Aminostratigraphy of Quaternary shorelines in the Mediterranean basin

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ABSTRACT

The age and correlation of shorelines around the Mediterranean basin have been addressed by analyzing the extent of isoleucine epimerization (aIle/Ile ratio) in protein preserved in molluscan fossils collected from raised marine deposits. The taxodont genera *Glycymeris* and *Arca* were selected as the primary taxa for this study because of their simple shell structure, reproducible aIle/Ile ratios, and ubiquitous occurrence. Direct comparison of aIle/Ile ratios in associated mollusks allows correlation of disjunct marine deposits and relative dating of sequential marine units in nearby areas that have similar thermal histories. The thermal gradient across the Mediterranean basin is, however, sufficiently high that shells from isochronous shorelines have significantly higher ratios at warmer than at cooler localities. Absolute dating, primarily U-series dates on corals directly associated with molluscan samples, provides an independent calibration of the amino acid data and compensates for dissimilar thermal histories.

AIle/Ile ratios in shells from 46 marine units cluster into 5 discrete groups (C, E, F, G, and K) that are related to positive sea-level events (interglacials/interstadials) associated with odd-numbered deep-sea isotopic stages. The most complete sequences are in southern Italy, where group C ratios in *Glycymeris* that average 0.30 are associated with the Neotyrrhenian, a post–last-interglacial (late stage 5), high–sea-level event. Group E ratios (0.38) are associated with classical Eutyrrhenian deposits from which four U-series coral dates (126 ± 7 ka) substantiate the correlation to isotope substage 5e. Group F ratios (0.50) are associated with U-series coral and mollusk dates between 200 and 300 ka; the deposits are tentatively correlated with stage 7. Deposits that have group G ratios (0.58) are correlated with stage 9. Shells from lower Pleistocene marine deposits that have ratios between 1.0 and 1.2 (group K) constrain the ages of the younger groups. An exponential decrease in the epimerization rate inhibits resolution of the older events. AIle/Ile ratios in last-interglacial deposits are similar in the northern and central region of the study area but increase sharply in southern Sicily, North Africa, and Crete, similar to the modern thermal gradient.

A lacuna between group G and group K is similar to gaps identified in California and Alaska, suggesting generally lower interglacial sea levels between stage 11 and sometime before the Brunhes/Matuyama boundary.

INTRODUCTION

The Quaternary raised shorelines of the Mediterranean basin have been objects of study for almost 80 yr (Hey, 1971, 1978). Early Mediterranean shoreline studies included those of Déperét (1906, 1918), DeLamothe (1911), and Gignoux (1913), who collectively concluded that terraces were cut during high stands of sea level against stable coastlines during the Quaternary. After 1948, when the Calabrian was added to the Pleistocene, the time-stratigraphic units of (oldest to youngest) Calabrian, Sicilian, Milazzian, Tyrrhenian, and Versilian were the major divisions of Quaternary marine events. These divisions were based on faunal changes as well as on the elevation of deposits and were considered interglacial counterparts of the Alpine glacial chronology. Attempts to correlate by altitude (Déperét, 1918; Zeuner, 1959), however, were hampered by local and regional tectonics and by the inherent complexity of the eustatic record. Largely on the basis of the rela-

tive abundance of a tropical molluscan fauna, the middle and late Pleistocene were later subdivided into the Paleotyrrhenian or T I, the Eutyrrhenian or T II, and the Neotyrrhenian cr T III (Bonifay and Mars, 1959).

The importance of the Senegalese (or *Strombus*) community as guide fossils was recognized early on by Gignoux (1913) and Issel (1914). This community, now common in coastal areas of West Africa, is thought to have "immigrated" into the Mediterranean during the middle and/or late Pleistocene. Important taxa in this fauna include *Strombus bubonius* (or *Strombus latus*), *Conus testudinarius, Natica lacetea, Natica turtoni,* and *Cantharus viverratus*.

Butzer and Cuerda (1962a, 1962b, and in press) deduced further complexity in the sea-level record from stratigraphic and paleontologic evidence on Mallorca and introduced the notion that strandlines may be reoccupied several times during high-frequency sea-level oscillations. In an attempt to attack the problem directly, Stearns and Thurber (1965, 1967) applied U-series dating of mollusks to the strandline deposits, although Kaufman and others (1971) later pointed out that there are serious inadequacies in U-series dating of mollusks. Renewed efforts by Bernat and others (1978, in press, unpub. data) Hoang and others (1978), and Radtke and others (1981, 1982) using U-series and electron spin resonance techniques to date mollusks still lack reliable independent means of confirmation.

The efforts of this study are aimed at filling the gap of a reliable independent geochronological method to date strandline deposits. In order to accomplish this goal, fossil mollusks and, in some cases, corals were collected from 46 marine deposits fronting the basin (Fig. 1) and were then analyzed for the extent of isoleucine epimerization (mollusks) and U-series disequilibrium (corals).
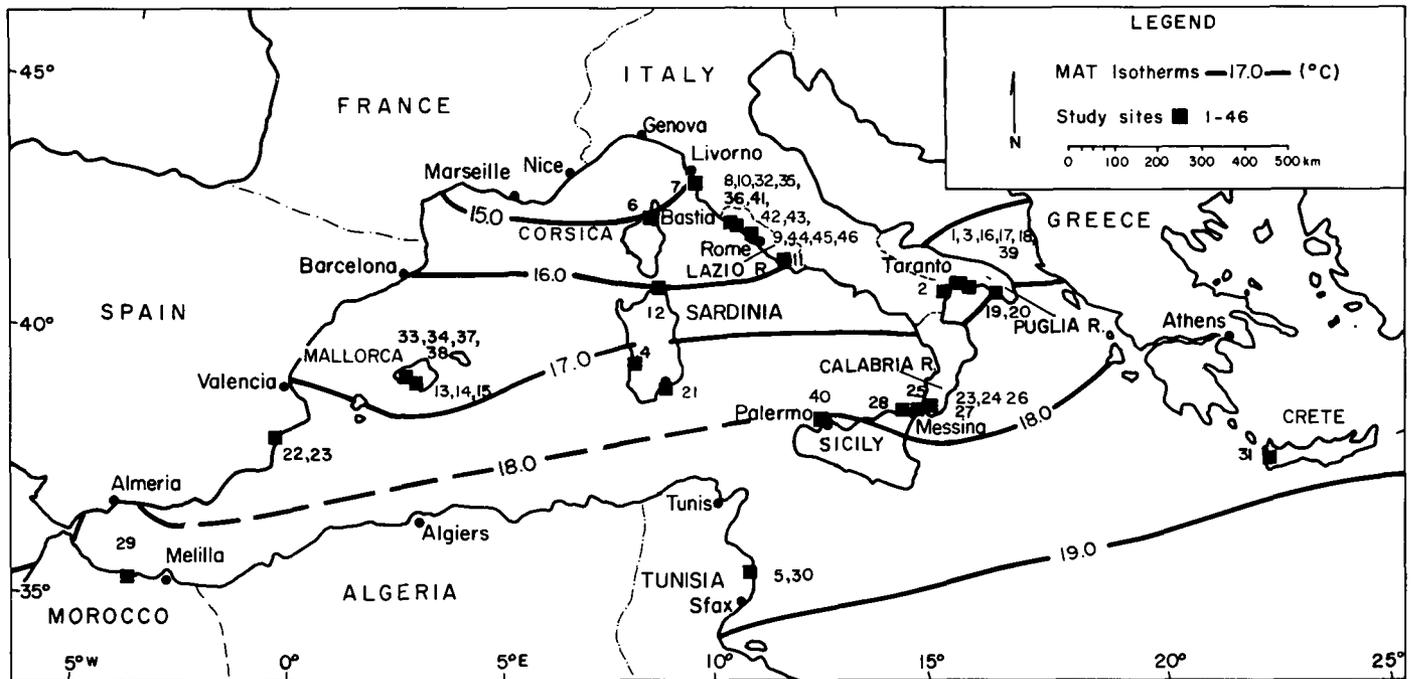
Figure 1. Location map of the western Mediterranean showing isotherms of present-day mean annual temperatures and the location of study sites. Locality numbers are identified in Table 2. (Data from Wernstedt, 1972.)

