DEPARTMENT OF MINES AND ENERGY SOUTH AUSTRALIA

REPT.BK.NO. 87/115 AMINOSTRATIGRAPHY OF THE LAST INTERGLACIAL IN SOUTHERN AUSTRALIA

GEOLOGICAL SURVEY

bv

C.V. Murray-Wallace R.W.L. Kimber A.P. BELPERIO (REGIONAL GEOLOGY)

and

V.A. Gostin

SEPTEMBER, 1984

DME.142/83

Proposed publication in SEARCH



CONTENTS	PAGE
AMINOSTRATIGRAPHY OF THE LAST INTERGLACIAL IN SOUTHERN AUSTRALIA	2
LARGS	4
MINIM COVE	4
DRY CREEK	5
PORT WAKEFIELD	6
DENIAL BAY	6
RESULTS AND DISCUSSION	6
ACKNOWLEDGEMENTS	9
REFERENCES	10
TABLE 1: Extent of amino acid racemisation in molluscan fossils of Last Interglacial age from southern Australia.	13
FIGURES	
Fig. No. Title	Plan No.
l Location of sample sites referred to in text. Open circles are Holocene samples, solid circles are Last Interglacial samples and triangles are Penultimate Interglacial samples.	S19480

Aminostratigraphy of the Last Interglacial in Southern Australia

C.V. Murray-Wallace^{1,2}, R.W.L. Kimber¹, A.P. Belperio³ and V.A. Gostin⁴

The application of amino acid racemisation reactions is explored for regional chronostratigraphic correlation of Last Interglacial marginal marine sediments in southern Australia. The extent of racemisation evident for a range of amino acids in several molluscan species which have experienced similar 'Effective Quaternary Temperature' histories (E.Q.T.), convincingly demonstrates the time equivalence of these sediments.

Time-dependent protein diagenetic reactions, in particular amino acid racemisation and epimerisation, have been extensively applied in Quaternary studies in the Northern Hemisphere (Williams and Smith, 1977; Schroeder and Bada, 1976; Wehmiller, 1982, 1984a,b; Rutter, 1985). Few studies however, have applied amino acid racemisation reactions in the dating of Australian Quaternary sediments (Kimber and Milnes, 1984; Belperio et al., 1984; Murray-Wallace, 1987; Murray-Wallace and Kimber, 1987). In this paper, we report the first comprehensive results from a range of coastal sections in southern Australia. These data will provide a valuable benchmark for subsequent amino acid racemisation studies as well as a useful adjunct to other geochronological investigations.

^{1.} CSIRO Division of Soils, Private Bag No. 2, Glen Osmond, South Australia, 5064.

^{2.} The N.W.G. Macintosh Centre for Quaternary Dating, The University of Sydney, N.S.W., 2006.

^{3.} South Australian Department of Mines and Energy, P.O. Box 151, Eastwood, South Australia, 5063.

Department of Geology and Geophysics,
 University of Adelaide,
 P.O. Box 498, Adelaide, South Australia, 5001.

Several species of molluscan fossils were analysed to determine the extent of racemisation of a range of amino acids. Results reported herein however, are for the mollusc species Anadara trapezia (Deshayes), Katelysia scalarina (Lamarck) and K. rhytiphora (Lamy). These species are considered particularly suitable for amino acid racemisation analyses because of their stout shells, which reduce the chances of contamination by non-indigenous amino acids. The molluscs were well buried, generally at depths greater than 1m.

Where possible, articulated specimens were selected for dating. To avoid both intrashell amino acid D/L ratio variation (Brigham, 1983; Murray-Wallace and Kimber, 1987) and analysing the same individual twice, only the hinges of left-hand valves were analysed. To reliably characterise the age of the deposits, numerous specimens were analysed from a single deposit (Table 1). Analyses were made for the 'total acid hydrolysate', a complex mixture of high molecular weight polypeptides, peptides and free amino acids.

