauna contains less than 20% northern (Dampierian) species and over 70% (Flindersian-Peronian) species. Kendrick (1960) suggested the unit was deposited in a shallow-marine gulf which occupied the site of the present-day Swan estuary, under similar temperatures to those prevailing today.

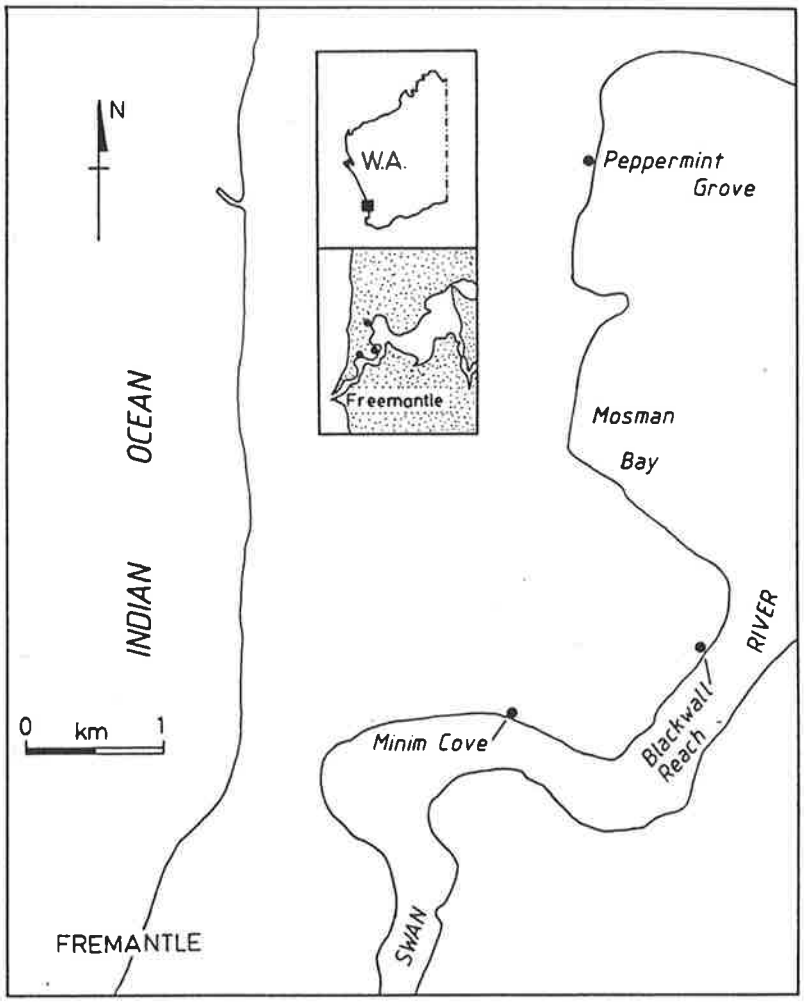


Figure 5.5 Location of the Minim Cove Member (Last Interglacial) and Peppermint Grove Member (Penultimate Interglacial) of the Tamala Formation, Swan River, Western Australia.

Fairbridge (1954) and Playford et al., (1976) assigned a Late Pleistocene age to the Peppermint Grove sediments. In contrast, in a preliminary study Hewgill et al., (1983) suggested a Penultimate Interglacial age for these sediments based on results from electron spin resonance dating.

Fossiliferous marine sediments at Minim Cove, approximately 4 km south of the Peppermint Grove exposure were considered to represent deeper water facies of this unit (Fairbridge, 1954). Electron spin resonance studies (Hewgill et al., 1983) however, are supported by the results of amino acid racemisation dating in this study which suggest that the Minim Cove sediments represent a Last Interglacial deposit.

5.4.2.3 Peppermint Grove: Amino Acid Racemisation Analyses

Molluscs collected for amino acid racemisation analyses included Anadara trapezia, Katelysia rhytiphora, Katelysia scalarina and Bassina pachyphylla. A combination of museum specimens and freshly collected materials were analysed. Analyses were made for the 'total acid hydrolysate' and free amino acids. The shells had been buried at depths between 0.25-0.5 m within an undercut section of the cliff exposure. In general, the molluscan fauna from this locality have partially leached surfaces and contain hardened surface encrustations of calcium carbonate derived from the overlying aeolian calcarenites. The shells analysed were approximately 3.5 m above mean sea level.

Representative analytical results are summarised in Tables 5.2a and b and in Figures 5.6a-d (see also Appendix Table 5.4). With the exception of aspartic acid, the free amino acids were consistently more extensively racemised than the 'total acid hydrolysate'. The anomalously high aspartic acid D/L ratios for the 'total' in relation to free amino acids resulted from the coelution of γ-amino-n-butyric acid with D-aspartic acid. This was

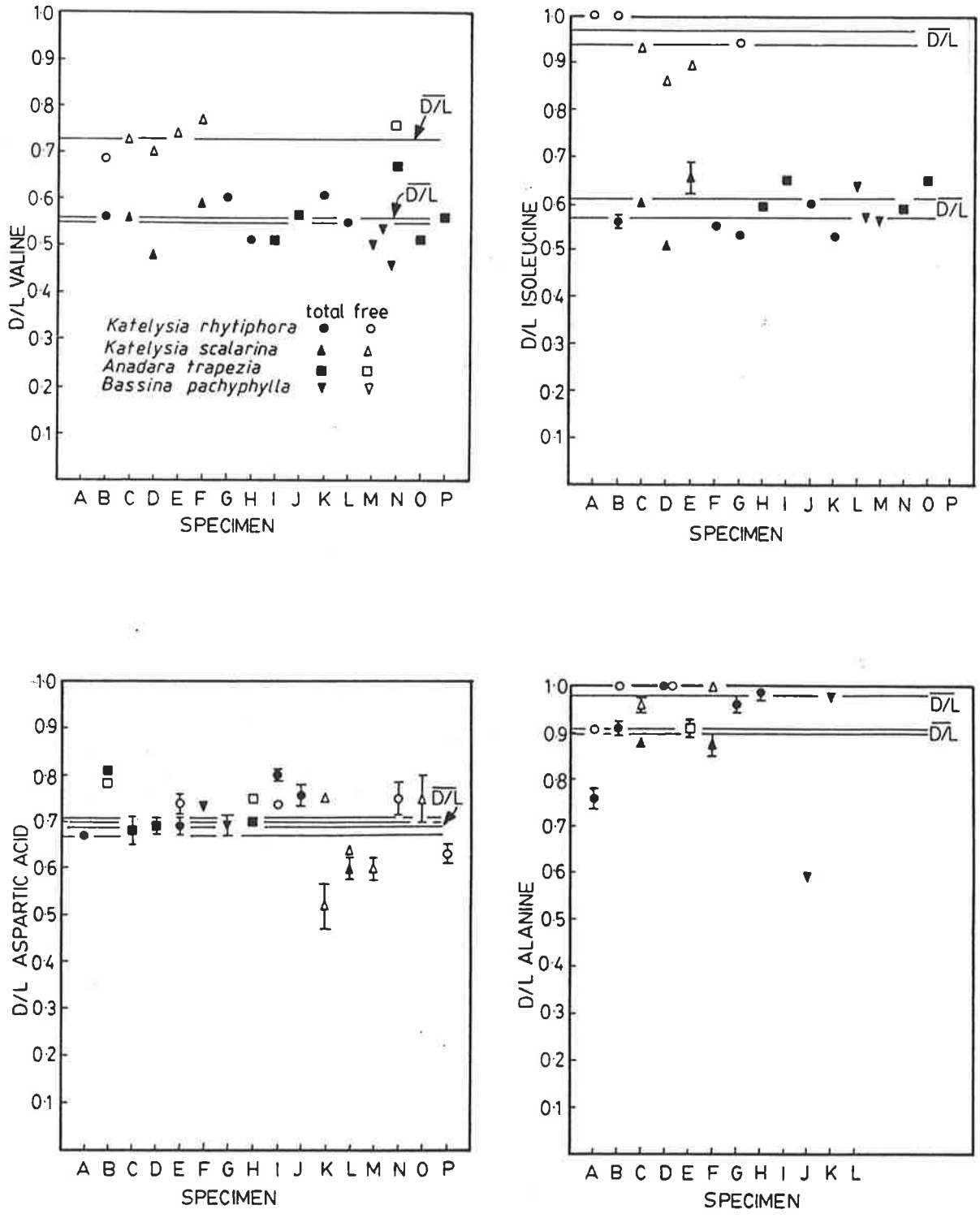


Figure 5.6 Extent of amino acid racemisation in molluscan fossils from the Peppermint Grove Member, Tamala Formation (Penultimate Interglacial). See Table 5.6 for mean D/L ratio values for Katelysia spp., and mixed species assemblages.

confirmed by analysis of amino acid standards, and studies using gas chromatography mass spectrometry (Kimber, unpublished data). These observations suggest that γ-amino-n-butyric acid was confined to the middle molecular weight peptide fraction of the 'total acid hydrolysate'. It is unlikely to be in the high molecular weight polypeptides, as hydrolysis would have to occur before they could react to form γ-ABA. Coefficients of variation for intershell D/L ratio variation were in accord with results for single deposits presented in Chapter 3.

Coefficients of variation for D/L ratios for Katelysia spp., tended to be lower for free amino acids than the 'total acid hydrolysate'. This was also evident in the 'mixed-genus' assemblage. In addition, coefficients of variation for D/L ratios both for the 'total acid hydrolysate' and free amino acids were higher in the 'mixed-genus' assemblage than Katelysia spp. (Table 5.2b). This is due to the increased variation introduced by different molluscan genera, which each have their characteristic rates of racemisation.

In accordance with equation 3.1, 10 individual shells (averaged for all amino acids) were required to reliably characterise the age of the strata at Peppermint Grove based on the amino acid data for the 'total acid hydrolysate'. This minimum number of individuals also applied for the free amino acid fraction. Valine, leucine and aspartic acid required the least number of individuals in order to satisfactorily characterise the age of the strata. Alanine and isoleucine required a significantly larger number of individuals (see Table 5.2a, footnote).

5.4.2.4 Blackwall Reach

Emergent fossiliferous marine strata occur some 2 km south of the Peppermint Grove exposure on the west bank of the Swan Estuary near Chidley Point (Figure 5.5). Anadara trapezia are particularly abundant at this locality and represent the dominant species in the molluscan fossil

Table 5.2a Extent of amino acid racemisation (epimerisation) in mollsucan fauna obtained from emergent fossiliferous marine strata, Peppermint Grove. Amino acid D/L ratios are for the 'total acid hydrolysate' and free amino acids.

Species	No. of individuals analysed	Total/ Free	Amino acid D/L ratios						
			ALA	VAL	ALLO /ISO	LEU	ASP	PHE	GLU
Anadara trapezia	3	T		0.48 ±0.04	0.55 ±0.13	0.53* ±0.02	0.76 ±0.03	0.82 ±0.12	0.62 ±0.02
Anadara trapezia	1	F		0.76 ±0.02	0.72 ±0.02	0.70 ±0.03	0.73 ±0.07	0.86 ±0.07	
Katelysia rhytiphora	5	T	0.91 ±0.10	0.57 ±0.04	0.56 ±0.03	0.68 ±0.05	0.75 ±0.08	0.89	0.63
Katelysia rhytiphora	4	F	0.99 ±0.05	0.73 ±0.04	0.98 ±0.10	0.81 ±0.06	0.73 ±0.02		
Katelysia scalarina	3	T	0.92 ±0.07	0.54 ±0.05	0.59 ±0.07	0.56* ±0.07	0.58 ±0.05		
Katelysia scalarina	4	F	0.96 ±0.05	0.74 ±0.03	0.96 ±0.12	0.77 ±0.06	0.74 ±0.09		
Bassina pachyphylla	3	T		0.50 ±0.04	0.59 ±0.04	0.55 ±0.09	0.72 ±0.03		

* Artificially low D/L leucine values due to the coelution of β-ALA with L-leucine

Minimum number of individuals required to reliably characterise the age of the marine strata at Peppermint Grove in accordance with equation 3.1.

	ALA	VAL	ALLO /ISO	LEU	ASP
'total acid hydrolysate'	19	5	15	10	7
free amino acids	6	2	20	7	11

Table 5.2b Comparison of grand means of raw data for Katelysia spp. with mixed assemblages for the Peppermint Grove sediments. Amino acid D/L ratios are for the 'total acid hydrolysate' and free amino acids.

Sample	Total/ Free	No. of individuals analysed	Amino acid D/L ratios ALA	VAL	ALLO /ISO	LEU	ASP	$\overline{CV}$
Katelysia spp.	total	9	0.91 ±0.08 (8.79%)	0.56 ±0.04 (7.14%)	0.57 ±0.05 (8.77%)	0.63 ±0.07 (11.11%)	0.67 ±0.09 (13.43%)	9.84%
	free	9	0.98 ±0.05 (5.10%)	0.73 ±0.03 (4.10%)	0.97 ±0.10 (10.30%)	0.78 ±0.08 (10.25%)	0.71 ±0.08 (11.26%)	8.20%
Mixed assemblage	total	14	0.90 ±0.13 (14.44%)	0.55 ±0.06 (10.94%)	0.61 ±0.12 (19.67%)	0.64 ±0.07 (10.94%)	0.69 ±0.08 (11.59%)	13.51%
	free	14		0.73 ±0.03 (4.16%)	0.94 ±0.11 (12.71%)	0.77 ±0.08 (10.68%)	0.70 ±0.08 (11.52%)	9.76%

Values in parentheses indicate coefficients of variation for individual amino acids

assemblage. A large proportion of the Anadara are articulated, although they are strongly leached, have a chalky appearance and easily crumble. The shells are set within a sandy clay and are covered by 1.5 m of pedogenically modified horizontally stratified clay rich sediments. The Anadara were approximately between 0.5-1.0 m above mean sea level. The highly leached character of these fossils is attributed to alternate wetting and drying due to tidal influence.

Given the close proximity of these strata to Peppermint Grove, a Penultimate Interglacial age was anticipated. To test this hypothesis, the extent of racemisation in Anadara trapezia was examined. Analyses were made for the 'total acid hydrolysate' and for free amino acids (Table 5.3).

Clearly the lack of internal concordance in the relative extent of racemisation (epimerisation) and the pronounced differences of amino acid D/L ratios between individuals support the suggestion that in situ leaching has affected the Blackwall Reach Anadara. This is not an unreasonable suggestion in view of the highly moistened nature of the host sediments. The lower D/L ratios evident in the 'total acid hydrolysate' for all amino acids in specimen number 1 compared with specimen 2 maybe attributed to the loss of free amino acids through leaching. This does not however explain the higher D/L ratios for free amino acids in specimen 1.

5.4.2.5 Minim Cove

Emergent fossiliferous shallow marine sediments crop out at Minim Cove, Mosman Park, on the northern bank of the Swan Estuary near Fremantle (Figure 5.5). Somerville (1920) briefly described these sediments although no indication was provided of their age. The marine sediments display horizontal lamination, emphasised by case hardening. As at other localities within the Perth Basin, the marine unit is capped by an aeolian calcarenite. Numerous solution channels, pipes and rhizoliths truncate bedding.

Table 5.3 Extent of amino acid racemisation (epimerisation) in Anadara trapezia, Blackwall Reach, Swan Estuary. Amino acid D/L ratios are for the 'total acid hydrolysate' (T) and free amino acids (F).

Fraction	Individual specimens	Amino acid ALA	VAL	ALLO /ISO	LEU	PRO	ASP
T	(1)	0.47 ±0.003	0.16 ±0.002	0.20 ±0.002	0.25 ±0.006		0.34 ±0.009
T	(2)	0.91 ±0.001	0.28 ±0.03	0.31 ±0.02	0.39 ±0.001	0.60 ±0.09*	0.57 ±0.001
F	(1)				0.77 ±0.05	0.72 ±0.09	0.69 ±0.04
F	(2)		0.39	0.36	0.50 ±0.04	0.56 ±0.07	0.50 ±0.02

* Hand integrated value based on peak height calculations

The marine sediment is highly siliceous and contains a diverse molluscan fossil assemblage. Only a small percentage of the sediment comprises calcium carbonate when the faunal content is excluded, although in places the calcium carbonate content, as matrix does reach approximately 54%.

The marine component represents a remnant of a sand barrier which formed within the mouth of the Swan Estuary under conditions of lower river discharge and good tidal exchange (G.W. Kendrick, Western Australian Museum, pers. comm., 1986).

Little work has been done on the marine sediments at Minim Cove. The earliest reference to these strata was by Somerville (1920) who described their elevated position by invoking uplift. Fairbridge (1953) favoured a Late Pleistocene age for the marine sediments at Minim Cove. This age was corroborated by Hewgill et al., (1983) who, using electron spin resonance dating correlated these sediments with uranium-series calibrated deposits of equivalent age (Veeh, 1966; Veeh et al., 1979; Szabo, 1979).

5.4.2.6 Minim Cove: Amino Acid Racemisation Analyses

Specimens collected for amino acid racemisation analyses were from a small undercut face of a rapidly eroding cliff on the north bank of the Swan Estuary (Figure 5.5). Mollusc species collected included Katelysia rhytiphora, Katelysia scalarina and Anadara trapezia. Katelysia spp., are abundant at this site, although Anadara trapezia is less common. The shells analysed were approximately 3 m above mean sea level, and buried beneath 2 m of sediment. All specimens were very well preserved with articulated and disarticulated shells represented. The disarticulated shells

were randomly oriented within the sediment. The shells were not coated with calcareous surface encrustations, a feature characteristic of the Peppermint Grove fauna.

Analyses were made for the 'total acid hydrolysate' and free amino acids. Representative results are presented in Table 5.4 and Figures 5.7a-e (see also Appendix Table 5.5).

As with the Peppermint Grove fauna, free amino acids were consistently more extensively racemised than the 'total acid hydrolysate' (Figure 5.7a-e). A species-effect on racemisation was not evident in the genus Katelysia based on data for both the 'total acid hydrolysate' and free amino acids. Systematic differences in D/L ratios between Katelysia rhytiphora and K. scalarina were not apparent and the variation evident can be explained in the context of intershell D/L ratio variation.

Coefficients of variation indicated that for the 'total acid hydrolysate', D/L ratio data for leucine and valine displayed the greatest concordance of results (Figure 5.7a and d).

Larger margins of error were evident for aspartic acid, alanine and isoleucine. For free amino acids, aspartic acid and leucine provided the greatest concordance with larger errors represented by alanine, valine and isoleucine. The largest differences between the extent of racemisation evident for free amino acids and the 'total acid hydrolysate' were observed for isoleucine (0.34) and leucine (0.29) respectively. Smaller differences were observed for valine (0.19), aspartic acid (0.09) and alanine (0.7). These data suggest that leucine and valine are particularly useful amino acids for characterising the age of deposits, in view of the excellent concordance of results. A similar conclusion was made by Wehmiller (1984b) for leucine. Valine however, has generally not been used in aminostratigraphic studies.

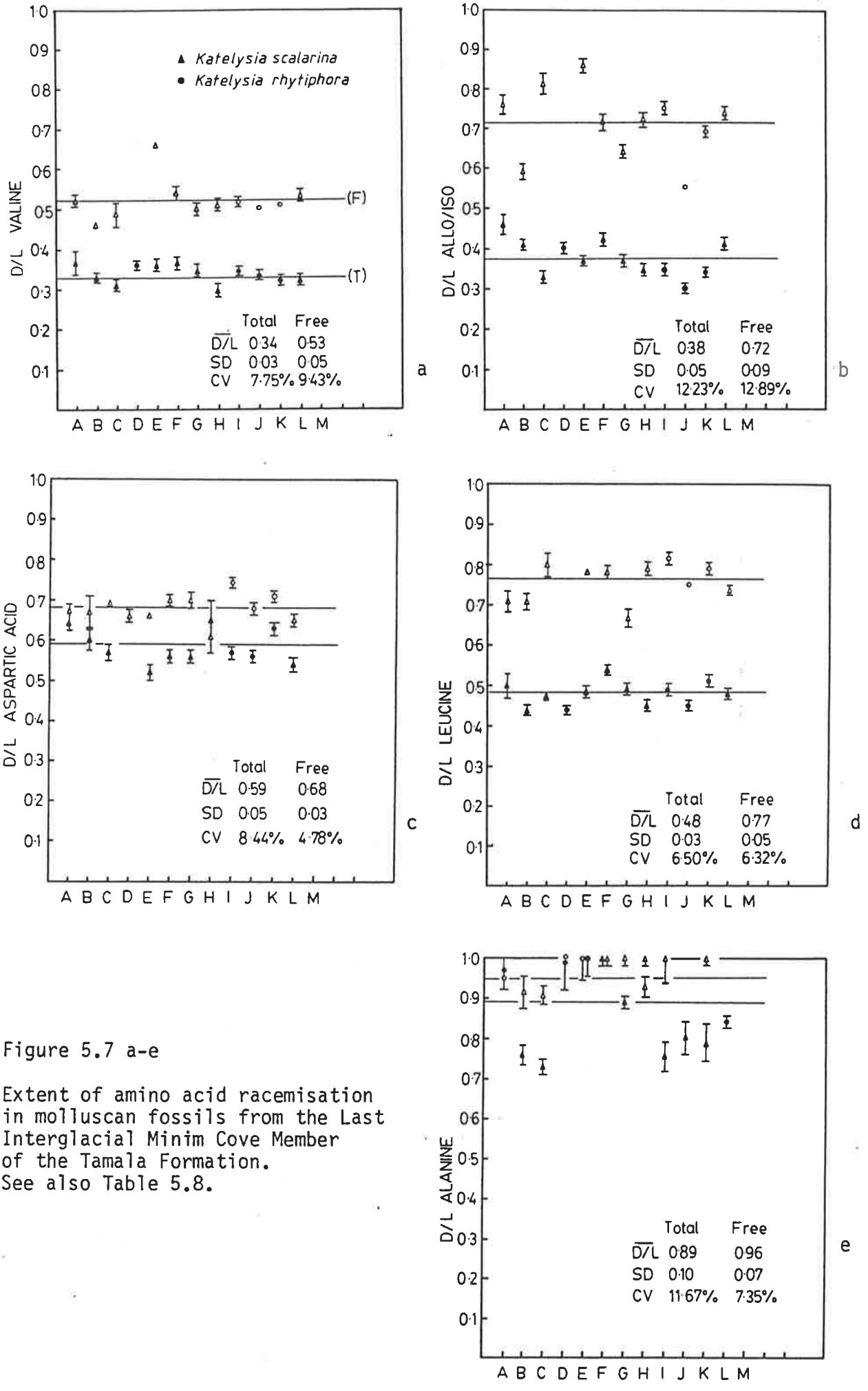


Figure 5.7 a-e

Extent of amino acid racemisation in molluscan fossils from the Last Interglacial Minim Cove Member of the Tamala Formation. See also Table 5.8.

That valine is a particularly useful amino acid for reliably characterising the age of strata is corroborated by equation 3.1. Using this equation to assess the minimum number of individual Katelysia specimens required to satisfactorily characterise the age of the Minim Cove sediments, indicated an average of 4 individuals for both the 'total acid hydrolysate' and free amino acids. The same number of individuals were necessary for aspartic acid and leucine. In contrast, isoleucine and alanine required 13 and 15 individuals respectively.

Table 5.4 Extent of amino acid racemisation (epimerisation) in Katelysia spp., from emergent fossiliferous marine strata, Minim Cove. Amino acid D/L ratios are for the 'total acid hydrolysate' and free amino acids. Results are presented for Katelysia rhytiphora and K. scalarina, and a grand mean of the raw data for both species is also presented. A species-effect is not evident in the genus Katelysia.

Species	No. of individuals analysed	Total/ Free	Amino acid ALA	VAL	ALLO /ISO	LEU	ASP
Katelysia rhytiphora	4	T	0.95 ±0.07	0.33 ±0.02	0.35 ±0.04	0.48 ±0.03	0.61 ±0.05
	3	F	0.99 ±0.02	0.51 ±0.01	0.67 ±0.10	0.79 ±0.03	0.71 ±0.02
Katelysia scalarina	8	T	0.86 ±0.10	0.34 ±0.03	0.39 ±0.04	0.49 ±0.03	0.58 ±0.05
	8	F	0.95 ±0.08	0.53 ±0.06	0.73 ±0.09	0.76 ±0.05	0.67 ±0.03
Katelysia spp. (grand mean)	12	T	0.89 ±0.10	0.34 ±0.03	0.38 ±0.05	0.48 ±0.03	0.59 ±0.05
Katelysia spp. (grand mean)	11	F	0.96 ±0.07	0.52 ±0.05	0.72 ±0.09	0.77 ±0.05	0.68 ±0.03

5.5 ROTTNEST ISLAND

Numerous studies have examined the lithostratigraphy of Rottnest Island (Figure 5.8) in the context of Quaternary sea level fluctuations (Fairbridge, 1953; Tiechert, 1950,1967; Veeh, 1966; Playford et al., 1976; Playford and Leech, 1977). In addition to lithostratigraphic evidence for sea level change, a variety of minor landforms including shore platforms have been described, although only a low degree of confidence can be placed in the latter (Hopley and Thom, 1983). Until the processes responsible for shore platform development for example, are understood, their potential as palaeosea-level indicators should be questioned (Hills, 1940).

Rottnest Island has figured prominently for its stratigraphic evidence for sea level change. According to Teichert (1950), the island's favourable position on the margin of the Western Australian Shield has meant that the island has experienced little tectonic instability during the Quaternary. Although these ideas have been contested in recent years (Playford and Leech, 1977), the island's lithostratigraphic record has been important in providing a time-framework for correlation with similar sediments on the mainland. In particular, the Rottnest Limestone (Fairbridge, 1953) has been equated with marine sediments in the Swan Estuary (Playford et al., 1976). Stratigraphic evidence for Quaternary sea level fluctuations are preserved in the Late Pleistocene Rottnest Limestone and the Middle Holocene Herschell Limestone (Playford and Leech, 1977).

The term Rottnest Limestone was used by Fairbridge (1953) in reference to a thin unit of coralline and shell-rich limestone that crops out at Fairbridge Bluff (named in honour of Rhodes W. Fairbridge) in Salmon Bay, Rottnest Island. The sediments interfinger with aeolian facies of the

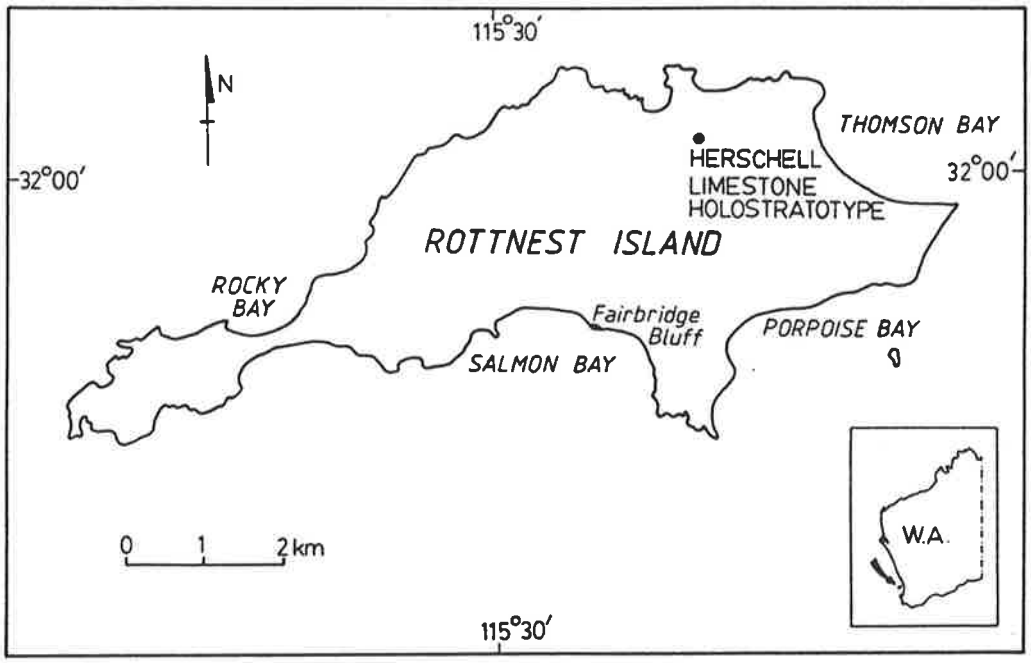


Figure 5.8 Rottnest Island, Western Australia

Tamala Formation. The total exposed thickness of the unit is approximately 3 m. According to Teichert (1950) branching species of Acropora predominate in the reefal sediments, mixed with some foloise types. Large colonies of Platygyra lamellina and Favites favosus are also present. Many corals are encrusted with Lithothamnium and represent a significant component of the reef framework.

Preliminary uranium/thorium ages on corals from the Rottnest Limestone provided an age of 100,000±20,000 yrs BP (Veeh, 1966). Szabo (1979) obtained ages on several corals and molluscs from the Rottnest Limestone and derived a mean age of 132,000±5,000 yrs BP. The Rottnest Limestone is therefore of Last Interglacial age (oxygen isotope stage 5e). Shell beds of equivalent age occur at Minim Cove, and according to Fairbridge (1953) were deposited when sea level was 7 m higher than contemporary mean sea level.

The Rottnest Limestone is here considered a marine coral reef facies of the Tamala Formation. The complex stratigraphic relationship of these sediments and restricted occurrence precludes the unit from being granted formation status. The unit does however have lithological characteristics distinguishing it from other marine facies in the Tamala Formation and is therefore suggested to merit member status in accordance with the lithostratigraphic principles outlined by Hedberg (1976) and Staines (1985).

5.5.1 Herschell Limestone

The Herschell Limestone refers to shell beds deposited in response to the Holocene transgression. These beds cropout along the margins of salt lakes on Rottnest Island, and disconformably overlie aeolian and marine sediments of the Tamala Formation and is in turn overlain by Holocene

dune, paralic and lacustrine sediments. The formation is named after Mount Herschell, and the holostratotype is situated in a small quarry 300 m southwest of the summit (31°59'45"S, 115°31'30"E). This section is 3 m thick, although only the upper 1.5 m is well exposed.

The Herschell Limestone is represented by a richly fossiliferous medium to fine grained skeletal-carbonate sand, containing abundant Katelysia scalarina, Katelysia rhytiphora and numerous Brachidontes spp. A detailed description of the macrofossil assemblage of the sediments was presented by G.W. Kendrick in Playford and Leech (1977). The sediments include shallow-marine and littoral deposits, and deposition is likely to have occurred when the existing salt lakes had a marine connection. According to Playford and Leech (1977), during the deposition of the Herschell Limestone, relative sea level was approximately 3 m higher than at present.

