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AGE AND AMINOSTRATIGRAPHY OF QUATERNARY COASTAL

DEPOSITS IN THE MEDITERRANEAN BASIN

by

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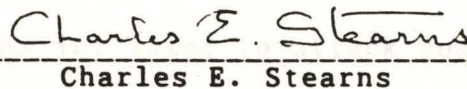This Thesis for the Doctor of Philosophy Degree by

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Age and aminostratigraphy of Quaternary coastal

deposits in the Mediterranean basin

Thesis directed by Associate Professor Gifford H. Miller

The Mediterranean has been a natural laboratory
for shoreline studies for nearly a century. From the
prodigious number of previous research programs,
several groups of raised shoreline deposits have been
identified that are related to early, middle, and late
Pleistocene marine transgressions. Inter- and
intra-regional correlations are complicated by localized
tectonic uplift and inadequate chronometry. This
investigation was initiated to attack some of the
outstanding dating problems by using the extent of
isoleucine epimerization in fossil shells contained in
shoreline deposits as an independent assessment of age.

The regional study includes 78 sites in Crete,
Italy, Sicily, Sardinia, Corsica, Tunisia, Spain,
Mallorca, Morocco and the Canary Islands. AIle/Ile
ratios have been determined in 762 shell samples of 23
genera, although the main contributions are based on
ratios from the genera Glycymeris, Arca, Astralium and
Patella. Six aminogroups (samples of equal age but

having variable temperature histories) have been defined
over the region and are labeled A, C, E, F, G and K with
increasing age. Eight U-series dates on the corals
Cladocora caespitosa and Astroides sp. obtained in this
study, and several other previously determined
radiometric dates have provided absolute age calibration
for some of the aminogroups.

Aminogroup A is defined from deposits
representing the Holocene beach-dune complex mainly from
coastal deposits in Mallorca. Aminogroup C includes
most previously identified Neotyrrhenian deposits and is
correlated to a late isotopic stage 5 (5a or 5c or both)
rapid and brief marine transgression. Aminogroup E, the
Eutyrrhenian, is positively correlated to isotopic stage
5e by seven coral dates averaging 126 ± 4ka (kilo anni).
Strombus bubonius and other "Senegalese fauna" are
intimately associated with the aminogroup E
transgression and the Eutyrrhenian. Little independent
evidence exists to imply an earlier or later than stage
5e presence of these exotic taxa. Future studies will
attempt to resolve some of these exceptional cases.
Aminogroups F and G are of mid Pleistocene age (cf.
Paleotyrrhenian) but ambiguous U-series dates can only
tentatively tie these aminogroups to isotopic stages 7
and 9 or 9 and 11. Amino acid epimerization kinetics
indicate that aminogroup G is less than 500ka old.

Aminogroup K represents multiple early Pleistocene deposits of Sicilian and Calabrian age.

This study demonstrates the potential of amino acid geochronology for dating and correlation of disjunct marine deposits distrubuted over a large area. Future studies will concentrate on obtaining additional absolute age calibration during the interval between 200 and 400ka. Further efforts will also focus on correlation of the coastal record with deep sea cores.

This thesis is dedicated to my parents
Fred and Josephine

Acknowledgements

Of all of those that inspired me to complete this thesis I would like to make particular mention of those who brought these years of pleasure and pain to this moment. Of course there are my parents who instilled something in me along time ago, probably during those '57 Chevy stationwagon trips to Yellowstone Park, that something remains in me and will always. They are the ones, and I love them so much. Chris and Eileen, my two younger sisters, also provided me with help and money and a reason to be proud of myself for this accomplishment. Chris also performed like a shining star in the field. Then there was Professor John F. Shroder who is my mentor. Jack is an inspired and marvelously enthusiastic teacher in his own right; he started this all when I slid into his geology class to complete a science requirement for my art major. Geology is an art.

Thanks (due mille grazie) to Butch, Sabine and Bepo for keeping me going, whether it be in choosing a menu in a Roman resturant, getting myself and equipment to Spain, or making life full (let us not forget the perfect life we sought, and the indescribable one presented to us). A special thanks to Tom Stotler and

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Strombus bubonius Lamarck. (= *le Kalan* Adanson).
Coquille de 100 à 150 mm., à callosité columellaire et labre très épais-
sis, ornée de tubercules, tantôt à peine marqués, tantôt bien dévelop-
pés et de quelques cordons spiraux grossiers et souvent peu visibles.
La suture est placée sur les tubercules, ce qui lui donne un aspect fes-
tonné. Coloration jaune fauve, parfois rosé, marbré de blanc.

CHAPTER I

INTRODUCTION

Preamble

The Mediterranean basin is ideally suited for
the study of Quaternary raised interglacial shorelines
not through constancy of the coastlines but through the
diversity of these features. A minimal tidal range (10
to 30cm) allows precise determination of ancient sea
levels. The warm temperate to subtropical maritime
climate encourages rapid induration and thus
preservation of marine deposits on predominantly
carbonate coastlines. On coasts with a greater
terrigenous input of siliceous sediments (e.g. Lazio
and Calabria coastlines), marine deposits remain
unconsolidated for longer periods resulting in reworking
of deposits and modification of morphological features.
High amplitude climatic changes through the Pleistocene
controled the development of molluscan faunas which vary
in fossil marine deposits from boreal to tropical. In
turn these faunal attributes can be utilized for

stratigraphic correlation.

What at first would appear to be a disadvantage in the study of raised shorelines in the Mediterranean, in many ways is essential for their preservation: tectonism related to the convergence of the African and Eurasian plates. The most intense vertical and horizontal movements are occurring adjacent to the Hellenic Trench south of the island of Crete and further west between Sicily and Calabria. Backarc volcanoes lie in a zone 100 to 300km north of the plate boundary. Mt.Vesuvius is included among them. The effect of this plate collision is felt far to the north of the basin. Where uplift dominates, marine deposits are commonly elevated to a level beyond the effect of subsequent marine erosion, aiding their preservation. Farther west in the Mediterranean basin, in areas such as Mallorca, Tunisia and Sardinia, relative stability predominates. Fewer fossil shorelines are preserved on stable coastlines where periodic high sea levels rise to similar elevations and destroy older deposits. If correlation can be achieved from the highly tectonic zones to the more stable ones, then not only can tectonic displacement be calculated, but also some inferences can be made on the absolute changes in sea level over the past several hundred thousand years.

The Mediterranean basin is a region in dynamic

flux; dynamic in climate, ecosystems and tectonics.
This project was designed with this overriding concept
in mind. Although there is considerable potential for
making absolute paleo-sea level determinations in the
Mediterranean, I have focused more on the correlation of
disjunct raised marine deposits across diverse geologic
and climatic settings through chronometry, bio-, litho-
and morphostratigraphy. The history of shoreline
studies in the Mediterranean has been plagued by the
inability to independently date the deposits. Déperét
(1918) and others were of the opinion that the elevation
of successive marine events was constant and that this
alone was sufficent to correlate high sea level
episodes. Notwithstanding their contribution to sea
level studies, early workers maintained that high
strandlines were the marine equivalent to fluvial
terrace sequences representing the major periods of
Alpine glaciation which we now know to be the opposite
phase of the climatic cycle.

The fundamental divisions of the Pleistocene at
the beginning of this project were the Calabrian and
Sicilian (early Pleistocene), the Milazzian (mid
Pleistoccene), the threefold Tyrrhenian (I, II and III;
mid and late Pleistocene), and the Versilian (Holocene).
These subdivisions have undergone a great deal of
scrutiny since 1981, and several major revisions have

been made as will be discussed later in this manuscript.
Litho- and biostratigraphy, geomorphology and
geochronology are the main tools used in subdividing the
marine transgressive-regressive cycles of the
Pleistocene.

The great classical works of Déperét (1918) and
Gignoux (1913) were based in large part on the
identification of subtle differences in the stratigraphy
and geomorphology of fossiliferous marine deposits.
Biostratigraphic correlation was also employed early on
in the study of sea level deposits in the Mediterranean
when it became clear that the basin was "invaded" by
alternating cold, banal (similar to today's fauna) and
tropical assemblages of mollusks and other invertebrates
through the Pleistocene. The narrow Gibraltar Strait
reduced oceanic mixing of Atlantic and Mediterranean
waters encouraging rapid surface water temperature and
environmental changes that promoted rapid development
and extinction of faunas. In addition to these
fluctuations, radical salinity changes were stimulated
by surges of glacial meltwater from Europe and Asia.
Entire continental shelves were repeatedly inundated and
exposed. This environmental dynamism was the driving
force behind the radical changes marine ecosystems.
This environmental dyanamism is reflected in the
diversity of marine organisms preserved in raised marine

deposits.

The need to know when these faunas occurred
prompted geologists in the 50's and 60's to begin dating
fossils and related sediments with radiometric methods.
Included are: C-14 and U-series on fossils and fission
track and K/Ar on volcanic sediments. The effective
range of C-14 on shells (30ka) is not adequate to
accomodate the 1.5 to 2 my of the Pleistocene. The
misuse of the C-14 method appears to have generated a
"ghost" sea level event centered around the finite
boundary of the method (see Richards, 1983; 1985).
U-series has a magnitude greater effective range than
C-14 and has been utilized in the Mediterranean for
dating mollusks (Stearns and Thurber, 1965; 1967; Bernat
et al, 1982; Hillaire-Marcel et al., 1986) and corals
(Dai Pra and Stearns, 1977; Brancaccio et al, 1978;
Hearty et al, 1986). Unfortunately, Kaufman et al
(1971) delivered a blow to U-series mollusk dating by
stating that the open system of the mollusk shell allows
migration of secondary uranium and thorium during
diagenesis. The Kaufman "obituary" was aimed at the
works of Stearns and Thurber (1965, 1967). It was
concluded that one-half of the mollusk dates are
probably valid dates; however, which half remains the
crucial question. U-series dating of corals has not
been widely applied in the Mediterranean due to the

sporadic distribution of corals in Pleistocene raised shoreline deposits. Solitary corals (<u>Astroides</u>) and branching type (<u>Cladocora caespitosa</u>) occur sporadically in the record, mainly during warm interglacials.

Dating volcanics in order to date marine events is inherently problematic. At least four reasons can be cited: 1) it is often difficult to associate pyroclastic deposits with marine events; 2) older volcanics are frequently reworked by marine action and thus would not render a reliable age of the marine event; 3) there are intrinsic analytical limitations of both fission track and K/Ar particularly at younger stages of diagenesis; and 4) there is a limited geographic extent of volcanic deposits in the Mediterranean. Nevertheless, a considerable number of publications dealing with dating of volcanics have stirred as much controversy as sea level problems they have solved.

In summary, the time range of the available methods are either too short, too great or are limited by occurrence of the analyzed material across the study area. This "hit and miss" chronometric gap has stimulated the inception of new methods that include electron spin resonance (ESR, cf. Radtke et al, 1983), thermoluminescence (TL, cf. Aitken, 1985), and the amino acid geochronology technique (cf. Blackburn,

1978); the lattermost being the subject of this work.

Amino acid geochronology

Amino acid geochronology (AAG) is effective in Mediterranean climates over a range of greater than 1my, with greatest resolution occurring during the first 500 ka (kilo anni) of the diagenetic history. The method can be applied to most deposits containing calcareous organisms (mollusks, foraminifera, ostracodes, etc) that are preserved in good condition. Amino acid dating is thus applicable to a majority of the known Pleistocene deposits in the Mediterranean. With proper calibration to radiometric dates, amino acid geochronology itself takes on an absolute dating potential that fills an enormous gap left by the inadequacies of other techniques now popular in the Mediterranean basin.

Abelson (1954; 1955) was the first to discover the presence of amino acids in fossil organisms. Later work by Hare and Mitterer (1967, 1969) focused on the use of racemization reaction of residual amino acids in fossils as a dating tool. In only the past ten to fifteen years there has been an exponential growth in the understanding and use of amino acid geochronology as a relative and absolute dating method. Thorough discussions and up-to-date references regarding the

technique, its applications, advantages and disadvantages can be found in Hare, Hoering and King (editors, 1980), Belknap (1979), Wehmiller, (1982; 1986), Hearty et al., (1986), Hearty (1986), Brigham (1985) and Miller and Mangerud (1986).

The AAG method has been most extensively applied in the Arctic, Europe and along the U.S. coasts (see discussions in Chapters 2 to 5). However, this and other new studies are extending the application to sites around the globe. In most applications the AAG method has aided or generated time stratigraphy previously unavailable, or provided thermal histories of critical sites.

Since temperature is the primary rate controlling variable in the racemization/epimerization reaction, its application in arctic areas is effective over several million years (at < 0°C effective diagenetic temperature). Unfortunately, the slowness of the reaction at low temperatures does not allow resolution of short term events. Conversely, due to the speed of the reaction in subtropical climates during the early stages of diagenesis, the method can resolve shorter events of a few thousand years, the typical time-frame of rapid positive sea level excursions, while the effective range in the Mediterranean climate remains at over a million years.

This study is the first comprehensive introduction of the method to the Mediterranean basin. There have been small AAG studies in the Mediterranean (Bartolini et al., 1984) but they were either inconsistent in the use of taxa or too localized to create much impact. Other laboratories (Scripps Institution of Oceanography and Università della Citta, Rome) have undertaken duplicate studies in the area (Bartolini et al., 1984), but their methodology and results are questioned (cf. Hearty, 1986, p. 65, "precautionary measures") and their persistant use of single shell analyses for absolute age assignment is strongly discouraged.

In the Mediterranean several genera of mollusks persist over a wide temporal and geographical range. After the initial field season, two related genera were chosen for detailed analyses. They are Glycymeris (G. violescens, G. bimaculata and G. glycymeris) and Arca (A. noae, A. tetragona and A. (= Barbatia) barbatia). Arca and Glycymeris inhabit slightly different niches in the littoral and sublittoral zones of most coastlines in the region, past and present. Other genera used in this study include Astralium, Cerastoderma, Patella, Cerithium, Spisula, Dosinia, Venus, Donax and Ostrea, representing a variety of habitats and salinity conditions. The shells were generally well preserved

and often articulated. Collections for analyses were taken from deep within the marine unit, usually at a depth of greater than one meter to reduce or eliminate the short term (diurnal and seasonal) heating cycles of the deposit.

In most cases the interior layers of the shell were used for the amino acid sample. The outer layers were mechanically removed with a Dremmel tool and the remaining portion further leached to reduce the possibility of contamination. All measurements of the amino acids in this study were of the total fraction (Total;free plus peptide-bound) of D-alloisoleucine/L-isoleucine (hereafter aIle/Ile) determined on an high-pressure liquid chromatography amino acid analyzer. Peak heights of aIle/Ile ratios were computed by a Hewlett-Packard 3390A Integrator.

Whenever possible, corals were collected from coeval marine deposits for uranium series dating. Cladocora caespitosa occurs most commonly in the Pleistocene marine record in the Mediterranean. This species is a branching form that prefers shallow, clear, well aeriated, and normal salinity waters. Several U-series analyses were performed on these corals by Dr. B. J. Szabo of the U.S. Geological Survey in Denver, Colorado, a collaborator throughout this project. These dates, as well as other radiometric dates from previous

studies in the Mediterranean were used to calibrate the amino acid ratios across a wide geographic range. The last interglacial marine deposits are most securely dated, but limited dates are available for older shorelines. This calibration allows extension of an "absolute age" dating capability to non-coraliferous or non-dated deposits through correlation of aIle/Ile ratios.

Amino acid terminology

Because of the scope of this study, there is a need to define a new terminology. AIle/Ile ratios cannot be directly compared across a thermally varied region, so 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" that represents 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 2-1) are used to calibrate sites across climatic boundaries and are the basis for aminogroup identification. (Hearty et al,

1986a, Chapter 2, this thesis).

Dimensionality of this research

This thesis is a complilation of several distinct papers making it advantageous for the reader to understand some overriding concepts that will unify the themes that pervade, although are not necessarily stated among the works contained herein. These concepts are introduced in the following paragraphs and figures and include: 1) a dimension of space (area); an inventory of the sites and samples analyzed across the study area; 2) a dimension of time; where multiple-aged groups dating from the Pleistocene are defined within the study area; 3) a dimension of temperature; the site-specific rate of epimerization is governed by the temperature history that has affected the samples since their deposition; 4) a biologic effect; the rate of epimerization may vary among different taxa; and 5) a lithologic effect; the potential for geochemical effects on the rate of epimerization exists and requires that these effects be evaluated. In light of these concepts, each amino acid ratio is viewed in a five dimensional framework, influenced by space, time, temperature taxonomy and lithology (Figure 1-1).

```
                        TIME
                         |
                         |
                         |
                         |
   TAXA-------->SAMPLE<------TEMPERATURE
                       /   \
                      /     \
                     /       \
                SPACE         LITHOLOGY
```
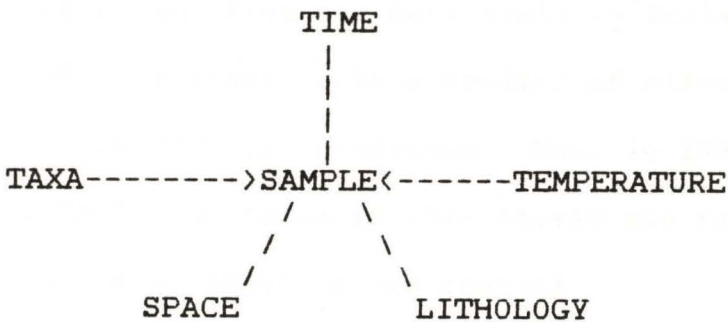
Figure 1-1: A conceptual view of the environmental
influences acting on a sample. The influences of time,
temperature, space, taxa and lithology are discussed in
the text.

Space:

After five years of research on raised
shoreline deposits in the Mediterranean a total of 762
samples from 78 sites (Figures 2-1, 3-1, 4-1 and 5-1)
have been analyzed from within an area of over 4 million
square kilometers. The sites range from Crete to
southern Spain, and from northern Italy to Tunisia. At
the onset of this study, only a handful of sites were
dated with chronometric techniques. Now, in 1987, over
100 sites, including those in this thesis and related
publications, have absolute age control.

Time:

From the aIle/Ile data, six major groups of
marine deposits (A,C,E,F, G and K) have emerged (Figure
2-4). These groups are bounded by or keyed to several
radiometric dates between 6,000 and 1,500,000 years B.P.
The most securely dated event is that of the
"Eutyrrhenian" (Bonifay and Mars, 1959) equivalent to
aminogroup E which occurred about 125,000 years ago.
Aminogroup C (or C/D) is younger but lies within the
last interglacial (sensu lato); aminogroups F and G are
clearly older than E, and represent mid Pleistocene
transgressions. Aminogroup K is a loosly defined
collection of ratios from the early Pleistocene. A
majority of the important areas producing multiple-aged

sequences are covered in this text while others are
reviewed in in current or pending publications.

Temperature:

A basic assumption in AAG is that temperature
is the primary rate-controlling factor. AIle/Ile ratios
increase with warmer present mean annual temperature (a
proxy for past thermal gradients) across the region.
Figure 2-3 is a map of contoured Glycymeris aIle/Ile
ratios from last interglacial deposits, many of which
are calibrated to U-series coral ages. A trend of
rapidly increasing aIle/Ile ratios associated with
present MATs greater than about 18.0°C is observed
across the study area. This increase may be
associated with the exponential effect of temperature on
the rate of epimerization. The plotting of aIle/Ile
versus MAT can be applied to any group of equal-aged
deposits determined from this study although the
greatest amount of data exists from aminogroup E
deposits.

Biologic effect:

Figure 1-2 is a plot of mean aIle/Ile ratios of
seventeen genera from Il Fronte and Bovetto, southern
Italy. U-series coral dates have demonstrated that
these sites are all of last interglacial age. In Figure

Southern Italy sites with present MAT's of 16.9 to 17.5°C.
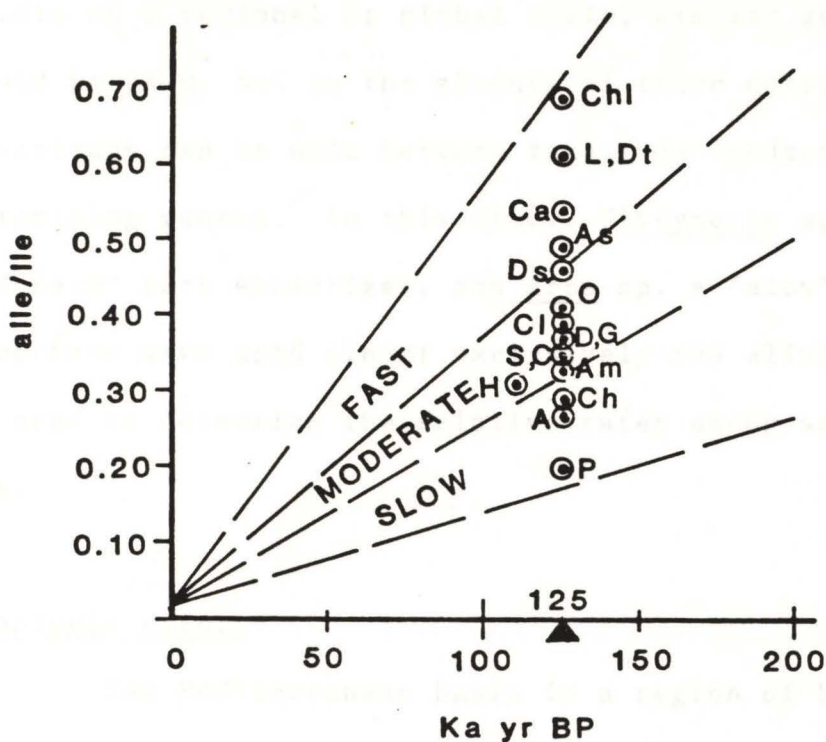
Figure 1-2: Relative rates of isoleucine epimerization (aIle/Ile) in seventeen taxa analyzed for this study. All of the genera were extracted from known last interglacial deposits free from surface heating effects. Slow, moderate and fast epimerizers are arbitrarly designated from this study. <u>Glycymeris</u> is considered a moderate epimerizer while <u>Arca</u> is designated a slow epimerizer.

1-2, groups of slow, moderate and fast racemizers have been determined in a relative sense. When comparing results on a regional or global scale, similar genera should be used, but in the absense of these data, comparisons can be made between taxa from "moderate" epimerizing genera. In this study, Glycymeris sp., a "moderate" rate epimerizer, and Arca sp. a "slow" epimerizer were used almost exclusively and eliminate the need to determine the relative rates among several taxa.

Lithologic effect:

The Mediterranean basin is a region of bed-rock diversity. The landscape is marked by geologic variation on a kilometric scale. Shoreline deposits also occur in a variety of sedimentary and lithologic settings, which are usually a function of the bedrock, tectonics and climate. In order to appraise the effect of various sediment types on the rate of epimerization, Glycymeris shell fragments were heated at 150°C in slurries of three sediment types (carbonate, volcanic and terra rossa soil) for 120 hours (Figure 1-3). The results of the experiment showed that under laboratory conditions, there was no distinguishable difference in the epimerization rate that could be attributed to the sediment types. The assumption is
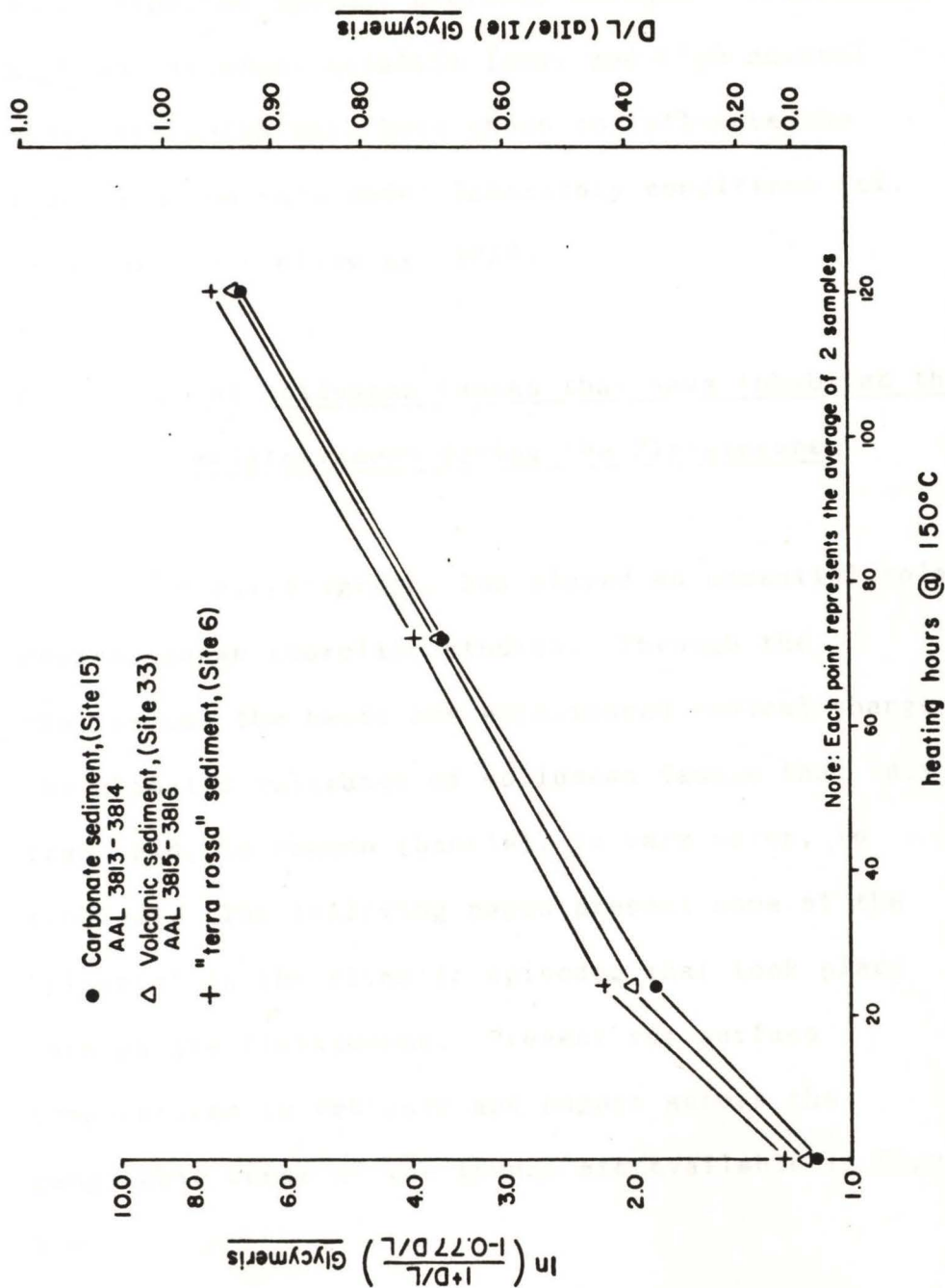
Figure 1-3: Relative epimerization rates of modern _Glycymeris_ shell fragments heated at 150°C for 120 hours in three different sediments. This experiment suggests that the nature of the enclosing sediments has little effect on the rate of epimerization.

therefore, that in a geologic setting, sediment type has little or no effect on the epimerization rate. This assumption, of course, excludes extreme circumstances of high pH, abundant metallic ions, and high natural radiation which have been shown to influence the epimerization rate under laboratory conditions (cf. Kriausakul and Mitterer, 1980).

The nature of molluscan faunas that have inhabited the Mediterranean during the Pleistocene

Biostratigraphy has played an essential role in Mediterranean shoreline studies. Through the Pleistocene the basin has experienced radical changes in the climatic tolerance of molluscan faunas that vary from cold, to common (banale), to warm water, to tropical. The following pages present some of the "players" in the climatic episodes that took place through the Pleistocene. Present sea surface temperatures in February and August across the geographic range of the faunas are available in Figure 1-4.

The "ospiti nordici" or northern guests:

The lower Pleistocene in the Mediterranean is subdivided on the basis of the waning influence of warm
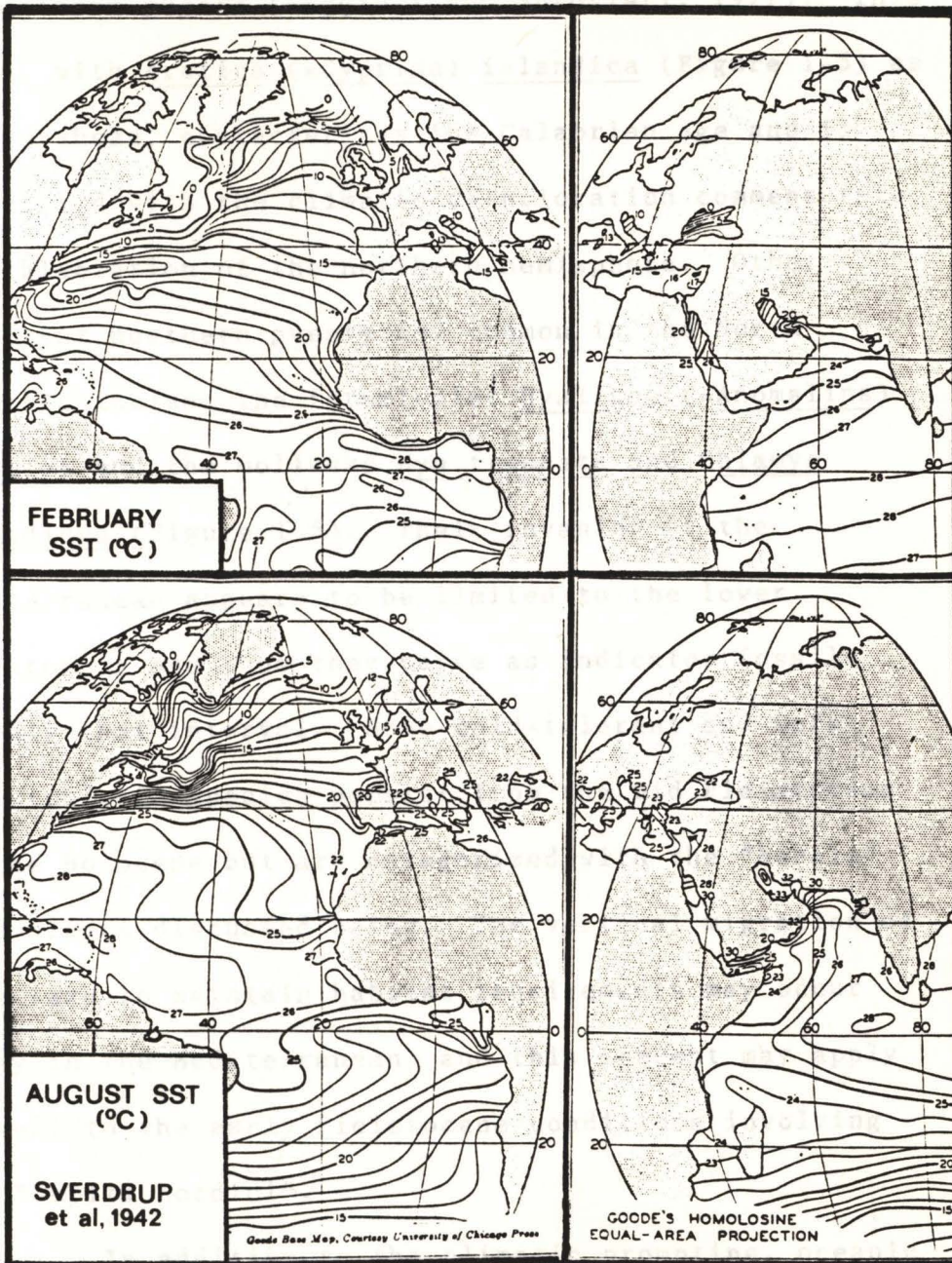
Figure 1-4: February and August sea surface temperatures in the Atlantic and Mediterranean from Sverdrup et al (1942). Sea surface temperatures span the present range of faunas that have inhabited the Mediterranean in the past. Included are cold, common, thermophilous and tropical faunas that are described in the following figures.

