

Amino acid geochronology of Pleistocene marine sediments in the Wanganui Basin: a New Zealand framework for correlation and dating

D. Q. BOWEN¹, B. PILLANS², G. A. SYKES¹, A. G. BEU³, A. R. EDWARDS⁴, P. J. J. KAMP⁵
& A. G. HULL³

¹*Department of Earth Sciences, University of Wales, Cardiff CF1 3YE, UK (email: bowendq@cardiff.ac.uk)*

²*Research School of Pacific and Asian Studies, Australian National University, Canberra, 0200, Australia*

³*Institute of Geological & Nuclear Sciences, PO Box 30368, Lower Hutt, New Zealand*

⁴*Stratigraphic Solutions, PO Box 295, Waikanae, New Zealand*

⁵*Department of Earth Sciences, University of Waikato, Hamilton, New Zealand*

Abstract: Amino acid analysis of indigenous protein preserved in fossil marine bivalves from Plio-Pleistocene sediments in the Wanganui Basin, North Island, New Zealand has provided an aminostratigraphy. D-alloisoleucine/L-isoleucine (D-alle/L-Ile) ratios were measured in the venerid marine bivalves *Tawera spissa* and *Austrovenus stutchburyi* that show progressively increasing D-alle/L-Ile ratios with increasing stratigraphical age. When calibrated by magnetostratigraphy, fission-track dating, radiocarbon dating, and coccolith biostratigraphy, these relative D-alle/L-Ile ages range up to c. 1 Ma. The aminostratigraphy provides a framework of correlation and dating for other sites in the New Zealand area where other methods of dating are unavailable, as well as facilitating correlation with oxygen isotope stratigraphy. This is the first calibrated aminostratigraphical sequence from a long sequence of sediments that cover a significant proportion of the Pleistocene.

Keywords: New Zealand, Quaternary, amino acids, dates, correlation.

Abelson (1954) discovered that amino acids contained in the indigenous proteins preserved in carbonate skeletons degrade progressively with time. Such changes may be used to estimate the time that has elapsed since the death of the organism. The principles of amino acid geochronology in carbonate fossils are discussed in Hare & Mitterer (1967) with comprehensive reviews by Miller & Brigham-Grette (1989) and Wehmiller (1989). Racemization refers to the inversion of L amino acids to the D configuration, but in the protein amino acid L-isoleucine racemization occurs about only one of the two chiral carbon atoms. This reaction, called epimerization, proceeds from an initial D/L ratio close to zero to an equilibrium ratio of about 1.3. The reaction rate is controlled by temperature and the nature of the proteins, a variable related to taxonomy and the extent to which the protein has degraded. The taxonomic variable, or species effect, may be minimized by using monospecific samples.

The integrated temperature at a site is the most important control on the reaction rate and thus the resolving power of the method. For example, at tropical sites with mean annual temperatures exceeding 25°C, age differences of c. 1 ka can be resolved within the Holocene, and between 5 and 10 ka for older samples; but equilibrium is reached after only 150–300 ka. At Arctic sites with mean annual temperatures of less than 10°C no measurable racemization is detected in Holocene samples, and equilibrium is not reached in less than 10 Ma. At mid-latitude sites, such as the USA, Britain and New Zealand, with mean annual temperatures greater than 10°C, the reaction rate is substantially lower and equilibrium takes about 2 Ma.

Amino acid geochronology has been successfully applied to Pleistocene marine and non-marine molluscs where other means of dating are not applicable or unreliable. It has, for

example, been widely applied to marine molluscs in mid-latitudes: in Europe by Bowen *et al.* (1985) and Miller & Mangerud (1985); in the Mediterranean by Hearty *et al.* (1986); western United States (Kennedy *et al.* 1982); eastern United States (Wehmiller & Belknap 1982) and Australia by Murray-Wallace & Kimber (1988). In Britain, it has also been applied to non-marine bivalves and gastropods (Bowen *et al.* 1989).

Samples were collected from Pleistocene marine sediments of the Wanganui Basin, New Zealand, a restricted geographical area where the integrated temperature effect on the fossils is the same, thus minimizing this source of variability. It was also intended to test the existing correlations across the Wanganui River (Beu & Edwards 1984), between Castlecliff and Landguard Bluff. To minimize any taxonomic variability the extent of epimerization was measured in two venerid marine bivalves, *Austrovenus stutchburyi* (Gray) and *Tawera spissa* (Deshayes), that yield similar D-alle/L-Ile ratios in the same stratigraphical units, thus showing that they epimerize at the same rate.

North Island, New Zealand (Fig. 1), contains thick Plio-Pleistocene marine sequences in emergent basins. Correlations between lithostratigraphical units in some of these basins and oxygen isotope stratigraphy have been previously proposed by Beu & Edwards (1984), Beu *et al.* (1987), and Pillans *et al.* (1994). The largest of these is the Wanganui Basin where biostratigraphic, magnetostratigraphic and fission-track dating is available. This combined chronology provides the geochronological calibration of the D-alle/L-Ile ratios measured on the marine fossils from precise lithostratigraphical units.