In this study two contrasting sedimentary units of the Herschell Limestone were recognised at the holostratotype (Figure 5.9). The lower unit (Unit-A) is richly fossiliferous containing a large assemblage of species. The shells are irregularly distributed throughout the sediment. Many of the molluscs are articulated and in growth position. In the quarry the thickness of exposure of this unit, although variable, is approximately 60 cm. The macrofauna are set within a medium to fine grained highly calcareous sand. Based on the number of articulated shells present this fossil assemblage is inferred as biocoenose. A thin albeit laterally persistent semi-indurated sandy layer overlies Unit-A. This layer contains few macrofossils and although its thickness is variable, it is generally in the order of 10-20 cm. Unit B overlies this sandy layer and has similar granulometric characteristics to Unit-A although it contains a thanatocoenose fossil assemblage. The sediments contain an abundant molluscan fauna, and the majority of the bivalves are disarticulated and stacked upon each other convex side upwards. Less matrix is evident in this sediment than in Unit-A.

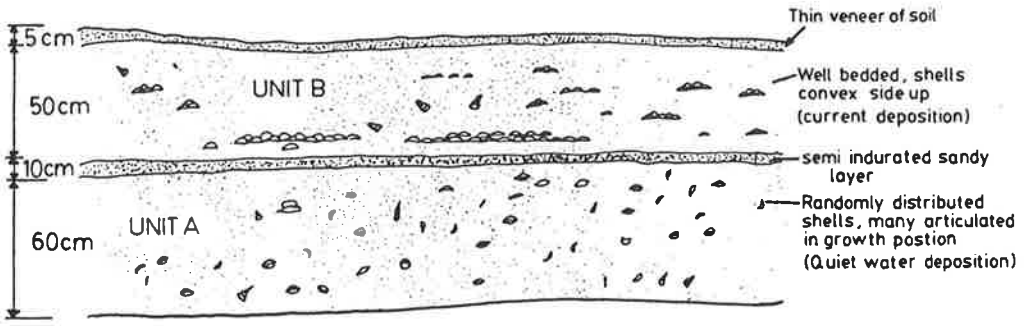


Figure 5.9 Diagrammatic representation of the Herschell Limestone Holostratotype illustrating an upper thanatocoenose and a lower biocoenose shell unit separated by a laterally persistent semi-indurated sandy layer. Radiocarbon dates from this section are presented in Table 5.9.

Katelysia spp., were collected from the lower unit (Unit-A) for amino acid racemisation analyses as these shells were well buried at a depth of 1 m. All macrofossils recorded from the Herschell Limestone are living species, and most of them still frequent the Rottnest-Fremantle area. The faunal difference between the two units is that the lower contains both Katelysia rhytiphora and Katelysia scalarina, whereas the upper unit contains only Katelysia scalarina (G.W. Kendrick, pers. comm., 1986).

Playford and Leech (1977) cited a range of radiocarbon ages without indicating whether the ages were marine environmentally corrected or were converted from radiocarbon years (bp) to sidereal years (BP). In addition, they failed to provide details of the stratigraphic context of the dated materials. The range of ages are listed in Table 5.5. Additional unpublished ages for molluscs from the Herschell Limestone are also outlined in Table 5.5 (G.W. Kendrick, unpubl. data, 1986).

Sample C of Kendrick and A of Playford and Leech (1977) both from the upper shell bed (Unit-B) are in close agreement, even though the error terms for these ages do not overlap. In addition samples A and B of Kendrick are consistent with B and C of Playford and Leech (1977). Based on radiocarbon evidence 'pooled' mean ages of 5580±626 and 3540±380 may be assigned to the lower and upper units of the Herschell Limestone respectively. Thus it would appear that the ages of the two units can be resolved based on radiocarbon dating.

An age of 5180±100 yrs BP was also reported by Playford and Leech (1977), obtained on bivalves from another undesignated locality adjacent Government House Lake on Rottnest Island.

In reference to the elevated position of the Herschell Limestone, suggestive of a relative 3 m higher Holocene sea level, Playford and Leech (1977) referred to an "Older Peron Submergence". Accordingly, this refers to a higher mean sea level experienced at Rottnest Island some 5,000-6,000 BP. During the "Older Peron Submergence" the now

Table 5.5 Radiocarbon ages obtained on molluscan fauna from the Herschell Limestone, Rottnest Island after Playford and Leech (1977) and unpublished data of Kendrick (1986, Western Australian Museum).

	Age	Species	Additional Information
(after Playford and Leech, 1977)			
(A)	3810±90 yrs	not indicated	top of unit
(B)	4950±160 yrs	not indicated	lower part of unit
(C)	5660±220 yrs	not indicated	upper part of unit

(after G.W. Kendrick, Western Australian Museum, unpublished data, 1986).

Rottnest Island conventional radiocarbon ages, Herschell Limestone. East face of the Mt Herschell quarry, collected by G.W. Kendrick, 19 March 1982.

(A) Sample A Shells of Tellina perna (Spengler) from carbonate sand, between 1.0-1.2 m below base of prominent cemented layer. SUA-1902 6410±80 yr BP.

(B) Sample B Shells of Katelysia rhytiphora (Lamy) from carbonate sand, between 0-0.2 m below base of prominent cemented layer, SUA-1903 5290±70 yr BP.

(C) Sample C Shells of Katelysia scalarina (Lamark) (disarticulated) from shell bed between 0.2-0.3 m above base of prominent cemented layer, SUA-1904 3270±60 yr BP.

restricted lakes on Rottnest Island had a marine connection. A subsequent fall of sea level and concomitant coastal dune migration led to the isolation of these lakes (Playford and Leech, 1977). This would appear to post-date the peak of the Holocene transgression documented along other parts of the Australian coastline, that have variously been dated at 6,500 radiocarbon years before present (Hopley, 1983). Although the cause of the "Older Peron Submergence" has not been established, the timing of this event may indicate a local hydroisotatic effect.

5.5.2 Herschell Limestone: Amino Acid Racemisation Analyses

Numerous articulated specimens of Katelysia rhytiphora and Katelysia scalarina were obtained for amino acid racemisation analyses from the lower unit of the Herschell Limestone. The shells had been buried at a depth of 1 m. Analyses were made for the 'total acid hydrolysate' and free amino acids (Table 5.6 and Appendix Table 5.6).

The shells were extremely well preserved. As low concentrations of free amino acids were anticipated, because of the young age of these fossils, entire single juvenile valves were analysed. As with older specimens studied, free amino acids were consistently more extensively racemised than the 'total acid hydrolysate'. In addition, relative intrageneric rates of racemisation were consistent with published results (Lajoie et al., 1980).

Accepting that a 'pooled' average radiocarbon age (calendar years) of 5580±626 BP for these molluscs is reliable, then the extent of racemisation would appear anomalously high for aspartic acid and alanine. In contrast, D/L ratios for leucine, valine and isoleucine are consistent with the radiocarbon age reported above and the approximate Mean Annual Temperature of 18°C for Rottnest Island. These data also compare favourably with Holocene data from Smoky Bay, South Australia (Table 4.14). The high coefficients of variation are likely to reflect genuine age

Table 5.6 Extent of racemisation (epimerisation) in Katelysia spp., from the Middle Holocene Herschell Limestone, Rottnest Island, Western Australia. Results are for the 'total acid hydrolysate' and free amino acids*.

	Amino acid D/L ratio				
	ALA	VAL	ALLO/ISO	LEU	ASP
'total acid hydrolysate'	0.42 ±0.12 (28.6)	0.09 ±0.02 (22.2)	0.13 ±0.04 (30.8)	0.15 ±0.04 (26.7)	0.37 ±0.05 (13.5)
free amino acids	0.69 ±0.06 (8.7)	0.24 ±0.04 (16.6)	0.26 ±0.08 (30.7)	0.34 ±0.11 (32.4)	0.52 ±0.05 (9.6)

* coefficients of variation for individual amino acids are indicated in parentheses

differences of individual shells. The coefficients of variation for all amino acids both for the total and free fractions were significantly higher than for Pleistocene samples studied. Thus, while age variation within Holocene sediments may be detected using amino acid data, the same resolution is not evident in Pleistocene sediments that may represent comparable time intervals (e.g., stage 5e of the marine oxygen isotope record).

5.6 ROE CALCARENITE: EUCLA BASIN

The term Roe Calcarenite is used in reference to richly fossiliferous, semi-indurated, medium to coarse grained calcarenites of Early Plei- age, deposited in the Eucla Basin (Lowry, 1970; Ludbrook,
The beds were first described by Tate (1879b) as "calciferous sandstone" with molluscs. The formation covers most of the Roe Plains, Western Australia. The Roe Calcarenite unconformably overlies the Miocene Abrakurrie Limestone, and in places the Eocene Wilson Bluff Limestone. The unit is mantled by soil and unconsolidated sand dunes. Although some variation is evident, the unit is generally 1.5-2 m thick, and attains a maximum thickness of 7.5 m in Eucla No.1 Well (Lowry, 1970; Ludbrook, 1978). In places, the calcarenite consists almost entirely of large tests of the foraminifer Marginopora vertebralis. Their large test size has been considered a function of warmer temperatures than prevail at present in southern Australia and water depth (J.M. Lindsay, pers. comm., 1986).

Ludbrook (1958) assigned a Pleistocene age (undifferentiated) to the Roe Calcarenite, based on the percentage of molluscs in the formation that belong to living species. Lowry (1970) briefly discussed the age of the Roe Calcarenite in the context of European Quaternary glacioeustatic sea levels and suggested the formation may have been deposited during the Mindel-Riss Interglacial (Oxygen Isotope Stage 7), Ludbrook (1978) subsequently examined the molluscan fossil assemblage of the Roe Calcarenite and identified some 265 species and sub-species, of which 65-70% of the living species are regarded as of Early Pleistocene age. Included in the fauna is the janthinid gastropod, Hartungia dennanti chavani, considered useful for biostratigraphic correlation because of its pelagic habit (Ludbrook, 1984). Hartungia also occurs in the Early Pleistocene Point Ellen Formation on Kangaroo Island (Milnes et al., 1983; Ludbrook, 1983).

As the endemic nature of the molluscan fauna in the Roe Calcarenite precluded stratigraphic correlation at an international level, Ludbrook (1978) compared the percentages of living species that are also present in the Roe Calcarenite with similarly obtained data for the Early Pleistocene Red Crag of East Anglia, which according to Beck et al., (1972) has a minimum age of 1.6 Ma. The similarity in these Lyellian percentages prompted Ludbrook to assign an Early Pleistocene age to the Roe Calcarenite. This age assessment should however be treated with caution. Within-basin environmental characteristics may determine species presence at only a local scale, and changes in these features could promote migration or extinction. The merit of Lyellian statistics should also be questioned. The approach does not involve correlation using index fossils or faunal assemblages, but simply a comparison of the ratios of living and fossil species with European Plio/Pleistocene stratal sequences.

5.6.1 Roe Calcarenite: Amino Acid Racemisation Analyses

Samples for amino acid racemisation analyses were obtained Madura, Western Australia (Figure 5.10). Species analysed included the molluscs Katelysia scalarina, Katelysia rhytiphora and the foraminifer Marginopora vertebralis. The specimens were from a collection of the Western Australian Museum and were kindly made available by Mr G.W. Kendrick. The specimens were from semi-indurated bioclastic carbonate sands, buried at depths of approximately 0.5 m. The mean annual air temperature at these sites is approximately 18.2°C. Analyses were made for the 'total acid hydrolysate' and free amino acids. Intrashell D/L ratio variation in the bivalves was avoided by analysing only the hinges. Similar sample amounts were used as in the Jandakot fauna. Representative results are presented in Table 5.1 and depicted in Figures 5.3a-d.

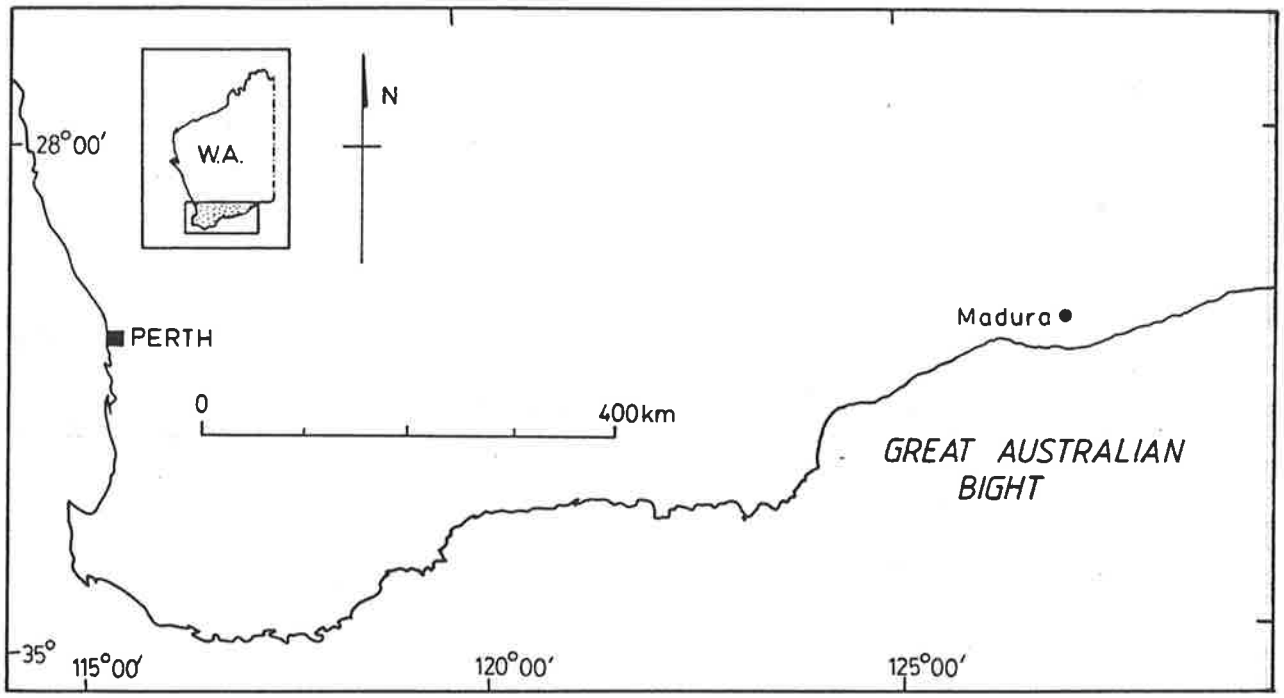


Figure 5.10 Location map of the Roe Calcarenite sample locality Madura, Western Australia.

Amino acid D/L ratios for the Roe Calcarenite fauna fall marginally below the 'racemic' condition. The relative extent of racemisation for individual amino acids in the Katelysia spp., is similar to younger Katelysia specimens studied in this investigation, and in general accord with other carbonate matrices (Lajoie et al., 1980). The anomalously low leucine D/L ratios resulted from coelution of β-alanine with L-leucine and was confirmed by analysis of amino acid standards, in conjunction with additional analyses on a Hewlett-Packard model 5890 gas chromatograph using a Chirasil-Val fused silica column.

Coefficients of variation for amino acid D/L ratios ranged between 4-14% for the 'total acid hydrolysate', and 5-20% for free amino acids. A similar range was evident in the Jandakot fauna. Amino acid D/L ratios for the 'total acid hydrolysate' were not significantly different from free amino acid values, a feature also evident in the Jandakot fauna. The significance of this observation was discussed in section 5.4.1.2.

Using equation 3.1, 14 individual shells were required to adequately characterise the relative age of the Roe Calcarenite based on amino acid D/L ratios for the 'total acid hydrolysate' to a precision of ±0.04. This compared favourably with the Jandakot fauna which required 15 individuals. In contrast, based on results for the free amino acid fraction, 31 and 27 individuals would have to be analysed from the Jandakot Member and the Roe Calcarenite respectively. This is most likely an expression of the labile nature of the free amino acid fraction, and highlights its susceptibility to leaching and preferential contamination effects.

These values represent averages for all amino acids. However, when individual amino acids were considered, alanine, valine and isoleucine provided the greatest precision for age assessments for both the Jandakot

Member and Roe Calcarenite. Aspartic acid provided good resolution for Katelysia spp., in the Roe Calcarenite, but rated poorly in the Jandakot Member. Results for phenylalanine and glutamic acid for the Jandakot Member are unrepresentative as they are for only one individual.

In the free amino acid fraction valine and isoleucine provided the greatest precision for the Jandakot Member, according to equation 3.1. Alanine, leucine, aspartic acid and valine gave the greatest precision for the Roe Calcarenite.

Amino acid analyses were also made on the foraminifer Marginopora vertebralis from the Roe Calcarenite. The specimens analysed were buried at a depth of 2 m. Despite their large test size (~1 cm) when compared with other foraminifera, it was necessary to analyse numerous individuals together in order to fulfil the requirement of sample weight. The reported D/L ratios therefore represent unweighted averages for approximately 20-30 individuals. Results of analyses are summarised in Table 5.7 and compared with younger specimens to serve as a basis for comparison.

The extent of racemisation evident in Marginopora vertebralis is consistently less than for Katelysia spp., of equivalent age (Table 5.7 cf., Table 5.1). Given that the D/L ratios reflect values for indigenous amino acids in Marginopora these data support the South Australian work, that the rates of racemisation in Marginopora vertebralis are significantly slower than in Katelysia spp., and other molluscan genera studied. A similar trend was evident in fauna from the Last Interglacial Glanville Formation in South Australia (Chapter 4).

Table 5.7 Amino acid D/L ratios ('total acid hydrolysates') for Marginopora vertebralis from the Plio/Pleistocene Roe Calcarenite, Roe Plains, Eucla Basin, Western Australia. Younger specimens provide a basis for comparison.

Sample age	Locality	MAT (°C)	Amino acid						
			ALA	VAL	ALLO /ISO	LEU	ASP	PRO	GLU
Modern	Great Barrier Reef, Queensland			0.02	0.02 ±0.007	0.03 ±0.01	0.08		0.05
Holocene (<2 ka)	Great Barrier Reef, Queensland	25.8	0.06 ±0.01		0.02	0.05 ±0.02	0.14 ±0.02	0.07 ±0.03	0.06
Late Pleistocene (Last Interglacial)	Glanville Formation, South Australia	18.0	0.30 ±0.05	0.10 ±0.02	0.14 ±0.02	0.15 ±0.01	0.36 ±0.03	0.27 ±0.02	0.23 ±0.01
Plio/Pleistocene Roe Calcarenite	Roe Plains, Western Australia	18.2	0.88 ±0.16	0.43 ±0.01	0.52 ±0.06	0.40 ±0.03	0.62 ±0.16	0.66*	0.48 ±0.05

* manually integrated based on peak height determinations.

5.7 AMINOSTRATIGRAPHIC RESULTS: DISCUSSION

Application of the aminostratigraphic approach in the study of Quaternary marine sediments within the Perth Basin has clarified some of the complex lithostratigraphic relationships and has provided a basis for chronocorrelation with South Australian marginal marine sediments. In addition, several important questions concerning the application of the amino acid racemisation reaction arose from this study and are addressed in Chapter 7.

5.7.1 The Perth Basin

Summary plots of analytical results (Figure 5.11a-c) indicate that valine and isoleucine reliably demonstrate the relative age relationships of the marine strata studied. Because of the coelution of β-alanine with L-leucine and γ-amino-n-butyric acid with L-aspartic acid and occasionally D-aspartic acid, less representative data were available and therefore results were not plotted for these amino acids.

Results for alanine suggest two possibilities. The first is that a 'racemic' condition is quickly obtained preventing Pleistocene deposits of different ages from being distinguished based on alanine enantiomeric ratio data. This may be due to a diagenetic contribution of alanine resulting from the dehydration of serine (Bada et al., 1978). That serine is not generally observed in molluscs of Last Interglacial age is consistent with this hypothesis. Alternatively, coelution of an unknown compound with D-alanine may have resulted in artificially high alanine D/L ratios in some instances, where rider peaks were recognised. In view of this caution was exercised with the interpretation of alanine D/L ratios in fossils older than the Last Interglacial.

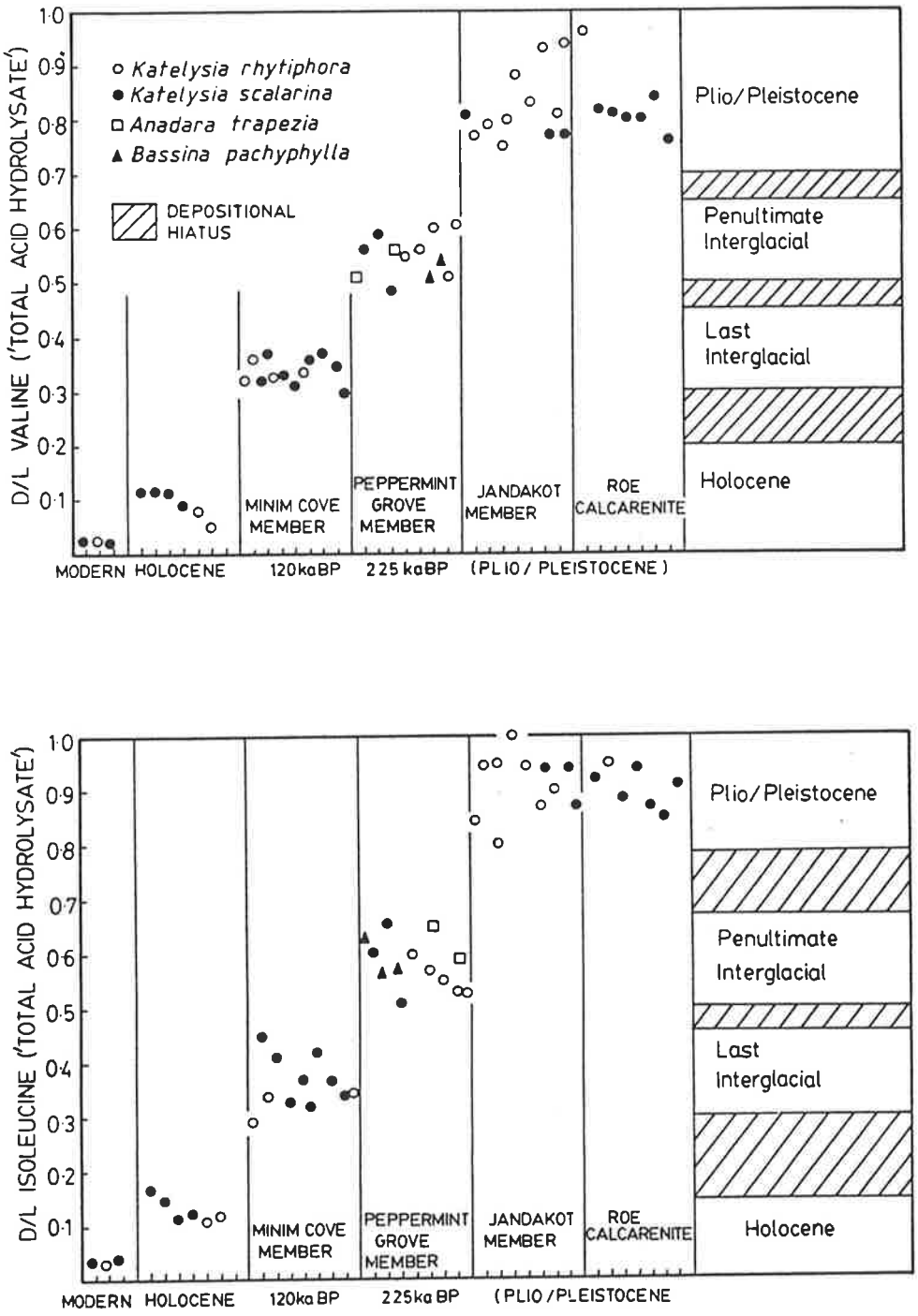


Figure 5.11a Summary plots of D/L ratio data for Quaternary molluscan fossils from Western Australia. D/L ratios are for the 'total acid hydrolysate' (Figure 5.11a) and free amino acids (Figure 5.11b).

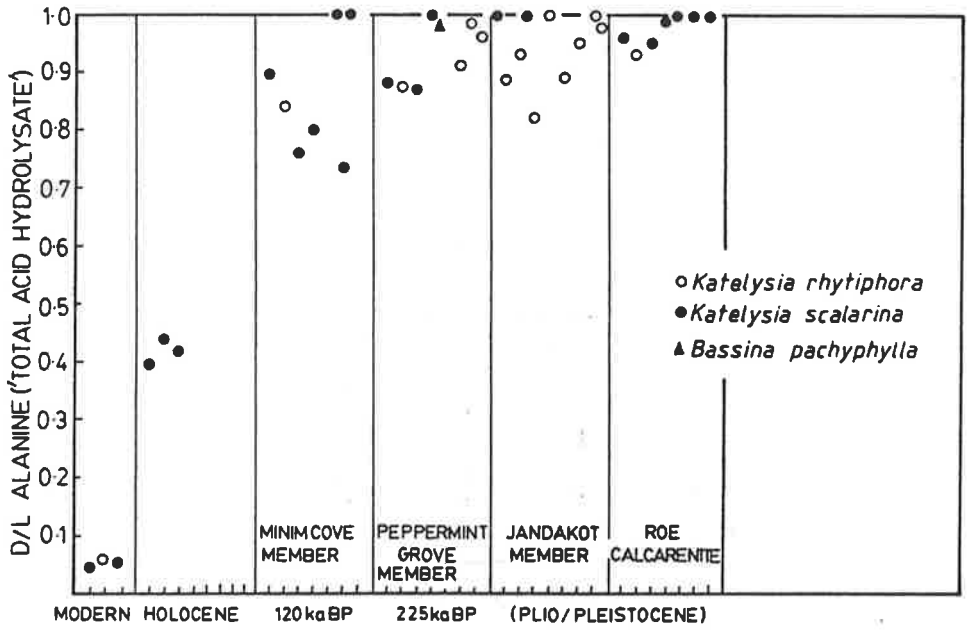


Figure 5.11 a (continued)

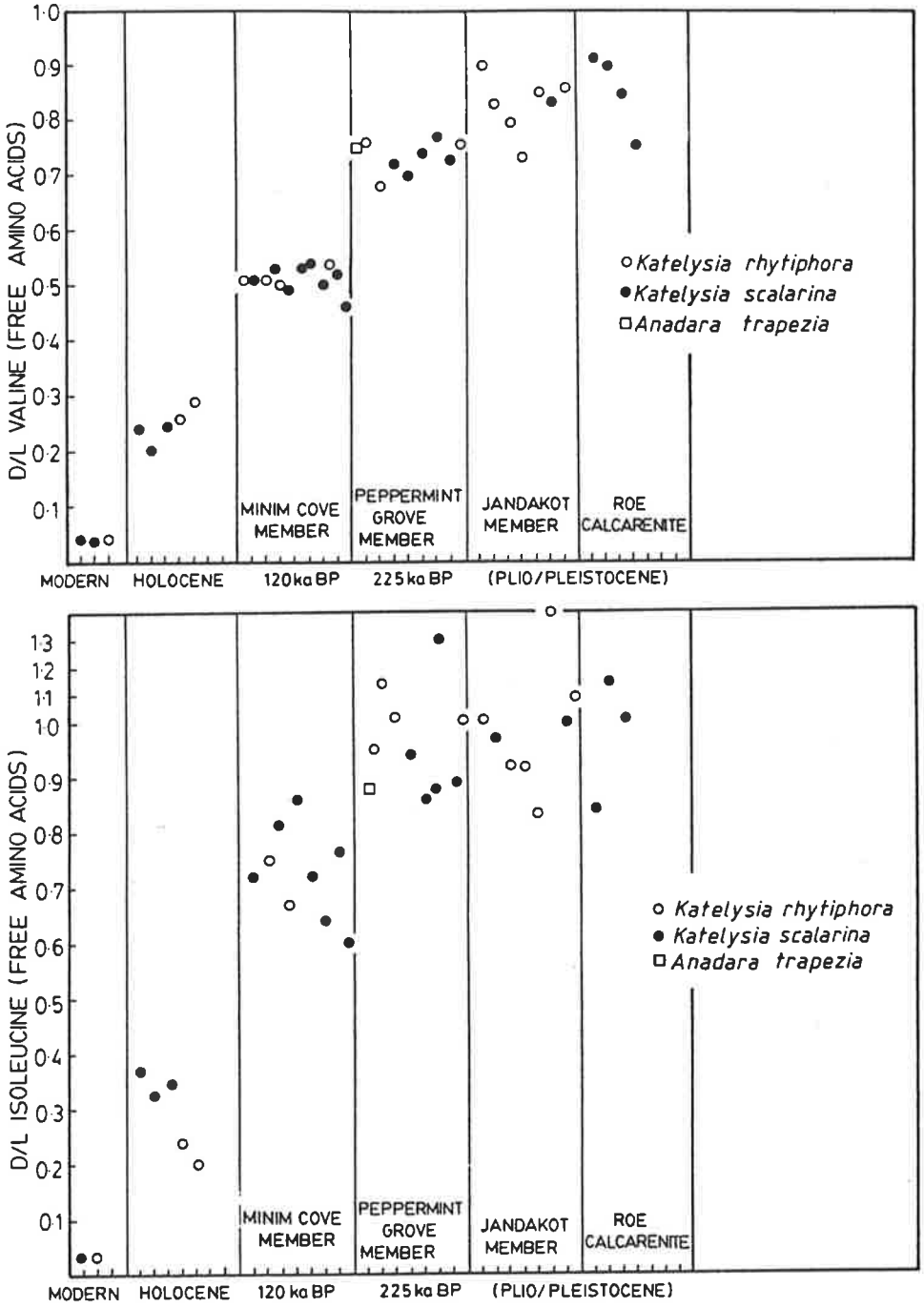


Figure 5.11b Free amino acids

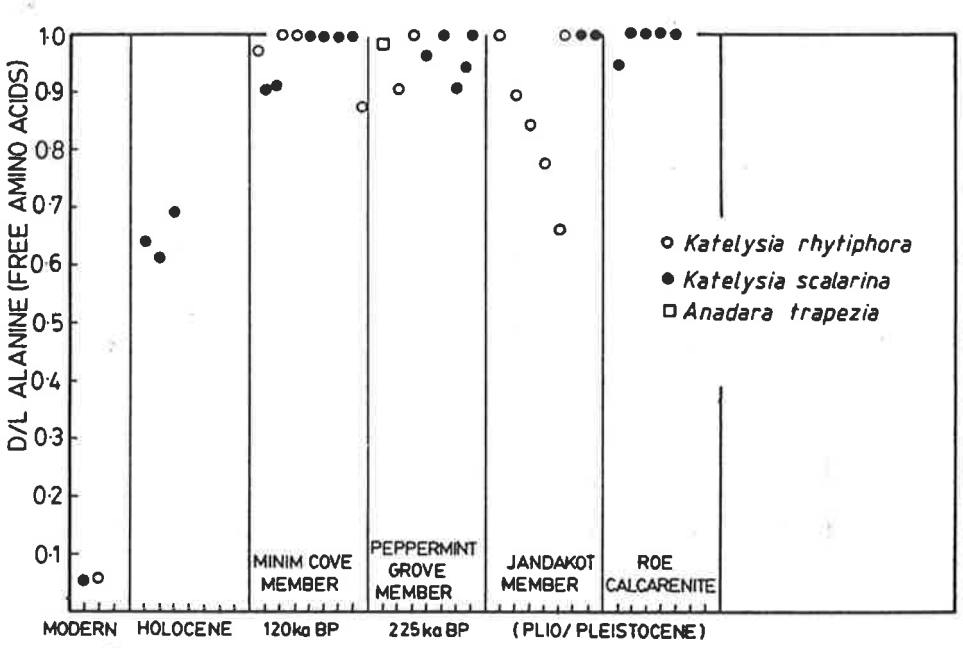


Figure 5.11 b (continued)

In a preliminary survey using electron spin resonance dating, Hewgill et al., (1983) assigned Last Interglacial and Penultimate Interglacial ages to the Minim Cove and Peppermint Grove sediments respectively. In both cases these age assessments were based on the total stratigraphic radiation dose experienced by Anadara trapezia since their incorporation in sediments. The total stratigraphic radiation doses for Anadara from the Peppermint Grove and Minim Cove sites were 27.9 and 15.5 krads respectively. These values were in close agreement with other molluscan species studied by Hewgill et al., (1983). Specimens of Tridacna maxima, from a calcarenite on the coastal plain west of Cape Range, had previously been dated using uranium-series dating by Veeh et al., (1979). This provided a basis for calibration of the electron spin resonance data. A suite of uranium-series age determinations were reported by Veeh et al., (1979) ranging between 138,000 to 110,000 yrs BP. The Tridacna maxima from this deposit yielded a total stratigraphic dose of 12.5 krad (Hewgill et al., 1983) which compared favourably with values obtained for Anadara trapezia from Minim Cove.