AMINO ACID GEOCHRONOLOGY

Amino acid geochronology can be used to provide relative ages of fossiliferous deposits or can be calibrated using other dating systems to provide absolute-age estimates. Amino acid enantiomeric ratios have been used to subdivide and correlate emergent marine deposits on the Pacific (Lajoie and others, 1980; Kennedy and others, 1982; Wehmiller and others, 1977) and the Atlantic (Belknap, 1979; Wehmiller and Belknap, 1982) coasts of North America, in the Canadian Arctic (Miller and others, 1977), in the British Isles (Miller and others, 1979), in Norway (Miller and others, 1983), and in the Mediterranean (Hearty and others, 1984). The method relies on the slow interconversion of L-amino acids, within the indigenous protein preserved in the carbonate matrix of molluscan shells, to increasing proportions of their respective D-configurations until an equilibrium mixture of D- and L-amino acids is attained.

In this study, we rely on the ratio of D-alloisoleucine to L-isoleucine (aIle/Ile) principally in the pelecypod genera *Glycymeris* and *Arca.* These genera were selected from a study of more than 20 taxa because of their well defined shell structure, frequency of occurrence, and inter- and intradeposit consistency of amino acid ratios, although careful sampling is required. AIle/Ile ratios in 8 functional and structural parts from a single *Glycymeris* shell varied
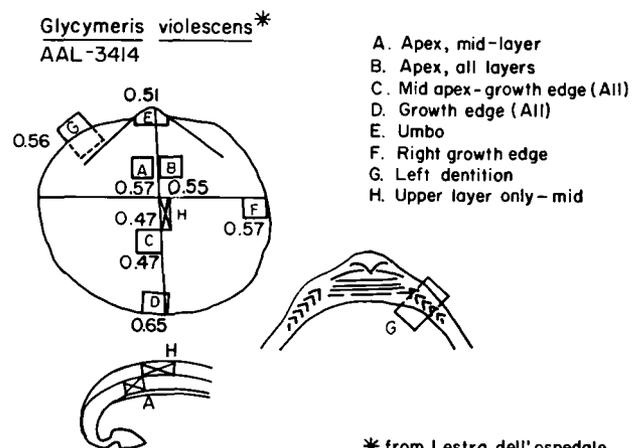
by 30% (Fig. 2). Because of the intrashell variability in aIle/Ile ratios, it is strongly recommended that sampling of *Glycymeris* be restricted to an interior structural layer which is isolated from the apex region of the shell (location A in Fig. 2). The same area in *Arca* shells was sampled.

Amino acids were extracted from an acid-cleaned fragment of each sample by decalcification in cold 7N HCl and subsequent hydrolysis in 6N HCl under N_2 at 110 °C for 22 hr. Amino acid separation was accomplished by automated ion-exchange high-pressure liquid chromatography with fluorescence detection and electronic peak integration. All amino acid data presented in this paper are a measure of the peak height aIle/Ile ratio in the total acid hydrolysate. From nearly all deposits, three or more individual shells (and in some cases, as many as 22) were analyzed.

The rate of isoleucine epimerization is temperature dependent; hence, measured aIle/Ile ratios can be directly compared only if samples have experienced similar postdepositional thermal histories. High-amplitude surface heating cycles may significantly accelerate the epimerization rate in shells contained in the upper 0.5 m of a deposit, resulting in an aIle/Ile

Figure 2. Intrashell variation of aIle/Ile ratios in a single *Glycymeris* shell from Lestra dell'Ospedale. For this study, all *Glycymeris* samples were taken from location A.

Glycymeris violescens*
AAL-3414

A. Apex, mid-layer
B. Apex, all layers
C. Mid apex-growth edge (All)
D. Growth edge (All)
E. Umbo
F. Right growth edge
G. Left dentition
H. Upper layer only-mid

*from Lestra dell'ospedale

(Site 41)

ratio higher than that in more deeply buried shells of the same age. To reduce this effect, sampling was generally restricted to recently cut natural and/or artificial exposures at depths of 1 m or more below the upper contact of the shell-bearing unit.

The epimerization rate is also taxonomically dependent; hence, the measured aIle/Ile ratios in different genera of the same age may differ considerably. No significant differences were noted between species of *Glycymeris (violescens, glycymeris,* and *bimaculata*) and *Arca (noae, tetragona, lactea,* and *barbatia*), the principal taxa used in this study (unpub. data from 15 sites; five having *Arca* spp., ten having *Glycymeris* spp.), but a consistent intergeneric difference in epimerization rate is apparent. The ratio of aIle/Ile in *Glycymeris* relative to the same ratio in coexisting *Arca* from 13 sites has been calculated to be 1.31 ± 0.07. This ratio, termed the "*Gly/Arca* index," can be used to correlate sites containing only *Glycymeris* with nearby sites containing only *Arca*. A *Glycymeris/Astralium* index of 0.71 ± 0.05 (3) (that is, for 3 shells analyzed) similarly allows conversion to *Glycymeris* aIle/Ile ratios if only *Astralium* is present.

TERMINOLOGY

Because aIle/Ile ratios cannot be directly compared across a thermally varied region, we have developed a regional chronostratigraphy from local aminostratigraphies (Miller and Hare, 1980) or aminozones (Nelson, 1978) that compare aIle/Ile ratios from nearby stratigraphic sequences that have uniform thermal histories. For regional correlations, we define *aminogroup* as representing a collection of equal-aged deposits, that due to dissimilar thermal histories, yield aIle/Ile ratios that vary relative to the long-term regional thermal gradient. Uranium-series ages (Table 1) are used to calibrate sites across climatic boundaries and are the basis for aminogroup identification.