In this paper results are presented for several Last Interglacial deposits from a range of coastal settings in southern Australia (Figure 1). These include the Minim Cove Member of the Tamala Formation in the Swan Estuary, Western Australia; the Glanville Formation neostratotype at Dry Creek north of Adelaide and equivalents at Denial Bay and Port Wakefield in South Australia; and samples from a well defined terrace at Largs in the lower Hunter Valley, New South Wales. With the exception of the Largs site, the age of these deposits has been established using other dating techniques supplemented by litho- and biostratigraphic correlations. The marine sediments at Largs have no formal lithostratigraphic name.

The analytical procedures undertaken follow those of Kimber and Griffin (1987) and Murray-Wallace (1987). The extent of racemisation (epimerisation) for a range of amino acids is presented in Table 1. Amino acid data were calibrated both internally and externally. Internal calibration involved comparison of the extent of racemisation in the

The marine sediments display horizontal lamination emphasised by case hardening, and are capped by an aeolian calcarenite. Numerous solution channels, pipes and rhizoliths truncate the bedding. The marine sediment is dominantly quartz sand and contains a diverse molluscan fossil assemblage.

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 them. This age was corroborated by Hewgill et al., (1983) who, using electron spin resonance dating correlated the strata at Minim Cove with uranium-series calibrated deposits on Rottnest Island (Veeh, 1966; Veeh et al., 1979; Szabo, 1979).

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. Mollusc species analysed included Katelysia rhytiphora and K. scalarina. The shells analysed were approximately 3m above MSL, and buried beneath 2m 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 a number of Last Interglacial marginal marine settings in southern Australia.

Dry Creek

Marine carbonate-rich sediments north of Adelaide containing abundant molluscan fossils and generally capped by an indurated carbonate crust were referred to by Firman (1969) as the Glanville Formation. These sediments contain the sub-fossils Anadara trapezia, Marginopora vertebralis and Pinctada carchariarum (Cann, 1978; Ludbrook, 1984; Belperio and Murray-Wallace, 1984). The Glanville Formation and equivalents occur extensively around the South Australian coastline and have been the subject of numerous studies (Cann, 1978; Belperio et al., 1983, 1984, 1985; Murray-Wallace,

ascribed Last Interglacial specimens with younger and older fossils. (Holocene and Penultimate Interglacial specimens). External calibration involved the comparison of amino acid racemisation data with independent dating techniques. To provide a basis for age calibration, modern molluscs as well as radiocarbon-calibrated Holocene and Penultimate Interglacial specimens were compared with the results for the Last Interglacial fossils. To establish the integrity of the analytical procedures undertaken in the CSIRO Soils laboratory, molluscs from an International Interlaboratory comparison (Wehmiller, 1984b) were analysed and the data were in general accord with the published results (Wehmiller, 1984b; Murray-Wallace, 1987). Mean Annual Air Temperatures (M.A.T.) for the sample localities are indicated in Table 1. All the Last Interglacial specimens were obtained within the latitudinal range of 31.56°S to 34.55°S. Mean Annual Temperatures of the sample sites varied within a range of approximately 2°C.

Largs

The earliest reference to the Largs site was by David and Etheridge (1890) who referred to the shell beds as raised a beach. The deposit contains a mixed assemblage of molluscan fossils with species from rocky coastlines, littoral and estuarine environments (Iredale, 1957). Radiocarbon dating indicates these sediments are older than 37,000 yrs BP.

Articulated and disarticulated, well-preserved specimens of Anadara trapezia were obtained from a small pit excavated within a well-defined terrace. The molluscs were buried 0.64m below a well-developed Holocene red-brown earth. This site is situated some 30km inland from the Pacific Ocean.

Minim Cove

Emergent fossiliferous shallow-marine sediments crop out at Minim Cove, Mosman Park, on the northern bank of the Swan Estuary near Fremantle.

1987; Murray-Wallace and Kimber, 1987). A Last Interglacial age has been assigned to the Glanville Formation based on uranium-series dating (Schwebel, 1978) and thermoluminescence and amino acid racemisation (Belperio et al., 1984).

Specimens of <u>Anadara trapezia</u> were collected from the neostratotype of the Glanville Formation from Dry Creek. Well-preserved, whole disarticulated specimens were obtained 3m below the ground surface. Only the hinge region of the bivalves were analysed.