However, the Penultimate Interglacial age suggested by Hewgill et al., (1983) for the Peppermint Grove sediments, was a relative age assessment and involved a comparison of the electron spin resonance results of uranium-series calibrated Last Interglacial marine strata with the results for the Peppermint Grove sediments. As a significantly higher value for the total stratigraphic dose was obtained on Anadara trapezia from the Peppermint Grove site, Hewgill et al., (1983) invoked established models of Quaternary global ice volumes and sea level fluctuations (Shackleton and Opdyke, 1973) to assign a Penultimate Interglacial age to these strata. Their age assessment therefore represents a minimum age as the strata could well be of pre-Penultimate Interglacial age or older using this reasoning.

Results of amino acid racemisation analyses in this study however, corroborate the age assessments of Hewgill et al., (1983). Based on the extent of racemisation of a range of amino acids the relative ages are in accord with the electron spin resonance data. Amino acids are consistently more extensively racemised in the Peppermint Grove than in the Minim Cove fauna (Table 5.2a cf. 5.4). This represents a significant advance as many workers still intuitively ascribe a Last Interglacial age to marine strata at Peppermint Grove (Playford and Leech, 1977). Additional evidence in support of the age of these strata is the similarity in D/L ratios for molluscan fossils of equivalent age from South Australia (see Section 5.7.2).

In addition to corroborating the results of electron spin resonance dating, this study has also clarified some aspects of the Quaternary lithostratigraphy within the Perth Basin. In particular, it is proposed that the Tamala Limestone (Playford et al., 1976) be renamed the Tamala Formation, in reference to the complex association of aeolian calcarenites and intercalated marine sediments that occupy the Swan Coastal Plain. This complex lithostratigraphic association developed from a succession of cyclic dune building episodes along the high energy coastline of Western Australia, and was intimitely related to Quaternary sea level fluctuations. Furthermore, several marine units merit Member status in accordance with the lithostratigraphic principles outlined by Staines (1985).

It is proposed herein that the emergent fossiliferous marine strata at Minim Cove and Peppermint Grove be granted Member status. Both these units are readily distinguishable from the aeolian facies of the Tamala Formation. However, their spatial distribution is difficult to establish and because dating techniques are required to distinguish these units, they cannot easily be mapped. In view of this, member status is assigned to them rather than formation status. In the case of the Peppermint Grove

sediments, this proposal represents a downgrading of their status for they were originally described as the Peppermint Grove Formation by Fairbridge (1954).

The relationship between the extent of racemisation (epimerisation) evident in the 'total acid hydrolysate' and free amino acids for valine and isoleucine respectively, for molluscs ranging from Plio/Pleistocene to Holocene in age is illustrated in Figure 5.12a and b. If the extent of racemisation was consistently equivalent for both the total and free with increasing fossil age, then the data should define a slope of 45°. Any departure from 45° would therefore indicate differences in the extent of racemisation, and as a corollary provide information regarding racemisation rates. Free amino acids both for valine and isoleucine are more extensively racemised (epimerised) than the 'total acid hydrolysate' for specimens ranging in age from 220 ka to Middle Holocene. In contrast, as outlined earlier in this Chapter, the extent of racemisation evident for free amino acids did not differ significantly from the 'total acid hydrolysate' for the Plio/Pleistocene specimens.

These data are therefore consistent with the model proposed by Mitterer and Kriausakul (1984) for the rate and degree (extent) of isoleucine epimerisation evident in different molecular size fractions. In particular, the data are important for they demonstrate that the relative kinetics evident in different molecular size fractions of isoleucine (Mitterer and Kriausakul, 1984) also applies for enantiomeric amino acids such as valine, as speculated by these authors. From these data however, arises the question; at what point does the extent of racemisation evident for the 'total acid hydrolysate' approach that of free amino acids? To address this question, molluscs with ages between Plio/Pleistocene and 220 ka would have to be analysed. However, the global occurrence of well preserved molluscs of this age is limited. Some workers (Blackwelder, 1981) have discussed the dearth of well preserved molluscs of this age in terms of a major depositional hiatus. This issue is further explored in Chapter 7.

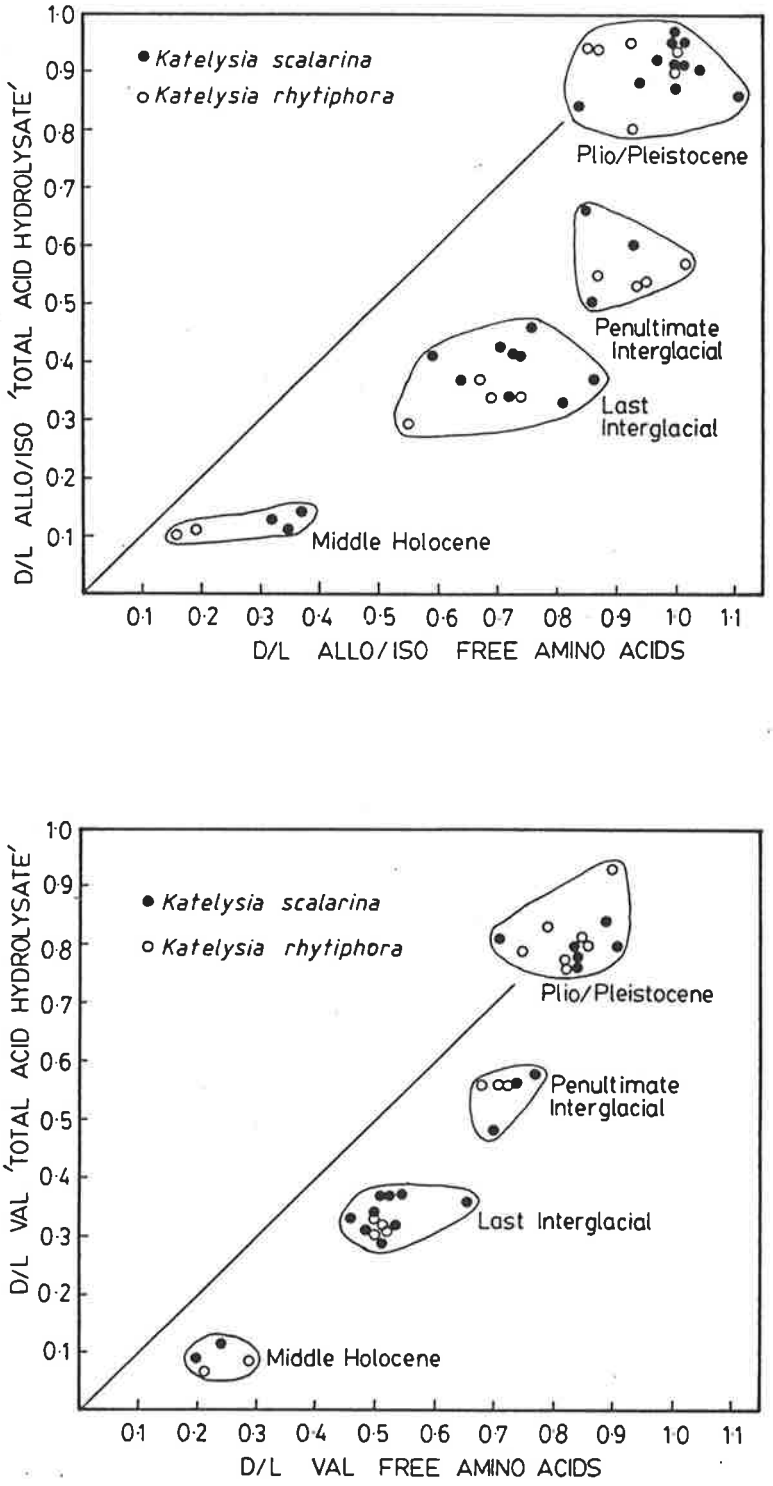


Figure 5.12 Summary plots comparing the extent of valine racemisation and isoleucine epimerisation for the 'total acid hydrolysate' against free amino acids.

In accordance with the aminostratigraphic principles outlined in Chapter 4, several aminozones were recognised within the Western Australian Quaternary stratal sequences. These are here referred to as the Jandakot-Roe, Peppermint Grove, Minim Cove and Herschell aminozones. Although a precise quantitative age cannot yet be delineated based on amino acid data, the Jandakot-Roe aminozone refers to sediments of Late Pliocene to Early Pleistocene age.

The Peppermint Grove, Minim Cove and Herschell aminozones are equated with stages 7, 5e and 1 of the marine oxygen isotope record respectively. In broad view these aminozones correspond to time intervals of 10 ka. It is here proposed that future studies invoke these terms to assign chronostratigraphic significance to Quaternary sediments where amino acid data suggest age equivalence. Therefore, Holocene sediments on the mainland irrespective of facies would be assigned to the Herschell aminozone. Similarly, sediments of Penultimate and Last Interglacial age would be equated with the Peppermint Grove and Minim Cove aminozones.

5.7.2 Intra-Continental Aminostratigraphic Correlation

In Chapter 2 it was outlined that aminostratigraphic studies are most reliable within small geographic regions that have experienced near uniform changes in their 'Effective Quaternary Temperature' histories. Although aminostratigraphic correlations over large distances have generally not been contemplated with the exception of studies investigating latitudinal effects, results presented herein suggest that provided independent age calibration and palaeoclimatic control is available, correlation of stratigraphic sequences using amino acid data is possible. This contention is supported by the chronocorrelation of the Jandakot Member of the Yoganup Formation (W.A.) with the Roe Calcarenite (W.A.); and the Minim Cove Member of the Tamala Formation (W.A.) with the Glanville Formation (S.A.). In addition, results for the Peppermint Grove Member of the

Tamala Formation (W.A.) and the "Older Pleistocene marine beds" (S.A.) further serve to highlight the potential of applying amino acid data in long distance chronocorrelations. These chronocorrelations are based on the extent of racemisation in Anadara trapezia and Katelysia spp. Results reported are for the 'total acid hydrolysate' (Tables 5.1, 5.8 and 5.9).

Chronostratigraphic correlation of Australian Early Pleistocene marine sediments has hitherto been hampered by a lack of techniques that could directly date molluscan fossils. The potential of applying amino acid racemisation to such problems is highlighted in the results for Jandakot Member of the Yoganup Formation and the Roe Calcarenite. Although these marine units are separated by a distance of some 1,000 km, the D/L ratios for the Katelysia spp., support the chronocorrelation of these deposits in broad view. This represents the first direct chronostratigraphic correlation of these units. To improve the precision of correlation, intrashell amino acid D/L ratio variation and a genus effect were avoided by analysing the hinge region of Katelysia spp. However, in accordance with the scheme presented in Chapter 3, effects or natural variation within a deposit and between site variation were unavoidable. Despite these sources of variation excellent concordance of results were obtained in the correlation of these deposits for both the 'total acid hydrolysate' and free amino acids. The difference between the mean D/L ratios for the Jandakot and Roe fauna for each amino acid both for the 'total acid hydrolysate' and free amino acids was generally less than intershell D/L ratio variation (Table 5.1) and therefore strengthens this chronocorrelation. The large difference between the mean D/L ratios for leucine from these two populations resulted from the coelution of β-alanine with L-leucine. Although this resulted in unrepresentative leucine D/L values for both the Jandakot and Roe fossils, the dilution effect of this was more pronounced in the Jandakot fauna. Contemporary mean annual air temperatures for both sites are approximately 18°C. This in

Table 5.8 Intracontinental aminostratigraphic correlation of Last Interglacial Marine Strata based on the extent of racemisation (epimerisation) in Katelysia spp. ('total acid hydrolysate').

Stratigraphic unit; locality	Contemporary M.A.T. (°C)	No. of individuals analysed	Amino acid D/L ratios VAL	LEU	ALLO /ISO	ASP
Minim Cove Member, Tamala Formation Perth Basin	18	12	0.34 ±0.03	0.48 ±0.03	0.38 ±0.05	0.59 ±0.05
Glanville Formation, Port Wakefield South Australia	17	4	0.36 ±0.05	0.39 ±0.09	0.42 ±0.01	0.56 ±0.14
Difference between mean D/L ratios			(0.02)	(0.09)	(0.04)	(0.03)

Table 5.9 Intracontinental aminostratigraphic correlation of Penultimate Interglacial Marine Strata based on the extent of racemisation (epimerisation) in Anadara trapezia ('total acid hydrolysate').

Stratigraphic unit; locality	Contemporary M.A.T. (°C)	No. of individuals analysed	Amino acid D/L ratios VAL	ALLO /ISO	LEU	ASP	PHE	GLU
Peppermint Grove Member, Tamala Formation Perth Basin	18	3	0.59 ±0.08	0.62 ±0.04	0.71 ±0.05	0.73 ±0.08	0.74 ±0.13	0.62 ±0.06
'Older Pleistocene Marine Beds' Redcliff, South Australia	18	4	0.48 ±0.04	0.55 ±0.13	0.53* ±0.02	0.76 ±0.03	0.82 ±0.12	0.62 ±0.02
Difference between mean D/L ratios			(0.11)	(0.07)	(0.18)	(0.03)	(0.08)	(0.00)

* D/L LEU values for the 'Older Pleistocene Marine Beds' are low, due to coelution of β-ALA with L-LEU

association with amino acid D/L ratio equivalence suggests these deposits may have experienced similar 'Effective Quaternary Temperature' histories.

The potential of intracontinental correlation is also apparent for marine strata of Penultimate Interglacial age (Table 5.9). Closer agreement between amino acid D/L ratios is evident in Katelysia spp. (Table 5.8) of Last Interglacial age from the Minim Cove Member of the Tamala Formation (W.A.) and the Glanville Formation (S.A.). The differences between the mean D/L ratios for these two populations compares favourably with intershell D/L ratio variation. Intrashell amino acid D/L ratio variation and a genus-effect were avoided by analysing only the hinges of Katelysia spp. Factors 5 and 6 of the scheme presented in Chapter 3 were unavoidable. The excellent concordance of results however, suggest that in this case, effects or natural variation within a deposit and between site variation assume less importance. These data are encouraging for they indicate that in some instances intershell D/L ratio variation may represent the largest margin of error in the correlation of deposits. This is a surprising observation however, in view of all the factors that influence molluscan racemisation, both at the molecular level and within and between outcrops.

5.8 CONCLUSIONS

The significant conclusions from this study include:

(1) The amino acid racemisation reaction has been successfully applied in resolving some of the complex lithostratigraphic relationships of Quaternary strata within the Perth Basin.

(2) Time equivalence of the Jandakot Member of the Yoganup Formation (Perth Basin) with the Roe Calcarenite (Eucla Basin) was demonstrated using amino acid data.

(3) Confirmation of Penultimate and Last Interglacial ages for the Peppermint Grove and Minim Cove Members of the Tamala Formation respectively.

(4) The application of amino acid racemisation in Intracontinental correlation of Penultimate Interglacial and Last Interglacial marine strata was demonstrated.

(5) The extent of racemisation evident in the molluscan fossils discussed in this Chapter, support the kinetic interpretations made in Chapter 4.

(6) An age cannot be firmly placed on the strata at Blackwall Reach in view of the strongly leached character of the Anadara trapezia

(7) Several aminozones are proposed and include the Jandakot-Roe, Peppermint Grove, Minim Cove and Herschell aminozones.

CHAPTER 6 HOLOCENE AMINOSTRATIGRAPHIC STUDIES: EAST COAST OF AUSTRALIA

6.1 INTRODUCTION

As both the foraminifer Marginopora vertebralis and the estuarine bivalve Anadara trapezia became locally extinct in South Australian coastal waters following the Last Interglacial, a pilot study was undertaken to examine the extent of racemisation evident in Holocene and modern specimens from the east coast of Australia where these fauna are still extant. It was also intended that the data obtained provide a basis for comparison with results of future aminostratigraphic studies from other Australian coastal localities. An additional aim was to further the understanding of the nature of molluscan racemisation kinetics in the context of the Australian Quaternary through studies of the D/L ratio variation with latitude.

6.2 HOLOCENE ANADARA spp., EAST COAST OF AUSTRALIA

6.2.1 Princess Charlotte Bay

Holocene specimens of Anadara (Tegillarca) granosa were obtained from three vibrocores at Princess Charlotte Bay, northern Queensland (PCB#1, 7 and 13) (Figure 6.1). Anadara (Tegillarca) granosa is common along Pacific Ocean coastlines (K. Gowlett, South Australian Museum, pers. comm., 1985). The mean annual air temperature at this locality is approximately 25.8°C. All specimens were very well preserved and the hinge region of either articulated or disarticulated whole shells were analysed. The majority of specimens were from Holocene subtidal and intertidal sediments, although some were excavated from a cliff section. All the shells were smaller than 4 cm (long-axis) and several juvenile specimens were analysed.

Analyses were made for the 'total acid hydrolysate' and free amino acids (Table 6.1). The relative extent of racemisation of different amino acids was in accord with other calcium carbonate matrices (Lajoie et al., 1980) and in general agreement with other mollusc species analysed in this study.

Some of the shells had pitted surfaces that may have resulted from solution weathering. However, the internal consistency in the relative extent of racemisation of different amino acids and the good concordance of D/L ratios in replicate samples suggest this feature did not result in contamination. Results for glutamic acid and phenylalanine were not available as L-glutamic acid coeluted with D-phenylalanine.

Comparison of the extent of racemisation in Holocene Anadara (Tegillarca) granosa from Princess Charlotte Bay with molluscs of equivalent age from southern Australia, permitted assessments of the

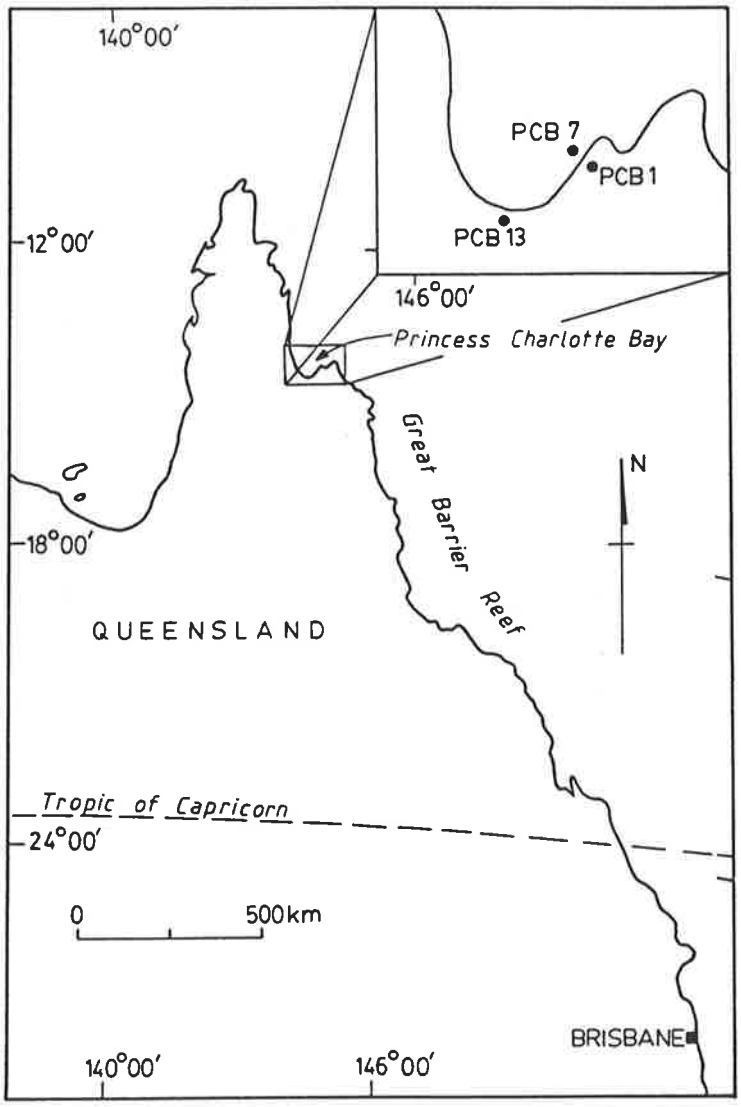


Figure 6.1 Princess Charlotte Bay: Location map of vibrocores

Table 6.1 Comparison of representative results of the extent of amino acid racemisation (epimerisation) in radiocarbon calibrated Holocene Anadara (Tegillarca) granosa, Princess Charlotte Bay, northern Queensland, with Holocene Katelysia spp., and Late-Pleistocene Anadara trapezia West Coast of South Australia and Gulf St Vincent. Amino acid D/L ratios are for the 'total acid hydrolysate' and 'free amino acids'. Calendric radiocarbon ages in parentheses.

Species	Location	M.A.T. (°C)	Age	Total (T) Free (F)	Amino acid D/L ratio				
					ALA	VAL	ALLO /ISO	LEU	ASP
Anadara (Tegillarca) granosa	Princess Charlotte Bay PCB#13 1.00 m	25.8	3860±80 bp (4325±140 BP)	(T)	0.56 ±0.03	0.14 ±0.002	0.17 ±0.005	0.27 ±0.005	0.50 ±0.005
				(F)		0.22	0.28	0.55	0.66 ±0.01
Anadara (Tegillarca) granosa	Princess Charlotte Bay PCB#1 2.25 m	25.8	2410±70 bp (2475±140 BP)	(T)	0.44 ±0.007	0.13 ±0.001	0.19 ±0.005	0.25 ±0.007	0.48 ±0.007
				(F)	0.63 ±0.07	0.22 ±0.006	0.37 ±0.05	0.47 ±0.01	0.60 ±0.04
Anadara (Tegillarca) granosa	Princess Charlotte Bay PCB#1 4.61 m	25.8	6530±80 bp (7430±130 BP)	(T)	0.53 ±0.02	0.17 ±0.006	0.23 ±0.01	0.29 ±0.005	0.52 ±0.01
Anadara (Tegillarca) granosa	Princess Charlotte Bay PCB#7 0.17 m	25.8	~2000 BP	(T)	0.29 ±0.008	0.07 ±0.004	0.09 ±0.006	0.15 ±0.003	0.33 ±0.003
				(F)	0.53 ±0.003	0.15 ±0.005	0.17 ±0.005	0.33 ±0.004	0.51 ±0.003
South Australia									
Katelysia rhytiphora	Tourville Bay	16.9	6490±170 bp (7370±180 BP)	(T)	0.23 ±0.01	0.08 ±0.002	0.12 ±0.002	0.16 ±0.02	0.23
Katelysia peronii	Tourville Bay	16.9	4540±100 bp (5200±140 BP)	(T)	0.14 ±0.006	0.07 ±0.001	0.09 ±0.002	0.13 ±0.01	0.24
Katelysia rhytiphora	Gulf St Vincent, Interstadial marine strata	16.0	Oxygen isotope Stage 3 ca. 40 kaBP	(T)		0.24 ±0.03	0.23 ±0.03	0.29 ±0.03	0.46 ±0.03
Anadara trapezia	Denial Bay	16.9	Last Interglacial 125 kaBP	(T)	0.64 ±0.07	0.33 ±0.02	0.44 ±0.03	0.44 ±0.01	0.64 ±0.02

influence of temperature on diagenetic racemisation. Because the genus Anadara is not extant in South Australian coastal waters, direct comparisons were not possible. However, comparison of the extent of racemisation in Anadara (Tegillarca) granosa with Katelysia spp., will partly overcome this problem. As a 'species-effect' on racemisation is not evident in the genus Katelysia, the inference was made that the same applies for the genus Anadara. Therefore, the relative rates of racemisation in both Anadara (Tegillarca) granosa and Anadara trapezia are held to be equal.

In Table 6.1 the extent of racemisation in Holocene Anadara (Tegillarca) granosa from Princess Charlotte Bay in northen Queensland, is compared with Holocene and Late Pleistocene Katelysia spp., and Late-Pleistocene Anadara trapezia from South Australia. The generally strongly leached and finely comminuted nature of molluscan fossils of Last Interglacial age from the Great Barrier Reef, precluded direct comparison with molluscs of equivalent age from southern Australia. Mean annual air temperatures at both sample localities are 25.8°C and 16.9°C respectively. Clearly, the Anadara from Princess Charlotte Bay are more extensively racemised for their age in comparison with the Katelysia spp. from southern Australia, even with a 'genus-effect' being taken into consideration. For example, the extent of racemisation evident in a 6,500 yrs old Katelysia rhytiphora is equivalent in broad view with a 2,000 yrs old Anadara (Tegillarca) granosa from Princess Charlotte Bay. The similarity in amino acid D/L ratios for these molluscs that are actually some 4,500 yrs different in age is the result of the significantly different temperature histories experienced during diagenesis (Table 6.1). The contribution of a genus-effect to these D/L ratio differences is minimal, and in no way is as significant as the differences introduced by the contrasting diagenetic temperature histories. A further example of the temperature effect on racemisation is illustrated in a comparison of a Last

Interglacial specimen of Anadara trapezia from South Australia with a 7000 yrs BP specimen of Anadara (Tegillarca) granosa from Princess Charlotte Bay (Table 6.1). The extent of racemisation in the Anadara from Princess Charlotte Bay would appear disproportionately high for their age if the diagenetic temperature history they experienced was not considered. A further example is illustrated in a comparison of the extent of racemisation in the 7,400 yrs BP Anadara (Tegillarca) granosa from Princess Charlotte Bay, with representative D/L ratios for Katelysia rhytiphora from Interstadial marine strata (oxygen isotope stage 3, 40 ka) from Gulf St Vincent. The mean annual air temperatures for these sites are 25.8 and 16°C respectively. Although the diagenetic temperature history for the molluscs from the Interstadial marine strata (S.A.) will have fluctuated in response to climatic change, it is likely that the Holocene specimens from Princess Charlotte Bay experienced a more equable diagenetic temperature history. Despite this however, and the additional complication of a genus-effect, the extent of racemisation in the 40,000 yr Katelysia rhytiphora is equivalent to the 7,400 yrs BP Anadara (Tegillarca) granosa from Princess Charlotte Bay. This relationship is also illustrated for aspartic acid in Figure 6.2, in which the extent of racemisation in Holocene Anadara (Tegillarca) granosa is compared with molluscs of different ages. Clearly, these examples illustrate that temperature effects are significant in relation to genuine age differences in explaining these observed D/L ratio differences.

Schroeder and Bada (1976) indicated that rates of racemisation doubled for approximately every 5°C rise in temperature. This notion was supported by Davies and Treloar (1977) who demonstrated that racemisation of aspartate for 1,000 years at 25°C resulted in ten times the extent of racemisation as 2,000 years at 12.5°C. Clearly, the results for Anadara from Princess Charlotte Bay are consistent with these observations.

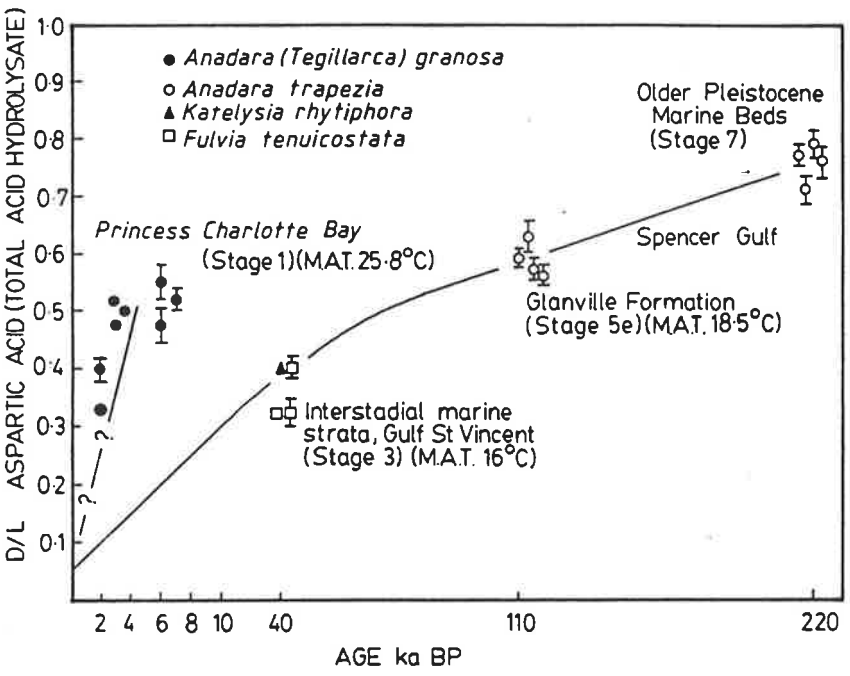


Figure 6.2 Schematic comparison of racemisation kinetic model curves for Anadara spp., illustrating the influence of different diagenetic temperature histories on the extent of racemisation. Mean Annual Air Temperatures (M.A.T.) are indicated for each sample locality. The first and second linear components of the 'non-linear' racemisation kinetic model presented for South Australian data are based on empirical results.

Ultimately a generalised racemisation kinetic curve for Australian tropical coastal and marine settings is sought for, in order to provide the basis of a predictive age assessment model (i.e., so that with a knowledge of the Effective Quaternary Temperature history and the D/L ratio, quantitative age assessments can be obtained). Difficulties arise however, with kinetic modelling. Problems associated with the data from Princess Charlotte Bay in particular, include the positioning of the transition zone in the molluscan racemisation kinetic model. Does the slope-break appear after 10 ka? Certainly linear kinetics are evident for the radiocarbon calibrated specimens to 7,400 Calendar years BP. This is supported by the linear plots of D/L ratios for the 'total acid hydrolysate' against free amino acids (Figures 6.3a-d).