Aminogroups of increasing age are identified in this study by capital letters "C," "E," "F," "G," and "K." Numerical notations (1, 2, 3, and so on) attached to letter identifiers (for example, E1, E2, and so on) represent bio- or lithostratigraphic facies subdivisions of aminogroups that show no significant age difference. The range of expected values of aIle/Ile ratios within a marine unit is partly a function of the duration of the marine event and must be considered as a significant portion of the intragroup variance. The mean *Glycymeris* and *Arca* value ($\bar{x}$), the standard deviation (σ) and the number of shells analyzed (n) will be presented in the format

TABLE 1. ANALYTICAL DATA AND CALCULATED URANIUM-SERIES AGES OF FOSSIL CORALS FROM MEDITERRANEAN SHORELINES

Location	Sample*	Uranium (ppm)	Activity ratios			Uranium-series age (k.a.)[†]
			$^{234}U/^{238}U$	$^{230}Th/^{232}U$	$^{230}Th/^{234}U$	
Mallorca						
Site 13 Son Grauet	H-C-3[§]	3.00 ± 0.05	1.070 ± 0.016	110 ± 44	0.702 ± 0.021	129 ± 7
Sardinia						
Site 21 Calamosca	S-C-4[§]	3.67 ± 0.07	1.112 ± 0.018	80 ± 18	0.735 ± 0.017SA	138 ± 7
Tunisia						
Site 30 Monastir	S-C-1[§]	3.48 ± 0.07	1.104 ± 0.017	204 ± 50	0.697 ± 0.021	126 ± 7[§§]
Southern Italy						
Site 1 Il Fronte, Mare Piccolo	H-C-1A[§,††]	4.20 ± 0.06	1.20 ± 0.017	217 ± 65	0.672 ± 0.020	117 ± 7
	H-C-1B[§,††]	4.14 ± 0.06	1.097 ± 0.016	82 ± 33	0.703 ± 0.021	128 ± 7
	H-C-2[§]	3.76 ± 0.06	1.114 ± 0.017	83 ± 33	0.682 ± 0.020	121 ± 7
Sicily						
Site 40 Tomasso Natale	S-C-3**	4.00 ± 0.06	1.074 ± 0.016	245 ± 100	0.918 ± 0.028	250 ± 30

Notes: Sites 1 and 13 collected by P. J. Hearty. Site 21 collected by C. Spano and A. Ulzega. Site 40 collected by G. Ruggieri. Site 30 collected by R. Paskoff. All analyses made by B. Szabo of the U.S. Geological Survey, Denver, Colorado.
*All coral samples have <3% calcite except sample S-C-4, which has 9% calcite.
[†]Calculated using half-lives of ^{230}Th and ^{234}U of 75,200 and 244,000, respectively.
[§]*Cladocora* sp.
**Astroides* sp.
[††]Portions of the same sample.
[§§]^{231}Pa date is determined to be 124,000 (+59,000, -28,000) yr; concordant with ^{230}Th date of 126,000 ± 7,000 yr within limits of experimental error.

"0.37 ± 0.02 (15)" in this paper. The results from all sites are summarized in Table 2.

ABSOLUTE AGE CALIBRATION

Mediterranean sites span a considerable temperature range (Fig. 1); hence, aIle/Ile ratios cannot be directly compared across the region. Independent age calibration is provided by uranium-series dates for solitary and branching corals from a suite of sites throughout the basin. Corals were collected from several sites (P. J. Hearty), and other corals were sent from deposits in Sardinia, Tunisia, and Sicily by cooperating scientists.

Unrecrystallized fossil corals are reliable materials for uranium-series dating because, unlike mollusks, they incorporate uranium into their carbonate exoskeletons during their life cycles (Ku, 1976). The measurement of the extent of the trend toward radioactive equilibrium of ^{230}Th with respect to ^{234}U permits the calculation of the time elapsed since the deposition of the fossil. The concentration of the uranium and the activity ratios of $^{234}U/^{238}U$, $^{230}Th/^{232}Th$, and $^{230}Th/^{234}U$ were determined by alpha spectrometry using analytical techniques similar to

those described by Szabo and Rosholt (1969). The relative abundances of calcite and aragonite were determined by X-ray diffraction. Limitations of the X-ray technique do not permit more accurate determination of the calcite content than <3% (trace). Sample S-C-4 contains ~9% calcite, but in light of amino acid data and bio- and lithostratigraphic considerations, the age of 138 ± 7 ka is within the acceptable age range of the deposit. Chemical and isotopic analyses of fossil corals, and the calculated uranium-series ages, are shown in Table 1. In all of the samples, the $^{230}Th/^{232}Th$ activity ratio is high, generally between 80 and 245, indicating little initial ^{230}Th. The average uranium-series age of the 6 coral samples from last-interglacial strandline deposits is 127 ± 4 ka, whereas a single date for a coral sample from the older Tomasso Natale locality (site 40) in Sicily (sample S-C-3) is 250 ± 30 ka.

LOCAL AMINOSTRATIGRAPHIES

Puglia Region, Southeast Italy

One of the most complete records of marine transgressions in the Mediterranean basin is pre-