This then provides an aminostratigraphy and amino acid geochronology (D-alle/L-Ile) as a framework for correlation with other areas of similar mean annual temperature. The

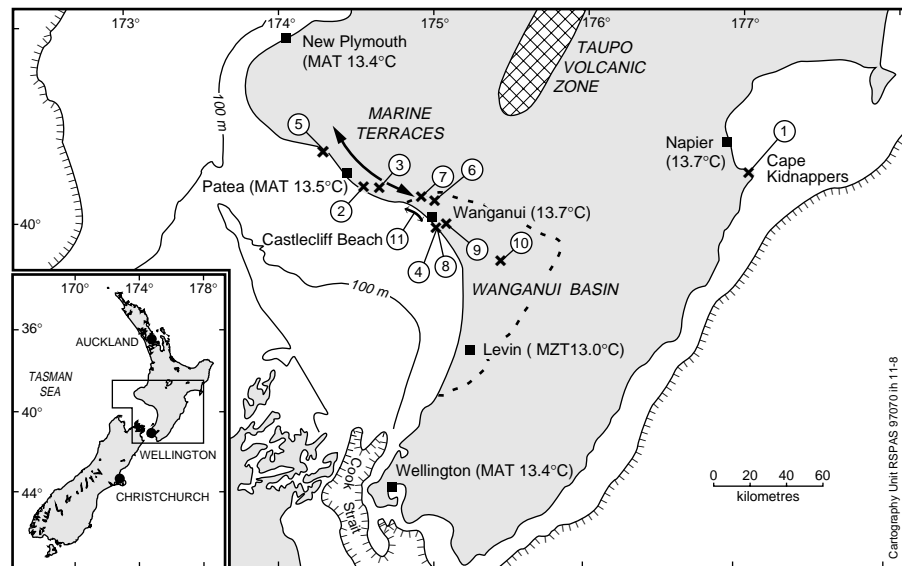


Fig. 1. Map showing locations of sampling sites. **Site 1.** Holocene marine terrace, Cape Kidnappers (Hull 1987). **Site 2.** Hauriri Marine Terrace, Waverley Beach (Pillans 1990). **Site 3.** Ngarino Marine Terrace, Waitotara valley (Pillans 1990). **Site 4.** Waipuna Delta Conglomerate, Wanganui East (correlated with Ngarino Marine Terrace by Beu & Edwards (1984), but could be younger—see text). **Site 5.** Ngarino Marine Terrace, Hawera (Pillans 1990). **Site 6.** Brunswick Marine Terrace, Brunswick Quarry (Pillans 1990). **Site 7.** Brunswick Marine Terrace, type section (Pillans 1990). **Site 8.** Landguard Formation, Landguard Bluff (Fleming 1953; Beu & Edwards 1984). **Site 9.** Windsor Shellbed, Wanganui East (Beu & Edwards 1984). **Site 10.** Rangitawa Shellbed, Rangitikei valley (Te Punga 1962). **Site 11.** Formations exposed in coastal cliffs at Castlecliff Beach, Wanganui (Fleming 1953; Beu & Edwards 1984). Mean annual temperatures (MAT) from the New Zealand Meteorological Service (1983).

example of correlation between the Wanganui Basin and Cape Kidnappers, Hawke's Bay, is presented, while other data for correlation between the Wanganui Basin and South Island (Kaikoura) is in preparation. Aminostratigraphy is not, however, invariably constrained to a single region where integrated temperatures are similar, but may be extended into other regions provided that independent age calibration of the amino acid ratios is available: for example, the western United States (Kennedy *et al.* 1982) and the Mediterranean Basin (Hearty *et al.* 1986).

Sample collection and laboratory methods

Fossil molluscs were collected from marine beds in the Wanganui Basin, North Island, New Zealand. The samples were sealed in plastic bags in the field, washed in the laboratory to facilitate species identification, and resealed until further analysis. The shells were cleaned of sediment mechanically and in an ultrasonic bath. Separation of the amino acids was done by chromatography on 25 × 0.24 internal diameter cm column packed with Durram DC4A ion exchange resin and maintained at approximately 65°C. Sample injection was by an LKB 2153 Autoinjector with 1291 dispenser accessory that provided variable sample volumes. The amino acids were eluted by a step gradient of 67 mM Sodium Citrate buffer pH 3.12, 3.8 and 33 mM Sodium Borate buffer pH 10.5 containing 170 mM NaCl and 2.7 mM EDTA. Buffer flow rate was maintained at 0.10 ml/min by an Eldex A-30-S pump at a back pressure of 400–700 psi depending on column age. Eluant from the column was mixed with OPA reagent, 0.49 M Potassium Borate Buffer pH 10.5 containing 1 ml of Brj 35/1 and 15 ml OPA solution (0.750 g OPA, 15 ml Methanol, 300 µl Mercaptoethanol). Reagent flow was maintained at 0.11 ml/min under nitrogen pressure and the reaction took place in a reaction coil (80 × 0.005 ID cm). The amino acids were detected as OPA derivatives by a Gilson 121 fluorometer. Control of sample injection, buffer switching and data collection was by an Apple IIe computer using IMI Chromatochart software in conjunction with IMI adalab card and chomadapt interface, a second adalab card monitored data with a five fold attenuation. The system plotted and