Comparisons of the extent of racemisation in the 'total acid hydrolysate' with free amino acids, for Anadara (Tegillarca) granosa from Princess Charlotte Bay are presented in Figures 6.3a-d. Regression analyses of these data and additional data presented in Appendix 6.1 convincingly demonstrate a linear relationship in the increasing extent of racemisation in both the 'total acid hydrolysate' and free amino acids with time. A comparison of the slopes of the regression lines for each amino acid permitted assessments of the relative increase in the extent of racemisation in free amino acids, in relation to the 'total acid hydrolysate' with time for different amino acids. These data suggest that the D/L ratios for the Anadara from Princess Charlotte Bay fall essentially within the first linear component of the 'non-linear' racemisation kinetic model.

Graphs of this nature provide an additional means of assessing racemisation kinetics. In particular, kinetic models such as those proposed by Kriausakul and Mitterer (1980) and Mitterer and Kriausakul (1984), which attempt to explain the extent of racemisation in different amino acid molecular size fractions can in part be assessed using these graphs. The

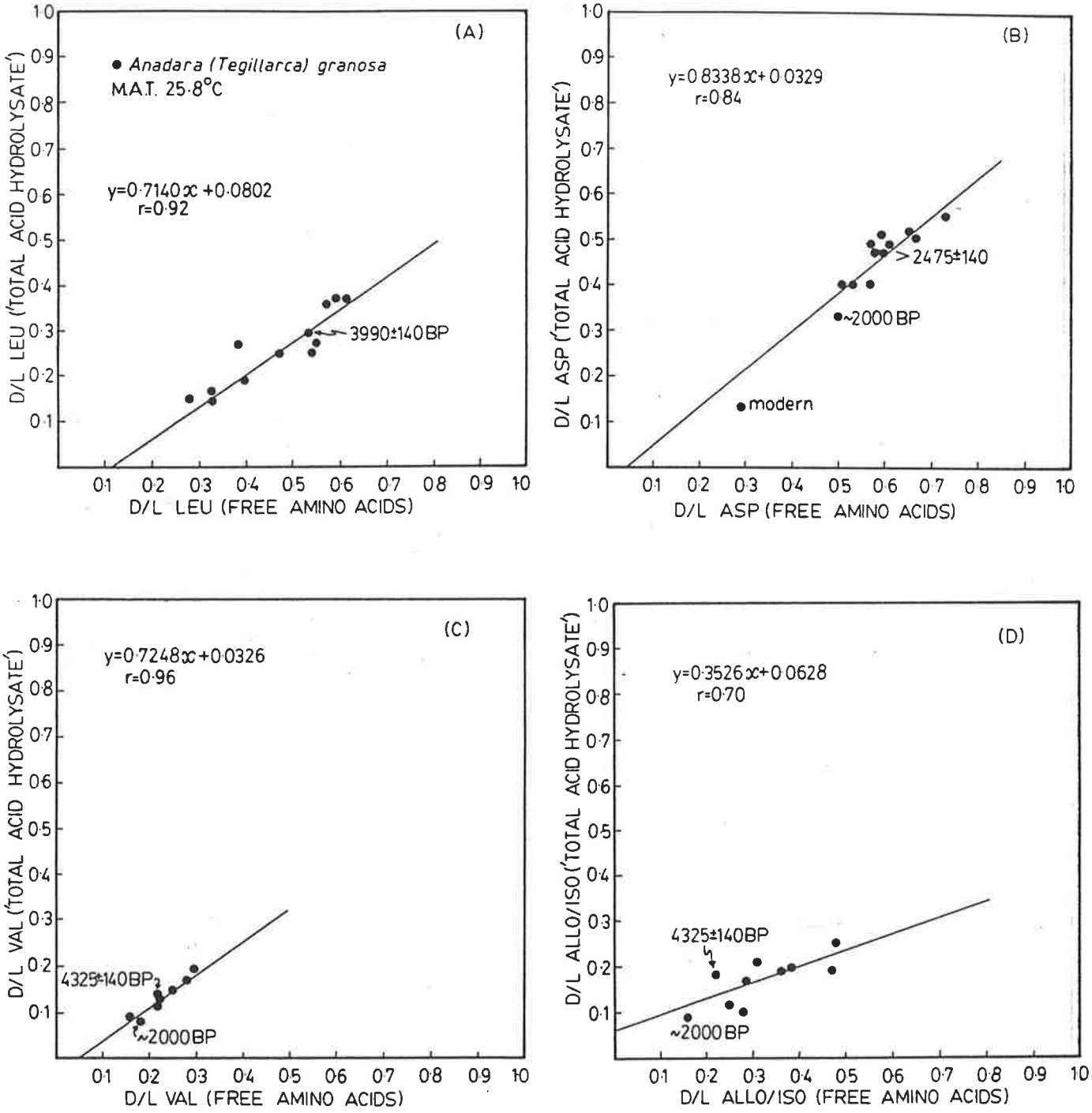


Figure 6.3 Summary plots of the extent of racemisation (epimerisation) evident in the 'total acid hydrolysate' against free amino acids. Where possible, radiocarbon calibration is indicated (ages cited in calendar years, BP). Results of linear regression analyses are also indicated.

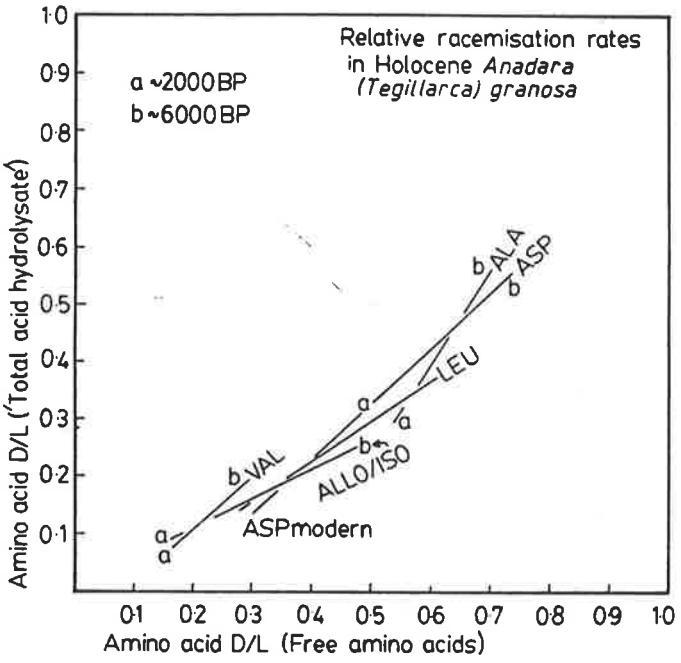


Figure 6.4 Composite plot of the relative slopes of linear regression data presented in Figure 6.3. (see text for discussion).

rationale is that graphs with slopes of 45° would suggest that the similarity in the extent of racemisation in both fractions was due to equivalent racemisation rates. However, it has long been recognised that free amino acids are generally more extensively racemised than the 'total acid hydrolysate' (Schroeder and Bada, 1976; Williams and Smith, 1977). In the graphs presented herein (Figures 6.3a-d), as free amino acids are represented on the abscissa, regression lines with slopes less than 45° will indicate that free amino acids are more extensively racemised than the 'total acid hydrolysate'. A composite plot indicating the relative slopes of the graphs in Figure 6.3 as well as data for alanine is presented in Figure 6.4. Individual lines represent regression lines of best fit with the end members a and b represented by D/L values for 2,000 and 6,500 yrs molluscs respectively. The contrasting slopes clearly highlight the different relative rates of racemisation for the total and free fractions for different amino acids. Crossing over, indicating changes in the rates of racemisation of different amino acids with time is also evident. These data are important for they indicate that depending on the age of fossils, differences in the relative extent of racemisation between amino acids may be anticipated. This observation is important for it suggests that relative rates of racemisation for different amino acids within an individual fossil may provide an unreliable criterion for assessing contamination. This is at variance with suggestions by Schroeder and Bada (1976).

That essentially linear racemisation kinetics apply for the Holocene Anadara from Princess Charlotte Bay, raises the question of when the transition zone commences. Wehmiller (1984a) noted that for leucine, linear kinetics applied from 0.0 to a D/L ratio of 0.2 for the mollusc Protothaca. This was followed by a progressive decrease in slope, a section of the curve referred to as the transition zone which continued to a leucine D/L ratio of approximately 0.35. A second essentially linear component then

follows with a slope approximately 10x less than the first linear component. In contrast, the data for Anadara from Princess Charlotte Bay indicate that essentially linear kinetics are followed through to leucine D/L ratios of 0.37 at least ('total acid hydrolysate') and 0.60 (free amino acids). The high correlation coefficient for leucine (r=0.92) demonstrates the strongly linear relationship of increasing D/L ratios with increasing fossil age. Similar relationships were evident for aspartic acid and valine, with weaker correlation for isoleucine.

A related question concerning the timing of the onset of the transition zone also arises. What are the relative contributions of a genus-effect and a diagenetic temperature history to the onset of this feature? This is a significant question for the timing and duration of the transition zone is important in quantitative age assessments. Only when a reliable understanding of the nature and rates of molluscan racemisation kinetics are understood will diagenetic racemisation be successfully applied in quantitative age determinations with a high level of confidence. The need for further research in this area is recognised.

Whilst systematic increases in amino acid D/L ratios with time were evident for the population of Anadara treated as a whole from Princess Charlotte Bay, only subtle differences were recognised in terms of down-core D/L ratio variation (Figure 6.5a and b). The extent of amino acid racemisation evident in radiocarbon calibrated Anadara (Tegillarca) granosa in core PCB#1 indicate that D/L ratios are only marginally higher in the 7,400 Calendar years (BP) specimen, than in the 2,400 yrs BP specimen. This is significant for it suggests that studies involving quantitative ages for Holocene fossils will experience resolution problems. For example valine D/L ratios for Anadara were 0.13 and 0.17 for 2,400 and 7,400 yrs BP respectively. Similar differences were also evident for

alanine, isoleucine, leucine and aspartic acid (Table 6.1). Molluscs that have experienced lower Holocene diagenetic temperature histories than the Princess Charlotte Bay specimens will exhibit even smaller differences in D/L ratios.

Results for Princess Charlotte Bay vibrocore #13 show the effect an elevated diagenetic temperature history has on molluscan racemisation. Clearly the samples from the cliff section (sample 13B and 13C, beach ridge facies) have experienced higher Effective Quaternary Temperature histories than the Anadara from the subtidal facies in core PCB#13 (Figure 6.5b).

6.2.2 East Coast Of Australia

In addition to the Anadara (Tegillarca) granosa from Princess Charlotte Bay, numerous specimens of Holocene Anadara trapezia were obtained from other localities along the East Coast of Australia. The samples represent a transect from Princess Charlotte Bay in northern Queensland (14°20'S, 144°07'E) to Quarantine Bay in southern New South Wales (37°04'S, 149°55'E) (Figure 6.6). Representative results for the 'total acid hydrolysate' and free amino acids are presented in Table 6.2.

Systematic latitudinal variation of amino acid D/L ratios could not be delineated owing to the restricted number of specimens available. Moreover, the likelihood of confidently recognising latitudinal D/L ratio variation in several of the Holocene specimens was low in view of the limited time for which different Effective Quaternary Temperature histories will have had an effect. In particular this applies mainly to the younger shells less than 2,000 yrs old. However, the radiocarbon calibrated D/L ratio data provide an indication of the extent of racemisation that would be anticipated in Holocene Anadara, both for the 'total acid hydrolysate' and

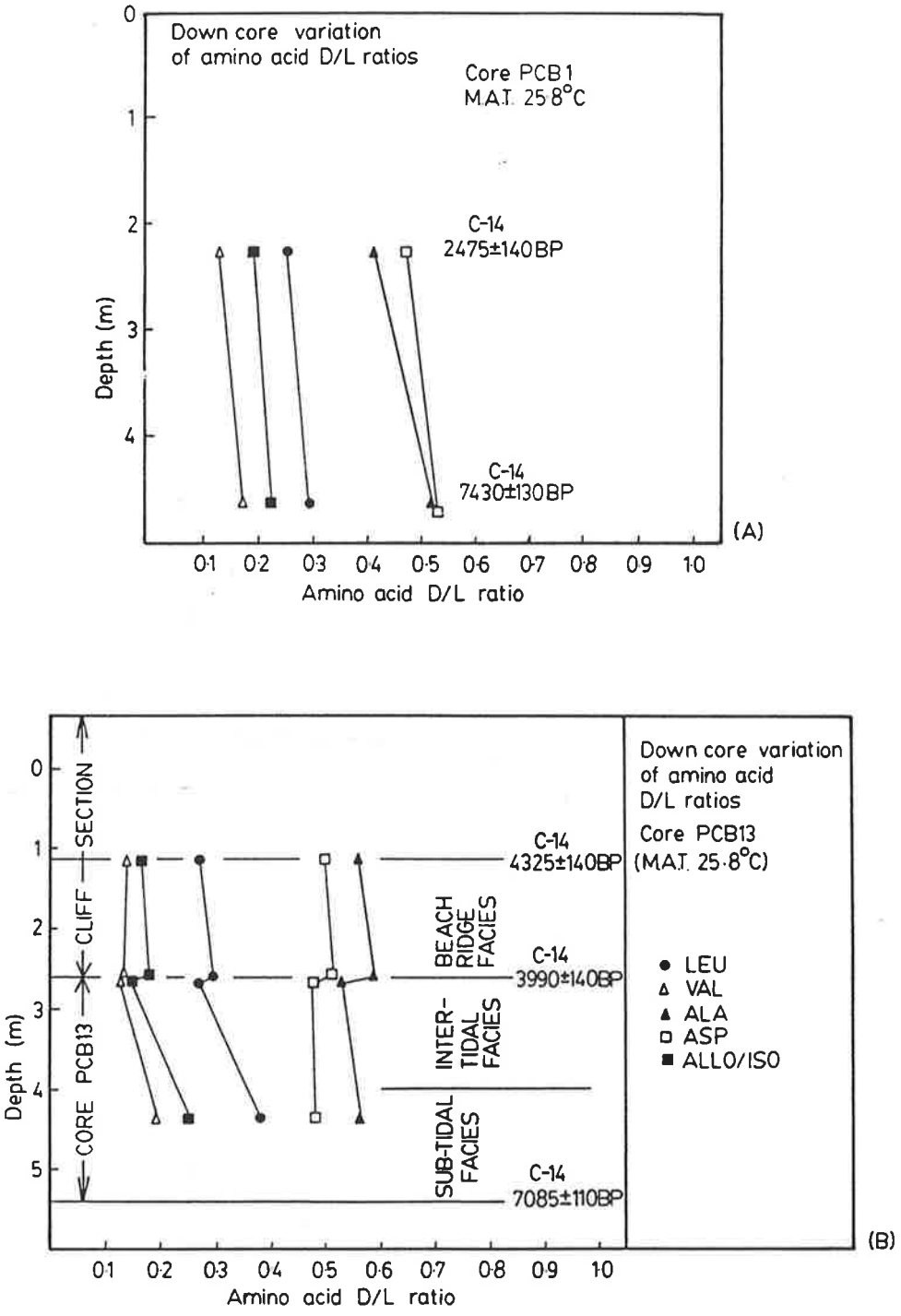


Figure 6.5 a and b.

Down-core variation of amino acid D/L ratios in Holocene Anadara (Tegillarca) granosa, Princess Charlotte Bay, Queensland.

free amino acids. Similar intrageneric relative rates of racemisation (epimerisation) for the 'total acid hydrolysate' and free amino acids were evident in both Anadara trapezia and Anadara (Tegillarca) granosa.

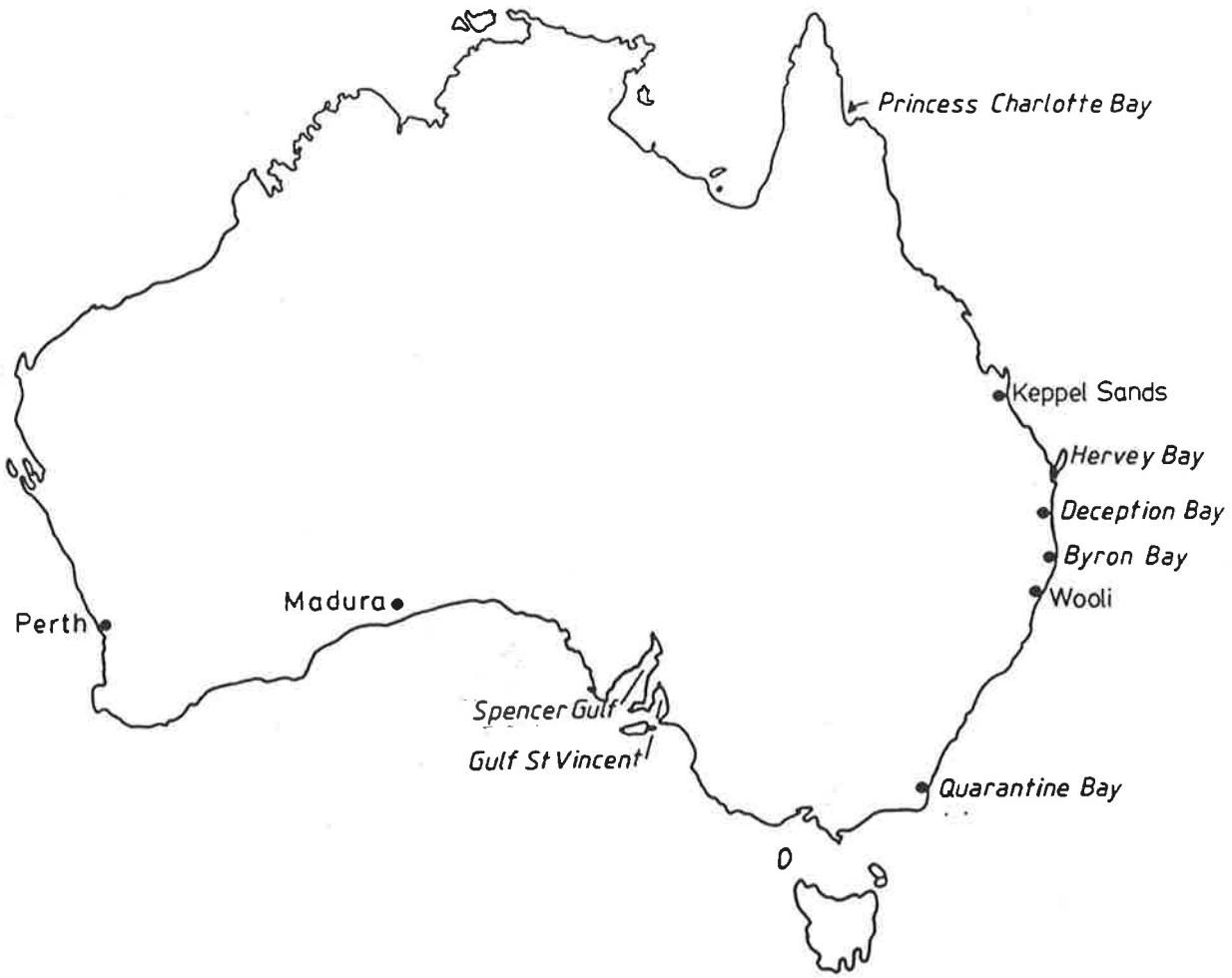


Figure 6.6 Sample localities of Anadara spp., East Coast of Australia. Mean Annual Air Temperatures (M.A.T.) indicated below. Temperature data based on Australian Climatic Averages (1975).

Locality	Latitude	Longitude	M.A.T.(^{o}C)
Princess Charlotte Bay	14^{o}20'	144^{o}07'	25.8
Keppel Sands	23^{o}20'	150^{o}48'	22.5
Hervey Bay	25^{o}06'	152^{o}49'	21.5
Deception Bay	27^{o}10'	153^{o}05'	21.5
Byron Bay	28^{o}39'	153^{o}37'	19.4
Wooli	29^{o}52'	153^{o}16'	19.4
Quarantine Bay	37^{o}04'	149^{o}55'	14.7

Table 6.2 Extent of amino acid racemisation in Holocene Anadara spp., from the East Coast of Australia. Amino acid D/L ratios are for the 'total acid hydrolysate' and free amino acids.

Species	location	MAT (°C)	Calendar age BP		Amino acid ALA	VAL	ALLO /ISO	LEU	ASP
Anadara (Tegillarca) granosa	Princess Charlotte Bay	25.8	2,475 ±140	(T)	0.44 ±0.007	0.13 ±0.001	0.19 ±0.005	0.25 ±0.007	0.48 ±0.007
				(F)	0.63 ±0.07	0.22 ±0.006	0.37 ±0.05	0.47 ±0.01	0.60 ±0.04
Anadara (Tegillarca) granosa	Princess Charlotte Bay	25.8	7,430 ±130	(T)	0.53 ±0.02	0.17 ±0.006	0.23 ±0.01	0.29 ±0.05	0.52 ±0.01
Anadara trapezia	Keppel Sands	22.5	~1,000	(T)	-	-	0.10 ±0.005	0.16 ±0.003	0.33 ±0.02
			3,000	(T)	-	-	0.18	0.32 ±0.008	0.52 ±0.02
Anadara trapezia	Hervey Bay	21.5	730±60[1]	(T)	0.20 ±0.04	0.04 ±0.001	0.04 ±0.02	0.07 ±0.001	0.33 ±0.005
			6,400±140	(T)	0.52 ±0.02	0.15 ±0.01	0.17 ±0.002	0.23 ±0.002	0.44 ±0.005
Anadara trapezia	Deception Bay	21.5	~5,000	(T)	0.36 ±0.01	0.07 ±0.004	0.07 ±0.007	0.12 ±0.001	0.37 ±0.01
				(F)	0.49 ±0.003	0.14 ±0.001	0.20 ±0.001	0.33 ±0.002	0.48 ±0.03
Anadara trapezia	Byron Bay	19.4	<7,000	(T)	0.49 ±0.06	0.19 ±0.002	0.21 ±0.006	0.33 ±0.003	0.42 ±0.005
				(F)	0.74 ±0.02	0.30 ±0.007	0.39 ±0.004	0.57 ±0.01	0.59 ±0.04
Anadara trapezia	Wooli	19.4	<6,000	(T)	0.42 ±0.008	0.13 ±0.003	0.16 ±0.001	0.24 ±0.001	0.42 ±0.02
				(F)	0.67 ±0.05	0.17 ±0.03	0.30 ±0.01	0.45 ±0.001	0.53 ±0.01
Anadara trapezia	Quarantine Bay	14.7	modern	(T)	0.08 ±0.02	0.02 ±0.008	0.02 ±0.002	0.03 ±0.001	0.11
				(F)	-	-	0.29 ±0.10*	0.13 ±0.01	0.13 ±0.005

* D/L ratios based on manually integrated peak height calculations
[1] Age in radiocarbon years (bp) (T) 'total acid hydrolysate' (F) free amino acids

6.3 HOLOCENE MARGINOPORA VERTEBRALIS, GREAT BARRIER REEF

As the foraminifer Marginopora vertebralis is now no longer living in South Australian coastal waters (Belperio and Murray-Wallace, 1984), Holocene and modern specimens were obtained from several localities from the Great Barrier Reef to afford comparison with specimens of Last Interglacial age (Glanville Formation) from South Australia (Chapter 4), and Plio/Pleistocene age from Western Australia (Roe Calcarenite: Chapter 5).

Representative results summarising the extent of racemisation in Holocene and modern Marginopora vertebralis are presented in Table 6.3. Results are for the 'total acid hydrolysate'.

To fulfill the requirements of sample weight, each analysis was made on approximately 20-50 individuals. Reported D/L ratios therefore represent unweighted averages for all these individuals. The cleaning procedure used on the Queensland Marginopora followed that outlined in Chapter 4.

Little downcore variation of amino acid D/L ratios was evident for the Marginopora from Core GBRVC#8. From this arose the question of whether this was a geological problem (e.g., rapid sedimentation rates so that only minor age variation is evident down profile) or whether it was a geochemical problem and reflected the poor age resolving ability of amino acid techniques, for this species.

All the available evidence suggests that this is a geochemical problem, for radiocarbon dating has distinguished a unidirectional age increase with increasing depth in sediment profile. In contrast, significant age differences based on the amino acid data would appear difficult to delineate in the species Marginopora vertebralis (Table 6.3). Data presented herein suggest that Marginopora rate poorly as a genus for studying age variation within Holocene sediments.

Table 6.3 Extent of amino acid racemisation in Holocene specimens of the foraminifer Marginopora vertebralis, from various localities, Great Barrier Reef, Queensland. Results are for the 'total acid hydrolysate'.

Locality	Depth in core (m)	Geologically expected age	Amino acid D/L ratios ALA	VAL	ALLO /ISO	LEU	PRO	ASP
Fantome Island	near surface	modern	-	0.02	0.02 ±0.007	0.03 ±0.01	-	0.05
Pipon Reef	near surface	<2 ka	0.06 ±0.008	0.04 ±0.02	0.03 ±0.005	0.05 ±0.02	0.07 ±0.02	0.11 ±0.03
Palms	Core BGRVC#8 1.00		0.26 ±0.01	0.08 ±0.02	0.07 ±0.01	0.07 ±0.004	0.22 ±0.003	0.34 ±0.02
	1.42	<5 ka	0.25	0.06	0.05	0.07	0.24 ±0.08	0.34 ±0.01
	2.54		0.36 ±0.05	0.09 ±0.009	0.09 ±0.008	0.09 ±0.01	0.23 ±0.04	0.40 ±0.03
	2.96		-	0.13	0.10	0.14	0.30	0.34 ±0.005
	3.32	4830±70 bp (env. corrected)						

6.4 CONCLUSIONS

(1) Representative Holocene and modern D/L ratios were reported for both the estuarine bivalve Anadara trapezia and the foraminifer Marginopora vertebralis.

(2) Data reported herein have improved the understanding that different "Effective Quaternary Temperature" histories can have on diagenetic racemisation for Australian coastal settings.

(3) As a corollary, the complex nature of molluscan racemisation kinetics is highlighted in the Anadara from Princess Charlotte Bay (e.g., the timing of the onset of the transition zone).

(4) Data reported herein suggest that the maximum age of datable fossiliferous materials from northern Queensland will be considerably younger than in southern Australia.

CHAPTER 7 AMINO ACID RACEMISATION DATING OF AUSTRALIAN QUATERNARY MARINE SEDIMENTS - ACHIEVEMENTS, PROBLEMS AND PROSPECTS

7.1 DISCUSSION AND SUMMARY

The future of amino acid racemisation dating in Australian Quaternary studies appear exciting and holds considerable promise. The need for a commercial dating facility is also recognised.

Despite the significant advances made in the application of amino acid racemisation dating, the Australian data dictate that a cautious approach should still be adopted in the application of the technique. Clearly, a large margin of error must be accounted for in aminostratigraphic studies. The necessity of studying large sample populations and implementing a sound statistical approach for age assessments is recognised. Amino acid D/L ratio working errors for within-species intershell variation from a single outcrop, was found to be less than 12%, for both the 'total acid hydrolysate' and free amino acids. These results are in general agreement with Wehmiller (1984b).

Larger margins of error arise in the chronocorrelation of isochronous units over widely separated localities. In particular, regional studies where multiple genera are involved, introduces variation due to differences in Effective Quaternary Temperature histories, as well as generic effects on racemisation. However, as the chronocorrelation of various Pleistocene marine units in southern Australia demonstrate, with careful sampling, these working errors can be reduced to a level comparable to within-species intershell D/L ratio variation for a single deposit (Factor 5 of the scheme presented in Chapter 3). Errors can also be minimised through careful field sampling.

The application of the amino acid racemisation reaction in marine stratigraphic studies in southern Australia has played an instrumental role in the recognition of Interstadial marine strata (oxygen isotope stage 3; 30-40 ka BP) from submarine cores, Gulf St Vincent. These results are of global significance as few examples of sediments of this age have been documented (Aharon, 1983; Chappell, 1983). In addition, amino acid data have successfully demonstrated the widespread occurrence of Last Interglacial and Penultimate Interglacial marine strata in southern Australia, and in so doing have served to simplify an otherwise complex lithostratigraphy. These results are important for they provide a useful adjunct for other dating techniques, and valuable time frameworks for coastal process studies, that work at scales of thousands of years.

Although the merit of applying amino acid data in geothermometry has been questioned (Williams and Smith, 1977; Davies and Treloar, 1977), results from southern Australia have demonstrated the usefulness of such an approach. Studies of Holocene and Late Pleistocene molluscan fossils, whose Effective Quaternary Temperature histories are relatively well understood, have provided an important test for assessing the suitability of amino acid data in geothermometry. Results from southern Australia also serve to highlight the application of amino acid data in the recognition of surface samples.

Despite incidental discussions, previous amino acid studies have not specifically addressed the problem of reworking of older fossils into younger sediments. Results for the benthic foraminifer, Marginopora vertebralis from Wardang Island, Spencer Gulf (Chapter 4) demonstrate that amino acid racemisation can present a powerful tool in recognising sediment reworking. These results are important as they provide a valuable adjunct in understanding sedimentation dynamics in the Quaternary.

Results from this study also highlight the importance of analysing free amino acids as a means of assessing the integrity of enantiomeric ratio data for the 'total acid hydrolysate'. This is of particular importance in situations where the moisture regime may disturb the amino acid signature of fossils through in situ leaching. In such instances, the moisture regime may represent a more important consideration than the diagenetic temperature history, when measuring the observed extent of racemisation in fossils.

Anomalously low D/L ratios evident in the 'total' fraction in some instances can be explained through the combined analyses of free amino acids and the 'total acid hydrolysate', in conjunction with their relative concentrations, as illustrated in the study of Marginopora from Wardang Island. It is therefore proposed that in future studies, laboratories routinely analyse free amino acids in conjunction with the 'total acid hydrolysate'.

Despite studies that have highlighted the potential dangers, of using 'total acid hydrolysate' (Kimber et al., 1986; Kimber and Griffin, 1987), results from this investigation suggest it presents a convenient and generally reliable chemical medium for age assessments, provided in situ leaching or contamination has not occurred. The merit of using the 'total acid hydrolysate' for relative age assessments of Quaternary strata is illustrated in Figure 7.1a,b and Figure 7.2 for a range of amino acids both for the 'total acid hydrolysate' and free amino acids. Representative D/L ratios for isoleucine for Katelysia spp., from various Quaternary deposits from the Perth Basin, Western Australia are compared with results from the northern hemisphere in Table 7.1. These data clearly indicate that the range of amino acid dating will not be as wide as in arctic settings, although potentially serves a greater range than in Florida. This issue is further explored later (Section 7.2).

