AN ORGANIC GEOCHEMICAL APPROACH TO PROBLEMS OF GLACIAL-INTERGLACIAL CLIMATIC VARIABILITY

by

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Submitted to the Massachusetts Institute of Technology/Woods Hole Oceanographic Institution Joint Program in Oceanography on May 13, 1988 in partial fulfillment of the requirements for the Degree of Doctor of Philosopy in Oceanography

ABSTRACT

The concentration and carbon isotopic composition ($\delta^{13}C$) of sedimentary organic carbon (C_{org}), N/C ratios, and terrigenous and marine $\delta^{13}C$-C_{org} end-members form a basis from which to address problems of Late Quaternary glacial-interglacial climatic variability in a 208.7 m hydraulic piston core (DSDP 619) from the Pigmy Basin in the northern Gulf of Mexico. Paired analyses of $\delta^{13}C$-C_{org} and N/C are consistent with the hypothesis that the sedimentary organic carbon in the Pigmy Basin is a climatically-determined mixture of C_3-photosynthetic terrigenous and marine organic matter, confirming the model of Sackett (1964). A high resolution (~1.4-2.7 ky/sample) $\delta^{13}C$-C_{org} record shows that sedimentary organic carbon in interglacial oxygen isotope (sub)stages 1 and 5a-b are enriched in ^{13}C (average ± 1σ values are -24.2 ± 1.2°/$_{oo}$ and -23.0 ± 0.8°/$_{oo}$ relative to PDB, respectively) while glacial isotope stage values 2 are relatively depleted (-25.6 ± 0.5°/$_{oo}$). Concentrations of terrigenous and marine sedimentary organic carbon are calculated using $\delta^{13}C$-C_{org} and C_{org} measurements, and terrigenous and marine $\delta^{13}C$-C_{org} end-members. The net accumulation rate of terrigenous organic carbon is 3.7±3.1 times higher in isotope stages 2-4 than in (sub)stages 1 and 5a-b, recording higher erosion rates of terrigenous organic material in glacial periods than interglacial periods. The concentration and net accumulation rates of marine and terrigenous C_{org} suggest that the nutrient-bearing plume of the Mississippi River may have advanced and retreated across the Pigmy Basin as sea level fell and rose in response to glacial-interglacial sea level change.

A study of selected organic biomarker compounds which could serve as tracers of terrigenous and marine sedimentary organic matter sources was performed by comparison with contemporaneous sedimentary organic carbon isotopic composition ($\delta^{13}C$-C_{org}). Organic carbon-normalized concentrations of total long chain (C_{37}-C_{39}) unsaturated alkenones and individual C_{27}-C_{29} desmethyl sterols were determined to be useful proportional indicators of preserved

marine and terrigenous organic carbon, respectively. The alkenones, whose source is marine phytoplankton of the class Prymnesiophyceae, generally occurred in higher concentrations in interglacial isotope stages 1 and 5a-b than in the intervening stages, including glacial stages 2 and 4. Sterols (C_{27}-C_{29}) of a dominantly terrigenous origin had lower concentrations during interglacial stages than in glacial stages. The sedimentary records of both terrigenous and marine organic carbon-normalized biomarker compound concentrations appear to be systematically altered by the remineralization of sedimentary organic carbon, as indicated by a simple, first-order organic carbon decay model. The sedimentary deposition of some terrigenous 4-desmethylsterols may be affected by differential hydraulic particle sorting as they are transported from river deltas across the continental shelf and slope to the hemipelagic Pigmy Basin. The marine phytoplanktonic alkenones which originate in the surface ocean and sink through the water column would not be subject to comparable particle sorting. The lack of any 4-desmethyl- or 4-α-methylsterol which was linearly related to the proportion of marine sedimentary organic matter (as scaled by $\delta^{13}C$-C_{org}) indicated that either (1) sedimentary diagenesis had obscured the biomarker/C_{org} versus $\delta^{13}C$-C_{org} record, or (2) the selected compounds were not proportional indicators of preserved marine organic carbon input.

The diagenetic alteration of the sedimentary sterol concentration records in which marine sterols were apparently more susceptible to degradation than terrigenous sterols was consistent with present-day sediment trap and recent (10^{-1}-10^{2}y) sediment core observations. Preferential preservation of terrigenous sterols may result in a biased sedimentary record of sterol input which could be misinterpreted as indicating solely terrigenous sterol sources. The value and limitations of a simple model which characterizes the effects of sedimentary diagenesis and source input changes on the relationship between organic carbon-normalized biomarker compounds and sedimentary organic matter carbon isotopic composition are discussed.

The potential occurrence of sterol double bond hydrogenations (Δ^5, Δ^{22}) in three classes of C_{27-29}-4-desmethylsterols was evaluated by examining the time series of expected product/precursor relationships with sterol data from the ~2-100kybp DSDP 619 record. Only the Δ^5-hydrogenations of the C_{29} sterols (24-ethylcholest-5-en-3ß-ol, 24-ethylcholesta-5,22-dien-3ß-ol) showed significant temporally-increasing trends. The 24-ethylcholestan-3ß-ol/24-ethylcholest-5-en-3ß-ol ($C_{29}\Delta^0/C_{29}\Delta^5$) ratio also positively correlated with paired sedimentary organic carbon isotopic composition ($\delta^{13}C$-C_{org}) values. This may be due to increased susceptibility to diagenetic transformation reactions by the organic matter accompanying finer grain-sized terrigenous sediment particles. A long-term source change of 24-ethylcholestan-3ß-ol relative to 24-ethylcholest-5-en-3ß-ol to explain the correlation with $\delta^{13}C$-C_{org} seems less likely since both compounds are predominantly of a terrigenous origin in the Pigmy Basin. A comparison of

histograms of stanol/stenol (Δ^0/Δ^5) ratios for the C_{27-29}-4-desmethylsterols indicates the following sequence in the relative degree of tranformation: $C_{27} > C_{28} > C_{29}$. The C_{27}- and C_{28}-sterols appear to have attained their respective degrees of transformation before ~2kybp, perhaps prior to deposition in the Pigmy Basin. However, differential rates of competing reactions of both the precursor and products may have obscured these simple transformation ratio records.

The sedimentary record of a ratio (U^K_{37}) of long chain (C_{37}) unsaturated alkenones is a useful indicator of glacial-interglacial climatic change in the Late Quaternary northern Gulf of Mexico where a planktonic foraminiferal $\delta^{18}O$-$CaCO_3$ record is complicated by meltwater and/or fluvial events (Williams and Kohl, 1986). Using laboratory temperature calibration data of the U^K_{37} ratio (Prahl and Wakeham, 1987), it is suggested that the minimum glacial surface mixed layer (SML) temperature was 8±1°C colder than the Holocene high SML temperature of 25.6±0.5°C in a Pigmy Basin hydraulic piston core (DSDP 619). However, this glacial-interglacial U^K_{37}-temperature difference was significantly larger than the differences predicted by either the foraminiferal $\delta^{18}O$ or foraminiferal assemblage temperature methods (0.8–2.0°C). A possible cause for this large difference is that the Prymnesiophyte assemblages in this area may vary in response to climatically-induced hydrographic changes. Interglacial periods may be dominated by pelagic Prymnesiophyte assemblages, while glacial periods may be dominated by neritic assemblages. Correlation of the U^K_{37} ratio with the sedimentary organic carbon composition ($\delta^{13}C$-C_{org}) is consistent with the predominance of preserved input of erosive terrigenous over marine organic carbon during glacial stages in the northern Gulf of Mexico when sea level was as much as 150m lower than in the present interglacial stage. Marine organic carbon burial dominated in warmer interglacial stages 1 and 5a-b.

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The interdisciplinary nature of my thesis research required the scientific and analytical expertise from many people. I am grateful to all of those who contributed their advice and assistance. Although one cannot often return such help directly, one hopes that the assistance received may be reciprocated by advising others as *crescat scientia vita excolatur*.

The scientific interests of my thesis committee reflect the interdisciplinary nature of this research. I thank all of them for the opportunity, freedom, and guidance to pursue the long-term climatic effects on sedimentary organic geochemical records. Bob Gagosian, my thesis supervisor, has advised me admirably in all aspects of the research, from writing the initial proposal, funding the work, coping with analytical and theoretical problems, to outlining and editing the thesis. John Farrington was readily available for discussions of this work which were helpful, insightful, and inspiring for me. Although John Hedges, from the University of Washington, and I communicated at less frequent intervals, his knowledge of bulk organic geochemical properties and his analytical assistance saved me from potential pitfalls. His reviews of this thesis have markedly improved it. Ed Boyle and Bill Curry have contributed paleoceanographic perspectives that have helped me to understand the value and limitations of this work. Although Lloyd Keigwin was not formally a member of my committee, I would like to thank him for stimulating discussions and analytical support.

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Finally, I would like to acknowledge friends and family who supported me through this project. Bruce Brownawell, Billy Spitzer, Martha Tarafa, Steve Morrill, and Bernward Hay have been good friends through many years. Barbara Jones, JoAnn Nicholson, Lynne Soughley and friends have made life in Woods Hole most enjoyable. My committee members have been more than staff members, but colleagues and friends. My mother and family have long supported and appreciated my scientific interests. Barbara Kamicker has been a good friend and advisor through most of my thesis; she is now my wife. I look forward to many years of stimulating discussions.

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Dedicated to

My Mother, Bob, and John

for the faith they had in me.

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CHAPTER 1

GENERAL INTRODUCTION

> "The empirical results just described have been widely accepted as confiriming the basic tenet of the astronomical theory, namely that orbital variations significantly influenced the climate of the earth during the Pleistocene Epoch. ... What is important is that a significant forcing function of climate has been identified unambiguously. A major opportunity is therefore at hand to identify the mechanisms by which different parts of the climate system respond to changes in radiative boundary conditions. The importance of this opportunity is that both the temporal and spatial structures of these changes can be specified exactly. Except for studies of the annual cycle, it is difficult to name another problem in climate dynamics where the primary external forcing terms are known so precisely."
>
> (Imbrie, 1982)

The scientific history of glacial-interglacial climatology began as a study of glacial geology on the continents. Later studies of micropaleontological, geochemical, and foraminiferal isotopic records of the surface ocean and, more recently, the deep ocean have begun to constrain theories about the physical properties and circulation of prehistoric oceans. Imbrie (1982) pointed out that the external forcing for glacial-interglacial climatic variations is one of the best characaterized mechanisms in climate dynamics. With that, a significant opportunity was at hand to investigate the physical effects of climatic change on primary production, deposition, and preservation of organic matter in Quaternary marine environments.

One of the most significant issues that has arisen from studies of glacial-interglacial climatic variability is the origin, distribution, and fate of marine and terrigenous organic carbon (Shackleton, 1977;

Broecker, 1982; Boyle and Keigwin, 1982). The production of marine organic carbon is often limited by nutrients (Riley, 1947; Huntsman and Barber, 1977) which may be provided by upwelling or riverine inputs. Equatorial upwelling increases as with trade wind velocity (Neuman and Peirson, 1966; Wyrtki, et al., 1976) so that strong trade winds result in high marine primary productivity (Brink, et al., 1980; Jones and Halpern, 1981). Conversely, relaxed trade wind velocities result in less upwelling and warmer sea surface temperatures in the eastern equatorial Pacific Ocean (Wyrtki, et al., 1976). Heavy rainfall along the western coasts of the Americas (Quinn and Burt, 1970) accompanies the decreased upwelling intensity and increased sea surface temperatures. The heavy rains erode terrigenous sediments and their associated organic material into the oceans. Quaternary sea level variations of approximately 150 meters cyclically exposed continental shelves to erosion during low sea level stands and submerged them in high sea level stands when they became depositional environments again (Broecker, 1982). With relatively simple climatological and oceanographic observations, one can construct reasonable hypotheses about the effects of glacial-interglacial climatic variability on the deposition of organic matter in deep-sea sedimentary environments.

There are numerous observations which suggest that there may have been significant temporal variations of organic matter input on the glacial-interglacial time scale in the equatorial oceans. On the continental slope and in nearshore basins of Central America and South America, glacial-interglacial variations of diatom concentrations and

species (De Vries and Schrader, 1981), concentrations of radiolaria and terrigenous quartz grains in marine sediments (Molina-Cruz, 1977), organic carbon concentration (Pedersen, 1983), $CaCO_3$ concentration (Adelseck and Anderson, 1978), and fish debris (De Vries and Pearcy, 1982) indicate cyclicity in organic matter input. In the equatorial Atlantic Ocean, even more data are available that record glacial-interglacial climatic changes. Multivariate statistical approaches to planktonic foraminiferal distributions have allowed detailed reconstructions of the Pleistocene Atlantic Ocean sea surface temperatures (CLIMAP, 1976; Gardner and Hays, 1976; McIntyre, et al., 1976; Crowley, 1981). The stable isotopic composition of planktonic foraminifera correlated with radiolarian and benthic foraminifera distributions, and sedimentary organic carbon content have been interpreted as upwelling indices in the equatorial Atlantic Ocean off northwest Africa (Berger, et al., 1978). Parkin and Padgham (1975) interpreted the presence of the qualitative indicators "charcoal sticks" and fungal hyphae, together with the "colour of sediment soak water" and sedimentary organic carbon content as "semiquantitative measures of land vegetation" over the last 700 ky in the northeastern equatorial Atlantic. The analyses of contemporary organic biomarker compound and stable isotopic methods will allow more precise determination of the sedimentary organic matter sources.

Studies of the carbon isotopic composition ($\delta^{13}C$) of benthic foraminiferal carbonates are not adequate in themselves to constrain the changes which occurred to carbon reservoirs during glacial-interglacial climatic variations. Marine and terrigenous organic

matter are about 20 and 26°/$_{oo}$ more negative in $\delta^{13}C$ (°/$_{oo}$ PDB), respectively, than $CaCO_3$-carbon so that it is not possible to make a unique statement about mineralization of which organic carbon reservoir may be causing the foraminiferal shifts of $\delta^{13}C$. This principle can be demonstrated by constructing carbon mass and carbon isotope balances of terrigenous and marine organic carbon, and dissolved inorganic carbon (Chapter 2, Appendix 2.1). At best, one could only state that the foraminiferal $\delta^{13}C$ changes are due to the mineralization of a given mass of marine organic matter, a smaller mass of terrigenous organic matter, or some linear combination of both. With combined analyses of bulk organic geochemical properties of sedimentary organic matter ($\delta^{13}C$-C_{org} and N/C ratios) and organic biomarker compounds in marine sediments, new insight may be gained into the climatically-controlled temporal variation of sedimentary organic matter accumulation.

Sedimentary organic matter carbon isotopic composition ($\delta^{13}C$-C_{org}) has been used to differentiate between marine and terrigenous sources in general (Craig, 1953; Sackett and Thompson, 1963; Sackett, 1964; Sackett and Rankin, 1970; Neuman, et al., 1973; Hedges and Parker, 1976; Joyce, et al., 1986). In an ~800ky Quaternary sediment core from the Sierra Leone Rise in the eastern north Atlantic, combined $\delta^{13}C$-C_{org} and C_{org} concentration analyses showed that there were cyclic glacial-interglacial variations in the preservation and, presumably, input of marine organic matter (Muller, et al., 1983). More recently, some individual organic compounds have been shown to be diagnostic for specific marine and

terrigenous faunal and floral inputs to sediments (MacKenzie, et al., 1982; Gagosian, 1983; Farrington, 1987); angiosperm versus gymnosperm sources (Hedges and Parker, 1976; Hedges and Mann, 1979a and b); leaf epicuticular wax input (Eglinton and Hamilton, 1967); dinoflagellate sources (Volkman, et al., 1984; Robinson, et al., 1984); and Prymnesiophyte algae, including coccolithophorid sources (Marlowe, et al., 1984a; Marlowe, et al., 1984b; Brassell, et al., 1986a; Brassell, et al., 1986b). Principles of organic molecular stratigraphy (Eglinton and Hamilton, 1967) developed in lacustrine sediments demonstrated the potential usefulness of organic geochemistry in addressing geologial problems (e.g., Reed and Mankiewicz, 1975; Ishiwatari and Ogura, 1984). However, relatively few systematic studies in Quaternary oceanography have utilized organic biomarker compounds in a quantitative fashion. In some recent investigations, organic biomarker compounds were used as source and molecular stratigraphic indices in Quaternary sediments. The sedimentary lignin compositional and concentration variations in an 11ky sediment core from Lake Washington, U.S.A., indicated long-term vegetation changes in the lake's watershed (Hedges, et al., 1982; Leopold, et al., 1982) The long chain (C_{37-39}) alkenones have been employed in newly developing areas of molecular stratigraphy and paleothermometry, and, perhaps, as quantitative source indices (Brassell, et al., 1986a: Brassell, et al., 1986b). These and other selected biomarker componds harbor great potential as organic matter source and depositional tracers, and as stratigraphic and paleothermometric measurements.

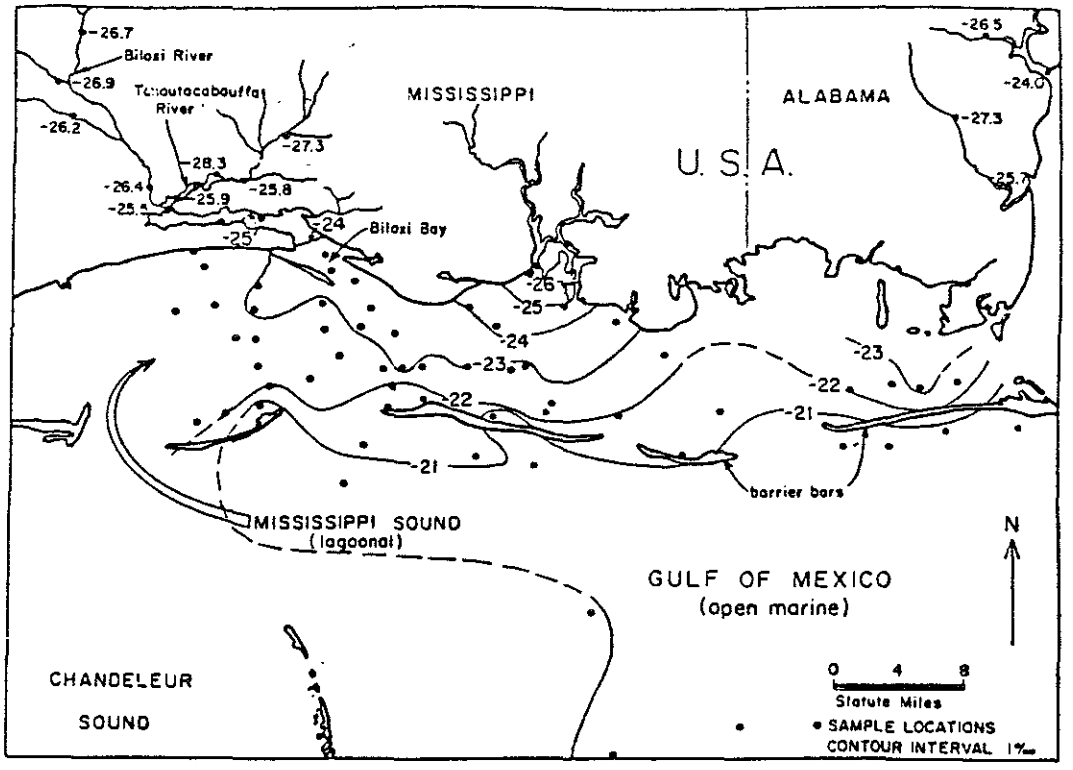
There is compelling evidence that a glacial-interglacial variation in the relative intensity of terrigenous versus marine organic matter deposition may be recorded in Gulf of Mexico sediments. A number of investigators (Sackett, 1964; Rogers and Koons, 1969; Sackett and Rankin, 1970; Neuman et al., 1973; and Joyce et al., 1986) have observed a 3-6°/$_{oo}$ increase in the sedimentary organic carbon isotopic composition since the Last Glacial Maximum (~20 kybp) in all major sedimentary provinces in the Gulf of Mexico. However, alternative hypotheses have been suggested to explain the variations in Quaternary $\delta^{13}C$-C_{org} records (Rogers and Koons, 1969), including (1) diagenetic carbon isotopic fractionation, and (2) temperature-dependent carbon isotopic fractionation by marine phytoplankton. Sedimentary mixing of C_3 (Calvin-Benson Cycle) and C_4 (Hatch-Slack) terrigenous organic matter could also produce the observed Quaternary $\delta^{13}C$-C_{org} variations. In the contemporary Gulf of Mexico, Hedges and Parker (1976) showed that lignin phenols are approximately a conservative mixing component (the terrigenous end-member) of sedimentary organic matter in a surface sediment $\delta^{13}C$-C_{org} gradient (-26°/$_{oo}$ onshore to -19°/$_{oo}$ farther offshore). The combined analyses of organic biomarker compounds (lignin phenols) and a bulk organic geochemical property ($\delta^{13}C$-C_{org}) supports the hypothesis of mixing of C_3-photosynthetic terrigenous and marine organic matter in surface sediments. In the present interglacial period, the terrigenous organic matter end-member is generally trapped on the continental shelves as indicated by the isopleths of $\delta^{13}C$-C_{org} (-26°/$_{oo}$ to

-22.5°/$_{oo}$) which radiate only a few tens of kilometers from estuary mouths onto the inner continental shelf (Sackett and Thompson, 1963; Schultz and Calder, 1976) (Fig. 1.1). In glacial times, however, the terrigenous influence ($\delta^{13}C$-C_{org} = -26°/$_{oo}$ to -22.5°/$_{oo}$) virtually covers the whole basin of the Gulf of Mexico (Newman, et al., 1973) (Fig. 1.2). Since the Mississippi River system drains a major fraction of the continental United States, combined analyses of organic biomarker compounds, sedimentary organic carbon concentration and its isotopic composition may allow a better understanding of organic matter sources than any of these measurements alone. The proper selection of organic biomarker compounds should also allow a determination of the marine and terrigenous $\delta^{13}C$-C_{org} end-members of Gulf of Mexico sediments. One should note that while in glacial eastern equatorial oceans the marine organic carbon contribution is believed to have increased because of increased upwelling (Muller and Erlenkeuser, 1983), in the glacial Gulf of Mexico, terrigenous input apparently dominate the basin due to erosion of terrigenous organic carbon-rich continental shelf sediments.

The main objective of this study was to use organic biomarker compounds and bulk organic geochemical techniques to qualify (sources) and quantify (marine and terrigenous organic matter accumulation) the effects of glacial-interglacial climatic variability on the deposition and fate of organic matter in a marine sedimentary environment. While this research was underway, selected compounds within one of the organic biomarker classes (alkenones) examined was found to potentially have paleoceanographically useful paleothermometric and

Fig. 1.1. Sedimentary organic carbon isotopic composition ($\delta^{13}C$-C_{org} in °/₀₀ PDB) in surface sediments of the northeastern Gulf of Mexico (from Sackett and Thompson, 1963)

Fig. 1.2. Sedimentary organic carbon isotopic composition ($\delta^{13}C$-C_{org} in °/₀₀ NBS-20) in the late Pleistocene sediments of the Gulf of Mexico, showing the dominance of terrigenous input from the Mississippi River system (from Newman, et al., 1983). Note that $\delta^{13}C_{NBS-20} = \delta^{13}C_{PDB} - 1.06$.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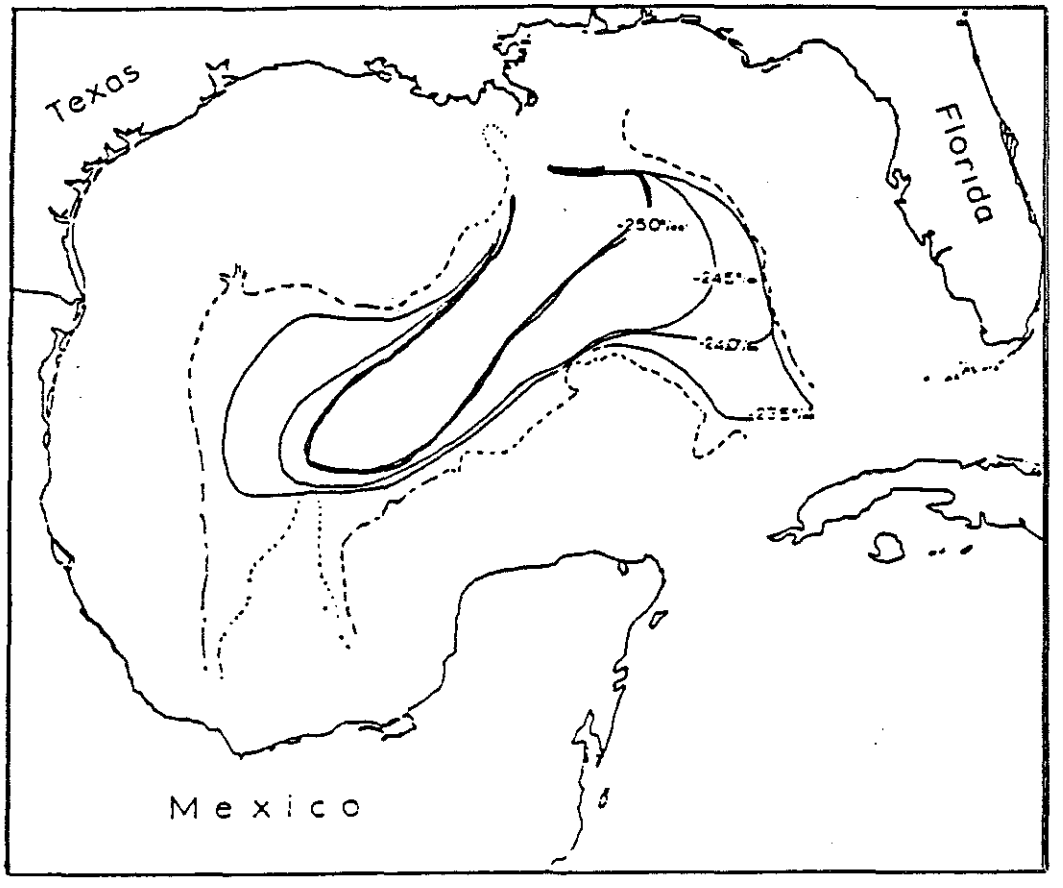
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molecular stratigraphic properties (Brassell, et al., 1986a; Brassell, et al., 1986b). These paleoceanographic properties were also evaluated in this study.

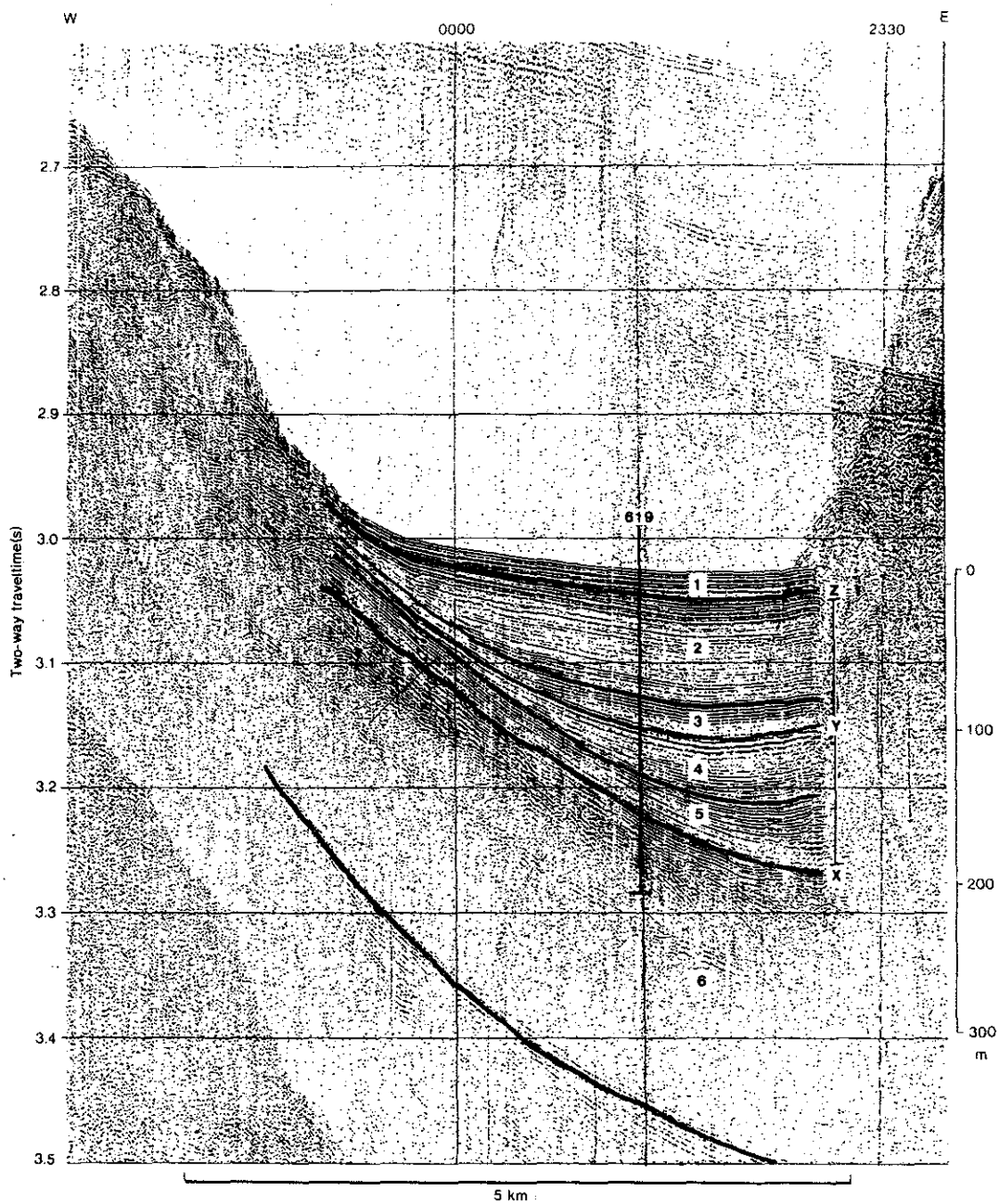
The Late Quaternary Gulf of Mexico is an opportune sedimentary environment in which to examine the relationship between bulk organic geochemical parameters and organic biomarker compounds since many previous investigations had shown large (3-6°/$_{oo}$) glacial-interglacial variations in sedimentary organic carbon composition (Sackett and Thompson, 1963; Sackett, 1964; Sackett and Rankin, 1970; Neuman, et al., 1973; Hedges and Parker, 1976; Joyce, et al., 1986). In addition, the proportions of the bulk sedimentary organic matter sources had apparently undergone large compositional variations. Hence, the organic biomarkers were also expected to record large concentration variations.

The present study focusses on sediment samples from a 208.7m hydraulic piston core collected from the Pigmy Basin in the hemipelagic northern Gulf of Mexico (Bouma, et al., 1986a)(see Fig. 2.1). The Pigmy Basin is a blocked canyon intraslope basin (Bouma, 1983) which is approximately 20km by 7km, with its major axis trending northeast to southwest. The basin has normally oxic bottom waters, a sill depth of ~1700m, and the basin floor at ~2300m (Bouma, et al., 1986b). The seismic stratigraphic profile of the Pigmy Basin is typical of hemipelagic sediments, with parallel and semi-transparent seismic reflectors above 3.24s; however, chaotic reflectors below 3.24s indicate core disturbance (Bouma, et al., 1986b), perhaps due to sediment density flows (Kohl, 1986; Williams and Kohl, 1986)(Fig. 1.3).

The lithology of the upper 151m of DSDP 619 is characterized by calcareous and noncalcareous clays, below which depth there are clays, muds, silts, and sands (Bouma, et al., 1986b). Further seismic, sedimentological, chronostratigraphical, geochemical, and geotechnical studies, and a drilling site summary are reported by Bouma et al. (1986a).

The results of this research are presented in four chapters, each with its own more specific introduction. In Chapter 2, bulk organic geochemical data and simple model calculations are used to quantify the general sources and accumulation of organic matter in the Pigmy Basin. In Chapter 3, the relationship between selected organic biomarker compounds and sedimentary organic carbon isotope composition is examined, and its paleoceanographic utility evaluated. In Chapter 4, potential steroid transformations are examined. The potential utility for alkenone (U^{K}_{37}) paleothermometry and molecular stratigraphy in a marginal sea environment is investigated in Chapter 5. Major results of this work are summarized and suggestions for further research are given in the final chapter.

Fig 1.3. Seismic stratigraphic profile and the late Pleistocene biostratigraphic zones at DSDP Site 619 in the Pigmy Basin (from Bouma, et al., 1986)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CHAPTER 2

THE SOURCES AND DEPOSTION OF ORGANIC MATTER IN THE LATE QUATERNARY PIGMY BASIN

ABSTRACT

The concentration and carbon isotopic composition ($\delta^{13}C$) of sedimentary organic carbon (C_{org}), N/C ratios, and terrigenous and marine $\delta^{13}C$-C_{org} end-members form a basis from which to address problems of Late Quaternary glacial-interglacial climatic variability in a 208.7 m hydraulic piston core (DSDP 619) from the Pigmy Basin in the northern Gulf of Mexico. Paired analyses of $\delta^{13}C$-C_{org} and N/C are consistent with the hypothesis that the sedimentary organic carbon in the Pigmy Basin is a climatically-determined mixture of C_3-photosynthetic terrigenous and marine organic matter, confirming the model of Sackett (1964). A high resolution (~1.4-2.7 ky/sample) $\delta^{13}C$-C_{org} record shows that sedimentary organic carbon in interglacial oxygen isotope (sub)stages 1 and 5a-b are enriched in ^{13}C (average ± 1σ values are -24.2 ± 1.2°/$_{oo}$ and -23.0 ± 0.8°/$_{oo}$ relative to PDB, respectively) while glacial isotope stage values 2 are relatively depleted (-25.6 ± 0.5°/$_{oo}$). Concentrations of terrigenous and marine sedimentary organic carbon are calculated using $\delta^{13}C$-C_{org} and C_{org} measurements, and terrigenous and marine $\delta^{13}C$-C_{org} end-members. The net accumulation rate of terrigenous organic carbon is 3.7 ± 3.1 times

higher in isotope stages 2-4 than in (sub)stages 1 and 5a-b, recording higher erosion rates of terrigenous organic material in glacial times. The concentration and net accumulation rates of marine and terrigenous C_{org} suggest that the nutrient-bearing plume of the Mississippi River may have advanced and retreated across the Pigmy Basin as sea level fell and rose in response to glacial-interglacial sea level change.

INTRODUCTION

The Mississippi River is the major source of sedimentary material to the Gulf of Mexico (Moody, 1967). The sources and deposition of organic matter accompanying the sediments in the Quaternary Gulf of Mexico have been examined in studies of sedimentary organic carbon isotopic composition ($\delta^{13}C$-C_{org}) and organic biomarker compounds. A number of investigators (Sackett, 1964; Rogers and Koons, 1969; Sackett and Rankin, 1970; Newman et al., 1973; and Joyce et al., 1986) have observed a 3-6°/$_{oo}$ increase in the sedimentary organic carbon isotopic composition since the Last Glacial Maximum (~20 kybp) in all major sedimentary provinces in the Gulf of Mexico. At least three interpretations have been considered to explain this carbon isotopic composition increase: (1) variations in the relative proportions of terrigenous and marine organic carbon inputs, (2) temperature-dependent fractionation of carbon isotopes by marine phytoplankton, and (3) diagenesis of sedimentary organic carbon. Sackett (1964) observed a 4.7°/$_{oo}$ increase in the carbon isotopic composition of

sedimentary organic matter over the last ~20 ky on the Sigsbee Knolls (core V3-127) in the northern Gulf of Mexico. He attributed the temporal $\delta^{13}C$-C_{org} increase to mixing of terrigenous and marine organic carbon sources by analogy with the apparent spatial mixing of terrigenous and marine organic carbon in Recent eastern Gulf Coast surface sediments. In the Pleistocene (0-2 My) Gulf of Mexico, Rogers and Koons (1969) observed typical $\delta^{13}C$-C_{org} ranges of -20 to $-22^{o}/_{oo}$ and -24 to $-26^{o}/_{oo}$ in a series of eleven periodic paleontologically-defined warm and cold stages, respectively. They considered sedimentary diagenesis an unlikely cause for the carbon isotopic variations because of the lack of a secular trend over the span of 2 My. With the oxygen isotopic composition of planktonic foraminifera as a temperature constraint, Sackett and Rankin (1970) concluded that the temperature variations predicted from the $\delta^{13}C$-C_{org} observations would be unrealistically high (35°C). Sackett's (1964) terrigenous and marine organic carbon mixing model was supported as a more plausible hypothesis. Finally, mixing of C_3 (Calvin-Benson Cycle) and C_4 (Hatch-Slack) photosynthetic terrigenous plant organic carbon could also produce the observed $\delta^{13}C$-C_{org} records. Paired stable carbon isotopic values and N/C ratios presented here will allow evaluation of all these hypotheses.

Paired analyses of selected organic biomarker compound concentrations and the carbon isotopic composition of contemporaneous sedimentary organic matter allow determination of marine and terrigenous carbon isotopic end-members. Hedges and Parker (1976) showed that the sum of six lignin component concentrations normalized

to sedimentary organic carbon concentration correlated well with sedimentary organic carbon isotopic compositions. With data from four offshore transects of surface sediments in the northwest Gulf of Mexico, they found that the carbon isotopic composition of the sedimentary organic matter approached -18.8°/$_{oo}$ PDB as lignin concentrations approached zero. That carbon isotopic value may be considered a model marine $\delta^{13}C$-C_{org} end-member for those recent surface sediments. Over a longer time scale (~100ky), the concentrations of total alkenones and five individual 4-desmethyl-sterols and normal C_{27-33} even numbered fatty alcohols were shown to be proportionately related to the sedimentary organic carbon isotopic composition (Chapter 3). Terrigenous and marine carbon isotopic end-members were calculated using those data. With (1) terrigenous and marine carbon isotopic end-members determined from these biomarker versus carbon isotopic relationships, (2) sedimentary organic carbon concentrations, and (3) a carbon isotope mixing model analogous to Calder and Parker's (1968), terrigenous and marine C_{org} concentrations are calculated for Pigmy Basin sediments (DSDP 619) which span from 2 to ~100 kybp. Net accumulation rates of terrigenous and marine sedimentary organic carbon by isotope (sub)stage are then examined.

In a global view of the fate of organic matter in the oceans, it can be shown (Appendix 2.1) that the remineralization of known masses of organic carbon can account for the 0.7°/$_{oo}$ carbon isotopic composition increase observed in benthic foraminifera shells between the last glacial stage and the present interglacial stage (Shackleton,

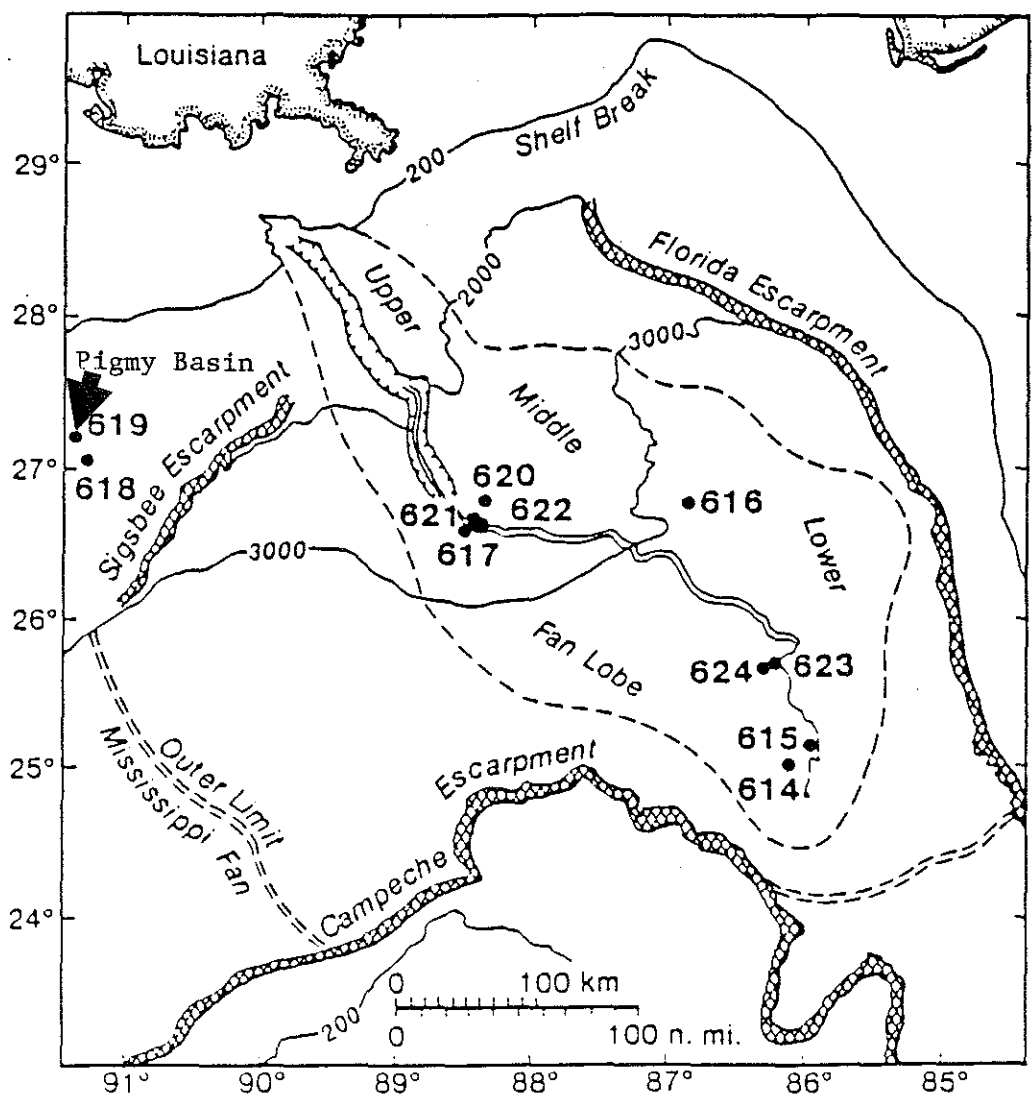
1977; Broecker, 1982; Boyle and Keigwin, 1982). Those masses are $9 \cdot 10^{17}$g of marine organic carbon with a $\delta^{13}C\text{-}C_{org}$ of $-19°/_{oo}$(PDB), $12 \cdot 10^{17}$g of terrigenous organic carbon with a $\delta^{13}C\text{-}C_{org}$ of $-26°/_{oo}$, or some linear combination of both types of organic carbon. Studies of the accumulation of organic matter in the Gulf of Mexico and other major sedimentary basins will help to constrain models of organic carbon transfer between major geochemical reservoirs.

EXPERIMENTAL

Samples

The Pigmy Basin is a blocked-canyon intraslope basin (Bouma, 1983) in the northern Gulf of Mexico which is approximately 20km by 7km with its major axis trending northeast to southwest. This oxic basin has a sill depth of ~1700m and the basin floor is at ~2300m. (Bouma, et al, 1986b). The samples examined in this study were from a 208.7 m hydraulic piston core collected by the Deep Sea Drilling Program's D/V Glomar Challenger from 2259 m water depth in this basin at 27°11.61'N, 91°24.54'W (Fig. 2.1). Using the sampling strategy described in Appendix II, a sampling interval of 1.9 ky was chosen to theoretically resolve 96 ± 2°/$_o$ of linear responses to orbitally-driven climatic change as short as 19 ky. Fifty-five ~50 g sediment samples from that core (DSDP Leg 96, Site 619) were collected for this study (Table 2.1) on the basis of a preliminary chronostratigraphy. The final chronostratigraphy discussed below, however, shows the average spacing of the first 29 samples is ~1.4 ky and the next 16 samples are spaced

Fig. 2.1 Map showing cored sites on Deep Sea Drilling Project Leg 96, including the Pigmy Basin (Site 619) at 27°11.61'N, 91°24.54'W.


Louisiana
Shelf Break
200
2000
3000
Florida Escarpment
Upper
Middle
Lower
Pigmy Basin
Sigsbee Escarpment
619
618
620
621
622
617
616
624
623
615
614
Fan Lobe
Escarpment
Outer Limit
Mississippi Fan
Campeche
0 100 km
0 100 n. mi.
29°
28°
27°
26°
25°
24°
91°
90°
89°
88°
87°
86°
85°

at ~2.7 ky. The last 9 samples are from an interval in which sediment density flows were indicated (Kohl, 1986; Williams and Kohl, 1986). The Shipboard Party (1986) reported that although the first core barrel was recovered nearly full, the sediment-water interface of DSDP 619 may not have been recovered. The sedimentation rates (described below) of interglacial substages 1 and 5a-b are similar to each other (81 and 73 cm/ky) as compared to the higher sedimentation rates of glacial stages 2 and 4 (230 and 250 cm/ky), supporting the contention that the core top loss may have been small. Samples marked "F" were frozen aboard the drilling ship. The other samples were collected from refrigerated storage at the DSDP Core Library at the Lamont-Doherty Geological Observatory five months later. The samples were subsequently stored at -40°C until they were analyzed. Seismic, sedimentological, chronostratigraphical, geochemical, and geotechnical studies and a drilling site summary on DSDP 619 are reported by Bouma, et al. (1986).

Methods

Sample Preparation for $\delta^{13}C$-C_{org}, N/C, and $CaCO_3$ Analyses

Wet sediment samples (~6 g) were dried for 16 hrs at 60°C in glass petri dishes which had been precombusted at 500°C in a muffle furnace for 16 hours. The sediment dry masses were measured and percent water lost calculated. One gram of dry sediment was saved for carbonate analysis. The remainder was used for $\delta^{13}C$-C_{org} and N/C analyses.

Carbonate carbon must be removed from sediment samples before organic carbon (C_{org}) and total nitrogen (N_{tot}) for N/C ratios,

and sedimentary organic carbon isotopic composition ($\delta^{13}C$-C_{org}) can be analyzed. Doubly-distilled 6M HCl which was diluted to 1M with potassium permanganate distilled water (Peltzer, 1979) was added with stirring to the dried sediment until visible degassing ceased and the pH of the mixture remained at 2.0 ± 0.5. The covered samples were stirred for ~16 hours on a shaker table and their pH values were re-measured. If the pH had increased above 2.5, doubly-distilled 6M HCl was added until the pH of the solution was 2.0 ± 0.25 and stirring was continued for 6 hours. The samples were then dried at 60°C for 16 hours. Permanganate distilled water was then added to the dry sediment and after stirring, the pH of the solution was tested. If the pH of supernatant solution were 2.0 ± 0.5, the sample was determined to be decarbonated. If the pH were greater than 2.5, the sample was re-acidified, shaken, and dried as before until the pH remained at 2.0 ± 0.5. The dried, decarbonated samples were powdered in a mortar with a pestle and were then ready for N_{tot}/C_{org} and $\delta^{13}C$-C_{org} analyses.

Carbonate Analysis

Carbonate concentration (mg $CaCO_3$/gds, where gds = grams dry sediment) was determined by the differential pressure bomb technique of Curry and Lohmann (1985), as modified from Jones and Kaiteris (1983). Briefly, a known mass (~500 mg) of dried sediment which had been powdered with a mortar and pestle was added to a side-arm flask. Three milliliters of 0.5 M HCl was added to the side-arm and the vessel was sealed. Pouring the acid from the side-arm onto the

sediment generated a CO_2 pressure which was measured and converted to mass $CaCO_3$. Twenty-three analyses of carbonate standards gave a 6.4°/$_{oo}$ (1σ) reproducibility associated with the carbonate concentration measurement.

Sedimentary Organic Carbon Stable Isotopic Analysis

A weighed mass (150-200 mg) of the decarbonated, dried, and powdered sediment samples was mixed with 1 g CuO wire and pulverized in stainless steel ball (WIG-L Bug) shakers. The powdered mixture was combusted for 1 hr at 900°C in quartz tubes that contained 0.5 g Cu and cooled to room temperature over 3 hr by the method of Minagawa, et al. (1984). Carbon dioxide generated by the combustion was separated from N_2, H_2O, and other gases on a high vacuum manifold by cryogenic distillation. Isotopic measurements on the purified CO_2 were made on a Finnigan MAT 251 isotope ratio mass spectrometer equipped with a triple collecting detector. Carbon isotopic values were corrected for $^{12}C^{17}O^{16}O$ interference to the $^{13}C^{16}O_2$ measurement by the method of Craig (1957).

The carbon isotopic results are given in the δ-notation relative to the Chicago PDB standard:

$$\delta^{13}C\ (°/_{oo}) = \left(\frac{R_S}{R_R} - 1\right) \cdot 1000 \quad ,$$

where R_S and R_R are $^{13}C/^{12}C$ ratios of sample and reference gases. The CO_2 reference gas was high purity tank CO_2. Analyses of two standards (NBS-21 graphite and NBS Solenhofen Limestone) were

within 0.11°/$_{oo}$ of the U.S. National Bureau of Standards' values. Three samples analysed in triplicate gave $\delta^{13}C$-C_{org} (1σ) reproducibility of ± 0.10°/$_{oo}$.

N/C Ratio Measurements

N_{tot}/C_{org} ratios were calculated from N and C concentrations measured on aliquots of the same decarbonated, dried, and powdered sediment samples used for $\delta^{13}C$-C_{org} analysis. Sediment mass-normalized concentrations of C_{org} or N_{tot} cannot be measured on the sediment samples prepared for $\delta^{13}C$-C_{org} and N/C analyses because of the hygroscopic salts produced by acidic decarbonation (Hedges and Stern, 1984). The N/C ratios of dried, decarbonated samples were, however, less susceptible to experimental errors in N_{tot} measurements because larger masses of N- and C-containing sediment can be introduced into the Perkin Elmer CHN analyzer than the atmospheric water-equilibrated samples prepared for N and C concentration analyses by Hedges and Stern's (1984) wet decarbonation method. The average reproducibility of 23 duplicate N/C ratios was 15°/$_{o}$.

Organic Carbon Analysis

Organic carbon (C_{org}) was analyzed by the aqueous acidification method of Hedges and Stern (1984), using a Perkin Elmer Model 240 Elemental Analyzer. Hedges and Stern (1984) cautioned that the decarbonation method employed should be adequate for dissolution of the carbonates in the samples. The decarbonation method used here was

adapted to compensate for the refractory nature of at least some fraction of the carbonates in this sample suite. Instead of the suggested five minutes of high-frequency sonication of the acidified samples, approximately 24 hrs of continuous stirring on a shaker table was employed for decarbonation. Two triplicate analyses of C_{org} samples gave an average variance ($100\sigma/\bar{X}$) of 4.1°/$_{o}$.

Sediment Wet Bulk Density

Sediment wet bulk densities (gds/cm^3 ws) are linearly interpolated in depth from data of the Shipboard Scientific Party of DSDP Leg 96 (Bouma et al., 1986). Wet-bulk density measurements were made with the cylinder technique described by Boyce (1976). The measurements were corrected for salt content assuming 35°/$_{oo}$ and water density of 1.024 g/cm^3.

Chronostratigraphy

The chronostratigraphy used in this study is based on the isotope (sub)stage boundary ages of Shackleton and Opdyke (1973) assigned to the DSDP 619 Globeriginoides ruber oxygen isotope record by Williams and Kohl (1986)(fig. 2.2). The Globeriginoides ruber oxygen isotope stratigraphy is compatible with two planktonic foraminiferal boundaries (Z/Y, Y/X) (Kohl, 1986), a phytoplanktonic boundary (Constance and Parker, 1986) and a volcanic ash layer (Y8) (Ledbetter, 1986) found in this core. Williams and Kohl (1986) assumed an age of 105ky for the bottom section of the core because of "the absence of a well-defined W Zone and lack of definition of the substages of Stage

5." An alkenone ratio (U^{K}_{37}) record (Brassell, et al., 1986) for DSDP 619 is also consistent with the glacial-interglacial history of this core (Chapter 5).

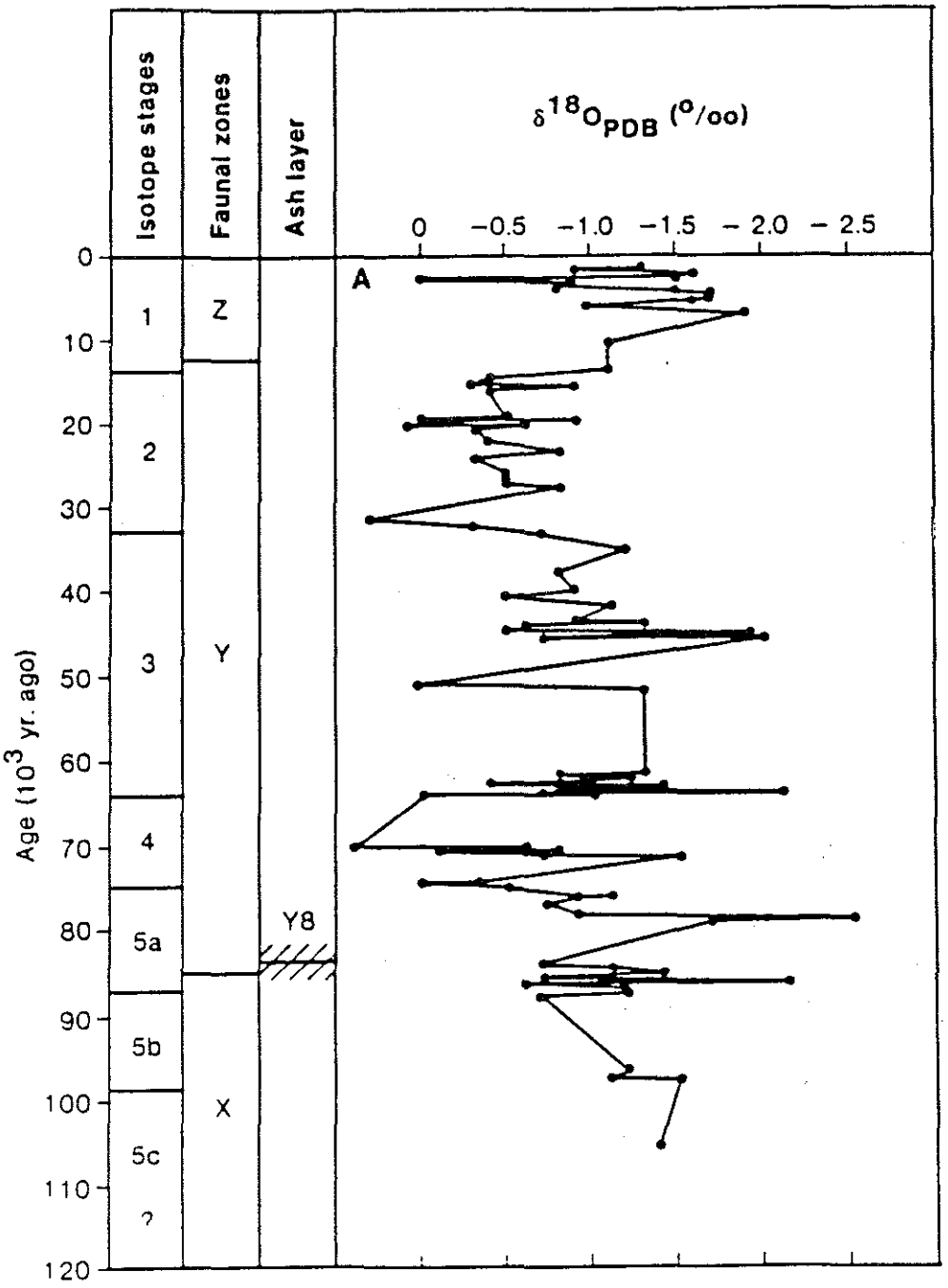
The planktonic foraminiferal boundaries which define the Ericson zonation are (1) the last appearance datum (LAD) of Globoratalia flexuosa at the X/Y boundary and (2) the LAD of the cold water planktonic foraminifera Globoratalia inflata and the reappearance of the warm water Globoratalia menardii complex at the Y/Z boundary. Kohl (1986) observed the Y/Z boundary at 5.0m and the X/Y boundary at 147m in DSDP 619. These faunal boundaries have been dated in other tropical and subtropical cores (Y/Z = 12 ky, Beard, 1973; X/Y = 85 ky, Thierstein et al., 1977) and the dates were assigned to those boundaries in DSDP 619.

The Gephyrocapsa spp./E. huxleyii phytoplanktonic boundary was dated at 85 ky by Theirstein et al. (1977) and observed by Constance and Parker (1986) in DSDP 619 at 141.74m.

Sufficient volcanic tephra for major elemental analysis was recovered from only one of the three ash layers observed in the Pigmy Basin core (Ledbetter, 1986). The ash layer at 142 mbs was analyzed for major element chemistry and was determined to be ash layer Y8 by comparison with type material analyzed by Rabek et al. (1985). Ash layer Y8 which was erupted from Lake Atillan Caldera, Guatemala, 84 ky ago is the most widespread late Pleistocene tephra in the Central American Region (Ledbetter, 1986).

The ages of the isotope (sub)stage boundaries assigned to DSDP 619 were used to calculate average linear sedimentation rates by isotope (sub)stage.

Fig. 2.2 Chronostratigraphy for the Pigmy Basin sediment core, DSDP 619, based on oxygen isotopic composition of Globigerinoides ruber (from Williams and Kohl, 1986), faunal boundaries (Kohl, 1986), volcanic ash layer Y8 (Ledbetter, 1986), and a phytoplanktonic boundary (Constance and Parker, 1986), as discussed in text.


Isotope stages
Faunal zones
Ash layer
$\delta^{18}O_{PDB}$ (‰)
0 −0.5 −1.0 −1.5 −2.0 −2.5
A
Age (10^3 yr. ago)
0
10
20
30
40
50
60
70
80
90
100
110
120
1
2
3
4
5a
5b
5c
?
Z
Y
X
Y8

RESULTS AND DISCUSSION

Sedimentation Rate by Isotope (Sub)Stage

Sedimentation rates were higher during glacial isotope stages 2 (230cm/ky) and 4 (250cm/ky) than in interglacial isotope (sub)stages 1 (85cm/ky), 5a (85cm/ky), and 5b (81cm/ky); isotope stage 3 had an intermediate rate (180 cm/ky) (fig. 2.3). The occurrence of higher sedimentation rates in glacial stages was presumably due to increased erosion of continental material during falling sea levels and low sea level stands (Broecker, 1982). This hypothesis is discussed further in relation to the deposition of organic matter components in the Pigmy Basin.

