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Amino Acid Dating of Quaternary Marine Terraces, Bahia Asunción, Baja California Sur, Mexico

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ABSTRACT

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In the area of Bahia Asunción, on the Pacific coast of Baja California peninsula, amino acid racemization dating has been used to estimate ages of mollusks from Quaternary marine terraces. Eighteen molluscan samples (of the genera *Tivela, Saxidomus,* and *Chione*) from ten localities have been analyzed. The high mean annual temperature for the region (greater than 20° C) has resulted in extensive racemization of samples from what are considered to be late Middle and Late Pleistocene terrace localities. Racemization of most amino acids is effectively complete by about 300,000 years. However, two amino acids, leucine and valine, demonstrate enough resolving power to be used to delineate different age groups among the terrace sites. Where these apparent groups are testable with stratigraphic or geomorphic evidence, they are generally consistent with the available geologic control. The ages estimated for the three aminostratigraphic groups recognized in this study are approximately 120,000, 200,000 and 300,000 years.

ADDITIONAL INDEX WORDS: *Quaternary marine terraces, Baja California Sur, Mexico, amino acid dating, aminostratigraphy, Vizcaino Peninsula.*

INTRODUCTION

Because mollusks are the most common macroinvertebrates found in Quaternary deposits, they have been used by numerous workers to apply and evaluate the amino acid racemization (AAR) dating method. This technique relies upon the conversion (racemization) of L-amino acids ("left-handed") present in living mollusk shells to an equilibrium mixture of 50% L-forms and 50% D-forms ("right-handed"). The amino acids represent the residuum of the original calcification protein, and the racemization of the amino acids is one of several diagenetic reactions that occur. D/L values increase from 0.0 to 1.0 with increasing age of the sample, and individual clusters of D/L values are often recognized as "aminostratigraphic units" or "aminozones" within "aminozones" within a geographic region (MILLER and HARE, 1980). WEHMILLER (1982) has recently reviewed many of the applications of amino acid racemization dating to Quaternary coastal chronologic problems.

Amino acid racemization dating has been employed extensively in studies of Quaternary deposits of the Pacific coast of the United States (WEHMILLER *et al.*, 1977; LAJOIE *et al.*, 1979; KARROW and BADA, 1980; KENNEDY *et al.*, 1982; and MUHS, 1983). Results from VALENTINE (1980), WOODS (1980), WEHMILLER and EMERSON (1980), and EMERSON *et al.* (1981), permit the extension of the United States aminostratigraphic sequences to lower latitudes (WEHMILLER, 1982: Figure 6). These studies have demonstrated that D/L ratios not only increase in samples of increasing age, but also in samples of equal age at lower latitudes (higher temperatures). In addition, D/L analysis of

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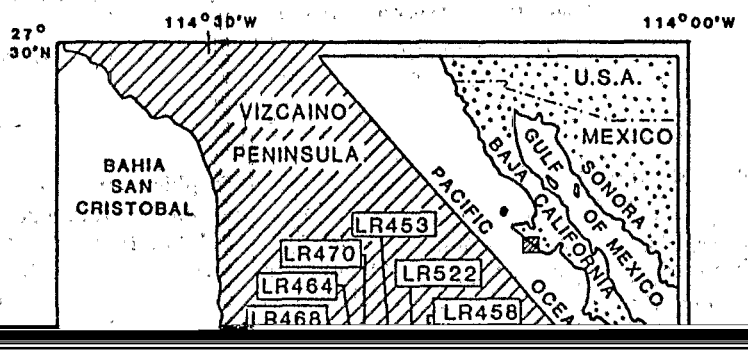
different amino acids and different genera have permitted relative intrageneric and intergeneric racemization rates to be established. This allows for the conversion of the results for one genus into equivalent results for another genus thus enabling direct aminostratigraphic comparison (LAJOIE *et al.*, 1980; WEHMILLER, 1982).