Port Wakefield

Numerous specimens of Anadara trapezia and Katelysia rhytiphora were obtained from a depth of 3m within a recent quarry exposure of well-bedded calcreted sandy gravels at Port Wakefield. The gravels display well-defined foresets of seaward dipping tabular cross stratification. A strongly indurated massive calcrete mantles the gravels and has a variable thickness of 0.5-1m. The calcrete is capped by a thin (<0.2m) veneer of red brown earth. The gravels represent a Last Interglacial beach-foreshore accretion unit and are equivalents of the Glanville Formation of the Adelaide region. Well-preserved articulated and disarticulated bivalves were collected for dating.

Denial Bay

Numerous specimens of Anadara trapezia were obtained from an undercut cliff face, below a well-indurated and laterally persistent nodular calcrete profile. The depth of burial was 1m. The host sediments are represented by bioclastic carbonates and correlate lithologically and palaeontologically with other occurrences of the Glanville Formation along the South Australian coastline.

Results and Discussion

The relative extent of racemisation for different amino acids in the samples studied is in accord with that for molluscan fossils of equivalent

age, studied from the northern hemisphere, as reported by Lajoie et al., (1980). Coefficients of variation for the amino acid data generally did not exceed 12%. The error terms are for one standard deviation and encompass analytical uncertainties and intershell amino acid D/L ratio variation for a given sample locality (Murray-Wallace, 1987). However, a larger margin of error may be expected with variation between sample sites. This results from environmental characteristics unique to a particular site and includes differences in the 'Effective Quaternary Temperature' history (E.Q.T.), moisture regime and pH. The Effective Quaternary Temperature history refers to the integrated kinetic effect of all temperatures to which a fossil has been exposed (Wehmiller, 1982). In addition, reworking and contamination may potentially introduce a larger margin of error.

A Late Pleistocene age is also clearly evident for the shells from Minim Cove, Denial Bay, Port Wakefield, Dry Creek and Largs, based on the extent of amino acid racemisation and comparison with the calibration samples. The greatest concordance of results between sample sites is evident for valine, with a coefficient of variation (C.V.) of 3%. This observation suggests that valine should be used more extensively in aminostratigraphic studies, particularly those requiring high precision with age resolution. Leucine and isoleucine provided less concordant results with C.V.'s of 6 and 9% respectively. Aspartic acid and glutamic acid displayed greater variation with C.V.'s of 10 and 13% respectively. The extent of leucine racemisation in the Last Interglacial specimens analysed in this study agree well with results for Anadara trapezia obtained by Belperio et al., (1984) in a chronological study of Quaternary marine sediments of northern Spencer Gulf.

The data presented herein clearly demonstrates a concordance in the extent of racemisation for the amino acids determined in mollusc samples from widely separated sites, independently assessed as Last Interglacial in age. Data for modern, Holocene and "Penultimate Interglacial" sediments effectively bracket the aforementioned amino acid results (Table 1). The

concordance of the amino acid data are therefore interpreted to represent a common age given the assumption that the integrated effect of all other parameters that may influence racemisation between sample sites were equable during their diagenetic history.

In part, the validity of this assumption can be assessed in the light of previous investigations (Schroeder and Bada, 1976; Williams and Smith, 1977; Lajoie et al., 1980; Wehmiller, 1984a), which indicate that the calcium carbonate matrix of shells acts as an effective chemical buffer, and in addition, retains indigenous amino acids for protracted periods. Furthermore, the pH range typically experienced in the environments studied has been demonstrated not to influence racemisation (Bada, 1985).

Although generic differences on the extent of racemisation have previously been observed in <u>Katelysia</u> spp. and <u>Anadara</u> spp., particularly for aspartic acid (Murray-Wallace and Kimber, 1987), the degree of statistical variation introduced by this factor was not sufficiently large to preclude stratigraphic correlation using these fossils.