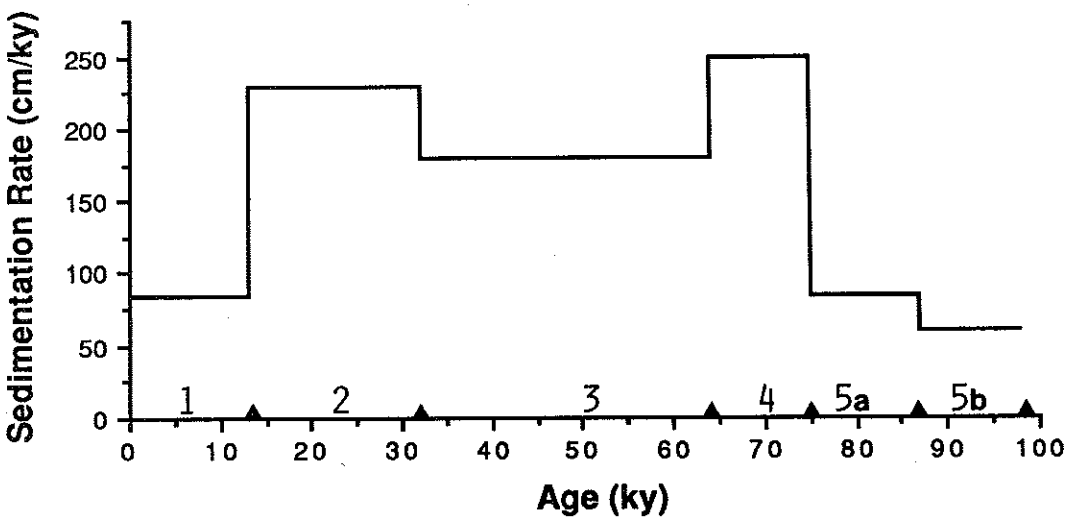
Time Series of Sedimentary Organic Carbon Isotopic Composition

The sedimentary organic carbon isotopic composition ($\delta^{13}C\text{-}C_{org}$) of 55 samples from the Pigmy Basin (DSDP 619) is presented as a time series (fig. 2.4) and in Table 2. The interglacial oxygen isotope stages 1 and 5a-b are characterized by relatively positive average ($\pm 1\sigma$) $\delta^{13}C\text{-}C_{org}$ values ($\delta^{13}C\text{-}C_{org}$ (stage 1) = $-24.2 \pm 1.2‰$, n = 9; $\delta^{13}C\text{-}C_{org}$ (substages 5a-b) = $-23.0 \pm 0.8‰$, n = 7), whereas stages 2 and 3 have comparatively negative average values ($\delta^{13}C\text{-}C_{org}$ (Stage 2) = $-25.6 \pm 0.5‰$, n = 13; $\delta^{13}C\text{-}C_{org}$ (Stage 3) = -25.2 ± 1.3, n = 18). Isotope stage 4 has two relatively negative values (avg. $\delta^{13}C\text{-}C_{org} = -25.3$) in the middle of the stage with relatively

positive values near the stage 4 boundaries ($\delta^{13}C$-C_{org} (3/4) = -22.80°/$_{oo}$; $\delta^{13}C$-C_{org} (4/5) = -21.90°/$_{oo}$). This time series is the highest resolution record of $\delta^{13}C$-C_{org} in the Gulf of Mexico spanning from the present interglacial isotope Stage 1 to the previous interglacial isotope substage 5b.

The temporal variation of $\delta^{13}C$-C_{org} is consistent with a glacial-to-interglacial climatically-forced mixing of terrigenous and marine organic carbon (Sackett, 1964) and the effects of the ~100 ky cycle of climatic change (Broecker and van Donk, 1970). It should be noted, however, that the $\delta^{13}C$-C_{org} values of the latest sample measured here (-24.1°/$_{oo}$ PDB at ~2ky) is significantly depleted in ^{13}C relative to a similar aged samples (-21.7°/$_{oo}$ PDB at ~2ky) in the Orca Basin (Northam et al., 1981) which is only ~30 km south of the Pigmy Basin. This relative depletion may reflect the potentially missing core top (Shipboard Party, 1986) and/or a greater predominance of terrigenous C_{org} input to the basin nearer the continental sediment source. A further comparison of Pigmy Basin and Orca Basin $\delta^{13}C$-C_{org} series also shows significantly more ^{13}C depleted (~1°/$_{oo}$) sedimentary organic carbon at ~10-20 kybp, indicating a relative predominance of terrigenous organic matter input into the shoreward Pigmy Basin over ~10 ky. Neuman (1973) also noted low $\delta^{13}C$-C_{org} values (-24 to -23°/$_{oo}$ PDB) near the tops of piston core records. She suggested that current scouring down to Pleistocene strata, sediment slumping, and coring losses as potential causes. In the rapidly sedimenting Pigmy Basin (Williams and Kohl, 1986), where sediment scouring seems an unlikely cause for the low $\delta^{13}C$-C_{org}

Fig. 2.3 Sedimentation rate by isotope (sub)stage in the Pigmy Basin core, DSDP 619.


Sedimentation Rate (cm/ky)
250
200
150
100
50
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

surface values, sediment slumping, core top loss, and/or increased terrigenous input are more likely possibilities.

At least three interpretations have been considered to describe the glacial-to-interglacial changes in $\delta^{13}C$-C_{org} in the Quaternary Gulf of Mexico--diagenesis of sedimentary C_{org}, temperature-dependent fractionation of C isotopes by marine phytoplankton, and variations in the relative amounts of terrigenous and marine C_{org}. Rogers and Koons (1969) examined the $\delta^{13}C$-C_{org} records of 24 gravity and piston cores and four 330 m drill cores in the northern Gulf of Mexico, with the longest record extended into the upper Pliocene (~2 My). They found that warm stages (as defined by planktonic foraminiferal assemblages) were characterized by $\delta^{13}C$-C_{org} values of -20 to -22°/$_{oo}$ PDB, whereas cold stages had $\delta^{13}C$-C_{org} values of -24 to -26°/$_{oo}$. They eliminated sedimentary diagenesis of C_{org} as a cause for $\delta^{13}C$-C_{org} variations since over the time spanned (~2 My) there was no secular monotonic trend in $\delta^{13}C$-C_{org} values. They concluded that the major cause of the $\delta^{13}C$-C_{org} variations was the temperature-dependent fractionation of carbon isotopes by phytoplankton. They considered mixing of terrigenous and marine C_{org} an unlikely cause.

Given the sedimentary $\delta^{13}C$-C_{org} variations in the northern Gulf of Mexico, Sackett and Rankin (1970) showed that the glacial-to-interglacial sea surface temperature variation predicted from the temperature-induced fractionation of carbon isotopes (35°C) would be implausibly large in light of the oxygen isotopic composition of contemporaneous planktonic foraminifera. Since Emiliani (1955) had

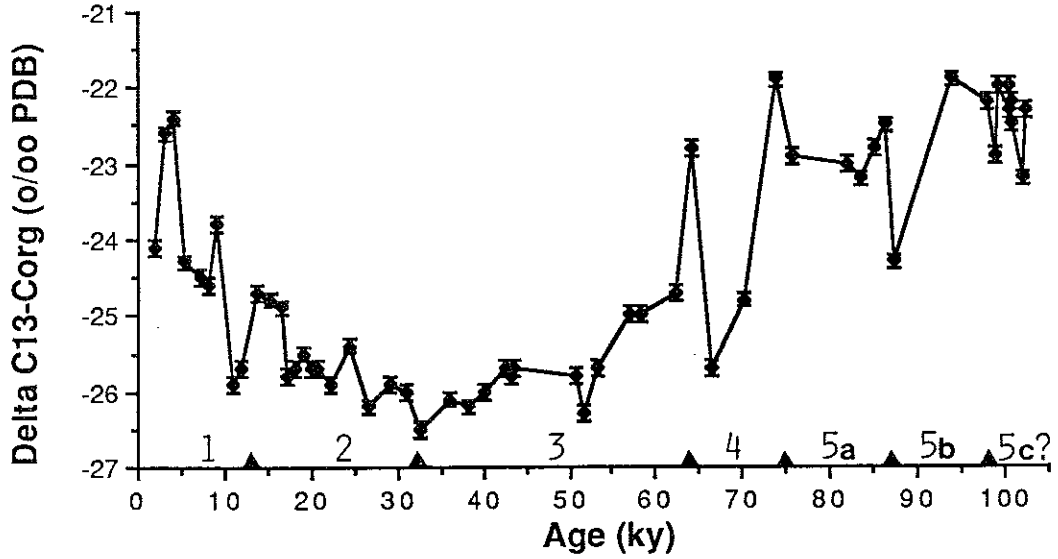
shown a temperature change of only 6-10°C from the last glacial to the present interglacial with the $\delta^{18}O$ of planktonic foraminifera in Caribbean surface waters, Sackett and Rankin (1970) favored the variation of relative proportions of terrigenous and marine C_{org} inputs as the cause of the temporal $\delta^{13}C$-C_{org} changes. Later, a foraminiferal assemblage-temperature transfer method (Brunner, 1982) and the foraminiferal oxygen isotopic temperature method using revised ice volume estimates (Chapter 5) indicated only small (0.8-2°C) Late Quaternary temperature variations in the northern Gulf of Mexico. These results make temperature-dependent carbon isotopic fractiontion an unlikely explanation for the large $\delta^{13}C$-C_{org} variations observed in the DSDP 619 core.

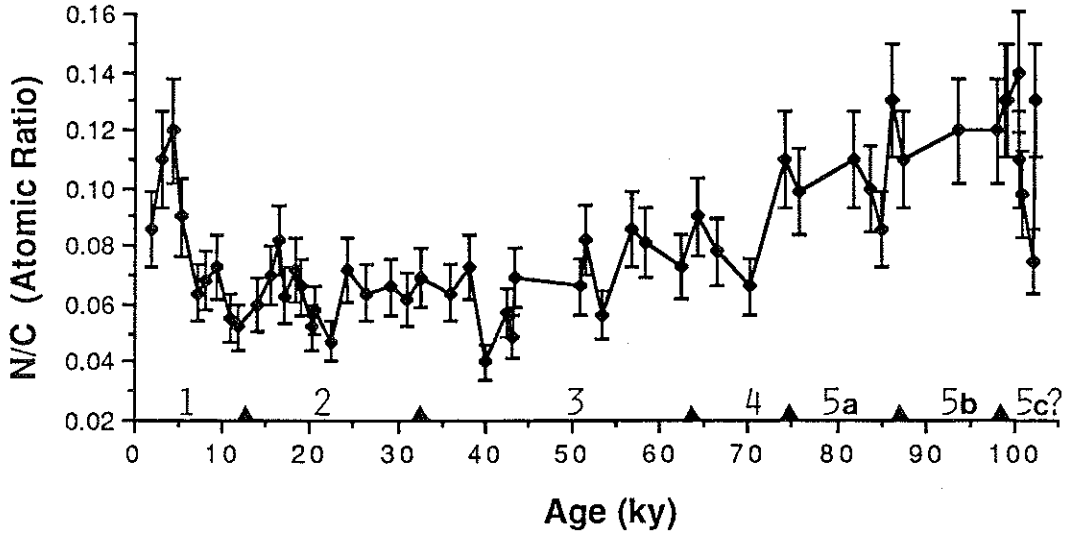
Neuman, et al. (1973) observed that the $\delta^{13}C$-C_{org} values of "olive grey, Pleistocene turbidite muds" were -22 to -24°/$_{oo}$ PDB and that the $\delta^{13}C$-C_{org} values for "orange and yellow, Holocene and interglacial foraminiferal oozes" were -20 to -16°/$_{oo}$. They assumed that the organic matter associated with terrigenously-sourced turbite muds contained mostly terrigenous C_{org} and the organic matter associated with marine-sourced foraminiferal oozes were dominated by marine C_{org}. The analysis of the $\delta^{13}C$-C_{org} records in 48 piston cores in all the major deep-water provinces of the late Quaternary Gulf of Mexico led them to conclude that the temporal $\delta^{13}C$-C_{org} variations were consistent with a model of sedimentary C_{org} deposition in which increased proportions of terrigenous C_{org} relative to marine C_{org} were deposited in glacial stages.

In a study of the depositional history of the late Quaternary deep

Fig. 2.4 Time series of the sedimentary organic carbon isotopic composition ($\delta^{13}C$-C_{org}) of DSDP 619 in the Pigmy Basin, showing relatively positive (marine) values in interglacial stages and relatively negative (terrigenous) values in glacial stages.

Fig. 2.5 Time series of N/C atomic ratios in the Pigmy Basin (DSDP 619) shows the general interglacial predominance of marine organic matter (typically, N/C ≅ 0.13-0.20) and the glacial predominance of terrigenous organic matter (typically, N/C ≅ 0.01-0.05).


Delta C13-Corg (o/oo PDB)
-21
-22
-23
-24
-25
-26
-27
1
2
3
4
5a
5b
5c?
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


N/C (Atomic Ratio)
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
1
2
3
4
5a
5b
5c?
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

western Gulf of Mexico, Joyce et al. (1985) supported the terrigenous and marine C_{org} mixing model as the mechanism to explain the glacial-to-interglacial variations in $\delta^{13}C$-C_{org}. Higher $CaCO_3$ content, increased sediment grain size, ~50°/$_o$ lower C_{org} concentrations, and more positive $\delta^{13}C$-C_{org} values were observed in the present interglacial (Ericson Z-zone) than the last glacial (Y-zone). They observed a positive correlation between $\delta^{13}C$-C_{org} and C_{org} concentration, with more negative (terrigenous) $\delta^{13}C$-C_{org} values (~-26°/$_{oo}$) corresponding to higher C_{org} concentrations (~6-11mgC/gds) and more positive (marine) $\delta^{13}C$-C_{org} values (~-22.5°/$_{oo}$) corresponding to lower C_{org} concentrations (~2-6mgC/gds). A similar linear trend was observed in DSDP 619 with C_{org} concentrations of ~9-12mgC/gds near -26.0°/$_{oo}$ and ~5-6mgC/gds at -22.5°/$_{oo}$ for samples less than 25ky old (discussed further below).

N/C Time Series

The N/C ratios of DSDP 619 sediments are presented as a time series (Fig. 2.5) and in Table 2. The interglacial (sub)stages 1 and 5a-b are characterized by relatively high values (N/C (stage 1) = 0.08 ± 0.02 ($\bar{X}$ ± 1σ), n = 9; N/C (substages 5a-b) = 0.11 ± 0.02). These N/C values approach those of planktonic organic matter (0.20-0.13; Redfield et al., 1963). The average N/C value of glacial stages 2-4 is 0.06 ± 0.02 which overlaps with the range of typical terrigenous plant and peat values of 0.01-0.05 (Waksman, 1933; Brenner et al., 1978). The N/C time series for the Pigmy Basin is consistent with the

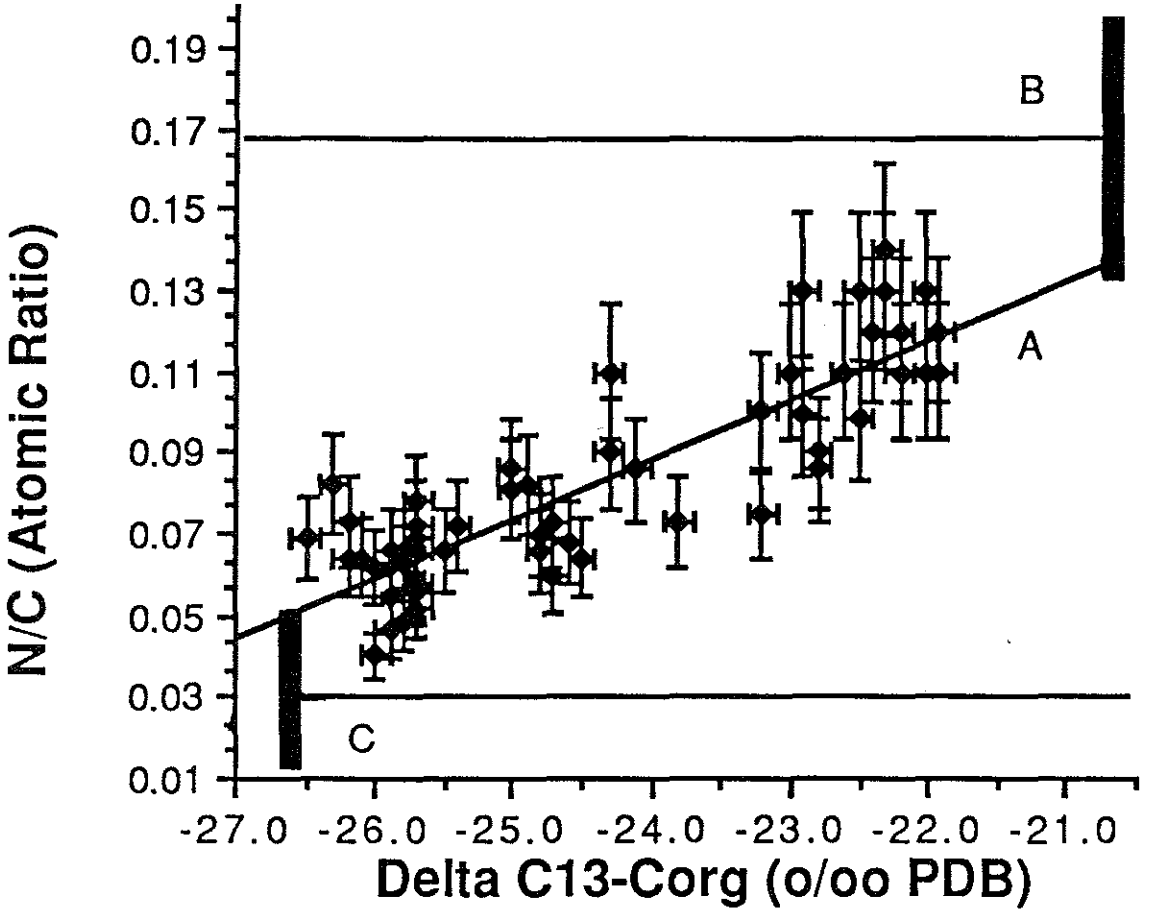
climatically-forced glacial-to-interglacial terrigenous and marine C_{org} mixing model, reflecting the general ~100ky climatic cycle.

N/C ratios are used here rather than the more typical C/N ratios for mathematical and graphical reasons. In a cross correlation graph of $\delta^{13}C$-C_{org} versus N/C, both parameters are essentially normalized to organic carbon content since in $^{13}C/^{12}C$ ratios ^{12}C composes ~99°/$_{o}$ of the total organic carbon. For graphical reasons, the use of N/C ratios of typical terrigenous and marine organic matter span similar ranges (0.07 versus 0.04 units, respectively) as opposed to C/N which expand terrigenous ranges (100 - 20 = 80 units) and compress the marine range (8 - 5 = 3 units).

$\delta^{13}C$-C_{org} versus N/C

A plot of the 55 paired $\delta^{13}C$-C_{org} versus N/C values from the Pigmy Basin core (DSDP 619) is shown in figure 2.6. A linear least squares regression of N/C on $\delta^{13}C$-C_{org} shows that the measurements are well correlated ($r^2 = 0.74$, $P < 0.0001$) by the statistical F-test for significance (Snedecor and Cochran, 1978). The correlation of N/C and $\delta^{13}C$-C_{org} values for the sedimentary organic matter in the Pigmy Basin (DSDP 619) is consistent with a mixing of C_3-photosynthetic (Calvin-Benson Cycle pathway of carbon fixation) terrigenous and marine organic matter sources. A linear regression line (labelled "A") through the paired data extrapolates through typical terrigenous (0.01-0.05) and marine (0.20-0.13) N/C values at empirically determined $\delta^{13}C$-C_{org} terrigenous (-26.6°/$_{oo}$ PDB) and marine (-20.6°/$_{oo}$) end member values (Chapter 3).

Fig. 2.6 This N/C versus $\delta^{13}C$-C_{org} plot shows that the composition of sedimentary organic matter in the Pigmy Basin (DSDP 619) for the last ~100ky is consistent with mixing of terrigenous and marine C_3-photosynthetic (Calvin-Benson Cycle) organic matter. The linear least squares regression line (A) is: $N/C = 0.015 \cdot \delta^{13}C\text{-}C_{org} + 0.44$ ($P < 0.0001$, $r^2 = 0.74$, $n = 55$). For comparison, typical N/C ratios of terrigenous (0.01-0.05) and marine (0.20-0.13) plants are given at $\delta^{13}C$-C_{org} terrigenous (-26.6°/$_{oo}$) and marine (-20.6°/$_{oo}$) end-member values (explained in text and given in Chapter 3). Constant marine N/C values with variable $\delta^{13}C$-C_{org} values (line B) would support temperature-dependent carbon isotopic fractionation as the cause of the Late Quaternary Gulf of Mexico $\delta^{13}C$-C_{org} variations. Constant terrigenous N/C ratios for all $\delta^{13}C$-C_{org} values would support the mixing of C_3 and C_4 terrigenous plant material as the cause of the $\delta^{13}C$-C_{org} variations (line C). Neither of the latter two hypotheses (represented by lines B and C) are supported by these data.


0.19
0.17
0.15
0.13
0.11
0.09
0.07
0.05
0.03
0.01
N/C (Atomic Ratio)
B
A
C
-27.0 -26.0 -25.0 -24.0 -23.0 -22.0 -21.0
Delta C13-Corg (o/oo PDB)

These data support the climatically-driven terrigenous and marine C_{org} mixture model and weaken other hypotheses for organic matter deposition in the late Quaternary Gulf of Mexico. If temperature-dependent fractionation of carbon isotopes by marine phytoplankton determined the Quaternary sedimentary $\delta^{13}C$-C_{org} values, constant marine N/C values (0.20-0.13) would be expected to co-occur with variable $\delta^{13}C$-C_{org} values (line B); this is not observed. This is consistent with the assertion that the maximum Quaternary surface water temperature variation in the Gulf of Mexico would cause only an ~1°/$_{oo}$ difference in $\delta^{13}C$-C_{org}, if it had any effect at all (Neuman, et al., 1973). If a climatically-determined mixture of C_3 and C_4 terrigenous organic matter caused the temporal $\delta^{13}C$-C_{org} variation, relatively constant terrigenous N/C values (0.01-0.05) would be observed across the range of $\delta^{13}C$-C_{org} values (line C); nor is this hypothesis supported.

In a review of sedimentary organic carbon isotopic results from coastal marshes to deep oceanic environments, Deines (1980) concluded that there was no convincing evidence for diagenetic alteration of the sedimentary $\delta^{13}C$-C_{org} records. Although the possibilty of diagenetic alteration of Quaternary $\delta^{13}C$-C_{org} records has been discussed (Rogers and Koons, 1969), the author is unaware of results supporting sedimentary diagenetic carbon isotopic fractionation as the cause of large $\delta^{13}C$-C_{org} variations (3-6°/$_{oo}$) as those observed in the Quaternary Gulf of Mexico sediments (Sackett, 1964; Rogers and Koons, 1969; Sackett and Rankin, 1970; Newman et al., 1973; and Joyce et al., 1986; this study). Rogers and Koons (1969)

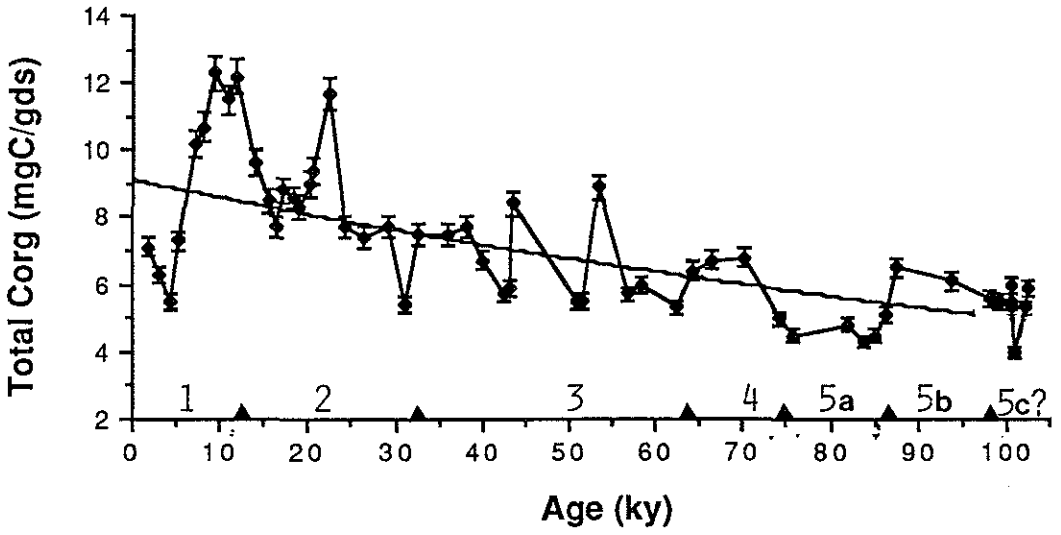
considered carbon isotopic fractionation during diagenesis as an insignificant problem affecting the $\delta^{13}C$-C_{org} record of 0-2 My old sediments since they did not observe a secular trend in $\delta^{13}C$-C_{org} values. However, a later study of the $\delta^{13}C$-C_{org} of the algal sapropelic sediments of the alternately aquatic, then marine Mangrove Lake in Bermuda indicated an overall decrease in $\delta^{13}C$-C_{org} of up to ~4°/$_{oo}$ over the last 5ky (Spiker and Hatcher, 1984). This research suggests caution in the interpretation of $\delta^{13}C$-C_{org} records solely in terms of organic matter sources, particularly in organic-rich sapropels. In that environment, secularly increasing $\delta^{13}C$-C_{org} values was due to preferential degradation of selected organic matter components (Spiker and Hatcher, 1984). This mechanism, however, would not explain the glacial-interglacial cyclic variation in $\delta^{13}C$-C_{org} and N/C values in the Pigmy Basin. Changes in organic matter sources are supported as a more probable cause for the correlation of the $\delta^{13}C$-C_{org} and N/C records than sedimentary diagenesis. Organic matter source changes are internally consistent with the inverse relations of terrigenous and marine organic biomarker compounds to $\delta^{13}C$-C_{org} (Chapter 3).

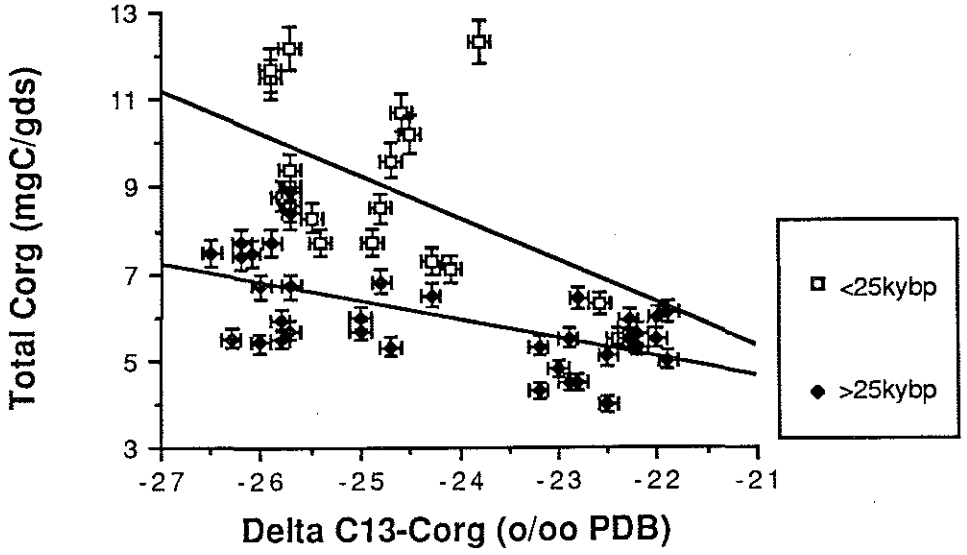
Organic Carbon Time Series

The organic carbon (C_{org}) concentration in DSDP 619 generally decreases from 9.2 ± 2.7 mgC/gds (n=9) in oxygen isotope stage 1 to 5.2 ± 0.8 mgC/gds (n=7) in isotope substages 5a-b (fig. 2.7 and Table 2.2). Alternative explanations for the general concentration decrease with age include a long-term C_{org} source change, sedimentary

Fig. 2.7 Organic carbon concentration time series of DSDP 619 in the Pigmy Basin. The hypothetical first-order decay curve (dashed line), $C_{org}(ky) = 9.2 \cdot \exp(-0.00610 \cdot ky)$ (with $\tau_{1/2}\text{-}C_{org}$ = 100 ky; $P<0.0001$, $r^2 = 0.48$, $n = 46$), is discussed in text.

Fig. 2.8 Cross-correlation plot of organic carbon concentration and the sedimentary organic carbon isotopic composition for the Pigmy Basin (DSDP 619) sediment core. Least squares linear regression lines for samples younger than 25ky ($C_{org} = -0.98 \cdot \delta^{13}C\text{-}C_{org} - 15$, $P = 0.022$) for those older than 25ky ($C_{org} = -0.41 \cdot \delta^{13}C\text{-}C_{org} - 4.0$, $P < 0.001$) are superimposed.


Total Corg (mgC/gds)
14
12
10
8
6
4
2
0
10
20
30
40
50
60
70
80
90
100
Age (ky)
1
2
3
4
5a
5b
5c?


Total Corg (mgC/gds)
13
11
9
7
5
3
-27
-26
-25
-24
-23
-22
-21
Delta C13-Corg (o/oo PDB)
<25kybp
>25kybp

diagenesis, or a combination of both processes. As previously noted, the significant ($P < 0.022$) positive correlation of C_{org} concentration with $\delta^{13}C$-C_{org} for samples younger than 25kybp was similar to the trend of sediments from the late Quaternary deep western Gulf of Mexico (Joyce, et al., 1985), supporting the hypothesis of climatically-driven mixing of terrigenous and marine C_{org} sources (Sackett, 1964). In DSDP 619, there is also a significant ($P < 0.001$) correlation for paired $\delta^{13}C$-C_{org} values and C_{org} concentrations older than 25kybp, but the C_{org} concentrations are generally lower at given $\delta^{13}C$-C_{org} values for these samples than those younger than 25kybp (fig. 2.8). The C_{org} differences are generally larger toward the more ^{13}C depleted (more terrigenous) $\delta^{13}C$-C_{org} values than toward the less ^{13}C depleted (more marine) $\delta^{13}C$-C_{org} values. If the C_{org} concentrations at given $\delta^{13}C$-C_{org} values of the original organic matter input were constant, the organic carbon difference between samples older and younger than 25kybp could be attributed to sedimentary C_{org} remineralization (diagenesis). Alternatively, the C_{org} concentrations at given $\delta^{13}C$-C_{org} values may have changed after 25kybp, with generally higher values toward the present (source change). This source change would have occurred at approximately the time (~25kybp) until which sea level was generally falling, exposing continental shelves to erosion, and after which sea level was generally rising, submerging the shelves again. The sediment sources to the northern Gulf of Mexico during sea level falls may have contained lower C_{org} concentrations at given $\delta^{13}C$-C_{org} values

than the sediment sources during sea level rises. However, mineralogical data for DSDP 619 are insufficient to differentiate sediment sources before and after ~25kybp.

There are four lines of circumstantial evidence supporting the remineralization of C_{org} in DSDP 619. (1) Catabolic reactions which consume C_{org} are indicated by the pore water chemistry. Sulfate concentrations generally decrease from 80°/$_{o}$ of normal seawater levels at 3 mbs (3.6 ky) to undetectable levels at 70 mbs (~40 ky) (Presley and Stearns, 1986). (2) Whelan, et al. (1986) showed experimental evidence of sulfate-reducing and methane-producing microorganismal activity in DSDP 619 by anaerobic sediment incubations with radiolabelled 2-^{14}C-acetate and ^{35}S-sulfate. (3) Below 70 mbs, generally increasing proportions of methane relative to total gases are observed, indicating microbial methanogenesis (Ishizuka et al., 1986). Stable carbon isotopic ratios of the methane (-94.8°/$_{oo}$ to -72.1°/$_{oo}$ PDB) from 76 to 178mbs in DSDP 619 are characteristic of methane produced by methanogenic bacteria (Pflaum, et al., 1986). This sequence of sulfate reduction overlying methanogenesis is typical of the later reactions of sedimentary diagenesis in coastal marine sediments (Martens and Berner, 1977; Martens and Crill, 1984). In the Pigmy Basin, however, these reactions occur over hundreds of meters rather than hundreds of centimeters, as in coastal environments. For comparison, the occurrence of physiologically active sulfate reducing bacteria has also been observed at great depths in continental geological units. Sulfate reducing and methanogenic bacteria were detected in deep

(1200-1800m) ground waters of the Madison Formation in the northern Great Plains of Montana, U.S.A. (Olson, et al., 1981). Other investigators report the occurence of active thermophilic sulfate-reducers in deep wells (2900-3200m) where temperatures ranged from 60° to 105°C. (4) The application of a first-order C_{org} remineralization model (Berner, 1980a) to (sub)stages 1-5b of the Pigmy Basin C_{org} record gives a decay half-life ($\tau_{1/2}$) of 100ky.

The C_{org} decay half-life calculated for the Pigmy Basin (100ky) is bracketed by the decay half-lives from other marine sedimentary environments. In the well constrained, nearly steady state sedimentary environment of Long Island Sound, Berner (1980b) found that an ~1ky C_{org} record could be modelled as a two component organic carbon system. A relatively labile fraction decayed away with a half-life of ~2y, while a more refractory fraction was remineralized with a half-life of ~600y. In a ~800ky Quaternary sediment core dominated by marine organic carbon from the Sierra Leone Rise in the eastern North Atlantic, Müller and Erlenkeuser (1983) observed generally decreasing C_{org} concentrations and attributed the decrease to organic carbon remineralization. They modelled the decrease with a first-order decay equation and found that the sedimentary organic carbon appeared to degrade with a half-life of ~1My, superimposed on the generally decreasing trends were glacial-to-interglacial periodic variations in C_{org} concentrations. The calculated decay half-life of sedimentary C_{org} in the Pigmy Basin (10^2ky) lies between those from the Long Island Sound (~10^0ky) and the Sierra Leone Rise (10^3ky).

A combined source change and diagenetic mechanism may explain both the apparent organic matter source change ($\delta^{13}C$-C_{org} and N/C) and the decrease in C_{org} concentration with age alone and with age for given $\delta^{13}C$-C_{org} values. If sedimentary organic matter which accumulated in the estuaries and on the continental shelf of the Gulf of Mexico during the last interglacial period (stage 5) underwent normal sedimentary diagenetic alteration, it would be relatively degraded compared to fresh, incoming material. As sea level fell during glacial periods and the continental shelf and estuarine sediments were eroded, partially degraded sedimentary organic matter would be delivered into the deep Gulf of Mexico. During sea level rises, the sedimentary organic matter delivered to the deep ocean may have been less degraded because fresh sediments would be replacing the eroded contintental shelves and estuaries as well as dispersing into the deep sea. In the Pigmy Basin, pore water geochemistry and microbiological data indicate that sedimentary C_{org} remineralization continues after burial. Even if the microbial processes were insufficent to account for the apparent C_{org} remineralization, a fraction of the C_{org} may have been previously degraded in the short-term burial in estuarine or continental shelf sediments.

In sum, the C_{org} concentrations of DSDP 619 generally decrease over the length of the record and the C_{org} concentrations at given $\delta^{13}C$-C_{org} values are generally lower before ~25ky than after that time. While a terrigenous C_{org} source change may be supported by further research, circumstantial evidence supports the occurrence of sedimentary C_{org} remineralization. A combined mechanism of (1)

partial C_{org} degradation during transport from the continent to the depositional basin and (2) continuing C_{org} remineralization within the basin may be a plausible explantion for the data. Sedimentary C_{org} remineralization in DSDP 619 is also supported by the predictable divergences (residuals) in organic biomarker/C_{org} versus $\delta^{13}C$-C_{org} relationships for a subset of these DSDP 619 samples (Chapter 3).

Concentrations of Terrigenous C_{org} and Marine C_{org}

The simultaneous use of lipid biomarker concentrations and $\delta^{13}C$-C_{org} values allows model calculations of terrigenous and marine C_{org} concentrations. Using a method similar to Calder and Parker (1968) to calculate the fractional concentration of terrigenous C_{org} in sediments, marine and terrigenous fractions of C_{org} in this Pigmy Basin core can be calculated

$$f_M = \frac{\delta^{13}C_1 - \delta^{13}C_T}{\delta^{13}C_M - \delta^{13}C_T} \qquad (3)$$

$$f_T = 1 - f_M \qquad (4)$$

where

f_M = marine fraction of total C_{org},

f_T = terrigenous fraction of total C_{org},

$\delta^{13}C_1$ = $\delta^{13}C$-C_{org} of a given sample,

$\delta^{13}C_T = \delta^{13}C\text{-}C_{org}$ of the terrigenous end member

$= -26.6 \pm 0.7°/_{oo}$,

and

$\delta^{13}C_M = \delta^{13}C\text{-}C_{org}$ of the marine end member

$= -20.6 \pm 2.2°/_{oo}$.

The concentrations of terrigenous and marine C_{org} concentrations can then be calculated by:

$$MC_{org} = f_M C_{org} \quad (5)$$

and

$$TC_{org} = f_T C_{org} \quad (6)$$

where

C_{org} = observed concentration of C_{org} (mgC/gds),

MC_{org} = marine C_{org} (mgC/gds), and

TC_{org}= terrigenous C_{org} (mgC/gds).

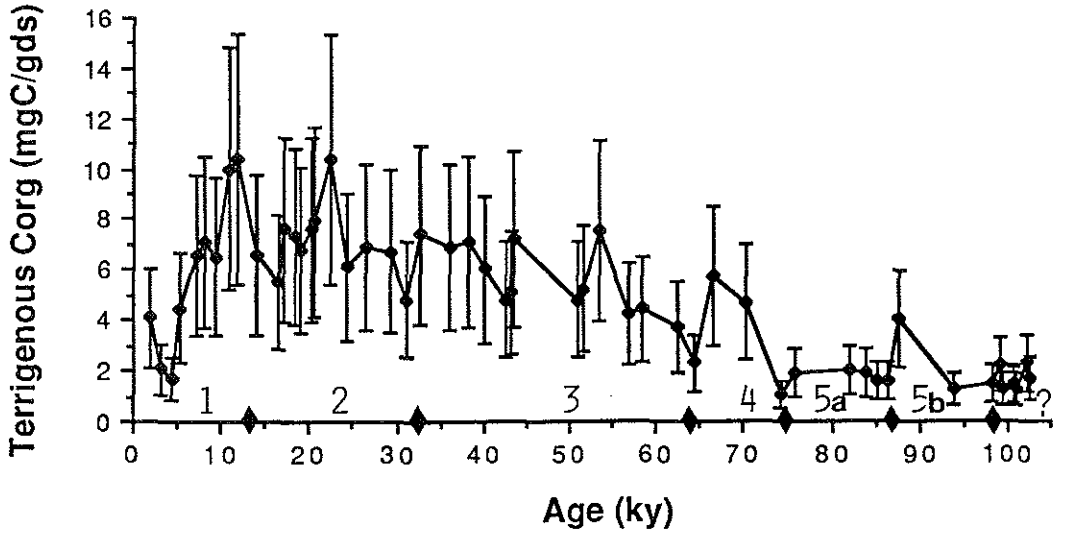
The terrigenous and marine $\delta^{13}C\text{-}C_{org}$ end member values were calculated by linear least squares regression analysis of organic carbon-normalized organic biomarker concentrations and $\delta^{13}C\text{-}C_{org}$ measurements (Chapter 3). By determining the $\delta^{13}C\text{-}C_{org}$ intercept of a total alkenone concentration/C_{org} versus $\delta^{13}C\text{-}C_{org}$ plot, a model terrigenous $\delta^{13}C\text{-}C_{org}$ end-member value (-26.6 ± 0.7 $°/_{oo}$) was determined. In an analogous fashion, a model marine $\delta^{13}C\text{-}C_{org}$ end member was calculated at $-20.6 \pm 2.2°/_{oo}$ using the average end member of two 4-desmethylsterols (24-ethylcholest-

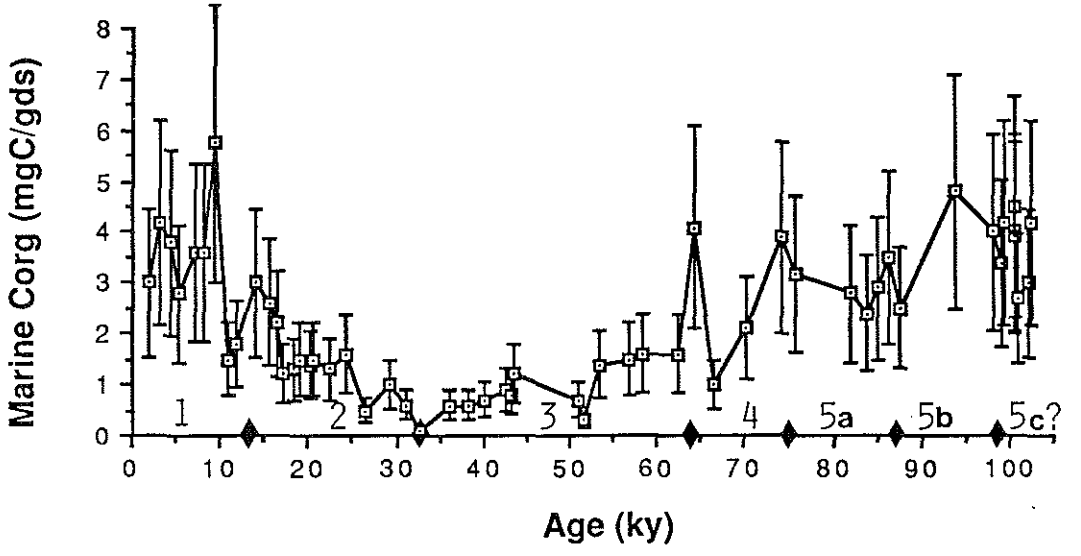
3ß-ol, -20.5 ± 2.1°/$_{oo}$; cholest-5-en-3ß-ol, -20.7 ± 2.2°/$_{oo}$) with the standard deviations added in quadrature. The standard deviations (1σ) for the $\delta^{13}C$-C_{org} end members were determined by the linear least squares regression method for evaluating the error in X for a given point Y (Snedecor and Cochran, 1978). In the present application, these standard deviations are considered maximum values because the residual trends in biomarker/C_{org} versus $\delta^{13}C$-C_{org} relationships cause systematic splaying from a simple linear relationship (Chapter 3). This splaying is mainly caused by differential digenesis between the biomarker compounds and C_{org}, and it decreases in magnitude near the $\delta^{13}C$-C_{org} end members (see Chapter 3). The projection of the error in Y (biomarker/C_{org}) onto the X-axis is therefore a high estimate of the standard deviation of the $\delta^{13}C$-C_{org} end members; non-linear statistical modelling should lower this estimate. The projected terrigenous end member (-26.6 ± 0.7°/$_{oo}$) corresponded well to the most negative $\delta^{13}C$-C_{org} values observed in the Pigmy Basin (-26.6 ± 0.1°/$_{oo}$ at ~33 kybp), but it is slightly depleted relative to the most negative value (-26.2°/$_{oo}$ at ~25 kybp, Northam et al., 1981) in the more seaward and perhaps less terrigenously-influenced Orca Basin. For comparison, the average $\delta^{13}C$-C_{org} (±1σ) values for 51 terrigenous C_3-photosynthetic plants is -28.0 ± 2.5°/$_{oo}$ (Smith and Epstein, 1971), overlapping the values observed here. The projected marine carbon isotopic end member is (within its estimate of variation) undifferentiable from Gulf of Mexico surface sediment $\delta^{13}C$-C_{org} values (-19 to -22°/$_{oo}$) which are interpreted as dominantly of a

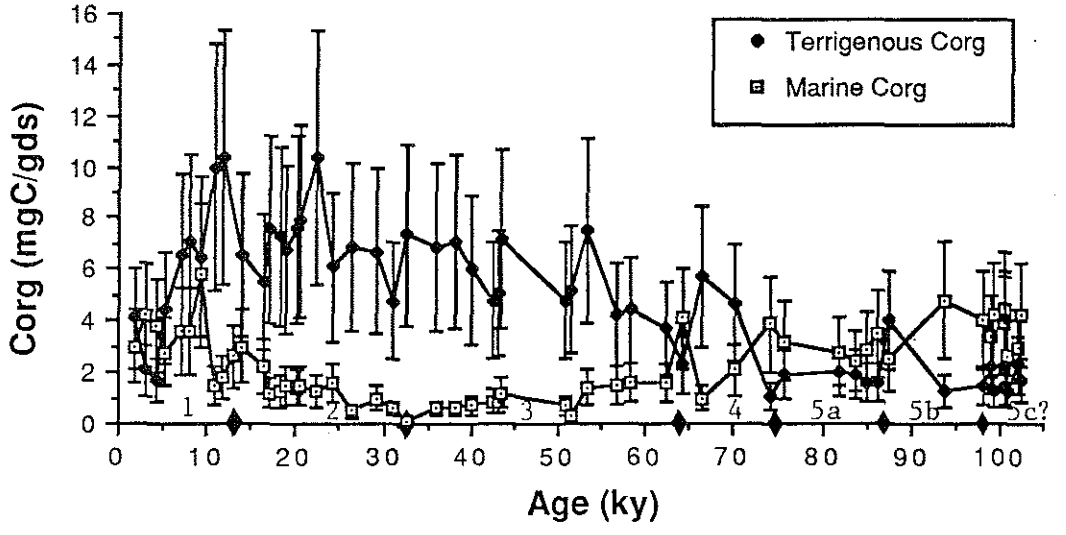
marine origin (Sackett and Thompson, 1963; Parker et al., 1972; Northam et al., 1981; Hedges and Parker, 1976). For comparison, the average (±1σ) of 10 species of C_3-photosynthetic marine phytoplankton is -18.9 ± 2.5 (Smith and Epstein, 1971).

Terrigenous C_{org} and marine C_{org} concentrations were calculated for DSDP 619 using observed $\delta^{13}C$-C_{org} values and C_{org} concentrations, equations 3-6, and the previously mentioned terrigenous and marine $\delta^{13}C$-C_{org} end members. Time series of terrigenous organic carbon (Fig. 2.9.a) and marine C_{org} (Fig. 2.9.b) concentrations show opposite trends. The average (±1σ variation added in quadrature) terrigenous C_{org} concentrations are 1.4±1.1 times higher in the glacial stages 2-4 than in the interglacial stages 1 and 5a-b. The average (±1σ) marine C_{org} concentrations are only 0.43±0.26 times as high in the glacial stages 2-4 as in the interglacial stages 1 and 5a-b. The concentrations of both terrigenous and marine C_{org} respond in opposite senses to a general ~100 ky cycle of glacial-interglacial climate change. Beyond the general climatically-related trends in marine organic carbon and terrigenous organic carbon concentrations, there also appears to be short-term events in those sedimentary records. Shortly preceding three cold-to-warm oxygen isotope stage transitions (2/1, 4/3, and 5a/5b), there are local concentration maxima (hereafter referred to as "spikes") in terrigenous organic carbon which are followed by marine organic carbon concentration spikes (fig 2.9.c). These terrigenous and marine organic carbon spikes may be directly or indirectly, respectively, a result of the glacial meltwater influx into the Gulf

Fig. 2.9 Terrigenous C_{org} (2.9.a) and marine C_{org} (2.9.b) concentration time series for DSDP 619 in the Pigmy Basin. Terrigenous C_{org} and marine C_{org} profiles show evidence of a opposite responses to the 100ky cycle of climatic change. Marine C_{org} spikes (local concentration maxima) follow terrigenous C_{org} spikes by ~2-4ky at three cold-to-warm stage transitions (2-to-1, 4-to-3, and 5b-to-5a) (2.9.c). The absence of marine C_{org} spikes in the interval ~60-15kybp may be due to a high turbidity plume of the Mississippi River which may have overlain the Pigmy Basin during low sea level stands. The (1σ) error bars are maximum values based on statistical linear least squares regression error in determination of the terrigenous and marine $\delta^{13}C$-C_{org} end members (discussed further in text).


Terrigenous Corg (mgC/gds)
Age (ky)
1
2
3
4
5a
5b
?


Marine Corg (mgC/gds)
Age (ky)
1
2
3
4
5a
5b
5c?


Corg (mgC/gds)
Terrigenous Corg
Marine Corg
Age (ky)
1
2
3
4
5a
5b
5c?

of Mexico.

Melting of the Laurentide ice sheet on the North American continent near the end of isotope stage 2 caused negative excursions up to ~2.4°/$_{oo}$ in $\delta^{18}O$ values of planktonic foraminifera (Kennett and Shackleton, 1975; Emiliani et al., 1978; Leventer et al., 1982; Williams, 1984). Average annual discharge of the Mississippi River into the Gulf of Mexico during the Laurentide ice sheet melting at the close of stage 2 is calculated to have been 1.8 to 4.0 times larger than the largest historically recorded flood, with probable annual peak floods twice as large (Emiliani et al., 1978).

William and Kohl (1986) observed a series of episodic negative excursions in the DSDP 619 G. ruber $\delta^{18}O$ record and interpreted them as glacial meltwater or fluvial events. Three of those events occurred near the 2/1, 4/3, and 5b/5a (sub)stage boundaries. Since such glacial and/or fluvial events would presumably transport increased amounts of terrigenous material into the sea, it is consistent that high concentrations of terrigenous organic carbon are found at these times. Shortly after the terrigenous organic carbon spikes (~2-4 ky), marine organic carbon spikes are observed. The marine organic carbon spikes may be due the shoreward movement over the Pigmy Basin of a standing primary productivity maximum following the turbidity maximum of the retreating Mississippi River offshore plume as sea level rose. As a contemporary analog for these surface water processes, a standing phytoplankton concentration maximum was observed seaward of the present-day Amazon River plume in the Atlantic Ocean (Milliman and Boyle, 1975). In the time span from ~60-15kybp,

there were 4–6 notable terrigenous C_{org} spikes which were not followed by marine C_{org} spikes. This difference could be because the hypothesized low salinity, high turbidity plume of the Mississippi River may have overlain the Pigmy Basin during glacial intervals, lowering marine production and marine organic matter input, while transporting in large amounts of terrigenous matter.

Net Accumulation Rates of Sedimentary Organic Carbon

The net accumulation rates of total sedimentary organic carbon, terrigenous organic carbon, and marine organic carbon by isotope (sub)stages are shown in Figures 2.10.a–c and given in Table 3. The net accumulation rate of each component is calculated by:

$$R = C\rho\omega \qquad (7)$$

where,

R = net accumulation rate ($gC/cm^2 \cdot ky$),

C = organic carbon concentration (gC/gds),

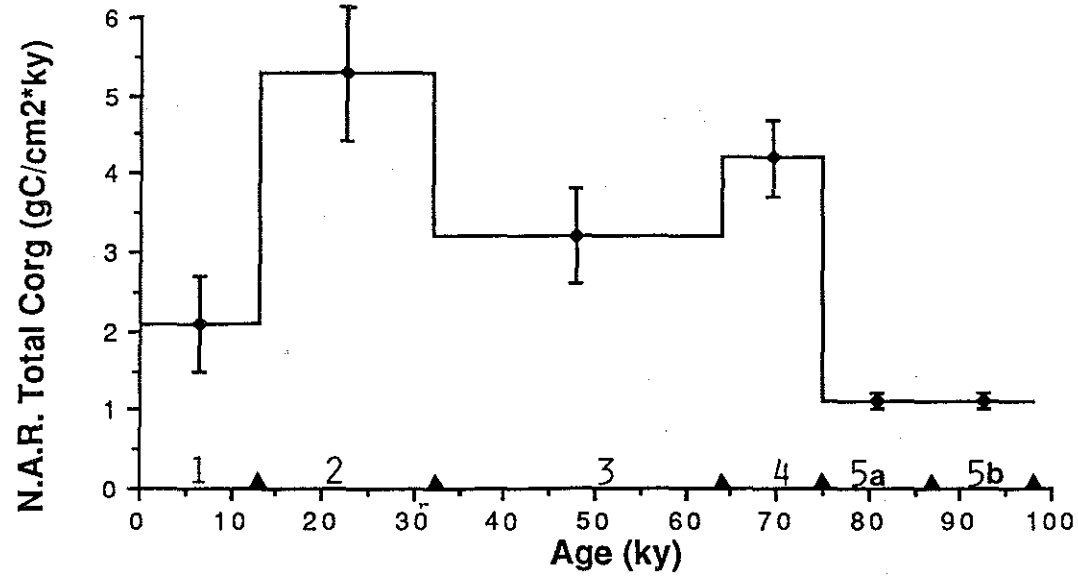
ρ = bulk density of total sediment solids (gds/cm^3 wet sediment), and

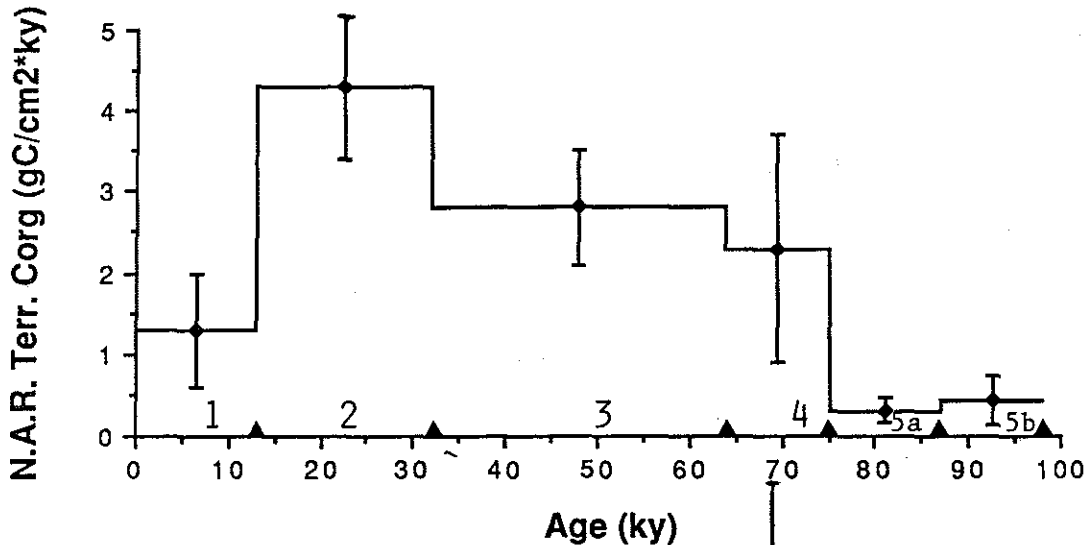
ω = sedimentation rate (cm/ky).

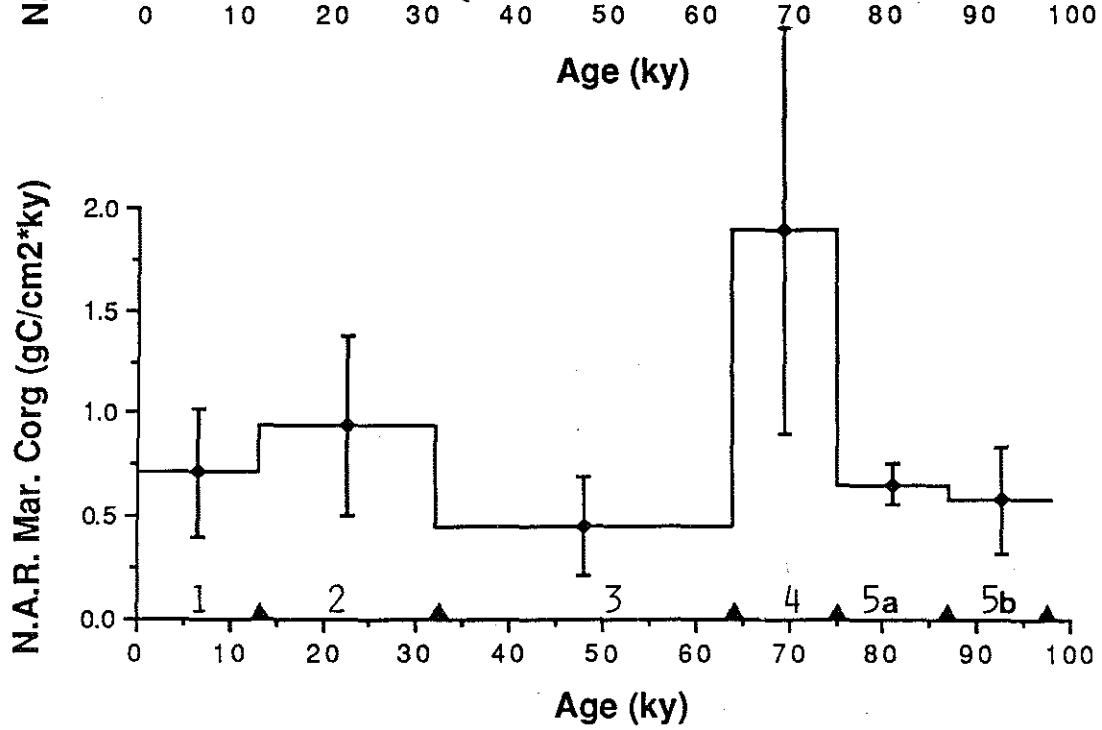
Net Accumulation Rate of Total Sedimentary Organic Carbon

The average ($\pm 1\sigma$) net accumulation rate of total sedimentary organic carbon (in $gC/cm^2 \cdot ky$) is low in interglacial stages oxygen isotope (sub)stages 1 (2.1±0.6, n=9) 5a (1.1±0.1, n=5), and 5b

Fig. 2.10 Net accumulation rates of total (2.10.a), terrigenous (2.10.b), and marine (2.10.c) organic carbon by isotope (sub)stage in the Pigmy Basin (DSDP 619).


N.A.R. Total Corg (gC/cm2*ky)
0
1
2
3
4
5
6
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


N.A.R. Terr. Corg (gC/cm2*ky)
0
1
2
3
4
5
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


N.A.R. Mar. Corg (gC/cm2*ky)
0.0
0.5
1.0
1.5
2.0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

(1.1±0.1, n=2), high in glacial stages 2 (5.3±0.9, n=13) and 4 (4.2±0.5, n=4) , and is an intermediate value in isotope stage 3 (3.2±0.6, n=13) (Fig. 2.10.a). The average (±1σ) net accumulation rate of sedimentary organic carbon is 2.6±1.3 times higher in glacial stages 2 to 4 than in interglacial (sub)stages 1 and 5a-b.

In the eastern North Atlantic, "estimated paleoproductivities" (in gC/m^2 y) were calculated increased (~2-5 times higher) in glacial periods relative to interglacials, using an equation which related sedimentary organic carbon preservation was proportionally related to the bulk sedimentation rate (Müller, et al., 1983). Since $\delta^{13}C$-C_{org} analyses showed that the sedimentary organic carbon was predominantly of marine origin, the authors interpreted the variations of water column decay-corrected organic carbon fluxes as changes in paleoproductivity. A later geochemical modelling study by Emerson (1985) suggested that within the range of typical deep ocean sedimentation rates (~0.1-5 cm/ky), bioturbational mixing was a much more significant factor influencing sedimentary organic carbon concentration than sedimentation rate. The reason for the enhanced C_{org} preservation was that deeper mixing of C_{org} into the sediments depleted pore water oxygen concentration, thereby reducing available oxidant to consume C_{org} (Emerson, 1985). However, at sedimentation rates above ~10 cm/ky, sedimentation rate was noted to significantly increase C_{org} preservation.

The carbon isotopic and N/C records of the Pigmy Basin core, however, show that there have been major sedimentary organic carbon sources changes through glacial-to-interglacial climatic variations.