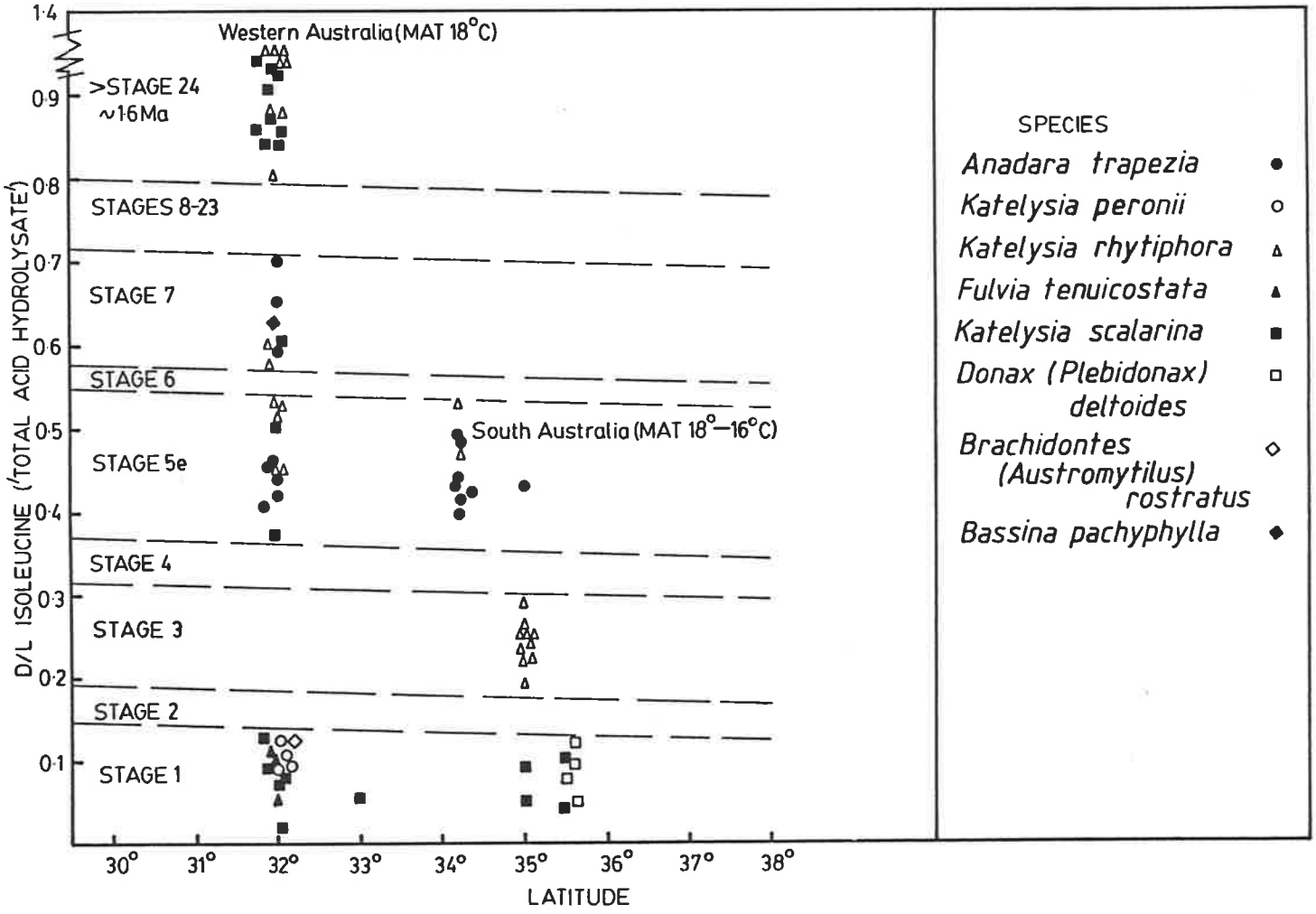


Figure 7.1a Summary plot of amino acid D/L ratios against latitude for Australian molluscan fossils of Quaternary age. Data are plotted within the framework of the marine oxygen isotope record. Data reported are for isoleucine and valine for the 'total acid hydrolysate'

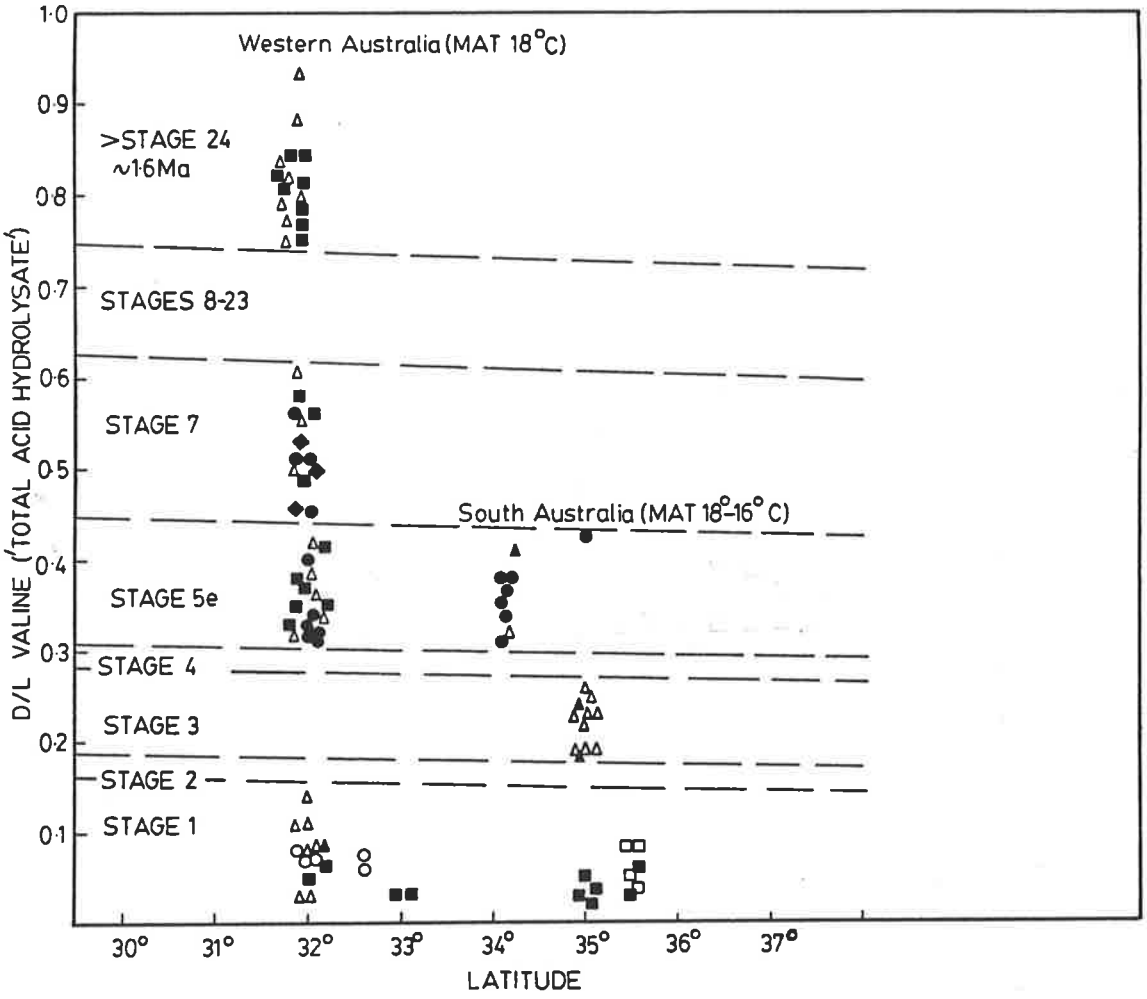


Figure 7.1 b Summary plot of valine D/L ratios against latitude

TABLE 7.1 Comparison of Australian amino acid data with results from the northern hemisphere, summarising the extent of isoleucine epimerisation in molluscan fossils. The extent of isoleucine epimerisation is representative of the extent of racemisation of other amino acids.

Authors	Mollusc Genus	Locality	Age(ka)	M.A.T.* (°C)	D/L
Keen et al., (1981)	Patella	Belle Hougue Cave, Jersey	120	12	0.123±0.024
Mitterer (1974,1975)	Mercenaria	Florida	120	20-24	0.71
"	"	"	ca. 2000	20-24	1.1
Szabo et al., (1981)	Various molluscs	Baffin Island, Canada	<10	-7 to -12	≦0.02
"	"	"	ca. 125-500	-7 to -12	0.10-0.20
This study	Katelysia	Perth Basin, Western Australia	5	18	0.13
"	"	"	125	18	0.38
"	"	"	225	18	0.57
"	"	"	1600	18	0.93

* M.A.T. - Mean Annual Temperature

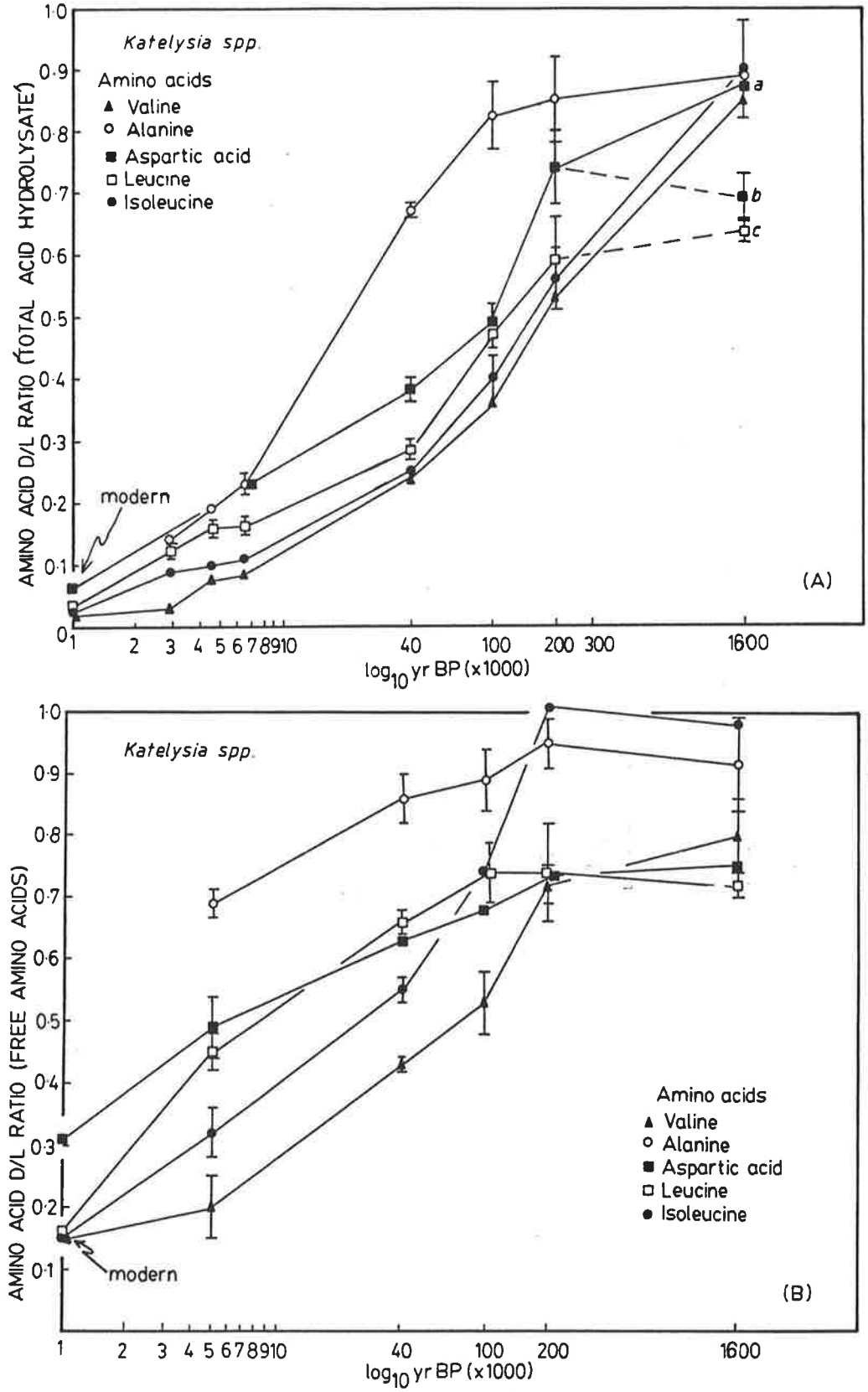


Figure 7.2 D/L ratio data for Katelysia spp., from Southern Australia (M.A.T. 18°C) ranging from Plio/Pleistocene to modern. D/L ratio data are for the 'total acid hydrolysate'(A), and free amino acids (a) Aspartic acid value obtained on a Hewlett Packard model 5890 gas chromatograph with a Chirasil-Val fused silica 25 m column and FID detector. (b) artificially low aspartic acid D/L ratio due to the coelution of γ-amino-n-butyric acid with L-aspartic acid. (c) artificially low leucine D/L ratio because of the coelution of β-alanine with L-leucine.

7.2 SIGNIFICANT QUESTIONS

Several significant questions have arisen from this research. In particular, the ability to distinguish subtle, albeit genuine age differences using amino acid data, a more detailed understanding of the nature of molluscan racemisation kinetics, particularly for fossils of great antiquity, and the upper and lower age limits of the technique for the dating of Australian fossiliferous materials are recognised as areas for future research.

Amino acid data from southern Australia highlight these problems. Composite plots of representative D/L ratios for valine and isoleucine (Figure 7.1a,b) demonstrate the difficulty of resolving genuine age differences for Interglacial marine sediments older than oxygen isotope stage 7 as well as distinguishing age differences for Interstadial marine strata younger than the Last Interglacial (oxygen isotope stages 5c and 5a). The results for valine and isoleucine are representative of other amino acids. Mean annual temperatures and sample localities are indicated in Figure 7.1a and b. As significant differences in mean annual air temperatures are not experienced between these localities, composite plots of the D/L ratio data are justified. The slope of the isochrons however, is empirically derived, and reflects minor differences in mean annual temperature with latitude.

Although representative D/L ratios for the Interstadial marine strata (oxygen isotope stage 3), from Gulf St Vincent and the Last Interglacial from southern Australia are significantly different, difficulties are likely to arise in distinguishing Interstadial peaks 5a and 5c based on amino acid data alone. Clearly, these data highlight the importance of studying large sample populations and applying a statistical approach for age assessments, as well as independent dating techniques to calibrate amino acid results. However, caution is even required with this approach, for statistical tests

of significance may not be sufficiently rigorous to resolve age differences based on subtle differences in amino acid D/L ratios. This would particularly apply where D/L ratio variation (e.g., within-species intershell variation), within a population is high. Although the possibility of improving age resolution may arise through reporting D/L ratios to three rather than two significant figures is recognised, this would necessitate the analysis of considerably larger sample populations as predicted by equation 3.1 and result in diminishing returns.

The problem of the age resolving ability of amino acid data is further illustrated in Figure 7.3. The ability to distinguish subtle age differences is greatly reduced when within-species intershell D/L ratio variation is large. This is because the D/L ratio error terms overlap despite the fact that the deposits in question may be of different ages. These problems are more pronounced in the second broadly linear component of the 'non-linear' racemisation kinetic model of Wehmiller (1984b), where racemisation rates are dramatically slower than in the first linear component or in the transition zone.

Unlike radionuclide decay, the time-dependent racemisation reaction is also strongly temperature dependent. In consequence, the datable timespan the technique may be applied is in part determined by local environmental factors and racemisation kinetics. A related issue concerns the lower limit for age assessments based on Australian amino acid data. Although the Effective Quaternary Temperature history is an important determinant, the nature of molluscan racemisation kinetics must also be considered. If the latter stage of the second-linear component of the 'non-linear' racemisation kinetic model (Chapter 2) is defined by an asymptote, then difficulties are likely to arise for age assessments for fossils with D/L ratios greater than approximately 0.75-0.80. Although these values represent an arbitrary cut-off, large error terms for intershell D/L ratio variation for values exceeding this cut-off will be difficult to distinguish statistically from a racemic condition.

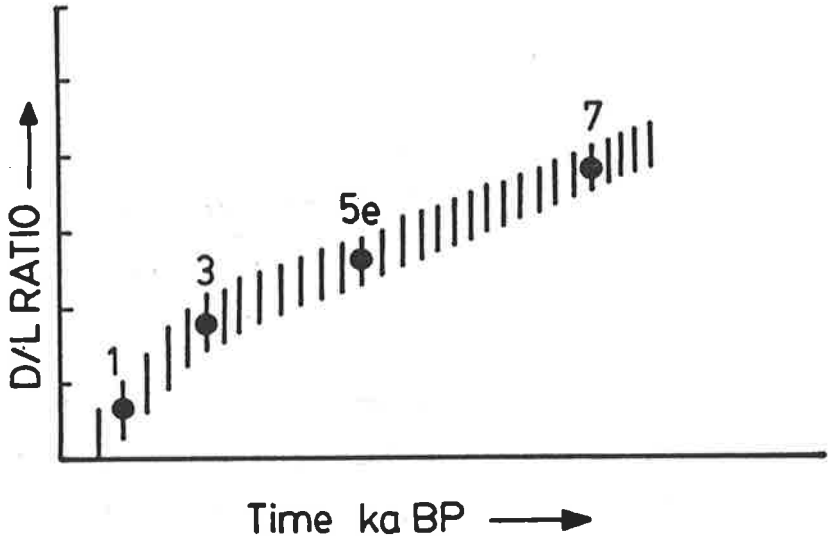


Figure 7.3 Diagrammatic representation of overlapping error terms of amino acid D/L ratios illustrating the problem of age resolution.
(see text for discussion).

In view of this, the minimum lower limit of amino acid racemisation for temperate climatic settings in Australia is very likely the Middle Pleistocene. This suggestion is highlighted by Figure 7.4, which depicts the potential datable age range for temperate climatic settings in Australia. These data would not apply for tropical settings as results from Princess Charlotte Bay (Chapter 6) indicate. Figure 7.4 assumes no reduction in the rates of racemisation from the 100,000 to 200,000 yr calibrated interval of this graph to the attainment of a racemic condition. Regression analyses of the D/L ratio data for valine, leucine and isoleucine ('total acid hydrolysate') indicate that a racemic condition would be attained within approximately 600,000 yrs for fossils that have predominantly experienced temperate climates during their diagenetic history. If the latter part of the kinetic pathway is defined by an asymptote, then the above suggestions would not strictly apply and the racemic state would be obtained within a longer period of time. However, the ability to resolve ages would be greatly reduced. Clearly, the need for further research in this area is recognised. These results are in marked contrast to results from arctic settings however, and they further serve to highlight the influence of different diagenetic temperature histories on racemisation (cf. Mitterer, 1974,1975; Szabo et al., 1981; and Wehmiller, 1982).

The above suggestions however, question the validity of the D/L ratio data for the Plio/Pleistocene Jandakot Member of the Yoganup Formation (Perth Basin, Western Australia) and the Roe Calcarenite (Roe Plains, Western Australia) discussed in Chapter 5. Representative D/L ratios for molluscan fossils from these sediments typically fall within the range of 0.80-1.0. Therefore, do these D/L ratios reflect results for indigenous amino acids? In addition, the question also arises concerning whether they represent a racemic condition, and reflect the ability of Katelysia spp., to maintain a racemic state for protracted periods? The good concordance of D/L ratios in replicate samples suggests that they are based on indigenous

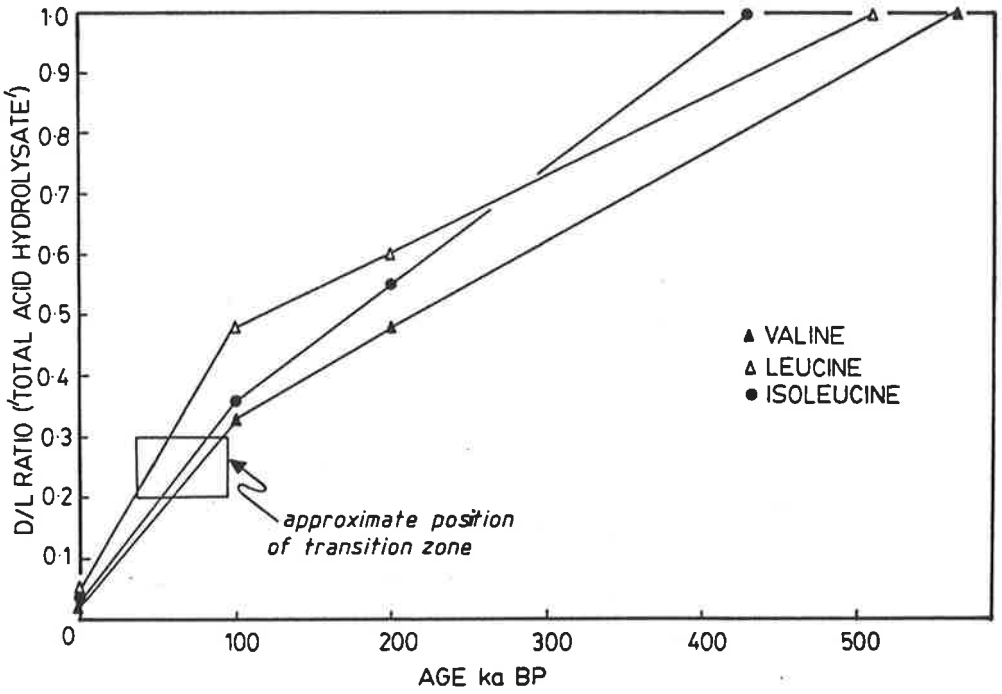


Figure 7.4 Potential dating range using amino acid racemisation data in temperate climatic settings in Australia (M.A.T. 18°C). The age range assumes no reduction in the rate of molluscan racemisation following the transition zone, and therefore suggests comparable rates as experienced in the calibrated (100-200 ka) interval of this graph. This age range represents the likely minimal dating range of the technique. This is due to the complex interrelationship between hydrolysis and molluscan racemisation.

amino acids. In addition, the absence of the less stable amino acids including serine and threonine, that would otherwise suggest contamination, when present in Pleistocene fossils also increases the validity of the results for the Plio/Pleistocene Katelysia spp.

To overcome the difficulties discussed in this section, mollusc specimens would be required from a continuous timespan throughout the Quaternary. Globally however, a dearth of well preserved molluscan fossils of Middle Pleistocene age and older is recognised. These are discussed by Blackwelder (1981) in the context of major depositional hiatuses.

Based on radiocarbon calibrated data (for the 'total acid hydrolysate') from southern Australia, the upper (or younger) limit of amino acid racemisation dating (i.e., confident distinction from modern), is approximately 1000 yrs, for temperate climatic settings. However, this value will differ in accordance with different diagenetic temperature histories, molluscan genera, amino acids selected and amino acid molecular size fractions studied (e.g., 'total acid hydrolysate', middle molecular weight polypeptides or free amino acids).

The selective analysis of D/L ratios from a given molecular weight fraction, with its characteristic rate of racemisation, may ameliorate the problem of resolution in amino acid dating. Because the 'total acid hydrolysate' is chemically, a very dynamic system comprising a complex mixture of high molecular weight polypeptides, smaller polypeptides and free amino acids, which each undergo racemisation at different rates, greater D/L ratio variation is likely to arise than would otherwise be evident if a discrete peptide fraction was analysed. Previous workers (Schroeder and Bada, 1976; Williams and Smith, 1977) have suggested analysing D/L ratios for only high molecular weight fossil polypeptides, as the suggested stability of this fraction would yield less variable D/L ratios in replicate samples.

However, Kimber et al., (1986) suggested that high molecular weight fossil polypeptides are less stable than previously considered. Accordingly, natural hydrolysis rapidly breaks down these larger molecules to middle molecular weight fossil polypeptides. Evidence from laboratory heating studies (Kimber et al., 1986) indicates the latter remains in the system for protracted periods and may therefore provide the greatest geochronometric utility. In contrast free amino acids represent an unsuitable fraction for dating because of their labile character. The isolation of middle molecular weight peptide fractions however would require dialysis, and present a time consuming procedure if routinely used in amino acid dating. In addition, the process may involve diminishing returns, as the improved accuracy resulting from this procedure might be minimal and not warrant the labour intensive laboratory preparation. The need for further research in this area is thus recognised.

In conclusion, although Wehmiller (1982, p.113) pointed out that;

> "Uncertainties in kinetic models, and the inability to calibrate these models with field samples represent a current weakness in both theoretical and applied concepts of amino acid racemization methods",

it is hoped that the present study has helped to resolve some of these problems using Australian examples and demonstrated the great potential of applying amino acid racemisation reactions in Quaternary studies.

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APPENDICES

APPENDIX 1 AMINO ACID RACEMISATION DATING: ANALYTICAL METHODS

Sample preparation and the derivatisation procedure used during the course of this research are outlined below in point form.

A1.1 Sample Preparation

(This procedure was used for shells and foraminifer.)

1.1 Molluscs are cut into approximately 1 gram portions after cleaning with dental tools. Dental tools are used to remove surface encrustations. Where possible the hinge is analysed (see Chapter 3).

1.2 Shell samples are then sonicated in a beaker with double distilled water for 1 minute. Supernatant is then decanted and this procedure is repeated.

1.3 The outer shell layer is dissolved in a beaker using approximately 30 ml of 1 M HCl for 30-40 seconds. The supernatant is then decanted and double distilled water is added to remove acid residue.

1.4 Shell samples are then placed on watch glasses and allowed to dry in a vacuum desiccator for 1 hour.

1.5 Samples are removed from vacuum desiccator and sample weight is recorded.

A1.2 ACID HYDROLYSIS

The following procedure is undertaken for preparation of the 'total acid hydrolysate'. Preparation of free amino acids does not involve step 2.3.

2.1 Samples are then placed in round bottom flasks and 1 ml of 8 M HCl spiked with the internal standard L-nor-leucine, is added to each vessel. The actual amount of internal standard added is 10 µl of 0.2 µ mole. Additional unspiked 8 M HCl is added until the shells are dissolved.

2.2 The dissolved shells are then transferred to 25 ml glass ampoules using pasteur pipettes, and the flasks containing the original solutions are rinsed with three small portions of unspiked 8 M HCl so that each ampoule is no more than half full.

2.3 Ampoules are then sealed under flame, placed in an aluminium block and heated in an oven at 110°C for 16 hours. (End of Day 1.)

2.4 Ampoules are removed from the oven and allowed to cool to room temperature. Samples are then transferred to 50 ml pear-shaped flasks using pasteur pipettes. During this transfer, samples are filtered using Whatman No.2 filter paper (Qualitative: 9 cm). Ampoules are rinsed three times with double distilled water and transferred to the pear-shaped flasks.

2.5 Samples are then evaporated on a rotary film evaporator using a water bath set at 40-45°C. A minimum volume of 1-2 ml of solvent is retained in the pear-shaped flask.

2.6 The remaining solvent is transferred to ion-exchange columns (Biorad AG50W-X8: 7-10 gms of cation exchange resin), using a pasteur pipette. Pear-shaped flasks are then rinsed 4 times with approximately 1.5 ml of 0.002 M HCl. (Cation exchange columns are cleaned immediately before loading with samples. The cleaning procedure involves the addition of 15 ml of 1.0 M HCl followed by 80-100 ml of double distilled water until no precipitate forms with $AgNO_3$ forms).

2.7 Cation exchange columns are eluted with 20 ml distilled water followed by 17 ml 2 M NH_4OH. The first 3-4 ml of 2 M NH_4OH are not collected. The remaining eluant is trapped in a 50 ml round bottom flask.

2.8 Flasks containing the eluants from the cation exchange columns are then snap shell frozen with liquid nitrogen, and placed on a freeze drier overnight. (End of Day 2.)

A1.3 DERIVATISATION: PROCEDURE

3.1 Samples are taken off the freeze drier. The dried sample residues are transferred with double distilled water into 3 ml reacti-vials. During this transfer, the samples are filtered using Whatman No.2 filter paper (7 cm: Qualitative).

3.2 Contents of the reactor vials are then evaporated with a stream of (Industrial) dry nitrogen to a minimum volume (~5 µl). This is achieved on a PIERCE Reacti-Therm heating module with a heated block at approximately 80°C. Reacti-vials are then placed in a vacuum deisccator for three hours.

(Esterification)

3.3 Samples are then removed from the vacuum desiccator and 1 ml of Propan-2-ol/HCl (3.3 M) is added to each reacti-vial using an automatic pipette (or pasteur pipette with a syringe attached). Each vial is then quickly flushed with nitrogen, capped tightly, swirled and then placed in an oven for 1 hour at 110°C.

3.4 Reacti-vials are removed from the oven and allowed to cool to room temperature before opening.

3.5 Solvent is removed to dryness with a stream of dry nitrogen using a PIERCE Reacti-Therm heating module. This procedure is performed at room temperature.

(Acylation)

3.6 250 µl of dichloromethane followed by 50 µl of pentafluoropropionic anhydride or trifluoracetic anhydride were added with automatic pipettes. Reacti-vials are then quickly flushed with nitrogen, capped tightly, swirled and placed in an oven at 110°C for 10 minutes.

3.7 The reacti-vials are taken out of the oven, allowed to cool to room temperature and then placed in a cooled aluminium block (-10°C). Reacti-vials are then uncapped and solvents are evaporated to dryness under a stream of dry nitrogen. (This procedure reduces differential evaporation of the relatively volatile pentafluoro-derivatives: see Kimber and Griffin, 1987).

3.8 Reacti-vials are then sealed with teflon caps after flushing with nitrogen. Samples are now ready for gas chromatography. (End of Day 3.)

A1.4 GAS CHROMATOGRAPHY

Amino acid derivatives were analysed by gas chromatography using a Packard-Becker model 419 gas chromatograph with a Chrompack 50 m length fused silica column, coated with the liquid stationary phase XE-60-s-Val-s-x-pea. Detection of the amino acid derivatives was achieved using a flame ionization detector (F.I.D.), with a nitrogen carrier gas. Individual amino acid peak heights and/or areas were recorded using an SP4100 Spectra-Physics Computing Integrator.

APPENDIX Table 2

Mollusc species analysed in this study

Species	Environmental setting
Anadara trapezia	- estuaries, mudflats
Anadara (Tegillarca) granosa	- estuaries, mudflats, tropical settings
Katelysia peronii	- sandy mud in midlittoral zone of estuaries
Katelysia rhytiphora	- sandy shores in the lower littoral zone
Katelysia scalarina	- sandy shores in the lower littoral zone
Fulvia tenuicostata	- sand and mud from 2-30 m water depth
Brachidontes (Austromytilus) rostratus	- rocky coasts, upper to mid-littoral zone
Brachidontes erosus	- rocky coasts, upper to mid-littoral zone
Anapella cycladea	- estuaries, tidal inlets or mudflats in mid-littoral zone
Ostrea angasi	- occurs generally at depths of 2-20 m on low to medium energy coasts
Donax (Plebidonax) deltoides	- abundant below surface of sandy beaches
Circumphalus disjecta	- sublittoral zone in sandy seagrass rich sediments (Posidonia australis facies)
Callucina lacteola	- subtidal habitats
Bassina pachyphylla	- sandy beaches
Foraminifera	
Marginopora vertebralis	- benthonic
Massilina milletti	- benthonic

Ecological distribution of species based on information provided in Ludbrook (1984).