A more serious question concerns the influence of repeated, alternate wetting and drying of fossils <u>in situ</u>, and the potential for loss of indigenous amino acids by leaching. This has been noted where fossils cropout in intertidal settings and experience diurnal changes in moisture regime (Murray-Wallace, 1987). Fossils that are permanently below the water table however, surprisingly appear unaffected by this. All the sample sites studied were not subject to alternate wetting and drying in the manner described above.

Thom et al., (1981) briefly discussed the Largs site as part of a wider study of the Late Quaternary geomorphic evolution of the Port Stephens - Myall Lakes area in central New South Wales. They noted the difficulty of delineating an age for the shell beds in view of the absence of corals suitable for uranium series disequilibrium dating. Radiocarbon dating however, on an articulated Anadara trapezia gave an age of >37,000

yrs BP, suggesting the molluscs may be of Last Interglacial age. The extent of amino acid racemisation evident in Anadara trapezia obtained from the Largs site clearly points to a Last Interglacial age for these strata.

Several palaeoclimatic inferences can also be made about the Late Quaternary in southern Australia from the amino acid data in the light of the assumptions previously discussed. All the Last Interglacial sample sites currently experience M.A.T.'s within the temperature range of 16.9 - 18.5°C. In view of the similarity of M.A.T.'s between sample sites, and the general concordance of amino acid D/L ratios for the Last Interglacial molluscan fossils, similar temperature differences between sample sites are likely to have been experienced during their diagenetic temperature history. Furthermore, the different sample sites are likely to have experienced similar Effective Quaternary Temperature histories since the Last Interglacial. In this context amino acid racemisation may provide a valuable adjunct to oxygen isotope studies of Quaternary palaeoclimatology.

Acknowledgements

A significant portion of this research formed part of a Ph.D. project by C.V. Murray-Wallace, undertaken jointly at the University of Adelaide and the CSIRO Division of Soils, South Australia under the supervision of Drs V.A. Gostin and R.W.L. Kimber. Mr G.W. Kendrick, Western Australian Museum kindly made reference samples available for dating, and assisted with fieldwork in the early stages of the project. Prof. B.G. Thom directed C.V. Murray-Wallace's attention to the Largs site. We thank Dr A.R. Milnes for critically reading the manuscript. A.P.B. publishes with permission of the Director General, South Australian Department of Mines and Energy.

References

- Bada, J.L. (1985) Racemization of Amino Acids. <u>In</u>, G.C. Barrett (ed.),

 <u>Chemistry and Biochemistry of Amino Acids</u> pp.399-414. Chapman and
 Hall.
- Belperio, A.P., Hails, J.R. and Gostin, V.A. (1983) A Review of Holocene Sea Levels in South Australia. <u>In</u>, D. Hopley (ed.)

 <u>Australian Sea Levels in the Last 15,000 Years: A Review</u>, Geography
 Department, James Cook Univ. Oc.Pap.3, pp.37-47.
- Belperio, A.P., Smith, B.W., Polach, H.A., Nittrouer, C.A., DeMaster, D.J., Prescott, J.R., Hails, J.R. and Gostin, V.A. (1984) Chronological Studies of the Quaternary Marine Sediments of Northern Spencer Gulf, South Australia, Mar.Geol. 61:265-296.
- Belperio, A.P. and Murray-Wallace, C.V. (1984) Comment: Wardang Island a refuge for Marginopora vertebralis? Trans.Roy.Soc.S.Aust. 108:227-228.
- Belperio, A.P. (1985) Quaternary geology of the Sandy Point and Outer

 Harbour St Kilda areas, Gulf St Vincent.

 Quart.Geol.Notes, Geol.Surv.S.Aust. 96:2-6.
- Brigham, J.K. (1983) Intrashell variations in amino acid concentrations and isoleucine epimerization ratios in fossil <u>Hiatella arctica</u>.