The accumulation of organic carbon in the Pigmy Basin is interpreted as a balance of erosive inputs from the Mississippi River drainage basin and water column primary production minus diagenetic remineralization. With terrigenous C_{org} and marine C_{org} concentrations calculated by equations 5 and 6, the net accumulation rates of those components have been calculated by equation 7 and can be individually examined.

Net Accumulation Rate of Terrigenous Organic Carbon

The average (±1σ) net accumulation rates of terrigenous organic carbon ($gC/cm^2 \cdot ky$) are higher in glacial stages 2 (4.3±0.8, n=13) and 4 (2.3±1.4, n= 4) than in interglacial stages 1 (1.3±0.7, n=9) and 5a (0.31±0.16, n=5), 5b (0.43±0.30, n=2) and the isotope stage 3 rate (2.8±0.7, n=13) is intermediate between those of glacial stages (fig. 2.10.b). In fact, the average (±1σ) terrigenous organic carbon rate is 3.7±3.1 times higher through stages 2 to 4 than in interglacial (sub)stages 1 and 5a-b. Since large amounts of sedimentary organic carbon buried in estuaries were eroded from the continents to the deep ocean at low sea level stands (Broecker, 1982), the observed increased rates of terrigenous organic carbon accumulation in the Pigmy Basin in isotope stages 2, 3, and 4 relative to interglacial (sub)stages 1, 5a, and 5b presumably record the climatically-varying continental shelf and estuarine erosion rates.

Net Accumulation Rate of Marine Organic Carbon

The average (±1σ) net accumulation rates of marine organic carbon ($gC/cm^2 \cdot ky$) in the Pigmy Basin are high in glacial stages 2

(0.94±0.44, n=13) and 4 (1.9±1.0, n=4), low in isotope stage 3 (0.45±0.24, n=13), and of intermediate values in interglacial (sub)stages 1 (0.71±0.31, n=9), 5a (0.65±0.10, n=5), and 5b (0.58±0.26, n=2) (fig. 2.10.c). Although the standard deviations (1σ) of most of the isotope (sub)stage-averaged net accumulation rates overlap (except those of (sub)stages 4 and 5b), the general trends in marine C_{org} are discussed.

The input of marine organic carbon to the Pigmy Basin is presumably due to water column primary production. The net accumulation rate of marine organic carbon in DSDP 619 is hypothesized to be a proportional remnant of the original primary productivity. In a study of organic matter preservation in diverse, normally oxic pelagic, hemipelagic, and marginal sea environments (Muller and Suess, 1979), organic carbon preservation in marine sediments was found to be proportional to the 0.30 power of the sedimentation rate by the expression:

$$C = \frac{0.030 \cdot R \cdot \omega^{0.30}}{\rho_s \ (1-\phi)} \qquad (8)$$

where,

C = organic carbon concentration,

R = primary production rate

ω = sedimentation rate

ρ_s = sediment bulk density, and

ϕ = porosity

This model was developed for sedimentary environments dominated by marine organic matter input. It may also be useful in the interpretation of the DSDP 619 marine organic carbon record since the

marine fraction has been differentiated from total organic carbon. After compensation for the differential effects of sedimentation rate change on organic matter preservation (with eqn. 8), the average net accumulation rate of marine organic carbon the interglacial glacial stage 1 in the Pigmy Basin equals (±2°/$_{o}$) that of glacial isotope stage 2. The average net accumulation rate of stage 4 would still remain higher than all of the other stages, after compensation for sedimentation rate changes. As previously mentioned, Emerson (1985) also suggested that increased sedimentary organic carbon preservation would be expected to occur in marine environments where sedimentation rates exceeded ~10 cm/ky. The average sedimentation rate in the Pigmy Basin (DSDP 619) from stage 1 to 5b is ~170 cm/ky, so that enhanced C_{org} preservation relative to more typical marine sedimentary environments would be expected. The mechanism to account for enhanced C_{org} preservation is presently unclear. Relatively fast burial below the depth of oxidative C_{org} remineralization may contribute to enhanced C_{org} preservation.

The putative increased rate of marine primary paleoproduction may have been caused by increased riverborne nutrient input to the euphotic zone (e.g., Diester-Haas et al., 1983) as the Mississippi River's offshore plume advanced and retreated over the Pigmy Basin. In fact, a low salinity plume that extended ~600 km westward from the Mississippi River delta was observed, carrying high phosphate and chlorophyll concentrations (Riley, 1937). The co-occurence of high phytoplankton concentrations with high phosphate concentrations near in the Mississippi River's offshore estuarine plume suggested that

the riverine nutrient input caused the regional high phytoplankton standing stock. As previously noted, a phytoplankton concentration maximum was observed to occur seaward of the high turbidity zone on the edge of the present-day Amazon River plume (Milliman and Boyle, 1975). In the Last Glacial Maximum (LGM), when sea level was about 150 m lower than today (Broecker, 1982), river waters were injected further out to sea relative to the present shoreline. The effect of sea level rise, compounded episodically by glacial meltwater outflows (Kennett and Shackleton, 1975; Emiliani et al., 1978; Leventer et al., 1982; Williams, 1984) and/or fluvial events (Williams and Kohl, 1986), may have caused a glacial offshore estuary to advance and retreat across the Pigmy Basin, leaving high net accumulation rates of marine organic carbon in the glacial periods as its phytoplankton maximum crossed the basin. Examination of the northern Gulf of Mexico's continental shelf topography west of the Mississippi River delta shows that a 150m sea level lowering would move the present shoreline ~300km seaward toward the Pigmy Basin. Seaward movement of the biologically productive offshore estuary toward the Pigmy Basin may account for increased net accumulation rates of marine organic carbon in glacial stage 4 and perhaps in stage 2. A possible explanation for the lowest average marine organic carbon net accumulation rate to have occurred in stage 3 is that the high turbidity plume of the Mississippi River may have overlain the Pigmy Basin through this interval, with its highly productive edges never crossing the basin. The high accumulation rates of terrigenous organic carbon during isotope stage 4 through 2 are consistent with this explanation.

CONCLUSIONS

The combined analyses of organic geochemical measurements give insight into the glacial-to-interglacial climatic effects on the sources and deposition of sedimentary organic matter in the Pigmy Basin in the northern Gulf of Mexico. Quantitative analyses of C_{org} concentration, $\delta^{13}C$-C_{org} values, and N/C ratios measurements allowed the following observations on organic matter deposition in the Late Quaternary Gulf of Mexico:

1. Paired analyses of $\delta^{13}C$-C_{org} and N/C of Pigmy Basin sediments show that the composition of the organic matter is a mixture of C_3-photosynthetic terrigenous and marine organic components. Other hypotheses to explain the glacial-to-interglacial $\delta^{13}C$-C_{org} increase since the Last Glacial Maximum in the Pleistocene Gulf of Mexico include temperature-dependent fractionation of carbon isotopes by phytoplankton, mixing of C_3 and C_4 plant material, and sedimentary diagenesis of sedimentary organic carbon. The two former hypotheses are unlikely because they would require approximately constant (marine and terrigenous, respectively) N/C ratios with variable $\delta^{13}C$-C_{org} values while a linear $\delta^{13}C$-C_{org} versus N/C relationship with a significant (non-zero) slope is observed. Sedimentary diagenesis is an improbable explanation since it would require an unprecedented, large (3-6°/$_{oo}$) and time-vaying degree of carbon isotopic fractionation for an oceanic sedimentary environment.

2. The correspondence between the $\delta^{13}C$-C_{org} and N/C time series and glacial-interglacial climatic cycles chronicled in the Pigmy Basin were consistent with Sackett's (1964) hypothesis of climatically-controlled mixing of eroded terrigenous organic carbon and phytoplanktonic-produced marine organic carbon composing the sedimentary organic carbon in the Quaternary northern Gulf of Mexico.

3. The simultaneous evaluation of C_{org} concentrations and $\delta^{13}C$-C_{org} measurements, and $\delta^{13}C$-C_{org} end-members (from paired $\delta^{13}C$-C_{org} and lipid biomarker analyses) allow calculation of terrigenous C_{org} and marine C_{org} concentrations.

4. The net accumulation rate of total sedimentary organic carbon is the sum of the net accumulation rates of eroded terrigenous organic carbon and contemporaneous primary production of marine organic carbon minus sedimentary remineralization. The average rate of total sedimentary organic carbon burial is 2.6±1.3 times higher in glacial stages 2 to 4 than in interglacial (sub)stages 1 and 5a-b.

5. Average (±1σ) terrigenous C_{org} concentrations are 1.4±1.1 times higher in glacial stages 2 to 4 than in interglacial (sub)stages 1 and 5a-b. The average net accumulation rate of terrigenous organic carbon was 3.7 ± 3.1 times higher in isotope stages 2 to 4 than in interglacial stages 1 and 5a-b. The higher accumulation rates of terrigenous organic carbon in stages 2 to 4 are presumably due to higher continental shelf and estuarine erosion rates caused during lowered sea level stands of glacial periods.

6. Average marine C_{org} concentrations are only 0.43 ± 0.26 as high in glacial stages 2 to 4 as in interglacial isotope (sub)stages 1

and 5a-b. However, the highest average net accumulation rates of marine organic carbon occurred in glacial stages 4 and 2, largely because of the sedimentation rate differences. After a model-dependent compensation for the differential effects of sedimentation rates on marine organic carbon preservation, the glacial stage 2 values nearly equalled those of interglacial substages 1 and 5a-b. The combined analyses of marine and terrigenous organic carbon concentratons and net accumulation rates suggest that a nutrient-bearing, low salinity plume of the Mississippi River may have advanced and retreated over the Pigmy Basin as sea level fell and rose, respectively, in the Quaternary northern Gulf of Mexico.

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APPENDIX 2.1

Calculation of Masses of Remineralized Terrestrial and Marine C_{org} to Cause the Glacial-to-Interglacial Increase in Benthic Foraminifera Shell $\delta^{13}C$ Values

The $\delta^{13}C$ of the total dissolved inorganic carbon (DIC) of the glacial (G) ocean was $0.7^{o}/_{oo}$ more negative than the present day interglacial (IG) ocean as indicated by isotopic measurements on benthic foramiferal shells (Shackleton, 1977; Broecker, 1982). Shackleton (1977) and Broecker (1982) have suggested that the glacial to interglacial $\delta^{13}C$ shift could be due to the mineralization of terrigenous organic matter (TOM). Since both TOM and marine organic matter (MOM) are significantly more depleted in ^{13}C than benthic foraminiferal carbonates, it is shown below that the glacial-to-interglacial foraminiferal variations in $\delta^{13}C$ may be due to mineralization of TOM, MOM, or some mixture of both types of organic matter.

Known:

$\delta^{13}C_{DIC,IG} = 0.0^{o}/_{oo}$ $\qquad$ $\delta^{13}C_{DIC,G} = -0.7^{o}/_{oo}$

$\delta^{13}C_{TOM} = -26^{o}/_{oo}$ $\qquad$ $\delta^{13}C_{MOM} = -19^{o}/_{oo}$

(All $\delta^{13}C$ values are given relative to the Chicago PDB standard)

$M_{DIC,IG} = 3.5 \times 10^{19}$ g C = Mass of DIC-C in the interglacial ocean

Mass Balance:

$$M_{DIC,G} + M_{TOM} = M_{DIC,IG}$$

Isotope Balance:

$$(\delta^{13}C_{DIC,G})(M_{DIC,G}) + (\delta^{13}C_{TOM})(M_{TOM}) = (\delta^{13}C_{DIC,IG})(M_{DIC,IG})$$

Unknown:

M_{TOM}, M_{MOM}, and $M_{DIC,G}$.

Solution:

$$M_{TOM} = M_{DIC}\frac{\delta^{13}C_{DIC,IG} - \delta^{13}C_{DIC,G}}{\delta^{13}C_{TOM} - \delta^{13}C_{DIC,IG}} \qquad (I)$$

$$M_{TOM} = 9.2 \times 10^{17} \text{ gC}$$

Or, substituting $\delta^{13}C_{MOM}$ for $\delta^{13}C_{TOM}$ in (I), we get:

$$M_{MOM} = 12 \times 10^{17} \text{ gC}$$

Hence, by only observing the $\delta^{13}C$ of benthic foraminiferal carbonates one cannot uniquely determine how much terrigenous or marine organic matter must be mineralized to cause the observed glacial to interglacial 0.7 $^{o}/_{oo}$ $\delta^{13}C$ change in the DIC pool.

APPENDIX 2.2

Signal Attenuation due to Averaging over Variable Length Time Spans

Often in the study of glacial-interglacial processes, sediment cores are recovered which contain shorter timespans than can be properly analysed by spectral analysis to discern the amplitude of a given signal. Since one of the main goals of this research was to quantify the temporal variation of sedimentary organic matter input to hemipelagic sediments, it was necessary to develop a quantitative framework to approach sampling sediment cores which may span fewer wavelengths (<10) than should be analyzed by spectral analysis. The astronomical theory of climatic responses (Imbrie and Imbrie, 1980; Berger, 1980; Imbrie, 1982) holds that the advance and retreat of glaciers are driven by the earth's orbital variations. The three dominant orbital parameters that drive the climate system are the precessional cycles (with periods of 19 and 23 ky), the obliquity cycle (with a period of 41 ky), and what is loosely referred to as the 100 ky eccentricity cycle (with 8 periods from 95 to 136 ky). The observations that (1) the shortest period of an orbital parameter included in the astronomical theory of paleoclimates is 19 ky, (2) the orbital parameters are sinusoidal, and (3) the simplest models of paleoclimatology involve linear responses to orbital parameters (Imbrie and Imbrie, 1980), lead one to ask how often it is necessary to sample a sedimentary record to resolve the amplitude of a simple linear response. That is, over what time span must one sample a given interval to resolve a linear response of the climate to sinusoidal astronomical forcing! The following mathematical treatment shows that a predictable fraction of the linear response amplitude to sinusoidal forcing can be derived from a given sampling period.

In order to determine what fraction of the amplitude of a sinusoidally-varying system of wavelength λ will be derived from sampling it over n equal intervals, maximum and minimum calculations were performed.

In the first case, the maximum fraction of the amplitude M (given as a fraction of the actual amplitude) that will be extracted by sampling a sinu- soidal wave of wavelength λ in n equal intervals of length λ/n is given by:

$$M = \frac{2\pi}{n} \int_{\left(\frac{n-2}{2n}\right)\pi}^{\left(\frac{n+2}{2n}\right)\pi} \sin\lambda d\lambda$$

$$M = -\frac{n}{2\pi}\left[\cos\left(\frac{n+2}{2n}\right)\pi - \cos\left(\frac{n-2}{2n}\right)\pi\right]$$

In the second case, the minimum fraction of the amplitude m (given as a fraction of the actual amplitude) that will be extracted by sampling a sinusoidal wave of wavelength λ in n equal intervals of length λ/n is given by:

$$m = -\frac{2\pi}{n}\int_{\frac{\pi}{2}}^{\left(\frac{2}{n}+\frac{1}{2}\right)\pi} \sin\lambda \, d\lambda$$

$$m = -\frac{n}{2\pi}\cos\left(\left(\frac{2}{n}+\frac{1}{2}\right)\pi\right)$$

Results of both of these equations form an envelope that rapidly approaches the full amplitude of the sinusoidal wave (see fig. 2.11 and Table 2.4).

The average amplitude recovered by sampling at intervals λ/n is $(M + m)/2$. The average correction factor to predict the actual amplitude from sampling intervals λ/n is $2/(M + m)$. Values of both of these parameters are given in Table 2.4.

Fig. 2.11 Graph of sampling frequency-dependent signal attenuation due averaging sinusoidal responses over variable length time spans. The upper curve describes the maximum amplitude resolvable for a given sample frequency. The lower curve delineates the minimum amplitude resolvable for a given sample frequency.

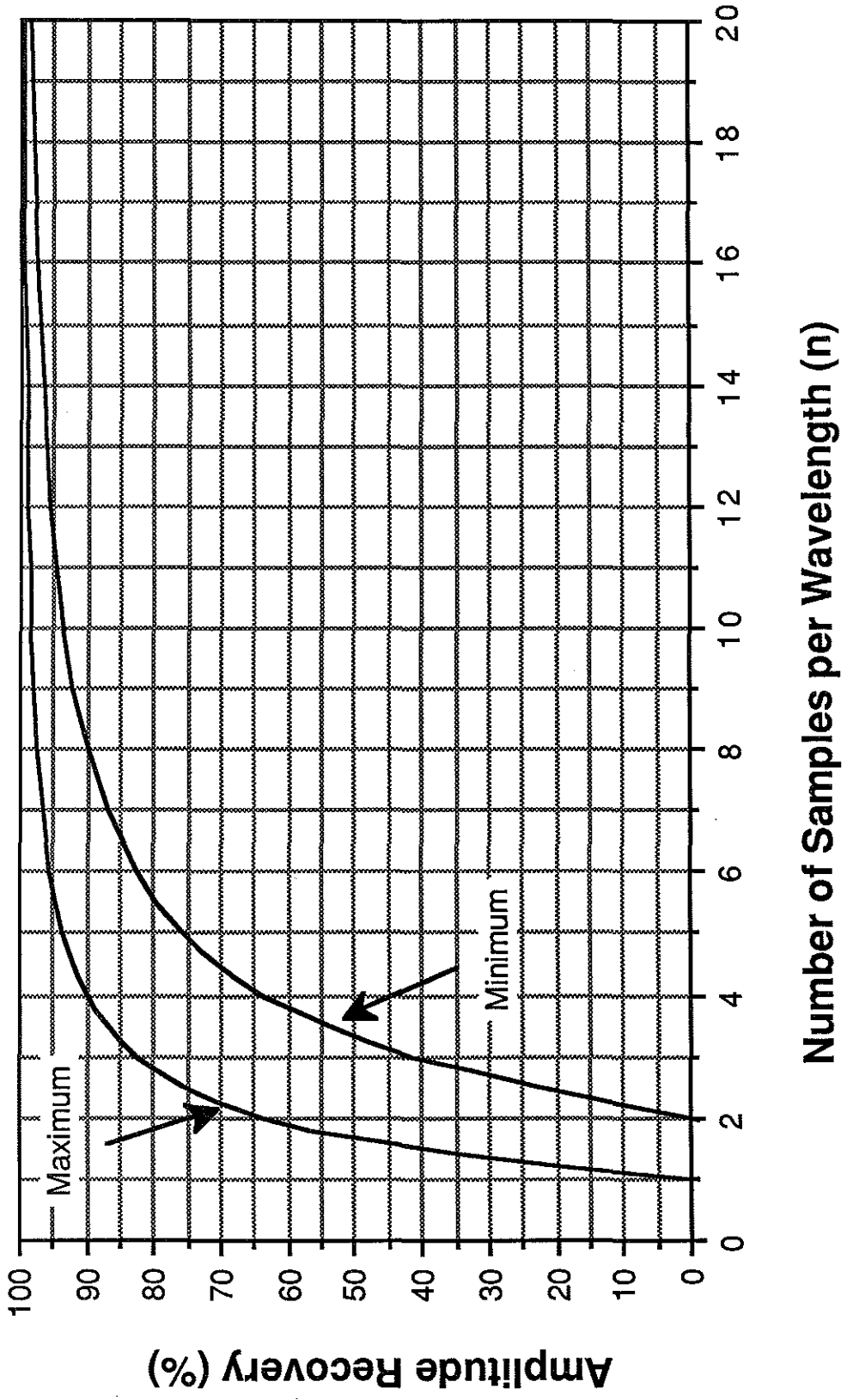

Amplitude Recovery (%)
100
90
80
70
60
50
40
30
20
10
0
Maximum
Minimum
0
2
4
6
8
10
12
14
16
18
20
Number of Samples per Wavelength (n)

TABLE 2.1

PHYSICAL PROPERTIES OF SEDIMENTS
PIGMY BASIN, D.S.D.P. CORE 619

Sample Number[a]	D.S.D.P. Identification (Core-Section:Interval in cm)	Depth (mbs)	Age[b] (ky)	Bulk Density (g/cm^3)
1	1-1:58-63	1.61	1.9	1.41
2	1-2:9-14	2.62	3.1	1.49
3	1-2:104-109	3.57	4.2	1.49
4	1-3:45-50	4.48	5.3	1.49
5	1-4:45-50	5.98	7.1	1.44
6	1-4:131-136	6.84	8.1	1.49
7	1-5:76-81	7.79	9.2	1.50
8	1-6:75-80	9.28	11.0	1.48
9	1-7:4-9	10.07	11.9	1.48
10	3-2:10-15	13.13	13.9	1.53
11	3-4:47-52	16.50	15.4	1.79
12	3-5:128-132	18.80	16.5	1.63
13	4-1:10-15	20.33	17.1	1.64
14	4-2:130-135	23.03	18.3	1.65
15	4-3:135-140	24.58	19.0	1.67
16	4-5:85-90	27.08	20.1	1.70
17F	4-CC:10-16	28.20	20.6	1.70
18	5-2:90-95	32.33	22.4	1.69
19F	5-CC:5-12	36.63	24.3	1.69
20	6-2:45-50	41.58	26.5	1.76
21F	6-CC:5-10	47.76	29.3	1.78
22	7-2:113-118	51.96	31.1	1.81
23F	7-CC:5-10	56.89	32.6	1.84
24	8-2:45-50	60.98	35.9	1.83
25F	8-CC:2-8	65.26	38.2	1.89
26	9-1:5-10	68.78	40.2	1.83
27F	9-CC:10-15	72.95	42.5	1.86
28	10-1:127-132	74.30	43.2	1.81
29F	10-2:44-49	74.97	43.6	1.81
30	11-1:11-16	88.14	50.9	1.81
31F	11-2:5-10	89.58	51.7	1.83
32	11-4:7-12	92.60	53.3	1.82
33F	12-2:5-10	99.18	57.0	1.80
34	12-3:90-95	101.53	58.3	1.78
35F	13-2:5-10	108.78	62.3	1.71
36	13-4:123-128	114.46	64.4	1.80
37F	14-2:5-10	118.38	66.5	1.81
38	15-2:5-10	127.98	70.3	1.86
39	16-2:5-10	137.58	74.1	1.71
40	16-4:813	140.61	75.9	1.78
41F	17-1:9-14	145.82	82.1	1.76
42	17-2:8-13	147.31	83.8	1.75

TABLE 2.1 (continued)

Sample Number[a]	D.S.D.P. Identification (Core-Section:Interval in cm)	Depth (mbs)	Age[b] (ky)	Bulk Density (g/cm^3)
43	17-2:116-121	148.39	85.1	1.76
44	17-3:76-81	149.49	86.4	1.76
45	17-4:12-17	150.35	87.6	1.81
46	18-1:45-50	155.89	93.9	1.81
47F	18-CC:0-5	158.27	98.2	1.80
48F	19-1:47-53	165.60	99.2	1.79
49	19-2:73-78	167.36	99.4	1.82
50	20-1:20-25	174.93	100.5	1.91
51F	20-2:2-7	176.25	100.7	1.95
52	20-2:110-115	177.33	100.8	1.95
53	20-3:5-7	177.76	100.9	1.95
54	22-1:50-55	187.83	102.2	1.95
55	22-2:15-20	188.98	102.4	1.95

[a]"F" denotes samples frozen upon collection; all other samples were obtained from D.S.D.P. refrigerated storage five months later.

[b]Ages of samples 1-47F were linearly interpolated from isotope (sub)stage boundaries 1-5b. Ages of samples 48F-55 were linearly interpolated between substage boundary 5b and an assumed core bottom age of 105ky (Williams and Kohl, 1986); high abundances of quartz sand, shallow water benthic foraminifera, and lack of datable horizons indicated sediment density flows through this interval (Kohl, 1986; Williams and Kohl, 1986).

TABLE 2.2

BULK ORGANIC GEOCHEMICAL RESULTS
PIGMY BASIN, D.S.D.P. CORE 619

Sample Number	Total C_{org} (mgC/gds)	$\delta^{13}C$-C_{org} (°/$_{oo}$ PDB)	N/C (Atomic Ratio)	$CaCO_3$ (mg/gds)	Marine C_{org} (mgC/gds)	Terrigenous C_{org} (mgC/gds)
1	7.1	-24.1	0.086	87	3.0	4.1
2	6.3	-22.6	0.110	159	4.2	2.1
3	5.5	-22.4	0.120	178	3.8	1.7
4	7.3	-24.3	0.090	127	2.8	4.5
5	10.2	-24.5	0.064	71	3.6	6.6
6	10.7	-24.6	0.068	90	3.6	7.1
7	12.3	-23.8	0.073	111	5.8	6.5
8	11.5	-25.9	0.055	60	1.5	10.0
9	12.2.	-25.7	0.052	33	1.8	10.4
10	9.6	-24.7	0.060	97	3.0	6.6
11	8.5	-24.8	0.070	80	2.6	5.9
12	7.7	-24.9	0.082	111	2.2	5.5
13	8.8	-25.8	0.063	133	1.2	7.6
14	8.6	-25.7	0.072	109	1.3	7.3
15	8.3	-25.5	0.066	120	1.5	6.8
16	9.0	-25.7	0.052	118	1.4	7.6
17F	9.4	-25.7	0.058	87	1.5	7.9
18	11.7	-25.9	0.047	132	1.3	10.4
19F	7.7	-25.4	0.072	101	1.6	6.1
20	7.4	-26.2	0.064	121	0.5	6.9
21F	7.7	-25.9	0.066	105	1.0	6.7
22	5.4	-26.0	0.062	135	0.6	4.8
23F	7.5	-26.5	0.069	159	0.1	7.4
24	7.5	-26.1	0.064	145	0.6	6.9
25F	7.7	-26.2	0.073	120	0.6	7.1
26	6.7	-26.0	0.040	171	0.7	6.0
27F	5.7	-25.7	0.057	130	0.9	4.8
28	5.9	-25.8	0.049	124	0.8	5.1
29F	8.4	-25.7	0.069	176	1.2	7.2
30	5.5	-25.8	0.066	84	0.7	4.8
31F	5.5	-26.3	0.082	260	0.3	5.2
32	8.9	-25.7	0.056	153	1.4	7.5
33F	5.7	-25.0	0.086	165	1.5	4.2
34	6.0	-25.0	0.081	145	1.6	4.4
35F	5.3	-24.7	0.073	133	1.6	3.7
36	6.4	-22.8	0.090	116	4.1	2.3
37F	6.7	-25.7	0.078	178	1.0	5.7
38	6.8	-24.8	0.066	102	2.1	4.7
39	5.0	-21.9	0.110	196	3.9	1.1
40	5.1	-22.9	0.099	96	3.2	1.9
41F	4.8	-23.0	0.110	33	2.8	2.0

TABLE 2.2 (continued)

Sample Number	Total C_{org} (mgC/gds)	$\delta^{13}C$-C_{org} (°/oo PDB)	N/C (Atomic Ratio)	$CaCO_3$ (mg/gds)	Marine C_{org} (mgC/gds)	Terrigenous C_{org} (mgC/gds)
42	4.3	-23.2	0.100	82	2.4	1.9
43	4.5	-22.8	0.086	165	2.9	1.6
44	5.1	-22.5	0.130	86	3.5	1.6
45	6.5	-24.3	0.110	120	2.5	4.0
46	6.1	-21.9	0.120	26	4.8	1.3
47F	5.6	-22.2	0.120	24	4.0	1.5
48F	5.5	-22.9	0.130	23	3.4	2.2
49	5.5	-22.0	0.130	23	4.2	1.3
50	5.5	-22.3	0.140	23	4.0	1.5
51F	6.0	-22.0	0.110	24	4.5	1.5
52	5.3	-22.2	0.110	15	3.9	1.4
53	4.0.	-22.5	0.098	21	2.7	1.3
54	5.3	-23.2	0.075	43	3.0	2.3
55	5.9	-22.3	0.130	61	4.2	1.7

Table 2.3

LINEAR SEDIMENTATION RATES AND NET ACCUMULATION RATES OF TOTAL, TERRIGENOUS, AND MARINE ORGANIC CARBON (C_{ORG}) BY ISOTOPE (SUB)STAGE

Isotope Stage or Substage	Linear Sedimentation Rate (cm/ky)	Number of Samples (n)	Net Accumulation Rate* (gC/cm^2ky)		
			Total C_{org}	Terrigenous C_{org}	Marine C_{org}
1	85	9	2.1±0.6	1.3±0.7	0.71±0.31
2	230	13	5.3±0.9	4.3±0.9	0.94±0.44
3	180	13	3.2±0.6	2.8±0.7	0.45±0.24
4	250	4	4.2±0.5	2.3±1.4	1.9±1.0
5a	85	5	1.1±0.1	0.31±0.16	0.65±0.10
5b	61	2	1.1±0.1	0.43±0.30	0.58±0.26

*$\bar{X}\pm 1\sigma$

TABLE 2.4

SAMPLING FREQUENCY-DEPENDENT AMPLITUDE ATTENUATION DATA

Number of Samples per Wavelenghth (n)	Percentage of Amplitude Sampled		Span of Max.-Min. (M-m) (%)	Span of Amplitde Sampled (%)	Average Correction Factor
	Maximum (M) (%)	Minimum (m) (%)			
1	0.00	0.00	0.00	0.00	0.00
2	63.67	0.00	63.67	31.84	3.14
3	82.70	41.37	41.34	62.03	1.61
4	90.03	63.67	26.36	76.85	1.30
5	93.55	75.68	17.87	84.62	1.18
6	95.49	82.69	12.80	89.09	1.12
7	96.68	87.09	9.59	91.88	1.09
8	97.45	90.02	7.43	93.73	1.07
9	97.98	92.05	5.93	95.02	1.05
10	98.36	93.53	4.84	95.94	1.04
11	98.65	94.62	4.02	96.63	1.03
12	98.86	95.46	3.40	97.16	1.03
13	99.03	96.12	2.91	97.57	1.02
14	99.16	96.64	2.53	97.90	1.02
15	99.27	97.06	2.21	98.16	1.02
16	99.36	97.40	1.95	98.38	1.02
17	99.43	97.69	1.74	98.56	1.01
18	99.49	97.93	1.56	98.71	1.01
19	99.55	98.13	1.41	98.84	1.01
20	99.59	98.30	1.29	98.95	1.01
21	99.63	98.45	1.18	99.04	1.01
22	99.66	98.58	1.08	99.12	1.01
23	99.69	98.69	1.00	99.19	1.01
24	99.71	98.79	0.93	99.25	1.01
25	99.74	98.88	0.86	99.31	1.01
26	99.76	98.95	0.81	99.35	1.01
27	99.77	99.02	0.76	99.40	1.01
28	99.79	99.08	0.71	99.43	1.01
29	99.80	99.13	0.67	99.47	1.01
30	99.82	99.18	0.64	99.50	1.01

CHAPTER 3

THE RELATIONSHIP BETWEEN SEDIMENTARY ORGANIC CARBON ISOTOPIC COMPOSITION AND ORGANIC BIOMARKER COMPOUND CONCENTRATION

ABSTRACT

A study of selected organic biomarker compounds which could serve as tracers of terrigenous and marine sedimentary organic matter sources was performed on samples from a 208.7 m hydraulic piston core from the hemipelagic Pigmy Basin in the northern Gulf of Mexico. Organic carbon-normalized concentrations of total long chain (C_{37}-C_{39}) unsaturated alkenones and individual C_{27}-C_{29} desmethyl sterols were determined to be useful proportional indicators of preserved marine and terrigenous organic carbon, respectively. The alkenones, whose source is marine phytoplankton of the class Prymnesiophyceae, generally occurred in higher concentrations in interglacial isotope stages 1 and 5a-b than in the intervening stages, including glacial stages 2 and 4. Sterols (C_{27}-C_{29}) of a dominantly terrigenous origin had lower concentrations during interglacial stages than in glacial stages. The sedimentary organic carbon-normalized concentration records of both terrigenous and marine biomarker compounds appear to be affected by the remineralization of sedimentary organic carbon, as indicated by a simple, first-order organic carbon decay model. The sedimentary deposition of some terrigenous desmethyl sterols may be affected by hydraulic particle sorting as they are transported from river deltas across the

continental shelf and slope to the hemipelagic Pigmy Basin. The marine phytoplanktonic alkenones which originate in the surface ocean and sink through the water column would not be subject to comparable particle sorting. The lack of any desmethyl- or 4-α-methylsterol which is linearly related to the proportion of marine sedimentary organic matter (as scaled by $\delta^{13}C$-C_{org}) indicates that either (1) sedimentary diagenesis has obscured the biomarker/C_{org} versus $\delta^{13}C$-C_{org} record, or (2) the selected compounds are not proportional indicators of preserved marine organic carbon input.

The diagenetic alteration of the sedimentary sterol concentration records in which marine sterols are apparently more susceptible to degradation than terrigenous sterols is consistent with present-day sediment trap and recent (10^{-1}-10^{2}y) sediment core observations. Preferential preservation of terrigenous sterols may result in a biased sedimentary record of sterol input which could be misinterpreted as indicating solely terrigenous sterol sources. The value and limitations of a simple model which characterizes the effects of sedimentary diagenesis and source input changes on the relationship between organic carbon-normalized biomarker compounds and sedimentary organic matter carbon isotopic composition are discussed.

INTRODUCTION

Organic biomarker compounds are often used as tracers of sedimentary organic matter sources (for reviews, see Brassell and Eglinton, 1981; Mackenzie et al., 1982; Gagosian, 1983; Volkman, 1986; Farrington, 1987). However, in only a few cases has the concentration

of a sedimentary organic biomarker compound been directly related to the composition of total sedimentary organic carbon (e.g., Gaskell et al., 1973; Hedges and Parker, 1976; Newman, 1976; and Pocklington and Leonard, 1979). The carbon isotopic composition of the total sedimentary organic carbon is often used to characterize the sources of terrigenous versus marine organic carbon (Sackett, 1964; Rogers and Koons, 1969; Sackett and Rankin, 1970; Newman et al., 1973; Northam et al., 1981; Joyce et al., 1986; and Chapter 2). Hedges and Parker (1976) showed that the organic carbon-normalized concentration of the sum of eight lignin components correlated negatively with the organic carbon isotopic composition of the surface sediments in the northern Gulf of Mexico. Beyond serving as a quantitative source tracer, the extrapolation of the normalized terrigenous biomarker concentration to zero allowed determination of the carbon isotopic composition ($\delta^{13}C\text{-}C_{org}$) of the sedimentary marine organic carbon end member. The discovery of organic biomarker compounds which when normalized to sedimentary organic carbon concentration are linearly related to the carbon isotopic composition of sedimentary organic matter would allow their application as tracers of the sources of terrigenous and marine organic matter in marine sedimentary environments and elucidation of the paleoclimatic and paleoceanographic effects on organic matter deposition.

The purpose of this research was to determine the relationship between concentrations of five classes of organic biomarker compounds (organic carbon-normalized) and the sedimentary organic carbon isotopic composition. If organic biomarker concentrations are found

to be related to $\delta^{13}C\text{-}C_{org}$, they may be used as quantitative tracers of organic matter deposition, with the additional potential benefit of greater source specificity than bulk organic geochemical measurements. Although a given organism may contribute biomarker compounds and bulk organic carbon to the sedimentary organic carbon inventory, the contribution may not be significantly related to the preserved sedimentary organic carbon isotopic composition because of either source changes or sedimentary diagenesis. The proportion of a biomarker compound relative to the bulk marine or terrigenous organic carbon may be variable, or differential diagenesis of either sedimentary organic carbon or biomarker compounds may have altered the original input biomarker/C_{org} ratio. Remineralization of organic carbon in marine sediments is a well characterized process (e.g., Berner, 1964; Berner, 1980). Diagenetic alteration or remineralization of organic biomarker compounds also affects their sedimentary concentration records (Lee, et al., 1977; Prahl, 1980; Gagosian et al., 1980; Mackenzie et al., 1982; Repeta and Gagosian, 1987; Farrington, et al, 1988). The diagenetic effects on the sterols discussed here are quantitatively evaluated elsewhere (Chapter 4).

The northern Gulf of Mexico was chosen as a location for this work because its wide spatiotemporal range in its sedimentary organic carbon isotopic composition. Sackett (1964), Shultz and Calder (1976), and Hedges and Parker (1976) have shown a $\delta^{13}C\text{-}C_{org}$ range from -18 to -25°/$_{oo}$ PDB in offshore transects of surface sediments. Downcore studies of the Quaternary variations of the $\delta^{13}C\text{-}C_{org}$ record show similar ranges, reflecting the glacial-interglacial

climatically-forced mixing of terrigenous and marine organic carbon in the pelagic and hemipelagic Gulf of Mexico (Sackett, 1964; Rogers and Koons, 1969; Sackett and Rankin, 1970; Newman et al., 1973; Northam et al., 1981; Joyce et al., 1986; and Chapter 2). The range of $\delta^{13}C$-C_{org} values (-21.9 to -26.6°/$_{oo}$ PDB) in the Pigmy Basin over a ~100 ky time span and the demonstration that the organic matter is a mixture of C_3-photosynthetic (Calvin-Benson Cycle) terrigenous and marine organic carbon (Chapter 2) made it an opportune sedimentary environment in which to evaluate the relationship between the organic carbon-normalized organic biomarker compounds and the sedimentary organic carbon isotopic composition.

The marine and terrigenous compounds selected for this study were chosen because of their source specificity, favorable preservational characteristics, and, in some cases, their known transformation pathways. The two classes of marine organic biomarker compounds examined here were the long chain unsaturated alkenones and the 4-α-methylsterols. The long chain (C_{37}-C_{39}) n-alkenones are characteristic marine organic biomarker compounds from the phytoplankton class Prymnesiophyceae, which includes the coccolithophorid Emiliania huxleyi (Volkman et al., 1979; Volkman et al., 1980; Marlowe, 1984a; Marlowe, 1984b). The alkenones have been found in marine sediments of Recent to Cretaceous ages (Boon et al., 1978; de Leeuw et al., 1979; Marlowe et al., 1984; Farrimond et al., 1986; Brassell et al., 1986; Farrington, et al., 1988). The phytoplanktonic alkenones from marine sediments have been shown to be useful in molecular stratigraphy, paleothermometry, and, perhaps, as a

quantitative indicator of preserved Prymnesiophyte input (Brassell et al., 1986a; Brassell et al., 1986b; Nichols and Johns, 1986; Prahl and Wakeham, 1987; Prahl et al., 1987; Farrington, et al., 1988). The 4-α-methylsterols, including dinosterol, are thusfar known to be biosynthesized mainly by dinoflagellates (Gagosian and Smith, 1979; Volkman, et al., 1984; Robinson et al., 1984). They have been found in lacustrine and marine sediments and have been used as indicators of dinoflagellate input (Boon et al., 1980; Gagosian et al., 1980; Brassell and Eglinton, 1983a; Brassell and Eglinton, 1983b; de Leeuw et al., 1983). An ~480 ky dinosterol concentration record from the Kane Gap region in the eastern equatorial Atlantic was characterized by generally low average values with episodic maxima (Brassell et al., 1986).

Three classes of terrigenous organic biomarker compounds examined herein are plant wax n-alkanes, n-alkanols, and selected desmethyl C_{27}-C_{29} sterols. The long chain (C_{21}-C_{35}) n-alkanes have long been recognized as components of land plant waxes (Eglinton et al., 1962; Eglinton and Hamilton, 1967; Dyson and Herbin, 1968; Herbin and Robins, 1968). They have been used as terrigenous organic matter indicators in a variety of sedimentary environments (Bray and Evans, 1961; Scalan and Smith, 1970; Gaskell et al., 1975; Gearing et al., 1976; Douglas and Eglinton, 1966).

Terrigenous long-chain (~C_{20}-C_{40}) n-alkanes are transported in the marine environment as particles , in suspension, and through the atmosphere in particles such as pollen grains, leaf wax, and aeolian dust (Simoneit and Eglinton, 1977; Gagosian, et al., 1981, 1987;

Schneider and Gagosian, 1985; Zafiriou et al., 1985; Prahl, 1985).

The long-chain (~C_{20}-C_{40}) n-alcohols co-occur with the long-chain n-alkanes as components of vascular plant waxes (Eglinton and Hamilton, 1967; Caldicott and Eglinton, 1973). They are commonly found in marine sediments (e.g., Bray and Evans, 1961; Aizenshtat, et al., 1973; Simoneit, 1978). Similar to the n-alkanes, they are transported in the marine environment in particulate and suspended phases (Prahl, 1986) and as particles through the atmosphere (Gagosian, et al., 1985; Schneider and Gagosian, 1985; Zafiriou et al., 1985).

Desmethyl sterols have numerous terrigenous and marine biological sources and have been found in the marine water column and underlying sediments (Gagosian, 1975; Gagosian and Heinzer, 1979; Brassell and Eglinton, 1983a,b; MacKenzie et al., 1983; Volkman, 1986). The co-occurrence of many specific sterols in both the terrigenous and marine biological realms, however, diminishes their usefulness as organic matter source tracers in the environment (Volkman, 1986). However, some C_{27}-C_{29} desmethyl sterols commonly occur in the epicuticular waxes of higher land plants (Scheuer, 1973; Goad, 1977) and can be useful terrigenous source indicators (Gaskell and Eglinton, 1977; Gagosian and Heinzer, 1979; Gagosian and Smith, 1979; Simoneit, 1981; De Leuuw, et al., 1983; Volkman, 1986; Volkman, et al., 1987). Sterols may undergo well-characterized tranformations which can be traced in the sediments even after the initial sedimentary input has been diagenetically altered (Gagaosian, et al., 1980; MacKenzie, et al., 1982).

While many sedimentary organic biomarker compounds have both terrigenous and marine sources, many terrigenous organic biomarkers are apparently better preserved (i.e., more refractory to sedimentary diagenetic degradation) than contemporaneously deposited marine compounds, perhaps because of their particle association with refractory plant biopolymers and waxes (Prahl et al., 1980; Gagosian, et al., 1982; Volkman et al., 1987). For example, 24-ethylcholest-5-en-3β-ol which has both terrigenous and marine sources appears to be preferentially preserved under the same sedimentary diagenetic conditions if it has a terrigenous rather than a marine source in the Peru upwelling region at 15°S (Volkman et al., 1987).

Within the terrigenous or marine classes of organic biomarker compounds, differential susceptibility to diagenetic processes affects the preserved record of organic biomarker deposition. Long chain n-alkanes (Wakeham et al., 1980), n-alcohols, and fatty acids (Johnson and Calder, 1973; DeBaar, et al., 1983) appear to be less susceptible to diagenetic transformation than their shorter-chain counterparts. The frequency of double bonds increases a compound's diagenetic lability, as indicated by the example of rapidly decreasing C_{25} alkenes/long chain ($>C_{25}$) n-alkanes and C_{37} alkene/C_{37} alkenone ratios with time in coastal Peru sediments (Volkman et al., 1987).

Differential preservation of marine versus terrigenous organic matter, and of certain classes of organic biomarker compounds will significantly bear upon the interpretation of results presented here.

EXPERIMENTAL:

Sedimentary Organic Carbon Isotopic Analysis

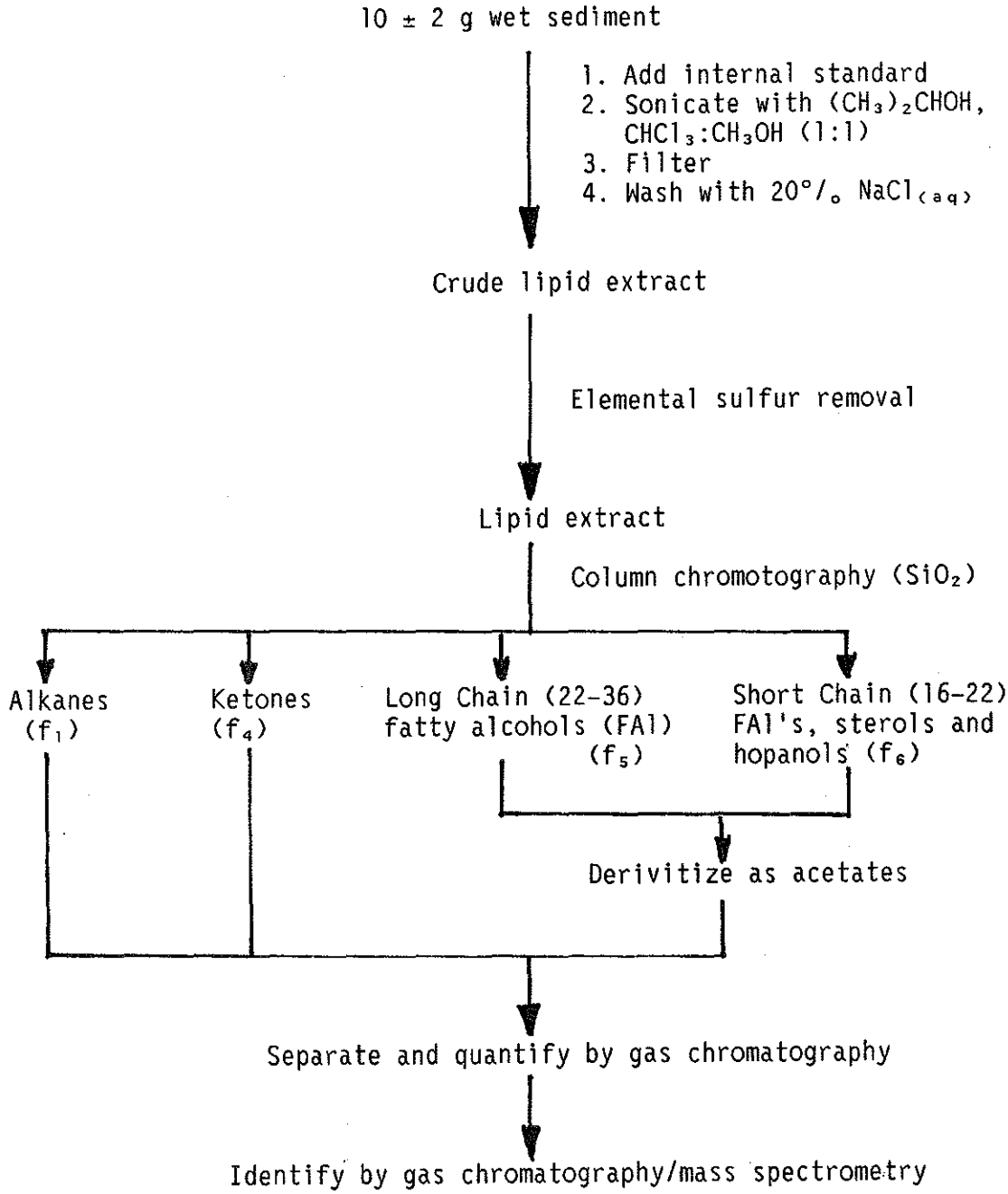
The carbon isotopic composition of sedimentary organic carbon ($\delta^{13}C\text{-}C_{org}$) was performed as previously described (Chapter 2). All $\delta^{13}C\text{-}C_{org}$ values are given relative to the Chicago PDB isotopic standard.

The Extraction, Separation, and Analysis of Sedimentary Lipids

Five classes of sedimentary lipids were extracted, separated, and analyzed from DSDP 619 sediment sample as outlined in Fig. 3.1 and described here.

Extraction Procedure. Approximately 10 ± 2 g wet sediment samples (~30°/$_o$ H_2O) were sonically extracted in an ice bath for three 10 min. intervals, once with 35 ml $(CH_3)_2CHOH$ and twice with 25 ml $CHCl_3$:CH_3OH (1:1, v/v), using a Tekmar P-500 Sonic Disruptor equipped with a 0.5 inch o.d. disruptor horn. Fifty microliters of a recovery standard solution (a hexane solution of 54.7 ng/µl 1-heptadecanol, 45.2 ng/µl 2-nonadecanone, and 52.6 ng/µl 1-heptadecanol) were added to each sediment aliquot in 50 ml screw-top centrifuge tubes at the beginning of the extraction procedure. After each sonication, the suspension was centrifuged and the supernatant solution decanted. The three extracts were combined, filtered through a pre-extracted Gelman A/E glass fiber filter to remove remaining suspended sediment, and washed with 120 ml of a 20°/$_o$ NaCl aqueous solution to partition polar species from the organic extract. The

Fig. 3.1. Schematic outline of lipid extraction, separation, and analytical procedures.


10 ± 2 g wet sediment
1. Add internal standard
2. Sonicate with $(CH_3)_2CHOH$, $CHCl_3$:CH_3OH (1:1)
3. Filter
4. Wash with 20°/$_o$ $NaCl_{(aq)}$
Crude lipid extract
Elemental sulfur removal
Lipid extract
Column chromotography (SiO_2)
Alkanes (f_1)
Ketones (f_4)
Long Chain (22-36) fatty alcohols (FAl) (f_5)
Short Chain (16-22) FAl's, sterols and hopanols (f_6)
Derivitize as acetates
Separate and quantify by gas chromatography
Identify by gas chromatography/mass spectrometry

organic fraction evaporated to dryness. Elemental sulfur was removed by a series of increasingly polar solvent elutions of the crude organic extract through an activated copper column. The combined eluants were evaporated to dryness on a rotary evaporator under vacuum at 45±5°C.

Lipid Class Separation. The sulfur-free organic extract was separated into compound classes by the long-column silica gel chromatographic technique of Peltzer and Gagosian (1987). The dried organic extract was eluted through a glass column (30 cm x 0.9 cm i.d. with a 250 ml reservoir bulb) containing 7 g of pre-extracted 5°/$_o$ deactivated silica gel (Bio-Rad, Bio-Sil A, 100-200 mesh) with a series of increasingly polar organic solvents. Four eluant fractions containing alkanes (f_1), ketones (f_4), long chain fatty alcohols (mainly C_{20}-C_{36}) (f_5), and short chain (C_{15}-C_{24}) fatty alcohols, sterols, and hopanols (f_6) were collected for structural and quantitative analyses.

Derivatization of Alcohols. n-Alcohols, sterols, and hopanols were acetylated by using the methods of Peltzer and Gagosian (1987). Briefly, lipid fractions f_5 and f_6 were dried and reacted with 20 µl acetic anhydride in 20 µl pyridine at 25°C for ~16 hr to form acetate esters of the alcohols. Addition of 0.5 ml hexane and 0.5 ml 3M HCl separated the acetate esters from excess reagents. The organic phase was combined with two additional 0.5 ml hexane extractions of the aqueous phase and the total extract was dried under a N_2

stream. The alcohol acetates were purified by the short glass column (12.5 cm x 0.6 cm i.d.) silica gel chromatographic procedure of Peltzer and Gagosian (1987).

Gas Chromatography. Gas chromatographic analysis was performed on a Carlo Erba 2150 gas chromatograph (GC) with a Varian Vista 401 Chromatography Data System. The GC was equipped with a flame ionization detector, an on-column injector, and a 30 m x 0.33 mm i.d. fused silica capillary column (J and W Scientific, Inc.) coated with a 0.1 μm DB-5 (95°/$_o$-dimethyl-(5°/$_o$)-diphenyl polysiloxane) liquid phase. Chromatographic separation was achieved with hexane as a solvent, H_2 as the carrier gas, and the following temperature program: 5 min. at 80°C, 80 to 220°C at 5°C/min., 220 to 325°C at 3.5°C, and 10 min. at 325°C.

Quantitation. Relative response factors (RRFs) for n-alkanes, n-alcohols, a ketone, and a sterol were determined by replicate analyses of standard solutions. The RRFs for even numbered nC_{20-36} and nC_{44} alkanes and 3-methyltricosane were determined relative to methyl nonadecanoate. The mean (n = 6) RRFs for eleven individual n-alkanes was sufficiently similar (C = 1.8°/$_o$, n = 11, where C = coefficient of variation (°/$_o$) $\equiv 100\sigma/\bar{X}$) that a constant RRF (1.27) was used for all n-alkanes. The RRFs for acetate esters of even numbered nC_{16-30} and nC_{17} alcohols and cholest-5-en-3ß-ol were determined relative to n-octacosane. The RRFs for 9 replicate analyses of an acetate-derivatized solution of 8 even-numbered

nC_{16-30} fatty alcohols were sufficently similar (1.07, C = ±3.4°/$_{o}$, n = 8) that the RRF for 1-heptadecanyl acetate relative to n-octacosane (1.06, C = ±0.32°/$_{o}$, n = 8) was used for all n-alcohols. The RRF of cholestenyl acetate relative to n-octacosane (1.08 , n = 3, C = ±1.6°/$_{o}$) was used to quantify sterol and hopanol concentrations. All alcohol concentrations are reported as underivatized alcohols. The RRF of 2-nonadecanone relative to n-octacosane was 1.42±0.044 (n = 8, C = ±3.1°/$_{o}$).

Internal standards were used for determining compound recoveries and quantitation. n-Octacosane was used as a quantitation standard for ketones, fatty alcohols, sterols, and hopanols; methyl nonadecanoate was used for alkanes. Internal standard recoveries ($\bar{X}$ ± 1σ, n, °/$_{o}$C) were 84 ± 11°/$_{o}$ (n = 53, C = 13°/$_{o}$) for 3 methyltricosane (alkane recovery standard), 84 ± 8°/$_{o}$ (n = 40, C = 9.0°/$_{o}$) for 2 nonadecanone (ketone recovery standard), and 75 ± 15°/$_{o}$ (n = 38, C = 20°/$_{o}$) for 1-heptadecanol (alcohol recovery standard). All concentrations (ng/gds) reported here were corrected to 100°/$_{o}$ recovery. The replicate analytical variance of sample (number 38) recovery-corrected concentrations were: 7.5°/$_{o}$ for odd-numbered nC_{27-33} alkanes (n = 5), 11°/$_{o}$ for total C_{37-39} di- and triunsaturated alkenones (n=3), and 16°/$_{o}$ for even-numbered nC_{26-32} alcohols (n=3). The reproducibility of individual sterol and hopanol concentrations was calculated at 17°/$_{o}$ by averaging the fractional concentration differences ($\sum[1-(X_1/X_2)]/n$) of 16 of those individual compounds in a duplicate sample (X_1,X_2) analysis; this value compares well with

the variance for n-alcohol concentrations (16°/$_o$). Detection limits for alkanes, ketones, and alcohols were 3 ± 0.5 ng compound/gds, based on minimum integrated peak areas and sediment sample masses.

Structural Elucidation. Structural determinations were based on comparison of gas chromatographic retention times, computerized gas chromatographic/mass spectrometric (C-GC-MS) analyses of samples and selected authentic standards, and comparison with published mass spectra. The authentic standards used were even-numbered nC_{20-36} and $nC_{40,44}$ alkanes, even numbered nC_{16-30} and nC_{17} fatty alcohol acetates, cholesteryl acetate, and 2-nonadecanone. The C-GC-MS instrument had a Carlo Erba 4160 gas chromatograph equipped with a 30 m x 0.32 mm i.d. glass capillary column (J and W Scientific) coated with DB-5 (95°/$_o$dimethyl-(5°/$_o$)-diphenylpolysiloxane). Chromatographic separations were achieved with hexane as a solvent, He as the carrier gas (3.6 ml/min), and the following typical temperature programs. For alkanes (f_1), the temperature program was: 3 min. at 70°C, 70 to 260°C at 3.5°C/min, 260 to 320°C at 4°C/min., and 10 min. at 320°C. For ketones (f_4) and alcohols (f_5 and f_6), the temperature program was: 3 min. at 80°C, 80 to 180°C at 20°C/min., 180 to 320°C at 3°C/min., and 20 min. at 320°C. The source of the Finnigan 4500 quadrupole filter mass spectrometer was operated in electron impact mode at 100°C, 50 eV electron energy, and 350 μA. The MS scanned repetitively from 50 to 650 a.m.u. at 1 scan/sec. Mass spectral data were collected and processed on a Data General 3/12

computer equipped with the Incos Data System. Mass spectra for comparison were found in the following publications (alkenones: de Leeuw, et al., 1979; n-alkanes and n-alcohols, McLafferty, F. W., 1980; hopanols: Dastillung, M., 1976). The fifteen individual sterol spectra required here are referenced in a compilation by de Leeuw and Baas (1986).

RESULTS AND DISCUSSION

Five classes of organic biomarker compounds were evaluated to test whether their organic carbon-normalized concentrations were significantly linearly related to the carbon isotopic composition of the contemporaneous sedimentary organic carbon ($\delta^{13}C\text{-}C_{org}$). The organic carbon-normalized concentration time series of biomarker compounds are described and discussed in their paleoceanographic context. For those organic biomarkers which were significantly related to sedimentary organic carbon isotopic composition, simple first-order organic carbon remineralization models were proposed to explain systematic deviations from the linear behavior of ideal terrigenous and marine organic matter tracers. The possible additional effect of hydraulic particle sorting on terrigenous biomarkers and sedimentary organic carbon is discussed as it bears upon the 4-desmethyl sterols' tracer properties. The sedimentary concentration records of other biomarker compounds which were determined not to be useful quantitative organic matter tracers are discussed and compared to terrigenous biomarkers which demonstrated useful tracer properties. Finally, a simple reconstructed

paleoceanographic history of organic matter deposition in the Late Quaternary Pigmy Basin is presented, based on the sedimentary records of organic biomarkers and bulk organic geochemical properties.

Marine Biomarkers

The Total C_{37-39} Alkenones/C_{org} Sedimentary Record.

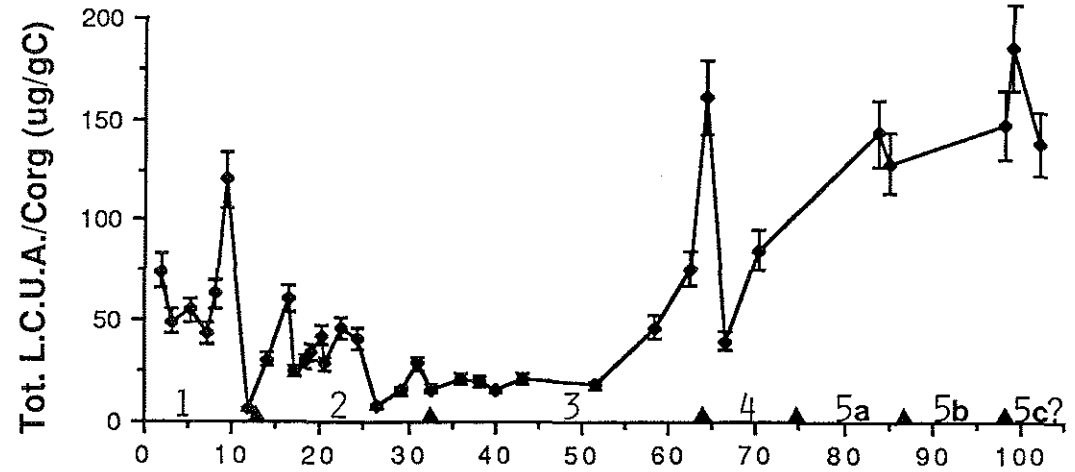
The total alkenone/C_{org} time series for the Pigmy Basin core (DSDP 619) is presented in Fig. 3.2.a. The general features of the time series are high values (~150 µg/gC) in the last interglacial (isotope substages 5a-b), with decreasing values to ~50 µg/gC into isotope stage 4. Total C_{37-39} alkenone/C_{org} values are lowest (~25 µg/gC) in isotope stage 3. They increase to ~40 µg/gC in glacial isotope stage 2. The total C_{37-39}alkenones/C_{org} values generally increase from ~10 to ~80 µg/gC through interglacial stage 1. Two total C_{37-39}alkenones/C_{org} values near two cold-to-warm transitions (the isotope stage 4-to-3 and 2-to-1 transitions) are noteworthy and will be further discussed later.