integrated the peaks and saved the raw data on disc from up to 16 analyses. The laboratory maintains comparability with other laboratories in the United States and in Norway using the Wehmiller international standard.

The Wanganui Basin

The Wanganui Basin occupies much of the onshore and offshore of southwestern North Island of New Zealand (Fig. 1). It contains a Plio-Pleistocene sedimentary succession up to 4 km thick. The succession is well-exposed in sea-cliffs northwest of Wanganui where stratotypes for the New Zealand Pleistocene stages are located (Nukumaruan 2.6–1.6 Ma, Castlecliffian 1.2–0.4 Ma, and Haweran 0.4–0 Ma). The Castlecliffian stratotype of Fleming (1953) was sampled as well as marine terraces of Haweran age between Wanganui and Hawera (Pillans 1983, 1990) (Fig. 1). In addition, the type Rangitawa Shell-bed in the Rangitikei Valley (Te Punga 1962), some 40 km east of Wanganui (Fig. 1), was sampled because fission-track ages (Kohn *et al.* 1992) and biostratigraphy (Fleming 1957) correlate it with the Putiki Shell-bed at the top of the Castlecliffian stratotype (Beu *et al.* 1987).

The Castlecliffian stratotype is a 12 km-long, nearly continuous exposure in 30–50 m high sea-cliffs. The beds dip at 2–4° to the southeast so that all of them are accessible at beach level. A gap in the sequence occurs across the mouth of the Wanganui River, but stratigraphic relationships between strata on either side of the river were inferred from drillhole data (Beu *et al.* 1987), now tested by aminostratigraphy (below). Figure 2 is a composite stratigraphical column that shows the levels of samples reported here.

The Castlecliffian stratotype consists of unconformity-bounded shallow marine (<100 m) units (Fleming 1953; Beu & Edwards 1984; Kamp & Turner 1990; Carter *et al.* 1991). Palaeoecological investigations by Beu & Edwards (1984) led to the conclusion that they accumulated during high stands