TABLE 2. AMINO ACID DATA, CURRENT SITE TEMPERATURE, AND FAUNAL NOTES

Site no./*Locality	MAT (°C)	Fauna	Glycymeris sp. x̄ ± σ (n)	Arca sp. x̄ ± σ(n)
Aminogroup C				
1. Il Fronte, IT	16.9	··	[0.25]	0.19 ± (1)
2. Piano San Nicola, IT	16.9	··	0.30 ± 0.02 (7)	··
3. Torre Casteluccia, IT	16.9	··	0.31 (1)	0.22 ± 0.02 (5)
4. San Giovani di Sinnis, SA	17.2	··	0.32 ± 0.01 (2)	0.34 (1)ʳ
5. Chebba Formation, TU	18.5	··	0.38 ± 0.02 (3)	··
Aminogroup E				
6. St. Florent, Arbitro, CO	14.7	··	[0.33]	0.25 ± 0.01 (6)
7. Buca dei Corvi, IT	15.2	S	0.35 ± 0.03 (15)	··
8. Cerveteri, IT	15.8	··	0.41 ± 0.01 (4)	0.27 ± 0.00 (1)
9. Cle. Olivastro, IT	15.8	··	0.37 (1)	··
10. Km 103, IT	15.8	··	0.40 ± 0.02 (2)	0.31 (1)
32. Pian di Spille, IT	15.8	S	[0.40]	0.32 ± 0.02 (4)
11. Latina Latium, IT	16.0	S, Sb	0.38 ± 0.04 (7)	0.30 ± 0.02 (3)
12. Sta. Teresa di Galluria, SA	16.0	··	0.36 ± 0.03 (3)	··
13. Son Grauet, MA	16.8	S, Sb	0.37 ± 0.03 (6)	0.28 ± 0.03 (5)
14. Cala Pi, MA	16.8	S, Sb	[0.35]	0.27 ± 0.01 (2)
15. Torre S'Estalella, MA	16.8	S, Sb	[0.44]	0.34 ± 0.02 (2)ʰ
33. Campo de Tiro "Neo," MA	16.8	S, Sb	0.42 ± 0.02 (6)	··
34. Cova de sa Gata, MA	16.8	··	0.44 ± 0.02 (3)	··
1. Il Fronte, Mare Piccolo, IT Site R	16.9	S, Sb	0.37 ± 0.02 (10)	0.27 ± 0.05 (22)
16. Site L, Mare Piccolo, IT (Massa San Pietro)	16.9	S, Sb	0.38 ± 0.01 (3)	··
17. Site S, Mare Piccolo, IT	16.9	S, Sb	0.35 (1)	0.29 (1)
18. Punta Penna, Mare Piccolo, IT	16.9	S, Sb	0.36 ± 0.01 (10)	0.29 ± 0.03 (2)
3. Torre Casteluccia, IT	16.9	··	0.39 (1)	0.26 (1)
19. Gallipoli, IT	17.2	S, Sb	0.41 ± 0.04 (12)	0.31 ± 0.03 (2)
20. Torre San Giovanni, IT	17.2	S, Sb	0.38 ± 0.02 (4)	··
21. Calamosca area, SA	17.5	S, Sb	0.40 ± 0.01 (6)	0.32 ± 0.02 (16)
22. La Caleta (E and W), SP	17.5	S, Sb	0.40 ± 0.02 (6)	0.31 (1)
23. La Marina, SP	17.8	S, Sb	0.40 (1) [0.42]	0.32 ± 0.01 (4)
24. Capo Pelloro, SI	17.8	S, Sb	0.41 ± (1)	··
25. Archi South, IT	17.8	··	0.40 ± 0.03 (10)	··
26. Ravagnese, IT	17.8	S, Sb	0.45 ± 0.01 (2)	0.32 (1)
27. Bovetto, IT	17.8	S, Sb	0.42 ± 0.04 (12)	··
28. Capo Milazzo, SI	17.8	S	0.41 ± 0.03 (2)	0.33 ± 0.04 (6)
29. Al Hoceima, MO	18.3	Sb	0.46 ± 0.02 (3)	··
30. Rejiche Formation, TU	18.5	S, Sb	0.49 ± 0.04 (20)	0.37 ± 0.02 (4)
31. Moni Krisokalitisas, CR	18.8	S, Sb	0.48 ± 0.04 (2)	0.35 (1)
Aminogroup F				
35. Cannelle, IT	15.8	··	0.47 ± 0.02 (5)	··
36. San Augustino Nuovo, IT	15.8	··	0.52 ± 0.01 (8)	··
37. Campo de Tiro "A," MA (main)	16.8	S, Sb	[0.51]	0.39 ± 0.04 (6)
38. Campo de tiro "B," MA (Cartnege)	16.8	S, Sb	[0.56]	0.43 ± 0.04 (8)
33. Campo de Tiro "Neo," MA	16.8	S, Sb	0.51 ± 0.01 (16)ʳ	0.40 ± 0.03 (4)ʳ
39. Carelli, IT	16.9	··	0.48 ± 0.02 (7)	··
40. Tomasso Natale, SI	18.0	S	[0.55]	0.42 ± 0.02 (3)
Aminogroup G				
41. Lestra dell 'Ospedale, IT	15.8	··	0.57 ± 0.03 (15)	0.51 ± 0.01 (3)
42. Tarquinia, IT	15.8	··	0.56 ± 0.02 (4)	··
43. San Pantaleo, IT	15.8	··	0.59 ± 0.04 (11)	··
10. Km 103, IT	15.8	··	0.56 ± 0.03 (3)	··
11. Latina Latium, IT	16.0	··	0.61 ± 0.03 (12)	··
3. T. Casteluccia, IT	16.9	··	[0.64]ᵃ	··
23. La Marina, SP	17.8	··	0.66 ± 0.04 (6)	··
Aminogroup K				
44. Valle de Sargia, IT	15.8	··	1.01 ± 0.10 (3)	··
45. Ponte Galleria Fm., IT	15.8	··	1.09 ± 0.12 (9)	··
46. Monte Mario Fm., IT	15.8	··	1.11 ± 0.04 (3)	··

Abbreviations:
MA = Mallorca
SP = Spain
IT = Italy
SA = Sardinia
CO = Corsica
SI = Sicily
TU = Tunisia
MO = Morocco
CR = Crete

r = reworking suspected
h = shallow depth of burial; heating suspected
a = converted from Gly/Astralium index = 0.71
S = Senegalese fauna
Sb = *Strombus bubonius*

Note: alle/Ile ratios are given as mean (x̄), standard deviation (σ), and number of shells analyzed (n). *Glycermeris* ratios in brackets are derived from *Arca* ratios converted to *Glycermeris*-equivalent ratios using the Gly/Arca index (1.31).

*Site references available upon request from P. J. Hearty.

served in the Puglia region of southeast Italy. The stratigraphy and paleontology of these shoreline deposits is well documented (Gignoux, 1913; Gigout, 1960a, 1960b, 1960c; Cotecchia and others, 1969); U-series coral dates for the transgressions are discussed by Dai Pra and Stearns (1977), and a detailed amino acid study in the area is presented by Hearty and Dai Pra (in press).

The Puglia region serves as a "type area" for an amino acid study in the Mediterranean basin because of the completeness of the sedimentary and fossil record both in the quiet embayment of Mare Piccolo and on the open coastline along the south coast of the Salentine Peninsula. The composite stratigraphic section synthesized from seven sections along the peninsula is presented in Table 3, as well as amino acid, U-series data and a probable correlation of the aminostratigraphy with the deep-sea record. Representatives of aminogroups C, E, F, and G are present in the region; 3 U-series coral dates equate amino-group E (0.37) with an age of 122 ± 4 ka. Aminogroup F at Carelli (site 39) at 0.48 is associated with a coral date of 290 ± 50 ka, whereas aminogroup G (0.64) at Torre Caste-luccia (site 3) is >300 ka (Dai Pra and Stearns, 1977).

Lazio Region, Central Italy

An extensive coastal plain north of Rome supports Pliocene to upper Pleistocene marine deposits that have stimulated numerous attempts to develop a comprehensive sea-level chronol-ogy (Bonadonna, 1967a, 1967b; Bonadonna and Bigazzi, 1970; Ambrosetti and Bonadonna, 1967; Conato and others, 1981; Conato and Dai Pra, 1980; Dai Pra, 1978; Ambrosetti and others, 1972, 1981). Our efforts were directed to-ward amino acid analyses of shells from key deposits to determine if discrete marine events could be distinguished and to extend the result-ant aminostratigraphy to fossiliferous sites of unknown age. Morphological shorelines are lacking, although several marine episodes can be distinguished from the measured alle/Ile ratios in *Glycymeris* that cluster at 0.39 ± 0.02 (10), 0.50 ± 0.03 (13), 0.58 ± 0.02 (33), and 1.08 ± 0.05 (15). These average *Glycymeris* ratios are correlated to aminogroups E, F, and G in Puglia and to aminogroup K (not collected in Puglia).