 <u>Geology</u> 11:509-513.
- Cann, J.H. (1978) An exposed reference section for the Glanville Formation. Quart.Geol.Notes, Geol.Surv.S.Aust. 65:2-4.
- David, T.W.E. and Etheridge, R. (1890) The Raised-beaches of the Hunter River Delta. Rec.Geol.Surv. N.S.W. 2(2):37-52.
- Fairbridge, R.W. (1953) <u>Australian Stratigraphy: Perth</u>.
 Univ.West.Australia. Text Books Board 516p.
- Firman, J.B. (1969) Quaternary Period <u>In</u>, L.W. Parkin (ed.)

 Handbook of South Australian Geology. pp.204-233 Geol.Surv.S.Aust.
- Hewgill, F.R., Kendrick, G.W., Webb, R.J. and Wyrwoll, K.-H. (1983) Routine ESR Dating of Emergent Pleistocene Marine Units in Western Australia.

- Search 14:215-217.
- Iredale, T. (1957) Recent Palaeontology. Aust.Zool. 11(4):347-350.
- Kimber, R.W.L. and Milnes, A.R. (1984) The extent of racemization of amino acids in Holocene and Pleistocene marine molluscs in southern South Australia: Preliminary Data on a time-framework for calcrete formation. Aust.J.Earth Sci. 31:279-286.
- Kimber, R.W.L. and Griffin, C.V. (1987) Further evidence of the complexity of the racemization process in fossil shells with implications for amino acid racemization dating. Geochim. et Cosmochim.Acta 51:839-846.
- Lajoie, K.R., Wehmiller, J.F. and Kennedy, G.L. (1980) Inter- and intrageneric trends in apparent racemization kinetics of amino acids in Quaternary molluscs. <u>In</u>, P.E. Hare, T.C. Hoering and K. King Jr (eds) <u>Biogeochemistry of Amino Acids</u> pp. 305-340, John Wiley, New York.
- Ludbrook, N.H. (1984) Quaternary Molluscs of South Australia, Department of Mines and Energy, South Australia. Handbook No. 9, 327p.
- Murray-Wallace, C.V. (1987) Evaluation and Application of the Amino Acid Racemisation Reaction in Studies of Quaternary Coastal and Marine Sediments in Australia. (Unpubl. Ph.D. thesis, Univ. Adelaide) 352p.
- Murray-Wallace, C.V. and R.W.L. Kimber (1987) Evaluation of the amino acid racemization reaction in studies of Quaternary marine sediments in South Australia. <u>Aust.J.Earth Sci.</u> 34, 279-292
- Rutter, N.W. (ed.) (1985) <u>Dating Methods of Pleistocene Deposits</u>

 and their problems. Geosci.Can. Reprint Series 2, 87p.
- Schroeder, R.A. and Bada, J.L. (1976) A review of the geochemical applications of the amino acid racemization reaction. <u>Earth-Sci.Rev.</u> 12:347-391.
- Schwebel, D.A. (1978) Quaternary stratigraphy of the south-east of South Australia. Unpubl. PhD Thesis, Flinders University of S.A.

- Myall Lakes Area, N.S.W. J. & Proc.Roy.Soc. N.S.W. 98:23-36.
- Thom, B.G., Bowman, G.M. and Roy, P.S. (1981) Late Quaternary Evolution of Coastal Sand Barriers, Port Stephens Myall Lakes Area, Central New South Wales, Australia. Quat.Res. 15:345-364.
- Veeh, H.H. (1966) Th^{230}/U^{238} and U^{234}/U^{238} ages of Pleistocene high sea level stand. <u>J.Geophys.Res.</u> 71:3379-3386.
- Veeh, H.H., Schwebel, D., van de Graaff, W.J.E. and Denman, P.D. (1979)

 Uranium-series ages of coralline terrace deposits in Western

 Australia. <u>J.Geol.Soc.Aust.</u> 26:285-292.
- Wehmiller, J.F. (1982) A Review of Amino Acid Racemization Studies in Quaternary Molluscs: Stratigraphic and Chronologic Applications in Coastal and Interglacial Sites, Pacific and Atlantic Coasts, United States, United Kingdom, Baffin Island, and Tropical Islands.