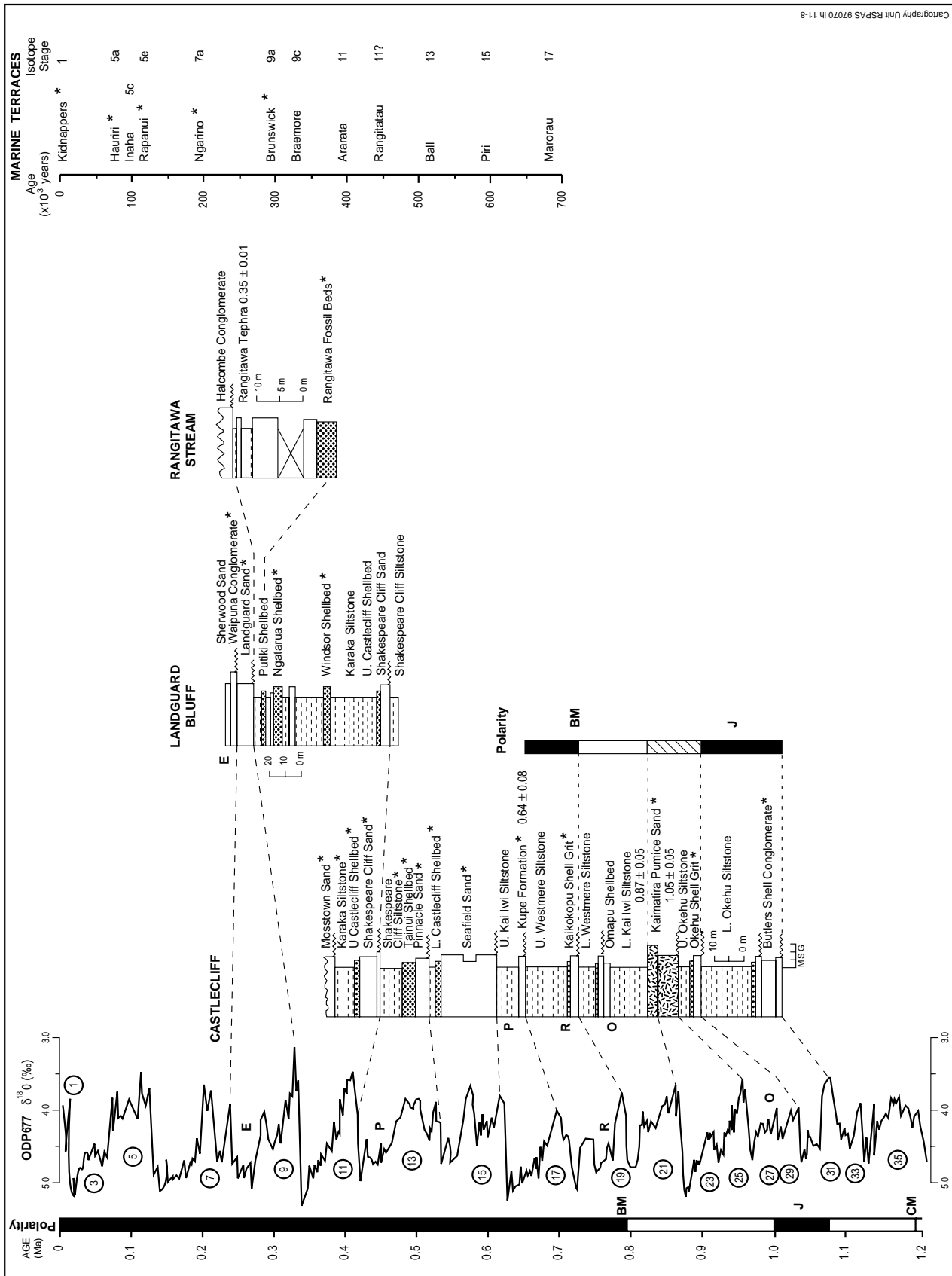


Fig. 2. Stratigraphic summary of sampling sites (sampled units are indicated by *). Oxygen isotope stages and polarity timescale after Shackleton et al. (1990) and Shackleton (pers. comm.). Lithostratigraphy of Castlecliff section after Carter et al. (1991); lithostratigraphy of Landguard Bluff section after Beu et al. (1987); lithostratigraphy of Rangitawa stream section after Bussell (1986); ages of marine terraces after Pillans (1983, 1990) and Hull (1987). Fission-track ages for tephra horizons after Kohn et al. (1992), Alloway et al. (1993) and Shane et al. (1996b). Biostratigraphic datums: E, FAD *Emiliania lacunosa*; P, LAD *Pseudoemiliania lacunosa*; R, LAD *Reticulofenestra asanoi*; O, FAD *Geophyrocapsa omega*.

Table 1. *D-alle/L-Ile ratios from Tawera spissa*

Lab no.	Stratigraphic unit*	D-alle/L-Ile	<i>n/N</i> †	Stage‡	Age
ABER-750	Holocene Terrace (1)	0.04 ± 0.01	3§	1	2.5
ABER-731	Hauriri Terrace (2)	0.24 ± 0.01	3/3	5a	74–83
ABER-1112	Ngarino Terrace (3)	0.50 ± 0.03	5/5	7	186–242
ABER-728	Ngarino Terrace (4)	0.37 ± 0.03	5/5	5e?	114–127
ABER-723	Ngarino Terrace (5)	0.47 ± 0.02	5/5	7	186–242
ABER-729	Brunswick Terrace (6)	0.49 ± 0.02	5/5	9	301–312
ABER-1114	Brunswick Terrace (7)	0.50 ± 0.03	2/2	9	301–312
ABER-726	Landguard Fm. (top) (8)	0.62 ± 0.03	3/3	9	312–334
ABER-727	Landguard Fm. (base) (8)	0.57 ± 0.01	3/3	9	312–334
ABER-733	Putiki Shellbed (9)	0.62 ± 0.04	5/5	11	364–427
ABER-734	Rangitawa Shellbed (10)	0.68 ± 0.01	3/3	11	364–427
LOND-418	Windsor Shellbed (9)	0.55 ± 0.04	5/5	9?	301–312
ABER-743	Mosstown Sand (11)	0.70 ± 0.05	2§	11	364–427
ABER-744					
ABER-737	Karaka Siltstone (11)	0.67 ± 0.05	5/5	11	364–427
ABER-724	Upper Castlecliff				
ABER-725	Shellbed (11)	0.76 ± 0.03	8/8	11	364–427
ABER-742	Shakespeare Cliff Sand (11)	0.73 ± 0.05	3/3	11	364–427
ABER-739	Shakespeare	0.75 ± 0.09	3§	11	364–427
ABER-740	Cliff Sand				
ABER-741	(base) (11)				
ABER-721	Shakespeare Cliff Siltstone (11)	0.70 ± 0.03	4/5	13	474–528
ABER-722	Tainui Shellbed (11)	0.75 ± 0.02	4/5	13	474–528
ABER-738	Pinnacle Sand (11)	0.67 ± 0.04	5/5	13	474–528
ABER-736	Lower Castlecliff Shellbed (11)	0.71 ± 0.09	4/4	15	568–621
ABER-732	Seafield Sand (11)	0.75 ± 0.04	3/5	15	568–621
ABER-730	Kupe Formation (11)	0.87 ± 0.02	5/5	17	659–712
ABER-745	Kaikokopu Shell Grit (11)	0.87 ± 0.01	3/3	19	760–787
ABER-746	Kaimatira Pumice Sand (11)	0.77 ± 0.02	2§	25	925–960
LOND-486	Okehu Shell Grit (11)	1.20 ± 0.03	5/5	29	1015–1030
LOND-484	Butlers Shell Conglomerate (11)	1.22 ± 0.08	5/5	31	1060–1080