Calibration of the racemization kinetics to the local effective temperature can be made by using amino acid analyses of samples from localities that have been independently dated. Because several of these localities now exist for the mid-latitude Pacific coast of North America, aminostratigraphic age estimates can be made by simple interpolation between the D/L data points for the 120,000 year dated sites (WEHMILLER, 1982). Kinetic models of racemization are needed to extrapolate to age estimates for otherwise un-dated localities, and can be tested with data from calibration localities and information on the climatic history of the region. The mid-latitude Pacific coast of North America has been an excellent region in which to study the combined effects of age and temperature on racemization. This is primarily due to the relative abundance of calibration sites and the moderate Late Pleistocene temperature change recorded in this region.

Solitary corals have been dated by Uranium-series methods at the following low terrace localities along the Pacific coast of North America: Cayucos, Calif. (VEEH and VALENTINE, 1967); Nestor Terrace, Calif. (KU and KERN, 1974); Eel Point Terrace, Calif. (MUHS and SZABO, 1982); and Magdalena Bay, Baja California Sur, Mexico (OMURA *et al.*, 1979). The dates on these samples appear to represent the 120,000 to 130,000 year high sea-stand that is recorded by the marine oxygen-isotope record (SHACKLETON and OPDYKE, 1973) and numerous tropical island coral terrace records (*e.g.*, BLOOM *et al.*, 1974). Also, on the Sonoran coast of the Gulf of California, several last interglacial radiometric dates have been obtained (BERNAT *et al.*, 1980). Absolute dating of mollusks and coral fragments by Uranium-series has provided several anomalous results from the Vizcaino Peninsula (ORTLIEB *et al.*, 1984).

Along the Vizcaino Peninsula, Baja California Sur, and, in particular, in the region of Bahia Asunción (Figure 1), a series of Quaternary marine terraces and superposed deposits exists that range in elevation from +2 to more than +100 meters



(TROUGHTON, 1974; ORTLIEB, 1978, 1979a, 1979b, 1980; MALPICA, 1980; and MALPICA *et al.*, 1981). The lowest terraces have been tentatively correlated on the basis of elevation and morphology and are thought to represent the last Middle to Late Quaternary high sea-stands corresponding to the oxygen-isotope curve of SHACKLETON and OPDYKE (1973)(ORTLIEB, 1978, 1979b, and 1979c). Since uplift rates have been relatively low in this region (less than 100mm/10^3 years) there is some overlapping of marine units deposited during several interglacial transgressions; generally these marine beds are separated by continental deposits. Where Pleistocene marine units occur in such stratigraphic sequences, the oldest deposit is the lowest one and elevation does not have the same meaning as in a flight of staircase terraces. No local faulting has been mapped within the study area.

The present investigation was undertaken to evaluate the utility of the amino acid racemization method in resolving discrete time intervals of marine deposition in a high temperature environment such as found along the Vizcaino Peninsula (current mean annual temperature is about 21° C). Since samples from terraces of different elevations are available, the consistency of the aminostratigraphy using various geologic criteria can be evaluated, and the effective age limits at these high temperatures can be determined. Three apparent aminostratigraphic units have been found for the Bahia Asunción region and they generally conform to local stratigraphic control. Based upon kinetic modeling, it appears that the amino acid racemization dating method reaches its limit of usefulness in this area by approximately 300,000 years.

METHODS AND RESULTS

Ten localities (Figures 1 and 2) were sampled by one of us (L.O.) in 1977. Eighteen mollusk samples (of the genera *Tivela*, *Saxidomus*, and *Chione*) were analyzed from these sites. Ideally, more samples should be studied to improve the statistics of each aminostratigraphic group. Amino acid enantiomeric (D/L) ratio analyses were made by gas chromatographic

derivative procedures used (Table 1), although a slight conversion has been made (see WEHMILLER and EMERSON, 1980) for the comparison of leucine D/L values obtained by the different techniques. The results reported in Table 1 represent the mean values of peak height ratio determinations from at least two chromatograms of each sample derivative. Precision of multiple sample analyses of well-preserved shells is usually between 5% and 10%, depending on the amino acid.