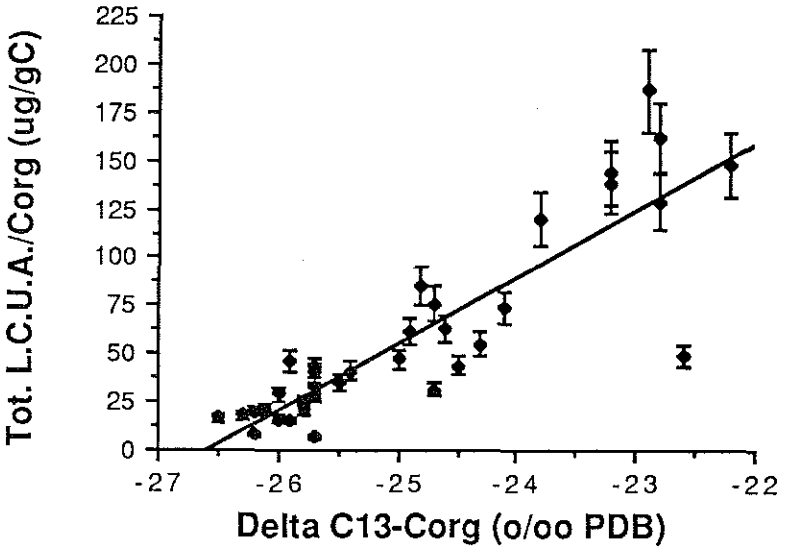
A graph of total C_{37-39} alkenones/C_{org} versus sedimentary organic carbon isotopic composition was plotted to test for a linear relationship between the biomarkers' fraction of the total sedimentary organic carbon and an index of marine versus terrigenous sedimentary organic carbon. The criterion used to test for a significant linear relationship was the statistical F-test which evaluates the null hypothesis that the correlation coefficient is significant (i.e., $r^2 \neq 0$) which is mathematically equivalent to testing that the slope of the least squares regression line is significant ($\beta \neq 0$) (Snedecor and

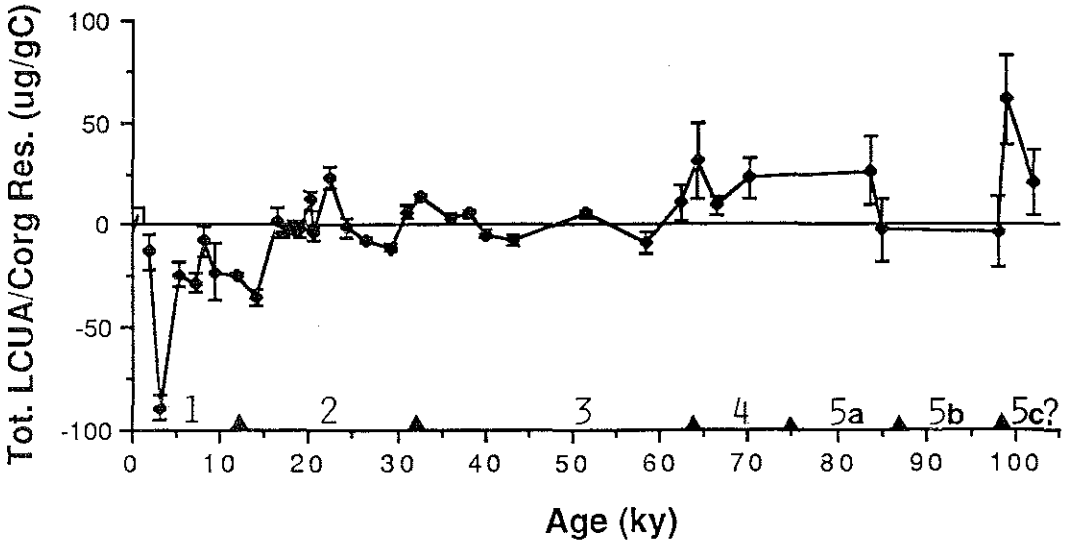
Fig. 3.2.a. Time series of total C_{37-39} alkenones/C_{org}.

Fig. 3.2.b. Total C_{37-39} alkenones/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. The least squares regression line is $34 \cdot \delta^{13}C$-C_{org} + 920 ($P < 0.001$, $r^2 = 0.76$, $n = 35$).

Fig. 3.2.c Time series of total C_{37-39} alkenones/C_{org} versus $\delta^{13}C$-C_{org} linear regression residuals.


Tot. L.C.U.A./Corg (ug/gC)
200
150
100
50
0
1
2
3
4
5a
5b
5c?
0
10
20
30
40
50
60
70
80
90
100


Tot. L.C.U.A./Corg (ug/gC)
225
200
175
150
125
100
75
50
25
0
-27
-26
-25
-24
-23
-22
Delta C13-Corg (o/oo PDB)


Tot. LCUA/Corg Res. (ug/gC)
100
50
0
-50
-100
1
2
3
4
5a
5b
5c?
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

Cochran, 1978). A statistical test for the use of linear regression when the X-variable is subject to error demonstrated that the experimental error in X ($\delta^{13}C$-C_{org}) relative to the error in Y (lipid biomarker/C_{org}), had an insignificant (<0.5°/$_{oo}$) effect on the slope determined by a least squares linear regression of Y on X. The same statistical analysis was applied to all other organic biomarkers examined in this study.

The graph of total C_{37-39}alkenones/C_{org} versus $\delta^{13}C$-C_{org} (Fig. 3.2.b) shows that the properties are to a first approximation linearly-related ($P<0.0001$, $r^2= 0.76$, $n = 35$). That is, the preserved record of total C_{37-39}alkenones/C_{org} concentration is directly proportional to the sedimentary organic carbon isotopic composition which has been used a quantitative measure of terrigenous and marine organic carbon (e.g., Calder and Parker, 1968; Shultz and Calder, 1976). In fact, fifty-five analyses of $\delta^{13}C$-C_{org} and N/C ratios from DSDP 619 were consistent with a climatically-forced mixing of terrigenous and marine C_3-photosynthetic (Calvin-Benson Cycle) organic matter sources (Chapter 2, Fig. 2.6). The linear relationship of total C_{37-39}alkenones/C_{org} to $\delta^{13}C$-C_{org} indicates that the total C_{37-39}alkenones/C_{org} ratio is a proportional indicator of preserved marine organic matter input in the Pigmy Basin, suggesting that these compounds are well preserved. There are indications from other studies that alkenones may be refractory to sedimentary diagenetic alteration. The observations that a ratio of alkenone compound unsaturation (U^K_{37}) records sea surface temperature and that ratio correlates with occurrence of

glacial-interglacial climatic cycles for approximately 100-500 ky (Brassell et al., 1986a,b; Prahl and Wakeham, 1987; Prahl et al., 1988; Chapter 5) also suggest that the alkenones are well preserved on long time scales. On a shorter time scale (~100y), U^{K}_{37} ratio reords from the Peru upwelling zone indicate that the alkenones have retained plausible U^{K}_{37} temperatures while other compounds (e.g., a branched alkene and polyunsaturated fatty acids) appear to have undergone significant diagenetic loss (Farrington, et al., 1987). Significant factors contributing to the alkenones apparently refractory character are their long carbon chain length (C_{37}-C_{39}), ketone functionalization, and, perhaps, their membrane and/or particle association (see e.g. Prahl et al., 1980; Volkman et al., 1987). The high molecular weight and carbon chain length of these alkenones may make them less susceptible to microbial degradation because high molecular weight (>600) are not easily transported across bacterial membranes (Gottschalk, 1986).

The total C_{37-39}alkenones/C_{org} versus $\delta^{13}C$-C_{org} linear regression residuals (i.e., observed values minus regression predicted values) when plotted as a function of time show a generally increasing trend with some notable exceptions (Fig. 3.2.c). This second order residual trend is superimposed on the significant ($P<0.0001$) linear relationship between organic carbon-normalized alkenone concentrations and sedimentary organic carbon isotopic composition. The extrapolation of the total alkenone/C_{org} ratio versus $\delta^{13}C$-C_{org} regression line to zero total alkenone/C_{org} concentration can be used to determine the terrigenous carbon isotopic end member for the

last ~100 ky in the Pigmy Basin. The terrigenous $\delta^{13}C$-C_{org} end member calculated for these data was -26.6 ± 0.7°/$_{oo}$ PDB. The estimate of variation in the end member was made by using the linear least squares method of calculating the error in X for a given regression value of Y (Snedecor and Cochran, 1967). The projected end member (-26.6 ± 0.7°/$_{oo}$) corresponded well to the most negative $\delta^{13}C$-C_{org} values observed in the Pigmy Basin (-26.6 ± 0.1°/$_{oo}$ at ~ 33 kybp; Chapter 2), but it is slightly depleted relative to the most negative value (-26.2 at ~25 kybp, Northam et al., 1981) in the more seaward and perhaps less terrigenously-influenced Orca Basin. For comparison, the average $\delta^{13}C$-C_{org} (±1σ) values for 51 terrigenous C_3-photosynthetic plants is -28.0 ± 2.5°/$_{oo}$ (Smith and Epstein, 1971), overlapping the values observed here. An improved estimate of the terrigenous end member variation with more elaborate statistical techniques would likely decrease the value because of C_{org} remineralization will cause splaying of the alkenone/C_{org} values from the mixing line with increasing $\delta^{13}C$-C_{org} values (explained further below and see Figures 3.3.b and 3.4.a). At the present level of approximation, however, a more elaborate analysis seems unwarranted.

If the decay rate of total C_{37-39} alkenones is small relative to the C_{org} decay rate, then the total C_{37-39}alkenones/C_{org} ratio for a given $\delta^{13}C$-C_{org} would increase with time (Fig. 3.2.a). The generally increasing value of total C_{37-39}alkenones/C_{org} versus $\delta^{13}C$-C_{org} residuals with time (Fig. 3.2.c) is consistent with more rapid remineralization of C_{org} than diagenetic loss of total

C_{37-39} alkenones. Although alkenones appear to be relatively refractory to diagenesis on this time scale, the bulk sedimentary organic carbon does not (Chapter 2). The generally increasing alkenone/C_{org} residual trend is consistent with the remineralization of sedimentary organic carbon.

Marine Biomarker/C_{org} versus $\delta^{13}C$-C_{org} Diagenesis Model

A simple, first-order diagenetic model is developed here as a illustration of how to assess the apparent general diagenetic alteration of organic carbon-normalized C_{37-39}alkenone sedimentary record. The model assumes that total sedimentary C_{org} decays with first-order kinetics (Berner, 1964; Jorgenson, 1979; Berner, 1980) and that the biomarker compounds considered here are well preserved relative to C_{org}. The latter assumption is confirmed by the significance ($P<0.0001$) of the total C_{37-39}alkenones/C_{org} versus $\delta^{13}C$-C_{org} linear regression. For simplicity of demonstration, the $\delta^{13}C$-C_{org} record is assumed to be a "sawtooth" (see e.g., Broecker and van Donk, 1970) with a pure marine end-member at 96 kybp, linearly mixing in time to a pure terrigenous end-member at 32 kybp, and returning to a pure marine end-member by the present. This simplification of the $\delta^{13}C$-C_{org} record reproduces the gross glacial-to-interglacial features of the observed $\delta^{13}C$-C_{org} record for DSDP core 619 (Chapter 2), in which the most positive $\delta^{13}C$-C_{org} values occur in interglacial stages and the most negative value near the isotope stage 2/3 boundary at ~32kybp. Additional support for this choice comes from the observed

24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} residuals changing sign from positive to negative values at ~32kybp (Fig. 3.5.c) and the model-predicted shape of the terrigenous biomarker residual time series (Fig. 3.6.c).

In the absence of C_{org} remineralization, the organic carbon-normalized concentration of an ideal marine biomarker is assumed to be linearly related to the $\delta^{13}C$-C_{org} ratios ranging from 0 to 100 units (e.g., μg/gC) (Fig. 3.3.a). This line ($t_{1/2}$ = ∞; i.e., no C_{org} decay) can be considered the original mixing line before C_{org} remineralization. The effect of the decay of C_{org} on the marine biomarker/C_{org} versus $\delta^{13}C$-C_{org} relationship (for 32 $\leq$ t $\leq$ 96 ky) can be modelled by the following equations:

$$M_f = \frac{M_{m1}}{\exp(-k(t-32))}, \qquad (1)$$

and

$$M_m \quad \frac{100}{64}(t-32) \qquad (2)$$

where,

M_f = marine biomarker/C_{org} concentration (μg/gC), ($0 \leq M_f \leq 100$)

k = first-order decay rate of sedimentary organic carbon (ky^{-1}),

t = age (ky) ($32 \leq t \leq 96$), and

M_{m1} = marine biomarker/C_{org} ratio as a function of time before C_{org} remineralization (ug/gC; $0 \leq M_m \leq 100$).

In the case of 32-to-96 kybp, 32 kybp is for model considerations (discussed below) the time of no diagenetic alteration of the marine biomarker/C_{org} concentration, so that from that point and backward

in time the marine biomarker/C_{org} values diverge from the original ratio at the time of burial.

These equations generate a family of curves which diverge from the original source mixing line on the marine biomarker/C_{org} versus proxy $\delta^{13}C$-C_{org} graph for t = 32 to 96 kybp with increasing time, decay rates, and fractional (percentage) marine C_{org} composition (Fig. 3.3.a).

The C_{org} remineralization model for application to the observed biomarker/C_{org} versus $\delta^{13}C$-C_{org} relationship over the time span of 0 to 32 kybp is developed by symmetry with the 32-to-96 kybp case. As in the previous case, the 0-to-32 kybp case also normalizes the diagenetic deviations from the original source mixing line for that time span to zero at 32 kybp. The normalization of biomarker/C_{org} diagenesis to 32 kybp is an auspicious choice because it approximates the time of (1) sign change of the residuals of the linear least squares regression line to the total alkenone/C_{org} and 24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} data (Figs. 3.2.c and 3.5.c, respectively) and (2) the minimum $\delta^{13}C$-C_{org} value in the DSDP 619 "sawtooth"-shaped record occurs at ~32kybp. The governing equations are analogous to those of the marine biomarker/C_{org} ratio decay equations (1 and 2):

$$M_f = \frac{M_{m2}}{\exp\,(k(32-t))} \qquad (3)$$

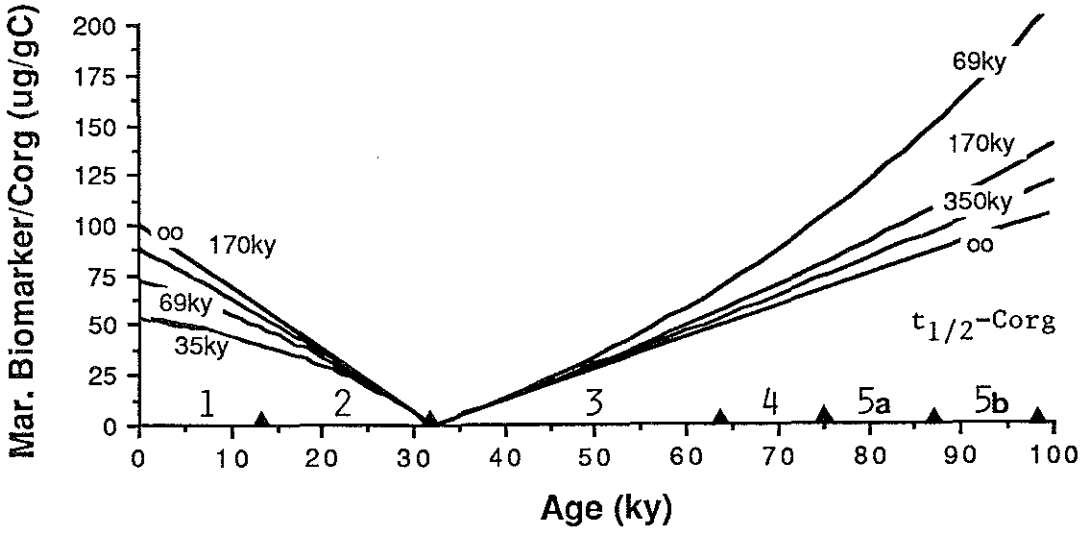
and

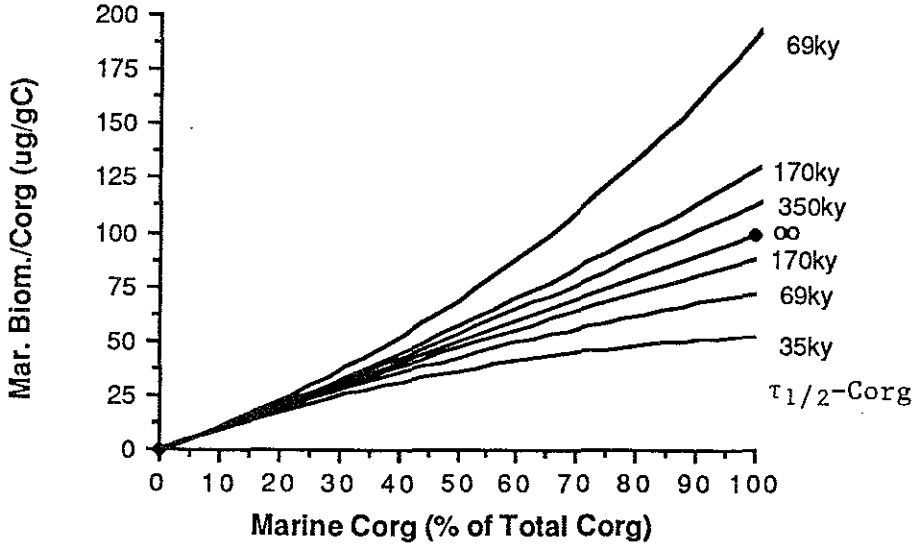
$$M_{m2} = \frac{100}{32}\,(32-t) \qquad (4)$$

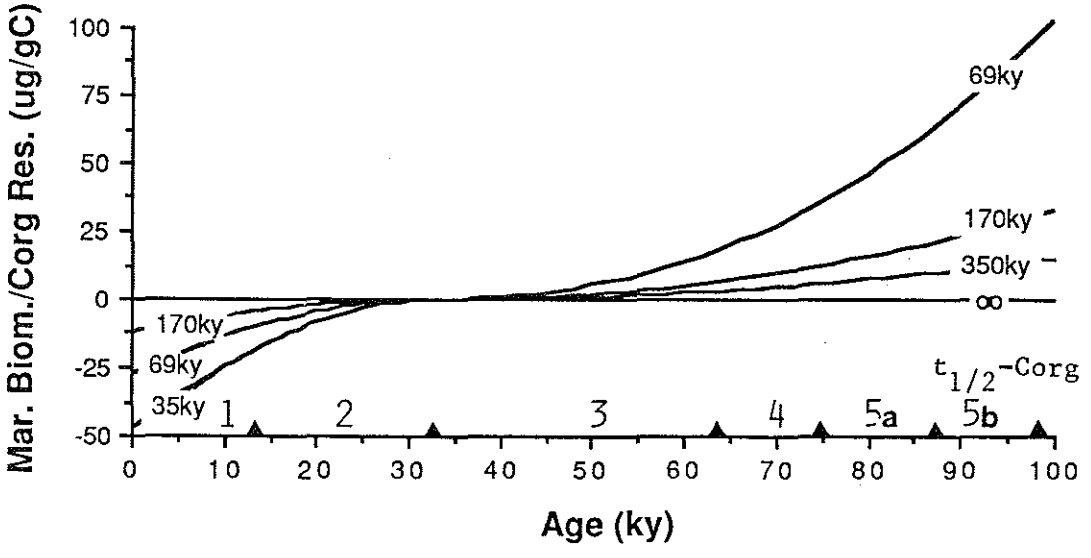
Fig. 3.3.a. Time series of ideal marine biomarker/C_{org} with superimposed effects of first-order C_{org} remineralization with various decay half-lives ($\tau_{1/2i}$; $\tau_{1/2} = \infty$ implies no C_{org} remineralization). This idealized model normalizes C_{org} remineralization to zero at 32 kybp and is further explained in text.

Fig. 3.3.b. Ideal marine biomarker/C_{org} versus fractional marine (versus terrigenous) C_{org} composition (proxy $\delta^{13}C$-C_{org} measure) with superimposed effects of first-order C_{org} decay half-lives ($\tau_{1/2i}$) (explained in Fig.3.3.a).

Fig. 3.3.c. Time series of ideal marine biomarker/C_{org} residuals (diagenetically-altered ($\tau_{1/2i}$) value minus original unaltered ($\tau_{1/2} = \infty$) value).


Mar. Biomarker/Corg (ug/gC)
200
175
150
125
100
75
50
25
0
0 10 20 30 40 50 60 70 80 90 100
Age (ky)
69ky
170ky
350ky
oo
oo
170ky
69ky
35ky
$t_{1/2}$-Corg
1
2
3
4
5a
5b


Mar. Biom./Corg (ug/gC)
200
175
150
125
100
75
50
25
0
0 10 20 30 40 50 60 70 80 90 100
Marine Corg (% of Total Corg)
69ky
170ky
350ky
oo
170ky
69ky
35ky
$\tau_{1/2}$-Corg


Mar. Biom./Corg Res. (ug/gC)
100
75
50
25
0
-25
-50
0 10 20 30 40 50 60 70 80 90 100
Age (ky)
69ky
170ky
350ky
oo
170ky
69ky
35ky
$t_{1/2}$-Corg
1
2
3
4
5a
5b

where,

t = age (ky), $(0 \leq t \leq 32$ ky),

M_{m2} = marine biomarker versus $/\delta^{13}C$ ratio as function of time before C_{org} remineralization $(0 \leq M_{m2} \leq 100)$,

M_0, k are as previously defined.

The main features of the effect of C_{org} remineralization on the biomarker/C_{org} versus $\delta^{13}C$-C_{org} relationship are illustrated in Fig. 3.3.b. The superimposition of C_{org} remineralization on the temporal sequence of marine source (total C_{37-39} alkenone/C_{org}) variations from 100 µg/gC at 96 kybp to 0 µg/gC at 32 ky and back to 100 µg/gC results in a splaying of the C_{org} remineralization half-life isopleths with increasing marine (versus terrigenous) C_{org} composition. Under ideal conditions of biomarker/C_{org} and $\delta^{13}C$-C_{org} sediment mixing and first-order C_{org} remineralization, the first-order remineralization constant (k) can be read from this type of graph. The C_{org} remineralization half-lives are given by

$$t_{1/2}\ (C_{org}) = \frac{-\ln\ (1/2)}{k}. \qquad (5)$$

The effect of diagenetic remineralization of C_{org} on the idealized "sawtooth" marine biomarker/C_{org} time series record is shown in Fig. 3.3.a. Increasing decay constants and temporal differences from the 32 ky time point result in increasingly positive deviations from the average source line for $t > 32$ ky and negative deviations for $t < 32$ ky. The deviations (or residuals) from the original biomarker/C_{org} demonstrate the effect of diagenetic

alteration (C_{org} remineralization). The main features of the diagenetically altered marine biomarker/C_{org} record are: (1) with increasing time, since C_{org} is decaying faster than the marine biomarker, the preserved marine biomarker/C_{org} record is skewed by C_{org} remineralization. Younger sediments have disproportionately lower marine biomarker/C_{org} ratios as compared to the average mixing line (over 0 to 96 kybp) than older sediments. The relatively faster degradation of C_{org} than the marine biomarker results in a diagenetic skewing of the marine biomarker/C_{org} sedimentary record. The extent of the diagenetic alteration can be partially assessed by a simple diagenetic model. (2) Increasing C_{org} remineralization rates (k) result in greater deviations from the original marine biomarker/C_{org} versus $\delta^{13}C$-C_{org} relationship for any given point in time. The linear regression residuals (diagenetically altered marine biomarker/C_{org} minus the average mixing line total C_{37-39} alkenone/C_{org} value) plotted as a function of time show the marine biomarker/C_{org} deviations (residuals) for given C_{org} remineralization constants (Fig. 3.3.c).

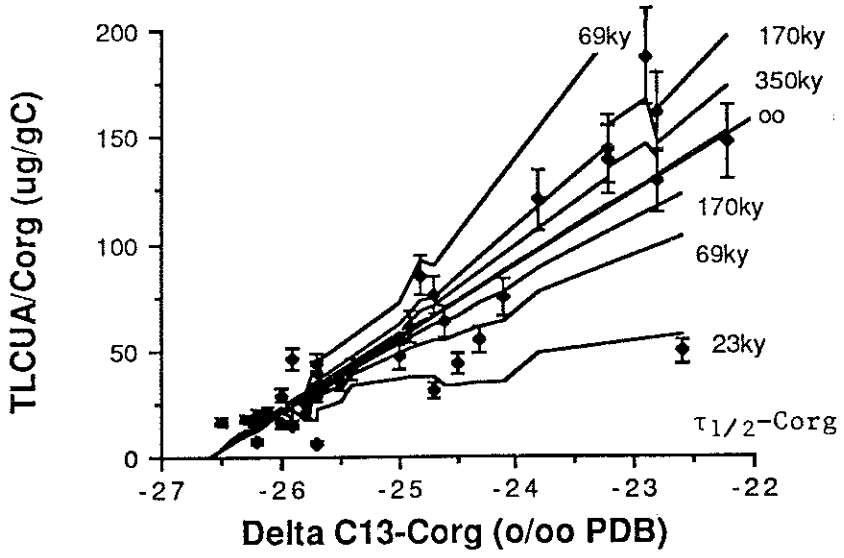
Application of the Marine Biomarker/C_{org} versus $\delta^{13}C$-C_{org} Diagenetic Model

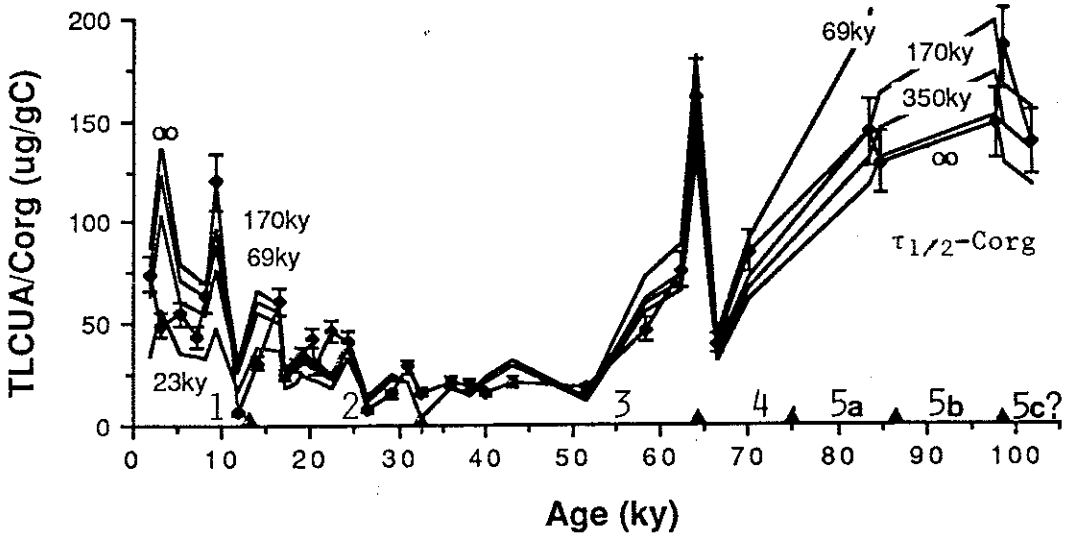
The extent of the diagenetic alteration of the marine biomarker/C_{org} record can be assessed in a general way by application of the first-order remineralization model described above. A linear least squares regression line was fitted to the observed data to approximate the average source line mentioned in the

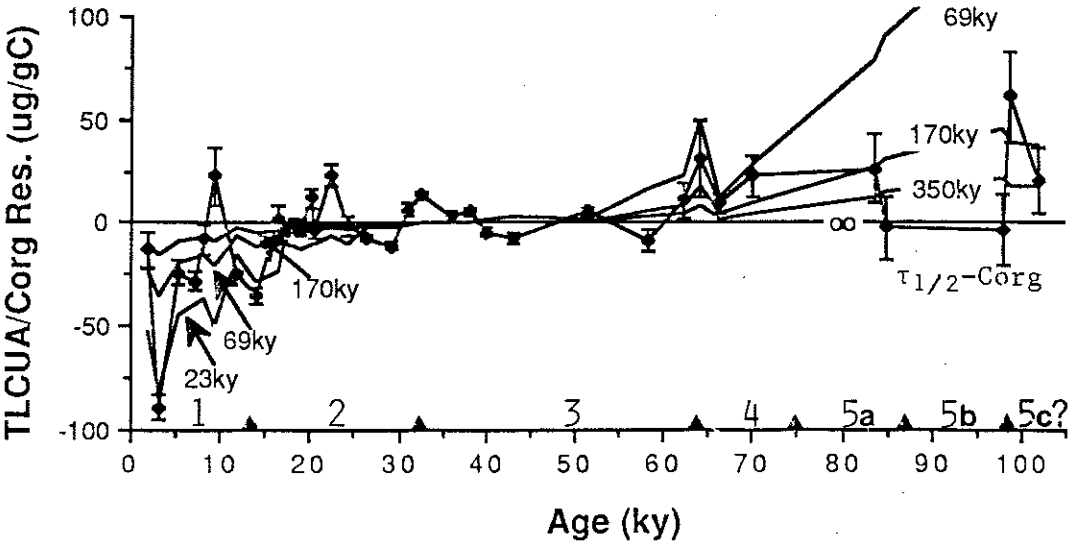
Fig. 3.4.a. Total C_{37-39} alkenone/C_{org} versus $\delta^{13}C$-C_{org} graph with superimposed least squares regression line approximation to average of 0-96 kyb mixing line) and time-dependent family of isopleths of constant first-order C_{org} decay half-lives ($\tau_{1/2_1}$).

Fig. 3.4.b. Time series of total C_{37-39} alkenone/C_{org} values with superimposed family of isopleths of constant first-order C_{org} decay half-lives ($\tau_{1/2_1}$) deviations (residuals) from linear least squares approximation to average (0 - 96 kybp) mixing line (same residuals as in Fig. 3.4.a).

Fig. 3.4.c. Time series of total C_{37-39} alkenone/C_{org} $\delta^{13}C$-C_{org} residuals with superimposed family of isopleths of constant first-order C_{org} decay half-lives ($\tau_{1/2}^{1}$).


TLCUA/Corg (ug/gC)
Delta C13-Corg (o/oo PDB)
69ky
170ky
350ky
oo
170ky
69ky
23ky
τ1/2-Corg


TLCUA/Corg (ug/gC)
Age (ky)
69ky
170ky
350ky
oo
170ky
69ky
23ky
τ1/2-Corg
1
2
3
4
5a
5b
5c?


TLCUA/Corg Res. (ug/gC)
Age (ky)
69ky
170ky
350ky
oo
170ky
69ky
23ky
τ1/2-Corg
1
2
3
4
5a
5b
5c?

idealized model previously discussed. If the observed total C_{37-39} alkenone/C_{org} versus $\delta^{13}C$-C_{org} linear regression line and the observed $\delta^{13}C$-C_{org} record are substituted for the model marine biomarker/C_{org} concentration ratio versus fractional marine/terrigenous composition of the sedimentary organic carbon and the "sawtooth" proxy $\delta^{13}C$-C_{org} record, respectively, we obtain:

$$M_D = \frac{34 * \delta^{13}C\text{-}C_{org} + 920}{\exp(-k_1(t-32))} \quad \text{for } (32 \leq t \leq 96) \qquad (6)$$

$$M_D = \frac{34 * \delta^{13}C\text{-}C_{org} + 920}{\exp(k_2(32-t))} \quad \text{for } (0 \leq t \leq 32) \qquad (7)$$

where,

$\delta^{13}C$-C_{org} = observed carbon isotopic composition of the sedimentary organic carbon at time t, and M_D, k_1, k_2, t are as previously defined.

The superposition of the family of isopleths of constant C_{org} remineralization rates (k) overlays the general trend of increasing linear regression residuals with increasing $\delta^{13}C$-C_{org} values (Fig. 3.4.a). Over the time spans of 0 to 32 ky and 32 to 96 ky, C_{org} remineralization constants of 0.004–0.03 ky^{-1} and 0.004–0.008 ky^{-1}, respectively, reproduce the general residual trends from the average mixing (linear regression) line. The remineralization constants correspond to C_{org}-decay half-lives ($t_{1/2}$ C_{org}) of 35 to 170 ky and 87 to 170 ky, respectively. However, the difference between the first-order organic carbon remineralization constants (k_1) in the younger (0 to 32 kybp) sediments ($k_1 \cong 0.012$ ky^{-1}) and in the older sediments ($k_2 \cong 0.006$ ky^{-1}) is not considered

significant at the present level of approximation; the average remineralization is sufficient for present purposes. The average C_{org} remineralization rate constant over the 0 to 96 ky interval ($k_1^{avg} = 0.012$ for $0 \leq t \leq 32$ky, and $k_2^{avg} = 0.06$ for $32 \leq t \leq 96$) and the previously noted ranges for k is 0.0072 ky^{-1}, which corresponds to a $t_{1/2}$-C_{org} of ~140 ky. These constants correspond well to the first-order remineralization rate constant of 0.0061 ky^{-1} and C_{org}-decay half-time of 100 ky derived from a first-order linear regression fit to the DSDP 619 C_{org} concentration time series (Chapter 2). This decay half-life (10^2ky) is bracketed by C_{org}-decay half-lives of ~10^0ky in Recent Long Island Sound sediments (Berner, 1980) and 10^3ky in Quaternary eastern equatorial sediments (Müller, et al., 1983).

A family of isopleths of constant C_{org} remineralization rates ($k_{1,\ldots n}$) overlies the total C_{37-39} alkenone/C_{org} time series (Fig. 3.4.b) and the residual time series (Fig. 3.4.c), reproducing the general features of the observed trends. The total C_{37-39} alkenone/C_{org} versus $\delta^{13}C$-C_{org} residual time series (Fig. 3.4.c) shows a generally increasing trend which is consistent with the remineralization of C_{org}.

If the residual trend were due only to diagenetic remineralization of C_{org}, the residual total C_{37-39} alkenone/C_{org} record should follow the isopleths of constant C_{org} remineralization rate. Large deviations from the general diagenetic trend (spikes) may be due to source changes; that is, the total C_{37-39} alkenone/C_{org} input ratio for any given $\delta^{13}C$-C_{org} value may have changed in time. In

this case, the total alkenones from prymnesiophyte phytoplankton may have been composed of a variable proportion of the accumulated marine sedimentary organic carbon over time. Positive deviations from the general diagenetic trend would indicate that the total C_{37-39} alkenones composed a larger proportion of the marine C_{org} than expected from the average total C_{37-39} alkenone/C_{org} versus $\delta^{13}C$-C_{org} relationship (Fig. 3.4.c); negative deviations would indicate less alkenone per unit marine C_{org} than the average ratio.

The 24-Ethylcholesterol/C_{org} Sedimentary Record

The 24-ethylcholesterol/C_{org} time series for the Pigmy Basin core (DSDP 619) is shown (Fig. 3.5.a) (24-ethylcholesterol = 24-ethyl-cholest-5-en-3ß-ol). The general features of the time series are low values (~30 µg/gC) in the last interglacial isotope substages (5a-b), with increasing values through stage 4 to maximal values (~90 µg/gC) in isotope stage 3. The 24-ethylcholesterol/C_{org} values generally decrease from stage 3 through stage 2 to low values (~20 µg/gC) in stage 1. Preceding the two local total C_{37-39} alkenone/C_{org} concentration maxima at the isotope stage 4-to-3 and 2-to-1 transitions (fig. 3.2.a) are local 24-ethylcholesterol/C_{org} maxima.

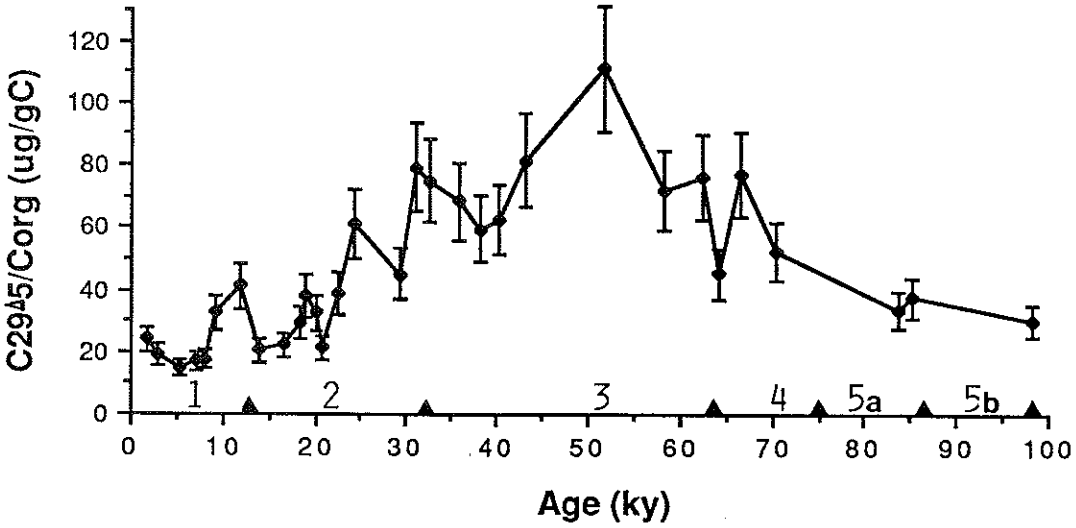
A cross correlation plot of 24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} (Fig. 3.5.b) shows that the organic carbon-normalized biomarker concentration and stable carbon isotopes are to a first approximation linearly-related ($P = 0.0033$, $r^2 = 0.26$, $n = 31$). That is, the diagenetically altered values of 24-ethylcholesterol/-C_{org} is inversely proportional to the sedimentary organic carbon

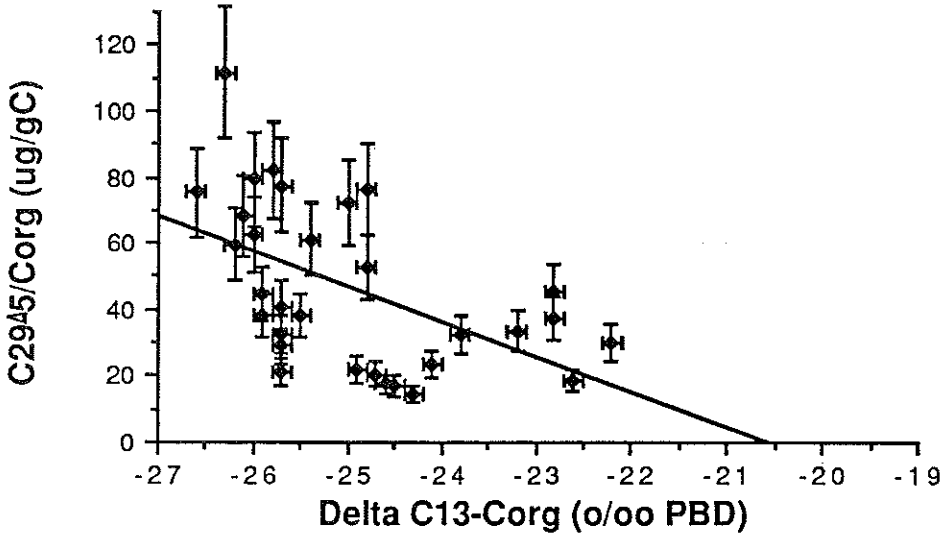
isotopic composition. As previously noted, the $\delta^{13}C$-C_{org} and N/C records of DSDP 619 are consistent with a sedimentary mixture of C_3-photosynthetic terrigenous and marine plants (Chapter 2). The linear relationship of 24-ethylcholesterol/C_{org} and $\delta^{13}C$-C_{org} indicates that 24-ethylcholesterol is a proportional indicator of preserved terrigenous organic carbon in the Pigmy Basin. The projection of the 24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} regression line to the zero 24-ethylcholesterol/C_{org} value gives an estimate of the carbon isotopic composition of the marine end member over the last ~100 ky in the Pigmy Basin. In a recent review article, 24-ethylcholesterol was shown to have significant terrigenous and marine sources (Volkman, 1986). However, 24-ethylcholesterol appears to be preferentially preserved under the same diagenetic conditions if it has a terrigenous rather than a marine source in the Peru upwelling zone at 15°S (Volkman, et al., 1987). By the linear least squares methods previously noted, the marine carbon isotopic end member was determined to be $-20.6 \pm 2.1‰$ PDB. The marine end members projected from the analysis of three other 4-desmethyl sterols discussed below range between -20.5 and $-21.7‰$. The (24-ethylcholesterol/C_{org}) projected marine carbon isotopic end member is (within its estimate of variation) undifferentiable from Gulf of Mexico surface sediment $\delta^{13}C$-C_{org} values (~$-19‰$ to $-22‰$ PDB) which are interpreted as dominantly of a marine origin (Sackett and Thompson, 1963; Parker et al., 1972; Northam et al., 1981; Hedges and Parker, 1976). For comparison, the average ($\pm 1\sigma$) of 10 species of C_3-photosynthetic marine phytoplankton is $-18.9 \pm 2.5‰$

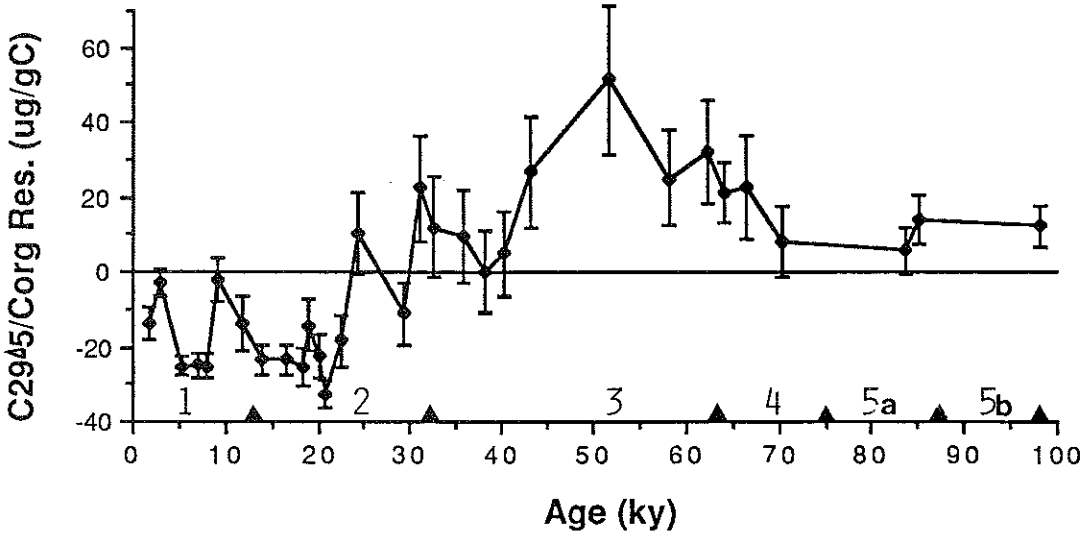
Fig. 3.5.a. Time series of 24-ethylcholesterol/C_{org}.

Fig. 3.5.b. 24-Ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. The least squares regression line is $-11 \cdot \delta^{13}C$-$C_{org} - 220$ ($P < 0.001$, $r^2 = 0.26$, $n = 31$).

Fig. 3.5.c. Time series of 24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} linear regression residuals.


C29Δ5/Corg (ug/gC)
120
100
80
60
40
20
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


C29Δ5/Corg (ug/gC)
120
100
80
60
40
20
0
-27
-26
-25
-24
-23
-22
-21
-20
-19
Delta C13-Corg (o/oo PBD)


C29Δ5/Corg Res. (ug/gC)
60
40
20
0
-20
-40
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

(Smith and Epstein, 1971). As previously noted for the estimate of variation of the terrigenous $\delta^{13}C$-C_{org} end member, diagenetic splaying of the 24-ethylcholesterol/C_{org} values from the projected $\delta^{13}C$-C_{org} end member increases the linear least squares estimate variation in the marine end member (see Figs. 3.6.a and 3.7.a). As with the estimation of variation in the terrigenous $\delta^{13}C$-C_{org} end member, and since the marine end member is extrapolated by 1.5°/$_{oo}$ beyond the least negative $\delta^{13}C$-C_{org} value, a more elaborate estimation of the end member variation is unwarranted.

The time series of 24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} linear regression residuals shows a generally sinusoidal trend (Fig. 3.5.c). If the decay rate of 24-ethylcholesterol (k_s) relative to the C_{org} decay rate (k_c) were small ($k_s/k_c \rightarrow 0$), the 24-ethylcholesterol/C_{org} ratio for a given $\delta^{13}C$-C_{org} value would increase with time. Therefore, the 24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} residuals would be expected to increase with time. The generally increasing 24-ethylcholesterol/C_{org} residual values with time are consistent with more rapid remineralization of C_{org} than diagenetic loss of 24-ethylcholesterol.

Terrigenous Biomarker/C_{org} versus $\delta^{13}C$-C_{org} Diagenesis Model

A simple, first-order diagenetic model for terrigenous organic biomarker compounds is developed here to as an illustration of how to assess the apparent diagenetic alteration of the 24-ethylcholesterol/C_{org} record. The model and its assumptions are analogous to the diagenetic model developed above for the marine

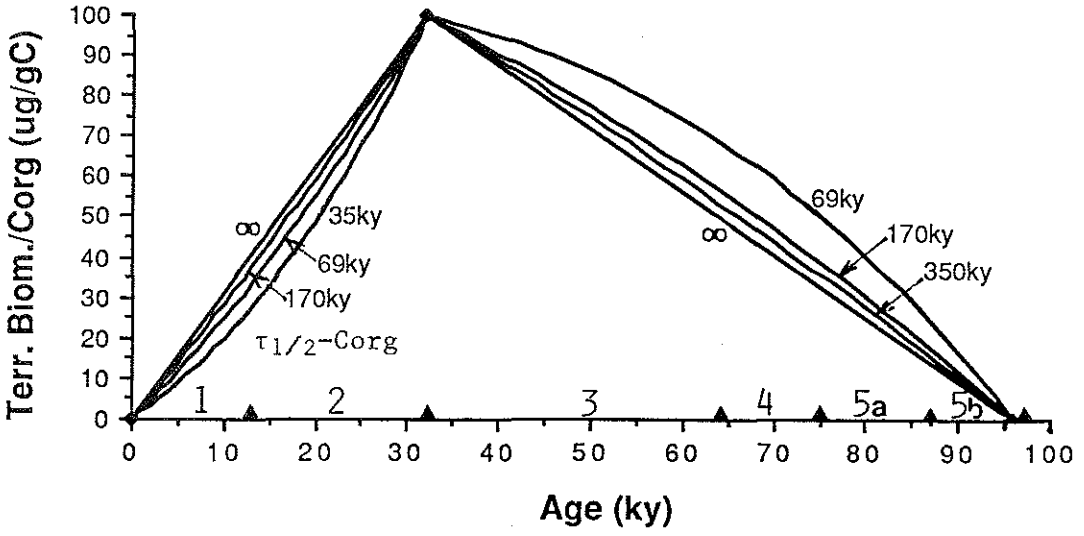
biomarkers (total C_{37-39} alkenones). First-order decay of C_{org} with time is assumed. 24-Ethylcholesterol is assumed to be well preserved relative to sedimentary organic carbon. This latter assumption is substantiated as indicated by the significance (P = 0.0033) of the linear regression of 24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org}. There is, however, circumstantial evidence (temporally-increasing stanol/stenol ratios) that 24-ethylcholest-5- en-3ß-ol and 24-ethylcholesta-5,22-dien-3ß-ol are undergoing diagenetic losses as they are hydrogenated to their respective stanols (Chapter 4), but the loss is relatively small (~15°/$_o$ over 100 ky) if the stenol → stanol tranformation is considered a closed system. In any case, the latter conjecture is implicit in using sterol ratios to infer degradation rates. The effect of the diagenetic transformation of 24-ethyl-cholesterol on the assessment of the C_{org} remineralization will be discussed in a following section.

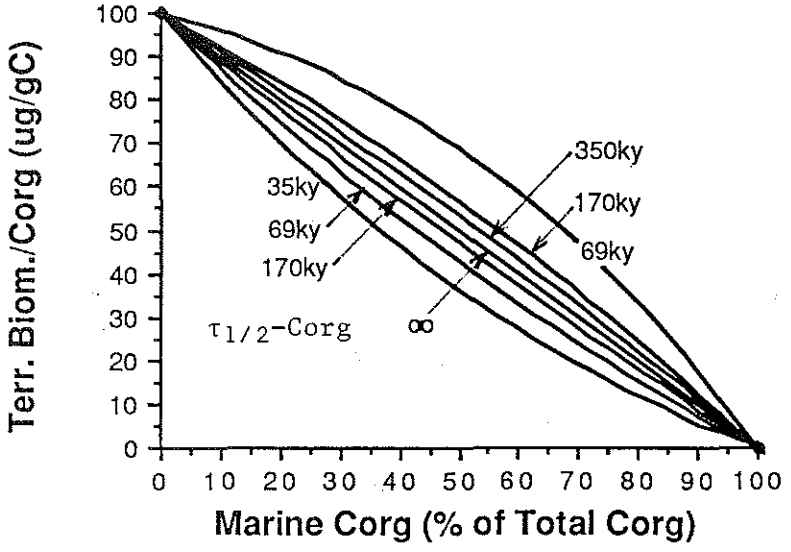
As a simple demonstration of the effect of C_{org} remineralization on a terrigenous biomarker/C_{org} record, the "sawtooth" (Broecker and van Donk, 1970) proxy $\delta^{13}C$-C_{org} record is assumed as in the marine biomarker/C_{org} case. In the absence of C_{org} remineralization, the organic-carbon normalized concentration of a well-preserved terrigenous organic biomarker compound is assumed to be linearly related to the co-occurring $\delta^{13}C$-C_{org} values, with biomarker/C_{org} ratios ranging from 0 to 100 units (Fig. 3.6.a). The line (marked "∞") may be considered the original biomarker/C_{org} concentration record for the time span 32 to 96 kybp. The effect of C_{org} decay on the terrigenous organic biomarker compound/C_{org} versus $\delta^{13}C$-C_{org}

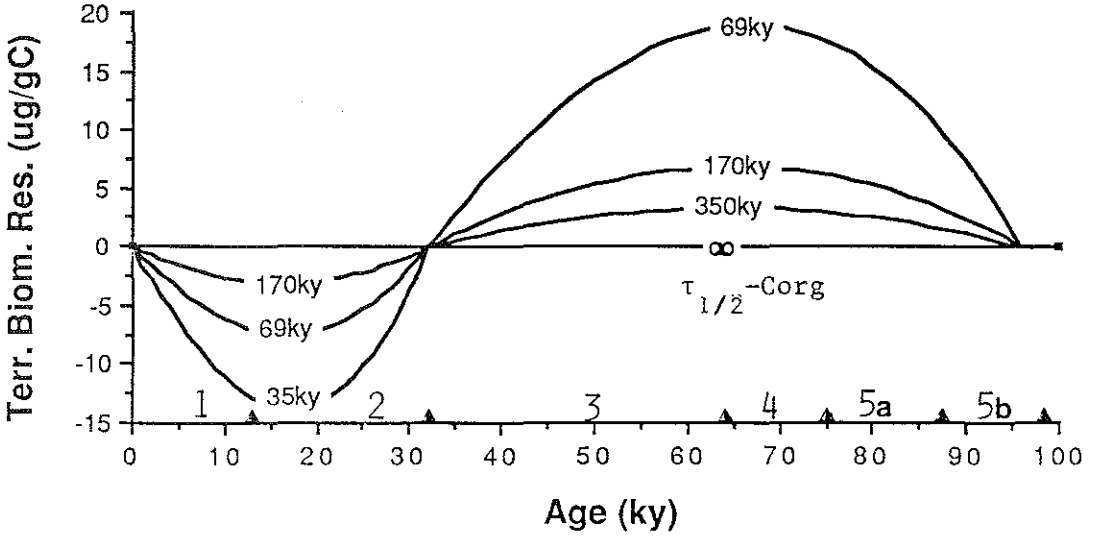
Fig. 3.6.a. Time series of ideal terrigenous biomarker/C_{org} with superimposed effects of first-order C_{org} remineralization with various decay constants (k_1; k = 0 implies no C_{org} remineralization). This idealized model normalizes C_{org} remineralization to zero at 32 kybp and is further explained in text.

Fig. 3.6.b. Ideal terrigenous biomarker/C_{org} versus fractional marine (versus terrigenous) C_{org} composition (proxy $\delta^{13}C$-C_{org} measure) with superimposed effects of first-order C_{org} decay half-lives ($\tau^{1}_{1/2}$) (explained in Fig. 3a).

Fig. 3.6.c. Time series of ideal terrigenous biomarker/C_{org} residuals (diagenetically-altered (k_1) value minus original unaltered (k = 0) value).


Terr. Biom./Corg (ug/gC)
Age (ky)
∞
35ky
69ky
170ky
τ1/2-Corg
69ky
170ky
350ky
1
2
3
4
5a
5b


Terr. Biom./Corg (ug/gC)
Marine Corg (% of Total Corg)
350ky
170ky
69ky
35ky
69ky
170ky
τ1/2-Corg
∞


Terr. Biom. Res. (ug/gC)
Age (ky)
69ky
170ky
350ky
∞
τ1/2-Corg
170ky
69ky
35ky
1
2
3
4
5a
5b

relationship is given by the equation:

$$M_f = \frac{M_{t1}}{\exp\left(-k\ t\ \frac{64}{100}\right)} \qquad (8)$$

$$M_{T1} = 150 - \frac{100}{64}\ t \qquad (9)$$

where,

M_f = terrigenous biomarker/C_{org} concentration (μg/gC) ($0 \leq M_f \leq 100$)

k = first-order decay rate of sedimentary organic carbon (ky^{-1}),

t = age (ky) ($32 \leq t \leq 96$), and

M_{T1} = °/$_o$ terrigenous C_{org} or (100-M_m)°/$_o$ marine C_{org}

= terrigenous biomarker/C_{org} ratio as a function of time in the absence of C_{org} remineralization ($0 \leq M_m \leq 100$).

A family of curves which diverges from and then converges to the average source line is generated with increasing time (from 32 to 96 ky), decay rates, and fractional (percentage) marine C_{org} composition (Fig. 3.6.a).

The rationale for the mathematics of 0-to-32 ky portion of the terrigenous organic biomarker compound/C_{org} versus $\delta^{13}C$-C_{org} versus C_{org} remineralization model is analogous to the model marine biomarker/C_{org} model described above (eqns. 3 and 4):

$$M_f = \frac{M_{t2}}{\exp\left(-k \bullet (32 - t)\right)}, \text{ and} \qquad (10)$$

$$M_{t2} = \frac{100}{32} t \qquad (11)$$

where,

t = age (ky) ($0 \leq t \leq 32$),

M_{t2} = terrigenous biomarker/C_{org} ratio as a function of time in the absence of C_{org} remineralization for $0 \leq t \leq 32$ ky, and M_f, k are as previously defined.

The general features of the effect of C_{org} remineralization on the terrigenous biomarker/C_{org} versus $\delta^{13}C$-C_{org} relationship are shown in Figure 3.6.b. The superimposition of C_{org} remineralization on the "sawtooth" record of terrigenous source (24-ethylcholesterol/-C_{org}) variations from 0 µg/gC at 96 kybp to 100 µg/gC at 32 kybp and to 0 µg/gC at the present results in a concave down family of C_{org} remineralization half-life isopleths over the time span of 96 to 32 kybp and a concave up family of C_{org} remineralization half-life isopleths over the period of 32ky to the present. Under ideal conditions of terrigenous biomarker/C_{org} versus $\delta^{13}C$-C_{org} mixing and first-order C_{org} remineralization, the remineralization constants (k) can be read from the graph (Fig. 3.6.b). The C_{org} remineralization half-time was described above (eqn. 5).

The effect of the diagenetic remineralization of C_{org} on the idealized "sawtooth" terrigenous biomarker/C_{org} time series record is shown in Fig. 3.6.a.

Increasing decay constants and temporal differences from the 32 ky time point result in positive deviations from the average source line for $t > 32$ ky and negative deviations for $t < 32$ ky. The deviations

from the average source line (i.e., k=0) represent the diagenetic alteration of the 24-ethylcholesterol/ C_{org} record. The diagenetic features of the terrigenous biomarker/C_{org} record are (1) positive deviations over the time span of 32 to 96 ky due to the faster relative decay of C_{org} versus 24-ethylcholesterol/C_{org}, and (2) negative deviations for the less than average decay of C_{org} over the time span of 0 to 32 ky.

Remineralization of sedimentary organic carbon and transformation of the terrigenous organic biomarker compound results in a diagenetic skewing of the terrigenous organic biomarker compound/C_{org} record. The extent of the diagenetic alteration of the terrigenous organic biomarker compound record can be assessed by a terrigenous organic biomarker compound versus $\delta^{13}C$-C_{org} residual model analogous to that developed for the marine organic biomarker compound/C_{org} versus $\delta^{13}C$-C_{org} residuals. The linear regression residuals (diagenetically altered terrigenous organic biomarker compound/C_{org} minus the average mixing line value) of a terrigenous organic biomarker compound versus $\delta^{13}C$-C_{org} relationship (Fig. 3.6.c) when plotted as function of time form the residual time series. The main features are (1) positive residuals over the 96 to 32 ky time span and negative residuals over the 32 to 0 ky time period, and (2) increasing residual absolute values with increasing C_{org} remineralization rate (k) at given $\delta^{13}C$-C_{org} values at given points in time.

Application of the Terrigenous Biomarker/Corg versus $\delta^{13}C$-C_{org} Model

The diagenetic effect of the decay of C_{org} on the 24-ethylcholesterol/C_{org} record can be assessed in an analogous fashion to the first-order remineralization model applied to the total C_{37-39} alkenone/C_{org} record. The observed 24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} linear regression line and the observed $\delta^{13}C$-C_{org} record can be substituted for the model terrigenous organic biomarker compound concentration ratio versus fractional marine/terrigenous composition of the sedimentary organic carbon and the sawtooth proxy $\delta^{13}C$-C_{org}. Doing this, we obtain:

$$M_D = \frac{-11 * \delta^{13}C\text{-}C_{org} - 220}{\exp(-k_1(t-32))} \quad \text{for } (32 \leq t \leq 96 \text{ ky}) \tag{12}$$

$$M_D = \frac{-11 * \delta^{13}C\text{-}C_{org} - 220}{\exp(k_2(32-t))} \quad \text{for } (0 \leq t \leq 32 \text{ ky}) \tag{13}$$

where,

$\delta^{13}C$-C_{org} = observed carbon isotopic composition of the sedimentary organic carbon at time t, and

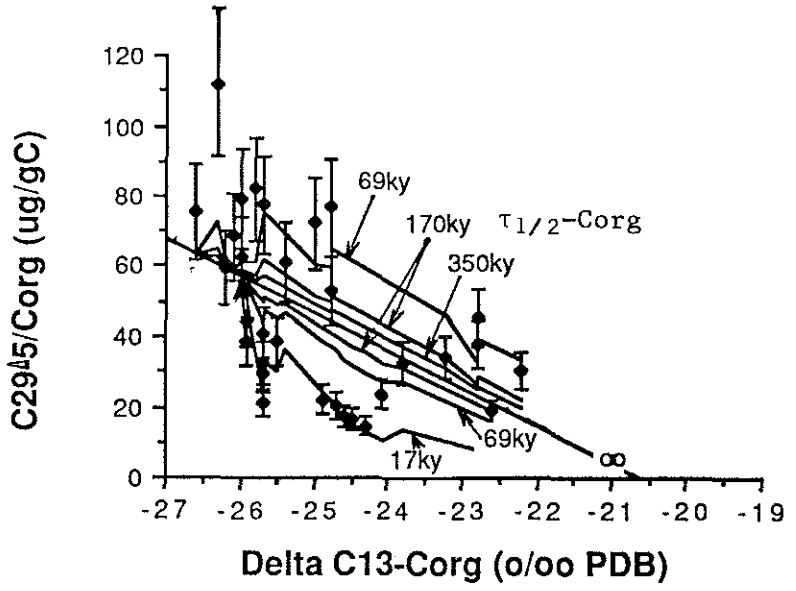
M_D, k_1, k_2, and t are as previously defined.