Pliocene faunas and the invasion of the "ospiti nordici" or northern guests (Ruggieri and Sprovieri, 1977). This fauna, with Arctica (=Cyprina) islandica (Figure 1-5) as a figurehead, characterizes the Calabrian age and is associated with the climatic deterioration commensurate with glaciation of the northern hemisphere. Other important northern guests now common in the North Atlantic include the foraminifer Hyalinea (=Anomalina) balthica and the mollusks Mya truncata and Chlamys islandicus (Figure 1-5). Their invasion of the Mediterranean appears to be limited to the lower Pleistocene and thus they serve as indicator fossils of only that interval. Some cold-tolerant and more opportunistic species persist from the mid Pleistocene to the Holocene but are catagorized with the "banale" assemblages discussed below. The vertical migration of some taxa to maintain habitat requirements may occur today in the Mediterranean, and this concept may apply as well to the early Pleistocene conditions involving the "ospiti nordici".

In addition to the climatic prompting, oceanic circulation near the western opening (Gibraltar) of the Mediterranean may have dictated the development and demise of now extralimital faunas. Certainly the modern Mediterranean behaves unlike any of the open oceans. The basin is now characterized by high temperature and
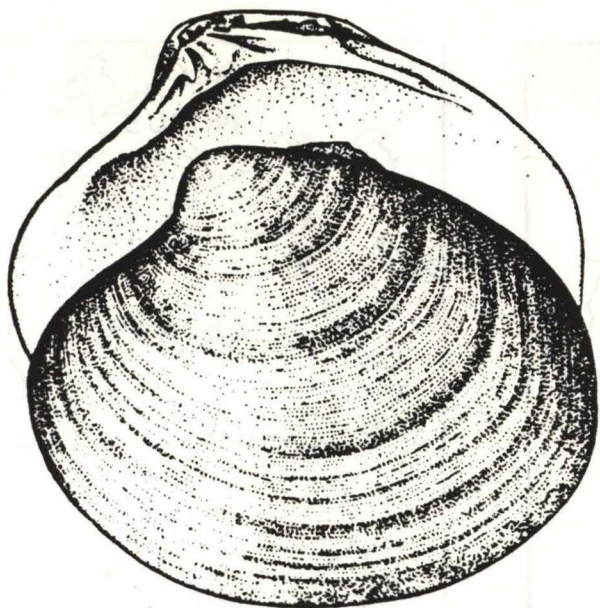
Cyprina (=Arctica) islandica (Linne)

Mya truncata (Linne)
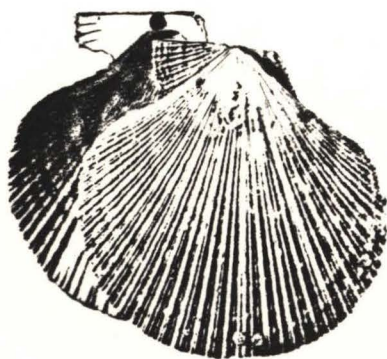
Chlamys islandicus (Muller)

Figure 1-5a: **Cold loving species that inhabited the Mediterranean during the Sicilian and Calabrian marine events of the early Pleistocene. (After Malatesta, 1963).**

Arctica islandica
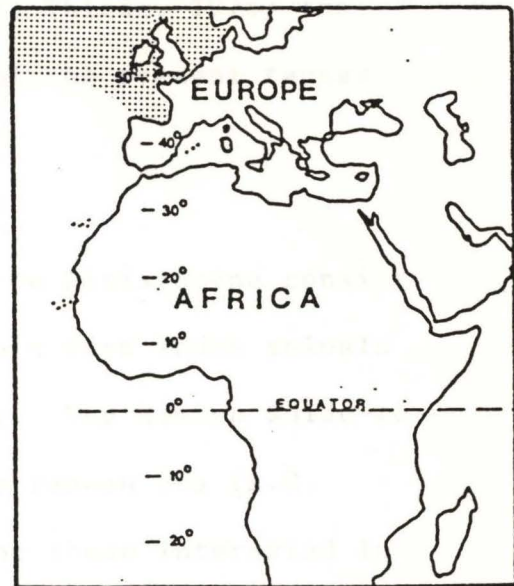
Mya truncata
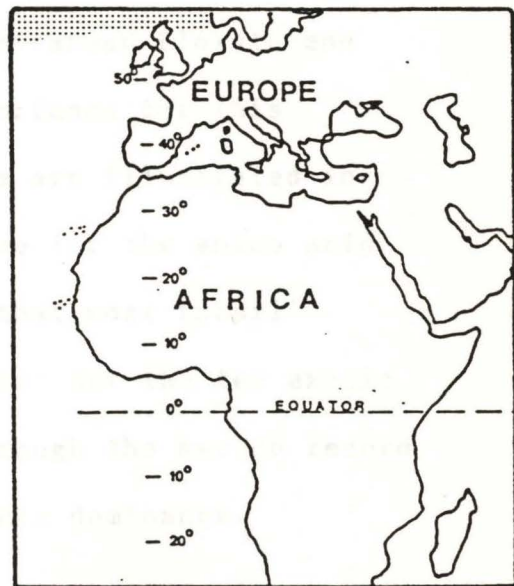
Chlamys islandicus

Figure 1-5b: Present range of cold-loving mollusks
(after McMillan, 1973 and Tebble, 1966).

salinity fluctuations, and frequent stagnations during
the Holocene (Thunnel et al, 1978; Thiede, 1978) that
certainly control the viability of the present faunas.

The "banale" fauna:

The "banale" faunas of the Pleistocene consist
of taxa generally indistinguishable from those animals
occupying the Mediterranean today. The Hamlyn Guide to
the Flora and Fauna of the Mediterranean Sea (A.C.
Campbell, 1982) is recommended for those interested in
the present day taxa. The ecologically tolerant nature
of these "banale" faunas is demonstrated by their
persistence throughout the Mediterranean Pleistocene
marine record and thus their importance for this
epimerization study. Banale taxa are illustrated in
Figure 1-6) in order of importance for the amino acid
study. It is essential to note that most fossil
assemblages are dominantly "banale" but the few exotic
types that occur sporadically through the marine record
of the Pleistocene overshadow their dominance.

A thermophilous fauna:

Gignoux (1913) identified a group of mollusks
that are "fréquentes aujourd'hui seulement dans les
parties les plus chaudes de cette mer, et qui, à
l'époque des Strombes, étaient au contraire abondantes
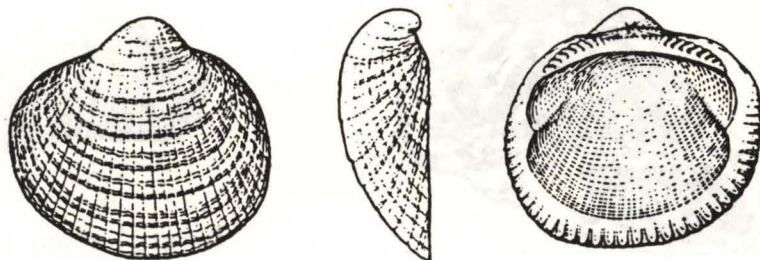
Glycymeris violescens (Lamark)
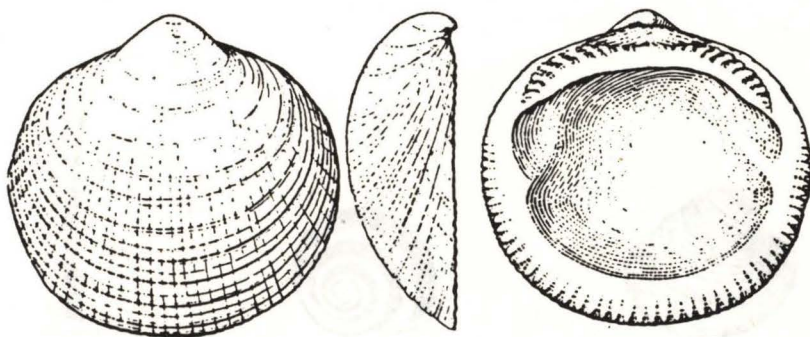
Glycymeris bimaculata (Poli)
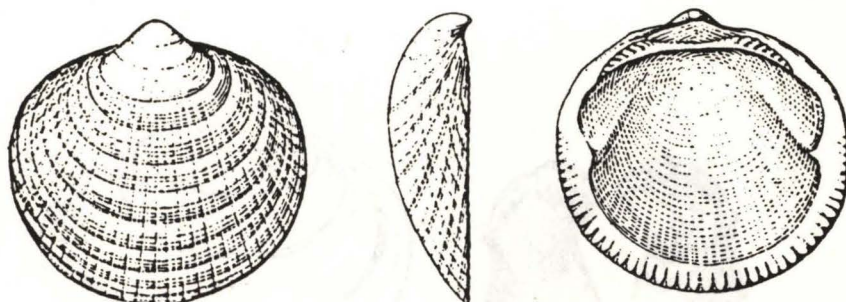
Glycymeris glycymeris (Linne)

Figure 1-6: Banale taxa that now inhabit the Mediterranean basin and constitute the principle specimens analyzed in this study.
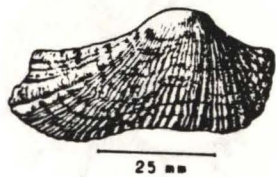
Arca noae (Linne)
(also A. tetragona)
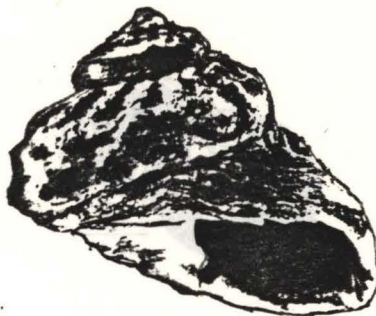
Astraea rugosa (Linne)

Dentalium sp.   Helix sp.   Chamalea gallina
(Linne)
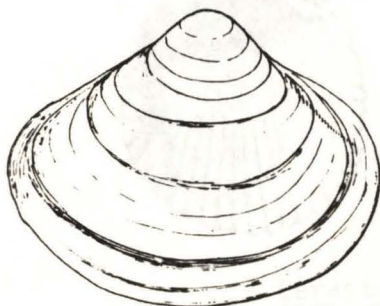
Spisula subtruncata   Ostrea sp.
(Da Costa)

Figure 1-6: (continued)
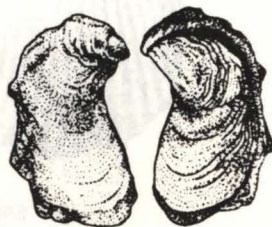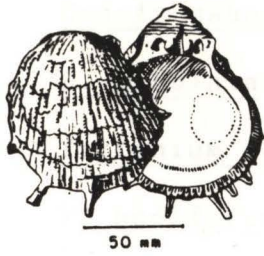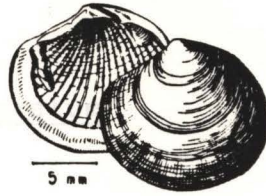
Spondylus sp.

Dosinia sp.
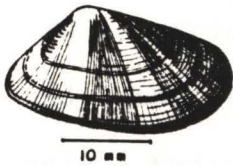
Donax sp.
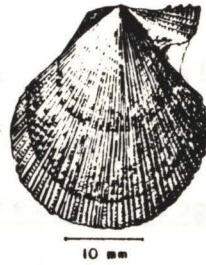
Chlamys sp.

Cerastoderma sp.

Figure 1-6: (continued)
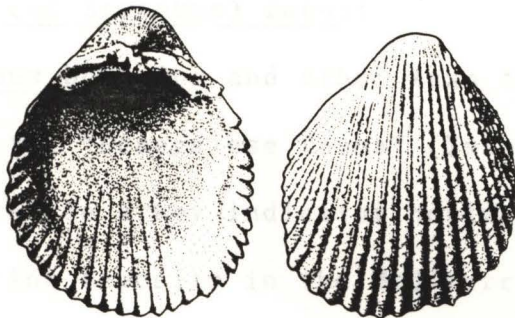
partout". Among these warmth-loving taxa are:

Spondylus gaederopus

Cassis saburon

C. undulata

Tritonium (=Cymatium) costatum

T. nodiferum

Panopaea glycymeris

Purpura (=Thais) haemastoma

The present range of these taxa is along the west African, African Mediterranean coast and in the Levant and Agean (Figure 1-7). Patella ferruginea is exclusively a Mediterranean member of this group. Little is known about its present habitat and range.

The Senegalese (or Strombus) fauna:

Strombus bubonius and other taxa that comprise what is termed the "Senegalese fauna" (Issel, 1914) (Figure 1-8) provide a key indicator horizon in late Pleistocene marine deposits in the Mediterranean basin. Gignoux's (1913) list included the following exotic taxa among "La faune des couches à Strombes":

Mytilus senegalensis (=M. charpentieri)

Conus testudinarius

Tritonidea viverrata

Arca geissei

Thias haemastoma (Linne)

Cymatium costatum (Born)
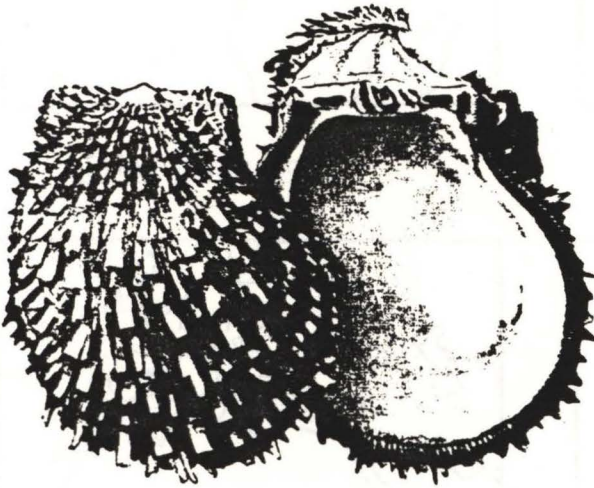
Spondylus gaederopus (Linne)
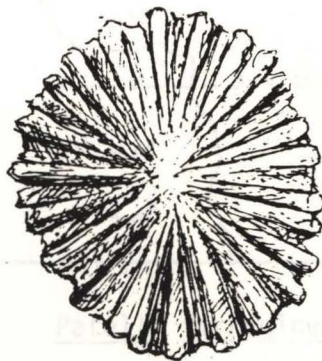
Patella ferruginea (Gmelin)

Figure 1-7a: Thermophilous taxa that now prefer warmer
areas in the Mediterranean but were widespread across the
basin during the last interglacial (after Gignoux, 1913).
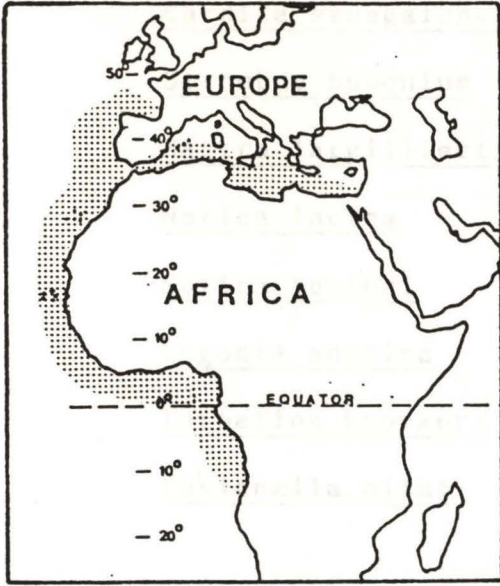
Thias haemastoma
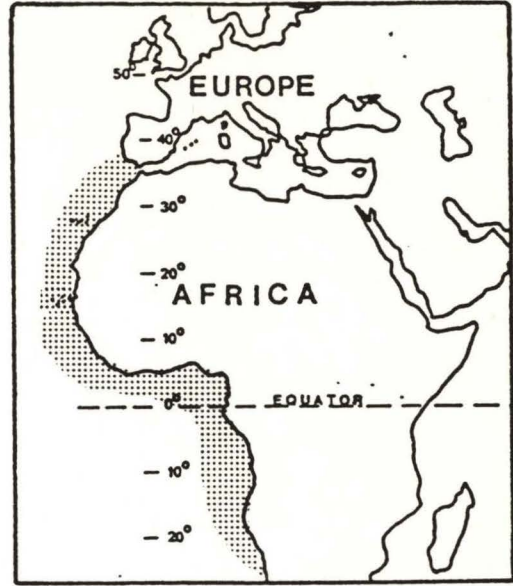
Cymatium costatum
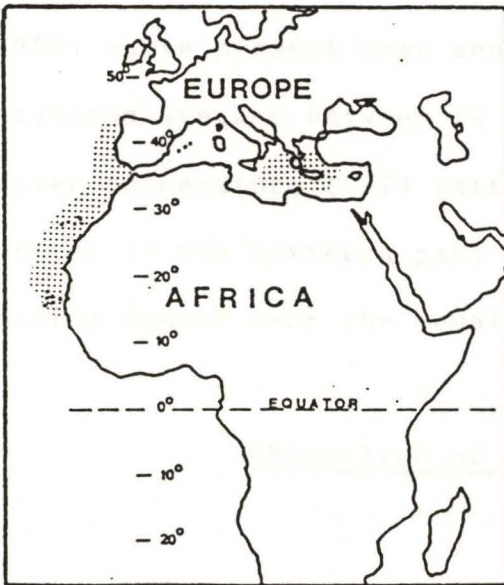
Spondylus gaederopus
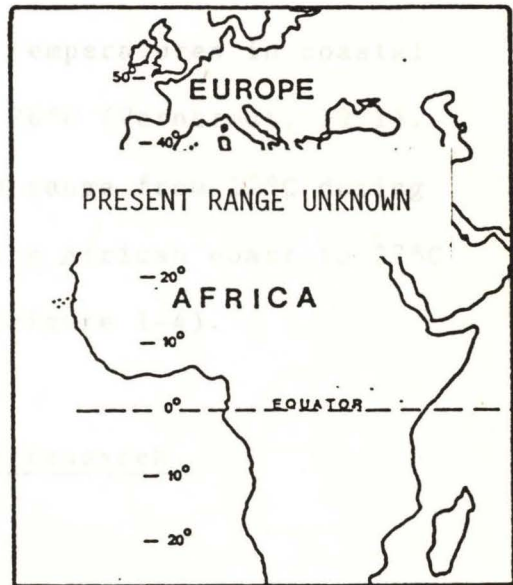
Patella ferruginea

Figure 1-7b: Present range of thermophilous taxa (after Nickles, 1950).

Tritonium ficoides

Cardita senegalensis

Strombus bubonius

Mactra largillierti

Natica lactea

Natica turtoni

Tugonia anatina

Tornatina knockeri

Pusionella nifat

Several of these taxa now reside in equatorial coastal waters of west Africa (Figure 1-8, Nickles, 1950) where present mean annual temperatures in coastal stations average between 21 and 26°C (Wernstedt, 1971). Water temperature (SST) extremes range from 17°C during winter in the northern part of the African coast to 27°C during summer near the equator (Figure 1-4).

Objectives of this research

The Mediterranean is the birthplace of shoreline studies. The central and western Mediterranean coastlines probably have the greatest density of previous studies (evaluated in Hey, 1971; 1978) of any region on the globe. The concentration of shoreline research in the Mediterranean is certainly the
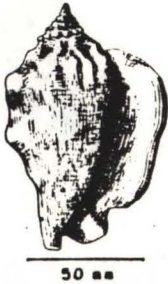
Strombus bubonius (LMK)

Conus testudinarius (Hwass)

Polynices lacteus (Guilding)

Polynices (=Natica)
Turtoni Smith

Figure 1-8a:(2 pages) – Some important members of the
Strombus or Senegalese fauna (after Gignoux, 1913) that
were abundant in the Mediterranean basin during the last
interglacial but are now extinct in the basin.

Cantharus viverratus (Kiener)
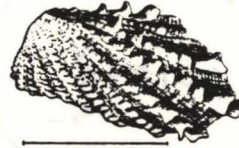
Cardita senegalensis (Reeve)
(Cardita = Benguina)

Arca Geissei (Dunker)

Figure 1-8a: (continued)
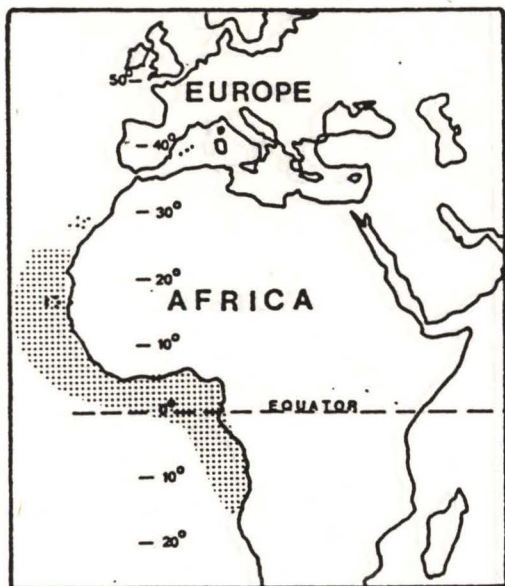
Strombus bubonius
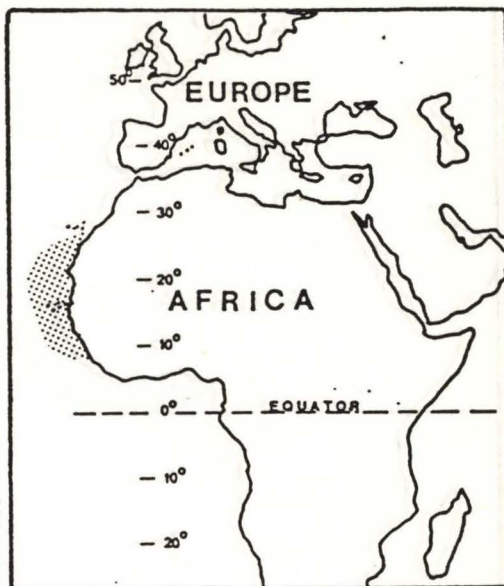
Conus testudinarius
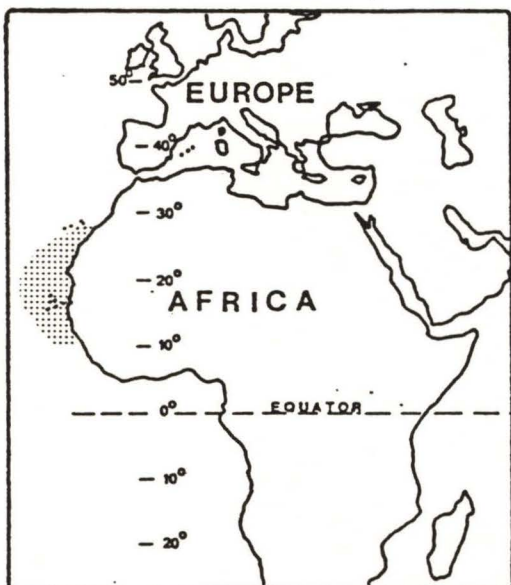
Polynices lacteus
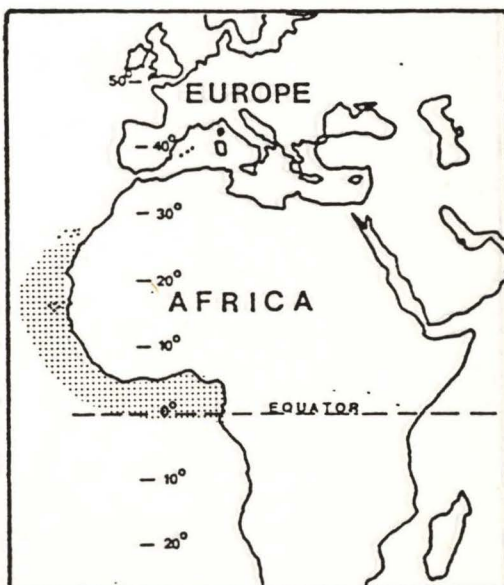
Polynices Turtoni

Figure 1-8b:(2 pages) – Present range of the Senegalese fauna along the west African coastline (after Nickles, 1950).
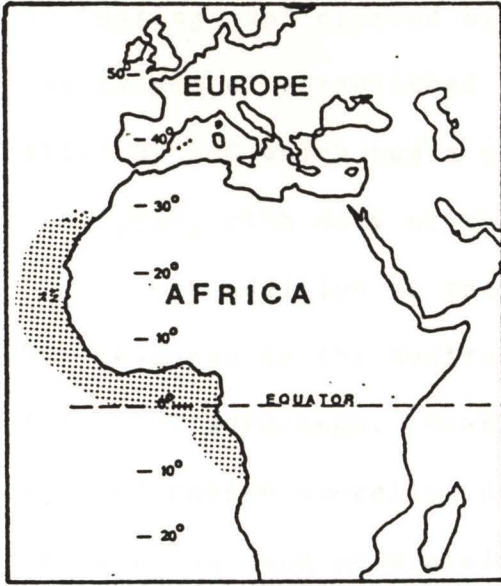
Cantharus viverratus

Cardita senegalensis

Arca Geissei

Figure 1-8b: (continued)
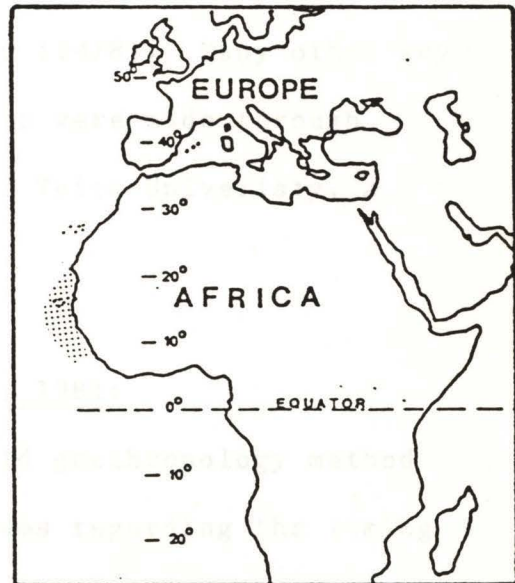
result of the splendidly preserved marine exposures. The "dating gap" created by the inadequate effective time ranges of established radiometric methods, can be filled by AAG which has a ca 1 my effective range, overlapping with many of the other methods.

In addition to the technological advances of this research in the Mediterranean, there is an historical advantage. Nearly a century of previous study of raised shoreline deposits offers a sizable stratigraphic and paleontologic data base on which future studies can be built. The initiation of this study in 1981 began with a flood of correspondence to many of the authors cited in Hey (1978). Many other key contacts with European scientists were made through Professor Charles E. Stearns of Tufts Univeristy, a member of this thesis committee.

The primary research objectives; 1981:

1) To use the amino acid geochronology method to attack the outstanding problems regarding the timing and amplitude of sea level changes. The focus would be on sites that contain abundant fossil shells and corals, contain multiple-event stratigraphy, and have a bearing on the sea level chronology;

2) To collect shells from deposits representing a broad geographical and age range, to determine the

aIle/Ile ratios and then to define aminogroups that
represent transgressive/regressive events of the
Pleistocene;

3) To determine the absolute age of the
aminogroups. This would be achieved through new
U-series dating of corals in coeval deposits, and/or
through correlation of amino acid analyzed deposits with
previously determined radiometric ages;

4) To evaluate the effect(s) on the rate of
isoleucine epimerization of non-uniform climatic
histories across the region;

5) To compare dated "aminogroups" (Hearty et
al., 1986a) to established sea level histories in
Mediterranean Europe and Africa to support or refute
present views on the sea level history;

6) To develop a bio-, litho- and
chronostratigraphic framework for future studies in the
region; and

7) To maintain a parallel laboratory
experimental program of pyrolysis using pertinent
taxa to more completely understand the kinetics
of isoleucine epimerization.

Secondary considerations: a collection of sea level
chronologies and their apparent correlation to
Mediterranean events

There are few data except for uranium-series ages to unify global sea level chronologies even though intuitively, they should be the same. Table 1-1 is an attempt to correlate from region to region around the globe. Some important questions arise regarding past correlations of marine events both in the Mediterranean and among key localities around the world. Most of these questions are addressed in this thesis (Chapters 2 through 5) or related publications. These questions lie within the finer detail of the objectives stated above and include the following :

1) What is the time interval bracketing the presence of the subtropical Senegalese fauna in the Mediterranean basin? Is it between 75 and 210ka as seen by Bonadonna (1967a), Ambrosetti et al, (1981), Butzer, (1983), and Hillaire-Marcel (1986) or was the presence of this fauna restricted to the peak of the last interglacial around 125ka? Earlier biostratigraphic studies associated the Senegalese fauna with one episode (Gignoux, 1913). Also, did the Senegalese fauna invade the basin several times in the past 300 ka, or is it restricted to one event during the last interglacial (sensu stricto)? Did individual members of this fauna "migrate" diachronously?

2) Are there several "Paleotyrrehnian" (pre-Strombus) events of the mid Pleistocene, and what

Table 1-1: Assembled sea level chronologies from the Mediterranean basin and other global studies.

Absolute Age*(ka)	Oxygen Isotope Shackleton & Updyke	Mallorca Butzer 1983 H T	France Bonifay & Mars 1959 Mallorca Fauna	Italy Ambrosetti et al. 1972 (Marine / Erosional)	N W Europe Paepe 1982 / Alpine	Morocco Biberson 1970 Stearns 1981	New Guinea Bloom et al. 1974	Barbados Bender et al. 1979	Macedonia Van der Hamen 1971	France Grand Pile Woillard 1978	Aminozone
0	1	A	Common Flandrian	Versilian	Flandrian		Terrace I	Mesotille 1968 and others		Preboreal	A
	2	B			Wurm		II			Lanterne	
	3			Pontian (Erosional)			IIIa, b				
	4						IV				
	5a		Rudimentary Thermophile				V	Worthing. 81	St. Germaine II		C
	5b			Erosional							
100	5c		Neotyrrhenian Partial or Absent Strombus fauna	3rd Strombus beach	early Weichselian Oultjian	late Ouljian	VI	Ventnor. 81	Drama	St. Germaine I	D
	5d			Erosional							
	5e		Eutyrrhenian Full Strombus	2nd Strombus beach	Eemian	early Ouljian	VIIa VIIb	Rendevous Hill BIII	Pangaion	Eemian	E
	6	C	Impoverished Sb Full Sb	Erosional	Saalian	Rabatian-Harounian		Durants Cave Hill Thorpe		Linexert	F
200	7		Paleotyrrhenian Partial or Absent Strombus fauna	1st Strombus beach	Holsteinian Riss II Elsterian			Husbands XI			G
	8	D	Common fauna P. terragionis fauna	Terra in Pietra	Cromerian			Unnamed XII			
300	9			Nomentanan Riss I							
	10			Tarquinian		Ouldyan-Anfatian					
	11			Flaminian Mindel							
400	12			Portuensian	Gunz Wallian	Maritian					
				Cassian							
700	1v			10 my Calabrian	Tiglian						
900											x
1100				2.5 my							

*non-linear scale

was the amplitude of their respective high sea levels?