Appendix Tables 2-6

(a) β-alanine riding under the L-leucine peak producing artificially low leucine D/L values

N.R. No replicate injection

* Manually integrated results based on peak height calculations

APPENDIX Table 3.1 Analytical Error (Gas Chromatography)
LOCATION Port Wakefield "Anadara Beds" Glanville Formation
SAMPLE ATRAP36AT1 (Depth of burial 2.5 m)
FRACTION ANALYSED "total acid hydrolysate"

Replicate injection	Amino acid D/L ratios					
	ALA	VAL	ALLO /ISO	LEU	PRO	ASP
T_0	0.7752	0.4086	0.5346	0.6060	0.6279*	0.6591
T_1	0.8390	0.4002	0.5495	0.6233	0.6279*	0.6746
T_2	0.8610	0.4042	0.5238	0.6108	0.6061*	0.6964
T_3	0.8279	0.4080	0.5411	0.6210	0.6800*	0.6637
T_4	0.8740	0.3739	0.5115	0.6078	0.6111*	0.6891
T_5	0.8747	0.4079	0.5342	0.6055	0.5938*	0.6707
24 hours T_6	0.8469	0.2941	0.4580	0.6024	0.6400*	0.6773
after T_0 T_7	Other peak heights too low to be resolved.				0.6407	0.6910

First injection immediately after derivatisation.
Subsequent injections on the hour.
* manually integrated based on peak height calculations.

APPENDIX Table 3.2 Intrashell D/L ratio variation in Anadara trapezia
LOCATION Port Wakefield, "Anadara Beds" (Glanville eq)
"total acid hydrolysate" and free amino acids

Depth (m)	Sample	Shell Section analysed	Geologically expected age	Amino acid D/L ratios ALA	VAL	ALLO /ISO	LEU	PRO	ASP
~2.5	ATRAP 30ATI (Total)	Hinge	120 ka	0.7899 ±0.0133	0.3831 ±0.0188	0.4964 ±0.0041	0.5511 ±0.0008	0.6052 ±0.0016*	0.5639 ±0.0007
~2.5	ATRAP 30AF1 (Free)	Hinge	120 ka	0.9641	0.4000* only one replicate injection available	0.4437	0.8712	0.7647*	0.7050
~2.5	ATRAP 30BTI (Total)	Central region	120 ka	0.8576	0.3696	0.5668	0.6265 ±0.0666	0.6296 ±0.0524	0.6041 ±0.0073
~2.5	ATRAP 30CT1 (Total)	Posterior growth edge	120 ka	0.8146	0.3811	0.4395	0.4974	0.6111*	0.5948
~2.5	ATRAP 30DT1 (Total)	Anterior growth edge	120 ka	0.7565 ±0.0062	0.3937 ±0.0057	0.5308 ±0.0103	0.5266 ±0.0018		0.6207 ±0.0064
~2.5	ATRAP 30ET1 (Total)	Central growth edge	120 ka	0.8792 ±0.113	0.4559 ±0.0029	0.6077 ±0.0032	0.5901 ±0.0122	0.5908 ±0.0042	0.6904 ±0.0007
~2.5	ATRAP 30FT1 (Total)	Central growth edge	120 ka	0.9464 ±0.0022	0.4347 ±0.0069	0.5867 ±0.0010	0.6153 ±0.0005	0.6563 ±0.0083	0.6652 ±0.0127

APPENDIX Table 3.2 (Continued)
LOCATION Port Wakefield "Anadara Beds" (Glanville eq)
Intrashell D/L variation in Anadara trapezia
(D/L ratios based on peak height calculations) ("total acid hydrolysate")

Depth (m)	Sample	Shell Section analysed	Geologically expected age	Amino acid D/L ratios ALA	VAL	ALLO /ISO	LEU	PRO	ASP
~2.5	ATRAP 31AT1 (Total)	Hinge	120 ka	0.8139 ±0.0030	0.3566 ±0.0210	0.4254 ±0.0055	0.5469 ±0.0037	0.6010 NR	0.6653 ±0.0108
~2.5	ATRAP 31BT1 (Total)	Central Region	120 ka	0.9334 ±0.0164	0.3709 ±0.0023	0.4636 ±0.0062	0.5618 ±0.0022	0.5864 ±0.0053	0.6787 ±0.0032
~2.5	ATRAP 31CT1 (Total)	Posterior growth edge	120 ka	-	-	0.3063	0.4599 ±0.0183	0.5737 ±0.0007	0.6430 ±0.0019
~2.5	ATRAP 31DT1 (Total)	Central growth edge	120 ka	0.7661 ±0.0097	0.3592 ±0.0195	0.4651 ±0.0262	0.5486 ±0.0155	0.6272	0.5929 ±0.0049
~2.5	ATRAP 31ET1 (Total)	Central growth edge	120 ka	0.9075 ±0.0313	0.4050 ±0.0010	0.4958 ±0.0165	0.5223 ±0.0010		0.5991 ±0.0057
~2.5	ATRAP 31FT1 (Total)	Anterior growth edge	120 ka	0.7777 ±0.0037	0.3964 ±0.0087	0.3444 ±0.0181	0.5810 ±0.0001		0.6271 ±0.0017

APPENDIX Table 3.2 (Continued)
LOCATION Port Wakefield "Anadara Beds" (Glanville eq)
Intrashell D/L variation in Anadara trapezia
(Free amino acids)

Depth (m)	Sample	Shell Section analysed	Geologically expected age	Amino acid D/L ratios					
				ALA	VAL	ALLO /ISO	LEU	PRO	ASP
~2.5	ATRAP 31AF1 (Free)	Hinge	120 ka	0.9871 NR	0.4874 NR	0.6332 NR	0.7589 ±0.0032	0.7852 ±0.0433	0.7810 ±0.0161
~2.5	ATRAP 31BF1	Central Region	120 ka	1.0329 ±0.0746	0.4851 ±0.0745	0.4963 ±0.0243	0.7297 ±0.0039	0.7853 ±0.0028	0.7691 ±0.0051
~2.5	ATRAP 31CF1	Posterior growth edge	120 ka	0.9117	0.4164	0.6085 NR	0.5970 ±0.0300	0.7565 ±0.0583	0.6601 ±0.0085
~2.5	ATRAP 31DF1	Central growth edge	120 ka	0.9264 ±0.0051	0.4944 ±0.0118	0.6853 ±0.0187	0.7322 ±0.0028	0.7416 ±0.0245	0.7067 ±0.0207
~2.5	ATRAP 31EF1	Central growth edge	120 ka	0.9357 ±0.0273	0.5078 ±0.0031	0.6613 ±0.0252	0.7496 ±0.0044	0.7477 ±0.0239	0.7102 ±0.0258
~2.5	ATRAP 31FF1	Anterior growth edge	120 ka	0.9446 ±0.0056	0.4626 ±0.0529	0.8750 ±0.0390	0.7945 ±0.0083	0.7588 ±0.0164	0.7743 ±0.0096

NR no replicate injection

APPENDIX Table 3.3 Within-Species Intershell D/L Ratio Variation in Anadara trapezia
LOCATION Port Wakefield, "Anadara Beds" "total acid hydrolysate"

Depth (m)	Sample	Geologically expected age	Amino acid D/L ratios							
			ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
2 m	ATRAP12AT1 (Total) (A)	120 ka	0.6558 ±0.0250	0.3014 ±0.0052	0.4300 ±0.0199	0.4364 ±0.0186		0.5903 ±0.0097	0.7527 ±0.0148	0.4238 ±0.0028
2 m	ATRAP12BT1 ("Total") (B)	120 ka	0.6448 ±0.0391	0.3686	0.4452 ±0.0428	0.4574 ±0.0165		0.6336 ±0.0269	0.7778 ±0.0445	0.4302 ±0.0034
2 m	ATRAP12CT1 (Total) (S)	120 ka	0.5404 ±0.0320	0.2036 ±0.0034	0.4051 ±0.0182	0.4674 ±0.0062		0.5788 ±0.0128	0.6522 ±0.0018	0.4565 ±0.0042
2 m	ATRAP12AF1 ("Free") (A)	120 ka	-	-	-	0.7433 ±0.0195		0.7647 ±0.0431	0.8599 ±0.0033	0.4661 ±0.0399
2 m	ATRAP12BF1 ("Free") (B)	120 ka	0.7310 ±0.0891	0.4575 ±0.0602	0.5987 ±0.0986	0.7126 ±0.0021		0.7539 ±0.0045	0.9287 ±0.0207	0.4929 ±0.0572
2 m	ATRAP12CF1 ("Free") (C)	120 ka	-	-	0.5870 ±0.0322	0.7105 ±0.0047		0.6922 ±0.0112	0.8319 ±0.0132	0.4046 ±0.0001
2 m	ATRAP30AT1 ("Total") (D)	120 ka	0.7899 ±0.0133	0.3831 ±0.0188	0.4964 ±0.0041	0.5511 ±0.0008	0.6052 ±0.0016*	0.5639 ±0.0007	-	-
2 m	ATRAP30AF1 ("Free") (D)	120 ka	0.9641	0.4000*	0.4437	0.8712	0.7647	0.7050	-	-
			only one replicate injection available							
2 m	ATRAP30AT1 ("Total") (E)	120 ka	0.8139 ±0.0030	0.3566 ±0.0210	0.4254 ±0.0055	0.5469 ±0.0037	0.6010 NR	0.6653 ±0.0108	-	-
2 m	ATRAP31AF1	120 ka	0.9871	0.4874	0.6332	0.7589	0.7852	0.7810	-	-
	("Free") (E)		NR	NR	NR	±0.0032	±0.0433	±0.0161		

APPENDIX Table 3.3 (Continued) Within Species Intershell D/L Ratio Variation in Anadara trapezia
LOCATION Port Wakefield, "Anadara Beds": Glanville Formation equivalent "total acid hydrolysate"

Depth (m)	Sample	Geologically expected age	Amino acid D/L ratios							
			ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
3 m	ATRAP07B1 (Total) (F)	110-120 ka	0.6875	0.3949	0.4629 ±0.0279	0.4826 ±0.0083		0.5779 ±0.0145	0.7828 ±0.0668	0.4119 ±0.0373
3 m	ATRAP07D1 (Total) (G)	110-120 ka	0.6743 ±0.0166	0.2606 ±0.0020	0.4240 ±0.0023	0.5325 ±0.0064		0.5064 ±0.0001	0.7499 ±0.0151	0.4264 ±0.0035
3 m	ATRAP07E1 (Total) (H)	110-120 ka	0.6813 ±0.0074	0.3084 ±0.0002	0.4268 ±0.0073	0.5207 ±0.0015		0.5433 ±0.0067	0.6633 ±0.0059	0.4385 ±0.0134
~2.5 m	ATRAP32AT1 (Total) (I)	120 ka	0.8055 ±0.0364	0.3884 ±0.0010	0.4833 ±0.0277	0.5498 ±0.0128		0.6384 ±0.0330		
	ATRAP32AF1 (Free) (I)	120 ka	0.8978 ±0.0227	0.4966 ±0.0298	0.6336 ±0.0167	0.7530 ±0.0107	0.7919 ±0.0175	0.7544 ±0.0185		
2.5 m	ATRAP33AT1 (Total) (J)	120 ka	0.8032 ±0.0028	0.3743 ±0.0083	0.4185 ±0.0194	0.5515 ±0.0072		0.6668 ±0.0012		
	ATRAP33AF1 (Free) (J)	120 ka	0.9606 ±0.0856	0.4504 ±0.0917	0.5871 ±0.0298	0.7311 ±0.0141	0.7996 ±0.0537	0.7886 ±0.0143		
~2.5 m	ATRAP34AT1 (Total) (K)	120 ka	0.9317 ±0.0819	0.3449 ±0.0267	0.3620 ±0.0007	0.5423 ±0.0030	0.5993 NRP	0.6792 ±0.0030		
	ATRAP34AF1 (Free) (K)	120 ka	0.9628 NRP	0.5100 NRP	0.5854 ±0.0328	0.6869 ±0.0176	0.7957 ±0.0428	0.7613 ±0.0060		

APPENDIX Table 3.4 Interlaboratory comparison of amino acid D/L ratios ("total acid hydrolysate")

Sample Code	Species	Injection No.	Geologically expected age	Amino acid D/L ratios ALA	VAL	ALLO /ISO	LEU	ASP
ILC-A (Total)	Saxidomus	1	~50 kaBP	0.4756	0.1134	0.1270	0.1978	-
		2		0.6018	0.1113	0.1259	0.1972	-
		3		0.5253	0.1152	0.1292	0.1952	-
		4		-	-	-	0.1684	0.4036
		x±SD		0.5342	0.1133	0.1274	0.1897	0.4036
				±0.0636	±0.0020	±0.0017	±0.0142	
ILC-B (Total)	Mercenaria	1	~100-250 kaBP	0.7929	0.3474	0.4408	0.4576	-
		2		0.7802	0.3520	0.4632	0.4694	0.5696
		3		0.8053	0.3467	0.4520	0.4492	0.6205
		4		0.8864	0.3567	0.4268	0.4428	0.6436
		x±SD		0.8162	0.3507	0.4457	0.4548	0.6112
				±0.0479	±0.0046	±0.0156	±0.0115	±0.0379
ILC-C (Total)	Mercenaria	1	1 Ma	1.0000	0.7195	0.8904	0.7573	0.8443
		2		0.9827	0.7249	0.9120	0.7603	0.8253
		3		0.9432	0.7328	0.9218	0.7656	0.8272
		4		0.9756	0.7193	0.8873	0.7679	0.8502
		x±SD		0.9754	0.7241	0.9029	0.7628	0.8368
				±0.0238	±0.0063	±0.0167	±0.0048	±0.0124

APPENDIX Table 3.5 Interlaboratory comparison with The University of Delaware
Location: Spencer Gulf, Gulf St Vincent and Queensland
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample Code	Species	Geologically expected age	Amino acid D/L ratios ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
Queensland 79/10		ATRAP 70AT1 (Total)	Anadara trapezia	modern	0.0745 ±0.0273	0.0219 ±0.0021	0.0176 ±0.0080	0.0440 ±0.0064		0.1323 ±0.0012	0.0239 ±0.0055	0.0458 ±0.0029
		ATRAP 70AF1 (Free)	Anadara trapezia	modern						0.2958		
Gulf St Vincent Glanville Formation 79/12	2 m	ATRAP 71AT1 (Total)	Anadara trapezia	125	0.9781 ±0.0703	0.3460 ±0.0039	0.3617 ±0.0084	0.4597 ±0.0031	0.7259 ±0.0253	0.6765 ±0.0155		
		ATRAP 71AF1 (Free)	Anadara trapezia	125		0.5073 ±0.0177	0.5332 ±0.0302	0.7243 ±0.0023	0.7792 ±0.0083	0.7557 ±0.0234		
SG#182 79/15 Spencer Gulf submarine core	2.20	ATRAP 72AT1 (Total)	Anadara trapezia	125	0.9032 ±0.0826	0.3905 ±0.0050	0.4342 ±0.0091	0.5164 ±0.0197	0.7168 *	0.6773 ±0.0400		
		ATRAP 72AF1 (Free)	Anadara trapezia	125		0.5543 ±0.0118	0.6244 ±0.0062	0.7518 ±0.0118	0.7624 ±0.0611	0.7706 ±0.0167		
SG#171 Spencer Gulf submarine Core	1.00	ATRAP 73AT1 (Total)	Anadara trapezia	125	0.8707 ±0.0182	0.3481 ±0.0001	0.4198 ±0.0109	0.4812 ±0.0059		0.6232 ±0.0289		
		ATRAP 73AF1 (Free)	Anadara trapezia	125	0.9371 ±0.0340	0.5526 ±0.0098	0.6237 ±0.0090	0.8005 ±0.0144	0.8013 ±0.0572	0.6961 ±0.0141		

APPENDIX Table 3.5 (continued) Interlaboratory comparison with The University of Delaware
Location: Spencer Gulf, Gulf St Vincent and Queensland
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample Code	Species	Geologically expected age	Amino acid D/L ratios							
					ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
Cultana beach ridge	near surface	ATRAP 74AT1 (Total)	Anadara trapezia	125	0.8372 ±0.0206	0.4330 ±0.0008	0.5391 ±0.0005	0.5816 ±0.0075		0.6821 ±0.0064		
		ATRAP 74AF1 (Free)	Anadara trapezia	125	0.9222 ±0.0053	0.5953 ±0.0402	0.7492 ±0.0006	0.8147 ±0.0031		0.7034 ±0.0008	0.4819 ±0.0052	0.0389 ±0.0003
Modern Anadara Queensland		ATRAP 70BT1 (Total)	Anadara trapezia	modern	0.1366 ±0.0088*	0.0137 ±0.0014*	0.0238 ±0.0021	0.0701 ±0.0026		0.1580 ±0.0046	0.0621 ±0.0043	0.0478 ±0.0004
Sample replicate to ATRAP70AT7F1		ATRAP 70BF1 (Free)	Anadara trapezia	modern				0.0948 ±0.0021		0.1000 ±0.0024		

APPENDIX Table 3.6 Modern Shells
Location: Gulf St Vincent, Semaphore Beach
Fractions analysed: "total acid hydrolysate"

Depth (m)	Sample Code	Species	Geologically expected age	Amino acid D/L ratios							
				ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
Surface of beach (modern)	FTCOS 20AT1 (Total)	Fulvia tenuicostata	Modern 'zero-age'		0.0167*	0.0288*	0.0469 ±0.0211	0.0526*	0.0713 ±0.0013		0.0340 ±0.0048
Beach surface (modern)	KSCAL 20AT1 (Total)	Katelysia scalarina	Modern 'zero-age'		0.0345 ±0.0056	0.0449 ±0.0045*	0.0446 ±0.0031*		0.2009 ±0.0023 (?)		0.0668 ±0.0023
Beach surface (modern)	GSTR1 20AT1 (Total)	Glycymeris (Tucetilla) striatularis	Modern 'zero-age'		0.0308*	0.0175*	0.0741*		0.2533 (?)		
Beach surface (modern)	KRHY 20AT (Total)	Katelysia rhytiphora	Modern 'zero-age'		0.0135 ±0.0024	0.0171 ±0.0025*	0.0337 ±0.0179		0.0708		
beach surface (modern)	MACA 20AT1 (Total)	Mactra australis	Modern 'zero-age'		0.0247*	0.0246*	0.0488*	0.0889*	0.0679	0.0998*	0.0327*
Quarantine Bay NSW Beach face	ATRAP 60AT1	Anadara trapezia	Modern	0.0752 ±0.0189	0.0178 ±0.0085	0.0203 ±0.0017	0.0327 ±0.0011		0.1143	0.0302 ±0.0103	0.0798 ±0.0129
	ATRAP 60AF1 (Free)	Anadara trapezia	Modern			0.2973 ±0.1040 (?)	0.1340 ±0.0115		0.1265 ±0.0052		

APPENDIX Table 4.1 Extent of racemisation in molluscan fossils from the Last Interglacial Glanville Formation, South Australia
Fractions analysed: total acid hydrolysate and free amino acids

Core	Location	Depth (m)	Sample	Species	Geologically expected age	Amino acid D/L ratios							
						ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
	Dry Creek	1.25	ATRAP 20AIT1 (Total)	Anadara trapezia	120 ka	0.7824 ±0.0096	0.4022 ±0.0109	0.4302 ±0.0311	0.4214 ±0.0046		0.7699	0.7316 ±0.0	0.5507 ±0.0
		1.25	ATRAP 20AIF1 (Free)	Anadara trapezia	120 ka				0.6805		0.7436	0.8628 ±0.0095	0.6844 ±0.0004
	Dry Creek	2 m	KSCAL GT1 (Total)	Katelysia scalarina	120 ka		0.4468 ±0.0162	0.5578	0.5333 ±0.0471		0.6672 ±0.0361	0.7605 ±0.0714	0.5163 ±0.0004
		2 m	KRHY GT2 (Total)	Katelysia rhytiphora	120 ka		0.4766 ±0.0039	0.5271 ±0.0046	0.5458 ±0.0020		0.6542 ±0.0095	0.6958 ±0.0043	0.5702 ±0.0053
	Quarry Exposure North of Port Wakefield 'South Hummocks'	1 m	ATRAP AT77 (Total)	Anadara trapezia	120 ka	0.7477 ±0.0864	0.2708 ±0.0146	0.3374 ±0.0034	0.4012 ±0.0279		0.6787 ±0.0590	0.5521	0.3704
		1 m	ATRAP AT78 (Total)	Anadara trapezia	120 ka	0.7657 ±0.0279	0.3146 ±0.0071	0.3851 ±0.0016	0.4436 ±0.0024		0.7838 ±0.0226 (a)	0.5718 ±0.0119	0.4133 ±0.0080
		1 m	ATRAP AT79 (Total)	Anadara trapezia	120 ka	0.8317 ±0.0395	0.2801 ±0.0038	0.3374 ±0.0022	0.4130 ±0.0056		0.7086 ±0.0055 (a)	0.4959 ±0.0082	0.4062 ±0.0062

APPENDIX Table 4.1 (Continued)

Core	Location	Depth (m)	Sample	Species	Geologically expected age	Amino acid D/L ratios							
						ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
	Port Wakefield "Anadara Beds"	3 m	KRHY O7A1 (Total)	Katelysia rhytiphora	110-120 ka	0.7136	0.2836	0.3871	0.4396		0.4761	0.6802	0.3739
		3 m	KRHY O7B1 (Total)	Katelysia rhytiphora	110-120 ka			0.3945 ±0.0549	0.4537 ±0.0149		0.4859 ±0.0326	0.7453 ±0.1063	0.3992 ±0.0221
		3 m	KRHY O7C1 (Total)	Katelysia rhytiphora	110-120 ka	0.7100 ±0.0149	0.3193 ±0.0622	0.4734 ±0.0168	0.5797 ±0.0046		0.4541 ±0.0649	0.6384 ±0.0868	0.3360 ±0.0081
		3 m	FTCOS O7A1 (Total)	Fulvia tenuicostata	110-120 ka	0.6126 ±0.0122	0.4179 ±0.1196	0.7411 ±0.0605	0.8375 ±0.0440		0.4096* ±0.0243	0.6799 ±0.0426	0.4581 ±0.0033
		3 m	KRHY O7D1 (Total)	Katelysia rhytiphora	110-120 ka	0.7616 ±0.0281	0.3719 ±0.0007	0.5370 ±0.0121	0.5629 ±0.0026		0.4588 ±0.0046	0.6407 ±0.0185	0.4273 ±0.0131
	Victor Harbor South Australia	5 m	ATRAP 21AIT1 (Total)	Anadara trapezia	120 ka	0.8056 ±0.0082	0.3287 ±0.0047	0.5000 ±0.0150	0.5907 ±0.0207	0.6029 ±0.0001	0.6088 ±0.0199		0.5744 ±0.1178
			ATRAP 21AIF1 (Free)	Anadara trapezia	120 ka	0.8806	0.4198 ±0.0449	0.5224 ±0.0036	0.7947 ±0.0142	0.7211 ±0.0666	0.6770 ±0.0425		0.4439 ±0.0578
		5 m	ATRAP 21AIT2 (Total)	Anadara trapezia	120 ka	0.7878 ±0.0185	0.3086 ±0.0143	0.3930 ±0.0116	0.5934 ±0.0094	0.5774 ±0.0203	0.6074 ±0.0134		0.5432 ±0.1470
			ATRAP 21AIF2 (Free)	Anadara trapezia	120 ka		0.4300 ±0.0088	0.5785 ±0.0020	0.7597 ±0.0010	0.7564 ±0.0190	0.7573 ±0.0247		0.4839 ±0.0464
	Denial Bay near Ceduna	~2 m	ATRAP 13AT1 (Total)	Anadara trapezia	120 ka	0.6971 ±0.0075	0.3140 ±0.0008	0.4605 ±0.0110	0.4506 ±0.0103		0.6648 ±0.0101	0.6619 ±0.0231	0.4752 ±0.0092
			ATRAP 13BT1 (Total)	Anadara trapezia	120 ka	0.5676 ±0.1159	0.3464 ±0.0120	0.4500 ±0.0206	0.4298 ±0.0182		0.6386 ±0.0182	0.7002 ±0.0334	0.4719 ±0.0031
			ATRAP 13CT1 (Total)	Anadara trapezia	120 ka	0.6643	0.3242	0.4089	0.4296		0.6259	0.7061	0.4706

APPENDIX Table 4.1 (Continued)

Core	Location	Depth (m)	Sample	Species	Geologically expected age	Amino acid D/L ratios							
						ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
	Denial Bay Ceduna	~2 m	ATRAP 13AF1 (Free)	Anadara trapezia	120 ka	Sample lost during derivatisation							
			ATRAP 13BF1 (Free)	Anadara trapezia	120 ka	0.8065 ±0.0658	0.4272 ±0.0624	0.6283 ±0.0152	0.5832 ±0.0235		0.7724 ±0.0134	0.5097 ±0.0030	0.4419 ±0.0228
			ATRAP 13CF1 (Free)	Anadara trapezia	120 ka			0.6869 ±0.1359	0.7314 ±0.0023		0.7932 ±0.0087	0.9165 ±0.0054	0.4946 ±0.0021
Sample 80a			ATRAP O2A1 (Total)	Anadara trapezia	120 ka	0.6182 ±0.0008	0.3328 ±0.0074	0.4492 ±0.0177	0.4777 ±0.0013		0.6457 ±0.0359		0.3373 ±0.0089
Sample 75a	Lake MacDonnell		KRHY 04H1 (Total)	Katelysia rhytiphora	120 ka	0.7872 ±0.0060	0.4202 ±0.0020	0.5348 ±0.0007	0.6548 ±0.0069		0.4662 ±0.0046		0.4435 ±0.0062
Sample 80b			ATRAP O2A2	Anadara trapezia	120 ka	0.6998 ±0.0023	0.3287 ±0.0006	0.4203 ±0.0089	0.4677 ±0.0110		0.6194 ±0.0204	0.6526 ±0.0663	0.4221 ±0.0344
Sample 58B	Tourville Bay		KSCAL 06A2 (Total)	Katelysia scalarina	120 ka	0.5232 ±0.0112	0.4162 ±0.0045	0.5037 ±0.0128	0.5812 ±0.0225		0.4991 ±0.0013	0.7049 ±0.0052	0.4384 ±0.0103
Sample 127	Lake Newland		KRHY 03H4 (Total)	Katelysia rhytiphora	120 ka	0.7543 ±0.0047	0.3533 ±0.0110	0.4506 ±0.0100	0.4723 ±0.0139		0.4642 ±0.0093	0.6798 ±0.0008	0.4087 ±0.0117

APPENDIX Table 4.1 (Continued)

Core	Location	Depth (m)	Sample	Species	Geologically expected age	Amino acid D/L ratios							
						ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
Sample 80(a)	Tourville Bay		KRHY O9A1 (Total)	Katelysia rhytiphora	120 ka	0.7876 ±0.0178	0.3864 ±0.0188	0.5210 ±0.0005	0.5620 ±0.0004		0.4851 ±0.0392	0.7612 ±0.0066	0.4656 ±0.0045
Sample 80(b)	Tourville Bay		KRHY O9B1 (Total)	Katelysia rhytiphora	120 ka	0.7793 ±0.0039	0.3654 ±0.0230	0.5314 ±0.0163	0.6118 ±0.0060		0.5401 ±0.0112	0.7671 ±0.0031	0.4899 ±0.0100
	Tourville Bay	1.5 m	ATRAP 15AT1 (Total)	Anadara trapezia	120 ka	0.8776 ±0.0126	0.4097 ±0.0088	0.4878 ±0.0262	0.4484 ±0.0151		0.6710 ±0.0012	0.7067 ±0.0248	0.8197 ±0.0116
		1.5 m	ATRAP 15AT1 (Free)	Anadara trapezia					0.6169 ±0.0497		0.7520 ±0.00345	0.8024 ±0.0395	0.7364 ±0.0274
	Tourville Bay	1.5 m	ATRAP 15A2T1 (Total)	Anadara trapezia	120 ka	0.8902 ±0.0106		0.6661 ±0.0145 (?)	0.4231 ±0.0253		0.6852 ±0.0367	0.7937 ±0.0395	0.8089 ±0.0072
		1.5 m	ATRAP 15A2F1	Anadara trapezia		0.9103 ±0.0252	0.5187 ±0.0165	0.6870 ±0.0212	0.5463 ±0.0040		0.7058 ±0.0069	0.7464 ±0.0007	0.5978 ±0.0300
	Tourville Bay		ATRAP O2A2 (Free)	Anadara trapezia	120 ka	0.8557 ±0.0052	0.4058 ±0.0128	0.7928 ±0.0360	0.7482 ±0.0063		0.7311 ±0.0098	0.9208 ±0.0124	0.4962 ±0.0264

APPENDIX Table 4.1 (Continued)

Core	Location	Depth (m)	Sample	Species	Geologically expected age	Amino acid D/L ratios							
						ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
	SG#84/2		ATRAP 01B1 (Free)	Anadara trapezia	120 ka	0.8641	0.5614		0.7374		0.6062		0.4688
Sample 80a	West Coast		ATRAP 02A1 (Free)	Anadara trapezia	120 ka	0.6507	0.4900	0.4902	0.6458 ±0.0132		0.6404 ±0.0117	0.8482 ±0.0116	0.4256 ±0.0181
	Hindmarsh River locality	1.5 m	ATRAP 01F1 (Free)	Anadara trapezia	120 ka	0.8234 ±0.0063	0.4096 ±0.0022	0.6246 ±0.0172	0.7145 ±0.0021		0.7909 ±0.0099	0.9111 ±0.0084	0.4906 ±0.0153
	RED 41		ATRAP 07D1 (Free)	Anadara trapezia	120 ka				0.7319		0.7075		
	Hindmarsh River locality	1.5 m	ATRAP 01T1 (Total)	Anadara trapezia	120 ka	0.5779 ±0.0671	0.2816 ±0.0376	0.3522 ±0.0459	0.4495 ±0.0494		0.6668 ±0.0402	0.6996 ±0.0716	0.4233 ±0.0088
	SG#84/2		ATRAP 01B1 (Total)	Anadara trapezia	120 ka	0.8534 ±0.0006	0.5399 ±0.0081	0.7802 ±0.0322	0.6466 ±0.0022		0.7409 ±0.0013	0.7903 ±0.0184	0.6733 ±0.0153

APPENDIX Table 4.2 Extent of amino acid racemisation in Anadara trapezia from the "Older Pleistocene marine beds", Redcliff, northern Spencer Gulf (Penultimate Interglacial)

Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample	Geologically expected age	Amino acid D/L ratios						
				ALA	VAL	ALLO /ISO	LEU	ASP	PHE	GLU
RED#41	1.30-1.35 m	ATRAP 17A1T1 (Total)	220 kaBP	0.8831 ±0.0195		0.7094 ±0.0208	0.5384 ±0.0005	0.7973 ±0.0200	0.8908 ±0.0015	0.6350 ±0.0070
		ATRAP 17A1F1 (Free)	220 kaBP					0.7743		
RED#40	0.90-1.00 m	ATRAP 18A1T1 (Total)	220 kaBP	0.8335 ±0.0867	0.5104 ±0.0097	0.5016 ±0.0228	0.5591 ±0.0151	0.7608 ±0.0280		0.6072 ±0.0528
		ATRAP 18A1F1 (Free)	220 kaBP			0.6865 ±0.0020	0.8324 ±0.0366	0.8270 ±0.0186		
RED#40	0.98-1.00 m	ATRAP 18A2T1 (Total)	220 kaBP				0.5133 ±0.0236	0.7186 ±0.0202	0.8920 ±0.0088	0.6324 ±0.0106
		ATRAP 18A2F1 (Free)	220 kaBP				0.7637 ±0.0381	0.7383 ±0.0363		0.5662 ±0.0056
RED#40	0.90-1.00 m	ATRAP 19A1T1 (Total)	220 kaBP	0.7776 ±0.0235	0.4548 ±0.0139	0.4484 ±0.0113	0.5119 ±0.0161	0.7732 ±0.0135	0.6773 ±0.1028	0.6005 ±0.0005
		ATRAP 19A1F1 (Free)	220 kaBP	0.7755 ±0.0099	0.4506	0.5112 ±0.0771	0.5856 ±0.0099	0.8092 ±0.0301	0.1334 ±0.0006	0.4475 ±0.0136

APPENDIX Table 4.3 Extent of amino acid racemisation in molluscan fossils from Interstadial Marine Strata
Location: Gulf St Vincent, Submarine Cores
Fractions analysed: "total acid hydrolysate"

Core	Depth (m)	Sample Code	Species	Geologically expected age	AAR age	Amino acid D/L ratios						
						ALA	VAL	ALLO /ISO	LEU	ASP	PHE	GLU
SV-4	0.58-0.60	KRHY 53AT1 (Total)	Katelysia rhytiphora	Late Pleistocene	30 ka	0.5774 ±0.0053	0.1927 ±0.0029	0.1937 ±0.0028	0.2930 ±0.0066	0.4521 ±0.0162		
	2.47	FTCOS 22AT1 (Total)	Fulvia tenuicostata	Late Pleistocene	30 ka	0.7148 ±0.0358	0.1913 ±0.0025	0.2210 ±0.0049	0.2840 ±0.0029	0.4092 ±0.0275		
	0.64	FTCOS 23AT1 (Total)	Fulvia tenuicostata			0.5213 ±0.0208	0.1060 ±0.0070	0.1079 ±0.0043	0.1999 ±0.0025	0.3242 ±0.0020		
SV-5	1.06	BERO 20AT1 (Total)	Brachidontes rostratus	Late Pleistocene	30 ka	0.4969 ±0.0388	0.3201 ±0.0058	0.5425 ±0.0318	0.5348 ±0.0100	0.4377 ±0.0047		
	0.25-0.27	CID 02AT1 (Total)	Circomphalus disjecta	Holocene <8		0.2431 ±0.0034	0.0465 ±0.0015	0.0553 ±0.0003	0.1094 ±0.0047	0.2569		
	3.69	KRHY 54AT1 (Total)	Katelysia rhytiphora	Late Pleistocene 10<x<110	30 ka	0.6908 ±0.0272	0.1965 ±0.0047	0.1813 ±0.0010	0.2947 ±0.0015	0.4556 ±0.0118		
	0.66	BRACH AT1 (Total)	Brachidontes erosus			-	0.3740 ±0.0052	0.3637 ±0.0236	0.3503 ±0.0612	0.5652 ±0.0344	0.5782	0.3593

APPENDIX Table 4.3 (Continued)

Core	Depth (m)	Sample Code	Species	Geologically expected age	Amino acid D/L ratios				
					ALA	VAL	ALLO /ISO	LEU	ASP
SV-4	0.64	FTCOS 24AT1 (Total)	Fulvia tenuicostata	Late Pleistocene ca. 40 ka	0.4355 ±0.0122	0.1246 ±0.0019	0.1534 ±0.0004	0.2246 ±0.0017	0.3214 ±0.0001
	0.58	KRHY 55AT1 (Total)	Katelysia rhytiphora	Late Pleistocene ca. 40 ka	0.6325 ±0.0020	0.2333 ±0.0039	0.2526 ±0.0112	0.3304 ±0.0077	0.4544 ±0.0021
	2.77	FTCOS 25AT1 (Total)	Fulvia tenuicostata	Late Pleistocene ca. 40 ka	0.7764 ±0.0374	0.2440 ±0.0049	0.2992 ±0.0047	0.3318 ±0.0100	0.4032 ±0.0015
SV-5	0.25-0.27	CIDO 3AT1 (Total)	Circomphalus disjecta	Holocene <8 ka	0.2107 ±0.0058	0.0619 ±0.0011	0.0756 ±0.0049	0.1190 ±0.0197	0.2759 ±0.0065
	surface grab sample from Gulf floor	GRAB 01AT1 (Total)	Mixed species assemblage	modern (sub-recent)	0.1856 ±0.0018	0.0474 ±0.0001	0.0614 ±0.0003	0.1050 ±0.0007	0.2231 ±0.0021
SV-1	0.34	CLAC 01AT1 (Total)	Callucina lacteola	Late-Pleistocene ca. 40 ka	0.2485 ±0.0018	0.1066 ±0.0004	0.1473 ±0.0023	0.2368 ±0.0025	0.3645 ±0.0042

APPENDIX Table 4.3 (Continued)

Core	Depth (m)	Sample	Species	A.A.R. age (ka)	Geologically expected age	Amino acid D/L ratios					
						ALA	VAL	ALLO /ISO	LEU	PRO	ASP
SV-5	3.50	KRHY 50AT1 (Total)	Katelysia rhytiphora	Late Pleistocene 30-40 ka?	100 > x > 10 Late Pleistocene	0.6831 ±0.0550	0.2633 ±0.0031	0.2601 ±0.0045	0.2799 ±0.0090		0.4574 ±0.0917
	1.38-1.42	KRHY 51AT1 (Total)	Katelysia rhytiphora	Late Pleistocene 30-40 ka?	100 > x > 10 Late Pleistocene	0.6832 ±0.0048	0.2474 ±0.0031	0.2535 ±0.0033	0.2878 ±0.0015		0.4265 ±0.0397
	0.54	KRHY 52AT1 (Total)	Katelysia rhytiphora	Late Pleistocene 30-40 ka?		0.6713 ±0.0114	0.2270 ±0.0036	0.2277 ±0.0004	0.2859 ±0.0010		0.4642 ±0.0090
	2.19	FTCOS 20AT1 (Total)	Fulvia tenuicostata	Late Pleistocene 30-40 ka?	100 > x > 10 Late Pleistocene	0.8617 ±0.1052	0.1819 ±0.0056	0.2355 ±0.0372	0.2871 ±0.0137		0.4301 ±0.0044
	2.00	FTCOS 21AT1 (Total)	Fulvia tenuicostata	Late Pleistocene 30-40 ka?	100 > x > 10 Late Pleistocene	0.8955	0.2304 ±0.0023	0.2567 ±0.0072	0.2801 ±0.0022	0.5081 ±0.0114*	0.4501 ±0.0047
	0.27	CDIS 01AT1 (Total)	Circomphalus disjecta	VAL 11548 ALLO/ISO 6928 LEU 5045 ASP 6719	<8 Holocene	0.2534 ±0.0344	0.0553 ±0.0011	0.0739 ±0.0024	0.0976 ±0.0050		0.2675 ±0.0016

APPENDIX Table 4.3 (Continued)

Core	Depth (m)	Sample Code	Species	Geologically expected age	Amino acid D/L ratios ALA	VAL	ALLO /ISO	LEU	PRO	ASP
SV-4	0.58-0.60	KRHY 56AF1 (Free)	Katelysia rhytiphora	Late Pleistocene	0.9405 ±0.0034	0.4335 ±0.0152	0.5547 ±0.0001	0.6669 ±0.0008	0.7656 ±0.0663*	0.6358 ±0.0384
SV-4	0.58-0.60	OST 01AF1 (Free)	Ostrea angasi	Late Pleistocene	0.8623 ±0.0058	0.6215 ±0.0047	1.0228 ±0.0054	0.7525 ±0.0202	0.7475 ±0.0150	0.6379 ±0.0218
SV-5	3.79	OST 02AF1 (Free)	Ostrea angasi	Late Pleistocene		0.3206	0.4962 ±0.0978	0.4674 ±0.0101		0.6775 ±0.0080
SV-4	0.58-0.60	KRHY 56AT1 (Total)	Katelysia rhytiphora	Late Pleistocene	0.7229 ±0.0107	0.2281 ±0.0005	0.2446 ±0.0014	0.3396 ±0.0011		0.4418 ±0.0057
SV-4	0.58-0.60	OST O1AT1 (Total)	Ostrea angasi	Late Pleistocene	0.7753 ±0.0010	0.3367 ±0.0021	0.4992 ±0.0093	0.4956 ±0.0036		0.4534 ±0.0241
SV-5	3.79	OST 02AT1 (Total)	Ostrea angasi	Late Pleistocene	0.9631	0.4293	0.5938 ±0.0045	0.3975 ±0.0156	0.6071*	0.4443 ±0.0074
SV-4	0.58-0.60	KRHY 57AT1 (Total)	Katelysia rhytiphora	Late Pleistocene	0.7376 ±0.0038	0.2844 ±0.0693	0.2603 NRA	0.3397 ±0.0042		0.5325 ±0.0176
		KRHY 57AF1 (Free)	Katelysia rhytiphora	Late Pleistocene	1.0418 ±0.0190	0.4162 ±0.0105	0.4305 ±0.0432	0.6020 ±0.0069		0.5909 ±0.0231

APPENDIX Table 4.4 Wardang Island and various other South Australian localities D/L ratios for the foraminifer Marginopora vertebralis ("total acid hydrolysate").

Sample Code	Depth (m)	Locality	Amino acid D/L ratios								
			ALA	VAL	ALLO /ISO	LEU	PRO	ASP	MET	PHE	GLU
MAVER 01A1 (Total)	2	Smoky Bay Eyre Pen.			0.0740	0.1562 ±0.0015	0.2679* ±0.0252	0.3422 ±0.0471		0.1979	0.1769
MAVER 51B1 (Total)	~2	Redcliff core 51	0.2500				0.2857	0.3655 ±0.0117			
MAVER 04A1 (Total)		Wardang Island Glanville Fm equivalent	0.2638 ±0.0141	0.0943 ±0.0088	0.1432 ±0.0105	0.1646 ±0.0062	0.2547* ±0.0066	0.3334 ±0.0003			0.2099 ±0.0076
MAVER 04E1 (Total)	surface sample	Wardang Island loose on tidal flat	0.1131 ±0.0006	0.0400 10.0021	0.0658 ±0.0004	0.0633 ±0.0011	0.0325 ±0.0002	0.1932 ±0.0002			0.1085 ±0.0003
MAVER 02A1 (Total)	surface sample	Wardang Island Tidal flat	0.0773 ±0.0114	0.0237 ±0.0002	0.0384 ±0.0013	0.0446 ±0.0025	0.1484 ±0.0134	0.1867 ±0.0004			0.1473 ±0.0278
MAVER 02A2 (Total)	Surface sample	Wardang Island Tidal flat	0.1195 ±0.0052	0.0353 ±0.0016	0.0549 ±0.0035	0.0584 ±0.0036	0.1384 ±0.0064	0.2152 ±0.0016			0.1512 ±0.0127
MAVER 02A3 (Total)	Surface sample	Wardang Island Tidal flat	0.0986 ±0.0018	0.0323 ±0.0020	0.0492 ±0.0028	0.0487 ±0.0007	0.0385 ±0.0129	0.1478 ±0.0014	0.0771 ±0.0217		0.0989 ±0.0025
KSCAL 25A1 (Total) Katelysia scalarina	Surface sample	Wardang Island Tidal flat reworked valve from Glanville Fm	0.7955 ±0.0087	0.4009 ±0.0233	0.4389 ±0.0040	0.3237 ±0.0161	0.5705 ±0.0170	0.6594 ±0.0094	0.4286 ±0.0252		0.5464 ±0.0042
MAVER 04A2 (Total)		Wardang Island Glanville Fm Equivalent	0.2451 ±0.0071	0.0744 ±0.0071	0.1161 ±0.0023	0.1342 ±0.0007	0.2937 ±0.0143	0.3057 ±0.0041	0.1323 ±0.0817	0.2187 ±0.0004	
MAVER 02A4 (Total)	Surface sample	Wardang Island Loose on Tidal flat				0.0659	0.1533*	0.1363	0.2139	0.0804	0.2980

APPENDIX Table 4.4 (Continued)
Location: Wardang Island
Fractions analysed: "total acid hydrolysate"
Amino acid D/L ratios in the foraminifer Marginopora vertebralis

Depth (m)	Sample	Location	Geologically expected age	Amino acid D/L ratios						
				ALA	VAL	ALLO /ISO	LEU	ASP	PHE	GLU
	MAVER 09F1 (Free)	loose on tidal flat	120 ka			0.4097	0.4854 ±0.0264	0.6007 ±0.0063	0.8103	0.2424 ±0.0245
	MAVER 09T1 (Total)	loose on tidal flat	120 ka	0.0848 ±0.0098	0.0180 ±0.0013	0.0418 ±0.0042	0.0361 ±0.0016	0.1499 ±0.0139		0.1043 ±0.0174
	MAVER 10F1 (Free)	loose on tidal flat	120 ka	0.3508	0.2222*	0.3333*	0.3255 ±0.0041	0.4019 ±0.0012		
	MAVER 10T1 (Total)	loose on tidal flat	120 ka	0.0990 ±0.0407	0.0279 ±0.0094	0.0610 ±0.0225	0.0465 ±0.0003	0.1451 ±0.0081	0.0770 (?)	0.1126 ±0.0173
	MAVER 11T1 (Free)	Reef Rock	120 ka	0.3419	0.2000	0.1874	0.2813 ±0.0442	0.4642 ±0.0472	0.5676	0.1824
	MAVER 11T1 (Total)	Reef Rock	120 ka	0.2687 ±0.0018	0.0781 ±0.0001	0.1438 ±0.0011	0.1530 ±0.0050	0.3192 ±0.0209	0.5409 ±0.0481	0.2325 ±0.0362

APPENDIX Table 4.4 (Continued)
Location: Wardang Island
Fractions analysed: "total acid hydrolysate"
Amino acid D/L ratios in the foraminifer Marginopora vertebralis

Depth (m)	Sample	Location	Geologically expected age	Amino acid D/L ratios						
				ALA	VAL	ALLO /ISO	LEU	ASP	PHE	GLU
	MAVER 12F1 (Free)	Reef Rock	120 ka				0.2530	0.4794 ±0.0125		
	MAVER 12T1 (Total)	Reef Rock	120 ka	0.2792 ±0.0445	0.1548 ±0.0168	0.1401	0.1546 ±0.0084	0.3899 ±0.0004	0.5025 ±0.0765	0.2391 ±0.0001
	MAVER 15AT1 (Total)	Reef Rock	120 ka	0.3750 ±0.0431		0.1112	0.1278 ±0.0136	0.4088	0.3843 ±0.0936	0.4859 ±0.0839
	MAVER 16AT1 (Total)	Wardang Is loose on	120 ka	0.1402	0.0286	0.0329 ±0.0018	0.0491 ±0.0055	0.2055 ±0.0060		0.2187 ±0.0059
	MAVER 16A1F1 (Free)							0.4535 ±0.0335		

APPENDIX Table 4.4 (Continued)
Location: Wardang Island
Fractions analysed: "total acid hydrolysate" and free amino acids
Marginopora vertebralis

Depth (m)	Sample	Location	Geologically expected age	Amino acid D/L ratios				
				ALA	VAL	ALLO /ISO	LEU	ASP
	MAVER 50AT1 (Total)	Loose on tidal flat	120 ka	extremely poor chromatograph trace				0.2192
	MAVER 51AT1 (Total)	Loose on tidal flat	120 ka	0.1497 ±0.0222	0.0301 ±0.0118	0.0446 ±0.0076	0.0344 ±0.0044	0.1725 ±0.0032
	MAVER 52AT1 (Total)	Loose on tidal flat	120 ka	0.0937 ±0.0705	0.0522 ±0.0001	0.0681 ±0.0011	0.0601 ±0.0005	0.2271 ±0.0022
	MAVER 53AT1 (Total)	Reef Rock Glanville Eq.	120 ka	0.3796 ±0.0107	0.1033 ±0.0004	0.1574 ±0.0021	0.1786 ±0.0024	0.3894 ±0.0890
	MAVER 54AT1 (Total)	Reef Rock Glanville Eq.	120 ka	0.6051 ±0.0756	0.1159 ±0.0353	0.1714 ±0.0404	0.0796 ±0.0090	0.3518 ±0.0078

APPENDIX Table 4.4 (Continued)
Location: Wardang Island
Fractions analysed: "total acid hydrolysate" and free amino acids
Marginopora vertebralis

Depth (m)	Sample	Location	Geologically expected age	Amino acid D/L ratios				
				ALA	VAL	ALLO /ISO	LEU	ASP
	MAVER 51AF1 (Free)	Loose on tidal flat	120 ka		extremely low peaks			0.4338
	MAVER 52AF1 (Free)	Loose on tidal flat	120 ka		extremely low peaks			0.5527
	MAVER 53AF1 (Free)	Reef Rock Glanville Eq.	120 ka	extremely low peaks			0.3967	0.6058
	MAVER 54AF1 (Free)	Reef Rock Glanville Eq.	120 ka					0.5345

NB. poor results were obtained for the "free amino acid fraction" due to too much sample being initially taken off for the total acid hydrolysate. Hence a poor recovery.

APPENDIX Table 5.1 Extent of amino acid racemisation in molluscan fossils from the Plio/Pleistocene, Jandakot Member, Yoganup Formation
Location: Jandakot, Perth, Western Australia
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample Code	Species	Amino acid D/L ratios							
				ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
Jandakot Bore	42.0-45.6 m (Total)	KRHY WAT4	Katelysia rhytiphora	1.1250 ±0.0363	0.8817 ±0.0105	1.0723 ±0.0785	0.5339 ±0.0567	0.7858 ±0.0940	0.7483 ±0.0242		
Jandakot Bore	42-45	KRHY WAT5 (Total)	Katelysia rhytiphora	0.9270 ±0.0095	0.7947 ±0.0062	0.9475 ±0.0124	0.6251 ±0.0039 (a)	0.7903 ±0.0724*	0.6444 ±0.0179 (b)		
Jandakot Bore	42-45	KRHY WAT6 (Total)	Katelysia rhytiphora	0.8223	0.7474	0.8701	0.6493 (a)	0.6667*	0.6055 (b)		
Jandakot Bore	42-45	KRHY WAF5 (Free)	Katelysia rhytiphora	0.7786	0.7393	0.8298	0.5325 (a)				
Jandakot Bore	42-45	KRHY WAF6 (Free)	Katelysia rhytiphora	0.6591 ±0.0079	0.4080 ±0.0130	0.3843 ±0.0084	0.2731 ±0.0064		0.4833 ±0.0260		

(a) β-alanine riding under the L-leucine peak producing artificially low D/L values

APPENDIX Table 5.1 (Continued)
Plio/Pleistocene Jandakot Member, Yoganup Formation
Location: Jandakot, Perth, Western Australia
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample Code	Species	Amino acid D/L ratios							
				ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
Jandakot Bore "Paulick's Bore"	38.8-48.8 m	KSCAL WAT50 (Total)	Katelysia scalarina	1.0640 ±0.0130	0.7704 ±0.1182	0.9396 ±0.0702	0.5950 ±0.0404 (a)		1.0166 ±0.0003		
	38.8-41.8 m	KSCAL WAF50 (Free)	Katelysia scalarina	0.8025 ±0.0079	0.2459 ±0.0043	0.1888 ±0.0090	0.2322 ±0.0021		0.6138 ±0.0164		
	38.8-41.8 m	KSCAL WAT5 (Total)	Katelysia scalarina	0.9552 ±0.0165	0.7798 ±0.0137	0.8744 ±0.0150	0.7393 ±0.0035		1.0543 ±0.0062		
	38.8-41.8 m	KSCAL WAF51 (Free)	Katelysia scalarina	1.0797 ±0.0257	0.8378 ±0.0109	1.0099 ±0.0029	0.8177 ±0.0075		0.7953 ±0.0153	0.8698 ±0.0080	0.6843 ±0.0054
	38.8-41.8 m	KRHY WAT52 (Total)	Katelysia rhytiphora	0.9727 ±0.0503	0.8098 ±0.0143	0.9520 ±0.0033	0.8013 ±0.0081		0.8347 ±0.0082		
	38.8-41.8 m	KRHY WAF52 (Free)	Katelysia rhytiphora	1.1575	0.8691	1.0925	0.8419		0.8572	0.8861	0.7838

APPENDIX Table 5.1 (Continued)
Plio/Pleistocene Jandakot Member, Yoganup Formation
Location: Jandakot, Perth, Western Australia
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample Code	Species	Amino acid D/L ratios							
				ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
		KSCAL WAT63 (Total)	Katelysia scalarina		0.8081 ±0.0025	0.8427 ±0.0410	0.6798 ±0.0116*		0.8394 ±0.0775	0.5880	0.7620
		KRHY WAT65 (Total)	Katelysia rhytiphora		0.8417 ±0.0083	0.9436 ±0.0178	0.7922 ±0.0386*		0.8558 ±0.0075	0.9508 ±0.0230	0.7829 ±0.0050
Jandakot Bore	42.0-45.6 m	KRHY WAT11 (Total	Katelysia rhytiphora	0.8895 ±0.0326	0.7693 ±0.0008	0.8000 ±0.0087	0.4474 ±0.0110 (a)	0.7047 ±0.0438	0.6579 ±0.0034 (b)		
		KRHY WAF11 (Free)	Katelysia rhytiphora	0.8989 ±0.0296	0.8313 ±0.0189	0.9281 ±0.0278	0.5870 ±0.0100 (a)	0.7615 ±0.0453	0.7558 ±0.0534 (b)		
Jandakot Bore	42 - 45.6 m	KRHY WAT12 (Total)	Katelysia rhytiphora	0.8991 ±0.0137	0.8314 ±0.0100	0.9558 ±0.0100	0.5443 ± (a)		0.6671 ±0.0010 (b)		
		KRHY WAF12 (Free)	Katelysia rhytiphora	0.8473	0.7993	0.9286	0.5959		0.6467 (b)		

APPENDIX Table 5.1 (Continued)
Plio/Pleistocene Jandakot Member, Yoganup Formation
Location: Jandakot, Perth, Western Australia
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample Code	Species	Amino acid D/L ratios							
				ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
Jandakot Bore, WA	42.0-45.6 m	KRHY WAT13 (Total)	Katelysia rhytiphora	0.9543 ±0.0146	0.9336 ±0.1151	0.9478 ±0.0273	0.5277 ±0.0006	0.7482 ±0.0276	0.6980 ±0.0126		0.6019 ±0.0249 (?)
		KRHY WAF13 (Free)	Katelysia rhytiphora	1.000 ±0.0212	0.9026 ±0.0020	1.0272 ±0.0010	0.7219 ±0.0090	0.7795 ±0.0208	0.7353 ±0.0277		
Jandakot Beds W.A.		KRHY WA38AT1 (Total)	Katelysia rhytiphora	1.000 ±0.0013	0.8180 ±0.0013	0.9017 ±0.0181	0.7522 ±0.0010		0.6726 ±0.0124		
		KRHY WA38AF1	Katelysia rhytiphora	1.000 ±0.0050	0.8517	1.000 ±0.0049	1.000 ±0.0050		1.000 ±0.0050		

APPENDIX Table 5.2 Extent of amino acid racemisation in molluscan fossils from the Plio/Pleistocene Roe Calcarenite, Madura, Western Australia

Location: Madura, Roe Plains, Western Australia

Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample Code	Species	Amino acid D/L ratios						
				ALA	VAL	ALLO /ISO	LEU	PRO	ASP	GLU
Recent excavation	0.5 m	KSCAL WAT31 (Total)	Katelysia scalarina	0.9944 ±0.0079	0.8067 ±0.0021	0.8675 ±0.0039	0.7875 ±0.0048		0.8160 ±0.0143	
		KSCAL WAT31 (Total)	Katelysia scalarina	0.9458					0.8741	
		KSCAL WAT31 (Free)	Katelysia scalarina			0.8448 ±0.0245	1.000 ±0.0100	0.8250 ±0.0118*	0.7614 ±0.0115	
		KSCAL WAT32 (Total)	Katelysia scalarina	1.0000 ±0.0009	0.8060 ±0.0019	0.8569 ±0.0059	0.7739 ±0.0036		0.7250 ±0.0314	
		KSCAL WAF32 (Free)	Katelysia scalarina	1.000 ±0.0403	0.9197 ±0.0054	1.1495 ±0.0552	0.9055 ±0.0026	0.7852*	0.8601 ±0.0418	
		KSCAL WAT33 (Total)	Katelysia scalarina	1.000 ±0.0160	0.8423 ±0.0003	0.9113 ±0.0062	0.7888 ±0.0115		0.9281 ±0.0340	
		KSCAL WAF33 (Free)	Katelysia scalarina	1.000 ±0.0515	0.8979 ±0.0247	1.0177 ±0.0314	0.8337 ±0.0081		0.7703 ±0.0923	

APPENDIX Table 5.2 (Continued)
Location: Madura, Roe Plains, Western Australia
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample Code	Species	Amino acid D/L ratios						
				ALA	VAL	ALLO /ISO	LEU	PRO	ASP	GLU
Roe Plains		KSCAL WAT14 (Total)	Katelysia scalarina	0.9579 ±0.0420	0.8097 ±0.0062	0.9216 ±0.0251	0.6196 ±0.0155		0.6991 ±0.0248	
		KSCAL WAF14 (Free)	Katelysia scalarina	1.000 ±0.0326	0.8451 ±0.0567	0.9793 ±0.0293	0.6457 ±0.0012	0.7799 ±0.0101	0.7764 ±0.0323	0.6179 ±0.0282 (?)
		KRHY WAT7 (Total)	Katelysia rhytiphora	0.9299	0.9666	0.8887 ±0.0563	0.6984 ±0.0555 (a)	0.7670 ±0.1723*	0.6541 ±0.0610 (b)	
		KSCAL WAT8 (Total)	Katelysia scalarina	0.9593 ±0.0452	0.8160 ±0.0011	0.9423 ±0.0026	0.7037 ±0.0153 (a)	0.8279 ±0.0078*	0.7416 ±0.0581 (b)	
		KSCAL WA39AT1 (Total)	Katelysia scalarina	1.0653 ±0.0053	0.7606 ±0.0050	0.7361 ±0.0050	0.9609 ±0.0050	0.7879 ±0.0100	0.8205 ±0.0100	
		KSCAL WA39AF1 (Free)	Katelysia scalarina		0.7114 ±0.0427	0.6442 ±0.0193	0.8090 ±0.0050	0.8258 ±0.0050	0.7422 ±0.0224	

APPENDIX Table 5.3 Extent of amino acid racemisation in Marginopora vertebralis from the Plio/Pleistocene Roe Calcarenite
Location: Roe Plains, Western Australia
Fractions analysed: "total acid hydrolysate"

Core	Depth (m)	Sample Code	Amino acid D/L ratios							
			ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
Roe Calcarenite	>2 m spoil from Madura rubbish dump pits	MAVER WAT3 (Total)	1.000	0.4156 ±0.0190	0.5076 ±0.0757	0.4201 ±0.0129	0.4688*	0.6177 ±0.0291	0.5683 ±0.0046	0.4753 ±0.0054
Roe Calcarenite	>2 m spoil from Madura rubbish dump pits	MAVER WAT2 (Total)	0.7671 ±0.0016	0.4385 ±0.0065	0.4635 ±0.0010	0.4085 ±0.0122		0.4482 ±0.0044		
Roe Calcarenite	>2 m spoil from Madura rubbish dump pits	MAVER WAT1 (Total)		0.4228 ±0.0769	0.5869 ±0.0816	0.3702 ±0.0100	0.6607*	0.7875 ±0.0937		

APPENDIX Table 5.4 Extent of amino acid racemisation in molluscan fossils from the Peppermint Grove Member, Tamala Formation (Penultimate Interglacial)
Location: Peppermint Grove, Western Australia
Fractions analysed: "total acid hydrolysate" and free amino acids

Sample Code	Species	Amino acid D/L ratios							
		ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
KSCAL WAT16 (Total)	Katelysia scalarina	0.8823 ±0.0010	0.5616 ±0.0059	0.6041 ±0.0008	0.5280 ±0.0056		0.5168 ±0.1007		
KSCAL WAF16 (Free)	Katelysia scalarina	0.9623 ±0.0093	0.7279 ±0.0009	0.9374 ±0.0077	0.7184 ±0.0191	0.7992 ±0.0012	0.7549 ±0.0006		
KSCAL WAT17 (Total)	Katelysia scalarina	1.0000 ±0.0886	0.4829 ±0.0090	0.5077 ±0.0094	0.5105 ±0.0008		0.6045 ±0.0169		
KSCAL WAT17 (Free)	Katelysia scalarina	1.0000 ±0.0122	0.7020 ±0.0028	0.8618 ±0.0201	0.7291 ±0.0008	0.7861 ±0.0160*	0.6387 ±0.0029		
KSCAL WAT18 (Total)	Katelysia scalarina					0.8017 ±0.0477*			
KSCAL WAF18 (Free)	Katelysia scalarina	0.9068 ±0.0124	0.7403 ±0.0073	1.1356 ±0.0208	0.8213 ±0.0006		0.4981 ±0.0236		

APPENDIX Table 5.4 (Continued)
Location: Peppermint Grove, Western Australia
Fractions analysed: "total acid hydrolysate" and free amino acids

Sample Code	Species	Amino acid D/L ratios							
		ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
ATRAP WA66AT1 (Total)	Anadara trapezia				0.6327 ±0.0623		0.7033 ±0.0027		
ATRAP WA66AF1 (Free)	Anadara trapezia	0.9897 ±0.0011	0.6925 ±0.0039	0.8866 ±0.0031	0.8685 ±0.0046	0.8700	0.7541 ±0.0039		
KRHY WAT19 (Total)	Katelysia rhytiphora	0.7650 ±0.0742	0.2636 ±0.0063	0.2288 ±0.0177	0.2442 ±0.0172		0.8062 ±0.0062		
KRHY WAF19 (Free)	Katelysia rhytiphora	0.9042	0.7650	1.1422					
KRHY WAT20 (Total)	Katelysia rhytiphora	0.9107 ±0.0204	0.5647 ±0.0060	0.5751 ±0.0200	0.6543 ±0.0050		0.7577 ±0.0986		
KRHY WAF20 (Free)	Katelysia rhytiphora	1.000 ±0.0100	0.6852	1.0215	0.8391 ±0.0785		0.7261		