Capo Milazzo, Sicily

Amino acid ratios and radiometric dating allow the correlation of marine deposits at Mil-azzo, Sicily (site 28) (of the Milazzian stage, Dépérét, 1918; DeLamothe, 1911), with *Strombus*-bearing deposits at Ravagnese (site 26) and Bovetto (site 27) in Reggio Calabria (Bonfiglio, 1972) and of these, in turn, with the well documented aminogroup E deposits at Mare Piccolo (P. J. Hearty and others, unpub. data).

The mean Milazzian *Glycymeris* alle/Ile ratio is 0.41 ± 0.03 (2), similar to the 0.42 ± 0.04 (12) aminogroup E ratio at Bovetto. The mean *Arca* ratio is 0.33 ± 0.04 (6) from Milazzo, resulting in a *Gly/Arca* index of 1.24. Reggio Calabria and Milazzo, separated by only 40 km, can be

TABLE 3. A COMPOSITE STRATIGRAPHIC SECTION FROM SEVEN SITES ON THE SALENTINE PENINSULA IN SOUTHEAST ITALY

Site no. (Table 2)	Description lithology and genesis	Glycymeris alle/Ile	U-series age (ka)	Isotopic stage	Aminozone	Litho- and biostratigraphic subdivisions
1	Estuarine marl; littoral	0.25*	· ·	5a/5c	C	C1
1, 3, 18	Marine/ terrestrial reddish calc. (derived); supra-littoral/sublittoral	0.30	· ·	5c/5e	C	C2
1, 3 16, 18 19, 20	White calcarenite with Strombus; sublittoral to littoral	0.37	122 ± 4 (3 samples)	late 5e	· ·	E1
1, 19	Yellow/grey silt, calcarenite with Ostrea beds; littoral	0.39*	· ·	mid-5e	E	E2
1	Derived clays and silts from Calabrian beds	0.35§	· ·	early 5e	· ·	E3
39	Calcarenite with Glycymeris; sublittoral to littoral	0.48	290 ± 50**	7-9	F	· ·
3	Detrital algal calcarenite; sublittoral	0.64†	>300**	9-11	G	· ·
1, 19, 20	Calabrian clays; shelf	· ·	· ·	· ·	K	· ·

Note: this table modified from Hearty and Dai Pra (in press).
*Gly/Arca index = 1.31.
†Gly/Astralium ratio = 0.71
§Gly/Dentalium ratio = 0.65.
**Dai Pra and Stearns, 1977.

considered under the same present climatic influence (~17.8 °C). Aminogroup E ratios for the same taxa in Puglia are lower [0.37 ± 0.02 (10) for Glycymeris and 0.27 ± 0.05 (22) for Arca] in keeping with the lower temperature in that area (16.9 °C).

We conclude that Milazzian stage deposits at the type locality are correlative with the last interglacial. Previous speculations about the age of these deposits range from Sicilian (Gignoux, 1913; Tongiorgi and Trevisan, 1953) to the Milazzian stage (Dépérét, 1918; DeLamothe, 1911) to Tyrrhenian II (Ottmann and Picard, 1954; Ruggieri and Sprovieri, 1977). The disagreement is probably related to the paucity of thermophilous taxa and the 60-m elevation of the deposits.

Mallorca

The combination of coastal marine and terrestrial deposits (littoral sands, eolianites, and red silts) on the seismically quiescent island of Mallorca (Fig. 1) provides a relatively complete record of sea-level events in the Mediterranean basin. These deposits have been largely deciphered by Butzer and Cuerda (1962a, 1962b) and Butzer (1975) at which time they intro-

duced the concept of marine-terrestrial hemicycles. Butzer (1983) has proposed a correlation between Mallorcan hemicycles and the deep-sea isotopic record. There remain certain ambiguities, however, regarding the absolute chronology of the marine deposits on Mallorca.

J. Cuerda and P. J. Hearty sampled numerous marine and terrestrial deposits on the shores fronting the Bay of Palma. Coral collected from the deposit at Son Grauet (site 13) yielded a U-series date of 129 ± 7 ka (Table 1) which provides a calibration to aminogroup E and isotope stage 5e. This deposit contains many of the notable Senegalese forms, including Strombus bubonius, Conus testudinarius, Polynices lacteus, and Cardita senegalensis (Cuerda, 1979) and other thermophilous taxa. Alle/Ile ratios in Glycymeris from this site are 0.37 ± 0.03 (6), and in Arca, 0.28 ± 0.03 (5). The Gly/Arca index is 1.32. Arca ratios from Cala Pi (site 14, Table 2) are similar to those from Son Grauet, supporting a correlation of the two aminogroup E sites.

The "classic Eutyrrhenian" sites at Campo de Tiro "A" (site 37) and "B" (site 38) were assigned a pre–stage 5 age by Butzer (1975) based on U-series mollusk dates (Stearns and Thurber, 1965, 1967). These sites yield aminogroup F

alle/Ile ratios in Arca averaging 0.41 ± 0.03 (14) (no Glycymeris). The Gly/Arca index predicts an alle/Ile ratio in Glycymeris of ~0.53, well above the measured aminogroup E Glycymeris ratio at Son Grauet of 0.37. The onlapping "Neotyrrhenian" deposits at Campo de Tiro (site 33) contain Glycymeris that have two populations of alle/Ile ratios, one at 0.42 ± 0.01 (6) and a second at 0.51 ± 0.01 (16). The mean ratio in Arca from the same deposit is 0.40 ± 0.03 (4), statistically similar to ratios in deposits at Campo de Tiro "A" and "B." The Gly/Arca index for the older populations (0.51/0.40) is 1.27. The interpretation of the Glycymeris that have ratios at 0.42 remains debatable but suggests an early stage 5 age like that for Son Grauet (0.37). Glycymeris from a Neotyrrhenian deposit at Cova de sa Gata (site 34, Cuerda, 1979) yielded alle/Ile ratios [0.44 ± 0.01 (3)] similar to those of the younger population in the Neotyrrhenian at Campo de Tiro. The concept of a "Neotyrrhenian marine transgression" originated at the Campo de Tiro site (Butzer and Cuerda, 1962a, 1962b) and a "post-Eutyrrhenian" (middle to late stage 5) age for such deposits in the Puglia region has been demonstrated from this survey, but we have yet to produce anything but Eutyrrhenian and/or older alle/Ile ratios from its type area at Campo de Tiro.

Crete

Many sites were investigated on the island of Crete (Fig. 2), but only Moni Krisokalitisas (site 31), on the western coast, produced Glycymeris and Arca shells. The only documented Strombus bubonius from Crete was found at the site among broken blocks associated with a platform at ~13.5 m above sea level. Alle/Ile ratios from Glycymeris that average 0.48 ± 0.04 (2) and one Arca of 0.35 from the Strombus layer are in accordance with the mean annual temperature (18.8 °C) and a last-interglacial age of the platform. The age and elevation of this level indicate little net uplift of the coast in the past 125 ka, supporting a style of intermittent uplift/subsidence as proposed by Pirazzoli and others (1981).