D-alle/L-Ile: mean and one standard deviation.

*Numbers in parentheses refer to localities shown on Fig. 1.

†*n*=number of analyses in mean; *N*=number analyses.

‡Oxygen isotope stage (see Fig. 2).

||Age range of oxygen isotope stage in thousands of years (from Bassinot *et al.* (1994) for stages 1–21; Shackleton *et al.* (1990) for older stages).

§One shell analysed *n* times.

of sea level during interglacials corresponding with odd-numbered oxygen isotope stages. They argued that ice-ages, corresponding with even numbered oxygen isotope stages, are represented by the unconformities when much of the basin was exposed to subaerial processes when contemporary shorelines lay well to the south. The younger Haweran marine beds in the marine terrace sequence are inferred to have accumulated during interglacial high stands of sea level (Pillans 1983; Pillans *et al.* 1988).

Geochronology

The primary geochronological control for the Castlecliffian stratotype is based on palaeomagnetic measurements that locate the Matuyama–Brunhes boundary (0.78 Ma) near the level of the Kaikokopu Shell Grit, and place the Jaramillo Subchron (0.99–1.07 Ma) within the Butlers Shell Conglomerate and Lower Okehu Siltstone (Turner & Kamp 1990) (Fig. 2). The ages are based on the astronomical timescale of Shackleton *et al.* (1990). The base of the stratotype, therefore, has an estimated age of 1.07 Ma. The top of the stratotype is estimated to be about 0.4 Ma based on the fission-track ages estimates of the Rangitawa Tephra (Kohn

et al. 1992; Pillans *et al.* 1996), that lies a few metres above the Rangitawa Shell-bed in the Rangitikei Valley. The Rangitawa Tephra also occurs in the non-marine coverbeds of the marine terrace sequence that were sampled west of Wanganui where it has a mean zircon fission-track age of 0.35 ± 0.04 Ma (Kohn *et al.* 1992).

Fossiliferous marine deposits of Holocene age do not occur at Wanganui, so Holocene specimens of *Tawera* were collected from an uplifted marine terrace at Cape Kidnappers, Hawke's Bay, some 150 km ENE of Wanganui (Fig. 1). Shells from this terrace have mean radiocarbon age estimates of *c.* 2500 BP (Hull 1987). Mean annual temperatures in the Kidnappers area are similar to those in the Wanganui Basin at sea-level, so it is assumed that they have experienced a similar integrated temperature history and similar rates of epimerization in fossil molluscs.

Samples were also collected from the sediments of the Wanganui marine terraces (Fig. 1). Using the age of the Rangitawa Tephra, D-alle/L-Ile age estimates from fossil wood and an uplift model the ages of the terraces were estimated as: Brunswick Terrace (0.31 Ma), Ngarino Terrace (0.21 Ma), Rapanui Terrace (0.12 Ma), and Hauriri Terrace (0.08 Ma) (Pillans 1983).

Table 2. D-allo/L-Ile ratios from *Austrovenus stutchburyi*

Lab no.	Stratigraphic unit*	D-allo/L-Ile	n/N†	Stage‡	Age
LOND-76	Rapanui Terrace (11)	0.98 ± 0.13	2/2	5e	114–127
LOND-70	Ngarino Terrace (5)	0.51 ± 0.03	5/5	7	186–242
LOND-77	Ngarino Terrace (5)	0.53 ± 0.12	5/5	7	186–242
LOND-71	Brunswick Terrace (6)	0.46 ± 0.04	5/5	9	301–312
LOND-66	Landguard Fm. (top) (8)	0.54 ± 0.04	4/4	9	312–334
LOND-67	Putiki Shellbed (9)	0.59 ± 0.04	3/3	11	364–427
LOND-71	Rangitawa Shellbed (10)	0.70 ± 0.02	3/3	11	364–427
LOND-419	Ngatarua Shellbed (9)	0.66 ± 0.16	4/4	11	364–427
LOND-417	Windsor Shellbed (9)	0.61 ± 0.11	5/5	9?	301–312
LOND-65	Mosstown Sand (11)	0.73 ± 0.08	3/3	11	364–427
LOND-68	Shakespeare Cliff Sand (11)	0.83 ± 0.05	4/4	11	364–427
LOND-69	Seaford Sand (11)	0.86 ± 0.05	3/3	15	568–621
LOND-483	Butlers Shell Conglom. (11)	1.22 ± 0.07	5/5	31	1060–1080
LOND-352	Kidnappers Terrace (1)	0.18 ± 0.01	4/4	5	71–127
	Te Awanga Beds (1)	0.94 ± 0.05	5/5	>15	>621
	Te Awanga Beds (1)	0.98 ± 0.03	5/5	>15	>621
LOND-75	Clifton Sand (1)	0.87 ± 0.09	5/5	>15	>621
LOND-73	Trig N Beds (1)	1.07 ± 0.02	5/5	>15	>621
LOND-74	Mt. Gordon Beds (1)	1.03 ± 0.02	5/5	>15	>621