 Quat.Sci.Rev. 1:83-120.
- Wehmiller, J.F. (1984a) Relative and Absolute Dating of Quaternary k Mollusés with Amino Acid Racemization: Evaluation, Applications and Questions. <u>In</u>, W.C. Mahaney (ed.) <u>Quaternary Dating Methods</u>. Elsevier Sci. Publ., Amsterdam, pp.171-193.
- Wehmiller, J.F. (1984b) Interlaboratory comparison of amino acid enantiomeric ratios in Fossil Pleistocene Molluscs. Quat.Res. 22:109-120.
- Williams, K.M. and Smith, G.G. (1977) A Critical Evaluation of the Application of Amino Acid Racemization to Geochronology and Geothermometry. Origins of Life 8:91-144.

TABLE 1

Extent of amino acid racemisation in molluscan fossils of Last Interglacial age from southern Australia. Amino acid D/L ratios are for the 'total acid hydrolysate'. Modern, Holocene and Penultimate Interglacial specimens provide a basis for comparison. Coefficients of variation are presented in parentheses.

	* *		•		of cimens	Amino	Acid D/L	Ratio		
Species	Locality	Age	(ka)	MAT (°C)	Speci	VAL	ALLO/ISO	TEO.	ASP	GLU
Anadara trapezia	Quarantine Bay, N.S.W.	mode	ern	14.7	2		0.02 +0.002 (10.0)	0.03 +0.001 (3.3)	0.11	**
Katelysia rhytiphora	Smoky Bay west coast of S.A.	7.1	1+0.2	18.0	3	0.08 +0.002 (2.5)		0.16 +0.02 (12.5)	0.23	0.10 +0.004 (4.0)
Anadara trapezia	Largs, N.S.W.	125		17.9	. 2	0.30 +0.01 (3.3)		0.43 +0.04 (9.3)	0.58 +0.04 (6.9)	0.43 +0.07 (16.2)
Anadara trapezia	Clanville Formation neostratotype Dry Creek, Adelaide	125		16.9	3	0.31 +0.01 (3.2)	0.39 +0.01 (2.56)	-	0.61 +0.01 (1.6)	0.54 +0.14 (25.9)
Anadara trapezia	Glanville Formation, Port Wakefie S.A.	125 eld,		. 17	12	+0.06	0.43 +0.02 (4.6)	0.51 +0.02 (3.9)	+0.03	0.43 +0.01 (2.3)
Katelysia rhytiphora	Glanville Formation, Port Wakefiel S.A.	125 .d,		17	6	0.32 +0.04 (12.5)	+0.07	0.51 +0.07 (13.7)	+0.02	0.38 +0.04 (10.5)
Anadara trapezia	Glanville Formation, Denial Bay, S.A.	125		16.9	6	0.33 +0.02 (6.0)	+0.03	0.44 +0.01 (2.2)	0.64 +0.02 (3.1)	0.47 +0.01 (2.1)
<u>Katelysia</u> rhytiphora	Minim Cove Swan Estuary, W.A.			18.5	8	0.33 +0.02 (6.0)	+0.02	0.48 +0.03 (6.3)	+0.05	-
<u>Katelysia</u> <u>scalarina</u>	Minim Cove Swan Estuary, W.A.			18.5	_	0.34 +0.03 (8.8)	+0.04	0.49 +0.03 (6.1)		-
Anadara trapezia	"Older Pleistocene marine beds" Redcliff, S.A	225	·- <u>-</u> -	19	4	0.48 +0.01 (2.0)	+0.02	-	0.76 +0.02 (2.6)	0.62 +0.02 (3.2)

VAL - valine, ALLO/ISO - D-alloisoleucine/L-isoleucine, LEU - Leucine, ASP - Aspartic Acid, GLU - Glutamic acid.

SADME

5194.60

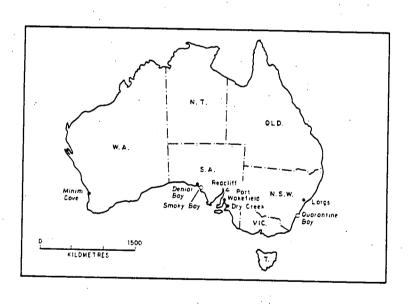


Figure 1.