3) Is there a Blackwelder (1981) lacuna between 0.4 and 1.1 my or is this phenemenon restricted to southeastern U.S. coastal plain? And where do mid Pleistocene events such as the Tarquinian (Bonadonna, 1967), Torre in Pietran (Stearns, 1978) (or Aurelian, Malatesta, 1978), Harounian and Anfatian (Biberson, 1970; Stearns, 1978) fit in the sea level chronology?

4) How many early Pleistocene marine events compose the aminozone K defined in this study?

5) What misinterpretations of the sea level record have occurred as a result of local or regional tectonics?

This work has dealt with many of the type localities in the Mediterranean basin including the type Calabrian, the type Milazzian, and the type Tyrrhenian (cf. Hearty et al, 1986a). This information combined with similar studies on type localities in the Atlantic (Miller and Mangerud, 1985; Hearty and Hollin, 1986a; 1986b), Tunisia (Miller et al, 1986), and New Guinea (Hearty and Aharon, submitted) will hopefully will shed some light on the validity of past correlations.

Organization of the thesis

An introduction, summary and conclusions

enclose four chapters of this thesis. The locations of
each of these four studies are illustrated in Figure
1-9.

Chapter 2 is a regional synthesis of the sea
level history of the western Mediterranean and the
chronologic implications of this survey. It is
essentially a manuscript of a paper by Hearty et al,
(1986) that appeared in the Bulletin of the Geological
Society of America. In this paper, several
"aminogroups" (defined in Chapter 2) ranging from the
last interglacial (aminogroups C, D and E), to mid
Pleistocene (aminogroups F and G) and the early
Pleistocene (aminogroup K) have been defined and
calibrated to absolute ages. A kinetic model of natural
epimerization in Glycymeris is also presented and
relates to other works presented here. Chapter 2 is, in
essence, a synthesis of this dissertation, while
Chapters 3, 4 and 5 deal with discrete areas that
contain critical stratigraphic sections producing data
that support the regional aminostratigraphy.

Chapter 3 centers around the littoral deposits
of the Salentine Peninsula in southeast Italy. In this
area, particularly within Mare Piccolo, beautifully
exposed stratigraphic sections contain molluscan faunas
and in situ corals. Amino acid and U/Th analyses form
the foundation for the conversion of the relative
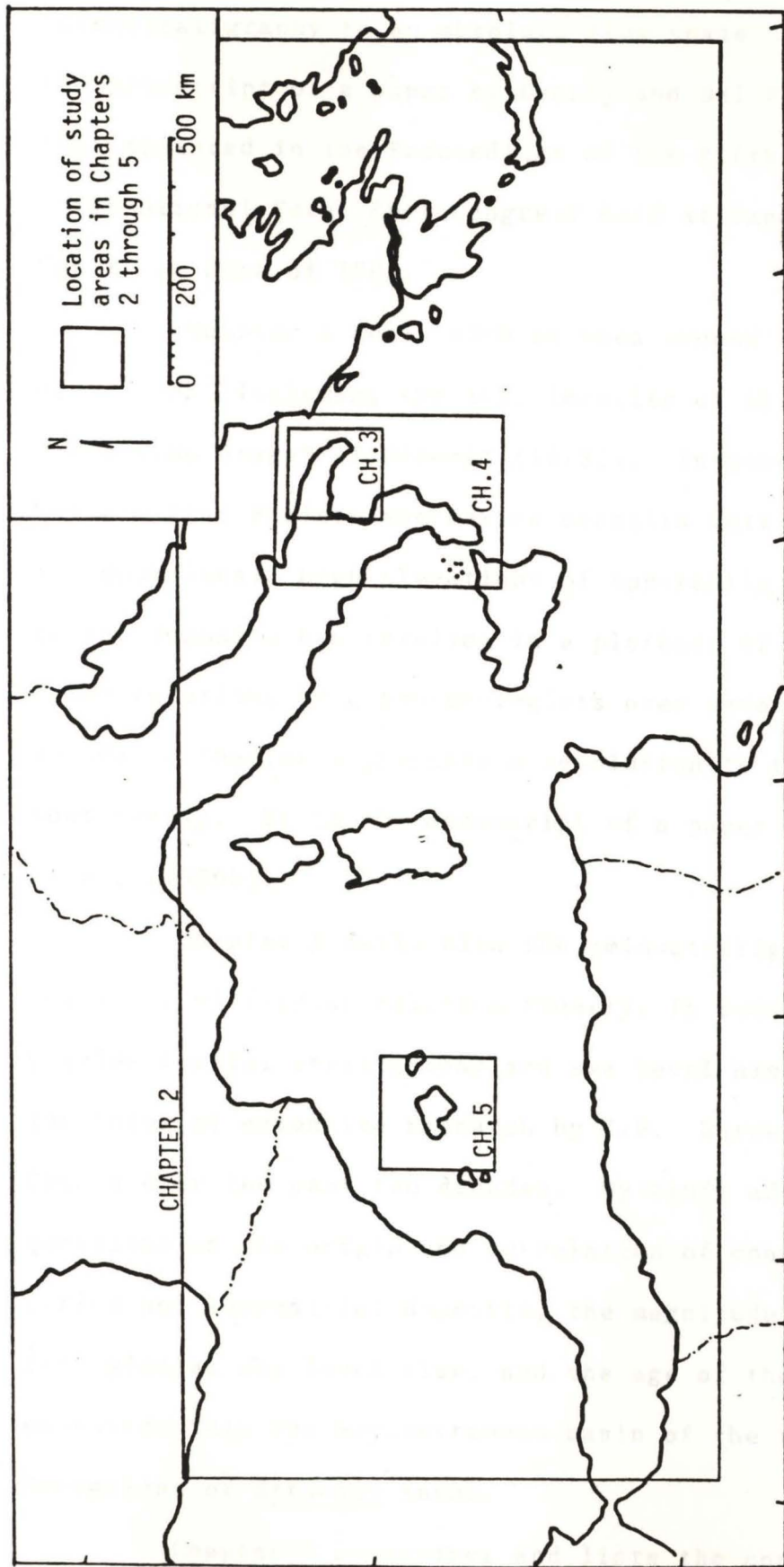
Figure 1-9: Location map of study areas of Chapters 2, 3, 4 and 5.

aminostratigraphy to an absolute time scale. This is
the manuscript of a paper by Hearty and Dai Pra (1985)
that appeared in the Proceedings of the Fifth
International Coral Reef Congress held at Papeete,
Tahiti in June of 1985.

Chapter 4 deals with an area around the Strait
of Messina (including the type locality of the
"Milazzian Stage" of Déperét (1918)). Intense tectonism
has elevated Pleistocene marine deposits well over 100m.
The anomalously high elevations of apparently youthful
marine deposits has resulted in a plethora of
interpretations by geochronologists over several
decades. Chapter 4 presents a resolution to the
controversy. It is the manuscript of a paper by Hearty
et al, (1986b).

Chapter 5 deals with the aminostratigraphy and
sea level history of Mallorca (Hearty, in press). The
complex coastal stratigraphy and sea level history were
the focus of extensive research by K.W. Butzer and Juan
Cuerda over the past two decades. My study addresses
questions on the origin and correlation of coastal
marine and terrestrial deposits, the magnitude of
interglacial sea level rise, and the age of the
expansion into the Mediterranean basin of the tropical
Senegalese or Strombus fauna.

Chapter 6 summarizes and lists the conclusions

of this basin-wide study. Global implications and
direction of future research are also discussed.

CHAPTER II

AMINOSTRATIGRAPHY OF QUATERNARY SHORELINES IN THE MEDITERRANEAN BASIN

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Abstract

The extent of isoleucine epimerization (aIle/Ile ratio) was determined in over 400 individuals of the common taxodont genera Glycymeris and Arca from Quaternary raised marine localities in Mallorca, Spain, Italy, Sardinia, Corsica, Sicily, Tunisia, Morocco and Crete. Comparison of aIle/Ile ratios enables correlation of disjunct marine deposits and relative dating of sequential marine units that have been affected by similar thermal histories. U-series and other dating techniques calibrate aIle/Ile ratios to absolute dates and thus correct for dissimilar thermal histories.

Five discrete aminogroups (C, E, F, G, K) are identified that relate to positive sea level events (interglacials and interstadials) and can be tentatively correlated to deep-sea isotopic stages and substages with the help of absolute dates. Deposits representing each of the five groups are present at sites in central and southern Italy, where because of their proximity and similar temperatures, aIle/Ile ratios can be directly compared. From this Italian "type area" the mean group C Glycymeris ratio is 0.30. These samples are associated with the Neotyrrhenian and are correlated

with isotope substage 5a or 5c. Four U-series coral
dates that average 127 ± 4 ka equate mean ratios of 0.38
(group E) with substage 5e and the Eutyrrhenian. A
major proliferation of fauna now residing on the coast
of Senegal occurred in the Mediterranean basin during
this high-sea-level interval. Mean group F ratios of
0.50 are related to coral and mollusk dates between 200
and 300 ka (i.e., stage 7 or 9). Group G ratios of 0.58
are tentatively equated with either stage 9 or stage 11.
Finally, group K is a collection of ratios between 1.01
and 1.11 representing several early Pleistocene marine
events. An exponential decrease in the epimerization
rate inhibits resolution of these older events.

AIle/Ile ratios in shells from last interglacial
deposits increase from north to south across the study
area, a trend that is positively correlated with present
mean annual temperatures.

Introduction

The Quaternary raised shorelines of the
Mediterranean basin have been the objects of study for
almost 80 years (Hey 1971; 1978). Early Mediterranean
shoreline studies included those of Deperet (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 the elevation of
deposits and were considered interglacial counterparts
of the Alpine glacial chronology. However, attempts to
correlate by altitude (Déperét, 1918; Zeuner, 1959) were
hampered by local and regional tectonics and by the
inherent complexity of the eustatic record. Largely on
the basis of the relative abundance of a tropical
molluscan fauna the mid and late Pleistocene were later
subdivided into the Paleotyrrhenian or T I, the
Eutyrrhenian or T II, and the Neotyrrhenian or 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 mid
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 1982) 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 et al. (1971) have pointed out that there are serious inadequacies in U-series dating of mollusks. Renewed efforts by Bernat et al. (1978; 1982a, b), Hoang et al. (1978) and Radtke et al. (1981; 1982) to date mollusks with U-series and electron spin resonance (ESR) techniques 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 occasionally corals were collected from 46 marine deposits around the basin (Figure 2-1) and were then analyzed for the extent of isoleucine epimerization (mollusks) and U-series disequilibrium (corals).

Amino acid geochronology
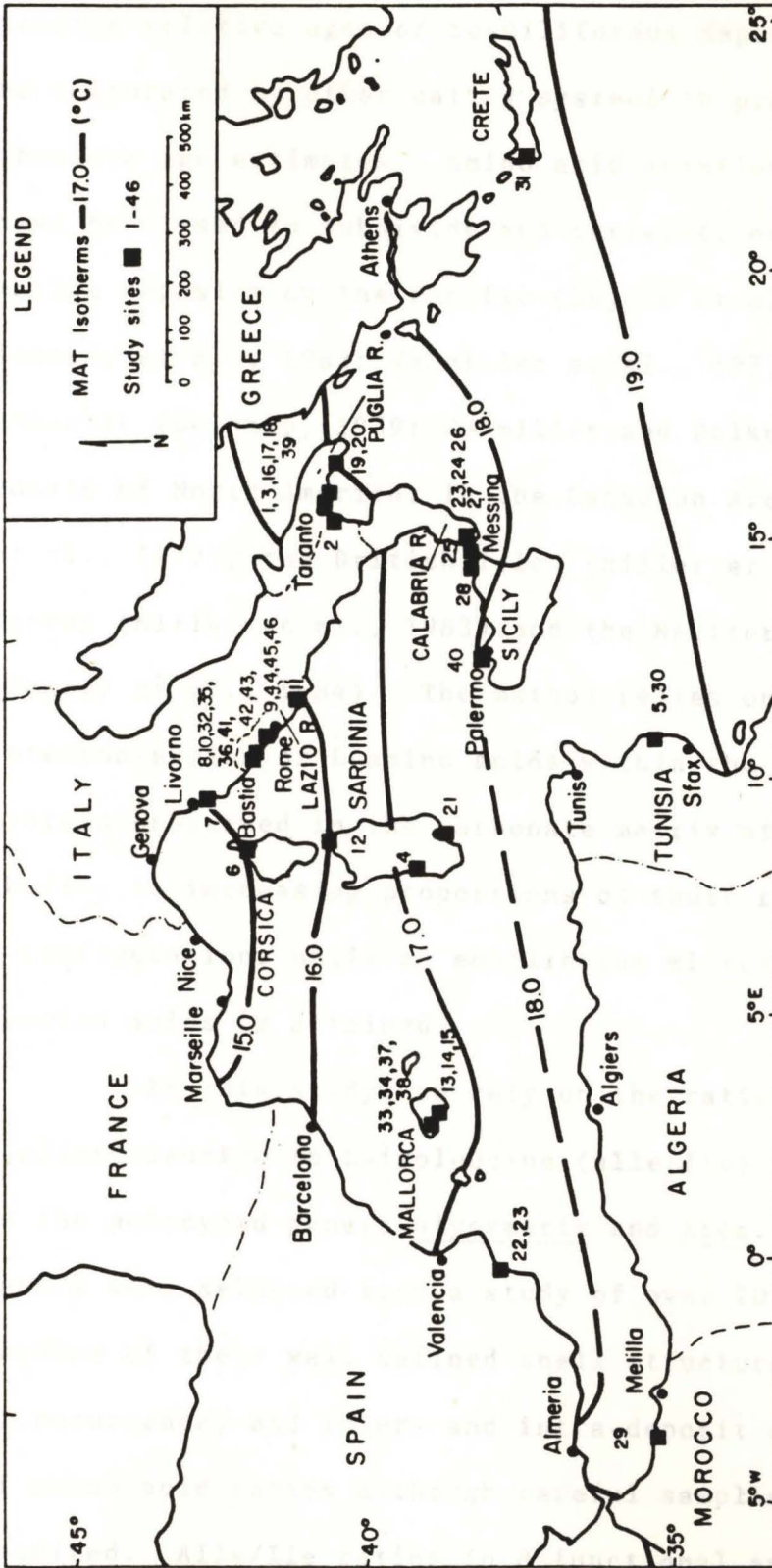
Figure 2-1: Location map of the western Mediterranean basin showing isotherms of present day mean annual temperatures and the loction of study sites. Locality numbers are identified in Table 2-2. (Climate data from Wernstedt, 1972.)

Amino acid geochronology (AAG) can be used to
provide relative ages of fossiliferous deposits or can
be calibrated by 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 et al., 1980;
Kennedy et al., 1982; Wehmiller et al., 1977) and the
Atlantic (Belknap, 1979; Wehmiller and Belknap, 1982)
coasts of North America, in the Canadian Arctic (Miller
et al., 1977), the British Isles (Miller et al., 1979),
Norway (Miller et al., 1983) and the Mediterranean
(Hearty et al., 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 over 20 taxa
because of their well defined shell structure, frequency
of occurrence, and inter- and intra-deposit 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% (Figure 2-2). Because of the intrashell
variability in aIle/Ile ratios it is strongly
recommended that sampling of Glycymeris be restricted to
an interior structural layer isolated from the apex
region of the shell (Location "A" in Fig. 2-2). The
same area was sampled from Arca shells.

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 (HPLC) 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 up to 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 post-depositional 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 a higher
aIle/Ile ratio than in more deeply buried shells of the
same age. To reduce this effect, sampling was generally

Glycymeris violescens*
AAL-3414
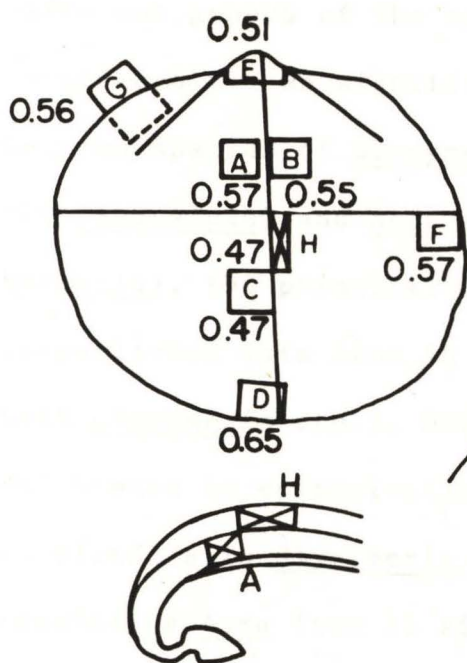
A. Apex, mid-layer
B. Apex, all layers
C. Mid apex-growth edge (All)
D. Growth edge (All)
E. Umbo
F. Right growth edge
G. Left dentition
H. Upper layer only - mid

0.51
0.56
0.57 0.55
0.47 H
0.47   0.57
0.65
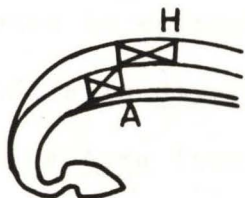
* from Lestra dell'ospedale
(Site 41)

Figure 2-2: 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" in the figure.

restricted to recently cut natural and or artificial
exposures at depths of one meter 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
(unpublished data from 15 sites; 5 with Arca spp., 10
with 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) similarly
allows conversion to Glycymeris aIle/Ile ratios when
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 aminogroups to represent 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 2-1) 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 etc.) attached to letter identifiers (e.g. E1, E2, etc.) 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 intra-group variance. The mean Glycymeris and Arca value (x), the standard deviation (σ) and the number of shells analyzed (N) will be presented in the format 0.37 ± 0.02 (15) in this paper. The results from all sites are summarized in Table 2-2.

Table 2-1: 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.

Table 2-2: Amino acid data, current site temperature (from Wernstedt, 1972) and faunal notes for 46 study sites in the Mediterranean basin.

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

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

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 *Glycymeris*-equivalent ratios using the Gly/Arca index (1.31).

Absolute age calibration

Mediterranean sites span a considerable temperature range (Figure 2-1), hence aIle/Ile ratios cannot be directly compared across the region. Independent age calibration is provided by uranium-series dates on solitary and branching corals from a suite of sites throughout the basin. Corals were collected from several sites (PJH), and others were sent by cooperating scientists from deposits in Sardinia, Tunisia, and Sicily.

Unrecrystallized fossil corals are reliable materials for uranium-series dating because, unlike mollusks, they incorporate uranium into their carbonate exoskeleton during the life cycle of the organism (Ku, 1976). Therefore the measurement of the extent of growth toward radioactive equilibrium of 230Th with respect to 234U permits the calculation of the time elapsed since the deposition of the fossil. The concentration of the uranium and the activity ratios of 234U/238U, 230Th/232Th and 230Th/234U were determined by alpha spectrometry using analytical techniques similar to those described by Szabo and Rosholt (1969). The relative abundance 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, 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 2-1. In all of
the samples the 230Th/232Th activity ratio is high,
generally betweeen 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, while a single date on 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 preserved
in the Puglia region of southeast Italy. The
stratigraphy and paleontology of these shoreline
deposits is well documented (Gignoux, 1913; Gigout,
1960a,b,c; Cotecchia et al. 1969); Uranium-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 (1985).

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 2-3 along with 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; three U-series coral dates equate aminogroup E (0.37) with an age of 122 ± 4ka. Aminogroup F at Carelli (Site 39) at 0.48 is associated with a coral date of 290 ± 50 whereas aminogroup G (0.64) at Torre Casteluccia (Site 3) is >300ka (Dai Pra and Stearns, 1977).

Lazio region, central Italy

An extensive coastal plain north of Rome supports Pliocene to late Pleistocene marine deposits that have stimulated numerous attempts to develop a comprehensive sea level chronology (Bonadonna 1967a, b; Bonadonna and Bigazzi 1970; Ambrosetti and Bonadonna, 1967; Conato et al., 1980; Conato and Dai Pra, 1980; Dai

Table 2-3: 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.

Pra, 1978; Ambrosetti et al., 1972; 1981). Our efforts were directed toward amino acid analyses of shells from key deposits to determine if discrete marine events could be distinguished, and to extend the resultant aminostratigraphy to fossiliferous sites of unknown age. Although morphological shorelines are lacking, several marine episodes can be distinguished from the measured aIle/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 aminogroup K (not collected in Puglia).

Capo Milazzo, Sicily (site 28)

Amino acid ratios and radiometric dating allow the correlation of marine deposits at Milazzo, Sicily (Site 28) (of the "Millazzian stage", Deperet, 1918; DeLamothe, 1911) with Strombus-bearing deposits at Ravagnese (site 26) and Bovetto (site 27) in Reggio Calabria (Bonfiglio, 1972), and these in turn, with the well documented aminogroup E deposits at Mare Piccolo (Hearty et al., 1986).

The mean Milazzian Glycymeris aIle/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 considered under the same present
climatic influence (ca. 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 "Milazzian stage" deposits at the
type locality are correlative with the last
interglacial. Previous speculations on the age of these
deposits range from Sicilian (Gignoux, 1913; Tongiorgi
and Trevisan, 1953), to their own Milazzian stage
(Déperét, 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
(Figure 2-2) 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) in which they
introduce the concept of marine-terrestrial hemicycles.

Recently, Butzer (1983) has proposed a correlation between Mallorcan hemicycles and the deep-sea isotopic record. However, there remain certain ambiguities regarding the absolute chronology of the marine deposits on Mallorca.

J. Cuerda and Hearty sampled numerous marine and terrestrial deposits around the Bay of Palma. Coral collected from the deposit at Son Grauet (site 13) yielded a U-series date of 129 ± 7 ka (Table 2-1) that 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. AIle/Ile ratios in Glycymeris from this site are 0.37 ± 0.03 (6) and 0.28 ± 0.03 (5) in Arca. The Gly/Arca index is 1.32. Arca ratios from Cala Pi (site 14, Table 2-2) 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 aIle/Ile ratios in Arca, averaging 0.41 ± 0.03 (14) (no Glycymeris). The Gly/Arca index predicts an aIle/Ile in Glycymeris of ca.

0.53, well above the ratio measured aminogroup E

Glycymeris ratio at Son Grauet of 0.37. The onlapping

"Neotyrrhenian" deposits at Campo de Tiro (site 33)

contain Glycymeris with two populations of aIle/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 with ratios at 0.42

remains debatable but suggests an early stage 5 age like

Son Grauet (0.38). Glycymeris from a "Neotyrrhenian"

deposit at Cova de sa Gata (site 34, Cuerda, 1979) also

yielded aIle/Ile ratios (0.44 ± 0.01 (3)) similar to the

younger population in the "Neotyrrhenian" at Campo de

Tiro. Although the concept of a "Neotyrrhenian marine

transgression" originated at the Campo de Tiro site

(Butzer and Cuerda, 1962a, b) and a "post-Eutyrrhenian"

(mid to late stage 5) age for such deposits in the

Puglia region has been demonstrated from this survey, we

have yet to produce anything but Eutyrrhenian and/or

older aIle/Ileratios from its type area at Campo de

Tiro. A more recent interpretation of the Mallorcan

data is contained in Chapter 5 of this thesis.

Crete

Although many sites were investigated on the island of Crete (Fig. 2-1), 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 ca. 13.5 m asl. AIle/Ile ratios from Glycymeris average 0.48 ± 0.04 (2) and one Arca of 0.35 from the Strombus layer are in accordance with the MAT (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 et al (1981).

Regional amino acid results

The regional amino acid results from 46 sites around the Mediterranean (Table 2-2) are classified into aminogroups according to the mean value, the apparent or known age and the present mean annual temperature. The number of aminogroup E sites is sufficient to support a contour map of aIle/Ile ratios (Figure 2-3). Uranium series coral dates of ca 125 ka calibrate this surface at six localities (Table 2-1). Within this region the aminogroup E surface can be used as a reference datum by which aIle/Ile ratios from new sites can be placed in a
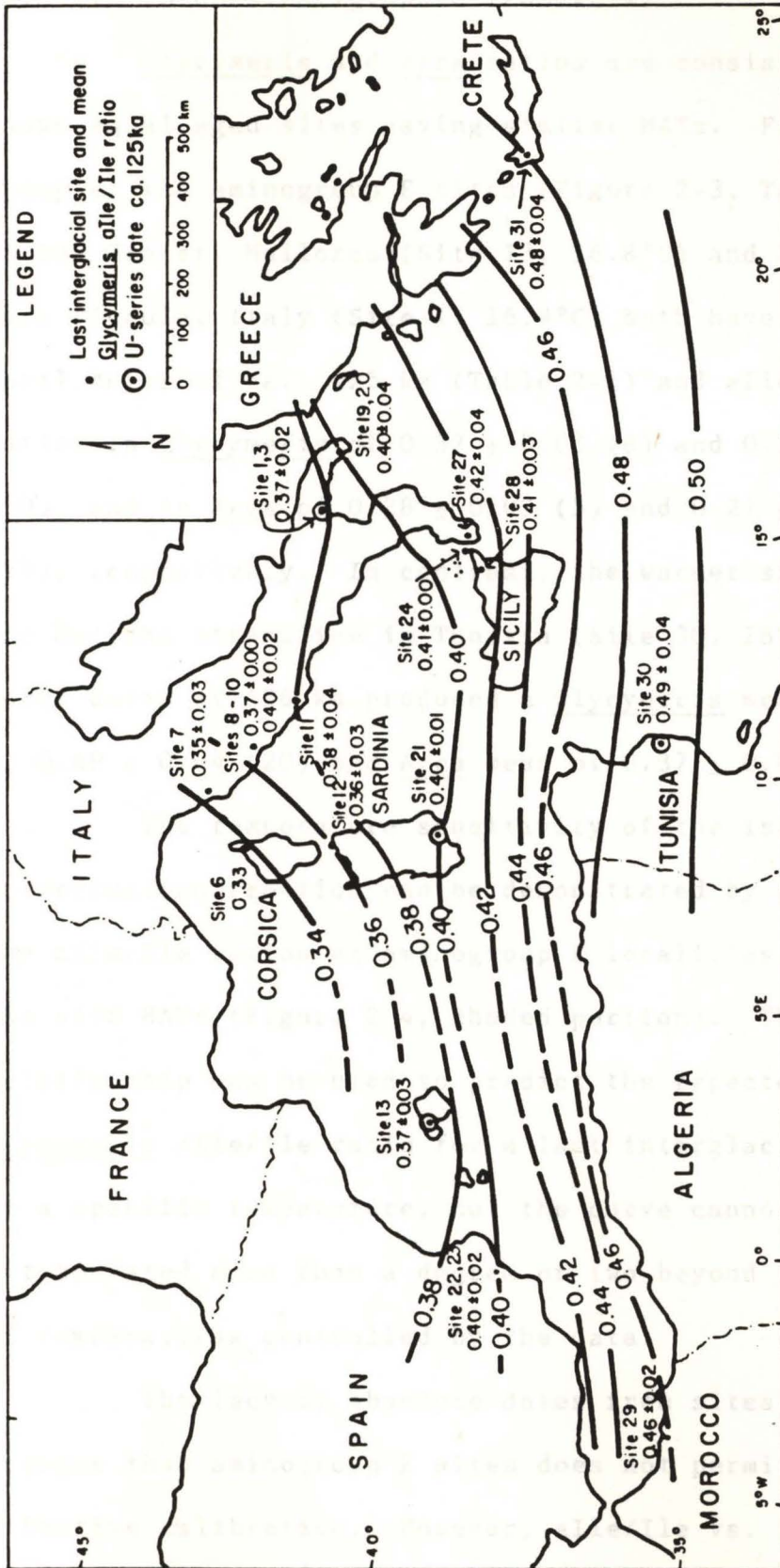
Figure 2-3: Map of contoured Glycymeris aIle/Ile ratios from last interglacial deposits. Note similarity between trends of isopleths in this figure and those of isotherms in Figure 2-1.

relative chronostratigraphic framework.