REGIONAL AMINO ACID RESULTS

The regional amino acid results from 46 sites on the shores fronting the Mediterranean (Table 2) are assigned to aminogroups according to the mean alle/Ile ratio, the apparent or known age, and the present mean annual temperature (MAT). The number of aminogroup E sites is sufficient to support a contour map of alle/Ile ratios (Fig. 3). Uranium-series coral dates of ~125 ka calibrate this surface at 6 localities
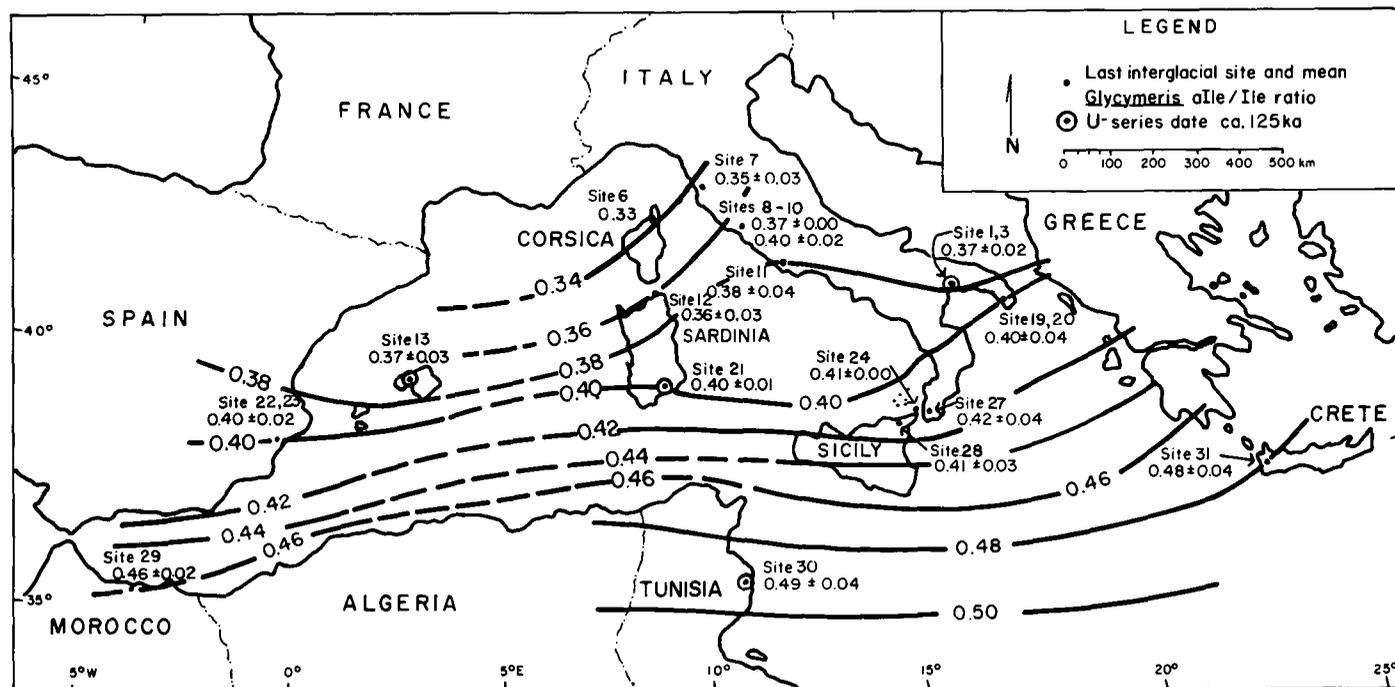
Figure 3. Map of contoured *Glycymeris* aIle/Ile ratios from last-interglacial deposits. Note similarity between trends of isopleths in this figure and those of isotherms in Figure 1.

(Table 1). Within this region, the amino-group E surface can be used as a reference datum by which aIle/Ile ratios from new sites can be placed in a relative chronostratigraphic framework.

Glycymeris and *Arca* ratios are consistent among known equal-aged sites having similar MAT's. For example, the aminogroup E sites (Tables 2 and 3) of Son Grauet, Mallorca (site 13, 16.8 °C) and Il Fronte, Mare Piccolo, Italy (site 1, 16.9 °C), both have U-series coral dates of ~125 ka (Table 1) and aIle/Ile ratios in *Glycymeris* of 0.37 ± 0.03 (6) and 0.37 ± 0.02 (10) and in *Arca* of 0.28 ± 0.03 (5) and 0.27 ± 0.05 (22), respectively. In contrast, the warmer sites of the Rejiche strandline in Tunisia (site 30, 18.5 °C) had coral dated at 126 ka and produced a *Glycymeris* mean ratio of 0.49 ± 0.04 (20) and an *Arca* mean of 0.37 ± 0.02 (4).

The temperature sensitivity of the isoleucine epimerization reaction can be demonstrated by plotting the aIle/Ile ratios at aminogroup E localities against the site MAT's (Fig. 4, shaded portion). This relationship can be used to predict the expected *Glycymeris* aIle/Ile ratio for a last-interglacial site of a specific temperature, but the curve cannot be extrapolated more than a degree or two beyond the range of temperatures controlled by the data.

The lack of absolute dates from sites older and younger than aminogroup E sites does not permit such effective calibration. AIle/Ile versus

MAT plots for older and younger sites, however, produce gradients parallel to that of aminogroup E (Fig. 4) suggesting a similar thermal history across the basin and supporting the relative age interpretation of the deposits. This interpretation is also supported by some U-series coral dates, stratigraphy, and paleontology

ABSOLUTE AGE OF THE AMINOGROUPS

We have established five discrete amino-groups in a relative chronology from widely scattered deposits related to intervals of high sea level during the past 1 m.y. We now attempt to establish an absolute chronology and a correlation with $\delta^{18}O$ core stages of the deep-sea stratigraphy.

Our primary calibration relies on the 6 U-series coral ages equating aminogroup E with core stage 5e and a marine transgression ~125 ka B.P. A linear kinetic model can be used to interpolate the age of aminogroup C. The lack of absolute ages and the uncertainties in the thermal history, however, preclude the precise dating of this event (or events). Our best estimate from the amino acid data is 90 ± 20 ka.

Amino acid data from aminogroup F indicate that the age of this marine event is greater than that of the last interglacial. Two U-series coral ages of 250 ± 30 (Table 1) and 290 ± 50 ka (Dai Pra and Stearns, 1977) from the amino-

group F sites of Tomasso Natale (site 40) and Carelli (site 39) support this interpretation and correlate the aminogroup F transgression with stage 7 or with stage 9. There are no amino-group F sites that have U-series ages of ~125 ka. Aminogroup F is positively correlated with a late middle Pleistocene event.