See Table 1 for footnotes.

Figure 2 summarizes the geochronology of the exposures that were sampled and correlates the Wanganui Basin beds with oxygen isotope stratigraphy. Correlation is based primarily on the Castlecliff magnetostratigraphy (Turner & Kamp 1990) and from the fission-track ages of interbedded tephtras (Shane *et al.* 1996b). More complete Castlecliffian sections, inland from the Wanganui coast provide further lithostratigraphic and magnetostratigraphic evidence (Pillans *et al.* 1994). The Kaimatira Pumice Sand consists of two cyclothem and a fission track date of 1.05 ± 0.05 Ma (Alloway *et al.* 1993) and its magnetostratigraphy (Pillans *et al.* 1994), correlate it with the uppermost Jaramillo Subchron.

First appearance datums (FADs) and Last appearance datums (LADs) of nannofossils from the Castlecliff sequence allow further correlation with oxygen isotope stratigraphy and the magnetostratigraphy of ocean sediments. These are as follows.

- (1) FAD of *Emiliania huxleyi* in the Waipuna Conglomerate (Beu & Edwards 1984) with an estimated age of 0.27 Ma in deep-sea cores (Thierstein *et al.* 1977).
- (2) LAD of *Pseudoemiliania lacunosa* in the Upper Kai-Iwi Siltstone with an estimated age of 0.46 Ma in deep-sea cores (Thierstein *et al.* 1977).
- (3) FAD of *Geophyrocapsa omega* that is recognized in deep-sea cores at the top of Jaramillo Subchron (0.97 Ma) (Young 1991). *G. omega* is present in both the Omapu Shell-bed and at the base of the Lower Kai Iwi Siltstone at the Castlecliff section, but cannot be related to the Kaimatira Pumice Sand because it does not contain identifiable nannofossils.
- (4) LAD of *Reticulofenestra asanoi* in the lowermost part of the Upper Westmere Siltstone (Edwards *et al.* 1995). *R. asanoi* is generally considered to have become extinct in deep-sea cores about 0.88 Ma (e.g. Wei 1993) during oxygen isotope stage 22, although its LAD has been reported close to the Matuyama–Brunhes boundary in the Sea of Japan (Muza 1992).

The positions of the *E. huxleyi* and *R. asanoi* datums, and the presence of *G. omega* in the Omapu Shell-bed and Lower Kai Iwi Siltstone is consistent with the correlations shown on Figure 2; but that of *P. lacunosa* is not. Its apparent position in older beds than would be expected is anomalous and is being investigated further.

Results and discussion

Tables 1 and 2 present the D-allo/L-Ile data for *Tawera spissa* and *Austrovenus stutchburyi* that forms the aminostratigraphy of the Wanganui Basin. Correlation with oxygen isotope stratigraphy is based on palaeomagnetic data, biostratigraphy and fission-track ages (above). In general, D-allo/L-Ile ratios of the taxa increase with increasing stratigraphical age.

The mean D-allo/L-Ile ratios for three sites (the Ngarino Terrace at site 4, the Windsor Shell-bed at site 9, and the Kaimatira Pumice Sand at site 11) were lower than expected.

Site 4, containing sediments ascribed to the Ngarino Terrace (Beu & Edwards 1984) is exposed in coastal cliffs east of the Wanganui river where stratigraphic correlations are uncertain because of the lack of outcrops. The D-allo/L-Ile ratio, however, indicates correlation with the Rapanui Terrace (sub-stage 5e), rather than stage 7. The site at which the presumed Windsor Shell-bed was sampled, is a poorly exposed outcrop on the east side of Wanganui River, and it is possible that it may be part of Brunswick Terrace (stage 9). This site, therefore, is excluded from the data set until the field relationships are further clarified. The D-allo/L-Ile ratio for the Kaimatira Pumice Sand, in which *Tawera* is rare, is based on duplicate analyses of a single shell, and until further specimens can be analysed from this unit, it is also excluded.