Glycymeris and Arca ratios are consistent among known equal-aged sites having similar MATs. For example, the aminogroup E sites (Figure 2-3, Table 2-2) 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 ca. 125 ka (Table 2-1) 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) coral dated at 126 ka produced a Glycymeris mean ratio of 0.49 ± 0.04 (20) and 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 MATs (Figure 2-4, 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. However, aIle/Ile vs. MAT plots for older and younger sites produce gradients parallel
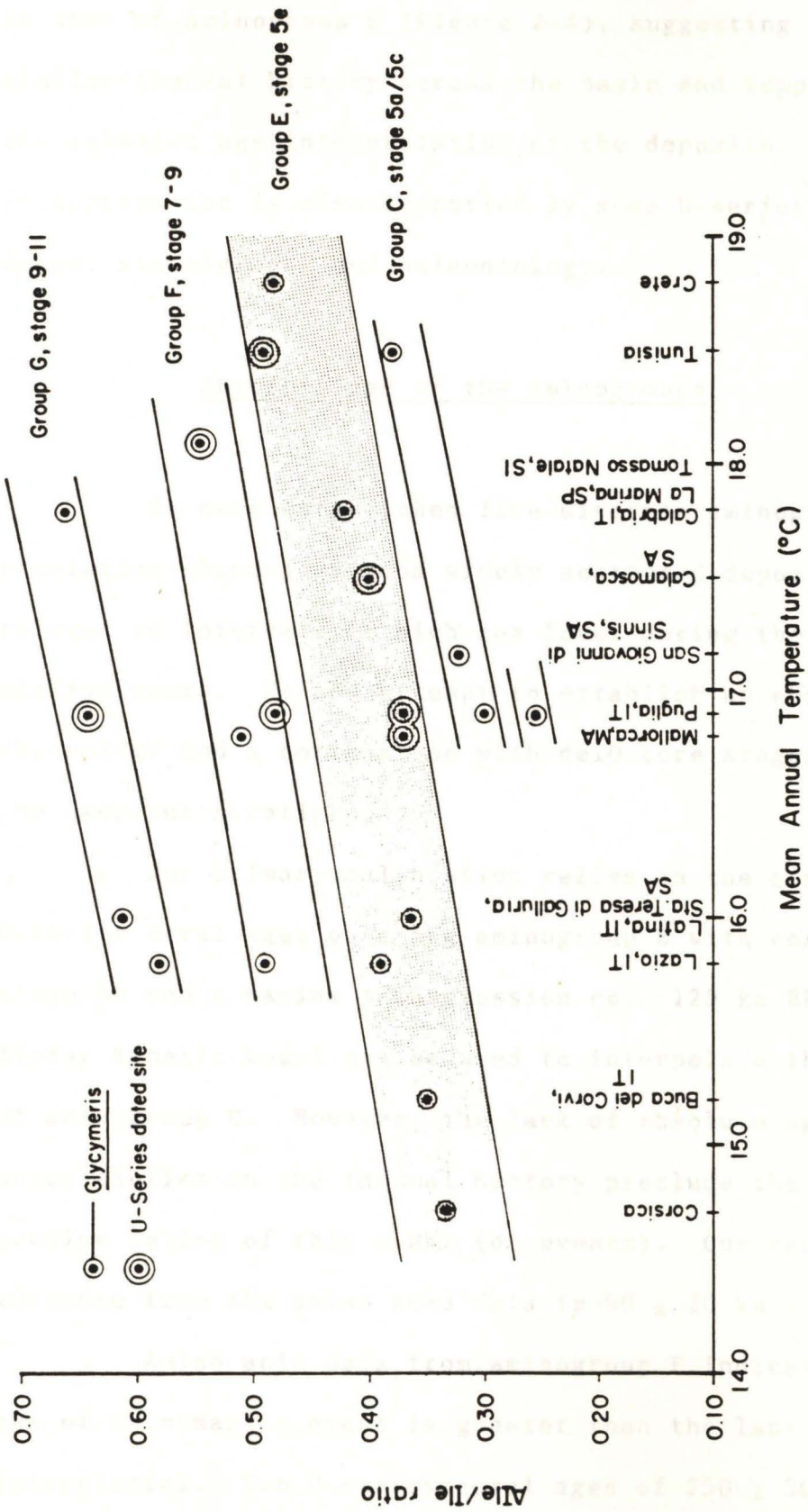
Figure 2-4: Plot of mean aIle/Ile ratios in Glycymeris ratios by group against present-day mean annual temperatures. The trend of increasing aIle/Ile ratios with temperature reflects the control of the temperature on the epimerization rate.

to that of aminogroup E (Figure 2-4), 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 aminogroups in a relative chronology from widely scattered deposits related to intervals of high sea level during the last million years. We now attempt to establish an absolute chronology and a correlation with del0 core stages of the deep-sea stratigraphy.

Our primary calibration relies on the six U-series coral ages equating aminogroup E with core stage 5e and a marine transgression ca. 125 ka BP. A linear kinetic model can be used to interpolate the age of aminogroup C. However, the lack of absolute ages and uncertainties in the thermal history 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 the age of this marine event is greater than the last interglacial. Two U-series coral ages of 250 ± 30 (Table 2-1) and 290 ± 50 (Dai Pra and Stearns, 1977)

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

Amino acid ratios from the older aminogroup G suggest a correlation with an interglacial immediately preceeding aminogroup F. A single U-series coral age of >300 ka has been determined on 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 my BP (Nicoletti, 1979; Everden and Curtis, 1965).

The epimerization history for Glycymeris is reconstructed over the past 1.3 my from mean aminogroup values and corresponding age estimates from sites having MAT's between 15.5 and 16.9°C (Figure 2-5). Aminogroup ages are correlated with warm intervals and isotopic events interpreted from foraminiferal assemblages (Cita et al., 1973) in a Tyrrhenian sea core. Curve 1 best satifies 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 (Hearty, unpub.

aIle/Ile

1.20 1.10 0.90 1.2my

Aminogroup K "window"

820 ka

OPTION 1 (preferred)   OPTION 2

C   AMINOGROUPS

1.20 1.10 0.90 0.80 0.70 0.60 0.50 0.40 0.30 0.20 0.10 0.00

1100 1000 900 800 700 600 500 400 300 200 100

Ka BP

AMINOGROUPS:
C = 0.30 ± 0.02(8)
E = 0.38 ± 0.02(47)
F = 0.50 ± 0.02(36)
G = 0.58 ± 0.02(45)
K = 1.09 ± 0.09(15)

GLYCYMERIS aIle/Ile
from sites 15.5–16.9°C

Warm
WT
Temperate
CT
Cold

from Cita et al., 1973

OP.2 C   E   E   F   G   F   G
OP.1 C   E

$$\left(\frac{1 + D/L}{1 - 0.77\ D/L} \right)$$

20.0 10.0 8.0 6.0 4.0 3.0 2.0 1.0

3 5 7 9 11

a c e

Figure 2-5: Mean aIle/Ile ratios of aminogroups C, E, F, G and K for sites that have present mean annual temperatures 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 E is fixed at 125ka and isotope stage 5e. Aminogroup C is younger, presumably 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 (210ka) establishes an epimerization curve (option 3), the slope of which could decrease with time but cannot increase. Extrapolated at a constant slope, option 3 intersects the aminogroup K "window" and is, therefore, possible. Mean aminogroup G ratios lie on the curve at 330ka (core stage 9). The alternative assignment of aminogroup F to stage 9 establishes a curve (option 4) that if extrapolated at a 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.

data) have shown that the epimerization rate is
exponentially decreasing over 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 aminogroup F is stage 7.

A significant time gap is represented between
ratios in aminogroups G (about 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 also recognized by Chappell
and Veeh (1978) on Atauro. It may correspond to
Blackwelder's (1981) "world-wide lacuna" between 0.4 my
(core stage 11) and 1.1 my. 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 et al. (1969), for stages 15 through 21 by
Stearns (1978), and for stages 13 through 21 by DSDP
552A (Shackleton et al., 1984).

Conclusions

Our interpretation of Mediterranean shorelines
is based on the correlation of deposits containing

aminogroup E aIle/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 (i.e. ca. 125 ka). We assume that all aminogroups are related to light del0 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 with aminogroup F ratios.

Aminogroup C, the Neotyrrhenian, onlaps aminogroup E, and is stratigraphically, paleontologically, and lithologically distinct. Aminogroup C deposits are typically thin, poorly developed, 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 aminogroup E deposits. <u>Strombus</u> may be associated with both aminogroups but unequivocal data has emerged only from last interglacial deposits. Aminogroup G deposits are generally found at higher elevations than younger aminogroups and do not contain Seneglese taxa.

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

1) AIle/Ile ratios from shells in nearby sites can be used to develop local aminostratigraphic zonations of the emerged strandline sequences. Calibration to sites with 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 on 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 with 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 last million-plus

years. Aminogroup C (Neotyrrhenian) is considered to be a mid-to-late-stage 5 event, aminogroup E (Eutyrrhenian) is dated to ca. 125 ka BP 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, comprised of ratios from deposits generally older than 800 ka, constrains the absolute ages of the younger groups.

4) This regional survey has produced sufficient data over a broad area to provide a template through which future local amino acid studies can be integrated into a regional chronological framework.

comments helped to clarify the presentation. J.T. Hollin was particularly helpful in developing many concepts contained in this paper. To all these people we extend our sincere gratitude.

CHAPTER III

AMINOSTRATIGRAPHY AND 230Th/234U DATING OF QUATERNARY

SHORELINES IN THE PUGLIA REGION OF SOUTHEAST ITALY

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Abstract

Amino acid racemization studies of the mollusk
genera <u>Glycymeris</u>, <u>Arca</u> and <u>Astralium</u>, uranium-series
analysis of <u>Cladocora caespitosa</u>, and bio- and
lithostratigraphy have distinguished four ages
(aminozones C, E, F, and G) of marine deposits in the
Puglia region of southeast Italy. Aminozone E, the
Eutyrrhenian, contains primary <u>Strombus bubonius</u> and
other Senegalese taxa, and has been U-series dated at
122 ± 4 ka and thus correlated with isotopic stage 5e.
A younger aminozone C, the Neotyrrhenian, lies within
stage 5 (5a or 5c). Two mid Pleistocene aminozones, F
and G, are tentatively correlated with stages 7 and 9.
An uplift rate of 0.20 ± 0.04 m/ka was calculated from
the well dated 122 ka, 28-35 m, stage 5e shoreline in
Mare Piccolo. Extrapolation of this rate to younger and
older strandlines supports our correlation of aminozone
E, F and G related shorelines with stage 5a or 5c, 7 and
9. A nearly continuous record of sea level changes
during state 5 has been interpreted from the data
generated through intensive stratigraphic studies at Il
Fronte, in Mare Piccolo.

Introduction

Mediterranean shoreline deposits have been the focus of a long history of research (Zeuner, 1959; Hey, 1971, 1978). The Puglia region, particularly the Salentine Peninsula, has been extremely productive in this area of Quaternary research. Early stratigraphic studies on a regional scale (Gignoux, 1913) aided in the definition of several marine events in the mid and late Pleistocene. Much of his effort concentrated on shoreline deposits in Puglia. Gignoux recognized the importance of Strombus bubonius and other subtropical west African taxa as index fossils. This fauna, termed the "Senegalese fauna" (Issel, 1914) was thought to have "immigrated" to the Mediterranean during interglacial periods toward the end of the mid Pleistocene and, to a greater extent, the late Pleistocene. Site-specific research conducted by Gigout (1960a, 1960b, 1960c), in Puglia created a foundation for later work.

The first attempt to establish a chronological framework in Puglia (Cotecchia et al. 1969) proved inadequate due to the limited time-frame of radiocarbon dating, but provided some useful stratigraphic data. More recently, Dai Pra and Stearns (1977) used U-series dating of corals (Cladocora caespitosa) from several Puglia deposits to establish the major elements of a sea level chronology. Our work in Puglia incorporates data

from these previous works and with the help of amino

acid geochronology, we have modified some of the

stratigraphic interpretations and provided a more

reliable chronological framework for the deposits in

Puglia representing a succession of sea level events.

In addition to the racemization study, U-series analyses

of corals, have provided absolute-age calibration of the

amino acid ratios allowing extension of the survey to

non-dated sites (Figure 3-1).

Geologic setting

The Salentine Peninsula is part of a broad

carbonate platform underlain by Cretaceous through

Pliocene limestones gently titled to the southeast with

minor normal faulting and some warping. This mildly

deformed platform is distinct from the intensely folded,

faulted and intruded Appenine complex to the west and

northwest. Mid to late Pleistocene calcarenitic marine

deposits generally lie unconformably upon early

Pleistocene silts and clays of Calabrian and Sicilian

age. These early Pleistocene marine deposits are often

found at elevations exceeding 100m and generally

maintain a deep-water character. This fact implies that

uplift has probably persisted since the early

Pleistocene. Such coastal uplift separates successive
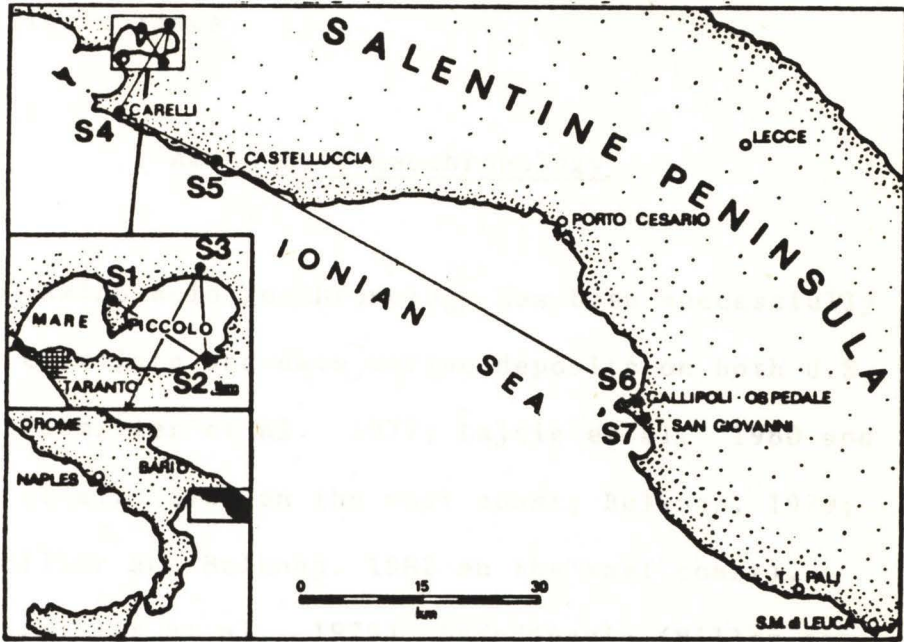
Figure 3-1: Location map of stratigraphic sections (Figure 3-2) discussed in the text, and geographical features.

marine deposits and protects them from subsequent
erosive high stands of sea level. In some islolated
areas, however, downwarping is evident and continuous
into historic times.

Amino acid geochronology

Amino acid geochronology has been successfully
used to correlate and date marine deposits on both U.S.
coasts (Wehmiller et al. 1977; Lajoie et al. 1980 and
Kennedy et al. 1983 on the west coast; Belknap, 1979;
and Wehmiller and Belknap, 1982 on the east coast),
Britian (Miller et al. 1979), Scandinavia (Miller et
al. 1983) and in the Mediterranean (Hearty et al.,
1986). This first amino acid racemization study in the
Puglia region is a subset of a regional study in the
Mediterranean basin (Hearty et al. 1984) and Hearty et
al. (1986).

We rely on the ratio of the non-protein amino
acid D-alloisoleucine to its protein diasteriomer
L-isoleucine (aIle/Ile ratio). This ratio increases
from near zero in a modern shell to an equilibrium ratio
of 1.30 ± 0.05. In Puglia, the aIle/Ile ratio in the
total (free plus peptide bound amino acids) fraction has
been determined in over 140 shells of eight genera
particularly Glycymeris and Arca. Astralium rugosum is

common in mid-Pleistocene deposits and has proven
equally effective for amino acid studies. It is
considered a faster racemizer when compared to
Glycymeris and Arca.

The fundamental assumption in amino acid
geochronology is that temperature is the primary
rate-controlling variable in the epimerization reaction.
Temporally equivalent shells will have similar aIle/Ile
ratios only if they have experienced similar
post-depositional thermal histories. In our program,
the samples are carefully collected to minimize the
possiblity of extreme thermal conditions. Sampling
generally is restricted to freshly man cut or man made
sections in which the shells have remained beneath 1 m
or more overburden since shortly after deposition.

Across the Mediterranean basin, the present mean
annual temperature (MAT) in coastal areas varies between
14°C and 20°C (Wernstedt, 1972). Because of the thermal
gradient across the region, aIle/Ile ratios cannot be
directly compared beyond local climatic zones; unless
calibrated by absolute dates (aminogroups as defined in
Hearty et al., (1986)). Along the Salentine Peninsula
the mean annual temperature is essentially constant
(16.9 to 17.2°C) and aIle/Ile ratios can be used
directly to develop a local aminostratigraphy. In this
study we will refer to discrete clusters of aIle/Ile

ratios as aminozones (Nelson, 1978), remembering that on

a regional scale these aminozones are subsets of and

correlative with aminogroups.

Outer layers of Glycymeris are mechanically

removed and the inner layer at the apex of the shell

further leached with HCl to reduce possible

contamination. Care was taken to sample precisely the

same area of the shell in every case. Experimental

results indicate that amino acid ratios may vary up to

30% in various functional parts and structural layers of

a single Glycymeris shell (Hearty et al., 1986). After

standard acid hydrolysis, amino acid residues in the

total fraction were separated on an automated

ion-exchange amino acid analyzer (Miller and Hare,

1980). Peak heights of the total fraction (free plus

peptide bound) aIle/Ile ratios are calculated by an H-P

3390 computing integrator.

Stratigraphy of Puglia marine deposits

Seven composite stratigraphic sections from Mare

Piccolo, Carelli, Torre Casteluccia and near Gallipoli

are presented in Figure 3-2. These litho- and

biostratigraphic sections resemble interpretations of

previous authors (Dai Pra and Stearns, 1977; Cotecchia

et al. 1969; Gigout 1960a, b, c) but revisions of some

S1
17m

S2
10m

S3
26m

S4
27m

S5
3m

S6
9m

S7
7m

0.36

0.25[1]

0.37

0.39[1]

0.35[3]

0.38

0.48

0.28[1]

0.39

0.64[2]

0.41

0.45

0.38

?

M. San Pietro

Carelli

Punta Penna

Il Fronte

T. Casteluccia

Gallipoli

T. San Giovanni

N.B. Superscripts
explained in Table 1.

Vertical Scale:
1meter
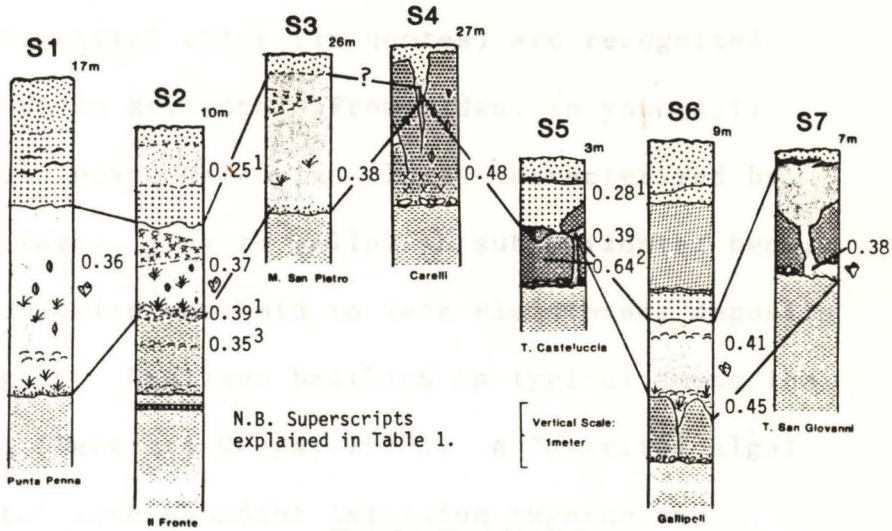
EQUIVALENT AMINOZONE

EXPLANATION OF UNITS

C — Holocene soil developed on underlying units

C — "Estuarine marl"

C — "Reddish calcarenite"

E — "Strombus beds"

E — "Ostrea beds"

E — "Transgressive unit"

F — "Calcarenites with Glycymeris"

G — "Detrital algal calcarenite"

— "Calabrian clays"

— Calcarenitic eolianite

— Shell hash

— Ash bed

— Articulated valve

— Calcrete lens

— Gradational contact

— Unconformity

— Cladocora caespitosa

Figure 3-2: Stratigraphic sections and Glycymeris data from localities on the Salentine Peninsula of southeast Italy.

stratigraphic relationships are suggested in light of
this study. Eight marine and transitional
marine/terrestrial units (in quotes) are recognized
among the seven sections. From oldest to youngest:
"early Pleistocene Calabrian clays" characterized by
silty to clayey, grey to yellowish subhorizontal beds,
commonly underlie most mid to late Pleistocene deposits
in the region. Hyalinea balthica is typical among the
microfauna (DeCastro-Coppa, 1979). A "detrital algal
calcarenite" with abundant Astralium rugosum and
Cladocora caespitosa fragments is best exhibited at the
Torre Casteluccia (section 5) 18 km southeast of Taranto
(Fig. 3-1). A "calcarenite with Glycymeris" and less
algal influence in the structure of the beds is present
in section 4 at Carelli 7 km south of Taranto and
contains articulated Glycymeris violescens and abundant
Astralium rugosum. The oldest bed of the last
interglacial complex at Il Fronte consists of reworked
Calabrian silts and clays and contains a diminutive
molluscan fauna. An angular unconformity separates the
early Pleistocene Calabrian beds from this
"transgressive unit" at Il Fronte. A unit of "Ostrea
beds" is gradational from the transgressive unit and is
characterized by calcareous silts and sands containing
in situ Ostrea, Mytilus, Chlamys and Cladocora. The
"Strombus beds" are also gradational from the Ostrea

beds and contain thermophilous mollusks in living position in a sedimentary matrix of a white calcarenite. In situ Cladocora caespitosa is abundant in the lower portion of this unit. At Gallipoli, the Strombus beds terminate at their upper contact with a 30 cm zone composed almost exclusively of mollusk shells including elements of the Senegalese fauna. The same horizon at Il Fronte contains discontinuous lenses of shell hash or coquina. "Reddish calcarenites" are separated from the underlying unit(s) by an irregular erosional surface. This unit is consistent in its position overlying the Strombus beds. At Il Fronte, Punta Penna and Gallipoli, there are abundant reworked marine shells, occasional vertebrate fossils and terrestrial gastropods including Helix. At Torre Casteluccia the reddish calcarenite is clearly a marine unit complete with articulated marine shells A bed of "estuarine marls" is paraconformable on the reddish calcarenites at Il Fronte. These beds are composed of brown to tan silts and clays with diminutive mollusk forms indicating euryhaline water conditions. A best example of the estuarine marls is exhibited near the mouth of a small river that debouches into Mare Piccolo near Il Fronte.

Aminostratigraphy of Puglia marine deposits

The amino acid data from the seven sections (Figure 3-2) on the Salentine Peninsula are presented in Table 3-1. The aminostratigraphy is based on aIle/Ile ratios from the genera Glycymeris, Arca and Astralium, but in some units other taxa (see Table 3-1) were analyzed where the principle genera were not available. Aminozones are defined as those fossiliferous deposits having distinct mean aIle/Ile ratios. In this case, we can distinguish aminozones C, E, F and G. Numerical subdivisions of aminozones (E1, E2, etc.) result from litho- or biostratigraphic differences among the units. Thus, the aminozones corresponding to the lithostratigraphic units (Fig. 3-2) noted above are: Calabrian clays = no amino acid determination but probably corresponds to the early Pleistocene aminogroup K of Hearty et al. (1986) based on the K/Ar date of DeCastro-Coppa (1971). A detrital algal calarenite at Torre Casteluccia is equivalent to aminozone G; The calcarenite with Glycymeris at Carelli is equivalent to aminozone F. The transgressive unit, the Ostrea beds and the Strombus beds all yield aminozone E ratios of last interglacial age. The reddish calcarenites and the estuarine marl are associated with a somewhat younger aminozone C.

Uranium-series calibration of amino acid ratios

Table 3-1: Alle/Ile ratios from Puglia sites located in
Figure 3-1. Mean annual temperature of the sites varies
between 16.9°C and 17.2°C.

Aminozone (this study)	Bio-Litho Unit*	Site and Section Number	Mean alle/Ile ratio, standard deviation (1σ) and number (N) of shells analyzed.				
			Glycymeris	Arca	Astralium	Dentalium	Spisula
C	C1	Il Fronte (2)	.25[1]	.19 (1)		.31 ± .02 (2)	.26 ± .01 (2)
	C2	T. Casteluccia (5)	.28 ± .02 (5)	.22 ± .03 (9)	.41 ± .03 (5)	.45 (1)	.32 ± .04 (3)
B	E1	Punta Penna (1)	.36 ± .01 (10)	.29 ± .03 (2)			
	E1	Il Fronte (2)	.37 ± .02 (10)	.27 ± .05 (22)		.61 ± .02 (4)	.35 ± .01 (3)
	E1	Massa San Pietro (3)	.38 ± .01 (3)				
	E1	T. Casteluccia (5)	.39 (1)	.26 (1)	.49 ± .03 (5)		
	E1	Gallipoli (6)	.41 ± .04 (15)	.31 ± .03 (2)			
	E1	T. San Giovanni (7)	.38 ± .02 (4)				
	E2	Il Fronte (2)	.39[1]				
	E2	Gallipoli (6)	.45 (1)	.30 ± .03 (5)			
	E3	Il Fronte (2)	.35[3]			.55 ± .01 (2)	.36 ± .02 (2)
F		Carelli (4)	.48 ± .02 (7)		.71 ± .03 (3)		
G		T. Casteluccia (5)	.64[2]		.91 ± .04 (3)		

*Numerical subdivisions based mainly on lithostratigraphic and biostratigraphic zonations.
[1] Interpreted from Gly/Arca index: Gly a/I = 1.31 Arca a/I.
[2] Interpreted from Gly/Astralium index: Gly a/I = 0.71 Astralium a/I.
[3] Interpreted from Gly/Dentalium index: Gly a/I = 0.65 Dentalium a/I.

Corals dated in this study have been processed by Dr. Barney Szabo, USGS, Denver, Colorado using analytical techniques similar to those described by Szabo and Rosholt (1969). The corals (<u>Cladocora</u> <u>caespitosa</u>) were collected in the field by Hearty and Dai Pra. The results of these analyses are presented in Table 3-2; the high 230Th/234Th activity ratios indicate negligible initial 230Th in these samples.

Multiple analyses of corals from Il Fronte (section 2, Fig. 3-2) demonstrate the reproducibility of the technique (Table 3-2). Two separate analyses were performed on a single collection of <u>Cladocora</u>. The two ages are not statistically different at the one sigma confidence level. A second sample of <u>Cladocora</u> was also dated and yielded a U-series age indistinguishable from the first sample. We feel that these three analyses demonstrate the integrity of this coral as a material for U-series dating. Also included in Table 3-2 are data produced by Dai Pra and Stearns (1977). Four U-series coral dates from the [same section] at Il Fronte are 87, 106, 130 and 154 ka (Table 3-2). Other Dai Pra and Stearns (1977) dates from Carelli (site 4) and Torre Casteluccia (site 5) broadly agree with our mid Pleistocene amino acid determination of the age of aminozones F and G at these localities.

Table 3-2: Analytical data and calculated uranium-series ages of fossil corals from several sites along the Salentine Peninsula. Samples H-C are from this study. Samples LJ are from Dai Pra and Stearns (1977).

Site	Sample No.	Uranium (ppm)	$\frac{234U}{238U}$	$\frac{230Th}{232Th}$	$\frac{230Th}{234U}$	U-series age (ka)
Il Fronte	H-C-1A	4.20 ± 0.06	1.20 ± 0.02	217 ± 65	0.67 ± 0.02	117 ± 7
Il Fronte	H-C-1B	4.14 ± 0.06	1.10 ± 0.02	82 ± 33	0.70 ± 0.02	128 ± 7
Il Fronte	H-C-2	3.76 ± 0.06	1.11 ± 0.02	83 ± 33	0.68 ± 0.02	121 ± 7
Il Fronte	LJ 483		1.15 ± 0.02		0.56 ± 0.02	87 ± 4
Il Fronte	LJ 481		1.13 ± 0.02		0.64 ± 0.03	106 ± 8
Il Fronte	LJ 505		1.12 ± 0.02		0.71 ± 0.03	130 ± 10
Il Fronte	LJ 487		1.14 ± 0.03		0.78 ± 0.03	154 ± 13
Carelli	LJ 410	3.00 ± 0.06	1.11 ± 0.03		0.95 ± 0.04	290 ± 50
T. Casteluccia	LJ 394	3.10 ± 0.06	1.09 ± 0.03		1.00 ± 0.04	>300

We conclude that aminozone E represents the last interglacial (substage 5e); aminozones E and F, predate the last interglacial, and aminozone C is significantly younger than 125 ka based on extrapolation of age from the U-series dated aminozone E at ca. 125 ka.

Discussion

Mare Piccolo (Punta Penna, Il Fronte and Frutteto):

The quiet embayment of Mare Piccolo offers an unusual opportunity to study a different style of sedimentation than on the open coastline. The marine strata within Mare Piccolo are generally horizontal and laterally persistent across the basin. During the early phase aminozone E (units E3, E2, Fig. 3-2), sedimentation was quiet allowing the preservation of fossils in their living position. This quiet trend continued up to the onset of deposition the Strombus beds (aminozone E, Table 3-1, Fig. 3-2) but is capped by an influx of coarser grained sediment containing broken shell material. This higher energy episode probably marks the topping of the Taranto Peninsula (ca. 25 m asl) by the rising sea. This magnitude of sea level rise would expose all of the Mare Piccolo sites to open ocean conditions in contrast to the breached basin of today. The 28-35 m asl last interglacial shoreline

recognized by Gignoux (1913), Dai Pra and Stearns (1977) and by Cotecchia et al (1969) is represented by the Frutteto section (26 m asl) in this study. The presence of Balanus, Patella and other littoral forms at Frutteto support the nearshore environment interpreted from this level. Punta Penna (17 m asl) and Il Fronte (10 m asl) represent progressively deeper water sedimentation during the Eutyrrhenian in the basin.

Carelli:

The change from lower to higher energy sedimentation can be seen between Mare Piccolo and the west side of the Taranto Peninsula at Carelli are from Glycymeris violescens in living position. Astralium data (Table 3-1) indicate that the Carelli deposits are younger than those at Torre Casteluccia, confirming the existence of at least two mid Pleistocene levels.

Torre Casteluccia:

A similar open ocean theme is revealed in the stratigraphy at Torre Casteluccia (site 3-5). Three cycles (aminozones C, E and G) of marien deposition, induration, and erosion are represented. Figure 3-2 (section 4) illustrates deposits that are successively reworked and removed by younger marine transgressions. The result is complex stratigraphic relationships that

change facies over short lateral and vertical distances.
Eutyrrhenian deposits are poorly represented at this
site, only one Glycymeris and one Arca have yielded
aminozone E ratios. No Strombus have yet been found in
the discontinous pods of Eutyrrhenian sediment.

Gallipoli:

Marine deposits at Ospedale di Gallipoli (site
6) have attracted Quaternary geologists and
paleontologists throughout the 20th century. Gignoux
(1913), Blanc (1953), Mirigliano (1953, 1956), Gigout
(1960c) and Cotecchia et al. (1969) have all attempted
to unravel what appears to a stratigraphy indicative of
several sea level events. The presence of Strombus beds
signal the Eutyrrhenian phase of the last interglacial
in deposits that rise to near 10 m asl. In our study,
numerous analyses of Glycymeris and Arca positively
correlate this phase with aminozone E at Il Fronte dated
at ca. 125 ka. Seventeen analyses were made of
Glycymeris and Arca shells from several different
sedimentary facies at Gallipoli. The mean aIle/Ile
ratios from all units lie within the standard error of
the overall Glycymeris mean of 0.41 ± 0.04 for the site.
A probable mid Pleistocene bed produced no usuable shell
material.

Torre San Giovanni:

This section on the southern edge of Gallipoli
(Fig. 3-1) records a mid-Pleistocene transgression
followed by the Eutyrrhenian Strombus event; aIle/Ile
ratios in Glycymeris from the younger sediments fall in
aminozone E. The stratigraphy at Torre San Giovanni
clearly demonstrates the motaring effect of successive
marine deposits around older reworked blocks (Figure
3-3). Strombus-bearing sediments completely encase
blocks of reef limestone of an older sea level event
similar to that observed at Ospedale di Gallipoli. This
style of shoreline sedimentation should be anticipated
on carbonate shorelines where "beach rock" formation is
rapid and wave energy is high.