Amino acid ratios from the older aminogroup G suggest a correlation with an interglacial immediately preceding aminogroup F. A single U-series coral age of >300 ka has been determined for an aminogroup G site at Torre Casteluccia (site 3; Dai Pra and Stearns, 1977). Aminogroup K sites are associated with K/Ar dates generally between 820 ka and 1.3 m.y. B.P. (Nicoletti, 1969; Everden and Curtis, 1965).

The epimerization history for *Glycymeris* is reconstructed for the past 1.3 m.y. from mean aminogroup values and corresponding age estimates from sites having MAT's between 15.5 and 16.9 °C (Fig. 5). Aminogroup ages are correlated with warm intervals and isotopic events interpreted from foraminiferal assemblages (Cita and others, 1973) in a Tyrrhenian Sea core. Curve 1 best satisfies the data and is, thus, preferred. Curve 2 would require an *increase* in epimerization rate at 0.60 to connect with the early Pleistocene "window" outlined by the aminogroup K data and associated independent dates. Pyrolysis experiments on *Glycymeris* (P. J. Hearty, unpub. data) have shown that the epimerization rate is exponentially *de-*
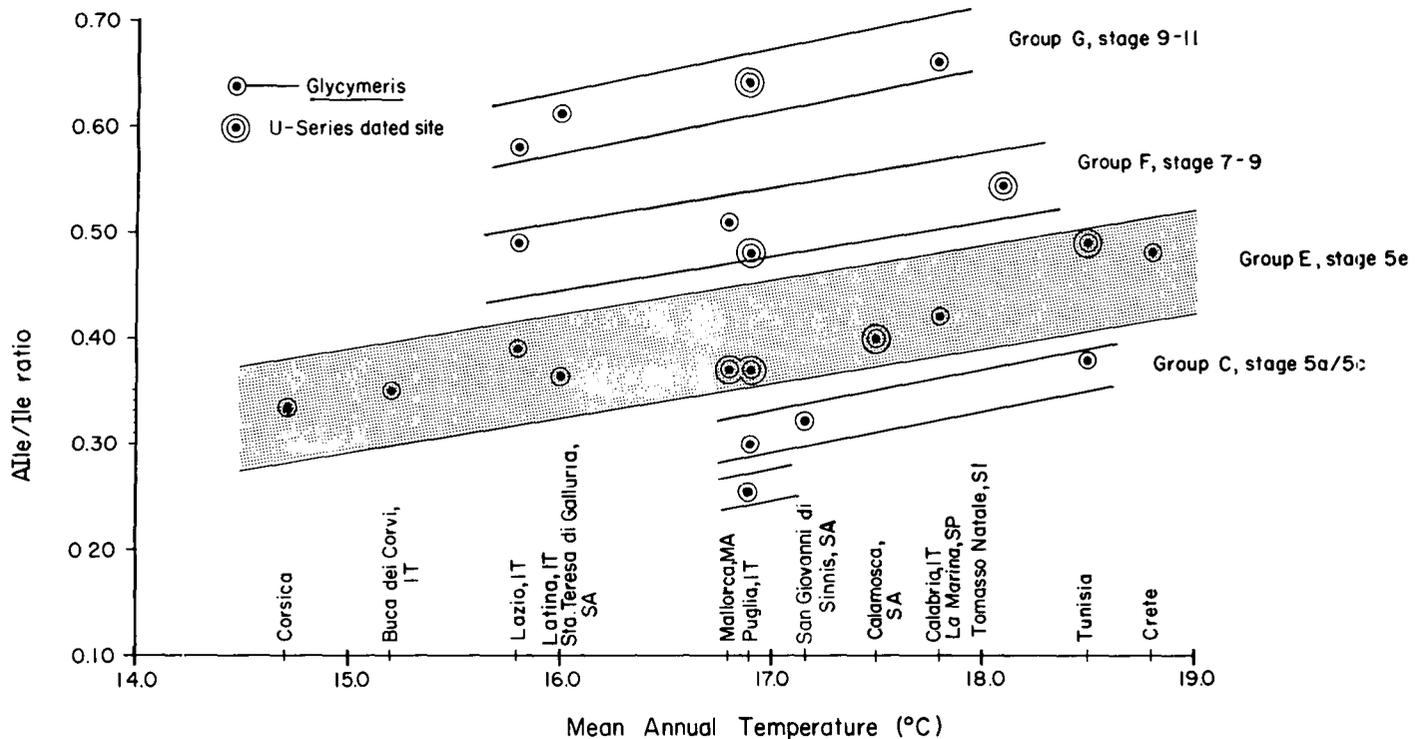
Figure 4. Plot of mean alle/Ile ratios in *Glycymeris* by group against present-day mean annual temperatures. The trend of increasing alle/Ile ratios with temperature reflects the control of the temperature on the epimerization rate.

creasing during this interval. From these data, it is certain that aminogroup G is no greater than 400 ka old. The most probable age assignments are that aminogroup G is stage 9 and that aminogroup F is stage 7.

A significant time gap is represented between ratios in aminogroups G (~0.60) and K (>1.00) and is similar to a lacuna found by Karrow and Bada (1980) and Muhs and Szabo (1982) in California strandline deposits; a similar gap was recognized by Chappell and Veeh (1978) on Atauro. This gap may correspond to Black-welder's (1981) "world-wide lacuna" between 0.4 m.y. (core stage 11) and 1.1 m.y. The paucity of dated littoral deposits in this interval may be partly an artifact of the availability of dating methods or preservation of deposits, but it may also confirm the predictions of generally lower interglacial sea levels (and lower temperatures) for core stages 13, 15, and 17 by Hays and others (1969), for stages 15 through 21 by Stearns (1978), and for stages 13 through 21 by Deep Sea Drilling Project 552A (Shackleton and others, 1984).

CONCLUSIONS

Our interpretation of Mediterranean shore-lines is based on the correlation of deposits containing aminogroup E alle/Ile ratios with the Eutyrrhenian event and the Senegalese fauna or "couches à *Strombes*" of Gignoux (1913). Uranium-series dates allow placement of aminogroup E in an absolute time scale (that is, ~125 ka). We assume that all aminogroups are related to light $\delta^{18}O$ excusions or odd-numbered isotope stages. *Strombus bubonius* is generally restricted to aminogroup E deposits or abraded "beach pebbles" in group C sediment. The only exception is at Campo de Tiro, where the U-series mollusk apparent age and stratigraphy of the deposits remain unclear; at Tomasso Natale, *Cantharus viverratus,* a Senegalese form, was found among corals dated at 250 ka (U-series) and *Arca* shells that yield aminogroup F ratios.

Aminogroup C, the Neotyrrhenian, onlaps aminogroup E, and is stratigraphically, paleontologically, and lithologically distinct. Amino-

group C deposits are typically thin, poorly developed, and laden with red silt; contain rough and angular clasts; and host a cool-marine fauna commonly mixed with terrestrial snails and/or reworked Eutyrrhenian (aminogroup E) shells. These characteristics have been noted by numerous authors and suggest a brief post-Eutyrrhenian high stand of the sea, with a large influx of reworked terrigenous terra rossa sediment.