Samples of *Austrovenus* from the Rapanui Terrace (sub-stage 5e) at Castlecliff Beach have D-allo/L-Ile ratios much higher than expected. They may, however, indicate re-working of the richly fossiliferous underlying beds of Mid- and Lower Pleistocene age.

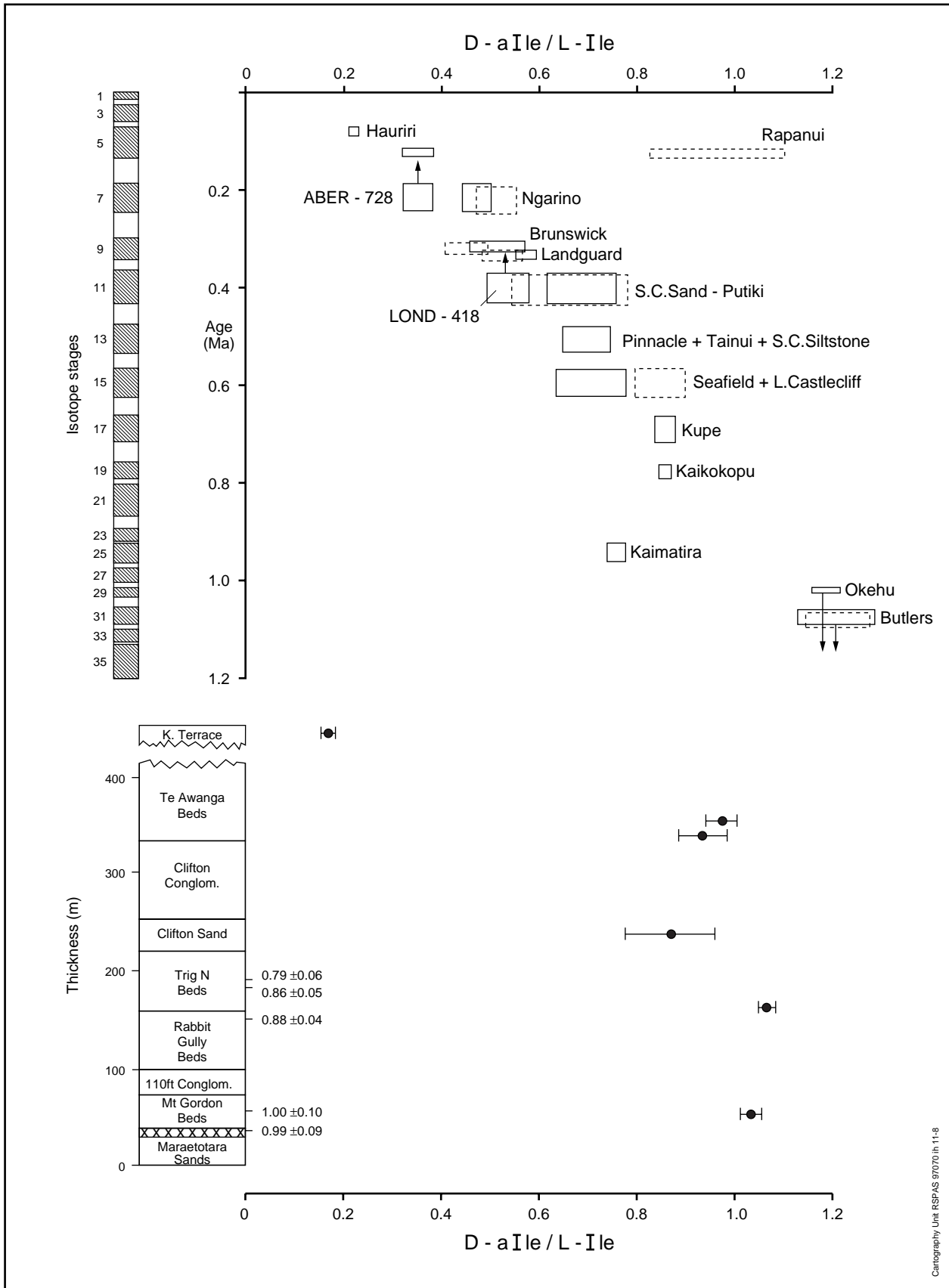


Fig. 3. (a) D-aIle/L-Ile ratios for *Tawera* (solid boxes) and *Austrovenus* (dotted) from Wanganui Basin plotted against oxygen isotope stage. D-aIle/L-Ile represents $\pm 1 \sigma$ for mean ratio; age range represents duration of correlative oxygen isotope stage (from Bassinot *et al.* 1994 and Shackleton *et al.* 1990). (b) Bottom: Cape Kidnappers section. Ages (Ma) from Shane *et al.* (1996a).