Implications for the local sea level and tectonic history

The sea level history since the last
interglacial, imprinted on coastlines of upward tectonic
movement, has been interpreted from the stratigraphy,
relative age and absolute age determinations at three
deposits in Mare Piccolo (cf. figure 3-4). The Il
Fronte section provides a continuous record through the
aminozone E (stage 5e) and again in aminozone C (stage
5c or 5a). The two episodes are separated by an

UNIT

D ▨ Red soils with lenses of
encrusted carbonate.

C ▨ Marine calcarenite with
Astralium rugosum.

B ▨ Marine calcarenite with
Glycymeris shells.

A ▨ Sicilian age calcarenite with
pebbles and shells.

▨ Reworked cobbles of unit "A".

▨ Strombus bubonius.

Figure 3-3: A sketch of the the Torre San Giovanni
Section (S7) demonstrating the "motaring effect" where
blocks of early Pleistocene beachrock is entirely
encompassed by younger last interglacial beach rock.
This style of sedimentation is common on high energy,
carbonate shorelines. The process involves deposition of
carbonate sediments, induration, erosion of tortuous
forms, and redeposition of sediments during subsequent
transgressions. Strombus bubonius was located near the
head of the arrow in the sketch.
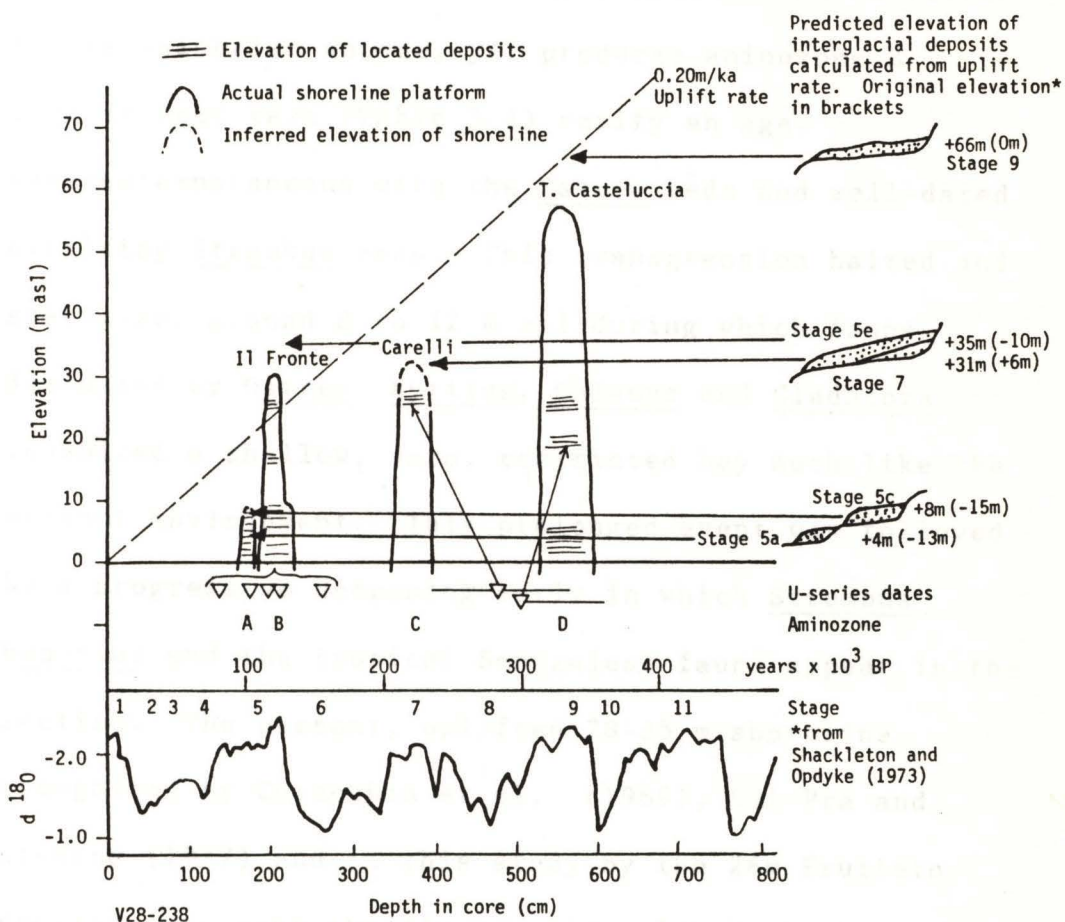
Figure 3-4: A possible correlation of oxygen isotopic events and strandlines on the uplifted southwestern coastline of the Salentine Peninsula. Given an uplift rate of 0.20 m/ka, determined from the well-dated last interglacial sites in Mare Piccolo, we estimate possible elevations of older and younger deposits. We have used estimated absolute elevations of each isotopic event from Shackleton and Opdyke (1973) and others.

unconformity developed during a period of subaerial
exposure.

The onset of aminozone E is signaled by
transgressive unit that maintains much of the character
of its Calabrian source, yet produces aminozone E
ratios: four taxa (Table 3-1) verify an age
penecontemporaneous with the Ostrea beds and well-dated
overlying Strombus beds. This transgression halted and
stabilized around 8 to 12 m asl during which fauna
dominated by Ostrea, Mytilus, Chlamys and Cladocora
inhabited a shallow, warm, restricted bay much like the
present environment. This prolonged event was followed
by a progressive deepening early in which Strombus
bubonius and the tropical Senegalese fauna appear in the
section. The present, uplifted 28-35 m shoreline
recognized by Cotecchia et al. (1969), Dai Pra and
Stearns (1977) and in this study by the 26m Frutteto
section, was near the final maximum level at which the
stage 5e transgression appears to have stabilized,
however, this strand may also have been developed and
occupied by previous high sea levels (Figure 3-4).
Discontinuous lenses of shell hash capping the
Eutyrrhenian sections in Mare Piccolo suggest that the
Taranto Peninsula at ca. 25 m was flooded by the rising
sea, exposing the Mare to open-ocean, high energy
conditions. Sea level then fell well below present sea

level during isotopic stage 5d.

Previous to and early in a mid/late stage 5 transgression, the reddish calcarenites resulted from reworking and redeposition of Strombus beds. The reddish color is probably incorporated from terra rossa soils developed on calcarenite during the 5d interval. At Torre Casteluccia, a reddish calcarenite contains articulated marine valves; producing aIle/Ile ratios clearly younger than the same taxa from the Strombus beds (aminozone E). Stabilization of the level of the aminozone C transgression is indicated by deposition of several meters of the estuarine marl at Il Fronte. The marl rises to about 10 m asl.

Acknowledging the potential for error in utilizing a Barbados-type model (Broeker et al. 1969; Bloom et al., 1975; Shackleton and Opdyke, 1973), in the case of Puglia, it remains advantageous to employ such a model to constrain our age estimates of strandlines associated with aminozones. If we accept the ca. 125 ka, stage 5e age of the strandline at 28-35 m and assign an original elevation of +10 ± 5 m, then an average uplift rate of 0.20 ± 0.04 m/ka (0.16 to 0.24 m/ka) is calculated. We also assume that the error (ca. ± 5 m) in original elevation estimates in a Barbados-type model are not cumulative and will fall within the error calculated from maximum (0.24 m/ka) and minimum (0.16

m/ka) uplift rates. We will use original sea level elevations collected from several sources averaging -10 ± 5 at 85 ka (5a), -10 ± 5 m at 105 ka (5c), + 10 ± 5 m at 125 ka (5e), -10 ± 5 m at 210 ka (7) and 0 ± 5 at 330 (9) for our calculations.

Extrapolating from stage 5e the uplift rate of 0.20 ± 0.04 m/ka our model predicts stage 5a deposits at 7 ± 4 m, 5c deposits at 11 ± 4 m, stage 5e at 35m, stage 7 deposits at 37 ± 8 m and stage 9 deposits at 66 ± 13 m. Strandlines are present in these intervals (10-15 m, 28-35 m and 55-60 m) and are associated with aminozones C, E and F, and G, respectively. We feel this test supports our correlation of aminozones C with 5a or 5c, E with stage 5e, F with stage F, and G with stage 9.

Acknowledgements

CHAPTER IV

AGE OF LATE QUATERNARY MARINE DEPOSITS OF SOUTHERN

ITALY DETERMINED BY AMINOSTRATIGRAPHY, FAUNAL

CORRELATION, AND URANIUM-SERIES DATING

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Abstract

Numerous studies on the 40 to 60 meter
strandline at Capo Milazzo, Sicily (ex-Milazzian stage)
yielded no consensus on its place in the Pleistocene sea
level chronology. The deposit has been considered to be
Sicilian (Sequenza, 1903; Gignoux, 1913; Tongiorgi and
Trevisan, 1953; Malatesta 1961-63), of its own
mid-Pleistocene Milazzian stage (Déperét, 1918;
DeLamothe, 1911), and Tyrrhenian II (Ottmann and Picard,
1954; Mars, 1956). Later independent studies at Capo
Peloro (Bonfiglio and Violanti, 1985), Ravagnese and
Bovetto (Bonfiglio, 1972) assigned a Tyrrhenian II age
to the marine beds there that contain Senegalese forms
including Strombus bubonius. Capo Milazzo, on the other
hand, is conspicuously lacking the Senegalese elements
although some warm-water forms are present. This is
probably a result of a unique shoreline facies on the
rocky peninsula of Capo Milazzo.

In light of this problem, a new method, amino
acid geochronology was introduced at fossiliferous sites
in southern Italy. The purpose of this investigation is
to determine if aIle/Ile ratios from deposits of unknown
age could be correlated to those of known age.

Paleontology and some radiometric dating are used to
support this correlation. Through these devices we can
confidently correlate the 40-60 m strandline at Capo
Milazzo with Eutyrrhenian (TII) deposits at Bovetto,
Capo Peloro, and Mare Piccolo.

Introduction

For nearly a century, controversy has surrounded
the placement of deposits at Capo Milazzo, Sicily in the
Pleistocene sea level chronology. These deposits, lying
40 to 60 meters above sea level, have been assigned a
Sicilian age; Gignoux, 1913; Tongiorgi and Trevisan,
1953; Malatesta 1961), a Milazzian age (Déperét, 1918;
DeLamothe, 1911), as well as a Tyrrhenian age (Ottmann
and Picard, 1954; Mars, 1956). The Milazzian stage name
has since been eliminated from the nomenclature and
replaced with an equally questionable term, the
"Paleotyrrhenian" (Bonifay and Mars, 1959). The reasons
for the questionable age of the marine beds at Capo
Milazzo are: 1) the presence of a dominantly "banale"
or common fauna having no true indicators of climate any
different than the present; 2) the anomalous 40-60 m
elevation of the deposits; and 3) the lack of adequate
absolute dates on the deposits. In addition, there are
two key sites in Calabria with abundant faunas but no

secure absolute ages.

Our efforts were to study the amino acid composition of shells from these sites to determine if this method could prove or disprove the previous speculations on the age of deposits at Milazzo. Although amino acid ratios can be used independently for relative dating; they are best used when calibrated to other dating systems (Carbon-14, U-series, K/Ar). We collected corals from Milazzo but found them to be either reworked or chemically altered. Attempts to U-series date calcareous algal nodules have met with questionable success. The nearest well-dated site in the region is at Mare Piccolo where several U-series coral dates have been obtained along with amino acid ratios on fossil mollusks. Our approach then is to compare amino acid ratios from Reggio Calabrian (Ravagnese and Bovetto), and Sicilian (Capo Milazzo and Capo Peloro) sites to the more secure and calibrated ratios from Mare Piccolo (Figure 4-1).

Amino acid geochronology

The geochronological potential of certain chemical reactions involved in the degradation of proteins in fossils was first recognized by Abelson (1955) and Hare and Mitterer (1967, 1969), and has been
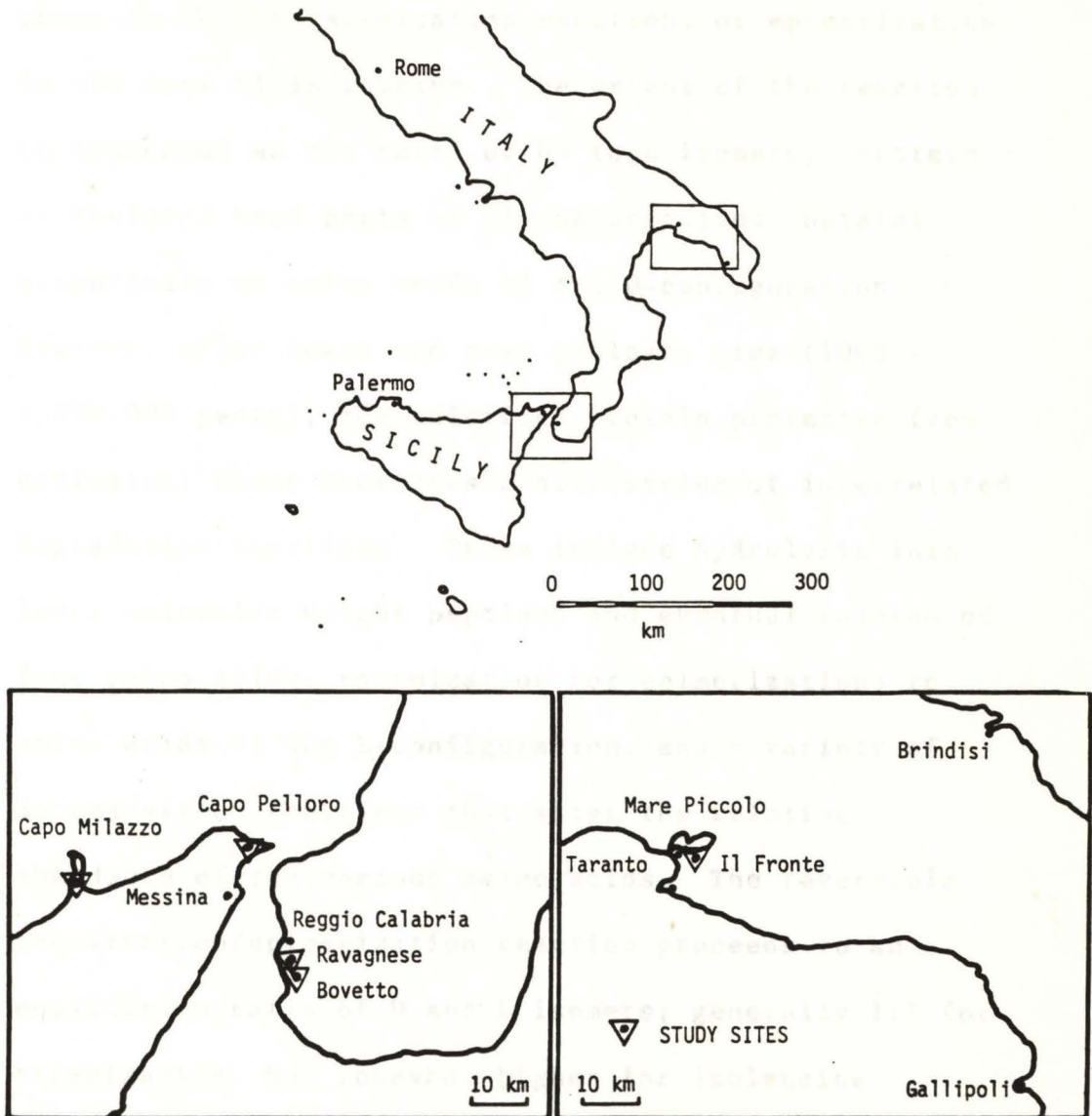
Figure 4-1: Location map of study sites mentioned in the text (indicated by triangles) and located near the Strait of Messina and the Gulf of Taranto.

the focus of an increasing number of investigations over the last decade. The most promising reaction has been shown to be the racemization reaction, or epimerization in the case of isoleucine. The extent of the reaction is expressed as the ratio of D- to L-isomers. Protein in skeletal hard parts of living organisms contains essentially no amino acids of the D-configuration. However, after death and over geologic time (1000 - 1,000,000 years), the calcified protein protected from biological decay undergoes a slow series of interrelated degradation reactions. These include hydrolysis into lower molecular weight peptides and eventual release of free amino acids, racemization (or epimerization) to amino acids of the L-configuration, and a variety of decomposition reactions that alter the relative abundance of the various amino acids. The reversible racemization/epimerization reaction proceeds to an equilibrium ratio of D and L isomers; generally 1:1 for racemization, but somewhat higher for isoleucine epimerization (1.3:1). This equilibrium value is reached at around 1.5 to 2.0 my in the climate of the Mediterranean basin. D-alloisoleucine to L-isoleucine ratios (aIle/Ile) have been determined in the total fraction (free amino acids plus those in the peptide-bound state that have been artifically released by heating the dissolved decalcified samples in 6N HCl

for 22 hours at 110°C) for the samples in this study.
The samples were analyzed on a automated ion-exchange
high pressure liquid chromatography amino acid analyzer
(Miller and Hare, 1980).

Uranium-series dating

The corals at Mare Piccolo were collected in
situ and identified as _Cladocora caespitosa_. The coral
samples were cleaned thoroughly by scraping,
hand-picking and ultrasonic scrubbing. The samples were
pulverized, heated for a period of about 6 hours at
900°C, and analyzed by alpha spectrometry using
analytical techniques (Szabo and Rosholt, 1969)
previously described. Abundance of calcite to aragonite
was determined by X-ray diffraction analysis.

The 230Th/232Th activity ratios in the corals
vary between 82 and 217 indicating that no initial 230Th
contamination had occurred (Table 4-1). The average
uranium-series age of the corals at Mare Piccolo is
122,000 ± 4,000 years and the average 234U/238U activity
ratio is calculated to be 1.156, a value concordant with
the average uranium ratio in modern ocean water of 1.14
± 0.02 (Ku et al., 1977). Because of the concordant
230Th/234U and 234U/238U results, the uranium-series
dates of these fossil corals from Mare Piccolo are

Table 4-1: Analytical data and calculated uranium-series ages of fossil corals from Mare Piccolo, southern Italy, and an algal nodule from Capo Milazzo, Sicily.

Locality	Field No.	Material	Percent calcite	Uranium (ppm)	Activity ratios				Uranium-series age (years)
					$\frac{234U}{238U}$	$\frac{230Th}{232Th}$	$\frac{230Th}{234U}$		
Il Fronte	TSh5b[2]	coral	<3	4.20 ±0.06	1.120 ±0.017	217 ±65	0.672 ±0.020		117,000±7,000
Il Fronte	TSh5b[2]	coral	<3	4.14 ±0.06	1.097 ±0.016	82 ±33	0.703 ±0.021		128,000±7,000
Il Fronte	TSh5a	coral	<3	3.76 ±0.06	1.114 ±0.017	83 ±33	0.682 ±0.020		121,000±7,000
Milazzo	ISh1e	algal nodule	100[3]	2.36 ±0.05	1.08 ±0.020	6.1 ±0.6	0.616 ±0.020		100,000±6,000[4]

1 All coral samples are Cladocora caespitosa.
2 Portions of the same sample.
3 It is unclear whether the carbonate is originally precipitated as calcite or aragonite.
4 The corrected 230Th/234U age of the sample is 83,000±5,000 yr. BP assuming an initial 230Th/232Th of 1.5 which is a reasonable number for the carbonate environment.

considered to be reliable.

A large (6 cm diameter) algal nodule composed of 100% calcite from Capo Milazzo was U-series dated by the same techniques yielding an age of 100 ± 6 ka* (Table 4-1). Because the chemistry of the nodule is reasonable for its age we suspect the carbonate may have been originally precipitated as calcite rather than through diagenesis from an original aragonitic composition. (* A corrected 230Th/234U age is 83 ± 5 ka indicating that the nodule was probably deposited between 83 and 100 ka.)

Amino acid methods

Species of the mollusk genera Glycymeris (G. violescens, G. bimaculata, and G. glycymeris) and Arca (A. noae, A. tetragona, A. lactea, and A. barbatia) were frequently found in death assemblages. At 11 Mediterranean sites where 168 Glycymeris and Arca were collected together, the ratio of Glycymeris (aIle/Ile) was determined to be 1.31 ± 0.06 times Arca (aIle/Ile) (Hearty et al., 1986). Least-squares analysis of this relationship between Gycymeris and Arca resulted in an R^2 value of 0.91, indicative of the strength of this index. The use of this index provides an internal check of the consistancy of the data within stratigraphic

units and among sites. Sites containing predominantly
Arca can then be compared to those containing only
Glycymeris and vice versa.

AIle/Ile ratios may vary up to 30% in various
parts of a single Glycymeris shell, but are consistent
from shell to shell if routinely sampled from the hard
inner layer at the apex of the shell (Hearty, 1986).
Outer layers of shells for this study were mechanically
removed, then the inner layers leached by 30% with 2N
HCl to remove parts that may be contaminated.

Only Glycymeris shells were found in the thick,
sandy deposits at Ravagnese and Bovetto. Conversely,
mostly Arca shells and only two Glycymeris valves were
discovered beneath the large boulders of the high
energy, rocky coastal environment of Capo Milazzo. It
appears the boulders were dislodged from the surf zone
and rolled seaward a short distance, coming to rest upon
and protecting finer sediments. These fine-grained
fossiliferous sediments (samples IShla, IShlb, and
IShle), collected for this study, are unusual among the
generally pebble to cobble-sized sediments winnowed by
the regressing sea at Capo Milazzo. Both Arca and
Glycymeris were analyzed from the deposits at Mare
Piccolo where the U-series dated corals were found in
situ together with the analyzed shells.

Paleontology

The deposits at Ravagnese and Bovetto provide paleontological evidence (Bonfiglio, 1972) that allows correlation with those at Mare Piccolo. The elevation of the Eutyrrhenian marine deposits in southwest Italy is exceeded only in the Mediterranean basin by similar Strombus-bearing sites at Corinth, Greece at over 200 m (Keraudren, 1971). Strombus bubonius is the key representative of the subtropical Senegalese fauna, which was present in the Mediterranean basin during the last interglacial, but is now restricted to the coastal areas near Cape Verde, Senegal. This coast of west Africa has a present mean annual temperature of ca. 24°C implying a 6°C increase in temperature during the Strombus interval in the Mediterranean basin. A greater abundance and diversity of the west African Senegalese forms have been associated with the Eutyrrhenian age whereas deposits impoverished in or lacking the exotic fauna, and bounding the Eutyrrhenian have been identified as Neotyrrhenian (younger) and Paleotyrrhenian (older) (Bonifay and Mars, 1959).

Strombus bubonius was recently discovered in sands with Glycymeris and Cerastoderma glaucum at Capo Pelloro, Sicily (Figure 4-1) at 84 m a.s.l. (Bonfiglio and Violanti, 1985). We thus designate a Tyrrhenian age

to this marine and brackish series previously assigned a Sicilian age by Gignoux (1913).

A list of mollusks from the same deposits as studied here is reported in Ruggieri and Greco (1965). Available are also complete lists of taxa collected by Gignoux (1913), Mars (1956) and Ruggieri and Greco (1965) in Ruggieri (1967). All taxa collected in this study are included in these lists. Apart from some species considered reworked, these lists include species now living in the Mediterranean Sea as well as some species frequently found in marine deposits of Tyrrhenian age. Some of these species, such as <u>Patella ferruginea</u> (GMEL), <u>Cypraea lurida</u> (L.), <u>Cymatium costatum</u> (Born) prefer warmer seas than exist today at Capo Milazzo. A recent finding of <u>Strombus bubonius</u> in deposits at Capo Pelloro gives credibility to the presence of <u>Strombus bubonius</u> and <u>Fissurella nubecola</u> reported in the lists of Power (1839a, 1839b) and Philippi (1836-1844) at Capo Milazzo. All the species at Capo Milazzo are strictly littoral, often from the intertidal zone (Ruggieri and Greco, 1965) and are limited to rocky and pebbly substrate. <u>Mytilus</u>-rich sediments at Capo Milazzo are generally very coarse, with mostly boulders and pebbles in a sand matrix. A high energy environment and a lack of terrigenous sedimentation some distance from the mainland can

explain the paucity of Senegalese mollusks such as
Strombus bubonius. Strombus bubonius is a littoral
species but prefers a coarse sand, rather than a rocky
bottom.

Sites near Mare Piccolo have been the object of
faunal studies since Gignoux (1913), continuing with
Blanc (1953) and Gigout (1960a, b), and more recent
studies by Cotecchia et al (1969) and Dai Pra and
Stearns (1977). Micropaleontological studies include
the recent works of De Castro-Coppa (1979). The radical
difference in sedimentary and biological facies between
Capo Milazzo and Calabria makes correlation difficult.
Paleontological data allow an easier correlation between
Bovetto, Ravagnese, Pelloro and Mare Piccolo based on
the Senegalese fauna. Correlation among these sites can
also be accomplished through our amino acid data with
adjustments made for slightly different integrated
thermal histories, as will be discussed later.

D. Violanti analyzed three sediment samples
(IShla, ISh1b, and IShle) collected from Capo Milazzo by
Hearty and Bonfiglio to determine if
micropaleontological data aid in interpretation of the
age of the deposits. The finer fraction for
micropaleontology was split from the same bulk samples
that contained shells used for amino acid geochronology.

Texturally, a coarse mode (> 250 μ) was dominant

in washed residues of IShla and IShle. Finer fractions
are common in only IShlb. The non-biogenic components
are mainly quartz, micas and metamorphic rocks.
Volcanic fragments and rare black or dark green crystals
(probably amphiboles) are present in ISh1b and IShle.

Half of each sample was then rewashed with H^2O^2
and distilled water, and sieved with a 151μ mesh. From
this fraction (< 151μ) taxonomical analyses of
foraminifera were carried out on an average number of
300 grains and/or specimens.

The biogenic residue consists mainly of
shallow-water skeletal debris: fragments and juvenile
tests of pelecypods are dominant, and echinoid fragments
(spines with rarer plates) are abundant. Gastropods and
bryozoans are common only in IShle, whereas small tests
and fragments of gastropods, bryozoans, ostracods,
anellids and sponge spicules are rare or absent in the
other two samples. Borings (probably by Natica) are
present in some tests of pelecypods in all three of the
samples.

The associated foraminiferal faunas display
marked differences from sample to sample as abundance,
diversity and plankton/benthos ratios change randomly.
The distribution of planktonic and benthonic
foraminifera and the relative presence in each sample
are listed in Tables 4-2 and 4-3. Planktonics are

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Table 4-2: A list of Planktonic foraminifera identified
in samples ISh1a, b and e from Capo Milazzo.

SPECIES SAMPLES	1a	1b	1e
Globigerina bulloides (d'Orbigny)	x	x	
" falconensis (Blow)		x	
" pachyderma (Ehrenberg)	x	x	
" parabulloides (Blow)		x	
" aff. praedigitata (Parker)		x	
" s.p.	x		x
Globigerinoides conglobatus (Brady)		x	
" elongatus (d'Orbigny)	x	x	
" gomitolus (Seguenza)	x	x	
" obliquus obliquus (Bolli)		x	
" obliquus extremus (Bolli and Bermudez)		x	
" ruber (d'Orbigny)	x	x	
" sacculifer (Brady)		x	
" trilobus (Reuss)	x	x	
Globorotalia crassaformis (Galloway and Wissler)		x	
" inflata (d'Orbigny)	x	x	
" margaritae (Bolli and Bermudez)		x	
" obesa (Bolli)	x		
" oscitans (Todd)		x	
" puncticulata (Deshayes)		x	
" Truncatulinoides exclesa (Sprovieri, Ruggieri and Unti)	x	x	
Globigerinita glutinata (Egger)		x	
Hastigerina siphonifera (d'Orbigny)		x	
Orbulina universa (d'Orbigny)	x	x	x
Sphaeroidinellopsis seminulina (Schwager)		x	

Table 4-3: A list of Benthic foraminifera identified in
samples ISh1a, b and e from Capo Milazzo.

SPECIES SAMPLES	1a	1b	1e
Articulina tubulosa (Seguenza)			x
" s.p.			x
Asterigerinata mamilla (Williamson)		x	
Cibicides floridanus (Cushman)		x	.
" lobatulus (Walker and Jacob)	x	x	x
" refulgens (de Montfort)		x	x
" wellestorfi (Schwager)		x	
Eggerella bradyi (Cushman)	x		
Elphidium aculeatum (d'Orbigny)		x	
" complanatum (d'Orbigny)			x
" crispum (Linn)	x		x
" macellum (Fichtel and Moll)		x	x
Lagena s.p.		x	
Miliolinella circularis (Bornemann)			x
Neoconorbina terquemi (Rzehak)		x	
Planorbulina mediterranensis (d'Orbibny)		x	
Planulina ariminensis (d'Orbigny)	x		
Pulenia quinqueloba (Reuss)		x	
Quinqueloculina agglutinans (d'Orbigny)		x	
" aff. bicornis (Walker and Jacob)			x
" lamarckiana (d'Orbigny)		x	
" seminulum (Linn)	x	x	
Rosalina globularis bradyi (Cushman)	x	x	x
Siphonina reticulata (Czjzek)		x	
Spirillina vivipara (Ehrenberg)		x	x
Spiroloculina canaliculata (d'Orbigny)	x		
Textularia conica (d'Orbigny)			x
" soldanii (Fornasini)			x
" s.p.	x	x	
Triloculina oblonga (Montagu)	x		
Uvigerina mediterranea (Hofker)			x
Valvulineria bradyana (Fornasini)		x	
" complanata (d'Orbigny)		x	

dominant in IShla. In contrast, they are rare in IShle, where benthonics are largely dominant. Foraminiferal assemblages are impoverished in both samples and species diversity is low. The sample IShlb is more representative at the Capo Milazzo area: the foraminiferal fauna is more abundant and diversified, displaying a plankton/benthos ratio of about 1:2. The planktonic fauna from sample IShlb consists of two populations of different ages. The "old" population contains: Globigerina parabulloides (Blow),Globigerinoides obliquus obliquus (Bolli), Globigerinoides obliquus extremus (Bolli and Bermudez), Globorotalia margaritae (Bolli and Bermudez), Globorotalia puncticulata (Deshayes), and Sphaeroidinellopsis seminulina (Schwager). On the basis of the occurrence of G. margaritae asociated with G. puncticulata this population can be attributed to zone M-Pl-3 of late Early Pliocene age. This zone is recorded from the region where the "Trubi" Formation has been described (Cita, 1975; Vismara and Stradner, 1977). The second younger population contains: Globigerinoides gomitolus (Seguenza), Globorotalia oscitans (Todd), Globorotalia truncatulinoides excelsa (Sprovieri, et al., 1974) which characterized the Mediterranean Pleistocene (Sprovieri, 1976; Sprovieri, et al., 1974). The occurrence of Globigerinoides ruber (d'Orbigny)

suggests that the younger population is correlated to a warm interval (Cita, et al., 1974). The inferred age of the younger population is then interglacial, probably Tyrrhenian. The older population has most likely been reworked from underlying Pliocene deposits.