Aminogroup F deposits generally are present at elevations similar to those of aminogroup E deposits. *Strombus* may be associated with both aminogroups, but unequivocal data have emerged only from last-interglacial deposits. Aminogroup G deposits are generally found at higher elevations than are younger aminogroups and do not contain Senegalese taxa.

The potential of amino acid geochronology for the subdivision, correlation, and dating of Mediterranean shallow-marine deposits is summarized as follows.

(1) Alle/Ile ratios from shells in nearby sites can be used to develop local aminostratigraphic

zonations of the emerged strandline sequences. Calibration with sites that have U-series coral dates allows the placement of the aminogroup E into an absolute time scale.

(2) The thermal gradient across the Mediterranean is sufficiently high that sites in different regions cannot be directly correlated on the basis of mollusk aIle/Ile ratios. Control for regional correlation is provided by U-series coral dates from Eutyrrhenian deposits in a wide range of current temperature regimes. These data allow the definition of aminogroups: correlative deposits that have aIle/Ile ratios that differ in proportion to the regional thermal gradient.

(3) The composite amino acid stratigraphy suggests at least five aminogroups representing high–sea-level events (C, E, F, G, and K) in the past million-plus years. Aminogroup C (Neotyrrhenian) is considered to be a middle-to-late stage 5 event, and aminogroup E (Eutyrrhenian) is dated to ~125 ka B.P., whereas a sparse grouping (aminogroup F) may be related to an isotope stage 7 event. Aminogroup G probably is equivalent to isotope stage 9. An early Pleistocene aminogroup K, comprising ratios from deposits generally older than 800 ka, constrains the absolute ages of the younger groups.

(4) This regional survey has produced sufficient data for a broad area to provide a template through which future local amino acid studies can be integrated into a regional chronological framework.
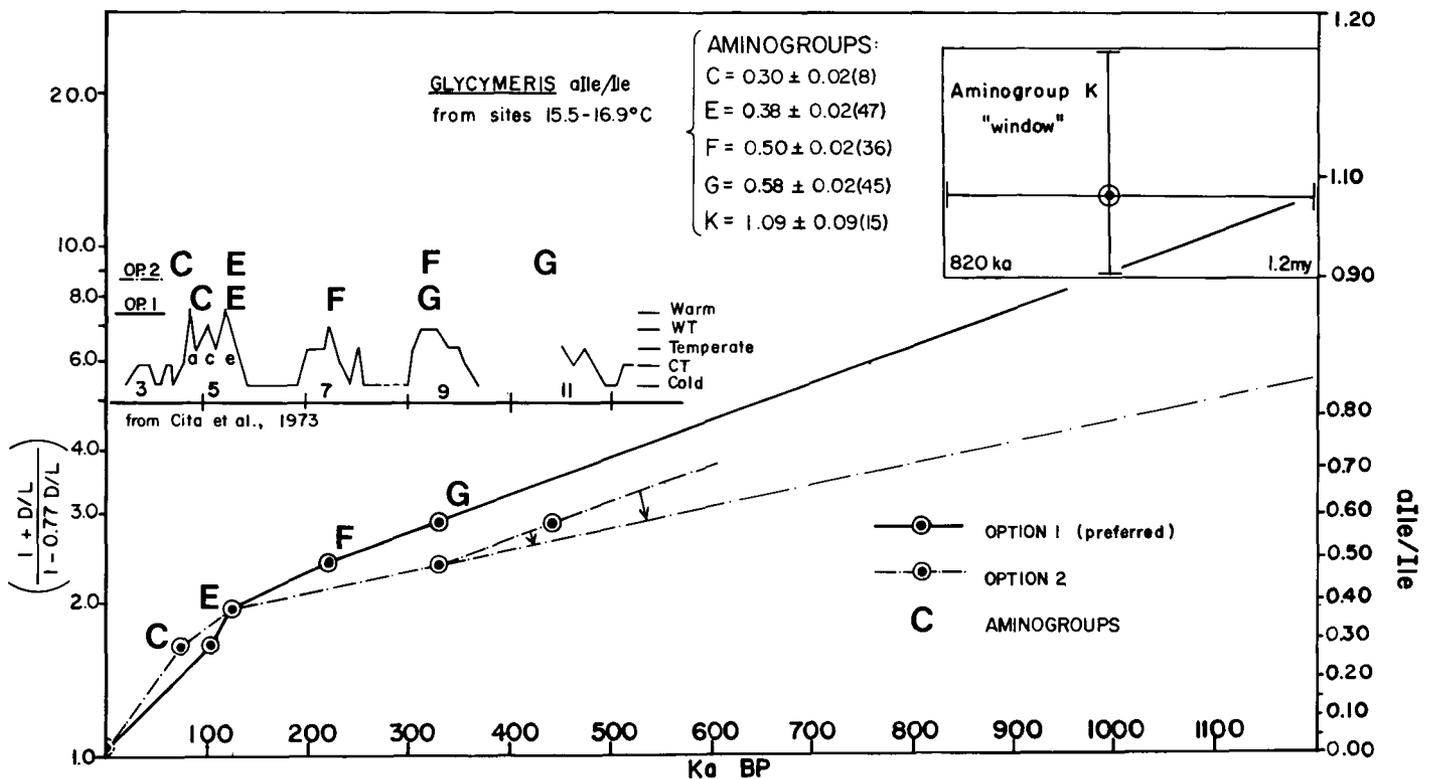
Figure 5. Mean aIle/Ile ratios of aminogroups C, E, F, G, and K for sites that have present MAT's between 15.5 and 16.9 °C plotted against (1) absolute age and (2) temperature variations in the Tyrrhenian Sea (Cita and others, 1973) and the oxygen-isotope substages to which they have been related. Aminogroup K appears as a "window" because of the large standard deviation in both mean aIle/Ile ratios and age.

Aminogroup E is fixed at 125 ka and $\delta^{18}O$ substage 5e. Aminogroup C is younger, presumably $\delta^{18}O$ substage 5a (option 1) or 5c (option 2). Variables in epimerization kinetics and reconstructed thermal histories prohibit a clear choice between these two options. Assignment of aminogroup F to core stage 7 (210 ka) establishes an epimerization curve (option 3), the slope of which could decrease with time but cannot increase. Extrapolated at constant slope, option 3 intersects the group K "window" and is, therefore, possible. Mean aminogroup G ratios lie on the curve at 330 ka (core stage 9). The alternative assignment of aminogroup F to core stage 9 establishes a curve (option 4) that if extrapolated at constant slope, falls well below the aminogroup K window. It could reach the window only if the slope increased with age, in violation of epimerization kinetics. We therefore reject option 4 (F = stage 9, G = stage 13) and accept option 3 (F = stage 7, G = stage 9) as the best interpretation of the available data.

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