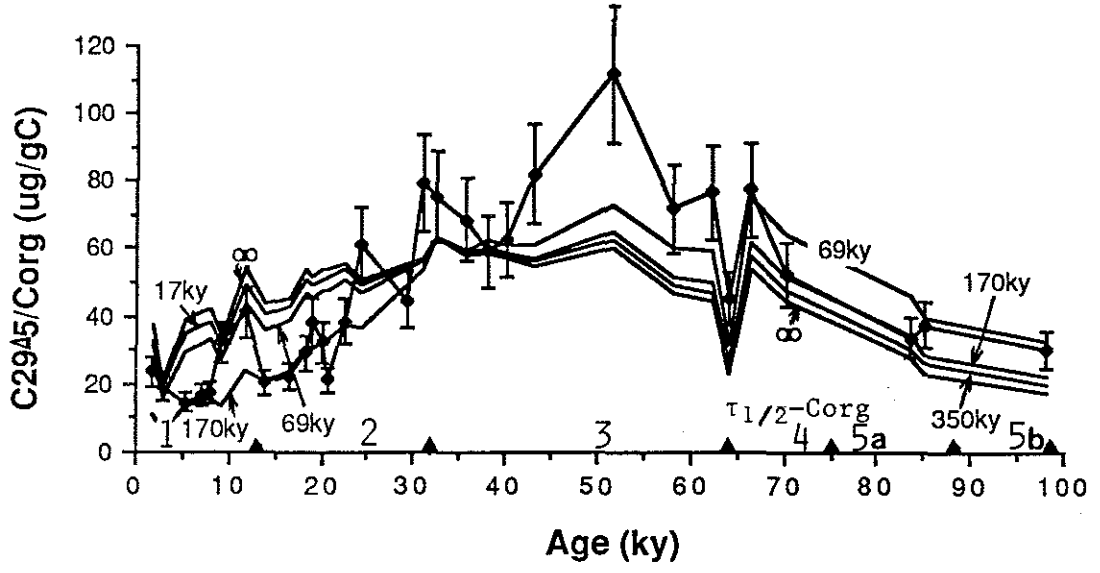
The family of isopleths of constant C_{org} remineralization rates (k) overlies the general lens-shaped pattern of residuals around the regression line (Fig. 3.7.a). The lack of data points in the center of the diagonal lens is consistent with faster remineralization of sedimentary organic carbon than the diagenetic transformation of the

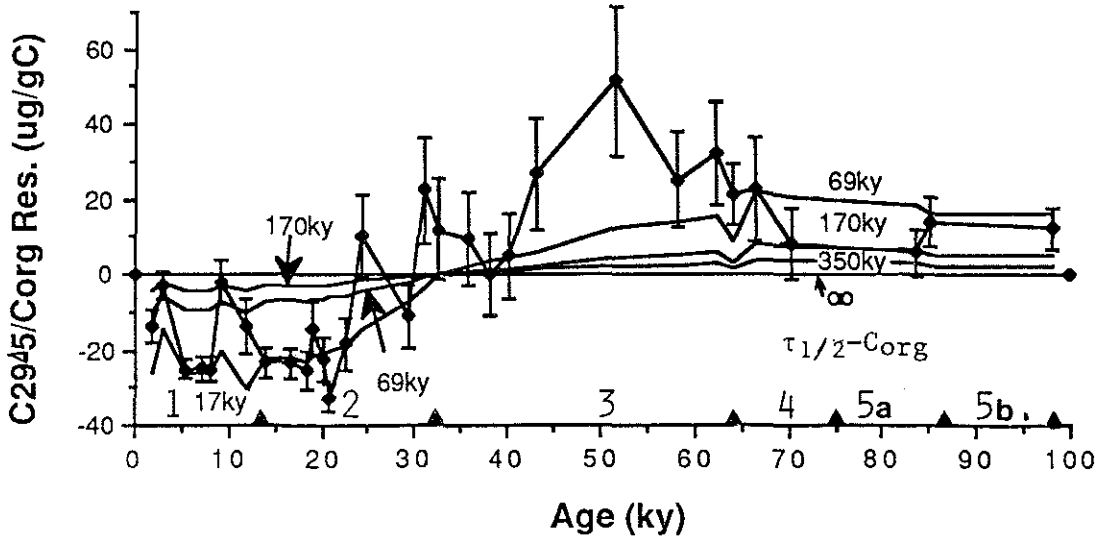
Fig. 3.7.a. 24-Ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} graph with superimposed least squares regression line (approximation of 0-96 kyb mixing line) and time-dependent family of isopleths of constant first-order C_{org} decay half-lives ($\tau^{1}_{i/2}$).

Fig. 3.7.b.. Time series of 24-ethylcholesterol/C_{org} values with superimposed family of isopleths of constant first-order C_{org} decay half-lives ($\tau^{1}_{i/2}$) deviation residuals from linear least squares approximation to average (0 - 96 kybp) mixing line (same residuals as in Fig. 7b).

Fig. 3.7.c. Time series of 24-ethylcholesterol/C_{org} $\delta^{13}C$-C_{org} residuals with superimposed family of isopleths of constant first-order C_{org} decay half-lives ($\tau^{1}_{i/2}$).


C2945/Corg (ug/gC)
120
100
80
60
40
20
0
69ky
170ky
τ1/2-Corg
350ky
69ky
17ky
∞
-27 -26 -25 -24 -23 -22 -21 -20 -19
Delta C13-Corg (o/oo PDB)


C2945/Corg (ug/gC)
120
100
80
60
40
20
0
17ky
∞
69ky
170ky
∞
1
170ky
69ky
2
3
τ1/2-Corg
4
5a
350ky
5b
0 10 20 30 40 50 60 70 80 90 100
Age (ky)


C2945/Corg Res. (ug/gC)
60
40
20
0
-20
-40
170ky
69ky
170ky
350ky
∞
τ1/2-Corg
1
17ky
2
69ky
3
4
5a
5b
0 10 20 30 40 50 60 70 80 90 100
Age (ky)

sterol (24-ethylcholesterol). This general pattern of residual distribution also occurs for four other individual sterols (cholesterol, 22-(E)-dehydrocholesterol, brassicasterol, and campesterol).

The C_{org} remineralization rates which span the range of most of the residuals can be read from the 24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} graph with the superposed isopleths (Fig. 3.7.a). These C_{org} remineralization constants (k) correspond to C_{org} decay half-times ($t_{1/2}$-C_{org}) of 87 to 17 ky and 116 to 33.2 ky. The average C_{org} remineralization constant over the 0 to 96 ky time span ($k = 0.024\ ky^{-1}$ for $0 \leq t \leq 32$ ky, and $k = 0.013\ ky^{-1}$ for $32 \leq t \leq 96$ ky) is ~$0.017\ ky^{-1}$, which corresponds to a $t_{1/2}$-C_{org} ~40 ky. The average C_{org} remineralization half-time by this analysis is much smaller than that of either the diagenetic model fit to total C_{37-39} alkenone/C_{org} versus $\delta^{13}C$-C_{org} data ($t_{1/2}$-$C_{org} \cong 140$ ky) or the first-order fit to the C_{org} concentration record ($t_{1/2}$-C_{org} = 100 ky). The apparent discrepancy of the best fitting range of C_{org} remineralization constants (k) will be discussed in the context of time series of 24-ethylcholesterol/C_{org} and 24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} linear regression residuals.

A family of isopleths of constant C_{org} remineralization rates (k) is superimposed over the observed 24-ethylcholesterol/C_{org} time series (Fig. 3.7.b). The observed 24-ethylcholesterol/C_{org} values are generally within ranges of the aforementioned remineralization rate in isotope stages 5a-b, 4, the latter part of 2, and 1.

Relatively large positive deviations (residuals) above the C_{org} remineralization isopleths occur in isotope stages 3 (~64 ky) and through the middle of stage 2 (~20 ky) (Fig. 3.7.c).

Hydraulic Particle Sorting as Potential Cause of High Glacial 24-Ethylcholesterol/C_{org} Residuals

In the case of the total C_{37-39} alkenone/C_{org} versus $\delta^{13}C$-C_{org} residual time series (Figs. 3.2.c and 3.3.c) the general increasing trend was attributed to the remineralization of C_{org} and the excursions from the general trends were attributed to source changes. Terrestrial organic biomarker compounds are subjected to at least one more process than marine compounds. Prahl (1985) has shown that a number of individual terrigenous organic biomarker compounds were selectively concentrated in different sedimentary regimes on the southern Washington continental shelf and slope. Wood plant tissue lignin, plant wax n-alkanes, and combustion-derived polycyclic aromatic hydrocarbons were associated with large average grain size sediment particles, while non-woody plant tissue lignins, fossil phenanthrenes, and diploptene were relatively concentrated in smaller average grain size particles. The compositional variations were attributed to differential hydraulic sorting of the particles carrying organic biomarker compounds in the marine sedimentary environment.

The large positive 24-ethylcholesterol/C_{org} deviations above the residual diagenetic trend from 25-65kybp may be due to a 24-ethylcholesterol/C_{org} source variation caused by sediment particle sorting. A time series of non-biogenic clastic particle size

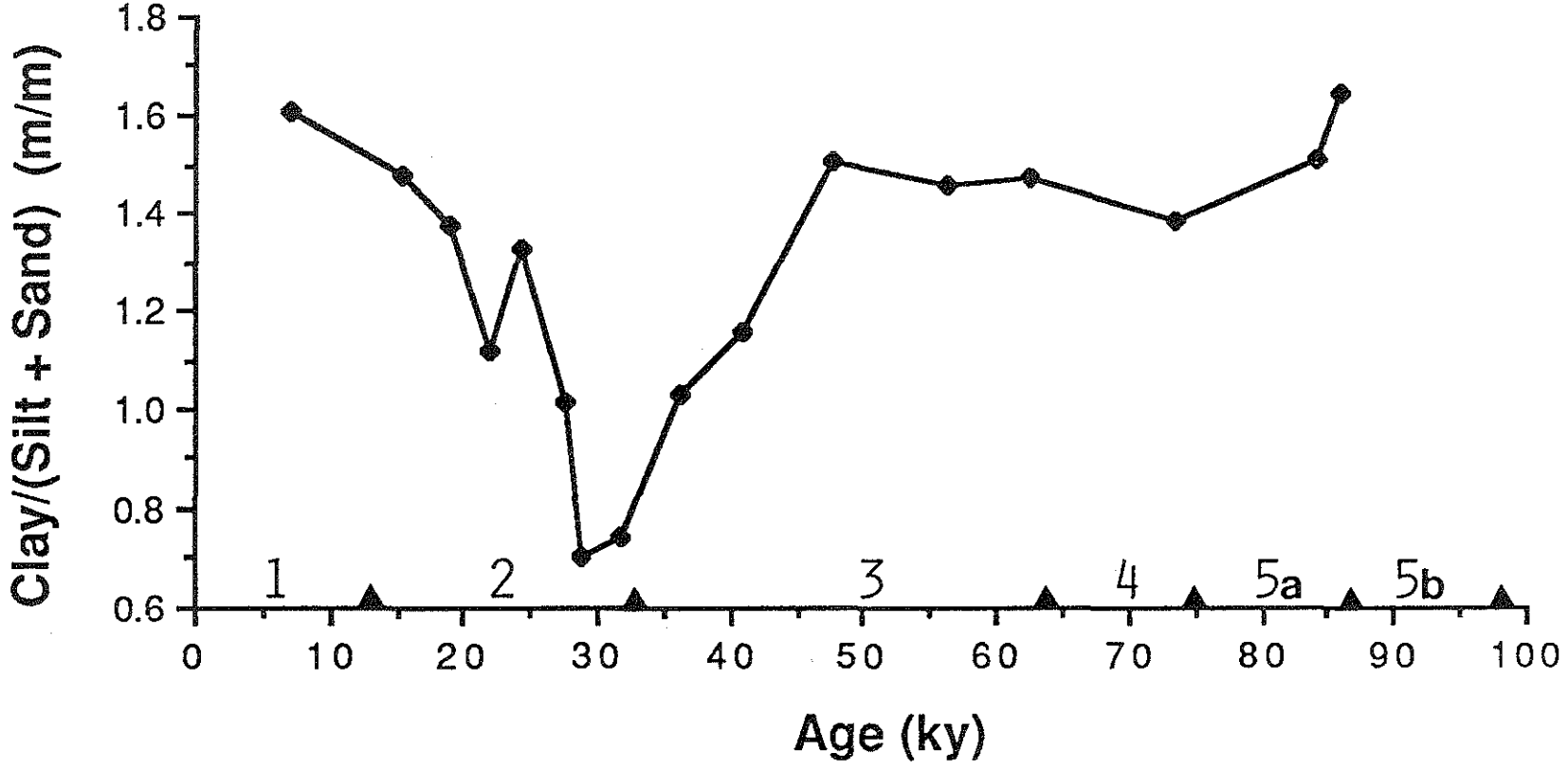
ratios ((clay/(silt+sand)) in the Pigmy Basin Core 619 shows generally finer sediments from 85–48 kybp and 15–5 kybp than during the intervening 48–15 kybp glacial period (Fig. 4.8) (calculated from Tieh et al., 1986). Particle sizes were coarsest from ~32–29 kybp. These observations are consistent with proportionally more coarser sediment particles reaching the Pigmy Basin during glacial low sea level stands than in interglacial high sea level stands. The organic carbon stable isotopic and N/C records show that the sedimentary organic matter during the time span of large positive deviations (~20–64 kypb) was predominantly (80–100°/$_{o}$) from terrigenous sources. The hydraulic particle sorting mechanism probably has little effect on marine-derived particles which fall through the water column as compared to terrigenous organic particles which are sorted with the terrigenous sediment enroute to depositional basins. There are at least three explanations which are consistent with the differential hydraulic particle sorting hypothesis which could account for the large positive deviations above the model residual trend.

First, the observation that the 24-ethylcholestan-3ß-ol/-24-ethylcholest-5-en-3ß-ol (stanol/stenol) transformation ratio increases with $\delta^{13}C$-C_{org} values is consistent with smaller terrigenous organic-bearing particles undergoing proportionally more transformation per unit time than larger particles (Chapter 4). More and larger terrigenous organic particles would be expected to be delivered to the glacial Gulf of Mexico with its higher terrigenous sedimentary organic carbon input and higher sedimentation and continental erosion rates (Chapter 2). Larger organic particles (with

lower active surface area per unit volume than smaller particles) arriving during glacial periods in the hemipelagic Gulf of Mexico would presumably be less susceptible to diagenetic alteration than smaller particles, resulting in higher 24-ethylcholesterol/C_{org} ratios at given $\delta^{13}C$-C_{org} values. The clay fraction of DSDP 619 forms a significantly smaller fraction relative to silt plus sand in glacial times, demonstrating a coarsening of sediment input during the erosive sedimentary regime of low sea level stands (Tieh, et al., 1986). Prahl (pers. comm.) has analogously observed that lignin oxidation products derived from an onshore-to-offshore transect of surface sediment particles have increased acid-to-aldehyde ratios with decreasing particle size. The lignin polymers carried on smaller, more hydraulically-sorted particles were interpreted to have been susceptible to proportionally more diagenetic transformation than larger particles. Another possibility is that the smaller lignin particles, besides having a larger surface area per unit volume, may be older than the larger particles and are thus more heavily diagenetically altered.

Secondly, the remobilization of sediments containing partially degraded organic constituents eroded from the continental shelves into the glacial hemipelagic Pigmy Basin may account for the high 24-ethylcholesterol/C_{org} residuals from ~25-65 kybp. The organic matter in continental shelf deposits during the last high sea level stand (isotope stage 5) was probably partially degraded during deposition there (also see Chapter 2). When sea levels dropped in glacial stages, the partially degraded sedimentary organic matter

Fig. 3.8 Time series of clay/(silt + sand) ratio (m/m) showing clastic particle coarsening during oxygen isotope stages 2 and 3 (sediment size data from Tieh et al. (1986); chronology from Chapter 2).


Clay/(Silt + Sand) (m/m)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

could have been eroded into the hemipelagic and pelagic basins. If 24-ethylcholesterol were degraded more slowly than sedimentary organic carbon, the greater degree of degradation (than the average ~0-100 kybp Pigmy Basin samples) would result in unusually high 24-ethylcholesterol/C_{org} values which would have high positive residual values.

Thirdly, the large positive deviations above the residual trend may be due to differential hydraulic sorting of 24-ethylcholesterol relative to sedimentary organic carbon. That is, proportionally more 24-ethylcholesterol than bulk terrigenous sedimentary organic carbon is transported to the hemipelagic Pigmy Basin in glacial low sea level stands than in interglacial high sea level stands. Since coarser, hydraulically-sorted terrigenous sediment is transported to the Pigmy Basin in glacial low sea level stands than in interglacial high sea level stands, the accompanying terrigenous organic matter may also have been hydraulically sorted. The observation of significant positive 24-ethylcholesterol/C_{org} deviations in the ~20-64 ky time span would be consistent with 24-ethylcholesterol-bearing particles being hydraulically sorted more similiar to a coarse fraction of sediment than the bulk sedimentary organic carbon. That is, the sedimentary organic carbon may be relatively more concentrated in the finer sediment particles than 24-ethylcholesterol which occurs in plant membranes.

The suggestion that differential hydraulic particle sorting is an operative mechanism in the western Gulf of Mexico is supported by measurements of lignin oxidation products and sedimentary organic

carbon isotopic composition. Hedges and Parker (1976) showed that there were high organic carbon-normalized concentrations of lignin phenols ($\lambda \equiv$ (mg (vanillyl + syringyl) phenols)/100 mg $C_{org} \cong 2$-6) on the continental shelf of the western Gulf of Mexico. Deep water surface sediment samples contained only ~1°/$_o$ of land-derived organic matter found in nearby continental shelf deposits. Hedges and Van Geen (1982) found that continental slope and abyssal Pleistocene sedimentary deposits in the western Gulf of Mexico and the Washington State coast contained only ~5°/$_o$ of the organic carbon-normalized lignin concentration found in sediments with similar $\delta^{13}C$-C_{org} values from adjacent continental shelves. They concluded that the two most likely explanations for differences were either that the ^{13}C-depleted organic matter was of marine origin as had been suggested by Rogers and Koons (1969) or that Pleistocene sediments were markedly depleted in vascular plant remains when they were deposited; sedimentary degradation of lignin was considered a less likely possibility in those sedimentary environments. The suggestion that Pleistocene ^{13}C-depleted organic matter was derived from marine sources is unlikely considering the approximate linear mixing of fifty-five $\delta^{13}C$-C_{org} and N/C paired analyses of Pigmy Basin DSDP 619 samples (Chapter 2). The linear mixing line is consistent with mixing of terrigenous and marine C_3-photosynthetic organic matter.

Lignin phenol (λ) measurements (Hedges and Ertel, 1982) on two Pigmy Basin DSDP 619 samples (J. Ertel, pers. comm.) give less than 3°/$_o$ of lignin expected at similar $\delta^{13}C$-C_{org} values in the modern Gulf of Mexico continental shelf sediments by comparison with

results of Hedges and Parker (1976). These low values (~3°/$_{oo}$) are comparable to those observed in Pleistocene deep-sea sediments from the western Gulf of Mexico (~5°/$_{oo}$) by Hedges and Van Geen (1982).

A third possibility to explain the apparent lignin depletion is diagenetic lignin degradation on a 10^{-1}-10^{5}y time scale. Significant (up to ~95°/$_{oo}$) diagenetic degradation of lignin components in Late Quaternary sedimentary sediments seems unlikely in light of a number of studies. Hedges, et al. (1988) found that the annual lignin flux through the Dabob Bay water column bracketed its sediment accumulation rate, indicating insignificant degradation on an annual to decadal time scale. Hedges and Mann (1979) found no evidence for appreciable lignin degradation over periods up to ~400 y on the Washington continental shelf and slope. Hedges et al. (1982) concluded that the acid/aldehyde ratio of lignin phenols from an 11-m Late Quaternary Lake Washington sediment core indicated only minimal in situ degradation over ~13 ky. Ishiwatari and Uzaki (1987) further supported the theory that lignin phenols are relatively diagenetically refractory by analyzing them over 700 m (0.6 My) in a Lake Biwa sediment core. Their work suggests that lignin phenols have a decay half-time of ~400 ky under Lake Biwa's sedimentary diagenetic conditions, assuming that the lignin decrease is due to its in situ degradation.

While ^{13}C-depleted sedimentary organic carbon and lignin degradation seem to be unlikely causes for the paucity of lignin phenols in Pleistocene Gulf of Mexico deep-sea sediments, differential hydraulic sorting remains a plausible mechanism for decoupling of

particles carrying woody plant tissue lignins from those bearing bulk sedimentary organic carbon, and, therefore, the decoupling of the Pleistocene-to-Holocene lignin-to-$\delta^{13}C$-C_{org} relationship.

An alternative explanation to differential hydraulic sorting of sedimentary particles causing the large positive 24-ethylcholesterol/C_{org} deviation is a climatically-induced 24-ethylcholesterol versus terrigenous C_{org} source change. Heusser (1986) found large variations in non-reworked pollen assemblages in the Pigmy Basin hydraulic piston core (DSDP 619) between glacial and interglacial stages. Glacial stages were characterized by higher relative frequency (percentage of total) of coniferous (pine (Pinus), spruce (Picea spp.), hemlock (Tsuga canadensis), and fir (Abies sp.)) than deciduous pollens. Oak (Quercus spp.) pollen frequency was higher in interglacial stages than in glacial stages. If higher 24-ethylcholesterol/C_{org} values were generated at given $\delta^{13}C$-C_{org} values from sediments emanating from coniferous forested regions than from to deciduous forested regions, the large positive 24-ethylcholesterol/C_{org} deviations above the diagenetic residual trend (Fig. 3.7.c) may be caused by a glacial-to-interglacial floral source change. The floral source change affecting the 24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} relationship may be due to the coniferous-deciduous arboreal change or other contemporaneous floral changes in grasses, understory plants, etc. The floral source change mechanism is presently not as well substantiated as the hydraulic particle sorting; however, it needs to be further investigated.

Limitations on the Biomarker/C_{org} versus $\delta^{13}C$-C_{org} Diagenesis Model

The basic tenet of the present biomarker/C_{org} versus $\delta^{13}C$-C_{org} diagenesis model is that a significant linear relationship must exist between a given organic carbon-normalized biomarker concentration and the carbon isotopic composition of the sedimentary organic carbon ($\delta^{13}C$-C_{org}) for a given sample suite. If there are characteristic $\delta^{13}C$-C_{org} marine and terrigenous end-members for that sample suite, and an organic biomarker compound from a known terrigenous or marine source, then a linear relationship between those parameters indicates that the biomarker/C_{org} ratio can be used as a quantitative indicator of the preserved fraction of either terrigenous or marine organic carbon, respectively. A time series of biomarker/C_{org} concentration ratios which are linearly related to the bulk sedimentary organic carbon composition ($\delta^{13}C$-C_{org}) is a temporal record of terrigenous or marine preserved sedimentary organic carbon. The most significant limitation on the use of organic carbon-normalized biomarker concentrations as a quantitative method in paleoceanography is the ability to establish a quantitative relationship between the normalized biomarker concentrations and the sedimentary organic carbon isotopic composition. The present model only quantitatively assesses the linear relationship between biomarkers/C_{org} and $\delta^{13}C$-C_{org} in terms of the significance ($P < 0.05$) a linear correlation coefficient (r^2). More sophisticated modelling techniques should allow statistical assessment of the second-order processes which are

superimposed upon the simple linear correlation model. With that, biomarker compounds (perhaps, the long-chain n-alkanes discussed below) which are sufficiently differentially labile from total sedimentary organic carbon that their first-order linear correlation to $\delta^{13}C$-C_{org} is insignificant may be determined to useful quantitative organic matter tracers. In testing for a linear relationship, the general source (i.e., terrigenous or marine) of the organic biomarker compound must be known. If the presumed linear relationship does not exist as tested by a statistical criterion for linearity, then two major possibilities should be considered. First, it is possible that the chosen organic biomarker concentration simply does not occur in constant ratio relative to its bulk (terrigenous or marine) organic carbon phase; that is, there was a source change. The distribution of some phytoplankton species (e.g., coccolithophorids, diatoms, and dinoflagellate) is known to be episodic on monthly to annual time scales and longer-term episodic source changes may be recorded in the sediment column. Therefore, the organic carbon-normalized record of their input may not demonstrate a readily discernible relationship to bulk marine organic carbon record. The second possibility that could preclude the establishment of linearity is differential rates of organic biomarker and sedimentary organic carbon diagenesis.

Differential diagenetic remineralization of sedimentary organic carbon and transformation of organic biomarker compounds complicates the quantitative interpretation of biomarkers in the sedimentary record. The application of a first-order biomarker/C_{org}

remineralization model (eqns. 1 and 3) is a systematic attempt to differentiate the general diagenetic trends superimposed on the organic biomarker concentration/C_{org} record from episodic excursions. The episodic excursions are presumably caused by source-related changes in the organic matter input ratio.

An ideal, diagenetically unaltered record of organic carbon-normalized biomarker would be one in which biomarker was preserved (or degraded) in direct proportion to its contemporaneously deposited bulk organic carbon source. That is, the biomarker and the bulk sedimentary organic carbon would diagenetically degrade at the same rate and a linear biomarker/C_{org} versus $\delta^{13}C$-C_{org} relationship would be maintained. Despite the diagenetic alteration of the biomarker and sedimentary organic carbon records, their ratio would remain quantitative proportional indicators of preserved terrigenous and marine sedimentary organic carbon input.

An additional factor influencing the preserved biomarker/C_{org} record is the relative diagenetic lability of terrigenous and marine sedimentary organic carbon.

Towards A General Biomarker/C_{org} Diagenesis Model

There is an increasing body of evidence which indicates that terrigenous organic matter may be more refractory to sedimentary degradation than marine organic matter (Prahl, et al., 1980; DeBaar, et al., 1983; Volkman, et al., 1987; Hedges, et al., 1988). In the biomarker/C_{org} remineralization model presented here (eqns. 1 and 3), terrigenous sedimentary organic carbon, marine sedimentary organic carbon, and mixtures thereof were implicitly assumed to decay at

constant rates ($k_{1,\ldots n}$) over specified time spans (0 to 32 ky, 32 to 96 ky). In principle, a more general solution of the biomarker/-C_{org} remineralization equations (eqns. 1 and 3) should allow the determination of the terrigenous C_{org} and marine C_{org} remineralization constants (k_t, k_m). The quantitative determination of the relative labilities of terrigenous and marine organic carbon would be aided by selection of particularly refractory biomarker compounds like lignin or, perhaps, the alkenones. The form of the equation to determine terrigenous and marine remineralization rates from a biomarker/C_{org} versus $\delta^{13}C$-C_{org} cross correlation plot is as follows:

$$M = \frac{M_d\,(\delta(t))}{\exp(-k_t t) + \frac{(\exp(-k_m t)-\exp(k_t t))\delta(t)}{\Delta\delta_{tm}}} \qquad (14)$$

where,

M = biomarker compound/C_{org} (µg/gC),

M_d = biomarker compound/C_{org} as a function of $\delta^{13}C$-C_{org}, (µg/gC), $\delta(t)$ = $\delta^{13}C$-C_{org} (°/$_{oo}$) as a function of time t,

t = age (ky),

k_t = first-order decay constant of terrigenous sedimentary organic carbon (ky^{-1}),

k_m = first-order decay constant of marine sedimentary organic carbon (ky^{-1}),

$\Delta\delta_{tm} = \delta^{13}C\text{-}C_{org}^{tem} - \delta^{13}C\text{-}C_{org}^{mem}$ (°/$_{oo}$),

tem = terrigenous end member, and

mem = marine end member.

Scaling an equation of this form (eqn. 14) by adjustment of the marine and terrigenous first-order decay constants to sufficiently constrained biomarker/C_{org} and carbon isotopic ($\delta^{13}C$-C_{org}) data would allow an assessment of the relative diagenetic labilities of marine and terrigenous sedimentary organic carbon. If, for example, marine C_{org} were remineralized faster than terrigenous C_{org} ($k_m > k_t$) under similar sedimentary diagenetic conditions, the effect on a marine biomarker/C_{org} versus (proxy) $\delta^{13}C$-C_{org} cross correlation plot (e.g., Fig. 3.3.b) would be to splay upward the C_{org} remineralization isopleths proportionally more upon approaching the marine end-member than upon approaching the terrigenous end-member.

The deviations from the average mixing line (residuals) would be proportionally larger at the marine end-member than at the terrigenous end-member as the difference between marine and terrigenous sedimentary organic carbon decay constants increased (i.e., $k_m - k_t \rightarrow \infty$). The residuals ($M_{res}$) from the average mixing line are defined by:

$$M_{res} = M_d\,(\delta(t))\left[\left(\frac{1}{\exp(-k_t t) + \frac{[\exp(-k_m t) - \exp(k_t t)](\delta(t))}{\Delta\delta_{tm}}}\right) - 1\right] \qquad (15)$$

In the special case of general biomarker/C_{org} remineralization model (eqn. 14) in which marine and terrigenous sedimentary organic carbon decay at the same rate ($k_t - k_m = 0$), the general equation simplifies to the first-order remineralization models (eqns. 1 and 3).

The presumed source changes in the total alkenone/C_{org} residual record (Fig. 9) which deviate from the generally increasing diagenetic

trend are sufficiently large that application of the general biomarker/C_{org} versus $\delta^{13}C$-C_{org} model (eqn. 14) to these data would be inappropriate.

The most general form of the organic biomarker concentration/-C_{org} equation (14) would also account for the potential diagenetic loss of biomarker compounds. At the present level of approximation, there is no unambiguous manner to account for a biomarkers' diagenetic loss. The stenol → stanol transformation ratios observed in this Pigmy Basin sediment core are consistent with reduction of stenols to stanols; however, it has not been demonstrated that the observed (transient state) concentrations are representative of quantitative transformation of a given stenol to its stanol (Chapter 4). There are other factors which may influence the observed stenol/stanol ratios. The diagenetic reactions which may further transform the stanols and transformation of stenols to products other than stanols (Gagosian, et al., 1980) would affect the observed transformation ratios. In addition, the methodological limitations of sample extraction efficiency (Lee et al., 1979; Lee et al., 1980; de Leeuw, 1983) may also affect the transformation ratio.

Other Alcohols Significantly Related to Sedimentary Organic Carbon Isotopic Composition

The relationship of organic carbon-normalized concentrations of three other 4-desmethylsterols and the normal C_{26-32} even numbered alcohols relative to sedimentary organic carbon isotopic composition is examined here. Cholesterol (cholest-5-en-3ß-ol), 22-(E)-dehydrocholesterol (cholesta-5,22E-dien-3ß-ol), brassicasterol (24-methyl-

cholesta-5-en-3ß-ol), and campesterol (24-methylcholesta-5-en-3ß-ol) have both terrigenous and marine biological sources (Scheuer, 1973; Goad, 1977). The nC_{26-32} even numbered fatty alcohols with high even/odd indicies (2-10) are derived from higher plant sources (Eglinton et al., 1962; Kolattukudy, 1976; Simoneit, 1978) and have been used as tracers of terrigenous organic matter in marine sediments (Gagosian, 1975; Gagosian and Heinzer, 1979; Brassell and Eglinton, 1983a,b; MacKenzie et al., 1983; Volkman, 1986) and in the marine atmosphere (Gagosian and Peltzer, 1987).

Time series of organic carbon-normalized concentrations of cholesterol, 22-(E)-dehydrocholesterol, campesterol, brassicasterol and nC_{26-32} even fatty alcohols (Figs. 3.9-13.a) are similar to that for 24-ethylcholesterol (Fig. 3.5.a). The general features of the time series are low concentrations (~10-50°/$_{oo}$) in the interglacial isotope (sub)stages 5a-b and 1 compared to maximum concentrations reached in the middle of isotope stage 3. The organic carbon-normalized concentrations generally increase from the last interglacial stage 5a-b to the middle of stage 3 and then decrease into late isotope stage 1. In all four of the 4-desmethylsterol/C_{org} time series, local concentration maxima (2-4 times the preceding and succeeding values) are observed near the glacial-interglacial stage 2 boundary.

Cross correlation plots of organic carbon-normalized concentrations of cholesterol, 22-(E)-dehydrocholesterol, campesterol, brassicasterol and the nC_{26-32} even fatty alcohols versus sedimentary organic carbon isotopic composition are presented here (Fig. 3.9-13.b).

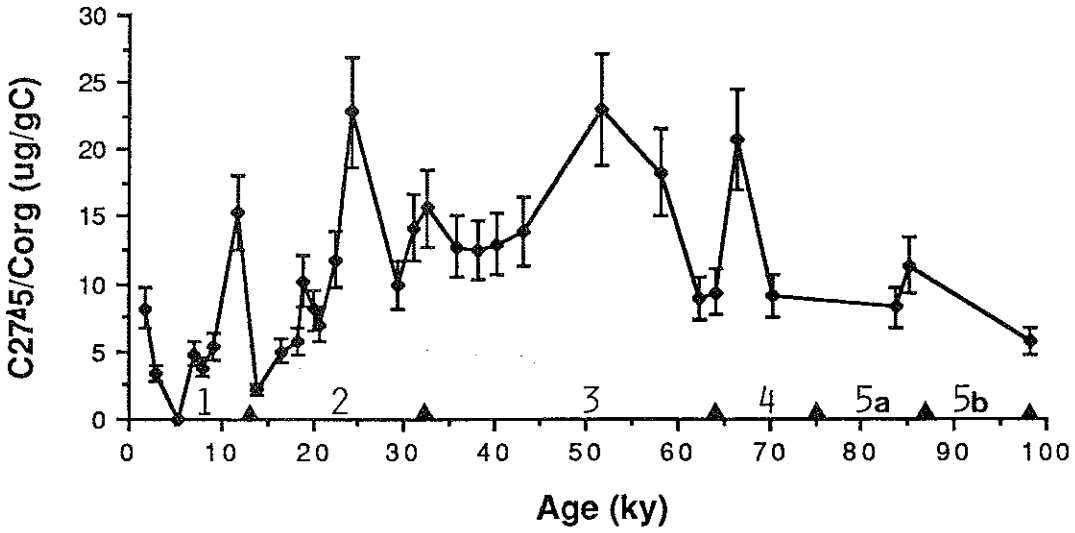
Application of the previously mentioned linear regression methods showed that these organic carbon-normalized organic biomarker compounds are to a first approximation ($P<0.05$) linearly related to sedimentary organic carbon isotopic composition. The linear relationship of cholesterol ($P=0.0039$), 22-(E)-dehydrocholesterol ($P=0.011$), campesterol ($P=0.016$), brassicasterol ($P=0.017$) and the nC_{26-32} even fatty alcohols ($P=0.045$) to $\delta^{13}C$-C_{org} indicates that these compounds are to a first approximation useful indicators of preserved terrigenous organic matter.

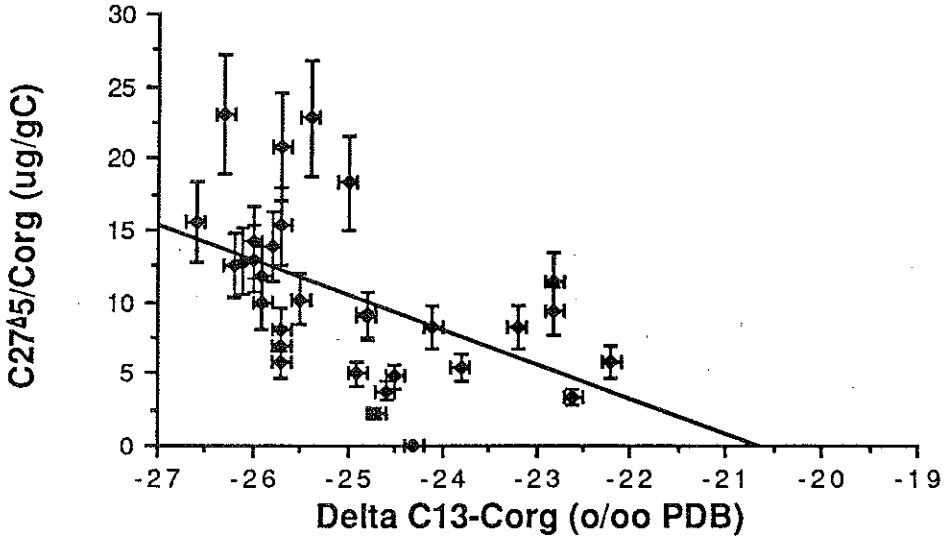
Time series of biomarker/C_{org} versus $\delta^{13}C$-C_{org} linear regression residuals for cholesterol (Fig. 9c), 22-(E)-dehydro-cholesterol (Fig. 3.10.c), campesterol (Fig. 3.11.c), brassicasterol (Fig. 3.12.c) and nC_{26-32} even fatty alcohols (Fig. 3.13.c) are presented below their respective concentration time series. All show a generally skewed sinusoidal trend similar to residual time series for 24-ethylcholesterol (Figs. 3.5.c and 3.7.c) and the idealized terrigenous biomarker (Fig. 3.6.c). Residual values are positive and generally increase to a maximum in the middle of stage 3. The residuals decrease and change their sign to negative values in the interval 40-20 kybp, whereafter they are generally negative. These residual trends are consistent with the effect of a higher sedimentary organic carbon remineralization rate than terrigenous organic biomarker transformation rate predicted by the idealized terrigenous biomarker/C_{org} model (eqns. 8-11 and Fig. 3.6.c) and observed for 24-ethylcholesterol (Figs. 3.5.c and 3.7.c). Generally high and positive residuals through intervals of 65-25 kybp similar to

Fig. 3.9.a Time series of cholest-5-en-3ß-ol/C_{org}.

Fig. 3.9.b. Cholest-5-en-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. The linear regression line is $-2.4 \bullet \delta^{13}C$-$C_{org} + 50$ ($P = 0.039$, $r^2 = 0.25$, $n = 31$).

Fig. 3.9.c. Time series of cholest-5-en-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} linear regression residuals.


C27 45/Corg (ug/gC)
30
25
20
15
10
5
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


C27 45/Corg (ug/gC)
30
25
20
15
10
5
0
-27
-26
-25
-24
-23
-22
-21
-20
-19
Delta C13-Corg (o/oo PDB)

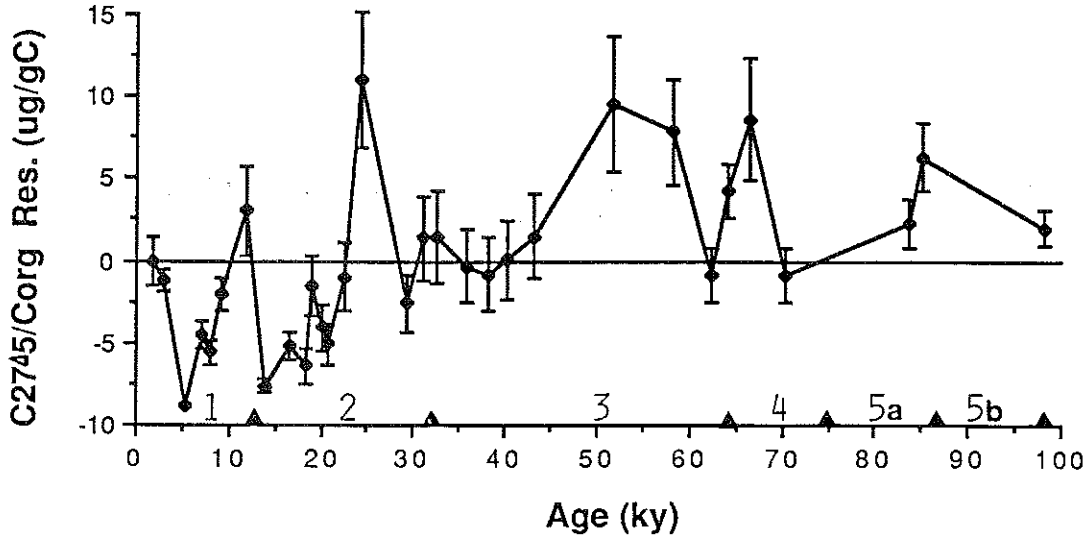
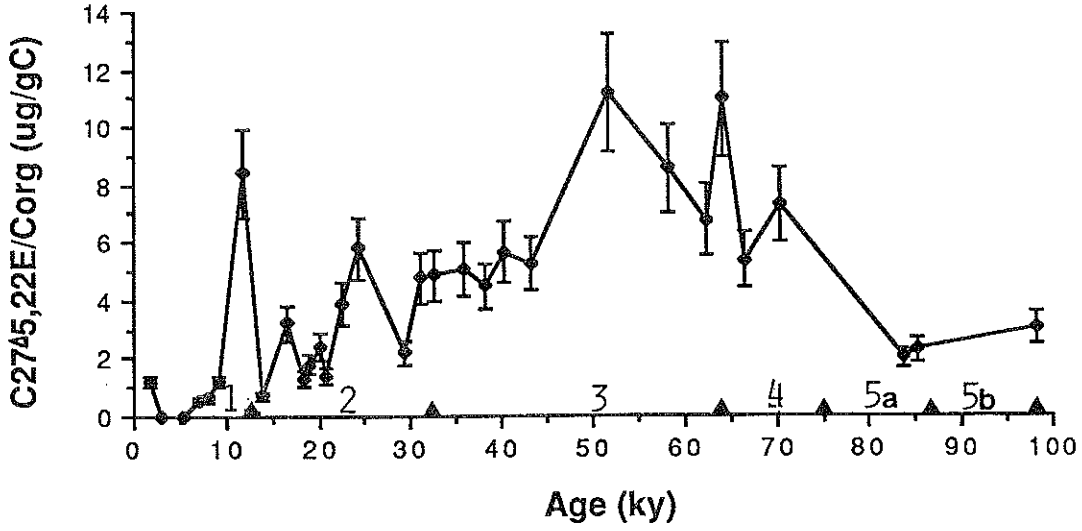
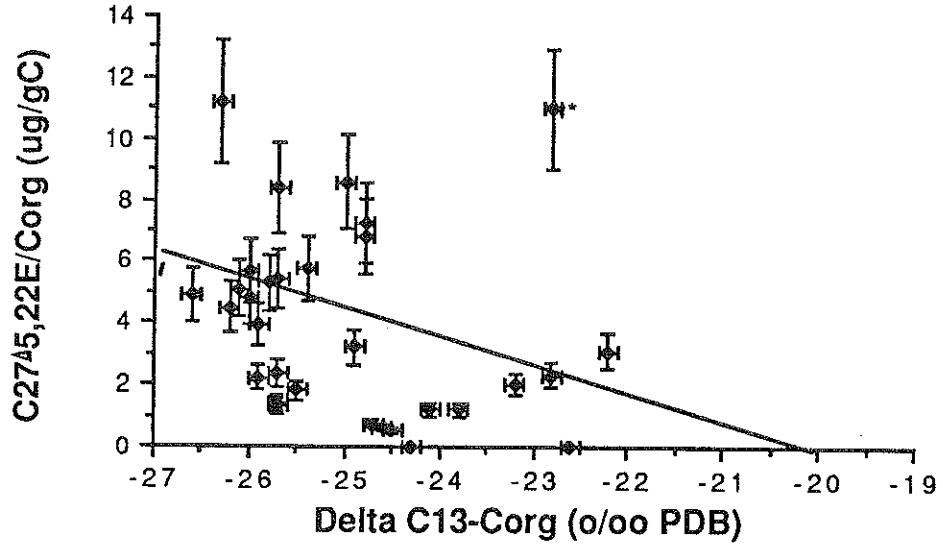

C27 45/Corg Res. (ug/gC)
15
10
5
0
-5
-10
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

Fig. 3.10.a. Time series of cholesta-5,22E-dien-3ß-ol/C_{org}.

Fig. 3.10.b. Cholesta-5,22E-dien-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. The linear regression line is $-1.1 \bullet \delta^{13}C$-$C_{org} + 50$ ($P = 0.011$, $r^2 = 0.21$, $n = 30$).

Fig 3.10.c. Time series of cholesta-5,22E-dien-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} linear regression residuals.


C27Δ5,22E/Corg (ug/gC)
14
12
10
8
6
4
2
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


C27Δ5,22E/Corg (ug/gC)
14
12
10
8
6
4
2
0
-27
-26
-25
-24
-23
-22
-21
-20
-19
Delta C13-Corg (o/oo PDB)

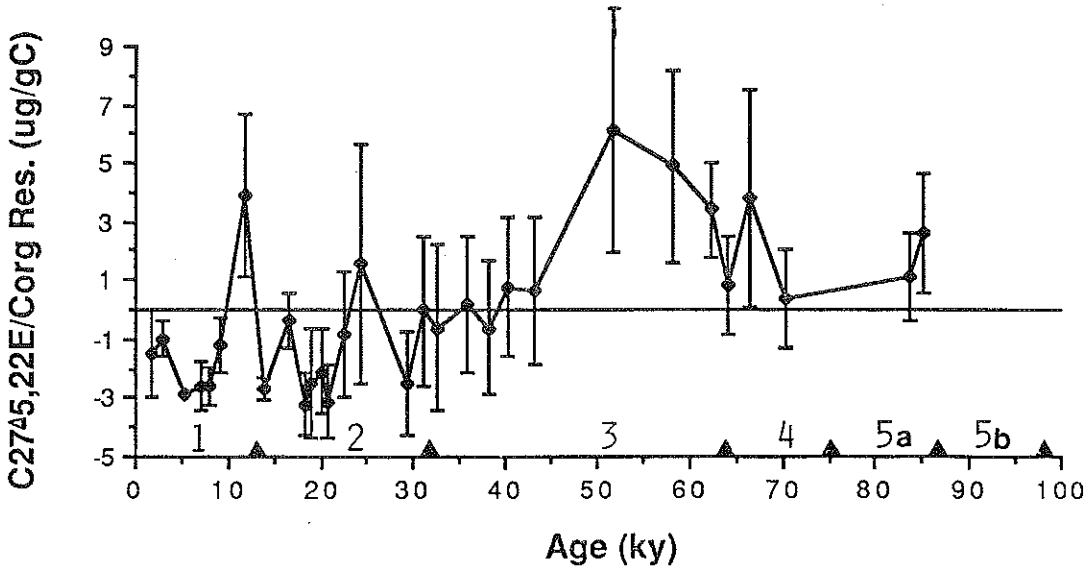
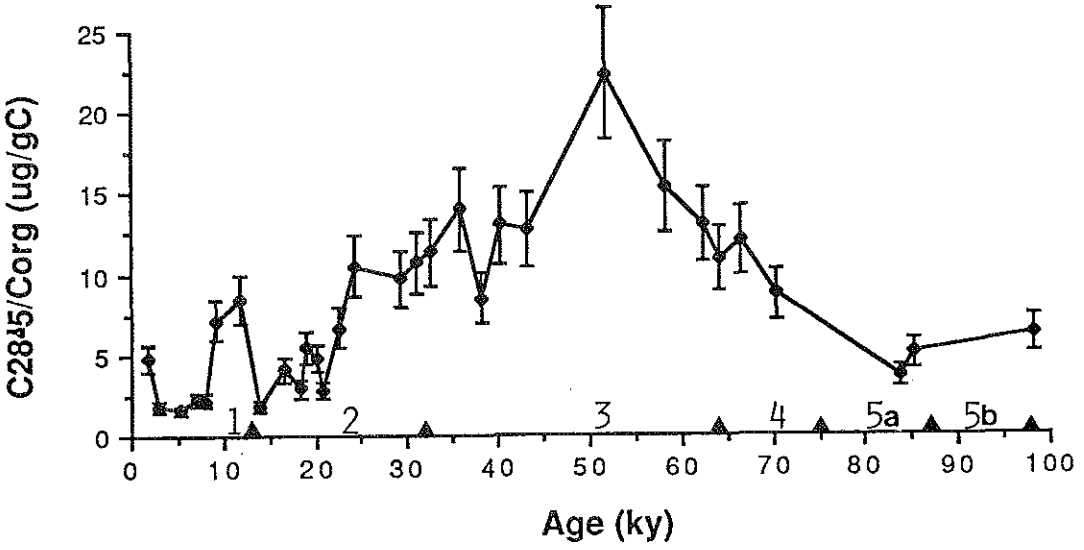
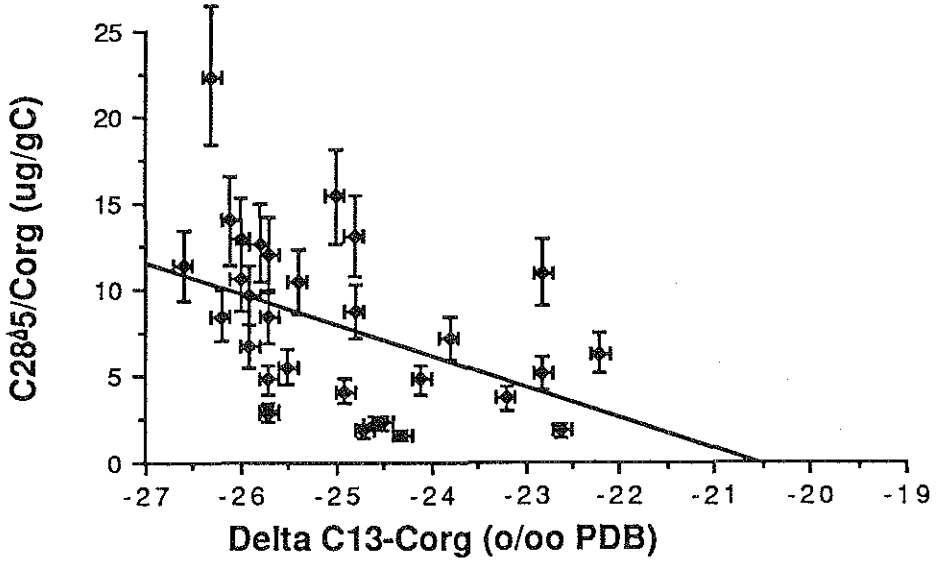

C27Δ5,22E/Corg Res. (ug/gC)
9
7
5
3
1
-1
-3
-5
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

Fig. 3.11.a. Time series of 24-methylcholesta-5-en-3ß-ol/C_{org}.

Fig. 3.11.b. 24-Methylcholesta-5-en-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. The linear regression line is $-1.8 \cdot \delta^{13}C$-C_{org} -36($P = 0.016$, $r^2 = 0.18$, $n = 31$).

Fig. 3.11.c. Time series of 24-methylcholesta-5-en-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} linear regression residuals.


C28Δ5/Corg (ug/gC)
25
20
15
10
5
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


C28Δ5/Corg (ug/gC)
25
20
15
10
5
0
-27
-26
-25
-24
-23
-22
-21
-20
-19
Delta C13-Corg (o/oo PDB)

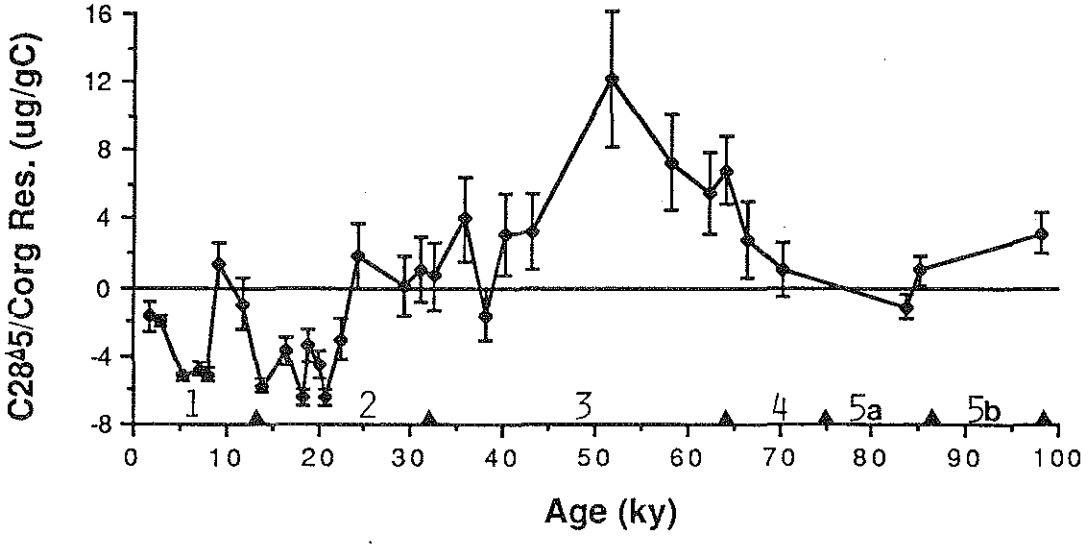
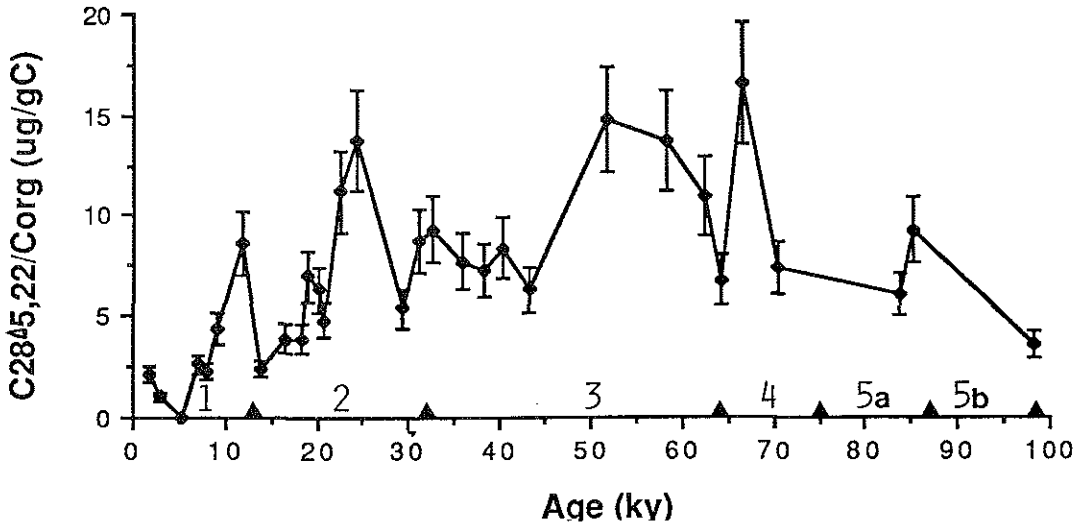
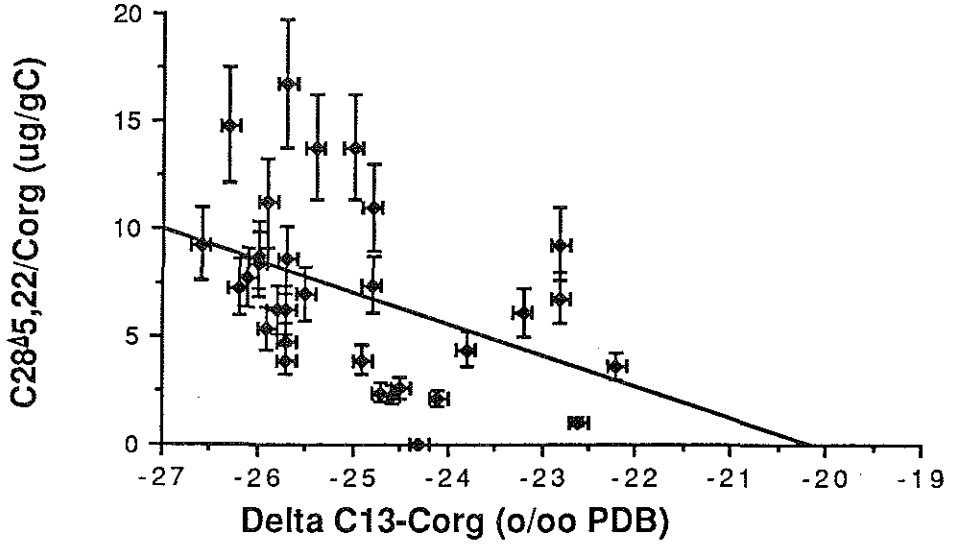

C28Δ5/Corg Res. (ug/gC)
16
12
8
4
0
-4
-8
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

Fig. 3.12.a. Time series of 24-methylcholesta-5,22-dien-3ß-ol/C_{org}.

Fig. 3.12.b. 24-Methylcholesta-5,22-dien-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. The linear regression line is $-1.5 \cdot \delta^{13}C$-$C_{org} + 30$ ($P = 0.017$, $r^2 = 0.18$, $n = 31$).

Fig. 3.12.c. Time series of 24-methylcholesta-5,22-dien-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} linear regression residuals.