Benthic foraminifera are commonly used to reconstruct the paleoenvironmental conditions; many authors have established different depth zones according to the more frequent or typical species. Parker (1958), Montcharmont-Zei (1968), and Cita and Zocchi (1978) have studied Pleistocene or Holocene benthic assemblages from Mediterranean sediments. All benthic species occurring in samples ISh-1a, ISh-1b, ISh-1e are typical of Assemblages 1 and 2, of Parker (1958) (Table 4-4); the most abundant species of Milazzo's samples display percentages comparable to those of Parker's Assemblage 1 which occurs shallower than 25 m in the eastern Mediterranean (Harbor of Piraeus, Greece).

Typical marine shallow water conditions are recognizable; different from the brackish, lagoon paleoenvironment inferred for the samples of Mortelle - near Capo Pelloro (Bonfiglio and Violanti, 1985).

We thus conclude on paleontological grounds that the deposits studied at Capo Milazzo belong to the Tyrrhenian within oxygen isotopic stage 5. The warmest interval was during stage 5e thought to be ca. 125 ka

Table 4-4: A comparison of abundance of foraminiferal taxa in Parker's (1958) Assemblages 1 and 2 with those found in our collections from Capo Milazzo. It is from the equivalence of Parker's Assemblage 1 and the Capo Milazzo sample that we conclude a less than 25m water depth.

===

The most abundant species in Parker's Assemblage 1 (shallower than 25 m) are:

Asterigerinata mamilla (4%)
Cibicides lobatulus (5%)
Elphidium crispum and variants (6%)
Miliolidae species (40%)
Peneroplidae (6%)
Planorbulina mediterranesis (13%)
Rosalina obtusa (7%)

The most abundant species in Parker's Assemblage 2 (51-205 m) are:

Asterigerinata mamilla (up to 13%)
Bolivina catanensis (up to 8%)
Cassidulina carinata (up to 14%)
Cassidulina cf. oblonga (up to 9%)
Cibicides lobatulus (up to 15%)
Elphidium complanatum (up to 7%)
Elphidium crispum (up to 7%)
Hanzawaia rhodiensis (up to 7%)
Miliolidae (up to 14%)
Neoconorbina terquemi (up to 7%)
Textularia sagittula (up to 9%)

The most abundant species in Milazzo's samples are:

Asterigerinata mamilla (about 2-5%)
Cibicides species (about 8%)
Miliolidae species (about 30%)
Planorbulina mediterranensis (about 10%)
Elphidium crispum (about 10%)

(Shackleton and Opdyke, 1973) which is a possible age of these deposits. This agrees with Ruggieri and Sprovieri (1977) who are now of the opinion that the Capo Milazzo 60 m deposits can be assigned to the Tyrrhenian cycle.

Aminostratigraphy

To further support the correlation provided by paleontology, we have used the analyses of over 50 shells (Table 4-5) to make an aminostratigraphic correlation. Six Arca barbatia shells analyzed from Milazzo gave a mean aIle/Ile ratio of 0.33 ± 0.04 and two Glycymeris gave a mean of 0.41 ± 0.04. A single Glycymeris from Capo Pelloro gave a 0.41 aIle/Ile ratio. AIle/Ile ratios in twelve Glycymeris from Bovetto average 0.42 ± 0.04 while two from Ravagnese have a mean of 0.45 ± 0.01. The Gly/Arca index is 1.24 from Milazzo and 1.27 if Bovetto and Milazzo shell ratios are combined as a unit lending further support to their correlation. AIle/Ile ratios from the U-series dated site at Il Fronte, Mare Piccolo, average 0.37 ± 0.02 for ten Glycymeris shells and 0.27 ± 0.05 for twenty-two Arca shells resulting in a Gly/Arca index of 1.37. A latitudinal increase in aIle/Ile ratios is observed from Mare Piccolo to Calabria and Sicily. Although mean values generally overlap at the 1o confidence level, we

Table 4-5: AIle/Ile data from the study sites in Sicily, Calabria, and the Mare Piccolo area of southeast Italy.

SITE and REFERENCES	Glycymeris aIle/Ile	Arca aIle/Ile	Gly/Arca index	MAT* °C	Fauna and environment	Absolute age (10³ yr)
		CALABRIA AND SICILY				
Capo Milazzo (see text)	.43 .38 x̄ = .41±.03	.30 .33 .41 .33 .28 .34 x̄ = .33±.04	1.24	17.8	warmer than present; dominantly high energy, rocky substrate forms	83 - 100±6
Capo Peloro Bonfiglio and Violanti (in press)	.41			17.8	warm; Stombus bubonius present	
Bovetto (Bonfiglio, 1972)	.37 .38 .41 .42 .37 .38 .42 .41 .43 .46 .48 .47 x̄ = .42±.04		1.27 (with Milazzo)	17.8	warm, sandy coast; Stombus bubonius and other Senegalese forms.	
Ravagnese (Bonfiglio, (1972)	.44 .46 x̄ = .45±.01			17.8	warm, sandy coast; Strombus bubonius and Senegalese forms.	
		IL FRONTE, MARE PICCOLO				
Il Fronte, Gigout (1960a, b) Dai Pra and Stearns, 1977)	.34 .37 .36 .39 .35 .38 .39 .35 .36 .37 x̄ = .37±.02	.24 .19 .25 .25 .26 .31 .26 .39 .31 .21 .31 .23 .26 .30 .24 .23 .20 .27 x̄ = .27±.05	1.37	16.9	warm, quiet inlet; Strombus bubonius and Senegalese forms.	122±4

*Climate data from Wernstedt, 1972.

feel the gradient is a real trend in the integrated thermal histories of the sites, reflected in today's MAT. The lower ratios at Mare Piccolo (0.37 for Glycymeris and 0.27 for Arca) are a function of a cooler temperature history compared to Calabria and Sicily. Current temperature differences between these two areas are about 1°C (Wernstedt, 1972 and Table 4-5).

The amino acid data support a last interglacial age for the deposits at Capo Milazzo. Amino acid ratios in Glycymeris from Milazzo, Capo Pelloro, Ravagnese, and Bovetto, all within 40 km distance, are not significantly different, supporting correlation of the deposits. The deposits at Capo Pelloro and Reggio Calabria have been assigned a Eutyrrhenian age (Bonfiglio, 1972; Bonfiglio and Violanti, 1985) and are correlative with Mare Piccolo deposits (300 km) on paleontological grounds: the presence of the Senegalese fauna. Micropaleontological studies also support a Tyrrhenian age for the Milazzian deposits. The last interglacial age of these deposits in southern Italy and Sicily is equivalent to a basin-wide designation of aminogroup E (Hearty et al., 1986).

This local correlation allows us to make inferences on the magnitude of tectonic uplift affecting the coastal sites since the last interglacial and earlier. If we assume all the sites are ca. 125 ka in

age, and originating from +6 m (Ku et al, 1974), then we calculate an average rate of uplift of 0.45 m/ka for Capo Milazzo, ca. 0.60 m/ka for Capo Pelloro and Ravagnese, 0.99 m/ka for Bovetto and 0.20 m/ka for Mare Piccolo. However, maximum shoreline elevations have not been determined for Capo Milazzo, Capo Pelloro and Ravagnese, making uplift values minimum estimates. In addition, there is a suggestion from the U-series date of 100 ± 6 ka (Table 4-1) that Capo Milazzo marine interval may be slightly younger than Stage 5e (possibly 5c) which would result in a higher rate of uplift. The uplift rate of 0.99 m/ka at Bovetto appears to have been effective since early Pleistocene based on the 1000-1400 m elevation of a terrace of that age (Raffy et al, 1981; Dumas et al, 1980) in the area.

Conclusions

There are several conclusions that can be drawn from this research:

1) The 40 to 60 meter strandline at Capo Milazzo, Sicily is correlated with Tyrrhenian marine deposits at Reggio Calabria (Ravagnese and Bovetto) and Capo Pelloro, all less than 40 km distant, and at Mare Piccolo (300 km away) by similarity of amino acid aIle/Ile ratios in fossil Glycymeris and Arca shells.

The mean Glycymeris aIle/Ile ratios from Milazzo and Bovetto are 0.41 and 0.42, respectively, and 0.33 for Arca from Milazzo. Mean Glycymeris and Arca ratios from Mare Piccolo are 0.37 and 0.27, respectively. Two Glycymeris from Ravagnese have a mean value of 0.45, and a single Glycymeris from Pelloro produced a 0.41 aIle/Ile ratio.

2) At Mare Piccolo, U-series dates on corals that average 122,000 yr BP, which calibrates mean aIle/Ile ratios of the deposits to deep-sea, oxygen-isotope stage 5, probably substage 5e (Shackleton and Opdyke, 1973). A calcareous algal nodule from Capo Milazzo yielded a U-series age between 83,000 and 100,000 yr. BP.

3) Biostratigraphic studies cannot conclusively correlate Milazzo and marine strandlines at Reggio Calabria but Reggio Calabria and Mare Piccolo are correlated through their mutual abundance of the Senegalese fauna. Patella ferruginea, Cyprea lurida, and Cymatium costatum have affinities to the Tyrrhenian and support the probable stage 5 deposition of marine beds at Capo Milazzo. The less developed Tyrrhenian fauna at Milazzo could be a result of the rocky, high energy environment there or possibly a cooler interval during Stage 5.

4) By knowing the age of the deposits at

Milazzo, Pelloro, and Bovetto we can calculate the rate
of uplift since the last interglacial ca. 125,000 yr
ago. We assume a sea level of +6 m relative to the
present about 125,000 yr ago (Veeh, 1966; Ku et al.,
1974). The most reliable datum is the maximum height of
Bovetto from which a rate of 0.99 m/ka is calculated.
The shoreline edge has not been located at Milazzo,
Ravagnese and Capo Pelloro so only minimum uplift rates
are calculated.

Acknowledgements

CHAPTER V

NEW DATA ON THE PLEISTOCENE OF MALLORCA

Abstract

Stratigraphic, geomorphologic and isoleucine
epimerization (aIle/Ile) studies at 14 sites in
Mallorca define four or possibly five aminozones (A, C,
E and F/G) of increasing age that are related to
transgressive-regressive marine cycles from the Holocene
to the mid Pleistocene. Calibration of aminozone E
(Glycymeris aIle/Ile mean from all sites = 0.41 ± 0.03
(n=38)) is provided by a 129 ± 7 ka U-series coral age
on Cladocora caespitosa from Son Grauet. Of the younger
aminozones, A relates to the Holocene transgression and
aminozone C to a mid to late isotopic stage 5 event (90
± 15ka) revealed only by supralittoral eolianites.
Assigning an age to the older, poorly resolved
aminozones F and G (called F/G in this case) is risky
without supporting radiometric data. But an age of
>180ka can be assigned to these aminozone(s) F/G based
on kinetic models and other examples in the

Mediterranean.

Several deposits, previously dated between 75 and >300 ka appear to belong to the last interglacial complex and aminozone E. A proposed revision of the positive sea level history of Mallorca shows multiple minor oscillations during the major last interglacial cycle and two mid Plestocene sea levels, one lower than present and the other at about 14m a.s.l.

Introduction

An extensive library of shoreline data has been generated in Mallorca (Butzer and Cuerda (1962a, 1962b and 1982), Butzer (1975, 1983), Cuerda (1975, 1979) Muntaner-Darder (1957) and Cuerda and Sacarés (1965, 1966). In addition to describing the stratigraphy and paleontology of hundreds of sites, Butzer and Cuerda introduced the concepts of a high frequency oscillations of sea level (hemicycles) over the mid and late Pleistocene and reoccupation of shoreline platforms by multiple high sea levels, and made observations on depositional processes associated with sea level oscillations. Cuerda has been personally responsible for assembling one of the largest systematized Pleistocene malacofaunal collections in the world from the Balearic Islands. These studies provide a valuable

bio-, morpho- and lithostratigraphic database upon which
this study builds.

Despite this excellent research foundation, the
interpretation of Mallorca's coastal stratigraphy and
sea level history remains controversial. Three particular
problems can be identified: 1) correlation of marine
events by biostratigraphy has been complicated
by the diversity of marine paleohabitats; 2)
highly variable wave energy has resulted in a diverse
coastal geomorphology from shallow bays and lagoons in
the Bay of Palma, to high-energy vertical coastal
profiles with notches and platforms on the exposed
southern and eastern coasts; and 3) the sites lack
a secure geochronology.

This study addresses these problems from a
stratigraphic point-of-view and also provides new
chronometric data related to the sea level record of
Mallorca. The main tool for dating and correlation of
marine and terrigenous deposits in Mallorca (Figure 5-1)
is amino acid geochronology which has been previously
shown to be effective in the Mediterranean (Hearty et
al, 1986; Miller et al, 1986; Hearty, 1986). The
conversion of L-isoleucine to D-alloisoleucine (aIle/Ile
ratio) is the principal reaction used in this study.
The grouping of the aIle/Ile ratios from deposits in
Mallorca define a number of aminozones. The difference

in aIle/Ile ratios is a function of their age since the thermal histories of the sites in Mallorca are assumed to be similar.

The Mallorcan data is presented in the context of extensive aminostratigraphic studies around the world. Such studies in Sardinia (Ulzega and Hearty, 1986), Tunisia (Miller et al, 1986) and Italy (Hearty and Dai Pra, 1985; 1986) provide epimerization models with related taxa in similar temperature regimes on relatively stable coastlines. In fact, there is a remarkable similarity among the physical- and chrono-stratigraphies of these sites. Other studies that use amino acid geochronology (AAG) for correlation and dating of shoreline deposits in many coastal localitites of the world include those in: California (Kennedy et al, 1982; Lajoie et al, 1980; Muhs and Szabo, 1982), Alaska (Brigham, 1983; 1985), the southeast U.S. coastal plain (McCartan et al, 1982; Wehmiller and Belknap, 1982; Belknap, 1979; Corrado et al, 1986 and Hearty and Hollin, 1986b), Bermuda (Harmon et al, 1983; Hearty and Hollin, 1986b), United Kingdom (Miller et al, 1979), Norway and Spitsbergen (Miller et al, 1983; Miller, 1982; Lehman, 1985), northwest Europe (Miller and Mangerud, 1985), South America (Peru), (Hsu et al, 1985; 1986), and the Mediterranean (Hearty et al, 1986; Hearty, 1986).

Amino acid geochronology

The geochronological potential of certain
chemical reactions involved in the degradation of
proteins in fossils was first recognized by Abelson
(1955) and further developed by Hare and Mitterer
(1967, 1969), and has been the subject of an increasing
number of investigations over the past decade. The most
promising reaction has been shown to be the racemization
reaction, or epimerization in the case of isoleucine.
The extent of the reaction is expressed a the ratio of
D- to L-isomers; D-alloisoleucine to L-isoleucine ratios
(aIle/Ile) in this case. Protein in skeletal hard parts
of living organisms contains essentially no amino acids
in the D-configuration. However, over geologic time,
the protein within a CaCO3 matrix undergoes a slow
series of interrelated degradation reactions, including
hydrolysis into lower molecular weight peptides and
eventual release of free amino acids, racemization (or
epimerization), and a variety of decomposition reactions
that alter the relative abundance of the various amino
acids.

The reversible racemization/epimerization
reaction proceeds to an equilibrium ratio of D and L
isomers; generally 1:1 for racemization, but somewhat

higher for isoleucine epimerization (1.3 : 1.0).

AIle/Ile ratios have been determined in the total

fraction (free amino acid plus those in the

peptide-bound state that have been artifically released

by heating the decalcified sample in 6N HCL for 22 hours

at 110°C). The aIle/Ile ratios are determined on an

automated ion-exchange HPLC amino acid analyzer (Miller

and Hare, 1980) with electronic peak integration on a

Hewlett-Packard 3390A integrator. The data is then

collected and reduced in a database system by a Digital

Equipment Corporation Pro 380 computer.

Shells were collected from as deep as possible

within the marine or terrestrial stratigraphic unit to

reduce or eliminate the diurnal and seasonal effects of

insolation and surface heating. In some cases, samples

were collected and analyzed up to the upper contact of

the marine unit in order to appraise the extent of

surface heating.

An intrashell variation of 30% (Hearty et al,

1986) is minimized when samples are consistently taken

from the same structural area (internal layer at the

apex) of the shell. Sample fragments of ~100mg are

leached an additional 30-50% with 2N HCl to reduce the

chance of contamination. Analytical procedures, factors

affecting D/L ratios, and guidelines are found in Hearty

et al, (1986) Hearty, (1986) and Miller and Mangerud
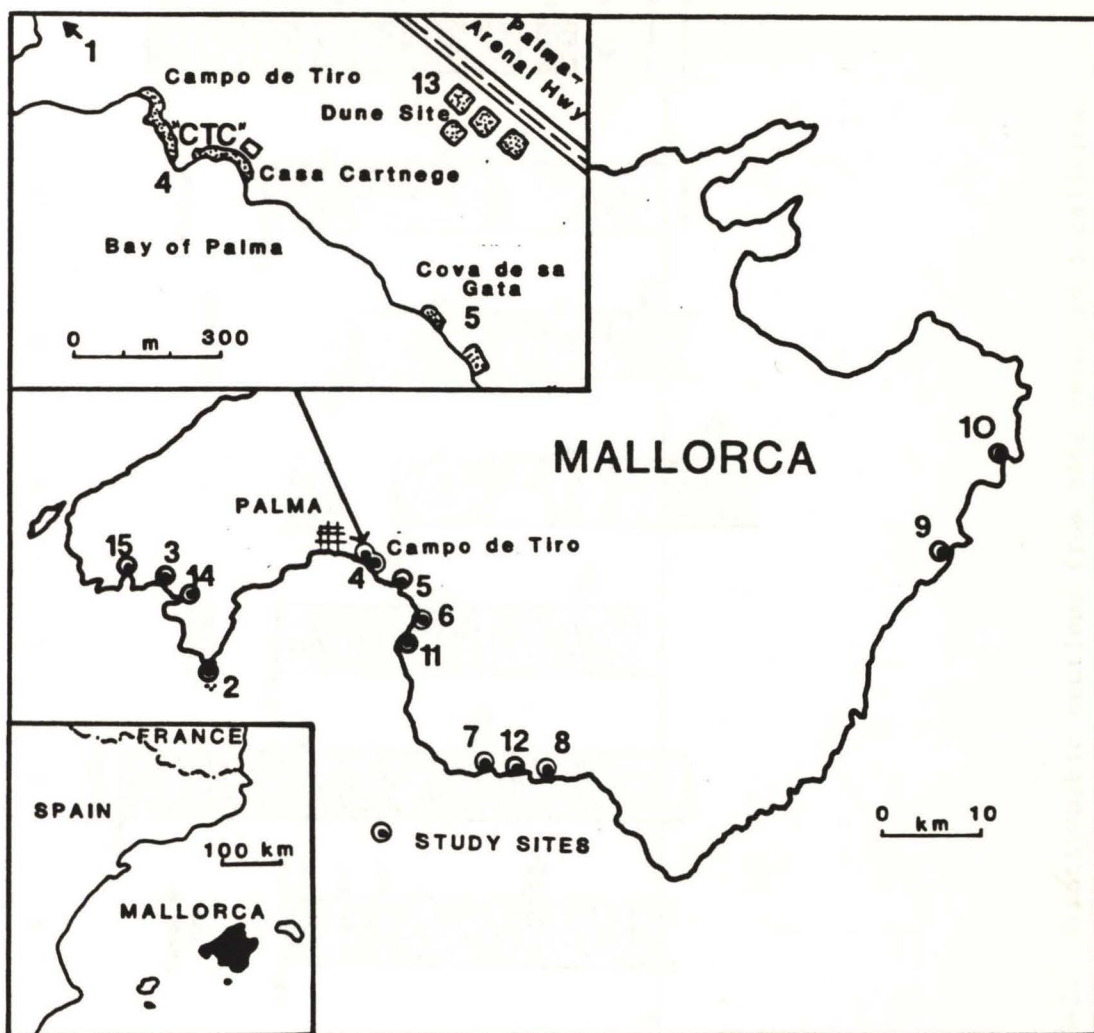
Figure 5-1: Location map of study sites in Mallorca. Site numbers related to figures and text are indicated.
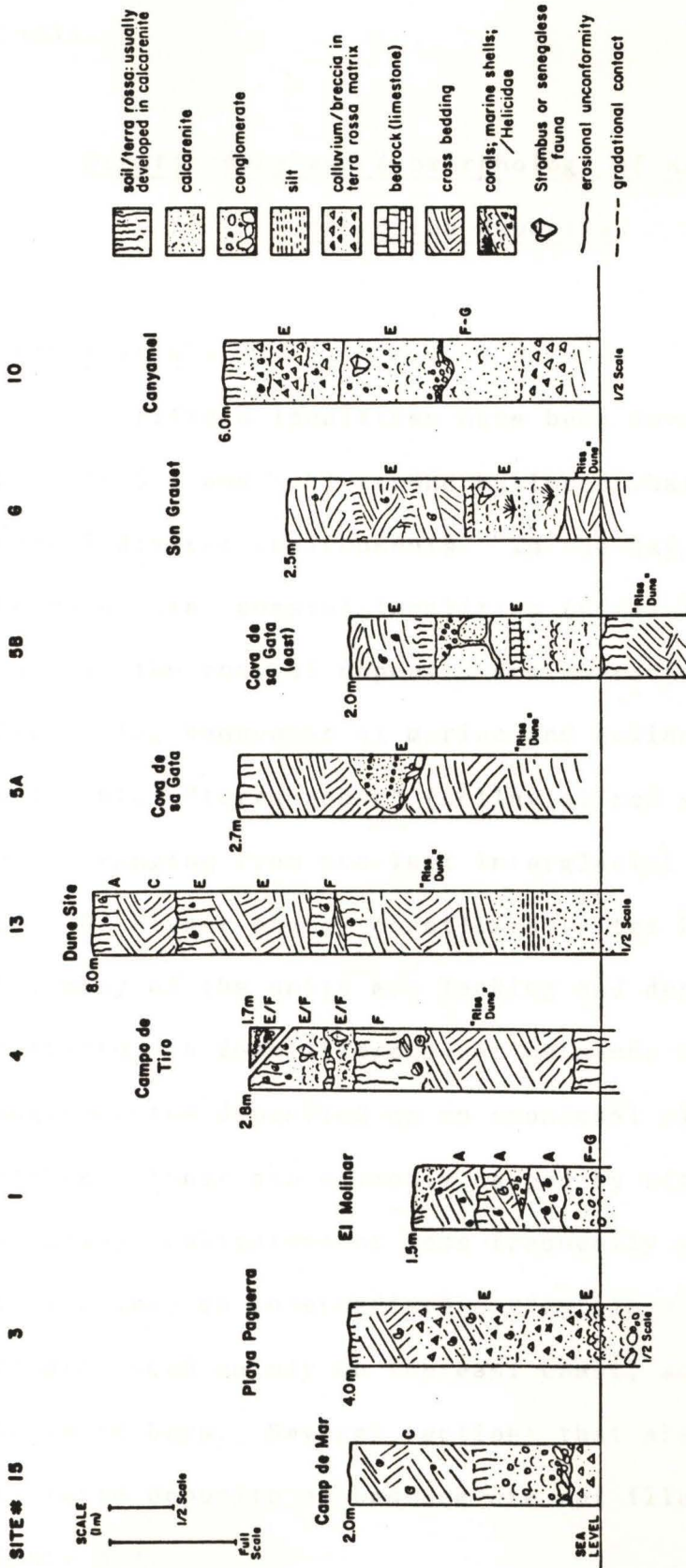
Figure 5-2: Stratigraphic sections from nine selected localities in Mallorca. Aminozones (from Table 5-1) are indicated in the figure.

(1985).

<u>Stratigraphy and geomorphology of Mallorcan</u>

<u>shoreline deposits</u>

<u>General view</u>

Fifteen localities have been investigated
(Figures 5-1 and 5-2) around Mallorca that represent
several diverse environments. In the Bay of Palma and
the more quiet coastal localities (sites 1,3, 4, 5, 6,
and 13), the coastal deposits are characterized by
alternating sequences of marine and eolian sands, and
continental "terra rossa" (colluvial red silts and
soils) ranging from pre-last interglacial to Holocene
age. On higher energy coastlines (sites 2, 7, 8, 14 and
15), many of the units are lacking and deposits are
restricted to fossiliferous marine sands and coarse
conglomerates deposited on an erosional platform or in
notches. These are commonly capped by either colluvium
(breccia), eolianites or less frequently soils. Sites
falling into an intermediate energy class (sites 9 and
10) are found mainly on the east coast, sometimes in
sheltered bays. Several sections that are only
scattered deposits on bedrock are not illustrated in
Figure 5-2.

Southwest coast --[(sites 2, 14 and 15) -Banco
   d'Ibiza, Paguerra, and Camp de Mar]

        The Camp de Mar and Paguerra sites are
similar in geomorphic position and stratigraphy
(Figure 5-2). Both are fossiliferous marine sands
and conglomerates deposited on erosional platforms
near sea level (0 to 1m). Camp de Mar marine
conglomerates are capped by a thin red soil, then an
eolianite. The marine conglomerate at Playa de Paguerra
is followed directly by colluvium (derived from the
nearby limestone cliffs) and then a mixed colluvium and
eolianite. At Banco d'Ibiza fossil deposits at 15 and
30m asl were discussed previously (Butzer and Cuerda,
1982). The 15m deposits contain Arca and lie well below
the 25m washing limit on the Banco d'Ibiza peninsula.
The deposits at 30m asl with Ostrea are problably
early Pleistocene or Pliocene in age based on the
composition of marine faunas.

Bay of Palma --[(sites 4, 13, 1, 5, 6 and 11) -Campo
   de Tiro-Cartnege, Dune site, Nautica Mus, Cova de sa
   Gata, Cova de sa Gata east, Son Grauet (Cova S'Anegat)
   and Cap Orenol].

        Coastal deposits at Campo de Tiro-Cartnege
(CTC) have been discussed since the early 1960's
(Butzer and Cuerda, 1962a, 1962b; Butzer 1975,

1984; Cuerda, 1975, 1979). One of the most complete
sequences (Figure 5-3) displays alternating marine and
continental influences, forced by both major and minor
oscillations of sea level. Forming the base of the
section is the so called "Riss dune" of Cuerda (1975;
1979) originally interpreted as a glacial age deposit.
In this study, it is interpreted as a supralittoral
eolianite. This upper shoreface sedimentary facies may
equate with a pre-last interglacial shoreline now
submerged in several meters of water. Similar eolianites
occur in several sections (Figure 5-2) and are correlated
to Campo de Tiro by stratigraphic position and textural
characteristics.

Above a deep red clayey "terra rossa" soil
developed on the dune sand lie two important marine
calcarenites (CTC I and II), that are separated
by a thin, brown soil that is probably equivalent to
the "Intra-Rejiche soil" of Paskoff and Sanlaville
(1983). A stratigraphically younger deposit
(CTC III), the "Neotyrrhenian" of Butzer and Cuerda,
(1982) and equivalent to the Chebba Fm at Hergla,
appears to be separated from CTC I and II by a
considerably greater period of time based on the
degree of development of the soil. The series is
capped by an alternating sequence of terra rossas and
eolianites, also well exposed at the Dune site (Figure

CAMPO DE TIRO-CARTNEGE (CTC)
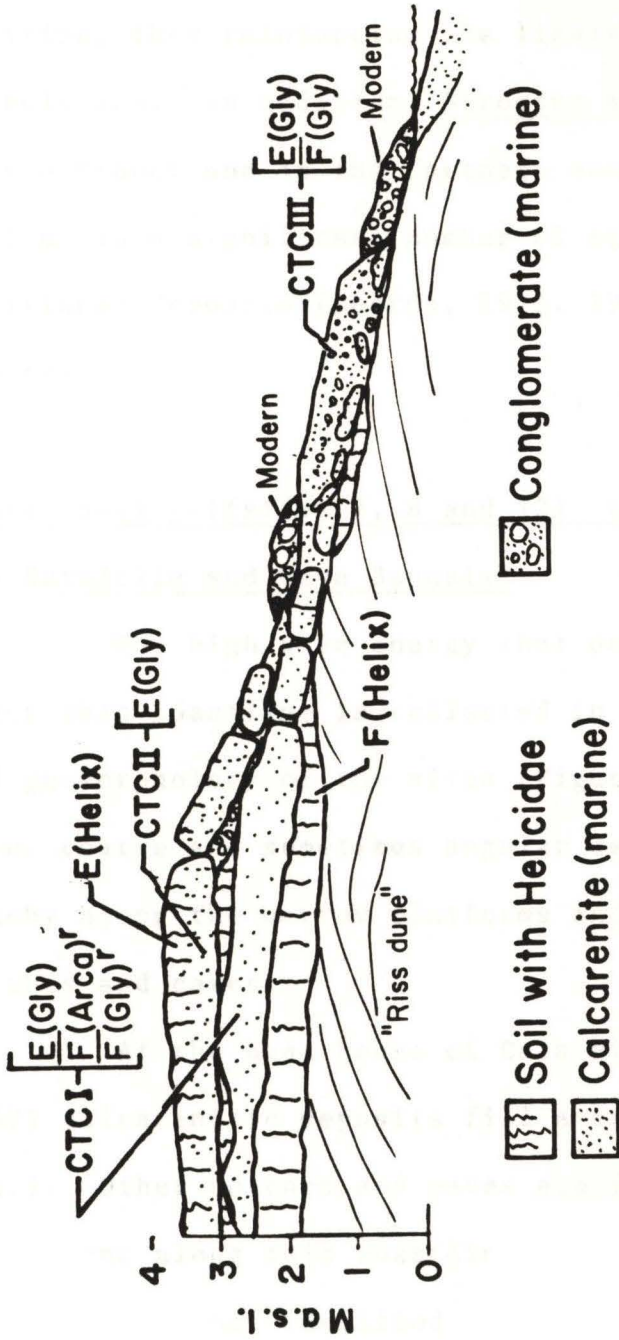
Figure 5-3: Stratigraphic cross-section of Campo de Tiro-Cartnege site (CTC) with aminogroups indicated. Three principle marine units are recognized in this section (CTC I, II and III) that are correlated to the last interglacial using the Glycymeris mean of 0.40 ± 0.03(n=13) equal to a 129 ± 7 ka coral age.

5-2, section 13).

In a geomorphic context, the deposits investigated around the Bay of Palma are in a similar position, thus reinforcing the likelyhood of their correlation. In addition, Strombus bubonius is present at Son Grauet and in the Cartnege series (CTC II) as well as in a significant number of equal geomorphically positioned deposits (Cuerda, 1975, 1979) between 0 and 10m asl.

South coast --[(sites 7, 8 and 12) -Cala Pi, Torre S'Estalella and Cava Bancals]

The high wave energy that dominates along this coastline is reflected in the stratigraphy and geomorphology of the sites (Figure 5-4). Thin, coarse and sometimes angular deposits are patchy along the narrow platforms and occasionally fill notches and caves.