DISCUSSION

The mollusks examined in this study generally had relative intrageneric racemization rates similar to those observed by LAJOIE *et al.* (1980): phenylalanine > alanine > proline > leucine > glutamic acid > valine. As the D/L values increased in the samples studied, these intrageneric trends became less pronounced and sometimes were inverted in the most extensively racemized samples. Valine, leucine, and glutamic acid were the only amino

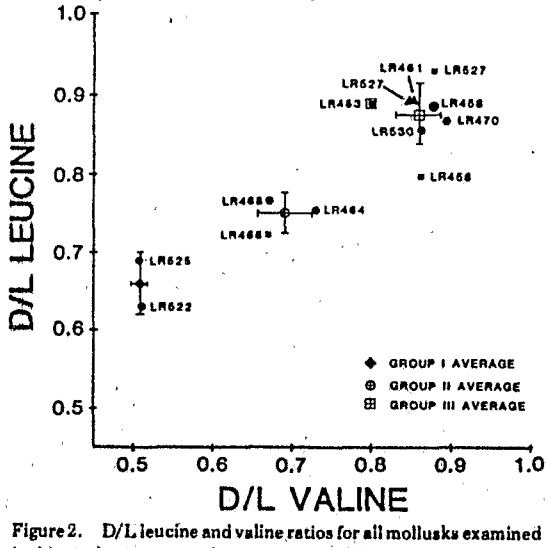


Figure 2. D/L leucine and valine ratios for all mollusks examined in this study. Average values are reported for multiple samples of the same species from the same locality. D/L leucine ratios for

acids that were not racemic in the oldest mollusks. Valine and leucine form three apparent clusters of D/L data (Figure 2). Glutamic acid data are generally consistent with these clusters but are more variable because of the systematic differences in the results from the two analytical methods used (WEHMILLER, 1984). Alanine, proline, phenylalanine, and aspartic acid are all so extensively racemized (or analytically variable, as in the case of aspartic acid) that they are of little value in aminostratigraphic applications at these temperatures.

The three well-resolved groups of leucine and

be directly comparable to *Tivela* or *Chione* results. Valine differentiates the three populations more clearly than leucine because of its slower rate of racemization.

The age represented by the lowest leucine-valine group in Figure 2 (Group I) is derived from the isochron shown in Figure 3 (modified from WEHMILLER, 1982). This isochron is drawn for one amino acid, leucine, and one genus, *Protothaca*, which is kinetically equivalent to *Chione* and *Tivela*, and it represents the D/L data for the "early Stage 5," 120,000 year calibration localities between cen-

1982 and elsewhere) for a given latitude and temperature range. Figure 3 can be used to determine if a D/L ratio group could be equivalent to 95,000 or 120,000 years by making the assumptions: (1) latitudinal gradients of effective temperature can be smoothly interpolated between calibration sites; and (2) effective temperatures for a local area can be considered equal (or nearly so) for samples of different ages but with the same present temperature. Other pairs of isochrons can be drawn for the probable range of D/L data that could be observed for samples deposited during Stages 3, 7, 9, etc. of the marine isotope record by using the ages proposed by SHACKLETON and OPDYKE (1973) for these stages. However, the use of the theoretical isochrons for age assignments greater than 120,000 years in Baja California, Mexico is currently limited because the leucine kinetic model has not yet been tested sufficiently in this region of relatively high mean annual temperatures.

The Group I leucine data fall in the early Stage 5 portion of the isochron band shown in Figure 3. Therefore, those data are interpreted to represent a time of deposition approximately 120,000 years before present. Other Baja California sites that fall within the same region of the 120,000 year isochron are those at Camalu (VALENTINE, 1980), Punta Santa Rosalillita (WOODS, 1980), Bahia Tortugas (EMERSON *et al*, 1980), and Magdalena Bay (WEHMILLER and EMERSON, 1980).