C28Δ5,22/Corg (ug/gC)
20
15
10
5
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


C28Δ5,22/Corg (ug/gC)
20
15
10
5
0
-27
-26
-25
-24
-23
-22
-21
-20
-19
Delta C13-Corg (o/oo PDB)

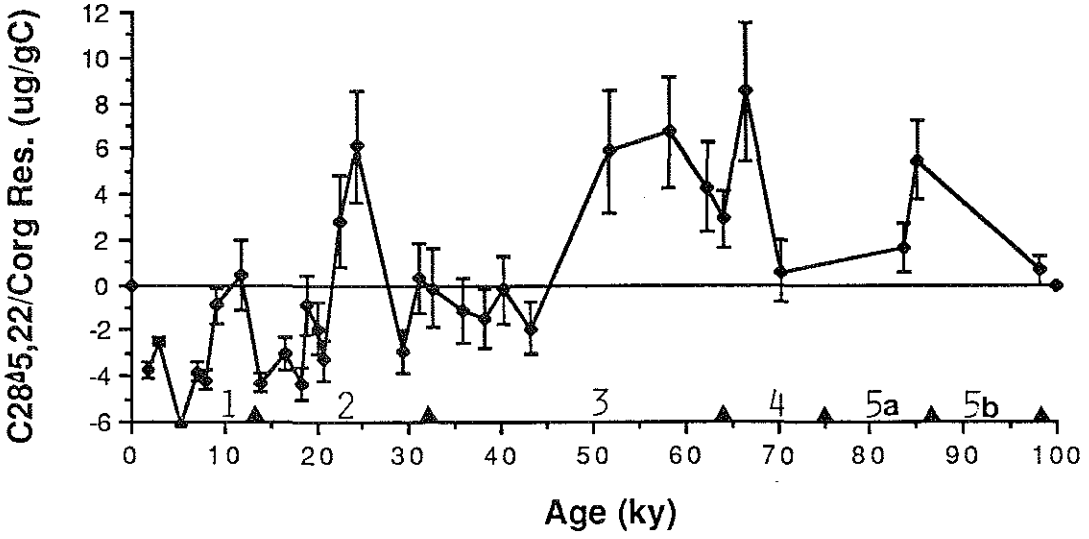
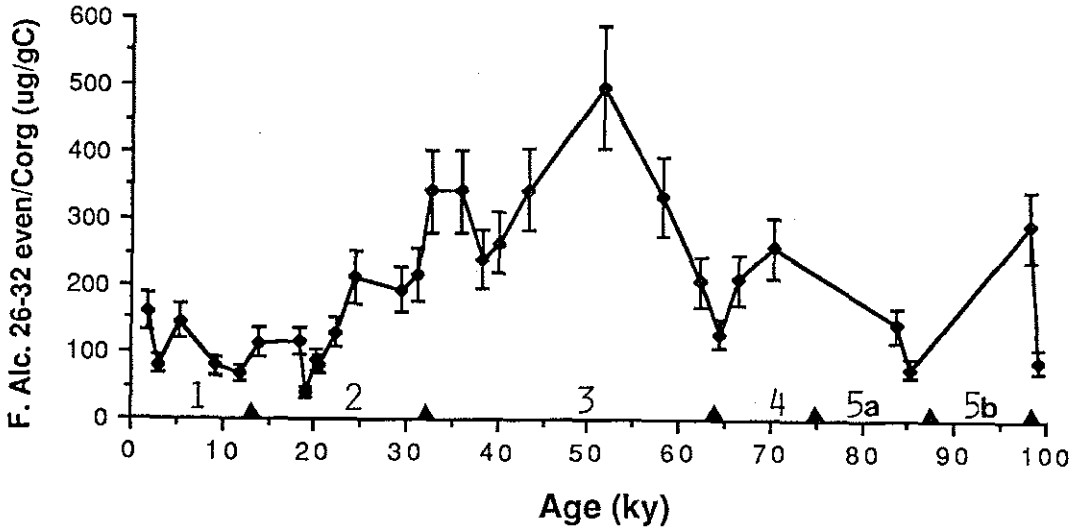
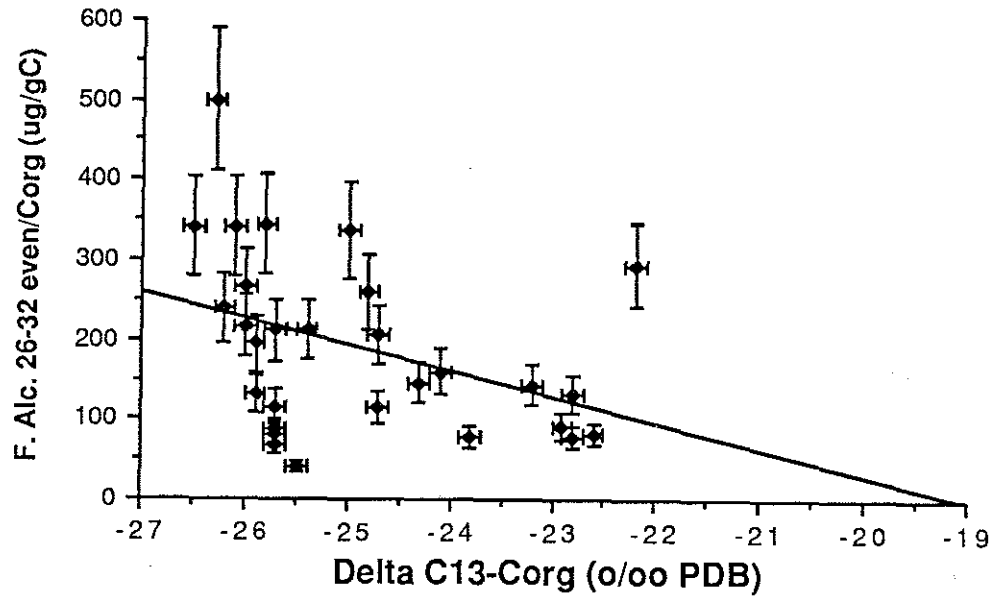

C28Δ5,22/Corg Res. (ug/gC)
12
10
8
6
4
2
0
-2
-4
-6
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

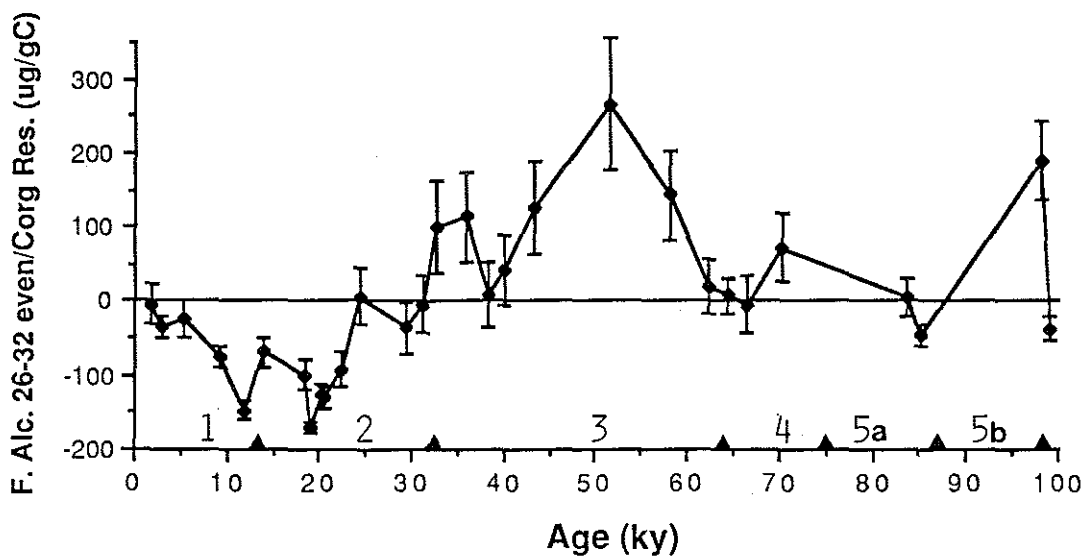
Fig. 3.13.a. Time series of nC_{26-32} even fatty alcohols/C_{org}.

Fig. 3.13.b. nC_{26-32} even fatty alcohols/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. The linear regression line is $-32 \cdot \delta^{13}C$-C_{org} -600 ($P = 0.045$, $r^2 = 0.14$, $n = 29$).

Fig. 3.13.c. Time series of nC_{26-32} even fatty alcohols/C_{org} versus $\delta^{13}C$-C_{org} linear regression residuals.


F. Alc. 26-32 even/Corg (ug/gC)
600
500
400
300
200
100
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


F. Alc. 26-32 even/Corg (ug/gC)
600
500
400
300
200
100
0
-27
-26
-25
-24
-23
-22
-21
-20
-19
Delta C13-Corg (o/oo PDB)


F. Alc. 26-32 even/Corg Res. (ug/gC)
300
200
100
0
-100
-200
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

24-ethylcholesterol residual time series (Fig. 3.7.c) were observed for the present four 4-desmethylsterol and fatty alcohol biomarkers. The high 24-ethylcholesterol/C_{org} concentration ratio relative to residuals predicted on the basis of organic carbon remineralization supported the hypotheses of either hydraulic particle sorting of terrigenous organic particles or a climatically-induced floral source change. The former hypothesis was supported by coarsening of Pigmy Basin sediments during the time span of 48 - 15 kybp. The latter hypothesis may be supported by the predominance of coniferous pollens and organic matter in glacial stages and deciduous pollens and organic matter during interglacials in the Pigmy Basin (Heusser, 1986). Both mechanisms working in concert could contribute to the high residual values during most of the 65-25 kybp interval.

Organic Biomarkers Insignificantly Related to Sedimentary Carbon Isotopic Composition

The organic carbon normalized concentrations of the following sterols, hopanols, and normal alkanes were insignificantly ($P > 0.05$) linearly related to the sedimentary organic carbon isotopic composition. With that, these compounds drop below a statistical threshold which makes them unutilizable as tracers of either terrigenous or marine organic matter for this sample suite. The concentration time series of each of the compounds in the Pigmy Basin and their sources will be discussed. Biomarker/C_{org} versus $\delta^{13}C$-C_{org} graphs are presented for each compound.

The $\Delta^{5,22}$-Desmethylsterols

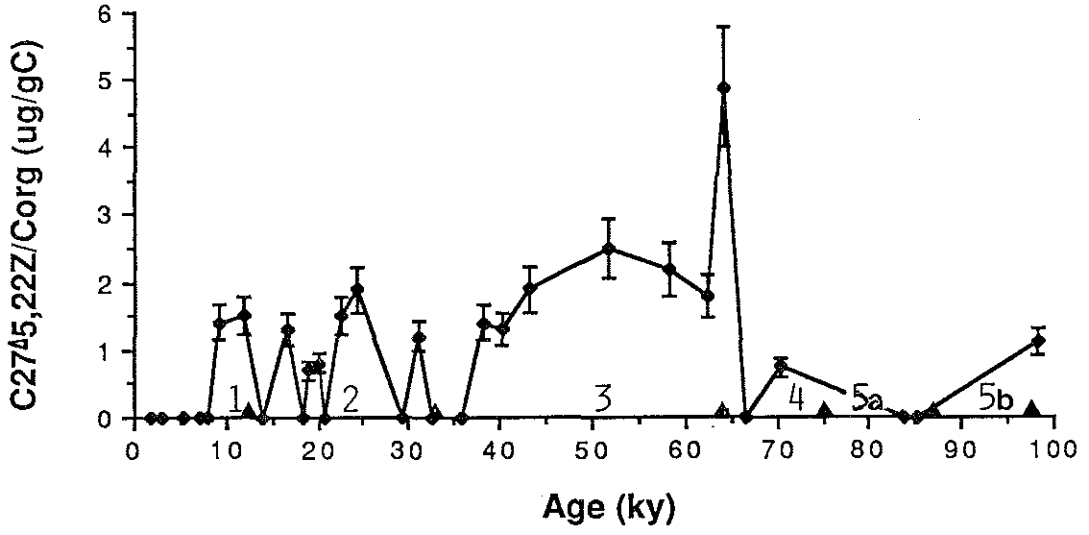
The C_{28-29}-$\Delta^{5,22}$-desmethylsterols have both terrigenous and

marine sources (Sheuer, 1973; Goad, 1977; Volkman, 1986). The organic carbon-normalized time series for 22-(E)-dehydrocholesterol (cholesta-5,22-dien-3ß-ol) and stigmasterol (24-ethylcholesta-5,22-dien-3ß-ol) are shown in Figures (3.14-15.a). Generally, low (< 50°/$_o$ of maximum) values are observed in isotope substages 5a-b, with concentrations increasing to maximum values by the middle of isotope stage 3. Thereafter, concentrations generally decrease into interglacial stage 1 with local maxima centered at ~25 and ~12 kybp.

Although the concentration time series have the same general features as the four previously discussed 4-desmethylsterols, none of these C_{27}- and/or C_{28}-$\Delta^{5,22}$-desmethylsterols is significantly ($P < 0.05$) related to the sedimentary organic carbon isotopic composition. The biomarker/C_{org} versus $\delta^{13}C$-C_{org} graphs of these sterols is shown in Figures (3.14-15.b). As previously hypothesized for four other 4-desmethylsterols, the effects of organic carbon remineralization, hydraulic particle sorting, and climatically-controlled floral source changes may combine to cause divergence from a simple biomarker/C_{org} versus $\delta^{13}C$-C_{org} linear relationship. Additional factors completing the sterol/C_{org} versus $\delta^{13}C$-C_{org} relationship are sedimentary sterol transformations, including microbial hydrogenation of double bonds and alcohol oxidation (Gaskell and Eglinton, 1975; Gagosian et al., 1980; Taylor et al., 1981). Temporally-increasing stanol-to-stenol ratios for some sterol pairs are consistent with sterol transformations occurring in this Pigmy Basin core (Chapter 4). The 24-ethylcholestan-3ß-ol/-/24-ethylcholest-5-en-3ß-ol ratio ($C_{29}\Delta^0/C_{29}\Delta^5$) for these

Fig. 3.14.a. Time series of cholesta-5,22-dien-3ß-ol/C_{org}.

Fig. 3.15.a. Time series of 24-ethylcholesta-5,22-dien-3ß-ol/C_{org}.


C27Δ5,22Z/Corg (ug/gC)
Age (ky)
1
2
3
4
5a
5b

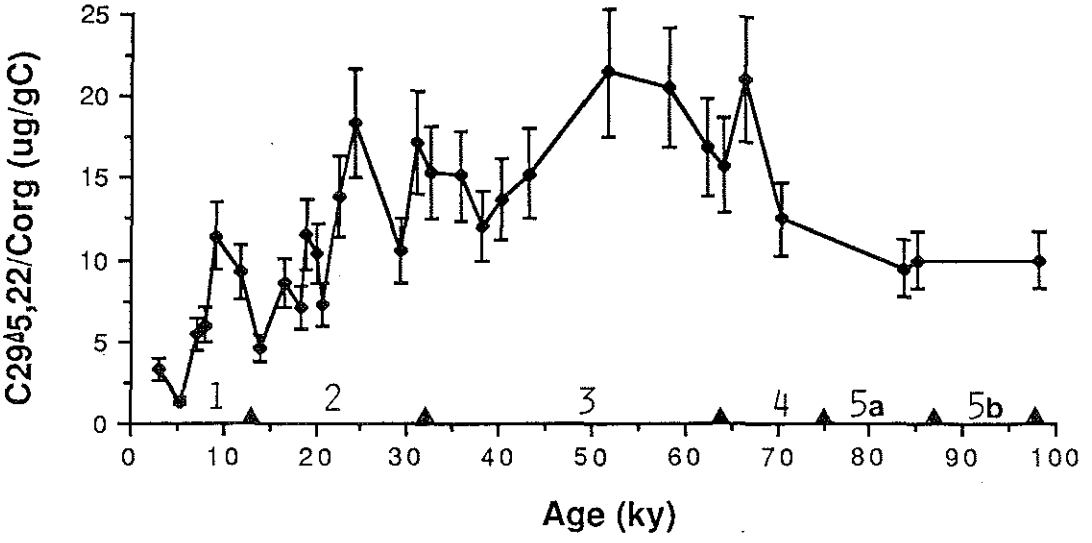
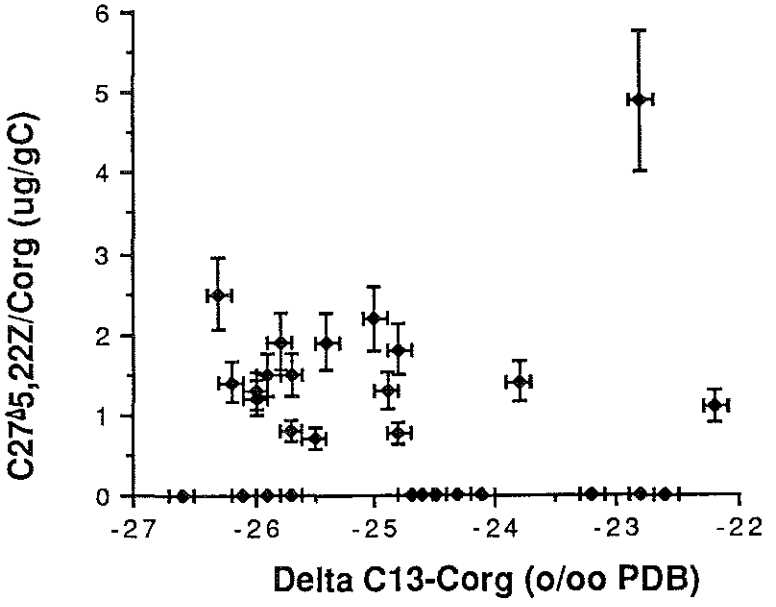
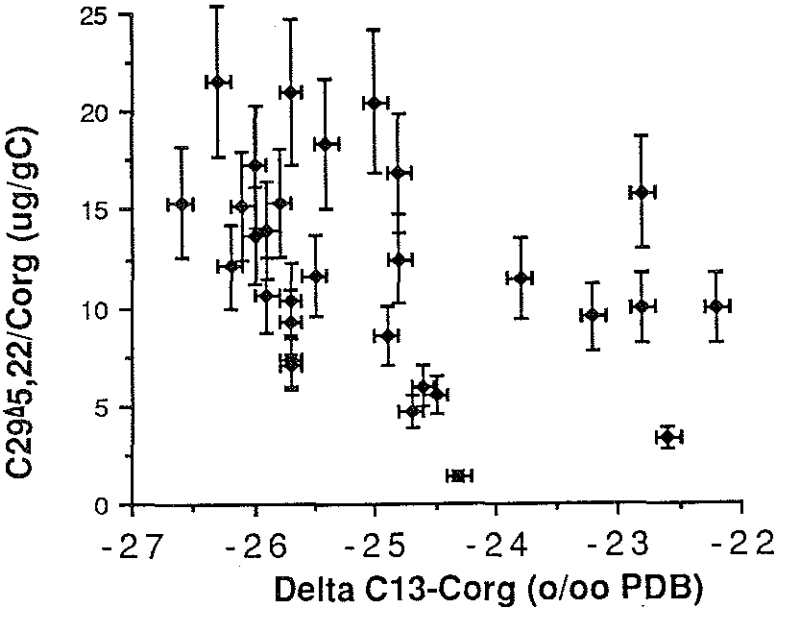

C29Δ5,22/Corg (ug/gC)
Age (ky)
1
2
3
4
5a
5b

Fig. 3.14.b. Cholesta-5,22-dien-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. There is no significant ($P < 0.05$) linear relationship between these properties.

Fig. 3.15.b. 24-Ethylcholesta-5,22-dien-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. There is no significant ($P < 0.05$) linear relationship between these properties.


C27Δ5,22Z/Corg (ug/gC)
6
5
4
3
2
1
0
-27
-26
-25
-24
-23
-22
Delta C13-Corg (o/oo PDB)


C29Δ5,22/Corg (ug/gC)
25
20
15
10
5
0
-27
-26
-25
-24
-23
-22
Delta C13-Corg (o/oo PDB)

Pigmy Basin cores are positively correlated with the paired carbon isotopic composition of the sedimentary organic carbon values, supporting the hydraulic particle sorting hypothesis since the sterols associated with coarser lithogenic particles had apparently undergone less transformation per unit C_{org} than those accompanying finer sediments (Chapter 4). The presence of two double bonds and an alcohol functional group on the C_{27-29} $\Delta^{5,22}$-sterols would make them more susceptible to sedimentary diagenetic transformation reactions than other less unsaturated desmethyl sterols.

The $C_{27-29}\Delta^{22}$-Desmethylsterols

The organic carbon-normalized concentration time series for the C_{27-29}-Δ^{22}-desmethyls are shown in Figs. 3.16-18.a. The C_{28-29}-Δ^{22}-4-desmethylsterol time series have features similar to their respective $C_{28-29}\Delta^{5,22}$-4-desmethylsterols. The concentrations are low (50-60°/$_o$) in isotope substages 5a-b compared to the higher average values reached in isotope stages 4 and 3. Thereafter, the concentration ratios decrease to ~0-10°/$_o$ of the high average values of stages 4 and 3. The decrease is not monotonic, however. At least two local maxima are centered at about 24 and 10 kybp. The $C_{27}\Delta^{22}$-desmethylsterol record is comparatively erratic because the compound concentration at times approached analytical detection limits. The general features of the $C_{27}\Delta^{22}$-desmethylsterol time series were low concentrations (~10-50°/$_o$ of the stage 3 maximum), with almost undetectable concentrations (<1 µg/gC) in stage 4, increasing to maximum values in stage 3. Toward the end of stage 3, concentrations often dropped

below detectable levels; local maxima, however, occurred at about 24 and 10 kybp.

The organic carbon-normalized concentrations of $C_{27-29}\Delta^{22}$-desmethylsterols were insignificantly ($P > 0.05$) related to sedimentary organic carbon isotopic composition (Figs. 3.16-18.b), so that they were not useful as either terrigenous or marine organic matter source tracers. In fact, these compounds may be diagnostic transformation products.

The $C_{27-29}\Delta^{22}$-4-desmethylsterols in subaqueous environments may be produced by the hydrogenation of $C_{27-29}\Delta^{5,22}$-4-desmethyl source sterols (Gaskell and Eglinton, 1976). Few original sources for the Δ^{22}-sterols have been determined. They have been found in a marine sponge (Bergman et al., 1945), a plant root (Takeda and Raper, 1958), and a slime mold (Heftmann et al., 1960). 22-Ethylcholest-22-en-3ß-ol is a metabolic transformation product of rat fecal bacteria (Eyssen et al., 1973) and was found in human feces (Eneroth et al., 1965). The $\Delta^{5,22} \rightarrow \Delta^{22}$-4-desmethylsterol hydrogenation hypothesis is considered a more likely origin for the C_{27-29}-Δ^{22}-4-desmethylsterols than the sources, considering the temporally-increasing stanol/stenol transformation ratios in this Pigmy Basin sediment core (Chapter 4).

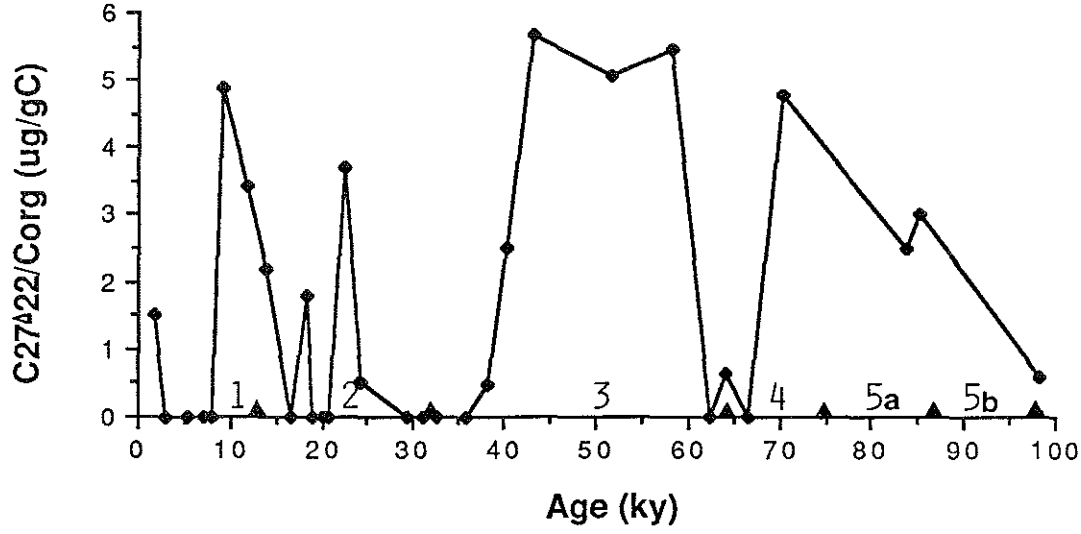
The C_{27-29}-4-Desmethylstanols

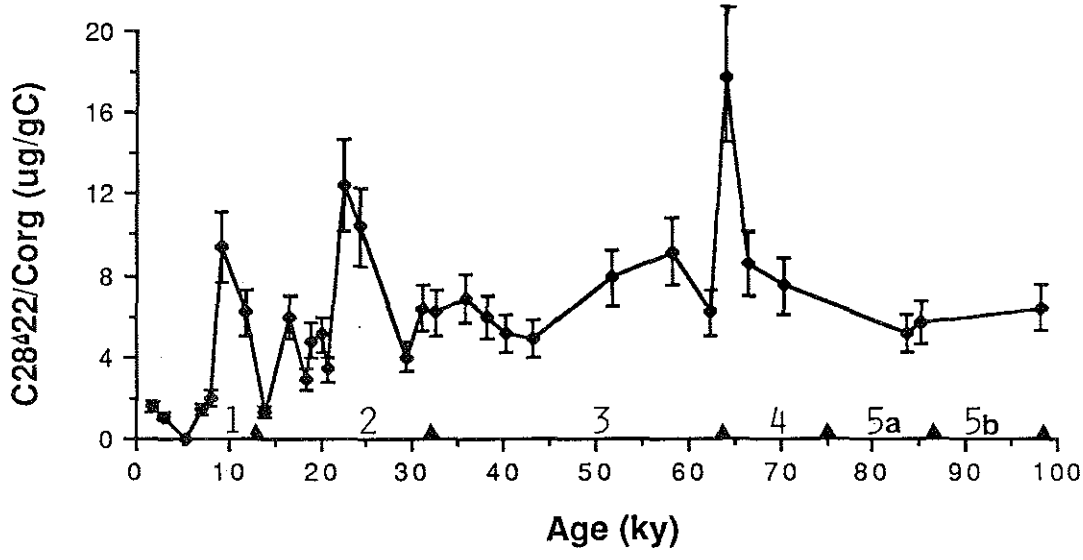
The organic carbon-normalized concentrations of the C_{27-29}-4-desmethylstanols are shown in Figs. 3.19-21.a. The concentrations of all the C_{27-29}-4-desmethylstanols increase from lower values

Fig. 3.16.a. Time series of cholesta-22-en-3ß-ol/C_{org}.

Fig. 3.17.a. Time series of 24-methylcholesta-22-en-3ß-ol/C_{org}.

Fig. 3.18.a. Time series of 24-ethylcholesta-22-en-3ß-ol/C_{org}.


C27Δ22/Corg (ug/gC)
0
1
2
3
4
5
6
0
10
20
30
40
50
60
70
80
90
100
Age (ky)
1
2
3
4
5a
5b


C28Δ22/Corg (ug/gC)
0
4
8
12
16
20
0
10
20
30
40
50
60
70
80
90
100
Age (ky)
1
2
3
4
5a
5b

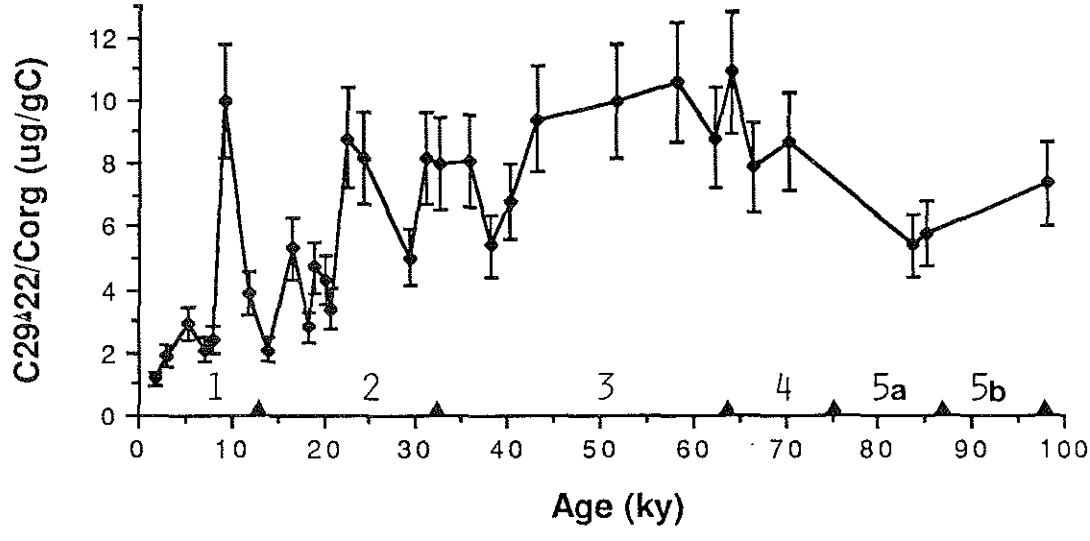
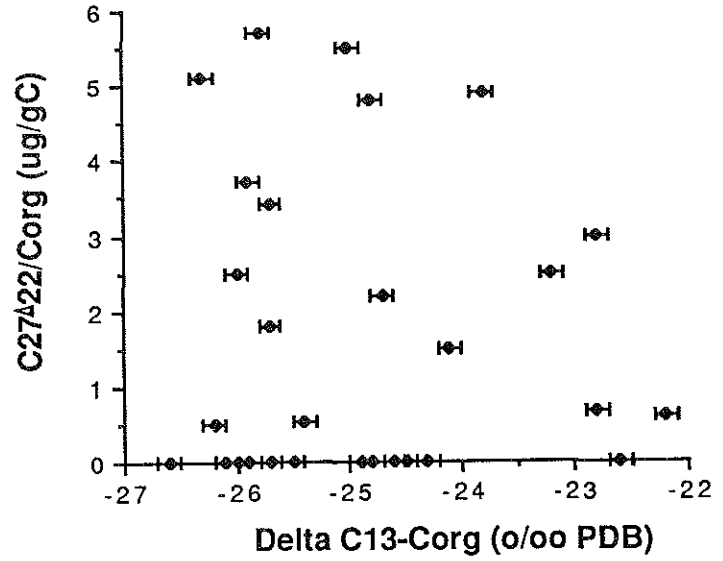
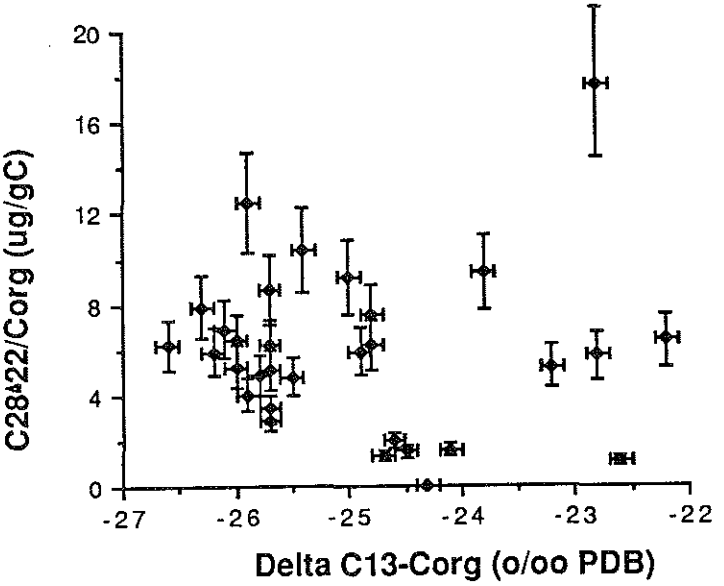

C29Δ22/Corg (ug/gC)
0
2
4
6
8
10
12
0
10
20
30
40
50
60
70
80
90
100
Age (ky)
1
2
3
4
5a
5b

Fig. 3.16.b Cholesta-22-en-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. There is no significant ($P < 0.05$) linear relationship between these properties.

Fig. 3.17.b. 24-Methylcholesta-22-en-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. There is no significant ($P < 0.05$) linear relationship between these properties.

Fig. 3.18.b. 24-Ethylcholesta-22-en-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. There is no significant ($P < 0.05$) linear relationship between these properties.


C27Δ22/Corg (ug/gC)
0
1
2
3
4
5
6
-27
-26
-25
-24
-23
-22
Delta C13-Corg (o/oo PDB)


C28Δ22/Corg (ug/gC)
0
4
8
12
16
20
-27
-26
-25
-24
-23
-22
Delta C13-Corg (o/oo PDB)

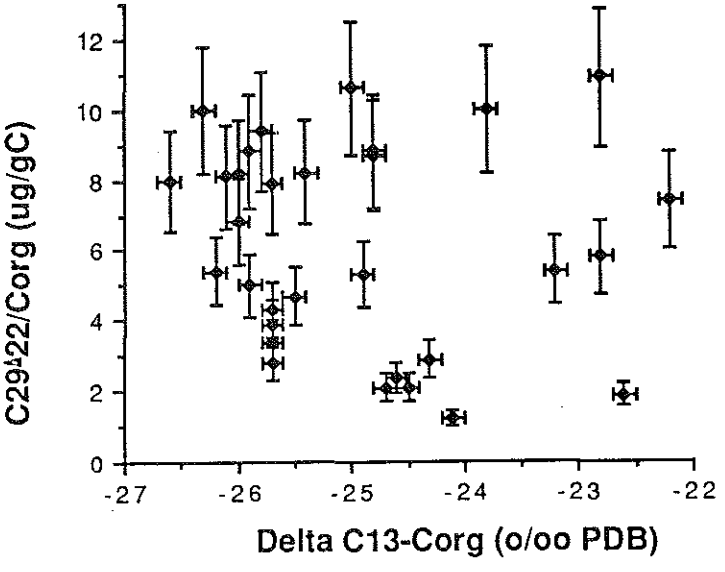
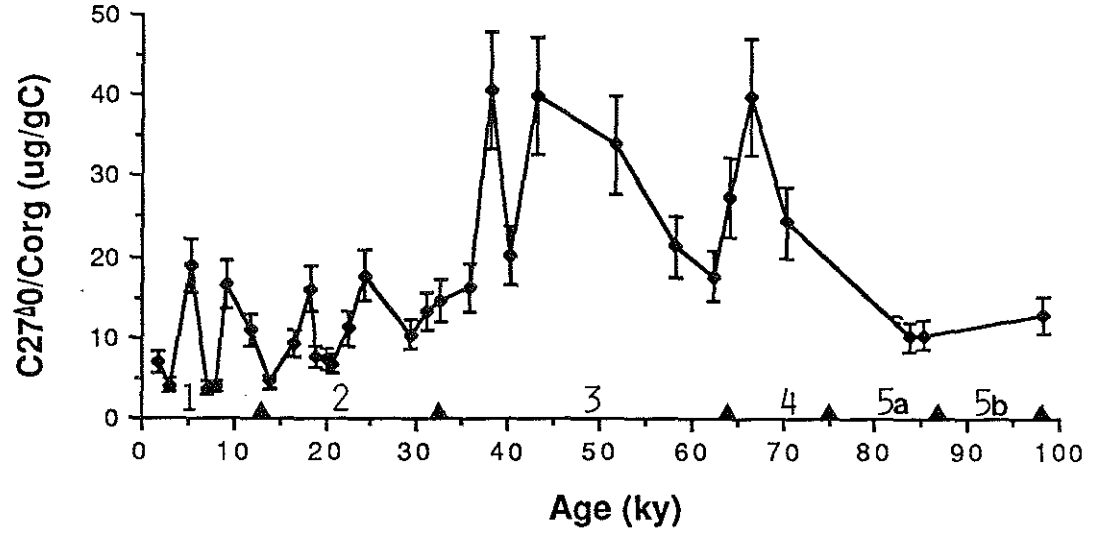
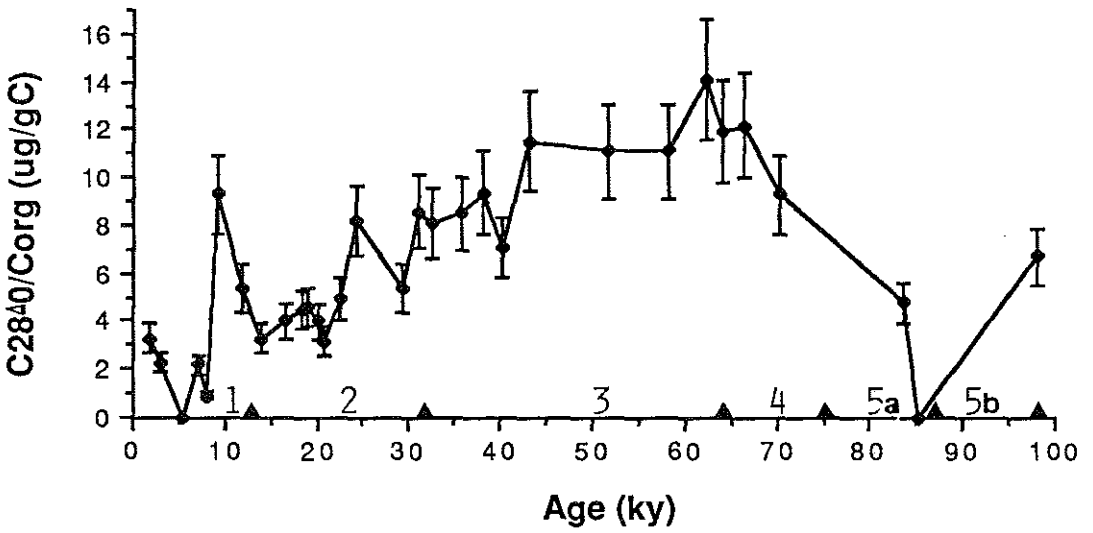

C29Δ22/Corg (ug/gC)
0
2
4
6
8
10
12
-27
-26
-25
-24
-23
-22
Delta C13-Corg (o/oo PDB)

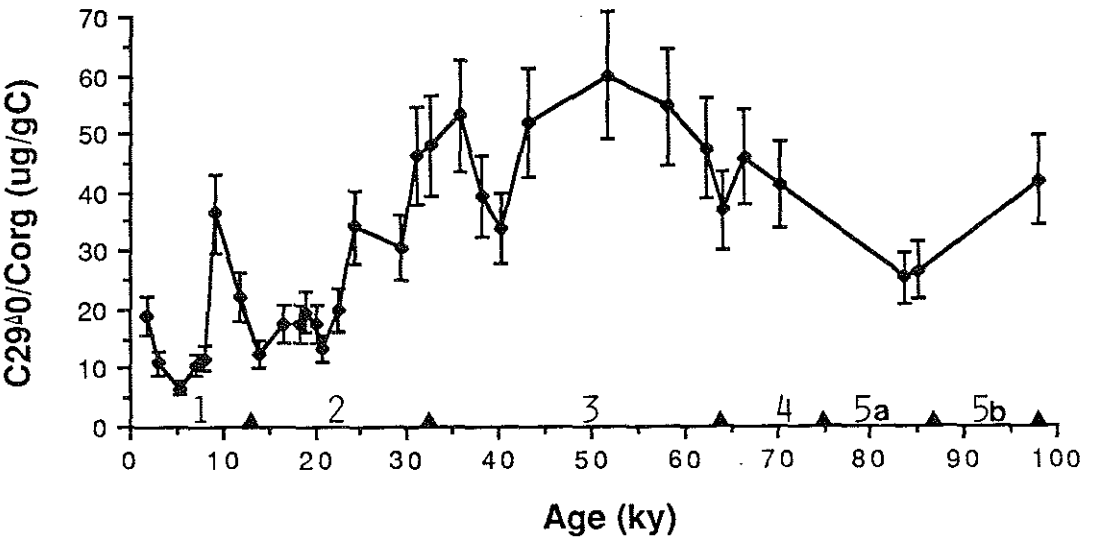
Fig. 3.19.a. Time series of 5α-cholesta-3ß-ol/C_{org}.

Fig. 3.20.a. Time series of 24-methylcholesta-22-en-3ß-ol/C_{org}.

Fig. 3.21.a. Time series of 24-ethylcholesta-22-en-3ß-ol/C_{org}.


C27Δ0/Corg (ug/gC)
50
40
30
20
10
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


C28Δ0/Corg (ug/gC)
16
14
12
10
8
6
4
2
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


C29Δ0/Corg (ug/gC)
70
60
50
40
30
20
10
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

(0-70°/$_{o}$ of the maximum observed value) in interglacial isotope substages 5a-b to maximum (100°/$_{o}$) values in stages 3 and 4. Thereafter, the concentrations decrease to 0-30°/$_{o}$ of the stage 3-4 maximum values in the latter half of interglacial stage 1. All of the C_{27-29}-4-desmethylstanols exhibit local maximum values centered at ~10 kybp which are at least three times the surrounding local minimum values.

The organic carbon-normalized concentrations of the C_{27-29}-4-desmethylstanols are insignificantly related to the sedimentary organic carbon isotopic composition (Figs. 3.19-21.b). They are therefore not useful in this study as quantitative terrigenous or marine organic matter tracers.

The C_{27-29}-4-desmethylstanols in sediments are derived from terrigenous and marine sources and from the hydrogenation of unsaturated sterols. The stanol/stenol ratio in many terrigenous and marine organisms is typically in the range of 0.1-0.2. The total stanol/total stenol ratio in the diatom Melosira granulata collected from the Japanese Lake Suwa was ~0.03 (Nishimura and Koyama, 1976). The total stenol/total stanol ratio of two higher plants (Zizania latifolia: 0.009; Potomageton crispus: 0.005), two phytoplankton species (Microcystus aeruginosa: 0.15; Melosira granulata: 0.012) and a zooplnakton species (Brachionus calyciflorus: 0.009) were all less than 0.15 (Nishimura and Koyama, 1977). The stanol/stenol ratios for six sterol pairs in Black Sea surface waters were in the range of 0.1-0.2 (Gagosian and Heinzer, 1979). These ratios were considered to be caused by stanol input directly from organisms (jellyfish:

Ballantine et al., 1976; red algae: Chardon-Lorriaux et al., 1975; echinoderms: Goad et al., 1972; and sponge: Nes and McKean, 1977) since stenol → stanol transformations would be expected to be slow in oxic surface water (Nishimura, 1978).

There are, however, occurrences of high stenol/stanol ratios in organisms. 5α(H)-Stanol/Δ^5-stenol ratios of ~0.5 were observed in cultured Minochrysis lutheri at stationary growth phase, while no measurable sterols were found when the culture was in exponential growth phase. Boon et al. (1983) reported a stanol/stenol ratio of ~0.5 in a cyanobacterial mat on the sediment surface of Solar Lake in Egypt.

The high (0.6-0.9) and temporally-increasing 24-ethylcholestanol/-24-ethylcholesterol ratio in the Pigmy Basin Core 619 suggested that a large proportion of the stanols were probably diagenetic transformation (reduction) products (Chapter 4).

None of the C_{27-29}-4-desmethylstanols was significantly ($P < 0.05$) related to the sedimentary organic carbon isotopic composition (Figs. 3.19-21.a). The combined effects of original source and stenol reduction inputs minus diagenetic stanol losses with the complications of particle sorting may have contributed to the lack of significance of the C_{27-29}-4-desmethylstanol/C_{org} versus $\delta^{13}C$-C_{org} regression.

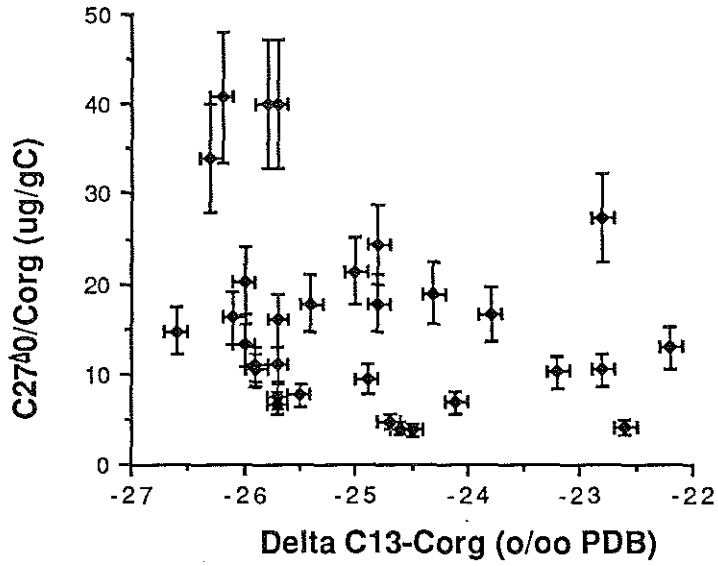
General Discussion of 4-Desmethylsterols

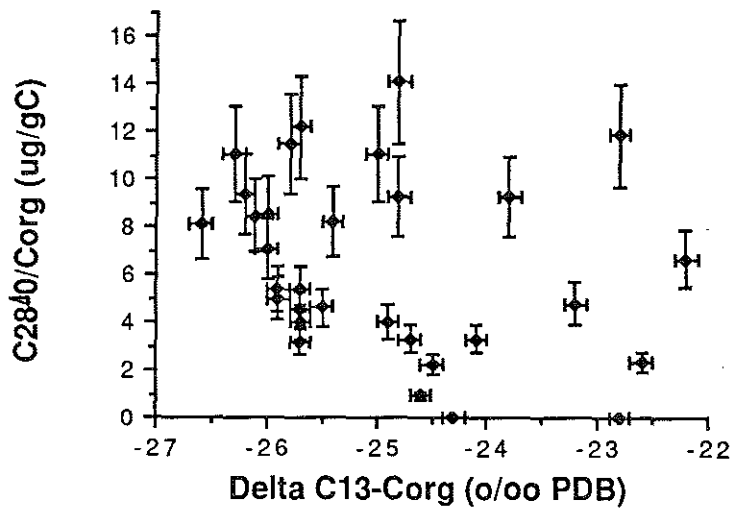
The somewhat arbitrary nature of the selection of a certain significance level ($P < 0.05$) of the statistical F-test to determine

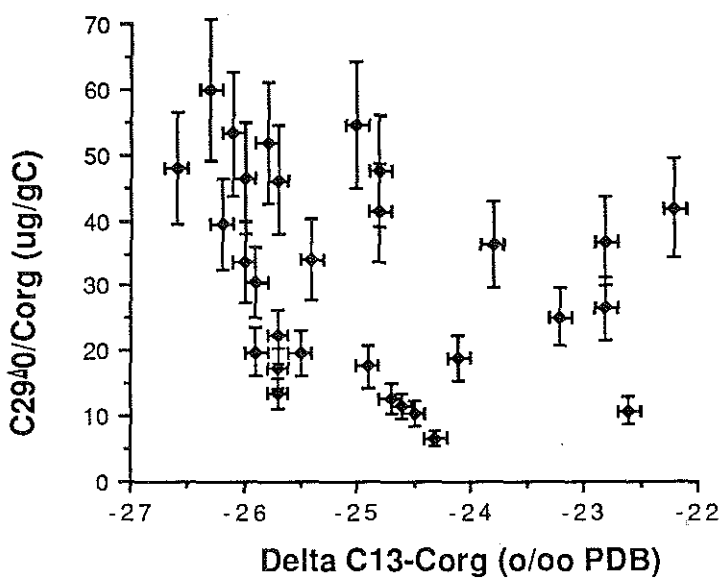
Fig. 3.19.b. 5α-Cholesta-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. There is no significant ($P < 0.05$) linear relationship between these properties.

Fig. 3.20.b. 24-Methylcholesta-22-en-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. There is no significant ($P < 0.05$) linear relationship between these properties.

Fig. 3.21.b. 24-Ethylcholesta-22-en-3ß-ol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. There is no significant ($P < 0.05$) linear relationship between these properties.


C27Δ0/Corg (ug/gC)
50
40
30
20
10
0
-27
-26
-25
-24
-23
-22
Delta C13-Corg (o/oo PDB)


C28Δ0/Corg (ug/gC)
16
14
12
10
8
6
4
2
0
-27
-26
-25
-24
-23
-22
Delta C13-Corg (o/oo PDB)


C29Δ0/Corg (ug/gC)
70
60
50
40
30
20
10
0
-27
-26
-25
-24
-23
-22
Delta C13-Corg (o/oo PDB)

the usefulness of organic carbon-normalized biomarkers as terrigenous or marine sources is recognized. More sophisticated modeling of organic carbon remineralization, hydraulic particle sorting, and floral source changes on the simple linear biomarker/C_{org} versus $\delta^{13}C$-C_{org} model should account for greater proportions of the regression variance; however, such modeling would requiire additional geochemical and sedimentolgical data.

Despite the fact that only five of the thirteen 4-desmethylsterols are significantly ($P < 0.05$) related to the sedimentary organic carbon isotopic composition, most of the thirteen 4-desmethylsterols have similar time series characteristics to the five useful tracers. Most of the 4-desmethyl sterols occurred in relatively low concentrations in glacial substages 5a-b. The concentrations generally increased to maximum values in isotope stages 3 or 4, whereafter they decreased to low values in the present isotope stage 1. The latter decreasing trend was frequently punctuated by two significant local maxima centered at ~11 and ~25 kybp.

Although terrigenous and marine sources have been noted for almost all of the 4-desmethyl sterols discussed above, five of them were linearly related to the sedimentary organic carbon isotopic composition in a manner expected of terrigenous organic biomarker compounds (negative slope and $\delta^{13}C$-C_{org} intercept = 19±3°/$_{oo}$ PDB). The time series characteristics of the others were similar to those four sterols. The widespread occurrence of 4-desmethylsterols in numerous phytoplanktonic algal classes, including the alkenone-producing Prymnesiophyceae (reviewed by Volkman, 1976),

indicates the marine 4-desmethylsterols were likely buried in the Pigmy Basin. The lack of a significant linear relationship between any of the previously discussed 4-desmethylsterols and sedimentary organic carbon isotopic composition which would have marine biomarker characteristics (a positive slope with a $\delta^{13}C$-C_{org} intercept of $-28.0\pm2.5‰$ PDB) suggests two possibilities about marine sterol preservation in the Late Quaternary Pigmy Basin. The first possibility is that the marine 4-desmethylsterols are more labile to sedimentary degradation than their terrigenous counterparts. The result of such differential susceptibility to degradation would be that the sedimentary concentration record of 4-desmethylsterols would be biased toward terrigenous sterol preservation. Therefore, an interpretation of 4-desmethylsterol records solely in terms of source inputs without consideration of superimposed diagenetic effects could be misleading. Evidence supporting the theory of preferential preservation of terrigenous over marine biomarker compounds in other subaqueous sedimentary environments has been noted by Volkman et al. (1987) and Wakeham et al., (1980). A second possibility is that the organic carbon-normalized concentrations of marine 4-desmethylsterols in the marine carbon isotopic end member are relatively low compared to the same ratio for the terrigenous 4-desmethylsterols of the same structure in the terrigenous $\delta^{13}C$-C_{org} endmember. Hence, when the two sources are mixed in the sediments the marine contribution is analytically indistinguishable compared to the terrigenous component. This latter possibility seems unlikely because marine organic matter probably contains more sterol per unit organic carbon than does

terrigenous organic matter.

The C_{27-29}-4α-Methylsterols

The organic carbon-normalized concentration time series for the C_{27-29}-4α-methylsterols are shown in Figures 3.22-24.a. The concentration of the C_{29}-4α-methylsterol in glacial substages 5a-b was relatively low (15-30°/$_o$) compared to the maximum (100°/$_o$) values reached near the stage 4/3 boundary. After a drop to undetectable levels (<0.5 μg/gc) at the beginning of isotope stage 3, concentrations increased to ~75°/$_o$ of the maximum value through the middle of isotope stage 3. Thereafter, the concentrations gradually decreased to undetectable levels near the isotope stage 2/1 boundary. The concentration then increased to the stage 3 maximum value near the end of stage 1.

The C_{27-28}-4α-methylsterol had some similar time series characteristics (Figures 3.22-23.a) although the C_{27}-4α-methylsterol often occurred in lower concentrations or were undetectable . Interglacial substages 5a-b were characterized by low (0-30°/$_o$) concentrations compared to the maximum value observed at the isotope stage 4/3 boundary. The maximum value observed at the 4/3 boundary was at least three times the preceding local minimum value. After that, the concentrations increased to about 20-50°/$_o$ of the maximum value and then decreased to undetectable levels at ~18 kybp. Two local maxima centered at about 10 and 5 kybp occurred in the C_{28}-4α-methylsterol record. Another local maximum at ~14 kybp was noted in the C_{27}-4α-methylsterol record.

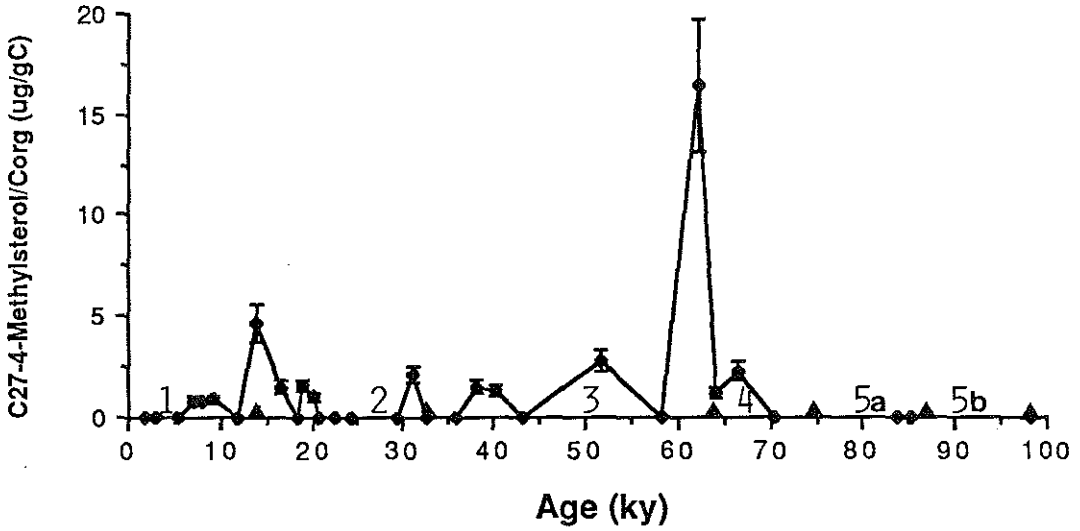
The organic carbon-normalized concentrations of each of the C_{27-29}-4α-methylsterols were insignificantly related to the sedimentary organic carbon isotopic composition (Figs. 3.22-24.b). These compounds were not considered as useful quantitative tracers of marine organic matter in the present study.

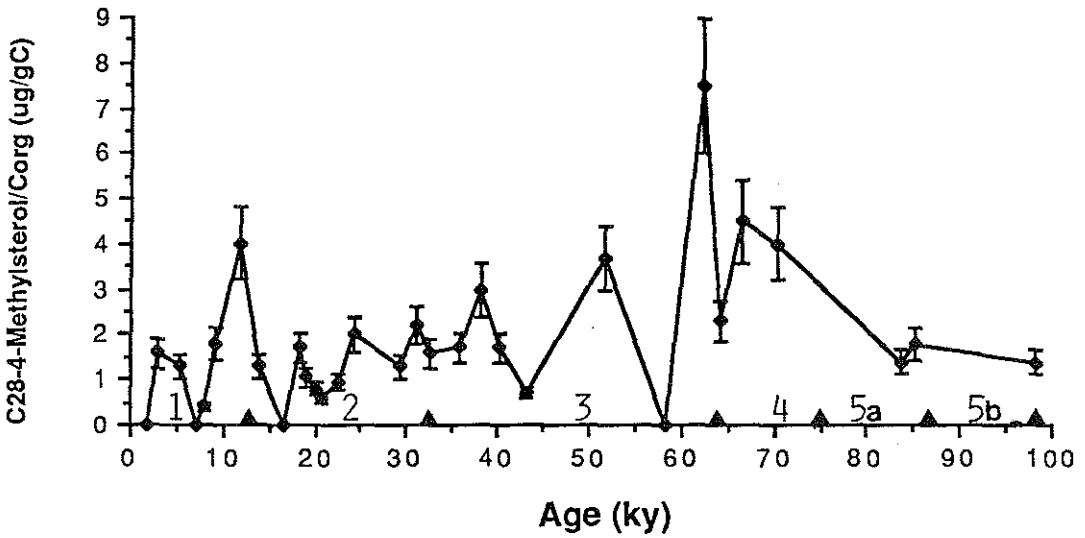
The C_{27-30}-4α-methylsterols are biosynthesized mainly by dinoflagellates and a few bacteria (Shimizu et al., 1976; Boon et al., 1979; Gagosian and Smith, 1979; Alam et al., 1979; Volkman et al., 1984; Robinson et al., 1984). Their occurrence in Pigmy Basin sediments probably indicates dinoflagellate organic matter input. Two possible reasons that C_{27-29}-4α-methylsterol concentrations were insignificantly related to the sedimentary organic carbon isotopic composition may be that (1) the production of 4α-methylsterols by dinoflagellate is not linearly related to the input of the total marine organic carbon, as scaled by $\delta^{13}C$-C_{org}, or (2) the C_{27-29}-4α-methylsterols are differentially degraded relative to the bulk marine organic carbon. The former hypothesis of the decoupling dinoflagellate production from the total marine organic carbon production was supported by the observation of the spatiotemporally episodic occurrence of dinoflagellates in the late Quaternary equatorial Atlantic Ocean (Brassell, 1986b) and in present-day surface waters. In the Kane Gap region of the equatorial Atlantic Ocean, seven C_{37-39} alkenones, the C_{24-33}-n-alkanes, and total chlorins were reported to have followed similar concentration trends during the last 0.5 My (Brassell, et al., 1986b). By contrast, dinosterol (C_{30}-4α-methylsterol) concentrations showed sharply defined local

Fig. 3.22.a. Time series of C_{27}-4α-methylsterol/C_{org}.

Fig. 3.23.a. Time series of C_{28}-4α-methylsterol/C_{org}.

Fig. 3.24.a. Time series of C_{29}-4α-methylsterol/C_{org}.