At the boat house of Cala Pi (Butzer and Cuerda, 1982) calcarenitic deposits fill a small notch at 3.5m a.s.l. Other notches and caves are frequent at similar elevations along this coastline and some contain Senegalese fauna. Rubified fossiliferous deposits at about 4.5 m near Torre S'Estalella are highly weathered and exposed, and are not typical, stratified marine deposits. We suggest that the Strombus-bearing
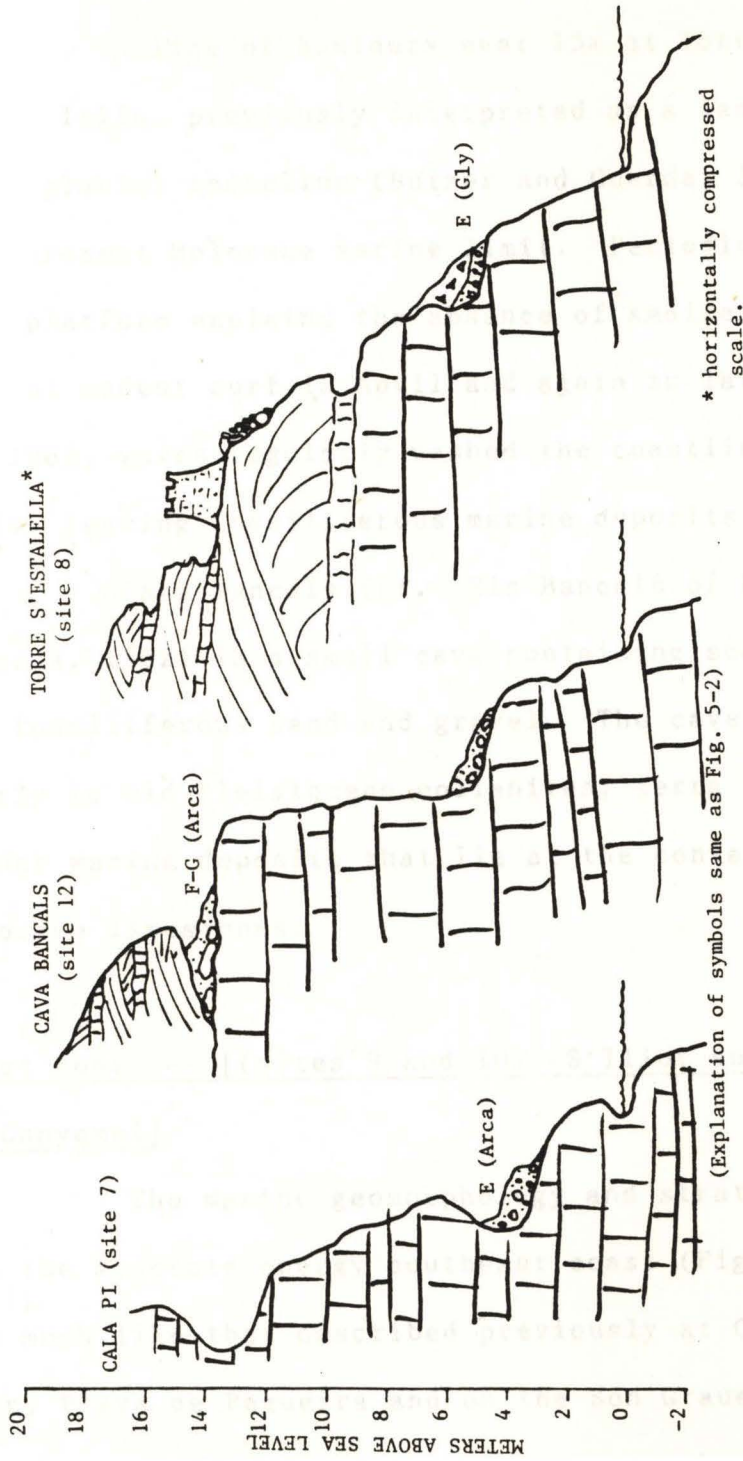
Figure 5-4: Stratigraphic profile from the high energy coastline of Cala Pi (Figure 5-1). AIle/Ile data from this area are sometimes higher due to the exposed condition of the deposits.

CALA PI (site 7)

E (Arca)

CAVA BANCALS (site 12)

F-G (Arca)

TORRE S'ESTELLELLA* (site 8)

E (Gly)

* horizontally compressed scale.

(Explanation of symbols same as Fig. 5-2)

METERS ABOVE SEA LEVEL

20 18 16 14 12 10 8 6 4 2 0 -2

sediments that occur up to 15m in this area were deposited by, and frequently reworked and churned by storms. A line of boulders near 15m at Torre S'Estalella, previously interpreted as a last interglacial shoreline (Butzer and Cuerda, 1962a), is the present Holocene marine limit. Periodic washing of the platform explains the absence of sediments. On a day of modest surf in April and again in late September of 1986, waves regularly washed the coastline at >5 m asl., leaving fossiliferous marine deposits at >10 m.

Cava Bancals (cf. Els Bancals of Butzer and Cuerda, 1982) is a small cave containing scanty deposits of fossiliferous sand and gravel. The cave is cut into early to mid Pleistocene eolianites, terra rossas and older marine deposits that lie at the contact with Miocene limestones.

East coast -- [(sites 9 and 10) -S'Illot and Canyamel]

The marine geomorphology and stratigraphy on the moderate energy southeast coast (Figure 5-5) is much like that described previously at Camp de Mar, Playa de Paguerra and on the Son Grauet-Cap Orenol coastline. The wave energy is greater than that in the Bay of Palma but significantly less than on the open coast of Torre S'Estalella and Banco d'Ibiza.
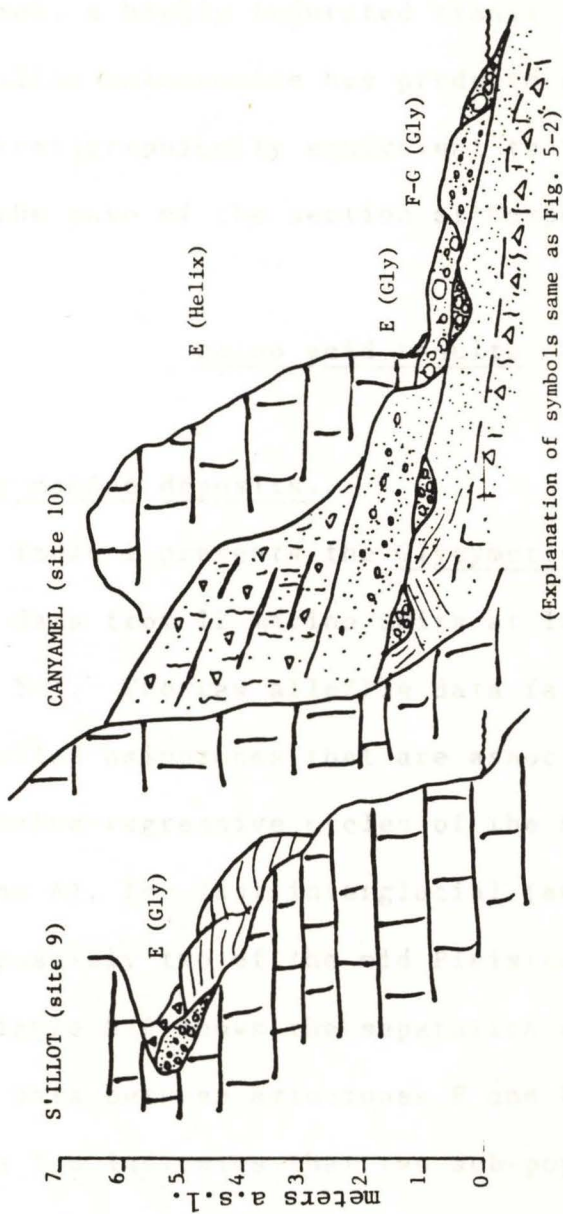
Figure 5-5: Stratigraphic profile of the S'Illot and Canyamel sites on the east coast of Mallorca.

At S'Illot, marine deposits rise to above 6m on platforms, and in several small caves and in notches (Figure 5-5). Further north at Canyamel, a marine unit with Strombus rises to about 3m. Below this marine unit at Canyamel, a highly indurated transitional marine/eolian calcarenite has produced rare Glycymeris and is stratigraphically equivalent to the "Riss dune" forming the base of the section at Campo de Tiro.

Amino acid results

Data from marine deposits.

Table 1 presents the Glycymeris and Arca aIle/Ile data from 12 marine units at localities listed in Table 5-1. The raw aIle/Ile data fall into several groups called aminozones that are associated with transgressive-regressive cycles of the Holocene (aminozone A), the last interglacial (aminozones C and E), and possibly two of the mid Pleistocene (aminozone F/G). Figure 5-6 shows the separation of populations of aIle/Ile data between aminozones E and F/G. The histogram in Figure 5-6 indicates that two sub-populations may be present in aminozone E. Previous studies have described a bipartite stage 5e event (Bloom et al., 1974; Hearty; 1986) during the same interval that in some locations is supported by stratigraphy. Although
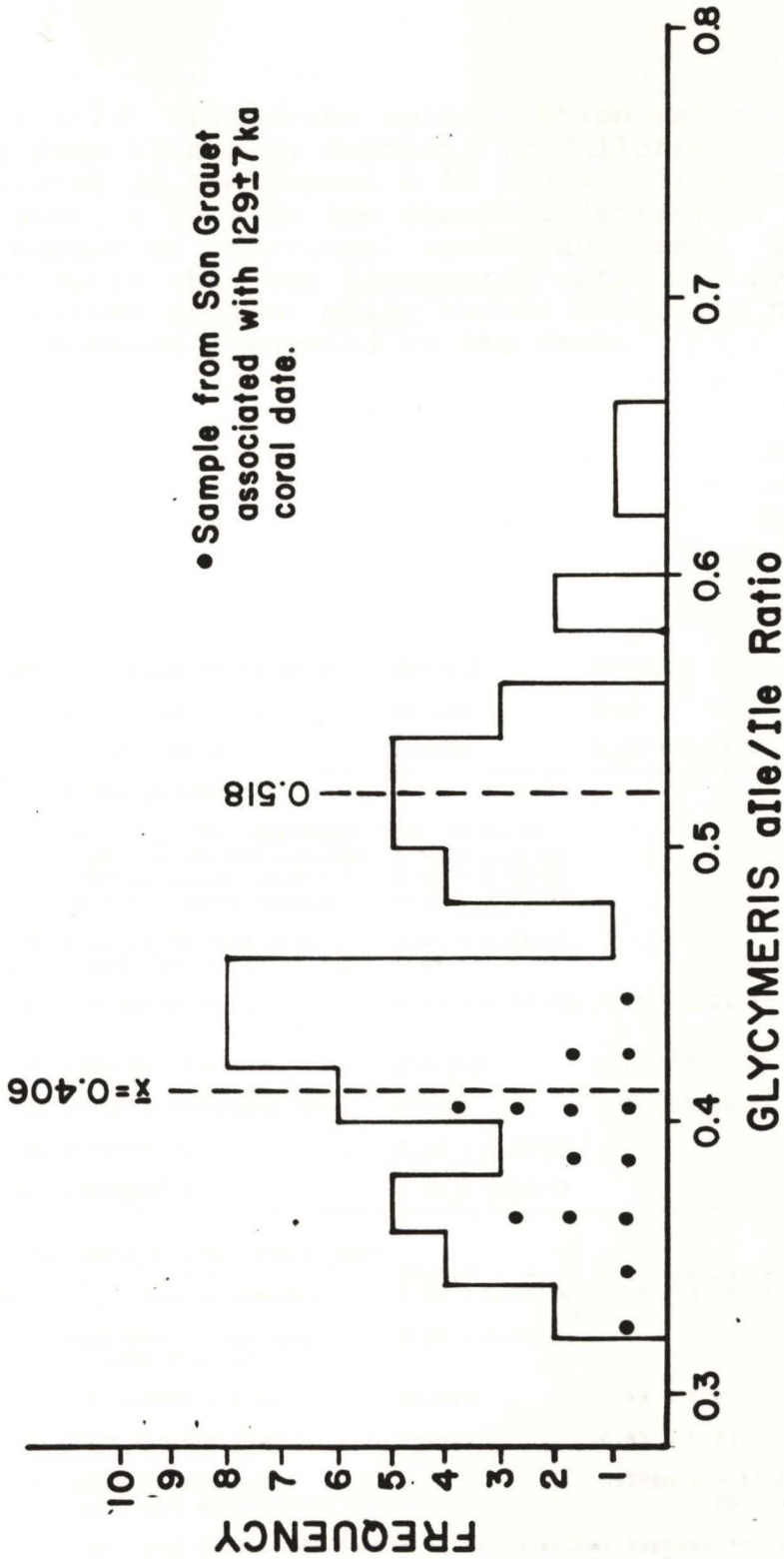
Figure 5-6: Histogram of aIle/Ile ratios from Glycymeris showing the distribution of values in aminozones E and F-G. There is a suggestion from the data that two groups may be represented in aminozone E which may be associated with minor oscillations of sea level between 135 and 118ka.

Table 5-1: Isoleucine epimerization (aIle/Ile ratio) data from 12 marine deposits in Mallorca. Data is presented in the format 0.40 ± 0.03 (3) where 0.40 is the mean, ± 0.03 is one standard deviation, and (3) is the number of individual shells analyzed. The symbol [ ] indicates that the _Glycymeris_ ratio has been converted from either _Arca_ or _Helix_ values according to relationships presented in the text.

A Z O N E	SITE # LOCALITY (elev.m)	GLY A/I	ARCA A/I	REMARKS
"A"	1. EL MOLINAR (1.5)	[0.09]	0.07	Holocene
	2. BANCO D'IBIZA	[0.13]	0.10 ± 0.01(3)	
	3. PLAYA DE PAGUERRA (1.0)	0.46 ± 0.02(3)		
	4. CAMPO DE TIRO- CARTNEGE (CTC) (0 to 4)			
	CTC III (Neotyrrhenian)	0.42 ± 0.01(6)		Sb?
	CTC II (peak intergl.)	0.43 ± 0.01(3)		Sb
	CTC I (early intergl.)	0.46 ± 0.03(3)		Sb
	5. COVA DE SA GATA (<2)	0.44 ± 0.04(3)		
"E"	EAST (CTC I equivalent)	0.44 (1)		
	6. SON GRAUET (1.2)	0.40 ± 0.03(13)	0.27 ± 0.02(9)	129 ± 7ka Sb
	7. CALA PI (3.5)	[>0.35] h	0.27 ± 0.01(2)	Sb
	8. TORRE S'ESTALELLA (5)	[0.44]	0.34 ± 0.02(2)	Sb
	9. S'ILLOT (6)	0.39 ± 0.05(3)		Sb
	10. CANYAMEL (3)	0.38 ± 0.03(4)		Sb
	4. CAMPO DE TIRO (reworked?)			
	CTC I and II	[0.54]	0.41 ± 0.05(14)	
"F/G"	CTC (Neotyrrhenian)	0.51 ± 0.03(16) h	0.40 ± 0.03(4)	
	10. CANYAMEL (lower unit) (A-zone F or G)	0.57 ± 0.01(2)		Exposed on surface
	11. CAP ORENOL (11.5)	[0.56]	0.43 ± 0.05(3)	
	12. CAVA BANCALS (14)	[0.59]	0.45 ± 0.03(6)	
"	1. BANCO D'IBIZA (30) (possibly much older)		OSTREA = 0.54,ND ND (3)	

ND = Not detectable levels of amino acids; typical in either very young samples, or extremely old samples. This deposit is possibly Pliocene in age.

the deposits representing mid Pleistocene

transgressions are stratigraphically and geomorphically

distinct, amino acid ratios do not clearly separate the

F and G aminozones. They will thus remain collectively

aminozone F/G until additional data can distinguish

them. Aminozone C representing the late last

interglacial is defined by Helix ratios in supralittoral

eolianites.

Uranium-series calibration

A uranium-series coral date of 129 ± 7ka on

Cladocora caespitosa (Table 5-2) was obtained from the

Son Grauet site (Hearty et al, 1986) and is equated with

Glycymeris mean aIle/Ile of 0.40 ± 0.03 (13) and Arca

ratios of 0.27 ± 0.02 (9). This date provides some

certainty that ratios within the range of 0.37 to 0.46

(Mallorca mean: 0.41 ± 0.04 (38)) for Glycymeris and 0.27

to 0.32 (0.29 ± 0.02 (13)) for Arca fall within the last

interglacial period. Hoang Chi-Trach (CNRS,

Gif-sur-Yvette, France) has recently determined the

U-series ages on three Glycymeris shells also from Son

Grauet provided by Hearty at 102 ± 7, 112 ± 7 and

135 +14/-10 ka (Table 5-2) (Hearty and Hoang, in

preparation).

Data from terrigenous deposits.

Table 5-2: Analytical data from uranium-series on
corals and mollusks, and isoleucine epimerization
(aIle/Ile) ratios from samples 4878A-C; the same
Glycymeris specimens U-series dated by Hoang Chi-Trach.
All samples were collected from the Strombus-bearing
calcarenites at Son Grauet.

```
----------------------------------------------------------------
URANIUM-SERIES CORAL DATA:
CLADOCORA CAESPITOSA FROM THE SON GRAUET, MALLORCA

H-C-3      <3%      3.00    1.070    110             0.702      129
(Szabo)           ± 0.05   ± 0.016   ± 44            ± 0.021    ± 7

----------------------------------------------------------------
URANIUM-SERIES MOLLUSK DATA:
GLYCYMERIS VIOLESCENS (4878A-C)

AMSh3      1.5%     0.508    1.22                     0.658     112
4878A             ± 0.015  ± 0.03                    ± 0.022    ± 7

BMSh3      <1%      1.066    1.26                     0.626     102
4878B             ± 0.033  ± 0.04                    ± 0.022    ± 7

CMSh3      <1%      0.488    1.18                     0.729     135
4878C             ± 0.017  ± 0.04                    ± 0.033   +14/-10

AILE/ILE DATA:
GLYCYMERIS VIOLESCENS (4878A-C)

4878A 0.40 |
           |                              SITE MEAN
4878B 0.43 } X = 0.42 ± 0.02 (3)      X = 0.40 ± 0.03 (13)
           |
4878C 0.43 |
```

<u>Helix</u> aIle/Ile ratios were determined from 13 eolianites and red soils listed in Table 5-3. <u>Helix</u> ratios averaging 0.39 from soils developed on last interglacial marine deposits (dated at 129ka) are interpreted to belong to an interval of low sea level at approximately 110 to 120ka.

<u>Helix</u> ratios from eolianites averaging 0.30 are keyed to a younger event, aminozone C, dated at approximately 90 ± 15 ka (mid or late stage 5), probably associated with a marine transgression that rose to a sea level slightly lower than present.

Synthesis of stratigraphic and geochronologic data

Figure 5-7 is a composite section illustrating the principal mid Pleistocene to Holocene lithostratigrapic units that are discussed in this study. Amino acid geochronology and U-series dating have allowed placement of these units into an absolute age framework. Correlations are based on age and stratigraphic position.

Reworking is a factor influencing variability of aIle/Ile ratios. Modern beaches are actively eroding older beach deposits and recycling marine shells as beach pebbles. At Campo de Tiro, two populations of shell ratios are present (Table 5-1). The younger is

Table 5-3: Isoleucine epimerization (aIle/Ile ratios)
data from 7 terrigenous deposits of soils, eolianites or
colluvium containing members of the family Helicidae
(i.e. Helix, Iberillus etc). Ages are estimated from
stratigraphic relationships with U-series coral dates
and calibrated Glycymeris values.

AMINOZONE V	SITE #	LOCALITY	HELICIDAE A/I	APP. AGE (KA)
	1.	NAUTICA MUS	0.03 ± 0.01(10)	<5
	13.	DUNE SITE	0.046 ± 0.01(3)	≤5
"C"	14.	PAGUERRA LOESS	0.29 ± 0.04(3)	70 to 110
	15.	CAMP DE MAR	0.30 ± 0.03(2)	
	13.	DUNE SITE	0.32 ± 0.05(2)	
	4.	CAMPO DE TIRO h (inter CTC soil)	0.49 ± 0.05(4)	
	4.	CTC (upper soil)	0.40 ± 0.03(2)	
"E"	13.	DUNE SITE (soil)	0.39 ± 0.02(5)	110 to 120
	5.	COVA DE SA GATA (eolianite)	0.44 ± 0.05(3)	
	6.	SON GRAUET (eolianite)	0.39 ± 0.02(3)	
	10.	CANYAMEL (soil)	0.35 ± 0.0_(5)	
post- "F"	4.	CAMPO DE TIRO (lowermost soil)	0.48 ± 0.03(3)	140 to 180
	13.	DUNE SITE (soil)	0.46 ± 0.03(3)	
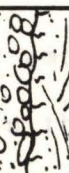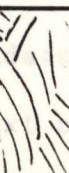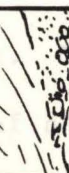
LITHOLOGY	SITE #	ISOTOPIC STAGE	FAUNA	ZONE	aIle/Ile HELIX	aIle/Ile GLYCY.	APPARENT AGE
Beach Sands	1		Banal	A			0–10
Soil	13	I		A	0.046		
Beach Dune Complex	2		Banal			[0.11]	60–
				C			110
Loess	14	5a/5c			0.29		
Eolianite	13,15		Banal		0.30		110
Soil CTC III	10	5a/5c	Partial Strombus or Banal		0.34	0.38 0.42	118
Beach-Dune Complex	4,10			E			110
Soil CTC II	4,6	5e 129ka	Strombus		0.39	0.43	
B-D Complex CTC I	(3–10)		Senegalese Fauna		0.44	0.46	135
B-D Complex	4			F-G			
Soil	4,13	7	Banal		0.47		150 180
Eolianite	4,13			G?		0.51	180
Marine	10	9	Banal				230
Beach Gravel	11,12		Banal			[0.58]	>300

Figure 5-7: A composite coastal stratigraphy from mid Pleistocene to the Holocene. Correlations with isotopic stages and apparent ages are tentative.

equated with the last interglacial period while the older group may involve reworking of submerged pre-last interglacial marine deposits. Apparently reworked shells belonging to a pre last interglacial aminozone are frequent in all units at Campo de Tiro. Miller et al. (1986) described an identical stratigraphic and geomorphic setting in Tunisia where mid Pleistocene aminozone F Glycymeris ratios are frequent in late Pleistocene marine deposits. Shackleton and Opdyke (1973) suggest that the stage 7 sea level is slightly below than present (-10m) which would agree both morphologically and geochronologically with the situation at Campo de Tiro and Rejiche, Tunisia. Older marine shells from Canyamel at 0.5m hint that a marine equivalent representing aminozone F (stage 7?) may lie submerged a few meters below present sea level.

This investigation provides an opportunity to compare results of independent methods that have been used on the same deposits (or equivalent marine units) in Mallorca. A comparison of the U-series mollusk and coral dates and the isoleucine epimerization data (Table 5-4) points out the trends among the data. The coral and the amino acid data (in the context of an extensive Mediterranean investigation) indicate an age of ca. 125 ka that is associated with a period of peak warmth during the early part of the last interglacial and

Table 5-4: A comparison of U-series coral and mollusk dates, and isoleucine epimerization ratios from several marine units in Mallorca.

SITE #	LOCALITY	GLY A/I	U-SERIES AGE (ka) M=mollusk C=coral	
4.	Campo de Tiro "B" (our CTC III)	0.42 ± 0.01(6) [0.54]*	220, 75	(M) ^
4.	Campo de Tiro "A" (our CTC I and II)	0.43 ± 0.01(3)	200	(M) ^
4.	Campo de Tiro "B" (our CTC I and II)	0.46 ± 0.03(3)	>300	(M) ^
6.	Son Grauet	0.40 ± 0.03(13)	129	(C) ^
9.	S'Illot	0.39 ± 0.05(3)	190	(M) ~
10.	Canyamel (upper) Canyamel (lower)	0.38 ± 0.0_(4)+ 0.57 ± 0.01(2)	>300	(M) ^
11.	Cap Orenol (11.5m)	[0.56]*	125	(M) ^

* = Converted to Glycymeris from Gly/Arca ratio of 1.32.
+ = Sample for mollusk date probably collected from upper unit at 3.3m (quote Butzer and Cuerda, 1982). Lower unit is exposed to maximum of only about 0.5 m.
^ = Securely collected from the same locality.
~ = Some doubt whether samples were collected from the same locality.

correlated with isotope stage 5e where as the mollusk

ages scattered between 75 and >300 ka.

Richards (1983, 1985) implied that the marine

deposits adjacent to the coastline in Mallorca were

similar to those in Tunisia dated at 25,000 to 30,000

years BP. Their similarity is not questioned but the

young age age conflicts with a number of U-series coral

and shell dates, and the amino acid data.

Epimerization kinetics.

When the mean aIle/Ile data are plotted against

apparent age, an epimerization curve is produced that

reflects a similar trend to that of pyrolysis

experiments (Figure 5-8). The pyrolysis curve is

generated by heating Glycymeris shells for 1,3,5, and 8

days at 130°C. The natural epimerization curve is

calibrated to the pyrolysis curve at 0.41 = 125ka = 72

hours. The pyrolysis and natural curves correspond well

up to about 180ka or 120 hours, where the pyrolysis rate

then begins to exceed the rate of natural epimerization.

This discrepancy could be explained by 1) the

nonlinearity of climate (which includes cold periods with

little epimerization) over geologic time in contrast to

the constant pyrolysis temperatures; or 2) by an

intrinsic difference between natural and high-

Figure 5-8: A plot of mean aIle/Ile ratios in <u>Glycymeris</u>
(natural and pyrolysis @ 130°C) and <u>Helix</u> versus time
(natural in ka BP and oven time in hours @ 130°C). The
relative epimerization rate in natural samples is
governed by climatic cycles that are symbolically
expressed on the horizontal axis. The pyrolysis and
natural data indicate a general correspondence in the
early phases of epimerization, but a divergence occurs in
late phases. This can be attributed to the difference
between the nonlinearity of natural epimerization as
controlled by climatic cycles and the pyrolysis curve
produced by linear (constant) oven heat.
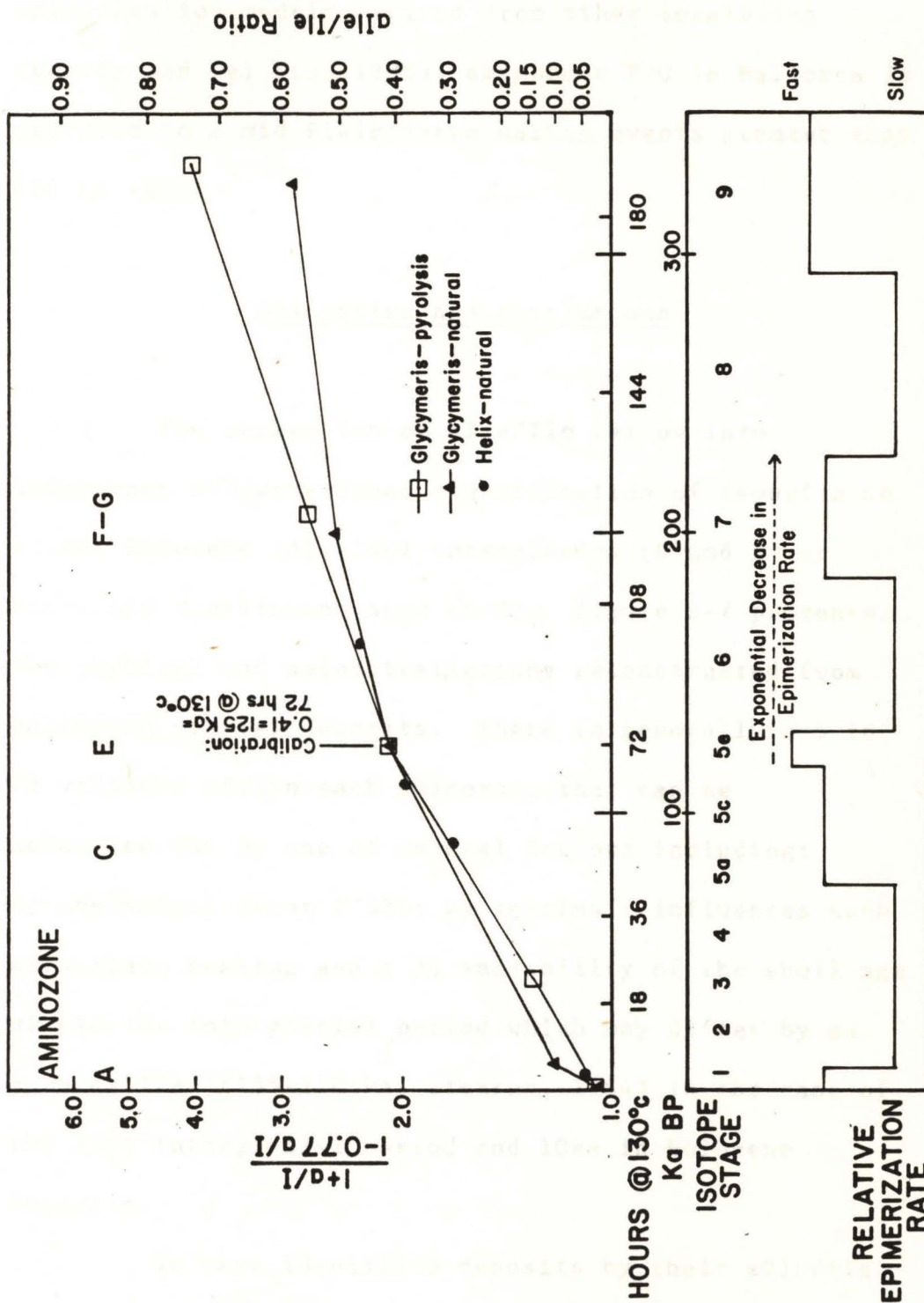
temperature induced epimerization kinetics. With
confidence in both pyrolysis experiments and natural
epimerization models derived from other localities
(Hearty and Dai Pra, 1985), aminozone F/G in Mallorca is
assigned to a mid Pleistocene marine events greater than
180 ka ago.

Discussion and conclusions

The separation of aIle/Ile ratios into
aminozones allows a broad classification of deposits in
either Holocene (A), last interglacial (C and E) or
older mid Pleistocene ages (F/G). Figure 5-7 presents
the physical and aminostratigraphy reconstructed from
Mallorcan coastal deposits. There is generally a 5 to
7% variance within each aminozone that can be
accounted for by one of several factors including:
1) analytical error (~3%); 2) intrinsic influences such
as surface heating and ; 3) variability of the shell age
within the interglacial period which may differ by as
much as 17ka (135-118 ka, Stearns, 1984) in the case of
the last interglacial period and 10ka in Holocene
deposits.

We have identified deposits by their aIle/Ile
ratios and correlated these deposits around the island
among diverse depositional enviroments. In summarizing

the results from this study, several key periods can be identified:

1) The Last Interglacial Period.