The Group II leucine data plot above all the Baja results thought to represent any portion of Stage 5. Because of the lack of calibration sites older than 120,000 years and the difficulty of extrapolating the kinetic model to D/L leucine values as high as those in either Group II or Group III, we can only tentatively propose an age of approximately 200,000 years (Stage 7) for the samples representing Group II. Elevation and morphologic characteristics of the Group II terrace suggest that it is older than the Group I terrace by a whole glacial/interglacial cycle (ORTLIEB, 1978, 1979a, 1979b). Because the valine and glutamic acid D/L values for the Group II samples are significantly greater than those observed in nearby Stage 5 samples (WEHMILLER and EMERSON, 1980; EMERSON *et al*, 1981), the Group II terrace must represent a pre-120,000 event rather than Groups I and II representing a late and early Stage 5 terrace complex.

Group III plots above the Group II average and can probably be assigned to either Stage 9 or Stage

Table 1. *Amino acid enantiometric (D/L) ratios from* Tivela, Saxidomus, *and* Chione *from Bahia Asunción, Baja California Sur, Mexico.*

Locality	Elevation (m)	Genus, sp.	Sample no.	Method*	LEU	GLU	PRO	VAL	ALA	PHE	ASP	Group
LR522	3	*Tivela* s.	78-67	B	0.630	0.620	0.740	0.510	0.910	0.810	—	I
LR525	12	..	80-2	B	0.689	0.626	0.765	0.506	0.835	0.818	0.679	I
LR468	6	..	80-25	P	0.768	0.751	nd**	0.672	1.030	0.689	0.660	II
LR468	6	*Sax.* n.	80-1	B	0.757	0.782	0.909	0.678	0.822	0.882	0.688	II
LR464	11	*Tivela* s.	78-52	B	0.765	0.700	0.843	0.730	0.980	0.940	—	II
LR458	10	..	78-60	B	0.880	—	0.870	0.900	1.070	0.960	—	III
LR458	10	..	79-20	B	0.893	0.991	0.953	0.857	0.856	0.992	0.807	III
LR458	10	*Sax* n.	79-21	B	0.828	0.973	0.900	0.862	0.831	0.973	0.798	III
LR461	12	*Chione* sp.	80-47	P	0.893	0.857	nd	0.891	0.898	0.748	—	III
LR461	12	..	80-48	P	0.894	0.825	nd	0.876	—	0.980	0.716	III
LR461	12	..	80-50	B	0.894	0.883	0.916	0.791	0.916	0.960	0.793	III
LR527	12-15	..	80-41	P	0.934	0.850	nd	0.907	1.020	0.784	0.748	III
LR527	12-15	..	80-55	P	0.853	0.773	nd	0.801	0.987	0.963	0.721	III
LR527	12-15	*Sax.* n.	80-40	P	0.958	0.798	nd	0.879	1.014	0.833	0.705	III
LR530	15	*Tivela* s.	80-59	B	0.858	0.928	0.940	0.862	0.995	0.989	0.861	III
LR470	30	..	78-56	B	0.870	0.870	0.910	0.895	0.960	1.000	—	III
LR453	32	*Sax.* n.	80-8	B	0.873	0.795	0.911	0.723	0.954	0.899	0.760	III
LR453	32	..	80-9	P	0.963	0.875	nd	0.882	1.000	0.852	0.805	III

*Methods: B—(+)-2-butyl derivative
P—isopropyl derivative; D/L leucine values listed have been converted to equivalent butanol leucine values using the

U of the marine isotope record (Figure 3). There- from the higher 200,000-year deposit or both

be controversial when used for U-series dating. Amino acid racemization dating provides internally consistent results which, in most cases, are in agree-

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aminoácidos, leunina y valina, muestran demasiada variabilidad como para ser usados para determinar los diferentes grupos de edades entre las localidades de las terrazas. Cuando estos grupos son comparables con evidencias aminoestratigráficas o geomórficas, son generalmente consistentes con el control geológico disponible. Las edades estimadas para los tres grupos aminoestratigráficos reconocidos es este estudio son aproximadamente 120.000, 200.000 y 300.000 años.--*Miguel A. Losada, Universidad de Santander, Santander, Spain*

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