C27-4-Methylsterol/Corg (ug/gC)
20
15
10
5
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


C28-4-Methylsterol/Corg (ug/gC)
9
8
7
6
5
4
3
2
1
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

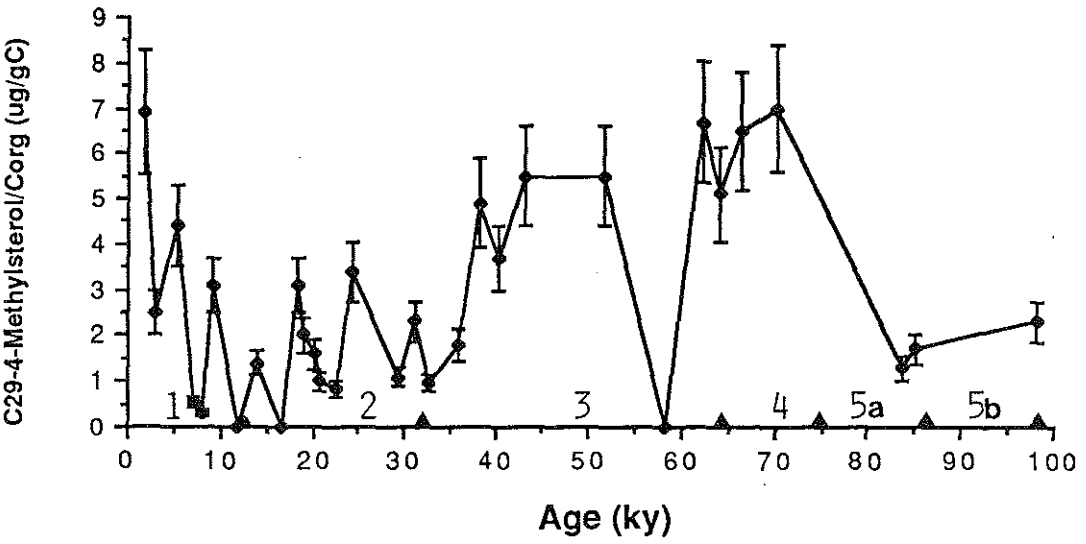
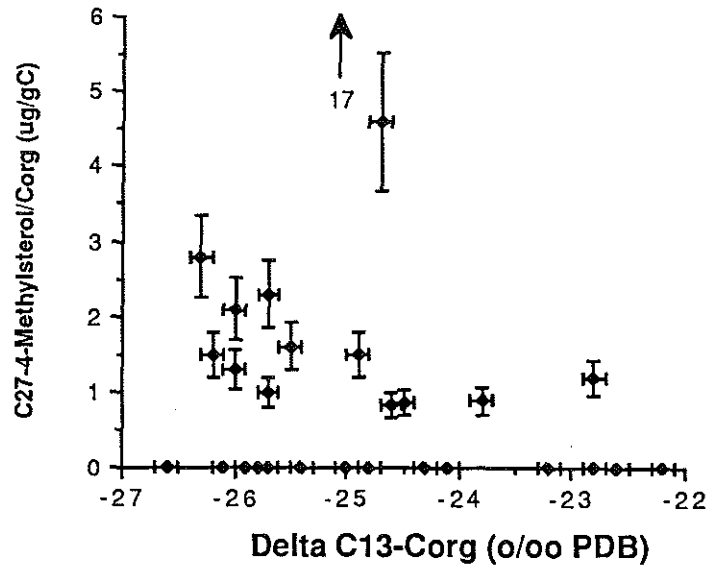
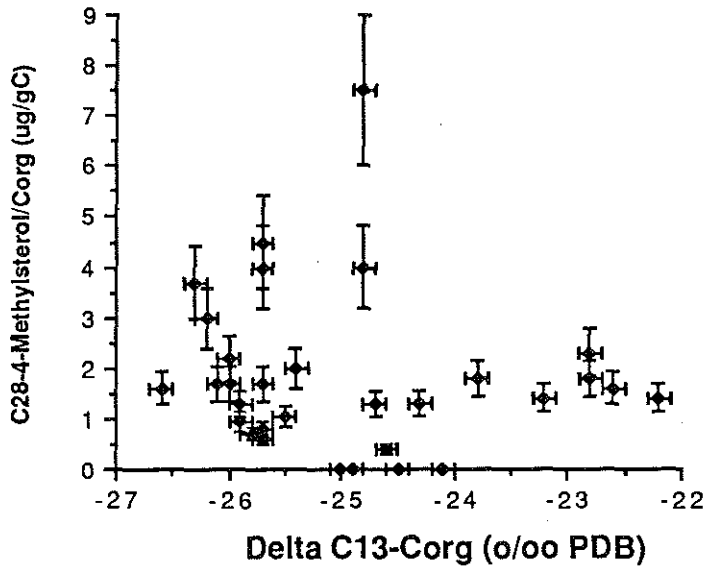

C29-4-Methylsterol/Corg (ug/gC)
9
8
7
6
5
4
3
2
1
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

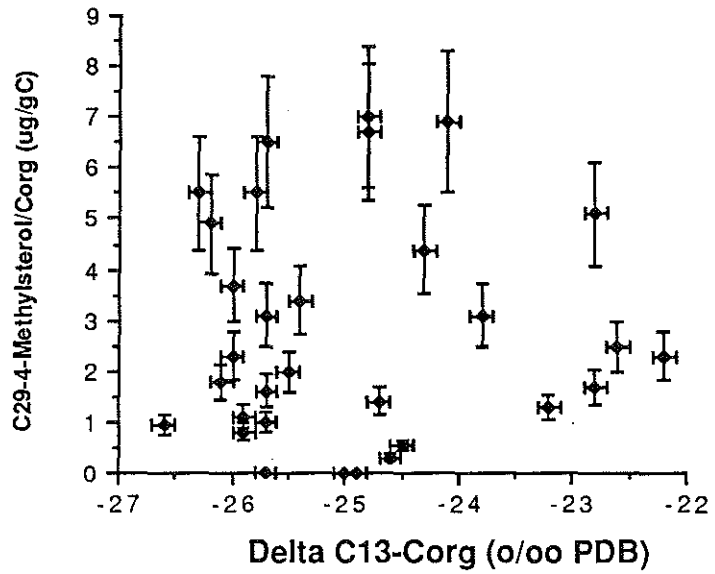
Fig. 3.22.b. C_{27}-4α-methylsterol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. There is no significant ($P < 0.05$) linear relationship between these properties.

Fig. 3.23.b. C_{28}-4α-methylsterol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. There is no significant ($P < 0.05$) linear relationship between these properties.

Fig. 3.24.b. C_{29}-4α-methylsterol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. There is no significant ($P < 0.05$) linear relationship between these properties.


C27-4-Methylsterol/Corg (ug/gC)
17
Delta C13-Corg (o/oo PDB)


C28-4-Methylsterol/Corg (ug/gC)
Delta C13-Corg (o/oo PDB)


C29-4-Methylsterol/Corg (ug/gC)
Delta C13-Corg (o/oo PDB)

maxima (5 maxima in ~500 ky), including one following the isotope stage 4/3 transition. The most prominent total C_{27-29}-4α-methyl-sterol concentration maximum in the Pigmy Basin also occurred shortly (~3 ky) after the isotope stage 4/3 boundary. The significance of these stage 4/3 local maxima at the time continental ice melting was unclear and warrants further investigation.

Hopan-31-ol and Hopan-32-ol

The organic carbon-normalized concentration time series in hopan-31-ol and hopan-32-ol are shown in Figs. 3.25-26.a. The concentrations were generally low (~30-65°/$_{\circ}$) in interglacial stages 5a-b compared to maximum values (100°/$_{\circ}$) reached in either isotope stages 3 or 4. Thereafter, the concentrations generally decrease to low values (~5°/$_{\circ}$ of the stage 3 or 4 maximum value) by the middle of stage 1, with a single point maximum at ~10 kybp standing at least three times higher than the surrounding values. By the latter half of isotope stage 1, the hopanol/C_{org} values returned to ~25-50°/$_{\circ}$ of their stage 3 or 4 maximum values.

The organic carbon-normalized concentrations of hopan-31-ol and hopan-32-ol were insignificantly ($P > 0.05$) related to the sedimentary organic carbon isotopic composition (Figs. 3.25-26.b), so that these compounds were not considered useful quantitative tracers for either terrigenous or marine organic matter.

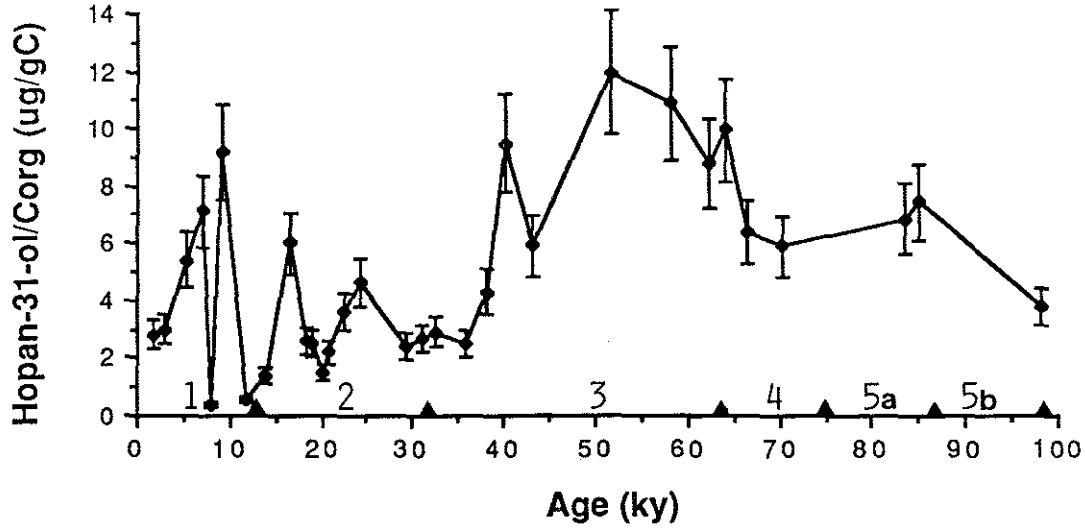
The hopanoids are widely distributed in nature (Ourisson et al., 1979; Rohmer et al., 1984). In fact, Ourisson et al. (1979) found hopanoids in every sedimentary organic matter sample that they

examined--including marine and lacustrine sediments, coals and shales, and petroleum, ranging in age from a few to 5 x 10^8 y. Some major sources of hopanoids are bacteria and cyanobacteria (blue green algae). Other sources include selected tropical trees, grasses, lichens, and ferns. The sources of many hopanols have yet to be well defined, including the sources for hopan-31-ol and hopan-32-ol (Dastillung et al., 1980). Those two hopanols were believed to be derived from bacteriohopane polyols which occur in many bacteria (Rohmer and Ourisson, 1976).

The organic carbon-normalized sedimentary record of hopan-31-ol and hopan-32-ol may be considered a qualitative record of bacteria input. The quantitative relationship to bacterial biomass, however, is presently unclear. The sedimentary records of hopan-31-ol and hopan-32-ol have some similar characteristics to those of the terrigenous biomarkers, the 4-desmethylsterols: low values in isotope stage 5a-b, increasing to maximum values in stages 3 or 4, then generally decreasing into the middle of stage 1, whereafter the concentrations increased toward the present. The significance of the general similarity of terrigenous biomarker and hopanol time series is speculative. Two possibilities are that (1) the hopanols accompanied terrigenous organic matter in its sedimentary transport from the continent to its deposition in the Pigmy Basin, or (2) the hopanol-producing bacteria grew preferentially in the Pigmy Basin sediments during times of predominant terrigenous (versus marine) organic carbon deposition.

Fig. 3.25.a. Time series of hopan-31-ol/C_{org}.

Fig. 3.26.a. Time series of hopan-32-ol/C_{org}.


Hopan-31-ol/Corg (ug/gC)
14
12
10
8
6
4
2
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

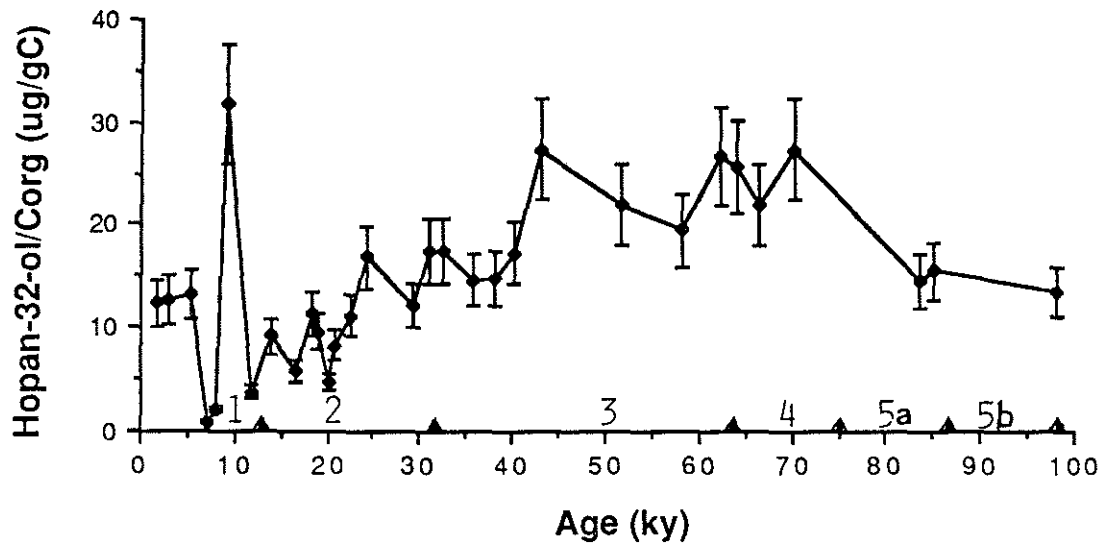
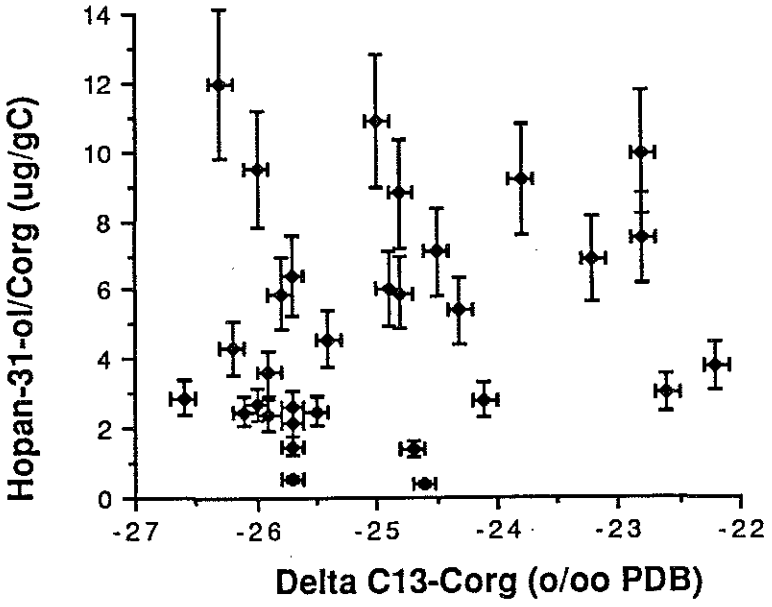
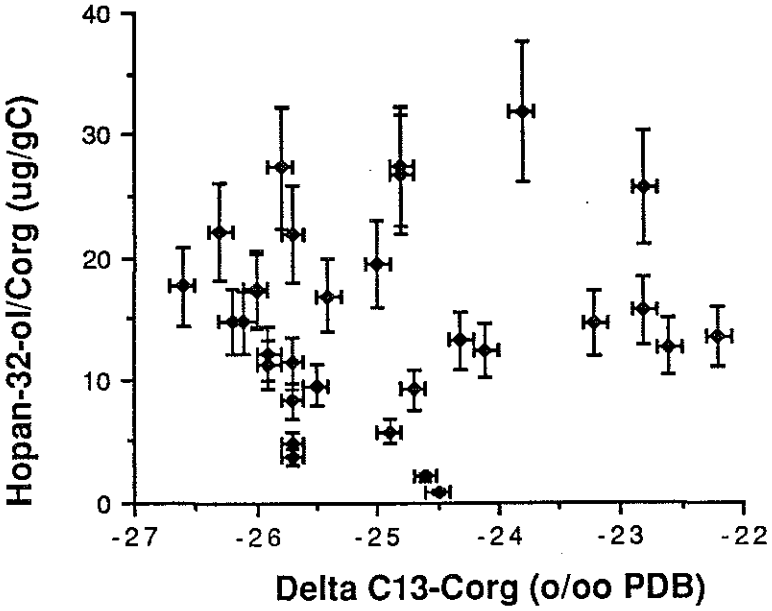

Hopan-32-ol/Corg (ug/gC)
40
30
20
10
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

Fig. 3.25.b. Hopan-31-ol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. There is no significant ($P < 0.05$) linear relationship between these properties.

Fig. 3.26.b Hopan-32-ol/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. There is no significant ($P < 0.05$) linear relationship between these properties.


Hopan-31-ol/Corg (ug/gC)
14
12
10
8
6
4
2
0
-27
-26
-25
-24
-23
-22
Delta C13-Corg (o/oo PDB)


Hopan-32-ol/Corg (ug/gC)
40
30
20
10
0
-27
-26
-25
-24
-23
-22
Delta C13-Corg (o/oo PDB)

Total nC_{27-33}-Odd Alkanes

The organic carbon-normalized concentration time series for the nC_{27-33} odd alkane is shown in Figure 3.27.a. The nC_{27-33} odd alkane concentrations were high (280-350 µg/C) in isotope stage 5b and decreased to a local minimum (180 µg/gC) in isotopic stage 5a, whereafter they increased to a maximum value (~390 µg/gC) in the middle of stage 3. The nC_{27-33} odd alkane concentrations then decreased to ~130 µg/gC near the isotope stage 2/3 boundary, with a local minimum (100 µg/gC) centered at ~18 kybp. The nC_{27-33} odd alkane concentrations increased from the stage 2/1 boundary to a local maximum at ~2 kybp.

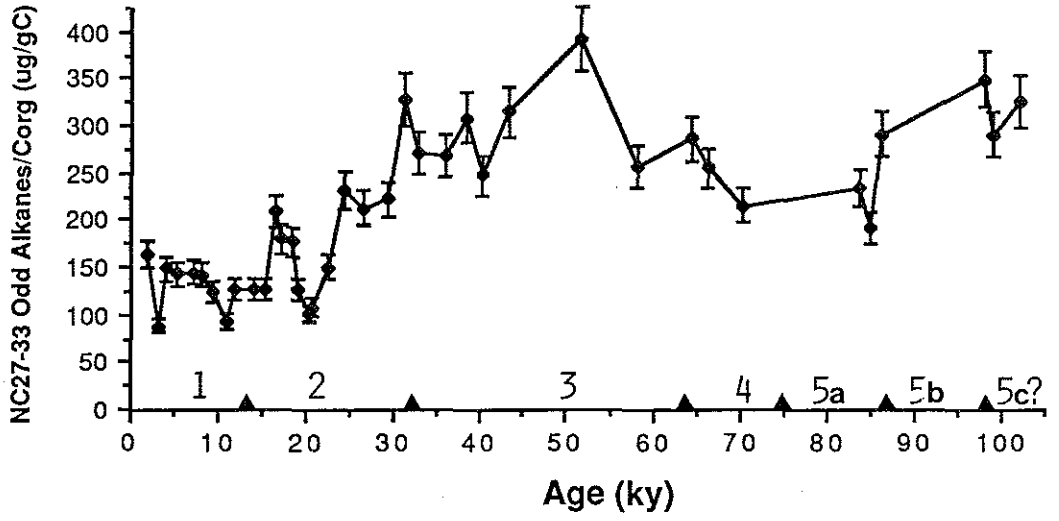
The nC_{27-33} odd alkanes were insignificantly correlated with the sedimentary organic carbon isotopic composition (Fig. 3.27.b). As a group, the nC_{27-33} odd alkanes were not useful quantitative tracers of either terrigenous or marine organic matter by this biomarker/-C_{org} versus $\delta^{13}C$-C_{org} linear correlation analysis. As discussed further below, the potentiallly diagenetically refractory long chain alkanes may be sigificantly better preserved than total sedimentary organic carbon, resulting in an insignificant linear correlation.

The long chain (C_{21-35}) n-alkanes with high (2-10) odd/even carbon preference indices are characteristic components of land plant waxes (Eglinton et al., 1962; Eglinton and Hamilton, 1967; Dyson and Herbin, 1968; Herbin and Robins, 1968). Long chain (C_{20-40}) n-alkanes with high carbon preference indices have been used as terrigenous organic matter tracers in many sedimentary environments (e.g., Bray and Evans, 1961; Aizenshtat, et al., 1973; Simoneit,

1978). They are transported through the environment as particles in the ocean (Prahl, 1986) and the atmosphere (Simoneit and Eglinton, 1977; Gagosian, et al., 1981, 1987; Schneider and Gagosian, 1985; Zafiriou et al., 1985; Prahl, 1985). The nC_{27-33} odd alkanes were chosen as a potential quantitative terrigenous organic matter tracers because these compounds occur in significantly (~2-10 times) higher concentrations than the adjacent even numbered homologues and they were preserved in many ancient sediments. The use this index assumes that there is insignificant preserved marine long-chain n-alkanes. In fact, however, long chain alkanes may be derived from marine bacteria, phytoplankton, and petroleum (as reviewed by Volkman, et al., 1983), which may dilute the nC_{27-33} odd alkanes as a terrigenous C_{org} tracer. Despite the fact that the nC_{27-33} odd alkane concentrations were insignificantly ($P > 0.05$) related to sedimentary organic carbon isotopic composition, they were significantly correlated with 24-ethylcholesterol ($r^2 = 0.55$, $P < 0.0001$, $n = 30$; Fig. 3.28) and a nC_{26-32} even fatty acid ($r^2 = 0.62$, $P < 0.0001$, $n = 28$; Fig. 3.29) concentration. The residuals of the 24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} linear regression were somewhat better correlated with the nC_{27-33} odd alkane concentrations than the 24-ethylcholesterol values ($r^2 = 0.66$, $P < 0.0001$, $n = 30$; Fig. 3.30). The latter correlation of the nC_{27-33} odd alkane/C_{org} data with the 24-ethylcholesterol/C_{org} residuals (previously interpretted as a biomarker/C_{org} diagenetic and particle sorting index) may be due to better preservation of the nC_{27-33} odd alkanes than the total sedimentary organic carbon. As previously noted, the long chain

Fig. 3.27.a. Time series of total nC_{27-33} alkanes/C_{org}.

Fig. 3.27.b. Total nC_{27-33} alkanes/C_{org} versus $\delta^{13}C$-C_{org} for paired analyses. There is no significant ($P < 0.05$) linear relationship between these properties.


NC27-33 Odd Alkanes/Corg (ug/gC)
400
350
300
250
200
150
100
50
0
1
2
3
4
5a
5b
5c?
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

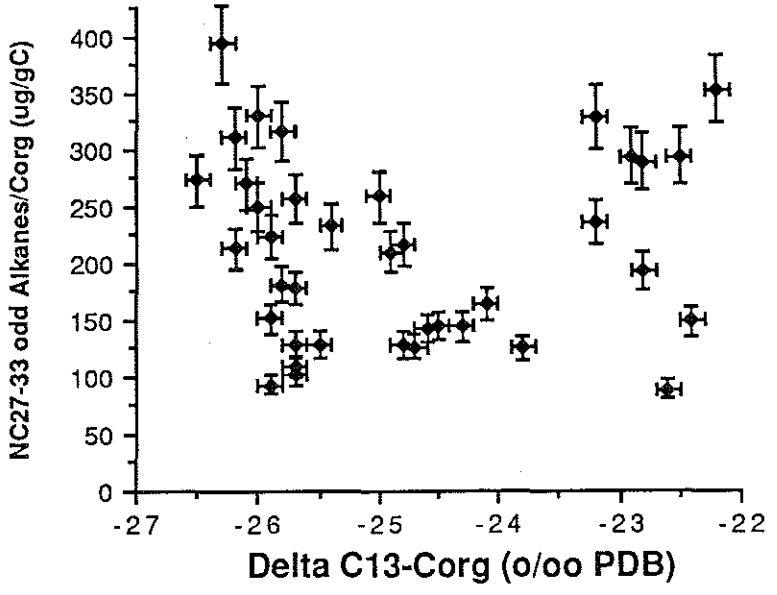
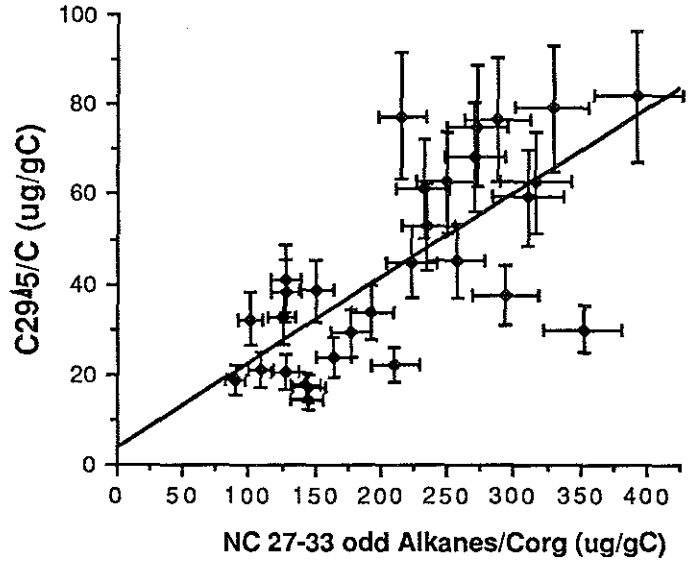
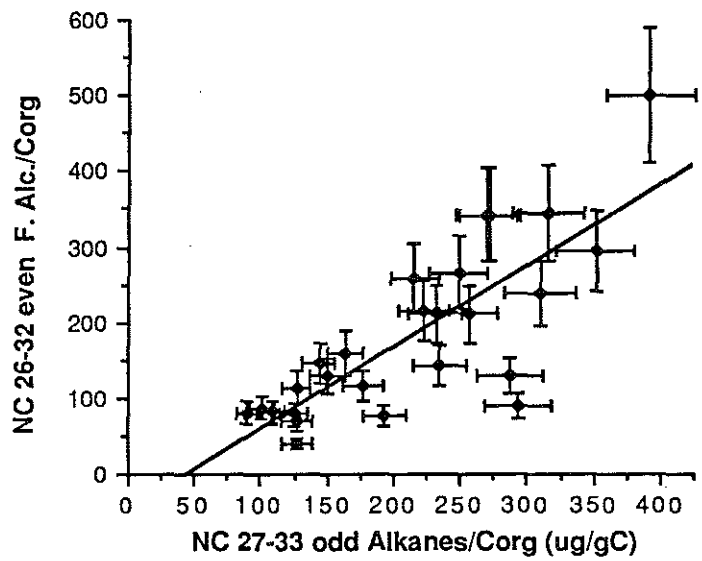

NC27-33 odd Alkanes/Corg (ug/gC)
400
350
300
250
200
150
100
50
0
-27
-26
-25
-24
-23
-22
Delta C13-Corg (o/oo PDB)

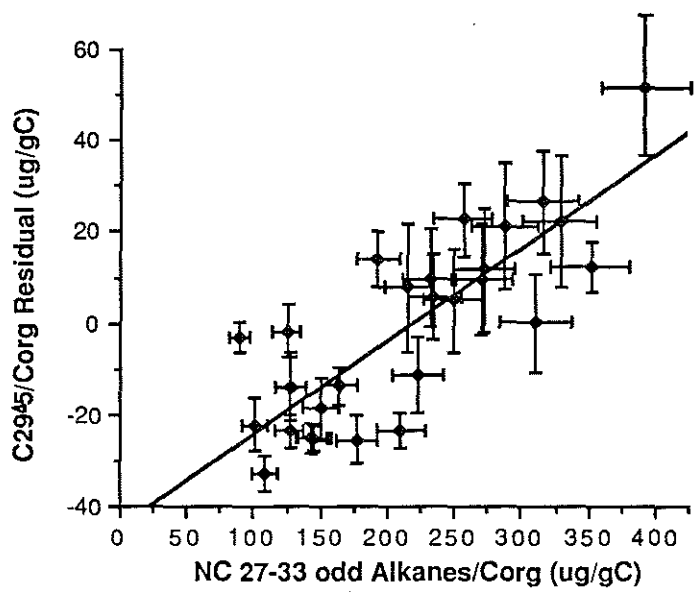
Fig. 3.28. Graph of 24-ethylcholesterol/C_{org} versus paired total nC_{27-33} alkanes ($0.19 \bullet \delta^{13}C\text{-}C_{org} + 3.8$; $P < 0.0001$, $r^2 = 0.55$, $n = 30$).

Fig. 3.29. Graph of nC_{26-32} fatty alcohols/C_{org} versus paired total nC_{27-33} alkanes ($1.1 \bullet \delta^{13}C\text{-}C_{org} - 46$; $P < 0.0001$, $r^2 = 0.62$, $n = 28$).

Fig. 3.30. Graph of 24-ethylcholesterol/C_{org} versus $\delta^{13}C\text{-}C_{org}$ residuals versus paired nC_{27-33} alkane/C_{org} ($0.20 \bullet \delta^{13}C\text{-}C_{org} - 45$; $P < 0.0001$, $r^2 = 0.66$, $n = 30$).


C2945/C (ug/gC)
NC 27-33 odd Alkanes/Corg (ug/gC)


NC 26-32 even F. Alc./Corg
NC 27-33 odd Alkanes/Corg (ug/gC)


C2945/Corg Residual (ug/gC)
NC 27-33 odd Alkanes/Corg (ug/gC)

nC_{27-33} odd alkanes have been found in ancient sedimentary environments, so that it is axiomatic that these compounds must be well preserved. This preservation may be the result of packaging with relatively refractory biopolymers of cuticular debris (Volkman, et al., 1987) and the lack of functional groups which inhibits enzymatic degradative reactions.

Since the maintenance of the proportionality of organic carbon-normalized biomarker concentrations relative to $\delta^{13}C$-C_{org} depends upon equal preservation (or degradation) rates of the biomarker compound and sedimentary organic carbon, if a biomarker were significantly more refractory than the contemporaneous sedimentary organic carbon, sedimentary diagenesis would obscure the biomarker's useful quantitative tracer (biomarker/C_{org}) quality. The following observations suggest three plausible hypotheses for the lack of a signficant nC_{27-33} odd alkane/C_{org} versus $\delta^{13}C$-C_{org} relationship. (1) The n-alkanes, by their occurrence in biological wax particulates and lack of functional groups are probably less susceptible to (micro)biological degradation than the bifunctionalized compounds, 24-ethylcholesterol and the monofunctionalized nC_{26-32} even fatty alcohols. (2) Organic carbon remineralization is probably occurring in the Pigmy Basin. (3) Temporally-increasing stanol/stenol ratios in Pigmy Basin circumstantially support the contention that sterol transformations are occurring in this core, maintaining the biomarker/C_{org} versus $\delta^{13}C$-C_{org} relationship (Chapter 4). The nC_{27-33} odd alkanes may be susceptible to hydraulic particle sorting at least to the same degree as the 4-desmethylsterols. The

combination of relatively refractory nC_{27-33} odd alkanes and labile sedimentary organic carbon, and source biomarker/C_{org} ratio changes caused by particle sorting and/or floral source changes could serve to degrade the nC_{27-33} odd alkanes potentially quantitatively useful biomarker versus $\delta^{13}C$-C_{org} tracer property. Two other potentially useful parameters that could be compared to $\delta^{13}C$-C_{org} are odd/even preference indices and "terrigenous" n-alkanes calculated with a model which allows separation of terrigenous from petrogenic n-alkanes. By constrast, relatively similar degradation rates of 4-desmethylsterols and sedimentary organic carbon may have served to maintain their quantitative tracer property.

A General Paleoceanographic Reconstruction of Organic Matter Deposition in the Pigmy Basin.

A general reconstructed history of the deposition of organic matter in the Late Quaternary Pigmy Basin was produced by a synthesis of the organic geochemical sedimentary records examined in this study. The combined analyses of bulk sedimentary organic carbon isotopic composition and N/C ratios allowed elucidation of the general glacial-interglacial organic geochemical trends in the Pigmy Basin. The addition of organic biomarker compound analyses allowed further specification of organic matter sources, the estimation of terrigenous and marine $\delta^{13}C$-C_{org} isotopic end members, the potential effects of hydraulic particle sorting, and a characterization of biomarkers' sedimentary diagenetic stability against transformations. Some significant observations mentioned previously are reviewed as a

context for this elementary reconstruction.

The existence of a significant porportionality between total C_{37-39} alkenones/C_{org} and $\delta^{13}C$-C_{org} suggested that total C_{37-39}alkenones and sedimentary organic carbon were preserved (or degraded) at nearly the same rate. A systematic residual trend was consistent with an independently calculated sedimentary organic carbon decay rate.

The organic carbon-normalized concentrations series of terrigenous biomarker compounds were also significantly linearly related to sediment organic carbon isotopic composition. These compounds also showed systematic residual trends from simple linear relationships to $\delta^{13}C$-C_{org}. The residual deviations, however, if interpreted only as a result of sedimentary organic carbon degradation rates (k = 0.035, $\tau_{1/2} \cong$ 20 ky) were unrealistically high compared to rates estimated from either the total C_{37-39} alkenones/C_{org} versus $\delta^{13}C$-C_{org} diagenesis model (k = 0.005, $\tau_{1/2} \cong$ 140 ky) or from a first-order degradation model applied to the sedimentary organic carbon record (k = 0.007, $\tau_{1/2} \cong$ 100 ky). The unusually high 4-desmethylsterol/C_{org} residual trend above a more typical sedimentary organic carbon decay rate (e.g. k =0.007, $\tau_{1/2} \cong$ 100 ky) was attributed to either hydraulic particle sorting and/or a climatically-induced floral source change. The hydaulic particle sorting mechanism could cause the usually high residual values observed in the ~20-65 kybp interval by the transport of a coarser organic carbon particle fraction with a higher than average 24-ethyl-cholesterol/C_{org} ratio for given $\delta^{13}C$-C_{org} values. This

hypothesis was supported by a coarsening of the terrigenous clastic sediment input to the Pigmy Basin in isotope stages 2 and 3 as compared to the preceding and succeeding stages.

Statistical analyses of terrigenous and marine biomarker/C_{org} versus $\delta^{13}C$-C_{org} allowed determination of average marine and terrigenous carbon isotopic end members. With these carbon isotopic end members, sedimentary organic carbon, and a linear mixing model, terrigenous and marine organic carbon records were calculated for the Late Quaternary Pigmy Basin (Chapter 2).

Combined sedimentary organic carbon isotopic composition and N/C ratio analyses allowed the determination that the sedimentary organic matter in the Late Quaternary Pigmy Basin was a climatically-forced mixture of terrigenous and marine C_3-photosynthetic (Calvin-Benson Cycle) organic matter. During interglacial periods (isotope (sub)-stages 1 and 5a-b), the global ice volume was small compared to that in glacial periods and the ocean covered the continental shelves. Terrigenous organic carbon and sediments were largely trapped in estuaries and on the continental shelves, and sedimentation rates in the Pigmy Basin were 2-4 times lower during interglacial stages 1 and 5a-b than in glacial stage 2. The interglacial Pigmy Basin and central Gulf of Mexico were dominated by the input of marine organic matter deposition.

In the glacial oceans, sea level was as much as ~150m lower than during interglacial stages, exposing most of the continental shelves. Continental shelf and estuarine erosion rates were higher, and the glacial stage 2 sedimentation rate was ~2-4 times higher than during

the interglacial stages (1 and 5a-b) in the Pigmy Basin. The high continental erosion rate caused a predominance of terrigenous organic carbon deposition in the glacial Pigmy Basin and central Gulf of Mexico.

The organic carbon-normalized concentration of total C_{37-39} alkenones was largely a proportional tracer of marine organic carbon and Prymnesiophyte plankton input to the Pigmy Basin. The interglacial substages 5a-b, which subsequently decreased into the beginning of stage 2. The proportion of marine carbon input (total C_{37-39} alkenones/C_{org}) generated local maxima shortly after the close of glacial stages 2 and 4.

The organic carbon-normalized concentrations of a population of 24-ethylcholesterol/C_{org} values were significantly related to sedimentary organic carbon isotopic composition, suggesting that this concentration ratio generally traced terrigenous organic matter burial in the Late Quaternary Basin. Interglacial substages 5a-b had low 24-ethylcholesterol/C_{org} values which generally increased into the middle of isotope stage 3 with a local maximum near the end of isotope stage 4, whereafter the value decreased into interglacial stage 1 with local maxima at about 10 and 25 kybp. Three similar local maxima at about 66, 25, and 10 kybp occurred to varying degrees in three of four other 4-desmethylsterol (cholesterol, 22-E-dehydrocholesterol, brassicasterol, and campesterol) which were also significantly related to the sedimentary organic carbon isotopic composition. The local maximum at ~10 kybp for brassicasterol was recognized, but there was significant local maxima at either approximately 66 and 25 kybp.

The onshore-offshore movement of a sediment-laden Mississippi River plume may have contributed to the occurrence of the local biomarker/C_{org} maxima in the Pigmy Basin sedimentary record. Meltwater spikes have significantly affected the stable oxygen isotopic composition of Gulf of Mexico surface waters at the close of glacial stage 2 and the beginning of isotope stage 1 (Kennett and Shackleton, 1975; Emiliani et al., 1978; Leventer et al., 1982; Fillon and Williams, 1984; Williams, 1984; Williams and Kohl, 1986). During the interval of about 10-11 kybp, a diversion of the meltwater flow from the Mississippi River to the St. Lawrence drainage system was hypothesized, causing the brief and cold Younger Dryas Event (Broecker et al., 1988). In the contemporary Amazon River plume, a standing diatom concentration maximum was observed in a narrow salinity range where suspended terrigenous sediment concentrations dropped nearly three orders of magnitude (Milliman and Boyle, 1975). The lowered turbidity of the surface water was considered to be a probable cause for the high diatom concentrations.

A hypothetical scenario is described here in which similar processes may have been occurring in the surface waters of the Pigmy Basin (Figs. 3.31 and 3.32). As global climate cooled and sea level fell, the turbid plume of the anticyclonic (counterclockwise) Mississippi River plume in the Gulf of Mexico moved off the Texas continental shelf seaward nearer the Pigmy Basin. The greater input of terrigenous sediment to the hemipelagic ocean caused an increased sedimentation rate and a predominance of terrigenous organic matter burial. An interval of ice melting in the latter part of glacial

Fig. 3.31. Block diagram of the interglacial Late Quaternary northern Gulf of Mexico and North America, showing some of the major processes affecting sedimentary organic carbon deposition in the Pigmy Basin over the last ~100 ky. The major features include: high sea level compared to the glacial case (Fig. 3.32), a predominance of marine organic matter preservation (total long chain unsaturated alkenone/C_{org} from fig. 3.2.a) over erosive terrigenous organic matter preservation (24-ethylcholesterol/C_{org} from fig. 3.5.a) input, counterclockwise seawater circulation over the Texas continental shelf, and withdrawn continental ice sheet.

INTERGLACIAL PERIOD

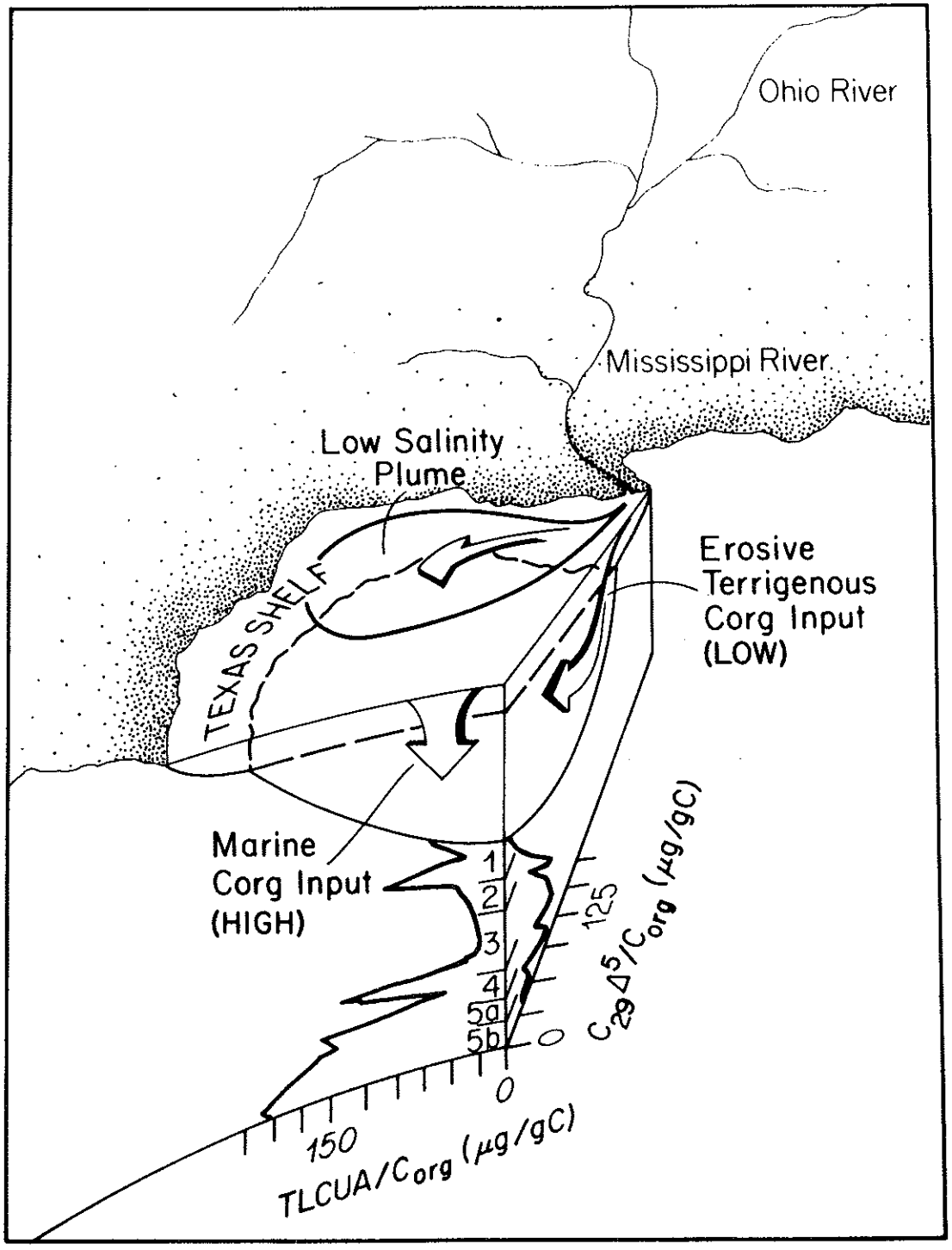
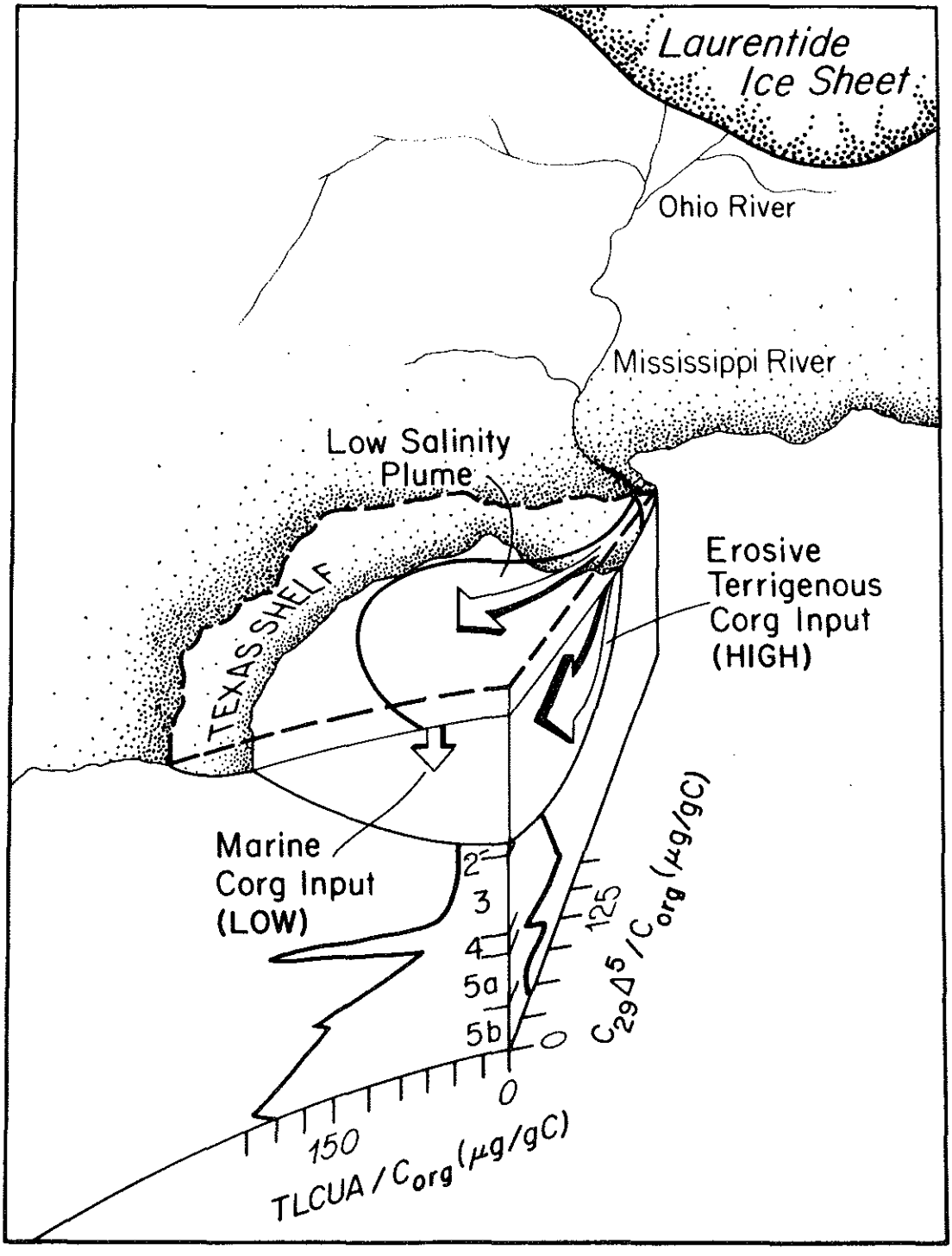


Fig. 3.32. Block diagram of the glacial Late Quaternary northern Gulf of Mexico and North America, showing some of the major processes affecting organic matter deposition in the last 100 ky. The major features include: sea level lowered ~150 m relative to interglacial intervals (see Fig. 3.31), a dominance of erosive terrigenous organic carbon preserved input (24-ethylcholesterol/-C_{org} from fig. 3.5.a) over marine organic matter preserved input (total long chain unsaturated alkenone/C_{org} from fig. 3.2.a), suggested seaward movement of the Mississippi River plume off the continental shelf toward the Pigmy Basin, and equatorward-advanced continental ice sheet.

GLACIAL PERIOD



isotope stage 4 caused erosion of continental sediment into the deep sea and local maxima of many 4-desmethylsterol/C_{org} in the Pigmy Basin. Following this putative meltwater event, a higher sea level and a retreat of the high turbidity plume, a standing marine primary production maximum moved over the Pigmy Basin. The advection of this productivity maximum left a record of high total C_{37-39} alkenone and $\delta^{13}C$-C_{org} values in the Pigmy Basin sediments. As global climate continued to cool, sea level fell to ~150m below the present level, and the increased erosion of continental material caused the highest sedimentation rates and the most negative $\delta^{13}C$-C_{org} values observed in this Pigmy Basin sediment core (DSDP 619). The high turbidity plume continued to overshadow the glacial Pigmy Basin, reducing total C_{37-39} alkenone/C_{org} values to low levels through stage 3 and into stage 2.

The deposition of terrigenous and marine organic matter recorded the general climatic warming trends of isotope stages 2 and 1. Marine organic matter became a larger proportion of the sedimentary organic carbon during this interval. A meltwater event at ~25 kybp caused the seaward movement of the turbid, low salinity plume. The deposition of continental material left local concentration in many 4-desmethyl-sterol/C_{org} records. These terrigenous organic matter maxima were followed by a higher total C_{37-39} alkenone/C_{org} ratio than was typical for the co-occurring $\delta^{13}C$-C_{org} value, suggesting that Prymnesiophytes became a larger than average source of marine organic carbon. Finally, as global climate warmed and the Laurentide Ice Sheet meltwaters poured into the Gulf of Mexico, the turbid plume of

terrigenous sediment and organic matter left a record of high 4-desmethylsterol/C_{org} ratios near the glacial-to-interglacial stage 2/1 boundary. With a decrease in the Mississippi River flow, the turbidity plume again retreated shoreward, followed by a maximum in Prymnesiophyte concentration which left a strong local total C_{37-39} alkenone/C_{org} maximum at ~10 kybp.

As sea level increased in the present interglacial period, the Mississippi River plume moved back onto the Texas continental shelf. Marine organic matter once again began to dominate the sedimentary record of the Pigmy Basin.

The general glacial-interglacial trends outlined in this hypothetical scenario were well substantiated by the organic geochemical records in the Pigmy Basin. Although the shorter term events noted in the reconstructed scenario were often confirmed by different techniques (biomarker/C_{org}, $\delta^{13}C$-C_{org}, residual biomarker/C_{org} values, and terrigenous and marine organic carbon concentrations), further study of their intensities and histories would give improved insight to their paleoceanographic significance.

Conclusions

The value of the combined analyses of organic biomarker compounds, organic carbon, and sedimentary organic carbon isotopic composition in discerning the organic geochemical record of glacial-interglacial climatic change was examined in a Late Quaternary (208.7m, ~100 ky) sediment core from the hemipelagic Pigmy Basin in the northern Gulf of Mexico.

1. The organic carbon-normalized concentrations of total C_{37-39} alkenone/C_{org} were significantly linearly related to sedimentary organic carbon isotopic composition, indicating that they were useful tracers of marine organic carbon on the 2-100 ky time scale. Interglacial isotope (sub)stages 5a-b, 1 and 2 were generally characterized by higher total C_{37-39} alkenone/C_{org} values than the intervening stages 4-2, with two local maxima succeeding isotopic stages 4 and 2.

2. A time-varying residual trend from the total C_{37-39} alkenone/C_{org} versus $\delta^{13}C$-C_{org} linear regression was consistent with the occurrence of two processes. The general decreasing trend with time was attributed to organic carbon remineralization. Episodic extrema may be attributed to source changes (i.e., time-varying total C_{37-39} alkenone/marine C_{org} ratios).

3. The organic carbon-normalized concentration of 24-ethylcholesterol/C_{org} was significantly related to sedimentary organic carbon isotopic composition, indicating that it was a useful terrigenous organic matter tracer in the 2-100 ky Pigmy Basin sedimentary record and perhaps in similar depositional environments.

Interglacial isotope stages 5a-b and 1 were characterized by lower 24-ethylcholesterol/C_{org} values than during the intervening stages 4-2, with a local maximum near the glacial-intergalcial stage 2/1 boundary.

4. The time-varying residual trend from the 24-ethylcholesterol/-C_{org} versus $\delta^{13}C$-C_{org} linear regression was consistent with the occurrence of a number of processes causing divergences from a simple mixing relationship. The general skewed sinusoidal trend in the residual time series was consistent with sedimentary organic carbon remineralization. Large, positive 24-ethylcholesterol/C_{org} residuals above the C_{org} remineralization trend in the ~20-65 kybp interval may have been caused by hydraulic particle sorting, deposition of partially-degraded organic matter, or climatically-induced floral source changes. The particle sorting hypothesis was supported by clastic sedimentological results which evidenced coarser particle deposition in the Pigmy Basin during near the glacial maximum than in interglacial stages. Climatically-induced floral source changes may also have contributed to or caused the positive residual trend. Episodic extrema were attributed to source changes.

5. Linear least squares regressions of observed biomarker/C_{org} ratios on $\delta^{13}C$-C_{org} values with first-order C_{org} remineralization kinetics approximated the idealized diagenetic models for organic carbon-normalized terrigenous and marine biomarker sedimentary records on the time scale of 2-100 ky. Processes (including C_{org} remineralization, hydraulic particle sorting, source changes, biomarker degradation, and differential marine and

terrigenous organic carbon remineralization) which cause divergences from the simple biomarker/C_{org} versus $\delta^{13}C$-C_{org} linear relationship may limit the application of this simple diagenetic model.

7. Four other desmethylsterols (cholesterol, 22-dehydrocholesterol, brassicasterol, and campesterol) and the nC_{26-32}even fatty alcohols were also significantly related to sedimentary organic carbon isotopic composition. Their residual trends were similar to that for 24-ethylcholesterol/C_{org}. The residuals may be attributed to C_{org} remineralization, hydraulic particle sorting, and/or floral source changes.

8. Eight other 4-desmethylsterols ($C_{27-29}\Delta^{22}$-, $C_{27\ and\ 29}\Delta^{5,22}$-, and $C_{27-29}\Delta^{0}$-4-desmethylsterols) when normalized to C_{org} followed the general trends of 24-ethylcholesterol/C_{org}, but were insignificantly related to sedimentary organic carbon isotopic composition. The similarity to the 24-ethylcholesterol/C_{org} record suggested that these 4-desmethylsterols also had a terrigenous plant origin. Sedimentary diagenesis, hydraulic particle sorting, and source changes may have contributed to the statistical insignificance of these biomarker compounds as quantitative tracers of organic matter determined by a linear least squares model.

9. There was an absence of 4-desmethylsterols which indicated marine biomarker/C_{org} characteristics (positive slope and $\delta^{13}C$-C_{org} intercept $\cong$ 19 $\pm$ 2°/$_{oo}$ PDB) relative to $\delta^{13}C$-C_{org}, despite the fact that most of the sterolsexamined had both terrigenous and marine sources. These observations implied that terrigenous

sterols were better preserved than marine sterols. The apparent differential diagenetic labilities of terrigenous and marine 4-desmethylsterols suggested that sedimentary sterol records may be biased in favor of terrigenous sterol preservation.

10. The combined analyses of selected organic biomarker compounds, sedimentary carbon isotopic composition, and sedimentary organic carbon concentrations allowed general paleoceanographic reconstructions of glacial and interglacial modes of organic matter deposition in the Late Quaternary Pigmy Basin.

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TABLE 3.1
Alkenone Time Series Data
Pigmy Basin, D.S.D.P. Core 619

Sample Number	Age (ky)	$\delta^{13}C_{org}$ (o/oo PDB)	37:2MK* (ng/gds)	37:3MK* (ng/gds)	38:2+3* MEK (ng/gds)	39:2+3* EK (ng/gds)	TLCUA# C_{org} (µg/gC)
1	1.9	-24.1	226	38	234	29	74
2	3.1	-22.6	134	17	140	19	50
4	5.3	-24.3	135	37	168	59	55
5	7.1	-24.5	205	82	145	19	44
6	8.1	-24.6	224	96	306	45	63
7	9.2	-23.8	447	184	669	180	120
9	11.9	-25.7	43	15	11	10	6.4
10	13.9	-24.7	99	34	145	19	31
12	16.5	-24.9	148	77	225	25	61
13	17.1	-25.8	85	45	68	21	25
14	18.3	-25.7	76	27	137	17	30
15	19.0	-25.5	91	47	136	27	35
16	20.1	-25.7	113	58	182	36	43
17F	20.6	-25.7	74	43	130	28	29
18	22.4	-25.9	163	81	255	47	46
19F	24.3	-25.4	102	47	147	19	41
20	26.5	-26.2	29[a]		31	23	7.7
21F	29.3	-25.9	34	18	62	7	16
22	31.1	-26.0	47	22	77	11	29
23F	32.6	-26.5	37	22	60	5	16
24	35.9	-26.1	48	24	77	10	21
25F	38.2	-26.2	41	22	72	20	20
26	40.2	-26.0	35	18	49	7	16
28	43.2	-25.8	34	26	54	10	21
31F	51.7	-26.3	34	12	48	7	18
34	58.3	-25.0	95	39	145	6	47
35F	62.3	-24.7	133	49	179	39	76
36	64.4	-22.8	333	145	494	66	162
37F	66.5	-25.7	72	44	124	28	40
38	70.3	-24.8	218	59	263	37	85
42	83.8	-23.2	241	41	279	56	140
43	85.1	-22.8	220	38	279	46	130
47F	98.2	-22.2	269	85	334	128	150
48F	99.2	-22.9	357	84	447	150	190
54	102.2	-23.2	267	50	350	76	140

*37:2MK = C_{37}-diunsaturated methylketone; 37:3MK = C_{37}-triunsaturated methylketone; 38:2+3MEK = Sum of the C_{38}-di- and triunsaturated methyl- and ethylketones; 39:2+3EK = Sum of the C_{39} di- and triunsaturated ethylketones.
#TLCUA/C_{org} = Total long chain (C_{37-39}) unsaturated alkenones/C_{org}
[a]37:2MK + 37:3MK

TABLE 3.2
NC_{27-33} Odd Alkanes and NC_{26-32} Even Alcohols
Pigmy Basin, D.S.D.P. Core 619

Name	Age (ky)	$\delta^{13}C$ (o/oo PDB)	NC 27-33 odd/C (µg/gC)	F.Alc. 26-32 even/C org (µg/gC)
1	1.9	-24.1	164	159
2	3.1	-22.6	89	81
3	4.2	-22.4	149	--*
4	5.3	-24.3	144	146
5	7.1	-24.5	145	--
6	8.1	-24.6	143	--
7	9.2	-23.8	125	78
8	11.0	-25.9	93	--
9	11.9	-25.7	128	68
10	13.9	-24.7	127	114
11	15.4	-24.8	128	--
12	16.5	-24.9	210	--
13	17.1	-25.8	181	--
14	18.3	-25.7	178	116
15	19.0	-25.5	128	40
16	20.1	-25.7	101	87
17F	20.6	25.7	109	82
18	22.4	-25.9	151	130
19F	24.3	-25.4	232	212
20	26.5	-26.2	213	194
21F	29.3	-25.9	223	216
22	31.1	-26.0	329	--
23F	32.6	-26.5	272	342
24	35.9	-26.1	270	342
25F	38.2	-26.2	310	239
26	40.2	-26.0	249	266
27	43.2	-25.8	316	345
28	51.7	-26.3	393	500
29	58.3	-25.0	258	337
30	62.3	-24.7	--	206
31	64.4	-22.8	288	130
32	66.5	-25.7	257	211
33	70.3	-24.8	216	259
34	83.8	-23.2	335	142
35	85.1	-22.8	193	77
36	86.4	-22.5	293	--
37	98.2	22.2	352	294
38	99.2	22.9	293	90
39	102.2	23.2	328	--

*Not determined

TABLE 3.3--Sterol and Hopanol Time Series Data

	A	B	C	D	E	F	G	H	I	J	K	L
1	Age	C13-Corg	C29Δ5	C29Δ0	C29Δ22	C29Δ5,22	C28Δ5	C28Δ0	C28Δ22	C28Δ5,22	C27Δ5	C27Δ0
2	(ky)	(o/ooPDB)	(ug/gC)	(ug/gC)	(ug/gC)	(ug/gC)	(ug/gC)	(ug/gC)	(ug/gC)	(ug/gC)	(ug/gC)	(ug/gC)
3	1.9	-24.1	23.7	19.0	1.2	0.0	4.8	3.3	1.6	2.1	8.2	6.9
4	3.1	-22.6	18.7	11.0	0.0	3.3	1.8	2.3	1.1	1.0	3.4	4.1
5	5.3	-24.3	14.6	6.7	0.0	1.4	1.6	0.0	0.0	0.0	0.0	18.9
6	7.1	-24.5	16.9	10.5	0.6	5.5	2.3	2.2	1.5	2.6	4.8	3.8
7	8.1	-24.6	17.5	11.6	0.6	6.0	2.2	0.9	2.0	2.3	3.8	3.9
8	9.2	-23.8	32.4	36.4	1.2	11.5	7.2	9.3	9.4	4.4	5.4	16.6
9	11.9	-25.7	41.0	22.3	8.4	9.3	8.4	5.4	6.2	8.6	15.3	11.0
10	13.9	-24.7	20.4	12.7	0.7	4.7	1.8	3.3	1.3	2.4	2.2	4.6
11	16.5	-24.9	22.1	17.6	3.2	8.6	4.1	4.0	5.9	3.9	5.0	9.3
12	18.3	-25.7	29.1	17.5	1.3	7.1	2.9	4.5	2.9	3.9	5.8	16.0
13	19.0	-25.5	38.2	19.7	1.8	11.6	5.5	4.6	4.8	7.0	10.2	7.6
14	20.1	-25.7	32.3	17.5	2.4	10.4	4.8	4.0	5.1	6.3	8.1	7.4
15	20.6	-25.7	21.2	13.5	1.4	7.3	2.8	3.2	3.4	4.8	7.0	6.7
16	22.4	-25.9	38.4	19.9	3.9	13.9	6.7	5.0	12.5	11.2	11.8	11.1
17	24.3	-25.4	61.2	34.1	5.8	18.4	10.5	8.2	10.4	13.8	22.8	17.7
18	29.3	-25.9	44.9	30.5	2.2	10.6	9.7	5.4	4.0	5.4	9.9	10.4
19	31.1	-26.0	79.3	46.4	4.8	17.2	10.7	8.6	6.4	8.8	14.2	13.2
20	32.6	-26.6	75.3	48.0	4.9	15.4	11.4	8.1	6.2	9.3	15.6	14.7
21	35.9	-26.1	68.5	53.2	5.1	15.2	14.0	8.5	6.9	7.7	12.8	16.2
22	38.2	-26.2	59.6	39.4	4.5	12.1	8.5	9.4	5.9	7.3	12.5	40.8
23	40.2	-26.0	62.9	33.7	5.7	13.7	13.0	7.1	5.2	8.4	13.0	20.3
24	43.2	-25.8	82.1	51.9	5.3	15.3	12.7	11.5	4.9	6.3	13.9	40.0
25	51.7	-26.3	111.7	60.0	11.2	21.5	22.4	11.1	7.9	14.8	23.0	34.0
26	58.3	-25.0	72.1	54.5	8.6	20.5	15.4	11.1	9.2	13.8	18.3	21.4
27	62.3	-24.8	76.7	47.4	6.8	16.9	13.1	14.1	6.2	11.0	9.0	17.7
28	64.3	-22.8	45.2	36.9	11.0	15.8	11.0	11.9	17.7	6.8	9.4	27.4
29	66.5	-25.7	77.5	46.1	5.4	21.0	12.1	12.2	8.6	16.7	20.8	40.0
30	70.3	-24.8	52.8	41.2	7.3	12.5	8.7	9.3	7.5	7.4	9.1	24.4
31	83.8	-23.2	33.7	25.3	2.0	9.5	3.7	4.8	5.2	6.1	8.3	10.1
32	85.1	-22.8	37.5	26.6	2.3	10.0	5.1	0.0	5.7	9.3	11.4	10.4
33	98.2	-22.2	30.1	41.9	3.1	10.0	6.3	6.7	6.4	3.6	5.8	12.9

TABLE 3.3--(Continued)

	M	N	O	P	Q	R	S	T
1	C27Δ22	C27Δ5,22Z	C27Δ5,22E	C27-4M	C28-4M	C29-4M	H-31-ol	H-32-ol
2	(ug/gC)	(ug/gC)	(ug/gC)	(ug/gC)	(ug/gC)	(ug/gC)	(ug/gC)	(ug/gC)
3	1.5	0.0	1.2	0.0	0.0	6.9	2.8	12.4
4	0.0	0.0	0.0	0.0	1.6	2.5	3.0	12.7
5	0.0	0.0	0.0	0.0	1.3	4.4	5.4	13.2
6	0.0	0.0	0.6	0.9	0.0	0.5	7.1	0.9
7	0.0	0.0	0.6	0.8	0.4	0.3	0.4	2.1
8	4.9	1.4	1.2	0.9	1.8	3.1	9.2	31.8
9	3.4	1.5	8.4	0.0	4.0	0.0	0.5	3.8
10	2.2	0.0	0.7	4.6	1.3	1.4	1.4	9.2
11	0.0	1.3	3.2	1.5	0.0	0.0	6.0	5.8
12	1.8	0.0	1.3	0.0	1.7	3.1	2.6	11.4
13	0.0	0.7	1.8	1.6	1.1	2.0	2.5	9.6
14	0.0	0.8	2.4	1.0	0.8	1.6	1.5	4.8
15	0.0	0.0	1.4	0.0	0.6	1.0	2.2	8.3
16	3.7	1.5	3.9	0.0	0.9	0.8	3.6	11.2
17	0.5	1.9	5.8	0.0	2.0	3.4	4.6	16.9
18	0.0	0.0	2.2	0.0	1.3	1.1	2.4	12.2
19	0.0	1.2	4.8	2.1	2.2	2.3	2.7	17.4
20	0.0	0.0	4.9	0.0	1.6	1.0	2.9	17.6
21	0.0	0.0	5.1	0.0	1.7	1.8	2.5	14.7
22	0.5	1.4	4.5	1.5	3.0	4.9	4.3	14.8
23	2.5	1.3	5.7	1.3	1.7	3.7	9.5	17.3
24	5.7	1.9	5.3	0.0	0.7	5.5	5.9	27.3
25	5.1	2.5	11.2	2.8	3.7	5.5	12.0	22.1
26	5.5	2.2	8.6	0.0	0.0	0.0	10.9	19.5
27	0.0	1.8	6.8	16.6	7.5	6.7	8.8	26.7
28	0.7	4.9	11.0	1.2	2.3	5.1	10.0	25.7
29	0.0	0.0	5.4	2.3	4.5	6.5	6.4	21.9
30	4.8	0.8	7.3	0.0	4.0	7.0	5.9	27.4
31	2.5	0.0	2.0	0.0	1.4	1.3	6.9	14.6
32	3.0	0.0	2.3	0.0	1.8	1.7	7.5	15.6
33	0.6	1.1	3.1	0.0	1.4	2.3	3.8	13.5

CHAPTER 4

4-DESMETHYLSTEROL TRANSFORMATIONS ON THE 10^3-10^5 YEAR SCALE

ABSTRACT

The potential reduction of sterol double bonds (Δ^5, Δ^{22}) in C_{27} to C_{29} 4-desmethylsterols was evaluated by examining the time series of expected product/precursor relationships with sterol data from the ~2-100kybp DSDP 619 record. Only the saturation of the Δ^5 bond of the C_{29} sterols (24-ethylcholest-5-en-3ß-ol and 24-ethylcholesta-5,22-dien-3ß-ol) showed significant temporally-increasing trends. The 24-ethylcholestan-3ß-ol/24-ethylcholest-5-en-3ß-ol ($C_{29}\Delta^0/C_{29}\Delta^5$) ratio also positively correlated with paired sedimentary organic carbon isotopic composition ($\delta^{13}C$-C_{org}) values. This may be due to increased susceptibility to diagenetic transformation reactions by the organic matter accompanying finer grain-sized terrigenous sediment particles. A long-term, secular source change of 24-ethylcholestan-3ß-ol relative to 24-ethylcholest-5-en-3ß-ol to explain the correlation with $\delta^{13}C$-C_{org} seems unlikely since both compounds are predominantly of a terrigenous origin in the Pigmy Basin. A comparison of histograms of stanol/stenol (Δ^0/Δ^5) ratios for the C_{27} to C_{29} 4-desmethylsterols indicates the following sequence in the relative degree of transformation: $C_{27} > C_{28} > C_{29}$. The C_{27} and C_{28}

sterols appear to have attained their respective degrees of transformation before ~2kybp, perhaps prior to deposition in the Pigmy Basin. However, differential rates of competing reactions of both the precursor and products may have obscured these simple transformation ratio records.