One of the important findings of this study is that many sites previously thought to be mid Pleistocene are stratigraphically and geochronometrically correlated to the last interglacial period. The depositional sequence of the last interglacial (<u>sensu stricto</u>) is most complete at Campo de Tiro-Cartnege (Figure 5-3). Three distinct marine units are present at CTC that are called "Cartnege I, II and III" and fall into aminozone "E" despite the age difference indicated by the soil between CTC II and CTC III. Unless all of the shells of CTC III are reworked from older deposits, we must assume that these units were generated by minor oscillations of sea level (between +10 and -10m) imposed on the major positive cycle during this period. Amino acid data also allow the assignment of several other units to aminozone E, which is calibrated to a U-series coral age of 129ka from Son Grauet.

The <u>Strombus</u> fauna is only associated with deposits producing aminozone E and mixed E and F/G ratios such as Campo de Tiro. Hearty (1986) reported that the Senegalese fauna occurred in nearly all of 50 sites belonging to the last interglacial aminogroup E

(dated at ca. 125ka) around the Mediterranean basin and found that rare occurrences of individual Senegalese forms were generally associated with ambiguous data. The Mallorcan studies have again supported the concept that no sites with exclusively mid Pleistocene ratios (aminogroup F or G) are associated with an abundance of Senegalese fauna.

2) Deposits younger than The Last Interglacial.

"Neotyrrhenian" marine deposits (in the sense of a late or post last interglacial age) have not yet been identified by aminostratigraphy in Mallorca. Marine deposits described as such in a stratigraphic sense (TIII or CTC III in this study) by Butzer and Cuerda (1982) have produced mixed ratios of aminozone E and F/G. However, the possiblilty exists that CTC III may be composed of entirely reworked shells of aminozones E and F/G, and may, in fact, belong to a younger event. A U-series shell date of 75ka (Stearns and Thurber, 1965; 1967) would support this hypothesis if verified. Unfortunately, at this time, until more sufficent data are produced, the question of the age of the Neotyrrhenian remains unanswered. Supralittoral eolianites have produced Helix ratios of aminozone C, which probably can be correlated to mid or late isotopic stage 5. Carbon-14 ages of 25,000 to 35,000 on the same shoreline

deposits (Richards, 1983, 1985) are considered to
reflect exchange of younger carbon rather than the
true age of the deposits.

Aminozone A is tied to the Holocene and, in the
case of Banco d'Ibiza, the early part of the Holocene
transgressive "hemicycle", perhaps 7 to 10kaBP. Intense
wave energy is responsible for deposition of Holocene
shells up to 15m a.s.l. on this and other exposed
coastlines including the controversial deposits near
Torre S'Estalella.

3) Deposits older than The Last Interglacial

Shells with aminozone F/G ratios are consid-
ered as reworked populations in last interglacial
marine deposits as well as indigenous populations in
older deposits. Shells producing aminozone F/G ratios,
associated with isotopic stage 7, may have been derived
from submerged deposits near Campo de Tiro
and at sea level at Canyamel. A remarkably similar
aminostratigraphy was described by Miller et al (1986)
in Tunisia. Aminozone F/G ratios have also been
obtained from deposits at 14m, indicating a mid
Pleistocene sea stand at this level. Based on the
interpretation of Arca ratios, the data suggest
that the 14m asl event is slightly older than deposits
at Canyamel and at Campo de Tiro.

Because of insufficient amino acid and radiometric data, we can not provide secure absolute ages for the older aminozones at this time but, within the regional framework of aminogroups (Hearty et al, 1986) and some kinetic constraints, we suggest a correlation of aminogroups F/G with isotopic stages 7 and/or 9.

4) Sea level history.

The sea level history of Mallorca is interpreted from the stratigraphy, geomorphology and geochronological data (Figure 5-9). A strong influence in this interpretation is the similarity of marine stratigraphic sequences in other "stable" coastlines of the world (cf. Hearty, 1986; Ulzega and Hearty, 1986; Hearty and Hollin, 1986 (a) and (b)). We derive our absolute age models from dated reef tracts in New Guinea (Chappell and Veeh, 1978; Bloom et al, 1974; Aharon, 1980; Chappell, 1983) and Barbados (Broecker et al, 1968) as well as from coral dated sites in the Mediterranean.

The sea level events that are interpreted from the stratigraphy of Mallorca and dated by amino acid and U-series dating are as follows (Figure 5-9)*:

a1) mid Pleistocene transgression with temporary halt at 14m asl (Cava Bancals);
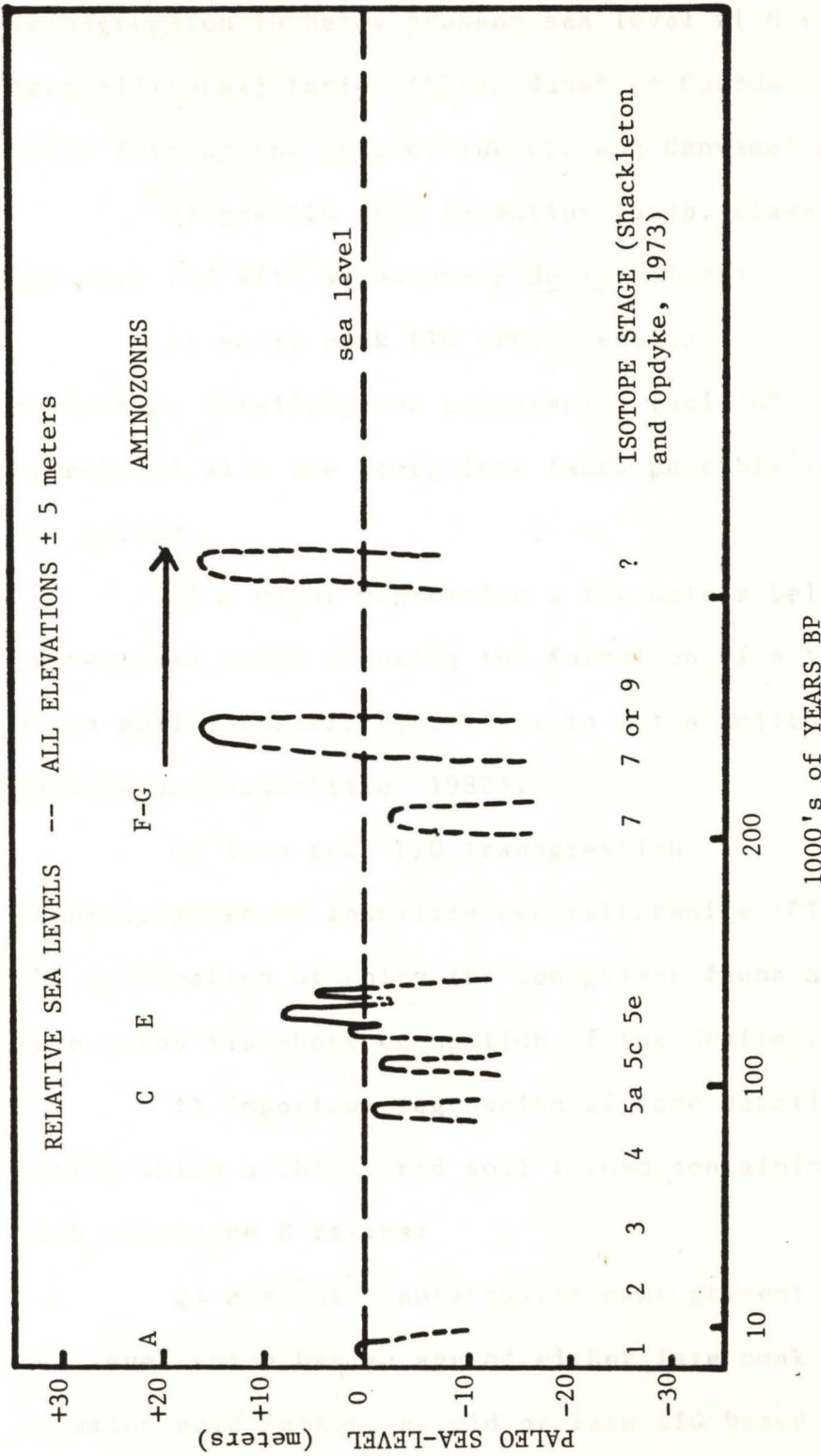
Figure 5-9: Proposed sea level curve synthesized from the stratigraphic, geomorphic and geochronologic data from Mallorca.

a2) penultimate? interglacial
transgression to below present sea level with eolianite
(supralittoral) facies ("Riss dune" of Cuerda, 1975,
1979) forming the base of the CTC and Canyamel sections;

b) pre-LIG soil formation (deep, clayey
and very red with aminozone F <u>Helix</u> ratios);

c) early peak LIG transgression
depositing fossiliferous calcarenite (unit CTC I)
associated with the Senegalese fauna possibly late in
the period;

d) a minor regression a few meters below
present sea level allowing the formation of a thin,
brown soil (probably equivalent to intra-Rejiche soil of
Paskoff and Sanlaville, 1982);

e) late peak LIG transgression
depositing second fossiliferous calcarenite (CTC II), at
the termination of which the Senegalese fauna appears to
have ended its short occupation of the Mediterranean;

f) important regression of some duration
during which a thick, red soil formed containing snails
with aminozone E ratios;

g) a brief transgression near present
sea level which has an age of either late peak LIG based
on amino acid ratios, or mid or late LIG based on
stratigraphy. An analoguous situation exists in Bermuda
(Hearty and Hollin, 1986b) where a stratigraphically

similar deposit (at Ft. St. Catherine) is coral dated at

85ka (Harmon et al, 1983);

      h) deposition of eolianites during late
LIG from a transgression near to but lower than present
sea level;

      i) Würmian regression, erosion and
deposition of continental sequence including soils and
colluvium; and

      j) Holocene transgression with minor
fluctuations of sea level and episodic eolian sand
deposition.

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*Definitions: LIG = last interglacial (sensu lato)
correlated to isotopic stage 5 or 135-75ka; peak
LIG = 135-118ka (Stearns, 1984) or isotopic stage 5e;
late LIG = early Würm or about 85-60ka; and Würm =
75ka to 10ka.

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5) Tectonic implications

      A synthesis of Mallorcan data support general
tectonic stability from the mid to late Pleistocene.
The geomorphic position of deposits producing aminozone
E ratios remains relatively constant occurring between 0
and 10m a.s.l. Minor variations ($\pm$5m) in elevation of
penecontemporaneous marine deposits can be explained by

1) variations in wave energy; 2) the distribution of shoreline facies (supralittoral, littoral, and sublittoral) deposited in a transect normal to the coastline; and 3) deposition during minor oscillations of sea level during the broader transgressive-regressive cycle.

6) U-series mollusk dates

A review of the U-series mollusk ages (Stearns and Thurber, 1965, 1967) indicates a possible conflict with amino acid ratios. The mollusk ages sometimes appear too young or too old but, in some cases, do not contradict the amino acid ratios.

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CHAPTER VI

SUMMARY AND CONCLUSIONS

Overview

This study demonstrates that the extent of
epimerization of isoleucine in mollusk fossils is an
effective tool for correlation of disjunct marine units
within a discrete area that has experienced a similar
thermal history; this is the concept of
aminostratigraphy (Miller and Hare, 1980). With the aid
of U-series dating on corals, several of these local
aminozones were placed in an absolute time scale and, in
the larger geographical picture, correlated to
aminogroups across the basin. These aminogroups have
subsequently been tied to major transgressive-regressive
sea level events and light isotopic intervals in a
global context.

The introduction of the amino acid method in
the Mediterranean did not proceed without problems. The
most significant hinderances during field studies
include the following: 1) locating fruitful deposits

considering the inherently patchy nature of the marine
record; 2) obtaining access to the highly urbanized,
often restricted coastlines; 3) locating shells of the
designated taxa; 4) finding samples in the field that
did not have obvious heating or other diagenetic
problems; and 5) unravelling geomorphological,
stratigraphic and facies relationships at the sections.
Once well preserved shell samples were located and
transported to the Amino Acid Laboratory in Boulder,
Colorado, a new set of difficulties were encountered
that included most importantly, the interpretation of
the results; there were difficulties with the
interpretation of multiple populations of ratios and the
occasional aberrant values. Were these digressions the
effect of surface heating, or chemical diagenesis, or
did they represent true differences in the age of the
shells? Each of these effects had its unique solution
that could only have been diciphired by the preparation,
analyses and detailed study of hundreds of shells and
the deposits containing them.

Despite several potential problems, a majority
of the data from deposits in the Mediterranean basin
fall into appropriate groups for their suspected or
known age and apparent thermal history. AIle/Ile ratios
demonstrate internal integrity by decreasing by
appropriate increments in stratigraphic section (e.g.

aIle/Ile ratios decrease regularly up 40m of sediment at Bovetto, southern Italy), or increasing up a flight of terraces generally known to increase in age.(e.g. Lazio coastline). In studies aimed at evaluating the surface heating effect, aIle/Ile ratios were shown to increase near the upper contact of marine units. In some cases (e.g. Gallipoli), it was demonstrated that overlying eolianites protected the thin fossiliferous marine deposits from surface heating effects. A shoreline process described as "mortaring" (Hearty and Dai Pra, 1985) brought to light the complexities of shoreline deposition on carbonate coastlines. This process involves the cyclic deposition of marine carbonates, erosion of a tortuous surface during transgressions, and redeposition of carbonate layers during subsequent regressions.

Amino acid geochronology, as indicated by the successful results of this study, can provide the needed answers to sea level problems by persistence in the field, care in sample selection and preparation, and diligence in the laboratory. Guidelines like those enumerated in Hearty (1986) should be considered at the onset of studies similar to this one. Adherence to such guidelines will certainly improve the data produced in the laboratory, but problems of interpretation will persist for a considerably longer time.

Contributions

Amino acid geochronology, biostratigraphy and
lithostratigraphy have been valuable tools for
correlation and dating of raised shorelines in the
Mediterranean basin. During the course of this thesis
research over 200 sites were studied, and data from
nearly 80 sites are presented here.

A majority of the objectives presented in the
introduction of this thesis have been satisfied. The
stated objectives (Introduction) and the resultant
contributions discussed thoroughly in each chapter, are
summarized below:

Objective 1: to use the amino acid
geochronology method to attack the outstanding problems
regarding the timimg and amplitude of sea level changes.
The focus would be on sites that contain abundant fossil
shells and corals, contain multiple-event stratigraphy,
and have a bearing on the sea level chronology.

A large number of sites were studied during the
three field seasons in the Mediterranean basin. Many of
these sites were important to the estabished sea level
chronology in the region. Included among the most
important are Campo de Tiro, Mallorca where Butzer and
Cuerda first revealed the complexity of sea level

changes in the mid and late Pleistocene; Calamosca,
Sardinia where the type locality of the Tyrrhenian was
established early in the century; Capo Milazzo, Sicily
where the now obsolete type section bearing its name was
identified; Bovetto and nearby sites along the Strait of
Messina that rank among the most uplifted last
interglacial sites (>140m) in the Mediterranean; Il
Fronte, southern Italy that Gignoux and others realized
was one of the more perfectly preserved late Pleistocene
marine sequences; and finally the terrace sequence on
the outskirts of Rome (Lazio region) that range in age
from the Pliocene to modern.

One of the products of this regional program
was the assignment of relative and/or absolute ages to
isolated marine deposits lacking stratigraphic context
and previous age determination. About half of the 78
sites investigated during this study fall into this
category. Included are sites that may have had some
previous work but have no time frame for their
deposition. Data from several of these isolated
deposits are presented in Table 2-2, in Hearty (1986),
Hearty (in press) and in Hearty and Dai Pra (1985;
1986). Worthy of mention are new aminogroup C
(Neotyrrhenian) sites: Piano San Nicola (So. Italy),
Panarea Island (28m, north of Sicily) and San Giovanni
di Sinnis (Sardinia), and aminogroup E (Eutyrrhenian)

sites: Archi South (Calabria, Italy), St. Florent (Corsica), and Santa Teresa di Gallura, Nora, Fradis Minoris, Cala su Turcu, Is Arenas and Sa Iletta (all of Sardinia; Ulzega and Hearty, 1986).

Objective 2: to collect shells from deposits representing a broad geographical and age range, to determine the aIle/Ile ratios and then to define aminogroups that represent transgressive/regressive events of the Pleistocene.

Nearly 800 analyses of isoleucine epimerization in species of Glycymeris and Arca from across the Mediterranean basin (see figures 2-1, 3-1, 4-1 and 5-1) resulted in at least six populations of aIle/Ile ratios that are distinct along latitudinal isotherms (based on current mean annual temperature) in the western Mediterranean.

I have assigned each aminogroup a letter identifier (aminogroups A,C, or C/D,E,F,G and K) that relate to, but are not fixed to light isotopic (negative) events defined from deep sea cores. Age differences are apparent between aminogroups, and these are supported by morpho-, litho- and biostratigraphic criteria. Aminogroup A is associated with the Holocene transgression. Aminogroups C and E are subdivisions of the last interglacial (s.l.) while aminogroups F and G relate to mid Pleistocene transgressions. Aminogroup K

represents several early Pleistocene events that are not yet individually resolvable with amino acid geochronology.

Objective 3: to determine the absolute age of the aminogroups.

Eight uranium-series dates on the branching coral Cladocora caespitosa (Table 2-1) and a solitary coral Astroides obtained during this study provide calibration of aminogroups E and F. Seven of the dates average 126 ± 4ka from deposits with aminogroup E ratios and tie this event to the peak of the last interglacial or isotopic stage 5e. This age is consistent with previous interpretations of the age of deposits bearing a thermophilous "Senegalese fauna" in the Mediterranean and a global view of warm climatic conditions during the last interglacial. Supported by its stratigraphic context and absolute age interpretation, the age of aminogroup C is younger than E and interpolated to an age of 90 ± 15 ka.

A single date from a mid Pleistocene deposit at Tomasso Natale near Palermo, Sicily of 245 ± 20ka, combined with the amino acid data from this site suggest a correlation of aminogroup F with stage 7 at approximately 180 to 250 ka (Imbrie et al, 1984). Other coral dates (Dai Pra and Stearns, 1977) have similarly been used to calibrate aIle/Ile ratios (Hearty and Dai

Pra, 1985). In the final appraisal, the extent of isoleucine epimerization is a consistent and reliable measure of the geologic age of deposits particularly when calibrated to the well-dated events, such as that of aminogroup E at ca. 125ka.

A large number of electron spin resonance (ESR, Radtke et al, 1983) and U-series mollusk dates (Stearns and Thurber, 1965, 1967; Bernat, 1982a; Hoang et al., 1978) are published from Mediterranean strandline studies. Ages from these techniques have not been used for calibration in this study. Their reliability was questioned (Kaufman et al, 1971) and has not since been demonstrated. While some are in broad agreement with aIle/Ile data, others are not. Regarding ESR from the Lazio region of northern Italy (Radtke et al, 1983), and U-series mollusk dates from Spain (Hillaire-Marcel et al, 1986), there is neither internal consistency among the ESR dates, nor correlation with amino acid data.

Objective 4: to evaluate the effect(s) on the rate of isoleucine epimerization of past climatic gradients across the region.

Since aIle/Ile ratios in fossil shells are a result of the integrated thermal history affecting the shell since deposition, and these thermal histories vary across the region, a collection of values from equal-age deposits across present climatic gradients should

reflect these integrated past gradients. This study has established such gradients for aminogroups C, E, F and G (best illustrated in Figure 2-2). When plotted against present mean annual temperatures, aIle/Ile ratios increase at the rate of approximately 0.03/°C. This gradient compares favorably with findings in California (Kennedy et al, 1982) and the southeast U.S. coastal plain (Hearty and Hollin, 1986b). However, this slope appears to flatten in cooler MAT's, and steepen in warmer MAT's as suggested by a recent compilation of global aIle/Ile versus MAT values (Hearty and Miller, in press). Regional differences in effective temperature can be calculated from aIle/Ile ratios across a climatic gradient (Miller et al, 1983), but these have not yet been determined for the Mediterranean basin.

Objective 5: to compare dated "aminogroups" (Hearty et al, 1986) to established sea level histories in the Mediterranean basin to support or refute present views on the sea level history.

Interpretation of paleosealevel is inherently problematic. It requires that evaluation be made regarding the age, the elevational indicators (finding the "zero" mark within beach stratigraphy), the tectonic history, the original paleosealevel, and other effects such as tides, hurricanes and tsunamis. Nonetheless, a fairly sustantial volume of data has been generated on

this subject during this study. We have established the precise or approximate ages of several aminogroups (Hearty et al, 1986, Hearty, 1986) from type localities in the Mediterranean basin. A monumental task in the basin is to establish which sites have been affected by tectonism, and which are the best indicators of paleosealevel.

By comparisons with other stable areas of the world (Ku et al, 1976; Harmon et al, 1983), it is likely that Sardinia and Mallorca are the most quiescent regions of the Mediterranean basin. Mallorca has offered the greatest amount of information on this subject (Chapter 5) where a comparison was made with Butzer and Cuerda's (1982) sea level scheme (Hearty, in press). And, despite countless assumptions, a synthesis of age and elevational data from both stable and unstable coastlines has also resulted in a sea level curve for the Mediterranean basin representing the past 250ka of geologic history (Hearty, 1986; Chapter 5).

As many as three sea levels previously thought to belong to separate interglacials (due to inaccurate dating or speculation on the age of deposits), are now certain to belong to minor oscillations of sea level during the last interglacial. New geomorphological and chronological evidence from Calabria, Italy (Hearty, Dumas and others, in press) supports two or three minor

oscillations of sea level during the Strombus interval and aminogroup E.This new information provides an explanation for the recurrence of a concept of "three Strombus levels" in the literature (see discussion below). In addition, amino acid data have provided support for a post-peak last interglacial high stand of sea level in several non-tectonic areas (Ulzega and Hearty, 1986; Hearty, 1986; Hearty and Hollin, 1986b; Miller et al, 1986; Hollin and Hearty, in press) in contradiction to assumed negative sea levels during that period calculated from constant uplift models (Bloom et al, 1974; Broecker et al, 1968) and isotopic interpretations (Shackleton and Opdyke, 1973).

Objective 6: to build a bio-, litho- and chronostratigraphic framework for future studies in the region.

A new amino-acid-based time framework is laid for future shoreline studies. An established dated network of several aminogroups will allow new sites to be incorporated into the framework and thus correlated to calibration "type sites" such as those at Il Fronte in the Puglia region of southern Italy. New research directions will be explored extending this framework, and additional stratigraphic, radiometric and epimerization data will strengthen the already existing one in the Mediterranean basin. In a recent synthesis

of last interglacial (s.l.) shoreline data from the Mediterranean basin, Hearty (1986) defined criteria characterizing the bio- and lithostratigraphy of deposits of the last interglacial period. This type of synthesis strengthens the ability of workers to correlate disjunct deposits with the aid of amino acid geochronology.

Objective 7: to maintain a parallel laboratory pyrolysis experimental program with pertinent taxa to more completely understand the kinetics of isoleucine epimerization.

During the course of the past five years, several hundred Glycymeris and Arca shells were heated at controlled temperatures (110, 130, 140 and 150°C) for specific time intervals (1, 3, 5, 8 and 16 days) and the aIle/Ile ratios analyzed to determine if epimerization kinetics under geological conditions, are reproduced under controlled laboratory ones. Preliminary comparisons between pyrolysis and natural conditions have been published (Hearty, 1986; Hearty, in press; Figure 5-8, this thesis) and the results indicate a general correspondence between the high and low temperature experiments, giving some hope for refinement of absolute age dating with the help of models. In natural epimerization, the aIle/Ile versus time curves tend to fall short of the pyrolysis ones when the two

curves are fixed to each other at known points. This discrepancy can be explained in part by the cyclic cold and warm in geologic time that slows and accelerates epimerization, compared to a constant influx of heat over time in the laboratory oven. This comparison has thus revealed that, in order to accurately calculate ages from natural epimerization models, a climatic temperature model must first be defined for each region. The publication of results of these and several other pyrolysis programs are forthcoming.

The age of the Senegalese fauna

Gignoux's (1913) original and unaffected view was that the Senegalese fauna, including Strombus bubonius occurred in the Mediterranean basin at a time "plus récent que tous les autres dépôts quaternaires". During the course of this investigation, Strombus (and related taxa) have been located or described from a considerable number of localities. Nearly 75% of all deposits of aminogroup E (ca. 125ka) contain members of the subtropical fauna. The remainder of the localities where Strombus has not been described lie generally in the northern parts of the basin, or are characterized by unusual paleoenvironmental conditions (e.g. euryhaline, high sedimentation, extremely high energy, or rocky

conditions). Without ambiguity, this study concludes that the Senegalese fauna is associated with a period of greater oceanic warmth in the Mediterranean basin centered around the peak of the last interglacial period, associated with aminogroup E, centered around ca. 125 ka. The magnitude of this interglacial warmth is reflected in pollen profiles (Woillard, 1978; Van der Hammen et al, 1967) and in high biogenic carbonate production (Hearty, 1986).

The presence of Strombus in deposits other than Eutyrrhenian is a source of great controversy. Strombus has been associated with deposits representing up to three interglacials dated between 75 and >200 ka (Bonadonna, 1967; Butzer, 1983; Hillaire-Marcel, 1986). A majority of the deposits from these studies have been visited and sampled by me, and mollusk aIle/Ile ratios measured. Of those deposits producing evidence for a multiple-interglacial occurrence of Strombus, nearly all contained either exclusively aminogroup E ratios, or a mixture of E, F and G ratios, suggesting reworking of older shells but provuding inconclusive evidence of older interglacial affinities of the Senegalese fauna.

The amino acid results also indicate that Strombus is found in aminogroup C deposits, but in all cases where found, the Strombus shells appear to be highly abraded fragments (often only the columella

remaining) that may be derived from older deposits. The
only deposits containing a member of the Senegalese
fauna (Cantharus viverratus) that has produced
unambiguous U-series coral dates and amino acid data
indicating an age greater than aminogroup E, is at
Tomasso Natale (Sicily). The occurrence of a single
member of the Senegalese fauna suggests that individual
species may migrate diachronously, which is not
unexpected. All other reportings of Strombus in
multiple-interglacial deposits are generally based on
uranium-series dating of mollusk shells, the dates from
which are highly suspect, and are not verified by
independent techniques.

In summary, amino acid and U-series coral dates
strongly support the contention that Strombus bubonius
and the Senegalese fauna reached their greatest
expansion during the peak of the last interglacial
period. Ambiguous data envelope the alternate
hypothesis that the exotic fauna occurred during
multiple interglacials in the Mediterranean basin. The
lack of tangible data to support a multiple-interglacial
occurrence of Strombus may either be a result of extreme
rarity or non-existence of the fauna during other
interglacials, or an artifact of spurious chronometric
techniques. The presence of abundant well-preserved
corals is in itself, evidence to support the association

of greater oceanic warmth with the occurrence of an exotic fauna. These corals, which provide the indisputable proof through U-series dating that <u>Strombus</u> occurred around 125 ka, are not generally abundant during earlier and later interglacials, nor are they abundant today. If the Mediterranean was warm enough to support a molluscan fauna now common only in equatorial regions (with MATs greater than 22°C), then it must have been warm enough to support plentiful corals. This is not the case in the Mediterranean Pleistocene with the exception of the last interglacial period. Basing the occurrence of the Senegalese fauna on unsupported U-series mollusk dates that have been demonstrated to be unreliable on geochemical (Kaufman et al, 1971) and on geological grounds (Hearty and Dai Pra, 1986; Hearty, in press; and Hearty et al, in press) is unfortunate considering the great stratigraphic works of those that have gone before us. The "burden of proof" lies with those who maintain a multiple-interglacial occurrence of the Senegalese fauna, to demonstrate with reliable, multiple and mutually supporting methods, that deposits bearing indigenous Senegalese fauna, are other than 125,000 years old.

<u>Future research</u>

This investigation was directed toward reconnaissance of numerous sites across the Mediterranean basin. There have been advantages wrought from a cursory regional approach. I have identified productive and problematic areas that now stimulate ideas and directions for future research within and beyond the Mediterranean basin. Focal points for future studies include:

1) A most obvious next-step is to correlate from coastal shoreline deposits to equivalent deposits recorded in deep sea cores. Since interglacial peaks are usually identifiable down core, these can be sampled for microfauna, both benthic and planktonic, and similarly sampled in dated coastal marine deposits. Many of the coastal marine deposits in areas of higher sedimentation (e.g. Lazio region and the Strait of Messina) contain abundant foraminifera of the planktonic and benthic varieties. A logical starting point is the last interglacial level which is readily identifiable in cores and well-dated in coastal sections. AIle/Ile ratios from coastal and deep sea equal-aged foraminifera are not expected to be the same, but are expected to record the temperature differences between coastal and bottom waters. Once this difference in diagenetic temperature history is established, further studies on several different interglacial levels would provide

important age constraints on marine deposits. An important by-product of this area of study would be a long record of isoleucine epimerization in cores that would provide new kinetic data on the inferred non-linearity of the epimerization reaction. Initial phases of this research are underway at INSTAAR.

2) A marriage of mutually temperature-sensitive oxygen isotope and epimerization techniques on mollusks from shoreline deposits in the Mediterranean would generate valuable data in a number of areas. Paleo-temperature gradients could be established from the interplay of these two techniques on equal-aged deposits across the region. Glycymeris that have been analyzed from a majority of the sites covered in this study would be available for isotopic analyses. Once equal-aged gradients were established, a series of multiple-aged sites could then be analyzed that would provide data on the differences in average temperature of several interglacial periods. A comparison with deep-sea epimerization and isotopic data would yield necessary verification of the temperature scheme.

3) Further studies would also include obtaining more U-series dates from aminogroups C and C/D age marine events. Corals can be often found in many such deposits in more southerly localities when deposits are subject to careful scrutiny and greater search-time. Better

absolute age calibration of amino acid sites result in

needed data on kinetic pathways of isoleucine

epimerization. Such data would allow more accurate

conversion of aIle/Ile ratios to absolute ages.

4) An absolute requirement of future studies is

to construct an integrated temperature history model

over at least the past 0.5my. This can be accomplished

through compilation of isotopic and pollen data from

several sources in and near the Mediterranean basin.

Further absolute age estimates with aIle/Ile ratios must

include, at minimum, a recognition of the role of

non-linear climatic pattern on diagenesis of amino

acids.

5) A new approach and application of amino acid

geochronology to neotectonism affecting coastal areas in

the Mediterranean is included in future research

objectives. Such research will concentrate on delimited

coastal segments that appear to have undergone

significant movement in the later Pleistocene. Tracing

and correlation of equal-aged deposits with amino acid

data will facilitate the calculation of relative uplift

rates.

6) Future efforts will continue to concentrate

on sequential marine seqences that constitute the basis

of sea level chronologies around the world. Such sites

include Bermuda, southeast U.S., New Guinea and the

Carribean. New sites will be incorporated into this epimerization network that has emerged from Mediterranean studies. Equatorial last interglacial deposits will soon be analyzed and will provide new data on the non-linearity of the epimerization reaction at much higher ambient temperatures. Such studies will also determine the geographical and climatic limitations of the method.

end

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