APPENDIX Table 5.4 (Continued)
Location: Peppermint Grove, Western Australia
Fractions analysed: "total acid hydrolysate" and free amino acids

Sample Code	Species	Amino acid D/L ratios							
		ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
KRHY WAT21 (Total)	Katelysia rhytiphora						0.6811		
KRHY WAF21 (Free)	Katelysia rhytiphora			0.5524	0.6246		0.5747		
KRHY WAT61 (Total)	Katelysia rhytiphora		0.6094	0.6036	0.7178		junk peak at this section		
KRHY WAT62 (Total)	Katelysia rhytiphora		0.5483	0.5260	0.6928		0.6692	0.8928	0.6324
BPAC WAT1 (Total)	Bassina pachyphylla	0.5815	0.5095	0.6377	0.9981		0.7369		
BPAC WAT2 (Total)	Bassina pachyphylla				junk peak interference				

APPENDIX Table 5.4 (Continued)
Location: Peppermint Grove, Western Australia
Fractions analysed: "total acid hydrolysate" and free amino acids

Sample Code	Species	Amino acid D/L ratios							
		ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
BPAC WAT3 (Total)	Bassina pachyphylla	0.9870	0.5369 ±0.0117	0.5719 ±0.0192	0.4036 ±0.0049		0.6964 ±0.0189		
BPAC WAT4 (Total)	Bassina pachyphylla		0.4546 ±0.0073	0.5654 ±0.0176	0.6144 ±0.0102			0.4440 ±0.0100	0.3849 ±0.0106
BPAC WAT5 (Total)	Bassina pachyphylla				Junk peak interference				
BPAC WAT6 (Total)	Bassina pachyphylla				0.5930				
KRHY WAT41 (Total)	Katelysia rhytiphora	0.9666 ±0.0111	0.6083 ±0.0013	0.5511 ±0.0071	0.7067 ±0.0464				
KRHY WAF41 (Free)	Katelysia rhytiphora	1.0498 ±0.0096	0.7217 ±0.0028	0.8706 ±0.0181	0.7386 ±0.0005		0.7510 ±0.0372		

APPENDIX Table 5.4 (Continued)
Location: Peppermint Grove, Western Australia
Fractions analysed: "total acid hydrolysate" and free amino acids

Sample Code	Species	Amino acid D/L ratios							
		ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
KRHY WAT42 (Total)	Katelysia rhytiphora	0.9875 ±0.0149	0.5115 ±0.0051	0.5322 ±0.0074	0.6055 ±0.0027		0.6982 ±0.0167		
KRHY WAF42 (Free)	Katelysia rhytiphora			0.9464	0.8379 ±0.0403		0.7493 ±0.0872	0.6587 ±0.0100	0.7318 ±0.0326
KSCAL WAT43 (Total)	Katelysia scalarina				junk peak contamination				
KSCAL WAF43 (Free)	Katelysia scalarina	1.000	0.7350	0.8870 ±0.0016	0.7557 ±0.0143		0.7010 ±0.1213		
KRHY WAT40 (Total)	Katelysia rhytiphora								
KRHY WAF40 (Free)	Katelysia rhytiphora	1.0331 ±0.0193	0.7662 ±0.0015	1.0083 ±0.0070	0.8923 ±0.0007		0.6314 ±0.0156		

APPENDIX Table 5.4 (Continued)
Location: Peppermint Grove, Western Australia
Fractions analysed: "total acid hydrolysate" and free amino acids

Sample Code	Species	Amino acid D/L ratios							
		ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
ATRAP WAT80 (Total)	Anadara trapezia	1.0092 ±0.0511	0.6788 ±0.1900	0.9960 ±0.0162	0.7605 ±0.0063		0.8149 ±0.0055	0.8800 ±0.0090	0.6886 ±0.0092
ATRAP WAF80 (Free)	Anadara trapezia		0.7582 ±0.0242	0.7198 ±0.0181	0.7260 ±0.0025		0.7862 ±0.0067	0.4008 ±0.0162	0.6063 ±0.0002
ATRAP WAT81 (Total)	Anadara trapezia		0.5129 ±0.0015	0.5921 ±0.0161	0.6728 ±0.0105		0.6801 ±0.0170	0.6106 ±0.0070	0.5836 ±0.0135
ATRAP WAF81 (Free)	Anadara trapezia				0.6996 ±0.0163		0.6816 ±0.0286	0.8714 ±0.0068	0.4626 ±0.0002
ATRAP WAT82 (Total)	Anadara trapezia		0.5674 ±0.0014	0.6505 ±0.0197	0.6845 ±0.0026		0.6900 ±0.0090	0.7372 ±0.0060	0.5875 ±0.0095
ATRAP WAF82 (Free)	Anadara trapezia			0.4495 ±0.0034	0.6626 ±0.0428		0.5727 ±0.0034	0.8557 ±0.0133	0.4598 ±0.0056
KSCAL WAT9 (Total)	Katelysia scalarina	0.8736 ±0.0529	0.5896 ±0.0047	0.6590 ±0.0391	0.6465 ±0.0313		0.6015 ±0.0202		
KSCAL WAF9 (Free)	Katelysia scalarina	1.00	0.7711	0.8905	0.8473		0.8205		

APPENDIX Table 5.5 Extent of amino acid racemisation in molluscan fossils from the Minim Cove Member, Tamala Formation (Last Interglacial)
Location: Western Australia, Minim Cove near Fremantle
Fractions analysed: "total acid hydrolysate" and free amino acids

Depth (m)	Sample Code	Species	Amino acid D/L ratios					
			ALA	VAL	ALLO /ISO	LEU	PRO	ASP
1 m	KSCAL WAT22 (Total)	Katelysia scalarina	0.7686 ±0.0405	0.3743 ±0.0286	0.4595 ±0.0248	0.5070 ±0.0504		0.6457 ±0.2051
1 m	KSCAL WAF22 (Free)	Katelysia scalarina	1.0075 ±0.0663	0.5240 ±0.0127	0.7670 ±0.0202	0.7113 ±0.0273		0.6691 ±0.0282
1 m	KSCAL WAT23 (Total)	Katelysia scalarina	0.8053 ±0.0490	0.3333 ±0.0072	0.4138 ±0.0010	0.4433 ±0.0040		0.6035 ±0.0426
1 m	KSCAL WAF23 (Free)	Katelysia scalarina		0.4686	0.5926 ±0.1188	0.7122 ±0.0105		0.6754 ±0.0313
1 m	KSCAL WAT24 (Total)	Katelysia scalarina	1.000 ±0.0100	0.3085 ±0.0232	0.3345 ±0.0058	0.4745 ±0.0022		0.5705 ±0.0275
1 m	KSCAL WAF24 (Free)	Katelysia scalarina	0.7862 ±0.0413	0.4926 ±0.0468	0.8184 ±0.0212	0.8072 ±0.0254		0.6957
1 m	KRHY WAT1 (Total)	Katelysia rhytiphora	0.8486 ±0.0100	0.3620 ±0.0076	0.4041 ±0.0071	0.4479 ±0.0046		0.6638 ±0.4500

APPENDIX Table 5.5 (Continued)
Location: Western Australia, Minim Cove near Fremantle
Fractions analysed: "total acid hydrolysate" and free amino acids

Depth (m)	Sample Code	Species	Amino acid D/L ratios					
			ALA	VAL	ALLO /ISO	LEU	PRO	ASP
	KSCAL WAT25 (Total)	Katelysia scalarina	1.0000 ±0.0025	0.3598 ±0.0004	0.3700 ±0.0050	0.4850 ±0.0170		0.5201 ±0.0100
	KSCAL WAF25 (Free)	Katelysia scalarina	1.0000	0.6606	0.8674	0.7870		0.6681
	KSCAL WAT26 (Total)	Katelysia scalarina	0.8993 ±0.0090	0.3774 ±0.0050	0.4219 ±0.0005	0.5484 ±0.0050		0.5603 ±0.0050
	KSCAL WAF26 (Free)	Katelysia scalarina	1.0000 ±0.0100	0.5431 ±0.0050	0.7233 ±0.0050	0.7844 ±0.0100		0.7022 ±0.0100
	KSCAL WAT27 (Total)	Katelysia scalarina	0.9347 ±0.0194	0.3481 ±0.0100	0.3730 ±0.0050	0.4926 ±0.0100		0.5667 ±0.0049
	KSCAL WAF27 (Free)	Katelysia scalarina	1.0000 ±0.0100	0.5034 ±0.0070	0.6469 ±0.0004	0.6676 ±0.0176	0.8009 ±0.0189	0.7050 ±0.0120

APPENDIX Table 5.5 (Continued)
Location: Western Australia, Minim Cove near Fremantle
Fractions analysed: "total acid hydrolysate" and free amino acids

Depth (m)	Sample Code	Species	Amino acid D/L ratios ALA	VAL	ALLO /ISO	LEU	PRO	ASP
	KSCAL WAT28 (Total)	Katelysia scalarina	0.7327 ±0.0140	0.2963 ±0.0006	0.3422 ±0.0035	0.4552 ±0.0128		0.6666 ±0.0675
	KSCAL WAF28 (Free)	Katelysia scalarina	0.9097 ±0.0256	0.5142 ±0.0001	0.7213 ±0.0140	0.7985 ±0.0181		0.6183 ±0.0437
	KRHY WAT29 (Total)	Katelysia rhytiphora	0.9957 ±0.1034	0.3235 ±0.0003	0.3494 ±0.0135	0.4946 ±0.0215		0.5707 ±0.0877
	KRHY WAF29 (Free)	Katelysia rhytiphora	1.0000 ±0.0512	0.5170 ±0.0001	0.7492 ±0.0006	0.8168 ±0.0005	0.8660 ±0.0731	0.7399 ±0.0011
	KRHY WAT30 (Total)	Katelysia rhytiphora	1.0000 ±0.0482	0.3351 ±0.0016	0.2980 ±0.0037	0.4472 ±0.0032		0.5616 ±0.0027
	KRHY WAF30 (Free)	Katelysia rhytiphora	1.0000 ±0.0500	0.5000	0.5511	0.7499		0.6880

APPENDIX Table 5.6 Extent of amino acid racemisation in molluscan fossils from the Middle Holocene Herschell Limestone, Rottnest Island
Location: Rottnest Island, Western Australia
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample Code	Species	Env. corrected age	Geologically expected age	Amino acid D/L ratios						
						ALA	VAL	ALLO /ISO	LEU	ASP	PHE	GLU
small quarry exposure	~0.5	KSCAL WAT70 (Total)	Katelysia scalarina	~5000 bp	Middle Holocene	sample lost during derivatisation						
small quarry exposure	~0.5	KSCAL WAT71 (Total)	Katelysia scalarina	~5000 bp	Middle Holocene		0.1151 ±0.0140*	0.1151 ±0.0140*	0.1631 ±0.0471	0.3562 ±0.0014	0.3556 ±0.0048	0.2012 ±0.0110
small quarry exposure	~0.5	KSCAL WAT72 (Total)	Katelysia scalarina	~5000 bp	Middle Holocene	0.4241 ±0.1158	0.0896 ±0.0050	0.1261 ±0.0018	0.1627 ±0.0005	0.4351 ±0.0011	0.3560 ±0.0186	0.1779 ±0.0026
		KSCAL WAF70 (Free)	Katelysia scalarina	~5000 bp	Middle Holocene	0.6985 ±0.0668	0.2054 ±0.0547*	0.3272 ±0.0468	0.4169 ±0.0037	0.7496 ±0.0107	0.6676	0.3153
		KSCAL WAF71 (Free)	Katelysia scalarina	~5000 bp	Middle Holocene				0.4744 ±0.0216	0.5737 ±0.0040	0.6273 ±0.0007	0.3088 ±0.0039
		KSCAL WAF72 (Free)	Katelysia scalarina	~5000 bp	Middle Holocene		0.2458	0.3564	0.4734	0.5363	0.6508	0.2869

APPENDIX Table 5.6 (Continued)
Location: Rottnest Island, Western Australia
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample Code	Species	Env. corrected age	Geologically expected age	Amino acid D/L ratios ALA	VAL	ALLO /ISO	LEU	ASP	PHE	GLU
Herschell Quarry	1 m	KRHY WAT73 (Total)	Katelysia rhytiphora	~5 ka see dates in Playford & Leech (1977)					0.1188 ±0.0165	0.3538 ±0.0210	0.4950	0.1682
Herschell Quarry	1 m	KRHY WAF73 (Free)	Katelysia rhytiphora	~5 ka			0.2620	0.2421	0.3220	0.5255	0.2645	0.2593
Herschell Quarry	1 m	KRHY WAT74 (Total)	Katelysia rhytiphora	~5 ka			0.0818 ±0.0147	0.1065 ±0.0157	0.1344 ±0.0067	0.3193 ±0.0044		
Herschell Quarry	1 m	KRHY WAF74 (Free)	Katelysia rhytiphora	~5 ka			0.2920	0.1669	0.1932	0.5158	0.2089	0.2622
Herschell Quarry	1 m	KRHY WAT75 (Total)	Katelysia rhytiphora	~5 ka			0.0560 ±0.0040	0.1131 ±0.0185	0.1143 ±0.0015	0.3434 ±0.0253		
Herschell Quarry	1 m	KRHY WAF75 (Free)	Katelysia rhytiphora	~5 ka			0.2125 ±0.0575	0.1829 ±0.0060	0.2398 ±0.0092	0.4157 ±0.0063	0.6380 ±0.0228	0.2363 ±0.0016
Herschell Quarry	1 m	KRHY WAT76 (Total)	Katelysia rhytiphora	~5 ka			0.2222*	0.2000*	0.2083	0.4295	0.2462	0.1753
Herschell Quarry	1 m	KRHY WAF76 (Free)	Katelysia rhytiphora	~5 ka					0.3023	0.5369	0.6197	0.2777

APPENDIX Table 6.1 Extent of amino acid racemisation in Anadara (Tegillarca) granosa, Princess Charlotte Bay, Queensland

Location: Princess Charlotte Bay, Queensland

Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample	Env. corrected C-14 age	Geologically expected age	Amino acid D/L ratios							
					ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
PCB#1	3.58 (4.61)	ATRAP 50A1T1 (Total)	6530± 80 bp	6.5 ka	0.5252 ±0.0247	0.1713 ±0.0058	0.2245 ±0.0107	0.2870 ±0.0049		0.5195 ±0.0114		
PCB#1	1.75 (2.25)	ATRAP 51A1T1 (Total)	0.90-1.0 m 2410±70 bp	~3 ka	0.4410 ±0.0067	0.1314 ±0.0011	0.1900 ±0.0050	0.2519 ±0.0007		0.4778 ±0.0070		
PCB#13	Top	ATRAP 52A±T1 (Total)		~modern	0.4355 ±0.0018	0.1268 ±0.0063	0.2106 ±0.0117	0.2510 ±0.0046		0.4796 ±0.0013		
PCB#1	1.75	ATRAP 51A1F1 (Free)		~3 ka	0.6290 ±0.0684	0.2232 ±0.0063	0.3733 ±0.0504	0.4703 ±0.0110	0.7550 ±0.0234*	0.6012 ±0.0422		
PCB#13	Top	ATRAP 52A1F1 (Free)			0.9180	0.2216	0.3103	0.5403 ±0.0086	0.7712 ±0.0205	0.4069 ±0.0192		
PCB#7	0.17	ATRAP 58AT1 (Total)		~2000 BP	0.2931 ±0.0079	0.0699 ±0.0044	0.0911 ±0.0061	0.1543 ±0.0028		0.3303 ±0.0029		
		ATRAP 58AF1 (Free)			0.5316 ±0.0026	0.1458 ±0.0050*	0.1667 ±0.0050*	0.3272 ±0.0043		0.5066 ±0.0025		

APPENDIX Table 6.1 (Continued)
Location: Princess Charlotte Bay, Queensland
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample	Env. corrected C-14 age	Geologically expected age	Amino acid D/L ratios							
					ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
PCB#7	0.24-0.28	ATRAP 56A1T1 (Total)		Holocene <6 ka ~2000 BP	0.2914 ±0.0094	0.0960 ±0.0060	0.1184 ±0.0003	0.1638 ±0.0002		0.4011 ±0.0078		
		ATRAP 56A1F1 (Free)			Peak heights too low			0.3277 ±0.0444	0.5439 ±0.1737*	0.5734 ±0.0023		
PCB#13	1.66-1.70	ATRAP 57A1T1 (Total)		~6000 BP	0.5351 ±0.0021	0.1960 ±0.0056	0.3219 ±0.0298	0.3759 ±0.0053		0.5517 ±0.0372		
		ATRAP 57A1F1 (Free)			Peak heights too low			0.6019 ±0.0247	0.8310 ±0.0034	0.7302 ±0.0089		
PCB#1	1.75	AGRAN AT4 (Total)	2410±70 BP	>2410±70 bp C-14 at 0.90-1.00 m	0.4820 ±0.0023	0.1498 ±0.0002	0.1953 ±0.0002	0.2722 ±0.0023		0.5130 ±0.0063		
		AGRAN AF4 (Free)			0.5482 ±0.0062	0.2450 ±0.0010	0.3778 ±0.0041	0.4775 ±0.0045		0.5912 ±0.0073		
PCB#7	0.17	AGRAN AT5 (Total)		<3000 BP (~2000 BP?)	0.3638 ±0.0134	0.0923 ±0.0013	0.1154 ±0.0005	0.1866 ±0.0023		0.4067 ±0.0095		
		AGRAN AF5 (Free)			0.5786 ±0.0233	0.1642 ±0.0020	0.2516 ±0.0050	0.3949 ±0.0069		0.5155 ±0.0050		

APPENDIX Table 6.1 (Continued)
Location: Princess Charlotte Bay, Queensland
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample	Env. corrected C-14 age	Geologically expected age	Amino acid D/L ratios							
					ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
PCB#13	1.66-1.70	AGRAN AT6 (Total)		~6000 BP	0.5645 ±0.0226	0.1955 ±0.0075	0.2531 ±0.0095	0.3780 ±0.0189		0.4743 ±0.0275		
		AGRAN AF6 (Free)			0.7023 ±0.0480	0.2910 ±0.0019	0.4792 ±0.0119	0.6148 ±0.0061		0.5844 ±0.0013		
PCB#7	0.34	AGRAN AT1 (Total)			0.5153 ±0.0423	0.0849 ±0.0042	0.1032 ±0.0014	0.1512 ±0.0006		0.4037 ±0.0045		
		AGRAN AF1 (Free)			0.5691	0.1830	0.2824	0.4075 ±0.0052	0.7778*	0.5369 ±0.0401		
PCB#13	Top of Core	AGRAN AT2 (Total)			0.7716 ±0.1679	0.1385 ±0.0274	0.1353 ±0.0301	0.2715 ±0.0050		0.4874 ±0.0050		
		AGRAN AF2 (Free)							0.7941 ±0.0416*	0.6129 ±0.0164		

APPENDIX Table 6.1 (Continued)
Location: Princess Charlotte Bay, Queensland
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample	Env. corrected C-14 age	Geologically expected age	Amino acid D/L ratios							
					ALA	VAL	ALLO /ISO	LEU	PRO	ASP	PHE	GLU
PCB#13	1.66-1.70	AGRAN AT3 (Total)			0.8900	0.1696 ±0.0129	0.1999 ±0.0154	0.3629 ±0.0042		0.4982 ±0.0106		
		AGRAN AF3 (Free)			0.8468 ±0.0050	0.2804 ±0.0142	0.4743 ±0.0047	0.5795 ±0.0050	0.7983 ±0.0100*	0.5714 ±0.0050		
PCB#13	~2.40 m in Cliff section CH-13C	AGRAN AT8 (Total)	3640±80 BP	3 ka	0.5827 ±0.0149	0.1401 ±0.0017	0.1832 ±0.0020	0.2961 ±0.0001		0.5150 ±0.0028		
		AGRAN AF8 (Free)	3640±80 BP	3 ka			0.2215 ±0.0325	0.5350 ±0.0021	0.7784 ±0.0208	0.6539 ±0.0037		
PCB#13	CH-13B	AGRAN AT9 (Total)	3860±80 BP	3 ka	0.5607 ±0.0336	0.1375 ±0.0023	0.1682 ±0.0050	0.2712 ±0.0050		0.5044 ±0.0050		
		AGRAN AF9 (Free)	3860±80 BP	3 ka		0.2232	0.2861	0.5506	0.7877	0.6682		
PCB#13	1.15 m in Core	AGRAN AT10 (Total)			0.5631 ±0.0253	0.1813 ±0.0183	0.2094 ±0.0041	0.3304 ±0.0001		0.4530 ±0.0050	0.2048	0.2334
		AGRAN AF10 (Free)				0.3197 ±0.0058	0.2620 ±0.0342	0.5010 ±0.0005		0.4564 ±0.0035	0.2261	0.1974

APPENDIX Table 6.2 Holocene and modern Anadara trapezia, East Coast of Australia
Location: East Coast of Australia (Transect)
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample Code	Species	Conventional C-14 age	Geologically expected age	Amino acid D/L ratios						
						ALA	VAL	ALLO /ISO	LEU	ASP	PHE	GLU
Quarantine Bay NSW	Beach face	ATRAP 60AT1 (Total)	Anadara trapezia		Modern	0.0752 ±0.0189	0.0178 ±0.0085	0.0203 ±0.0017	0.0327 ±0.0011	0.1143	0.0302 ±0.0103	0.0798 ±0.0129
		ATRAP 60AF1 (Free)			Modern			0.2973 ±0.1040 (?)	0.1340 ±0.0115 (?)	0.1265 ±0.0052		
Wooli, northern NSW	4 m below AHD	ATRAP 61AT1 (Total)	Anadara trapezia		Holocene <6 kaBP	0.4216 ±0.0080	0.1306 ±0.0030	0.1645 ±0.0010	0.2452 ±0.0003	0.4203 ±0.0212	0.0728 ±0.0113	0.2219 ±0.0167
		ATRAP 61AF1 (Free)				0.6690 ±0.0547	0.1720 ±0.0266	0.3017 ±0.0113	0.4577 ±0.0004	0.5314 ±0.0104	0.2330 ±0.0183	0.2152 ±0.0218
Wooli, northern NSW	5 m below AHD	ATRAP 62AT1 (Total)	Anadara trapezia		Holocene <6 kaBP	0.5006 ±0.0233	0.1279 ±0.0020	0.1514 ±0.0003	0.2536 ±0.0097	0.3867 ±0.0103	0.0372 ±0.0037	0.2439 ±0.0691
		ATRAP 62AF1 (Free)				0.5331 ±0.0125	0.2064 ±0.0101	0.2799 ±0.0077	0.4527 ±0.0218	0.4773 ±0.0031	0.1059 ±0.0031	0.1191

APPENDIX Table 6.2 (Continued)
Location: East Coast of Australia (Transect)
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample Code	Species	Conventional C-14 age	Geologically expected age	Amino acid D/L ratios						
						ALA	VAL	ALLO /ISO	LEU	ASP	PHE	GLU
Byron Bay NSW	Beach face	ATRAP 63AT1 (Total)	Anadara trapezia		Modern	0.4995 ±0.0644	0.1903 ±0.0022	0.2141 ±0.0060	0.3258 ±0.0031	0.4197 ±0.0472	0.0438	0.2451
		ATRAP 63AF1 (Free)	Anadara trapezia			0.7387 ±0.0192	0.2987 ±0.0066	0.3926 ±0.0044	0.5668 ±0.0094	0.5853 ±0.0365	0.1915 ±0.0168	0.2657 ±0.0301
Keppel Sands, Queensland		ATRAP 64AT1 (Total)	Anadara trapezia		1000-3000 yrs BP			0.1036 ±0.0051*	0.1601 ±0.0034	0.3272 ±0.0204	0.1330 ±0.0058	0.1910 ±0.0112
		ATRAP 64AF1 (Free)	Anadara trapezia					0.1813	0.3239 ±0.0075	0.5219 ±0.0158	0.8128 ±0.0620	0.2647 ±0.0130
Deception Bay, Queensland		ATRAP 65AT1 (Total)	Anadara trapezia		ca. 5000 yr BP	0.3601 ±0.0100	0.0667 ±0.0004	0.0689 ±0.0007	0.1154 ±0.0002	0.3716 ±0.0097	0.0263 ±0.0081	0.1279 ±0.0107
		ATRAP 65AF1 (Free)	Anadara trapezia			0.4876 ±0.0034	0.1417 ±0.0013	0.1969 ±0.0011	0.3362 ±0.0015	0.4766 ±0.0336	0.2012 ±0.0166	0.1760 ±0.0193
Torquay, Hervey Bay	2 m	ATRAP QLT50 (326142)	Anadara trapezia	730±60 bp	<2500 BP	0.2004 ±0.0499	0.0412 ±0.0005	0.0448 ±0.0267	0.0739 ±0.0002	0.3336 ±0.0048		

APPENDIX Table 6.2 (Continued)
Location: East Coast of Australia (Transect)
Fractions analysed: "total acid hydrolysate" and free amino acids

Core	Depth (m)	Sample Code	Species	Conventional C-14 age	Geologically expected age	Amino acid D/L ratios						
						ALA	VAL	ALLO /ISO	LEU	ASP	PHE	GLU
Moore Pk Hervey Bay	2.8-2.9 m	ATRAP QLT51 (107032)	Anadara trapezia	5620±90 bp	<1000 BP	0.5206 ±0.0160	0.1418 ±0.0126	0.1725 ±0.0018	0.2328 ±0.0020	0.4387 ±0.0050		
Woodgate, Hervey Bay	2.8-3.2 m	ATRAP QLT52 (216013)	Anadara trapezia	1010±50 bp	<1000 BP	0.3338 ±0.0093	0.0451 ±0.0050*	0.0304 ±0.0010	0.0595 ±0.0062	0.2524 ±0.0050	0.0977 ±0.0022	0.0826 ±0.0010
Woodgate, Hervey Bay	0.8-1.2 m	ATRAP QLT53 (201013)	Anadara trapezia	1050±70 bp	<1500 BP	0.1611 ±0.0015	0.0714 ±0.0050*	0.0749 ±0.0227*	0.0707 ±0.0009	0.2307 ±0.0180	0.0997 ±0.0490	0.0736 ±0.0005
Moore Pk Hervey Bay	1.7 m	ATRAP QLT54 (115012)	Anadara trapezia	750±50 bp	<1000 BP	0.3504 ±0.0050*	0.0381 ±0.0009*	0.0285 ±0.0049	0.0501 ±0.0009	0.2432 ±0.0010	0.1091 ±0.0034	0.0897 ±0.0051

APPENDIX Table 6.3 Extent of amino acid racemisation in Holocene and modern Marginopora vertebralis Great Barrier Reef, Queensland.
Location: Great Barrier Reef, Queensland.
Fractions analysed: "total acid hydrolysate"

Core	Depth (m)	Sample Code	Geologically expected age	Amino acid D/L ratios						
				ALA	VAL	ALLO /ISO	LEU	PRO	ASP	GLU
GBRVC#12 Cleveland Bay#2	0.26-0.36	MAVER 40AT1 (Total)	<6 ka	0.2321 ±0.0253*	0.0967 ±0.0120*	0.0893 ±0.0084*	0.0862 ±0.0196	0.2409 ±0.0634	0.3281 ±0.0041	
		MAVER 40AF1 (Free)		Peak heights too low : unresolvable					0.2442	
GBRVC#7 PALMS#3	0.05	MAVER 41AT1 (Total)	<6 ka	0.1771 ±0.0147*	0.0310 ±0.0066*	0.0470 ±0.0093*	0.0607 ±0.0093	0.1650 ±0.0133	0.2417 ±0.0052	
		MAVER 41AF1 (Free)		Peak heights too low : unresolvable						
GBRVC#8 PALMS#4	1.00	MAVER 42AT1 (Total)	<6 ka	0.2606 ±0.0086*	0.0657 ±0.0081	0.0832 ±0.0109*	0.0750 ±0.0058	0.2168 ±0.0426*	0.3284 ±0.0077	
		MAVER 42AF1 (Free)		Peak heights too low : unresolvable						

APPENDIX Table 6.3 (Continued)
Location: Great Barrier Reef, Queensland.
Fractions analysed: "total acid hydrolysate"

Core	Depth (m)	Sample Code	Geologically expected age	Amino acid D/L ratios						
				ALA	VAL	ALLO /ISO	LEU	PRO	ASP	GLU
Pipon Reef, Great Barrier Queensland		MAVER 01C1 (Total)		0.0609		0.0684	0.0957 ±0.0162	0.1261	0.0627	
		MAVER 01C2 (Total)		0.0705 ±0.0187		0.0368 ±0.0205	0.0514 ±0.0095	0.1261	0.0627	
		MAVER 01C3 (Total)		0.0542 ±0.0074	0.0402 ±0.0289	0.0285 ±0.0008	0.0627 ±0.0602	0.0849	0.1150 ±0.0896	
GBRVC#12 Cleveland Bay	0.26-0.36	MAVER 40BT1 replicate to MAVER 40AT1	<6 ka			0.1026 ±0.0165*	0.1091 ±0.0054*	0.2121 ±0.0279*	0.3473 ±0.0053	
GBRVC#7 Palms#3	0.05	MAVER 41BT1 replicate to MAVER 41AT1	modern	0.2644 ±0.0118*	0.0421 ±0.0006*	0.0358 ±0.0018*	0.0323 ±0.0178	0.1241 ±0.0058*	0.2624 ±0.0005	

APPENDIX Table 6.3 (Continued)
Location: Great Barrier Reef, Queensland.
Fractions analysed: "total acid hydrolysate"

Core	Depth (m)	Sample Code	Geologically expected age	Amino acid D/L ratios ALA	VAL	ALLO /ISO	LEU	PRO	ASP	GLU
GBRVC#8 Palms#4	1.00	MAVER 42BT1 replicate to MAVER 42AT1	<6 ka		0.0909	0.0625	0.0694 ±0.0006	0.2212 ±0.0408*	0.3566 ±0.0045	
GBRVC#8	1.42	MAVER 43AT1		0.2500*	0.0588*	0.0455*	0.0714 ±0.0010*	0.2353 ±0.0832*	0.3418 ±0.0104	
GBRVC#8	2.54	MAVER 44AT1		0.3635 ±0.0517*	0.0935 ±0.0092*	0.0930 ±0.0085	0.0894 ±0.0145*	0.2349 ±0.0449*	0.3955 ±0.0328	
GBRVC#8	2.96	MAVER 45AT1			0.1250*	0.1000*	0.1418*	0.3000*	0.3421 ±0.0051	
Fantome Island GBR		MARG QT80 (Total)	modern	0.1377 ±0.0986		0.0197 ±0.0094	0.0187 ±0.0017		0.0808	0.0559
Fantome Island GBR		MARG AT81 (Total)	modern	0.1509	0.0175	0.0104	0.0370			