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The two oldest beds (Okehu Shell Grit and Butlers Shell Conglomerate) are the only ones sites for which the species *T. subsulcata* was analysed, whereas *T. spissa* was analysed at all other sites. *T. subsulcata* and *T. spissa* are not known to occur together at any other site, so it is not possible to evaluate any taxonomic effect on epimerization. In addition, there appears to be considerable re-working of fossils from older strata into the oldest part of the Castlecliff section. Typical *T. subsulcata* occurs only in Nukumaruan beds, and although shells related to *T. subsulcata* occur in the Haweran shell-beds in Cook Strait (Fig. 1), it seems likely that the two oldest samples represent re-worked Nukumaruan specimens. The higher than expected D-alle/L-Ile ratios in the two *T. subsulcata* samples apparently result from this re-working. These sites, in addition to the Rapanui site (above) highlight an important application of amino acid analysis for the identification of re-worked fossils.

The similarity in D-alle/L-Ile ratios for samples from the Ngarino and Brunswick terraces was unexpected: the Ngarino Terrace has an age of 210 ka, and Brunswick Terrace has an age of 310 ka according to the age model of Pillans (1983), which should result in statistically different D-alle/L-Ile ratios. It is noted, however, that the two sample sites for the Brunswick Terrace (sites 6 and 7) occur at an elevation of c. 130 m above present sea-level, whereas the sites for the Ngarino Terrace (sites 3 and 5) are less than 60 m above present sea-level. Such a difference in elevation would imply that the Brunswick sites have experienced a lower mean long term temperature history than the Ngarino sites: some 0.5°C lower based on present lapse rates (NZ Meteorological Service 1983). Such a difference in temperature would mean that the D-alle/L-Ile ratios could be some 10% too low relative to the Ngarino sites. Indeed, all our other sampling sites are within 50 m of present sea-level, and the Brunswick ratios could be similarly lowered relative to these.

To test aminostratigraphical (D-alle/L-Ile) correlations, samples of *Austrovenus* were collected from the sequence of marine Pleistocene beds at Cape Kidnappers, Hawke's Bay (Fig. 1). Figure 3b shows the D-alle/L-Ile ratios plotted against stratigraphical units in the Cape Kidnappers sequence. Except for the sample from the Cape Kidnappers Terrace (see Geochronology), all samples have D-alle/L-Ile ratios greater than 0.8 which indicate ages greater than 0.6 Ma (Fig. 2). Fission-track age estimates from the Cape Kidnappers sequence were 0.32 Ma (base of the Trig N Beds), 0.36 Ma (Rabbit Gully Beds), 0.47 Ma (Mt Gordon Beds), and 0.85 Ma (the Kidnapper Tuff) (Seward 1975).

Subsequently, however, isothermal plateau fission-track and $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Shane *et al.* 1996a) suggested that the first estimates were probably affected by partial track fading that resulted in anomalously young ages. Black (1992) located the Matuyama–Brunhes boundary (0.78 Ma) within the Rabbit Gully Beds, but Shane *et al.* (1996a) consider that some palaeomagnetic samples may have been affected by a strong normal polarity overprint, in which case the M/B boundary could lie somewhat higher in the sequence. Correlation of D-alle/L-Ile ratios on *Austrovenus* between Wanganui and Cape Kidnappers, however, is consistent with the general position of the Matuyama–Brunhes boundary in the Cape Kidnappers sequence that confirms the aminostratigraphic correlations.

Beu *et al.* (1987) reported the occurrence of the coccolith *Pseudoemiliana lacunosa* in the Te Awanga Beds at Cape Kidnappers that points to an age greater than 0.46 Ma. Lewis (1971) considered the terrace at the Cape Kidnappers locality

at an elevation of 140 m was likely to be last interglacial in age (oxygen isotope sub-stage 5e at c. 125 ka). But the D-alle/L-Ile ratios point to an oxygen isotope stage 5a age for the terrace similar to the Hauriri Terrace (80 ka) at Wanganui.

Conclusions

At temperate mid-latitude sites, such as New Zealand, the British Isles and the United States aminostratigraphy, and its derivative amino acid geochronology, is widely applicable because the moderate rate of epimerization (Miller & Mangerud 1985; Miller & Brigham-Grette 1989) is able to resolve the age of Mid- and Late Pleistocene deposits sufficiently for correlation with oxygen isotope stratigraphy. The results presented here are the first D-alle/L-Ile sequence from an independently dated long sequence of rocks spanning the Late, Mid- and Early Pleistocene for marine molluscs.

These data provide a framework for further aminostratigraphical correlations and dating in the New Zealand region, especially for areas that experienced a similar temperature history and for which no other means of dating is available. Such a framework is most easily applied to other parts of the North Island where long term mean annual temperatures are similar (within 0.5°C) to Wanganui, as illustrated by the Cape Kidnappers example discussed above. Correlation with other areas is also possible provided that local calibration of the aminostratigraphy is possible by other means as has been accomplished on the west coast of the United States between southern California and Washington (Kennedy *et al.* 1982).

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