INTRODUCTION

The processes influencing the relative abundance of saturated and unsaturated steroidal alcohols in nature have been inferred from environmental distributions and laboratory studies. Some bacteria have the ability to transform stenols into stanones, via stenone and stanone intermediates (Schubert and Kaufmann, 1965; Rosenfeld and Hellman, 1971; Eyssen et al., 1973; Eyssen and Parmentier, 1974). The increasing stanol/Δ^5-stenol ratios with depth in Quaternary (Ogura and Hanya, 1973) and contemporary lacustrine sediments (Gaskell and Eglinton, 1975, 1976; Nishimura and Koyama, 1976) were taken as circumstantial evidence for the occurrence of stenol → stanol transformations. Laboratory cultures of fresh lacustrine sediments and anaerobic sewage sludge (Gaskell and Eglinton, 1975) and microbial enrichments of anaerobic marine sediments (Taylor et al., 1981), with radiolabelled 4-^{14}C-cholesterol demonstrated the ingrowth of the C_{27}-stanol, supporting the suspected $C_{27}\Delta^5$-stenol → $C_{27}\Delta^0$-stanol transformation. Steroid distributions and transformations have also been extensively studied in the oceanic water column and marine sediments (Gagosian and Smith, 1979; Lee

et al., 1980; Gagosian et al., 1980; De Leeuw et al., 1983). Studies of sterol distributions in marine sediments have allowed elaboration of mechanistic pathways for microbial or chemical transformations in seawater or sediments (Gagosian, et al., 1980; MacKenzie, et al., 1982). With model transformation pathways as a guideline, geochemists can evaluate possible sterol transformation ratios in nature as circumstantial evidence for specific reactions.

The C_{27} to C_{29} 4-desmethylstanols are derived from terrigenous and marine sources and from the transformation of unsaturated sterols. The stanol/stenol ratio in many terrigenous and marine organisms is typically in the range of 0.1-0.2. The total stanol/total stenol ratio in the diatom Melosira granulata collected from the Japanese Lake Suwa was ~0.03 (Nishimura and Koyama, 1976). The total stanol/total stenol ratio of two higher plants (Zizania latifolia: 0.009; Potomageton crispus: 0.005), two phytoplankton species (Microcystus aeruginosa: 0.148; Melosira granulata: 0.012) and a zooplnakton species (Brachionus calyciflorus: 0.009) were all less than 0.15 (Nishimura and Koyama, 1977). The stanol/stenol ratios for six sterol pairs in Black Sea surface waters were in the range of 0.1-0.2 (Gagosian and Heinzer, 1979). These ratios were considered to be caused by stanol input directly from organisms (jellyfish: Ballantine et al., 1976; red algae: Chardon-Lorriaux et al., 1975; echinoderms: Goad et al., 1972; and sponge: Nes and McKean, 1977) since stenol → stanol transformations would be expected to be slow in oxic surface water (Nishimura, 1978).

There are, however, a few isolated occurrences of high stanol/-

stenol ratios in some organisms. 5α(H)-Stanol/Δ^5-stenol ratios of ~0.5 were observed in cultured Minochrysis lutheri at stationary growth phase, while no measurable sterols were found when the culture was in exponential growth phase. Boon et al. (1983) reported a stanol/stenol ratio of ~0.5 in a cyanobacterial mat on the sediment surface of Solar Lake in Egypt.

In this study, sterol data collected for a quantitative assessment of their bulk organic matter tracer properties (Chapter 3) were evaluated for the possible occurrence of two double bond (Δ^5, Δ^{22}) reductions by evaluating time series records of their transformation ratios.

II. METHODS

Samples

The samples used in this study were from a 208.7m hydraulic piston core collected by the D/V Glomar Challenger in the normally oxic Pigmy Basin (2259m water depth at 27°11.61'N, 91°24.54'W) in the northern Gulf of Mexico. The sampling of this core was described in Chapter 2.

Sterol Analysis

The procedures for the extraction, separation, and analysis of the sterols were previously described (Chapter 3). Briefly, the sterols were sonically extracted with $(CH_3)_2CHOH$ and $CHCl_3$:CH_3OH (1:1) from 10±2g wet sediment samples. 1-Heptadecanol was used as an

internal recovery standard for the sterols. The sterols were derivatized to acetate esters using the methods of Peltzer and Gagosian (1987). Gas chromatographic analysis was performed on a Carlo Erba 2150 gas chromatograph with a Varian Vista 401 Chromatography Data System. Forty sterol analyses gave 75±15°/. (C = 20°/., where the variance C ≡ 100σ/$\bar{X}$) recovery of the alcohol recovery standard. The detection limit for the sterols was 3 ± 0.5 ng compound/gds, based on minimum integrated peak areas and sediment sample masses. The triplicate variance of three different C_{29}-sterol ratios ranged from 15 to 21 °/$_{oo}$. The variances of the C_{27}- and C_{28}-sterols were difficult to evaluate because in many instances one or both members of the potential transformation pair approached detection limits. The variance of the the C_{28}-sterol ratios was estimated at ~25°/$_{oo}$. The triplicate variance of the cholestan-3ß-ol/cholest-5-en-3ß-ol pair was 34°/$_{oo}$, characteristic of errors in ratios present at low concentrations. Structural determinations were based on gas chromatographic retention times and computerized gas chromatographic/mass spectrometric (C-GC-MS) analyses of samples and selected authentic standards and comparison with published mass spectra.

Sedimentary Organic Carbon Isotopic Analysis

Sedimentary organic carbon isotopic analysis ($\delta^{13}C$-C_{org}) was described in Chapter 2. All $\delta^{13}C$-C_{org} values are given relative to the Chicago PDB isotopic standard.

Chronostratigraphy

The chronostratigraphy used in this study is based on the isotope

(sub)stage boundary ages of Shackleton and Opdyke (1973) assigned to the DSDP 619 Globeriginoides ruber oxygen isotope record by Williams and Kohl (1986). Additional chronostratigraphic constraints for DSDP 619 include planktonic foraminiferal boundaries (Z/Y, Y/X) (Kohl, 1986), a phytoplanktonic boundary (Constance and Parker, 1986) and volcanic ash layer (Y8) Correlated by major element chemistry to a major eruption of the Guatamalan Lake Atitlan Caldera (Ledbetter, 1986). An alkenone ratio (U^{K}_{37}) record (Brassell, et al., 1986) for DSDP 619 is also consistent with the glacial-interglacial history of this core (Chapter 5).

RESULTS AND DISCUSSION

The C_{29} 4-Desmethylsterols

The time series of four potential sterol reduction pathways are examined here. Since there are possibly two sites for double bond saturation in these 4-desmethylsterols (Δ^5, Δ^{22}), each of these two reactions will be examined for the Δ^5 and $\Delta^{5,22}$-sterols. A diagram of the major structural sterol transformations discussed here is shown in Figure 4.1.

The Δ^5 Reductions

The time series of potential $\Delta^5 \rightarrow \Delta^0$ and $\Delta^{5,22} \rightarrow \Delta^{22}$ double bond reductions were evaluated by examination of 24-ethylcholestan-3ß-ol/24-ethylcholest-5-en-3ß-ol ($C_{29}\Delta^0/C_{29}\Delta^5$) (Fig. 4.2) and 24-ethylcholest-22-en-3ß-ol/-24-ethylcholesta-5,22-dien-3ß-ol ($C_{29}\Delta^{22}/C_{29}\Delta^{5,22}$) time series

(Fig. 4.3). Although both the $C_{29}\Delta^0/C_{29}\Delta^5$ and $C_{29}\Delta^{22}/C_{29}\Delta^{5,22}$ time series show episodic excursions, the stanol/stenol ratios generally increase with age. The general temporal ratio increases were determined to be significant ($P<0.05$) by application of the statistical F-test to a linear least squares regression result of sterol ratios (Y) on age (X). The F-test evaluates the null hypothesis that the correlation coefficient is significant (i.e., $r^2 \neq 0$), which is mathematically equivalent to testing that the slope of the linear least squares regression line is significant ($\beta \neq 0$) (Snedecor and Cochran, 1978).

Temporally-increasing stanol/stenol ratios are circumstantial evidence consistent with the occurrence of stenol → stanol transformations. However, secular source changes may also result in temporally-increasing time values, and intermediate and alternative reaction pathways may also obscure stanol/stenol records of stenol → stanol transformation reactions. Although secular changes in stanol/stenol records may be due to secular (monotonic) sterol source changes, this explanation seems implausible in the Pigmy Basin. During the interval in which $C_{29}\Delta^0/C_{29}\Delta^5$ and $C_{29}\Delta^{22}/C_{29}\Delta^{5,22}$ ratios were generally linearly increasing, paired sedimentary organic carbon isotopic and N/C values showed that glacial-interglacial climatically-forced organic matter source changes (Chapter 2) in the characteristic shape of the simplified "sawtooth" climate model (Broecker and van Donk, 1970) were simultaneously occurring. Glacial periods were dominated by erosive terrigenous organic matter input and interglacial periods were characterized by

Fig. 4.1 Potential 4-desmethylsterols double bond reductions examined in this study. Solid arrows show Δ^5-hydrogenations. Dashed arrows show Δ^{22}-hydrogenations. The compounds shown are 24-ethylcholest-5,22-dien-3ß-ol (I), 24-ethylcholest-5-en-3ß-ol (II), 24-ethylcholest-22-en-3ß-ol (III), and 24-ethylcholestan-3ß-ol (IV).

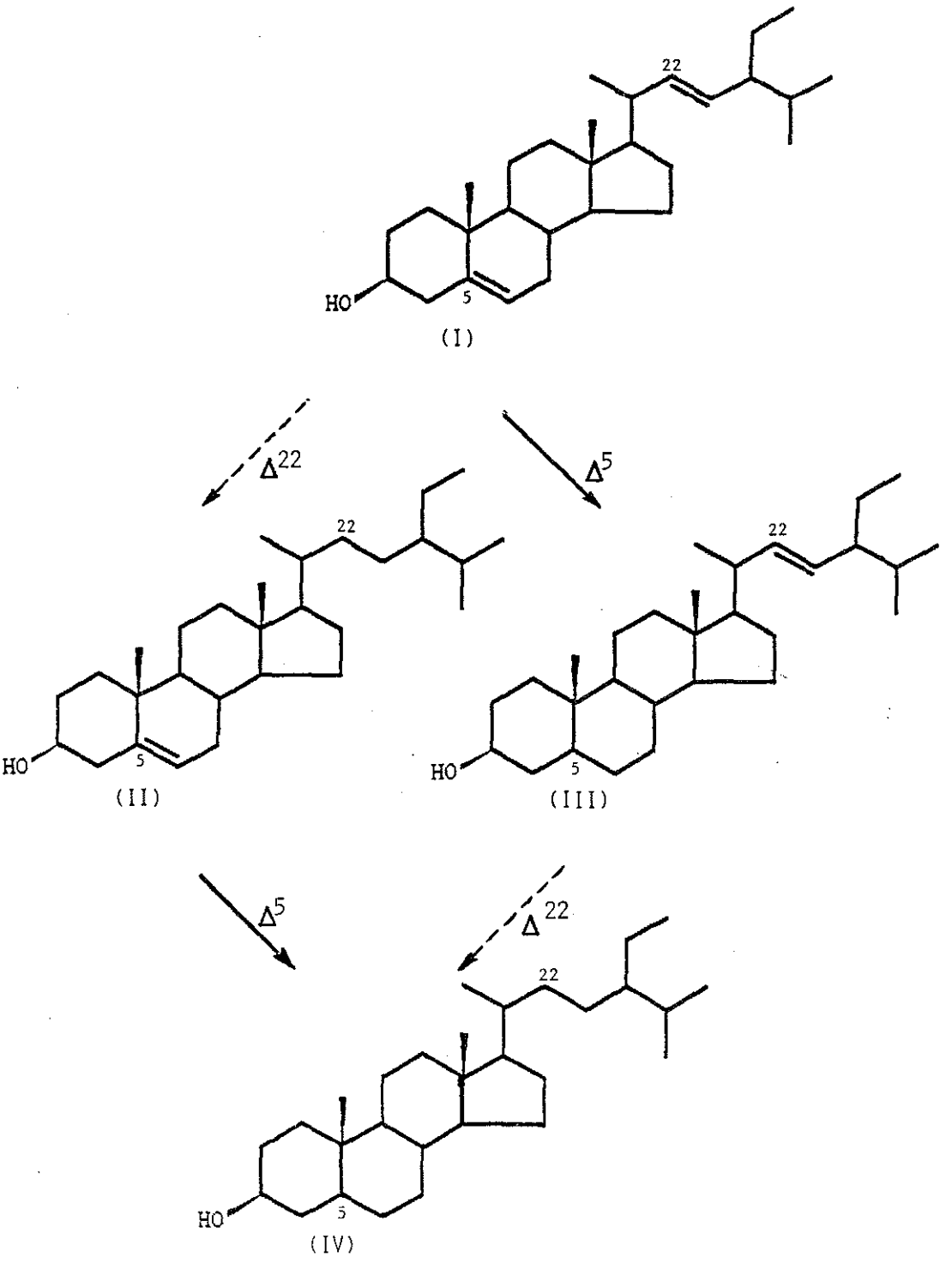
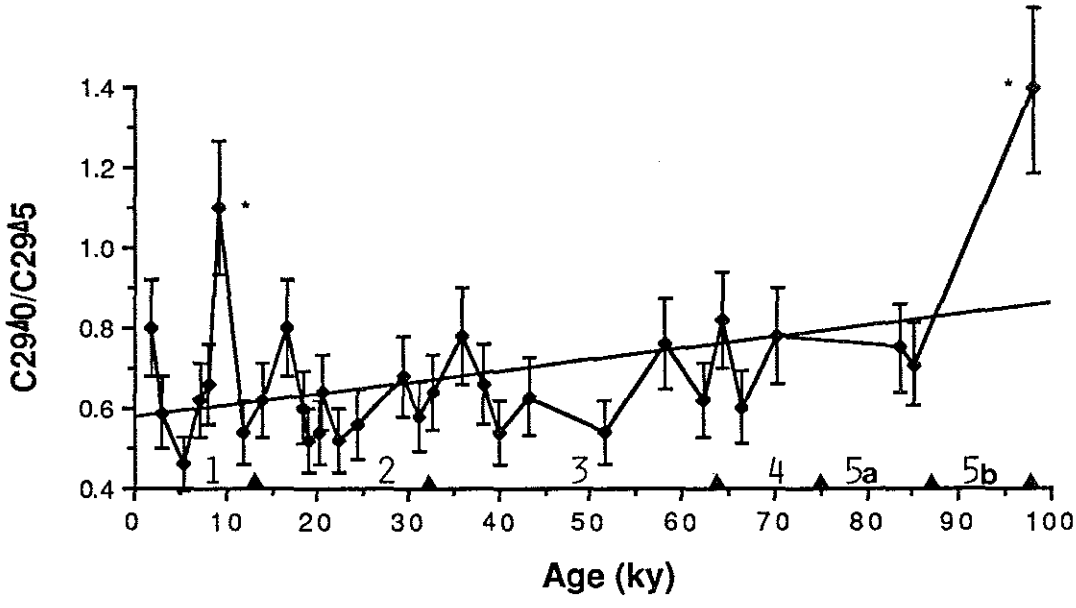
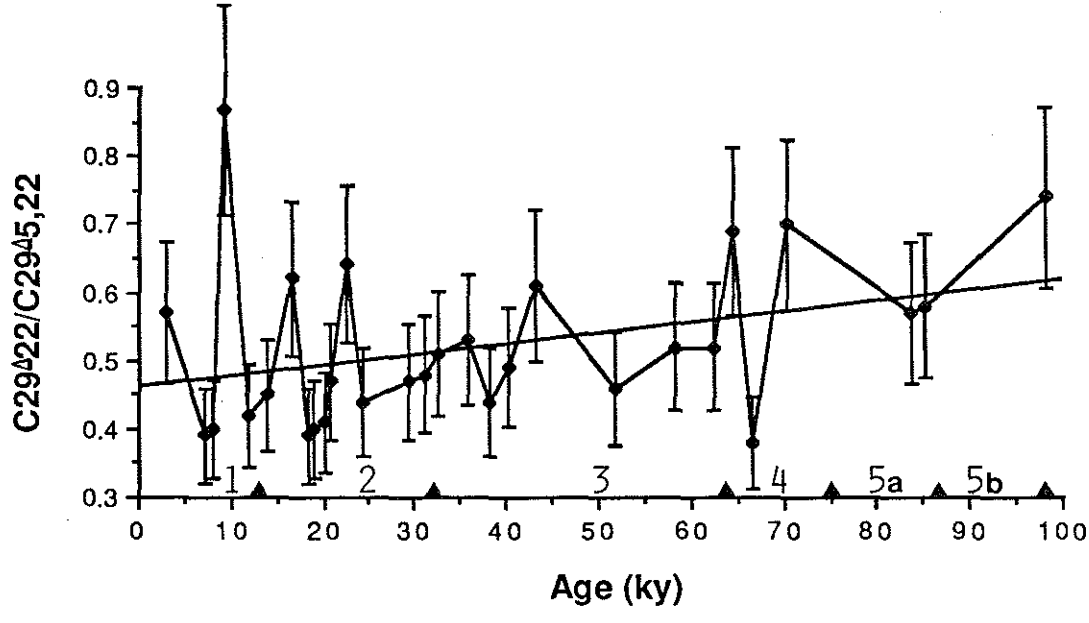

22
HO
5
(I)
Δ22
Δ5
22
HO
5
(II)
22
HO
5
(III)
Δ5
Δ22
22
HO
5
(IV)

Fig. 4.2 24-ethylcholestan-3ß-ol/24-ethylcholest-5-en-3ß-ol ($C_{29}\Delta^0/C_{29}\Delta^5$) ratio time series for the Pigmy Basin DSDP 619 sediment core. $C_{29}\Delta^0/C_{29}\Delta^5$ ratio increases significantly ($P<0.05$) with age, with or without potential sediment slump samples (*). Linear regression line for all data is shown: $C_{29}\Delta^0/C_{29}\Delta^5 = 0.0028 \cdot t + 0.58$, where t = age in ky.

Fig. 4.3 24-ethylcholest-22-en-3ß-ol/24-ethylcholest-5,22-dien-3ß-ol ($C_{29}\Delta^{22}/C_{29}\Delta^{5,22}$) ratio time series.


C29/40/C29/45
1.4
1.2
1.0
0.8
0.6
0.4
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


C29/22/C29/45,22
0.9
0.8
0.7
0.6
0.5
0.4
0.3
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

high proportions of marine organic matter input. It seems improbable that while sedimentary organic matter sources underwent major terrigenous versus marine source changes that two sterols (the stanol/stenol pair) could undergo a secular monotonic change, resulting in temporally-increasing stanol/stenol ratios.

The reactions of numerous intermediate stenol → stanol transformations and alternative stenol and stanol transformation pathways may obscure the sedimentary record of the simple stenol → stanol transformations by providing other sinks for the stenol precursors and other sources for stanol products. In fact in Recent sediments, stenones and stanones are proposed intermediates in stenol → stanol transformations; steradienes, steratrienes, and sterenediols are other possible stenol transformation products; and sterenes are possible dehydration products of stanols (reviewed in Gagosian et al., 1980). Despite these other reactions, the generally increasing stanol/stenol trends support the occurrence of the $C_{29}\Delta^5$ → $C_{29}\Delta^0$ and $C_{29}\Delta^{5,22}$ → $C_{29}\Delta^{22}$ transformations.

Episodic excursions in the product/precursor time series may be due to abrupt source changes or time-varying diagenetic (redox, microbial activity) conditions at burial. Turbidite flows of older, previously buried material into the Pigmy Basin (Kohl, 1986; Williams and Kohl, 1986) may also have transported in a more heavily transformed (i.e., higher product/precursor ratio) sterol suite than was being deposited under typical conditions. A major discontinuity in sedimentation was recognized beyond 98ky (157mbs) in D.S.D.P. Core 619 (Kohl, 1986). Significant discontinuities in magnetostratigraphy

and calcareous nannofossil in situ/reworked ratios, and other parameters also occurred at ~10-14ky (~8-12mbs) (Bouma, et al., 1986). The anomalously high stanol/stenol ratios at ~9ky (7.8mbs) and beyond 98ky (>157m) may be caused by turbidite input.

The Δ^{22} Reductions

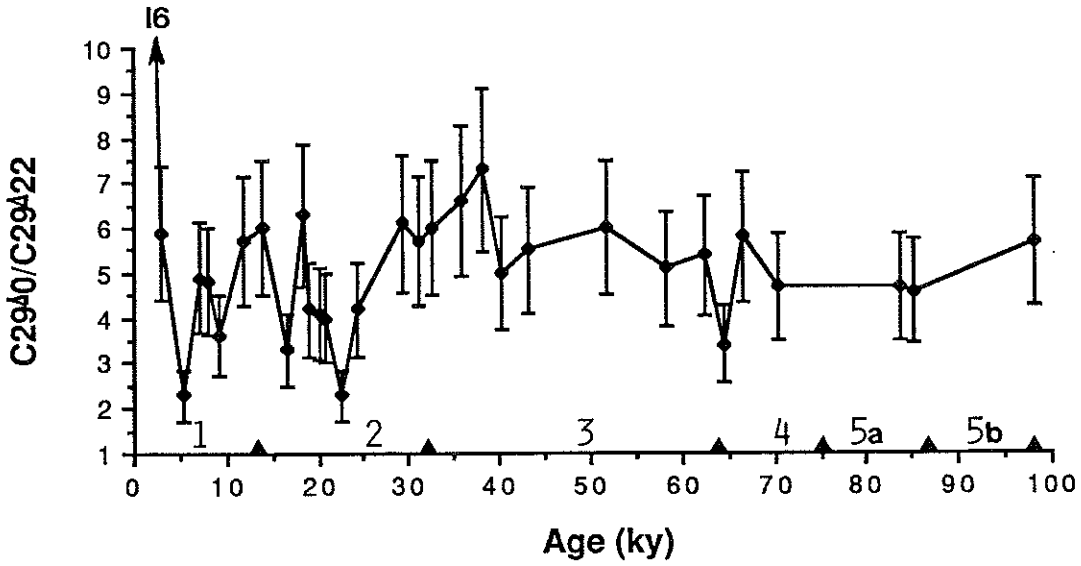
The potential occurrence of $\Delta^{22} \rightarrow \Delta^{\circ}$ and $\Delta^{5,22} \rightarrow \Delta^{22}$ double bond reductions were evaluated by examination of the 24-ethylcholestan-3ß-ol/24-ethylcholest-22-en-3ß-ol ($C_{29}\Delta^{\circ}/C_{29}\Delta^{22}$) (Fig. 4.4) and 24-ethylcholest-5-en-3ß-ol/-24-ethylcholesta-5,22-dien-3ß-ol) ($C_{29}\Delta^{5}/C_{29}\Delta^{5,22}$) (Fig. 4.5) time series in the Pigmy Basin. On the basis of these transformation ratio records, neither of these reactions appeared to be a significant ($P<0.05$) linear function of time.

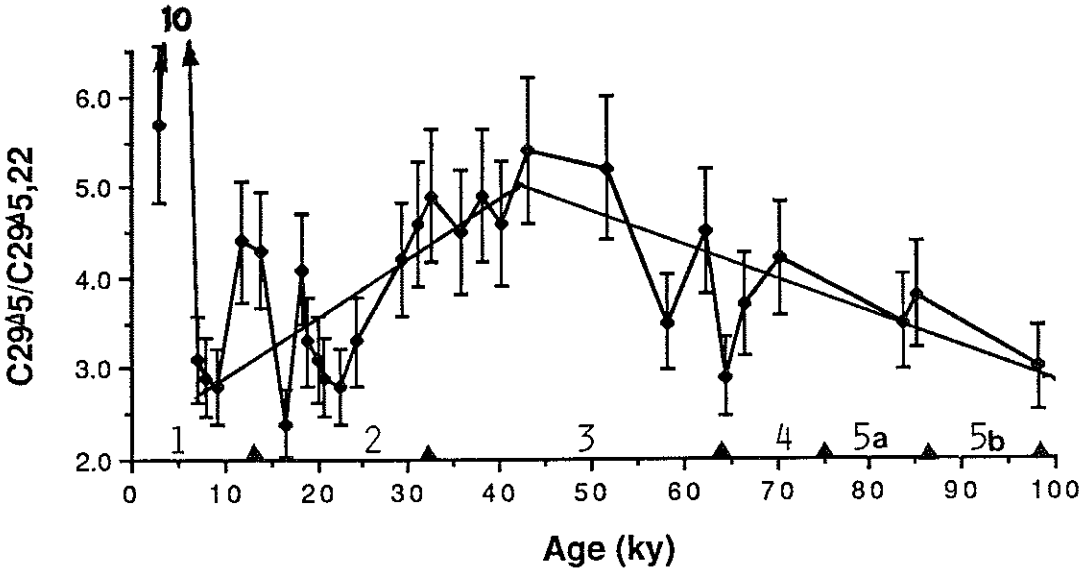
Three possible reasons for the apparent insignificance of the transformation time series are differential transformation rate kinetics, sterol source changes, and the input of previously (before ~2ky) degraded sterols. Controlled laboratory chemical experiments showed that steroid Δ^{5}-hydrogenations proceeded more rapidly than Δ^{22}-hydrogenations (Augustine, 1972). The sedimentary records of both Δ^{22}-reductions reactions (Figs. 4.4 and 4.5) may be insignificant functions of time while the Δ^{5}-reductions (Figs. 4.1 and 4.2) were temporally- increasing functions because the hydrogenation of Δ^{5} has a lower energy relative to Δ^{22}.

The $C_{29}\Delta^{22} \rightarrow C_{29}\Delta^{\circ}$ reaction may be difficult to discern by the evaluation of a $C_{29}\Delta^{\circ}/C_{29}\Delta^{22}$ time series because of the

Fig. 4.4 24-ethylcholestan-3ß-ol/24-ethylcholest-22-en-3ß-ol ($C_{29}\Delta^{0}/C_{29}\Delta^{22}$) ratio time series.

Fig. 4.5 24-ethylcholest-5-en-3ß-ol/24-ethylcholest-5,22-dien-3ß-ol ($C_{29}\Delta^{5}/C_{29}\Delta^{5,22}$) ratio time series. Linear regression lines are significant ($P<0.05$) and may indicate a glacial-interglacial source change.


I6
C2940/C29422
10
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
90
100
1
2
3
4
5a
5b
Age (ky)


10
C2945/C2945,22
6.0
5.0
4.0
3.0
2.0
0
10
20
30
40
50
60
70
80
90
100
1
2
3
4
5a
5b
Age (ky)

combined effects of digenetic transformations and source variations. Each compound was probably at least partially (e.g., $C_{29}\Delta^{22}$) or dominantly ($C_{29}\Delta^{\circ}$) a sedimentary diagenetic product and each can be further transformed to other diagenetic steroids (Gagosian et al., 1980; MacKenzie et al., 1982). In addition, the Δ^5-reductions (Figs. 4.2 and 4.3) were apparently significant reactions in this core, producing $C_{29}\Delta^{22}$ and $C_{29}\Delta^{\circ}$, so that the potential evidence for the $C_{29}\Delta^{22} \rightarrow C_{29}\Delta^{\circ}$ may be obscured by the products from other reactions (see fig. 4.5). The $C_{29}\Delta^{5,22} \rightarrow C_{29}\Delta^{5}$ transformation would be difficult to discern by the $C_{29}\Delta^{5}/C_{29}\Delta^{5,22}$ record because (1) both of these compounds can be significant components of the original source sterols (Volkman, et al., 1987) so that only a small fraction of the observed $C_{29}\Delta^{5}$ may be a reduction product and (2) the previously mentioned $C_{29}\Delta^{5}$ reduction to $C_{29}\Delta^{\circ}$ and the production of intermediates may have obscured the product/precursor ratio of the $C_{29}\Delta^{5,22} \rightarrow C_{29}\Delta^{5}$ transformation by consuming some fraction of the $C_{29}\Delta^{5}$. Finally, although there is not an increase in either of the Pigmy Basin $C_{29}\Delta^{\circ}/C_{29}\Delta^{22}$ or $C_{29}\Delta^{5}/C_{29}\Delta^{5,22}$ time series, the possibility that the transformations may have occurred prior to the beginning of this record (~2kybp) can not excluded. In fact, the total stanol/total stenol record of a sediment core from Lake Suwa, Japan, asymptotically approached a value of ~0.5 in 600y, suggesting that a large proportion of diagenetic sterol reduction reactions may occur in a relatively short period of time. The average $C_{29}\Delta^{22}/C_{29}\Delta^{5,22}$ ratio for the DSDP 619 samples (0.57±0.30, n =

30) was generally higher than those observed in the free (0.2), esterified (0.3), and residual (0.4) fractions of surface sediments of the Black Sea (de Leeuw, et al., 1983). If the terrigenous sterol sources were similar, this comparison suggests that the sterols deposited in the Pigmy Basin have been previously (before ~2ky) transformed. There is circumstantial evidence supporting early or pre-depositional diagenetic alteration of total organic carbon in the Pigmy Basin. Previous burial and degradation in the estuarine and continental shelf sediments of the northern Gulf of Mexico was suggested as a cause for generally lower C_{org} for older (>25kybp) as compared to younger (<25kybp) samples (Chapter 2). Sterols, a component of the total organic carbon, would also presumably be subject to diagenetic alteration.

If the $C_{29}\Delta^5/C_{29}\Delta^{5,22}$ ratio were considered as an organic matter source index, the $C_{29}\Delta^5/C_{29}\Delta^{5,22}$ time series may be interpreted as a record of glacial-interglacial climatic effects on sterol deposition. There are two significant ($P<0.05$) temporal trends in the $C_{29}\Delta^5/C_{29}\Delta^{5,22}$ time series, excepting the last two samples (1.6.-2.6kybp), that may be a result of glacial-interglacial climatic change. The $C_{29}\Delta^5/C_{29}\Delta^{5,22}$ ratio generally increased from low values (~3) in the last interglacial substage 5b to maximum values (~5) in the latter half of isotope stage 3, whereafter the values generally decreased to low values (~3) in stage 1, before the unusually high values (5.7, 12) after ~3 kybp. The unusually high values may be due to young, relatively untransformed $C_{29}\Delta^5$ input.

Climatically-induced floral source changes and/or differential

hydraulic particle sorting were cited as possible causes for the high 24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} linear regression residuals in their glacial Pigmy Basin record (Chapter 3). Viewed simply as an organic matter source indicator, the $C_{29}\Delta^5$/-$C_{29}\Delta^{5,22}$ record may be interpreted as supporting the floral source change mechanism. This hypothesis is also supported by a dominance of deciduous pollen frequency in interglacial periods and coniferous pollen in glacial periods in the same Pigmy Basin core (Heusser, 1986; also see Chapter 3). However, a coarsening of non-carbonate clastic grains in glacial periods as compared to interglacial periods, supported the differential hydraulic sorting of organic particles (Chapter 3).

Differential Hydraulic Particle Sorting Hypothesis

Paired analyses of $C_{29}\Delta^\circ/C_{29}\Delta^5$ ratios and sedimentary organic carbon isotopic composition values and the contention that both $C_{29}\Delta^5$ and $C_{29}\Delta^\circ$ are terrigenous organic biomarkers support the differential hydraulic particle sorting hypothesis in the Late Quaternary Pigmy Basin. A linear least squares regression of $C_{29}\Delta^\circ/C_{29}\Delta^5$ on paired $\delta^{13}C$-C_{org} values is significantly positively correlated whether all the paired values are considered ($P=0.0014$, $n=30$) or if two potential sediment slump samples are removed ($P=0.056$, $n=28$) (Fig. 4.6). The $C_{29}\Delta^\circ/C_{29}\Delta^5$ was also shown above to be a significant increasing function of age, presumably due to stenol → stanol transformations. The observation that the organic carbon-normalized concentration of $C_{29}\Delta^5$

($C_{29}\Delta^5/C_{org}$) in the Pigmy Basin was to a first approximation linearly related to $\delta^{13}C$-C_{org} is consistent with the hypothesis that this sterol had a terrigenous origin (Chapter 3). Although $C_{29}\Delta^\circ/C_{org}$ was not significantly ($P>0.05$) linearly related to $\delta^{13}C$-C_{org}, $C_{29}\Delta^\circ/C_{org}$ concentration was well correlated ($P<0.0001$, $r^2 = 0.82$) with $C_{29}\Delta^5/C_{org}$ concentrations (fig 4.7), circumstantially supporting the contention that $C_{29}\Delta^\circ$ was largely derived, either directly or via transformation pathways, from terrigenous sources.

With these observations, the argument in favor of hydraulic particle sorting can be constructed. The time series of $C_{29}\Delta^\circ/C_{29}\Delta^5$ supported the occurrence of the $C_{29}\Delta^5 \rightarrow C_{29}\Delta^\circ$ (stenol → stanol) transformation. Since both $C_{29}\Delta^5$ and $C_{29}\Delta^\circ$ are probably terrigenous organic biomarkers and their transformation ratio ($C_{29}\Delta^\circ/C_{29}\Delta^5$) generally increased with $\delta^{13}C$-C_{org} (i.e., toward the marine $\delta^{13}C$-C_{org} end member), the $C_{29}\Delta^5$ that was nearer to the marine $\delta^{13}C$-C_{org} end member (~-21°/$_{oo}$ PDB) environment appears to have been more susceptible to reduction than the $C_{29}\Delta^5$ that remained near the terrigenous end member (~-27°/$_{oo}$ PDB). In the Pigmy Basin, sedimentation rates were higher (Chapter 2) and the non-carbonate clastic sediment grains were coarser in glacial periods than in interglacial periods (Chapter 3). If sedimentary organic matter particles were differentially hydraulically sorted as were the clastic sediment grains, coarser organic matter particles would reach the glacial Pigmy Basin and only finer grained organic particles would reach the Pigmy Basin in

interglacial periods. The organic compounds on finer particles with higher surface areas would presumably be more susceptible to molecular transformations than larger particles with less surface area. This hypothetical combined differential hydraulic particle sorting and molecular transformation mechanism would account for the significant correlation of $C_{29}\Delta^{o}/C_{29}\Delta^{5}$ with both sedimentary organic carbon isotopic composition and age.

Additional support for the differential hydraulic particle sorting mechanism came from two sources. Differential hydraulic particle sorting was offered as a mechanism to explain unusually high $C_{29}\Delta^{5}/C_{org}$ (residual) values in the glacial Pigmy Basin (Chapter 3). The glacial excess of $C_{29}\Delta^{5}/C_{org}$ over the expected (linear regression) ratio could be explained if $C_{29}\Delta^{5}$ were transported in the aqueous environment on coarser particles than the bulk sedimentary organic carbon (C_{org}). Low sea levels in glacial periods relative to interglacial periods allowed coarser sediment particles (Chapter 3) and presumably more $C_{29}\Delta^{5}$ relative to C_{org} to reach the hemipelagic Pigmy Basin. Prahl (pers. comm.) has analogously observed that lignin oxidation products derived from an onshore-to-offshore transect of surface sediment particles have increased acid-to-aldehyde ratios with decreasing particle size. The lignin polymers carried on smaller, more hydraulically-sorted particles were interpreted to have been susceptible to proportionally more diagenetic transformation than larger particles.

The C_{27}- and C_{28}-4-Desmethylsterol Transformations

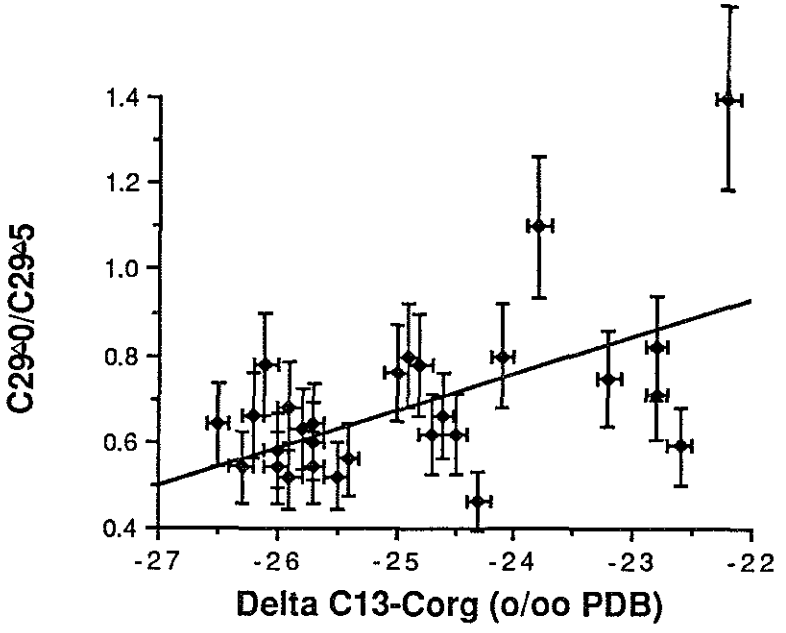
The time series of four potential sterol reduction pathways analogous to those for the C_{29}-4-desmethylsterols (Fig. 4.1) were examined for the C_{27}- and C_{28}-4-desmethylsterols (Figs. 4.8-4.15). The Δ^0/Δ^5 and $\Delta^{22}/\Delta^{5,22}$ ratio time series were examined as indicies for the Δ^5-double bond reduction reactions. The $\Delta^5/\Delta^{5,22}$ and Δ^0/Δ^{22} time series were examined as evidence for the occurrence of Δ^{22}-double bond hydrogenation. None of those potential pathways were evidenced by temporally-increasing product/precursor ratios. There are, however, some relatively short-term (~20-50 ky) trends in C_{28} transformation ratio records whose potential significance is beyond the scope of this study. Episodic maxima (e.g., at ~10-14 kybp, 60-64 kybp, and ~ 98 kybp) may be due to ancient sediment density flows transporting more heavily transformed sterol suites into the Pigmy Basin. Except for the C_{27} stanol/stenol ($C_{27}\Delta^0/C_{27}\Delta^5$) ratio record, the remaining potential C_{27} transformation ratio time series do not show an interpretable trend. This is largely because concentration detection limits are approached. The latter data are presented in the interest of balanced presentation as the sterols occur in a wide spectrum of concentrations, and as a guide to future studies.

The Frequency Distribution of C_{27} to C_{29} Stanol/Stenol Ratios

The frequency distributions of C_{27-29} stanol/stenol (Δ^0/Δ^5) ratios are presented in the form of histograms (Figs. 4.16.a-c). The cholestan-3ß-ol/cholest-5-en-3ß-ol ($C_{27}\Delta^0/C_{27}\Delta^5$) ratios span

Fig. 4.6 24-ethylcholestan-3ß-ol/24-ethylcholest-5-en-3ß-ol ($C_{29}\Delta^0/C_{29}\Delta^5$) versus $\delta^{13}C$-C_{org}. Linear regression line is: $C_{29}\Delta^0/C_{29}\Delta^5 = 0.086 \bullet \delta^{13}C\text{-}C_{org} + 2.8$ ($P=0.0014$, $r^2=0.31$).

Fig. 4.7 24-ethylcholestan-3ß-ol/C_{org} versus 24-ethylcholest-5-en-3ß-ol/C_{org} plot shows that 24-ethylcholestan-3ß-ol and 24-ethylcholest-5-en-3ß-ol are highly correlated, indicating that 24-ethylcholestan-3ß-ol as well as 24-ethylcholest-5-en-3ß-ol are probably terrigenous organic biomarker compounds. Linear regression line is: $C_{29}\Delta^0/C_{org} = 0.57 \bullet C_{29}\Delta^5/C_{org} + 4.4$ ($P<0.0001$, $r^2=0.82$).


C29Δ0/C29Δ5
1.4
1.2
1.0
0.8
0.6
0.4
-27
-26
-25
-24
-23
-22
Delta C13-Corg (o/oo PDB)

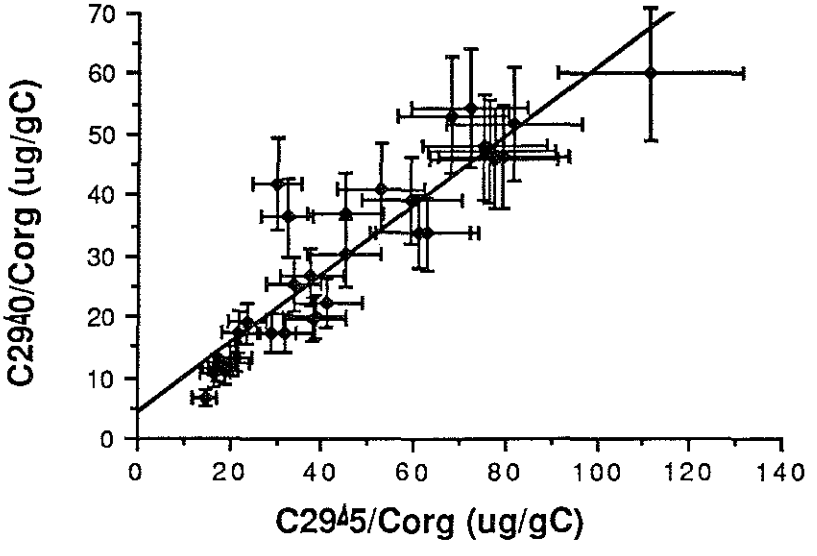
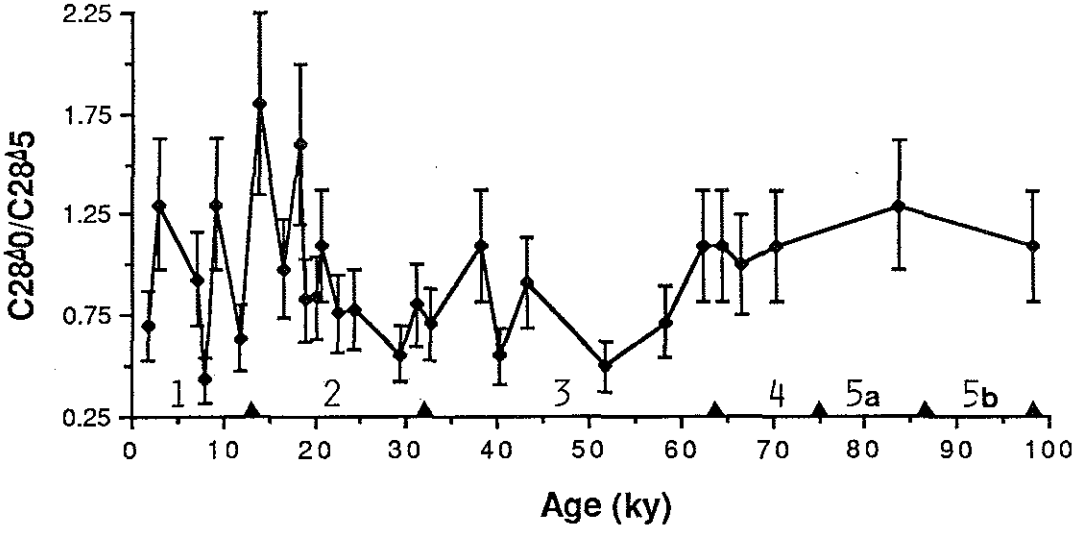

C29Δ0/Corg (ug/gC)
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
C29Δ5/Corg (ug/gC)

Fig. 4.8 24-methylcholestan-3ß-ol/24-methylcholest-5-en-3ß-ol ($C_{28}\Delta^{0}/C_{28}\Delta^{5}$) ratio time series.

Fig. 4.9 24-methylcholest-22-en-3ß-ol/24-methylcholest-5,22-dien-3ß-ol ($C_{28}\Delta^{22}/C_{28}\Delta^{5,22}$) ratio time series.


C28^40/C28^45
2.25
1.75
1.25
0.75
0.25
0
10
20
30
40
50
60
70
80
90
100
Age (ky)
1
2
3
4
5a
5b

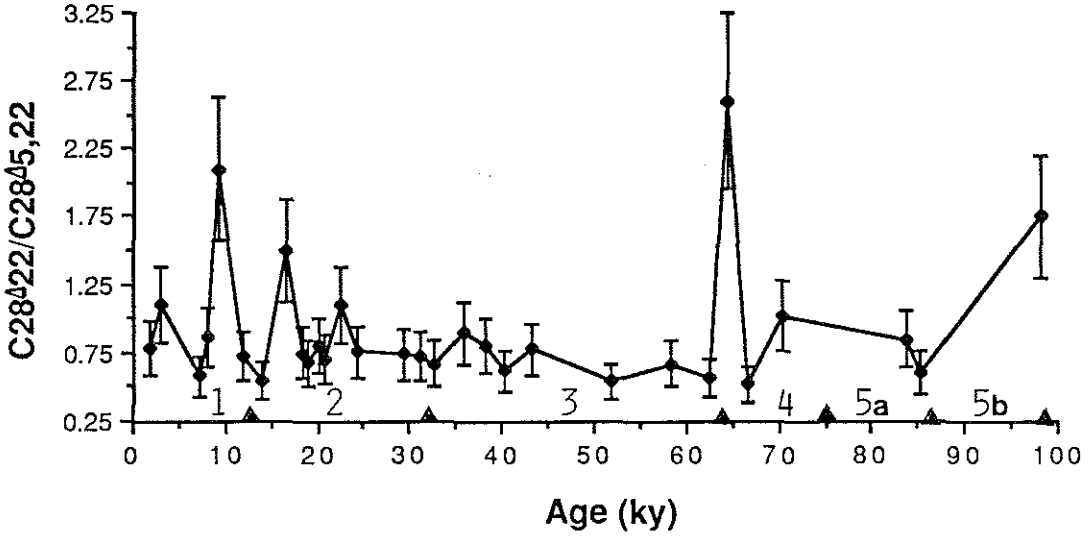
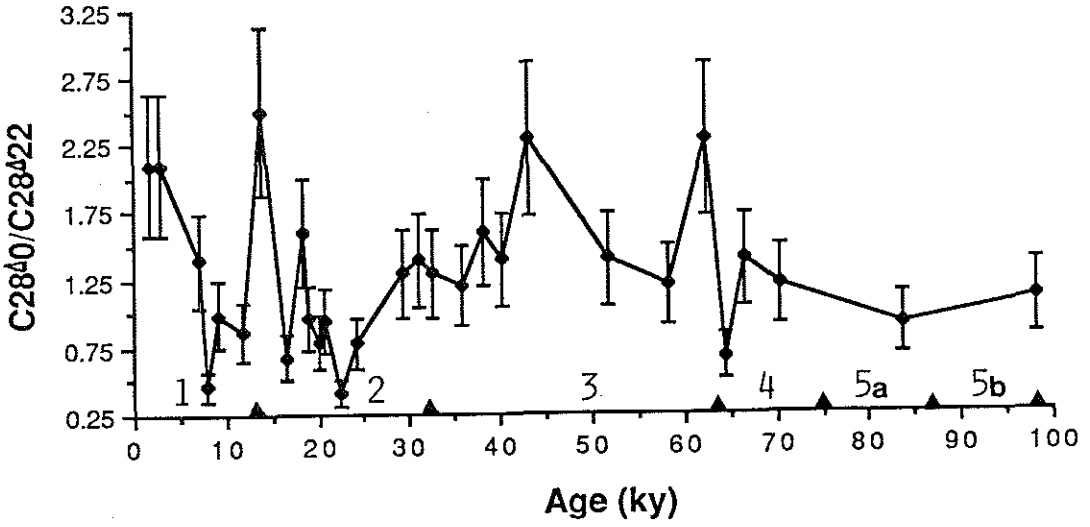

C28^22/C28^45,22
3.25
2.75
2.25
1.75
1.25
0.75
0.25
0
10
20
30
40
50
60
70
80
90
100
Age (ky)
1
2
3
4
5a
5b

Fig. 4.10 24-methylcholestan-3ß-ol/24-methylcholest-22-en-3ß-ol ($C_{28}\Delta^{0}/C_{28}\Delta^{22}$) ratio time series.

Fig. 4.11 24-methylcholest-5-en-3ß-ol/24-methylcholest-5,22-dien -3ß-ol ($C_{28}\Delta^{5}/C_{28}\Delta^{5,22}$) ratio time series.


3.25
2.75
2.25
1.75
1.25
0.75
0.25
C28^40/C28^22
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

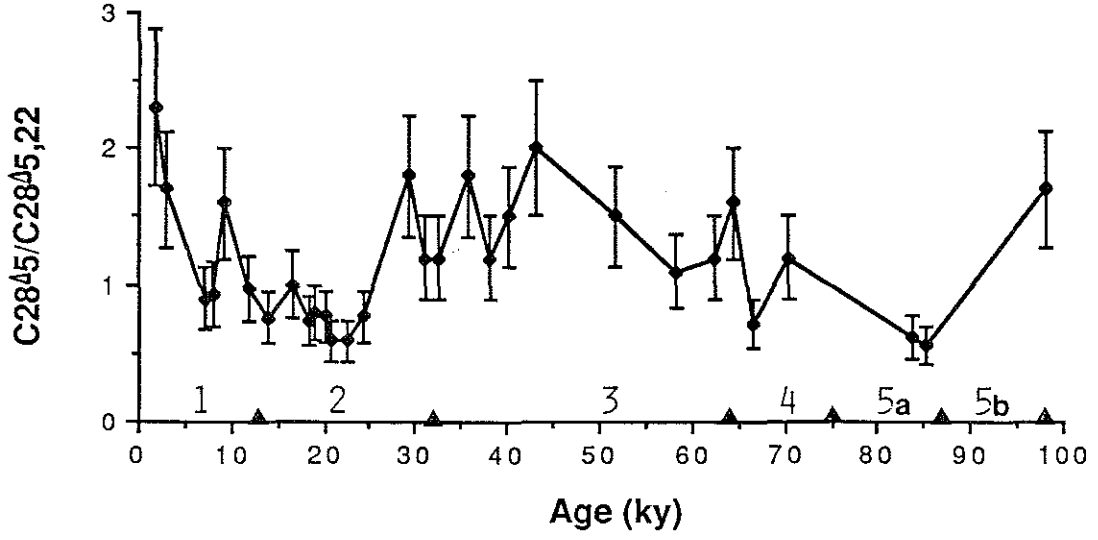
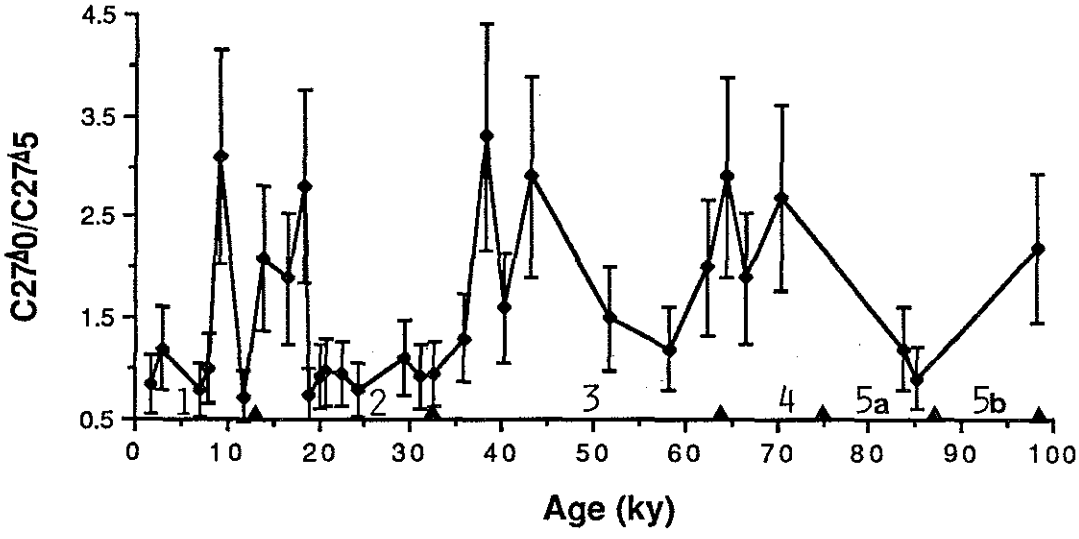

3
2
1
0
C28^45/C28^45,22
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

Fig. 4.12 Cholestan-3ß-ol/cholest-5-en-3ß-ol ($C_{27}\Delta^0/C_{27}\Delta^5$) ratio time series.

Fig. 4.13 Cholest-22-en-3ß-ol/cholest-5,22-dien-3ß-ol ($C_{27}\Delta^{22}/C_{27}\Delta^{5,22}$) ratio time series.


C27Δ0/C27Δ5
4.5
3.5
2.5
1.5
0.5
0
10
20
30
40
50
60
70
80
90
100
Age (ky)
1
2
3
4
5a
5b

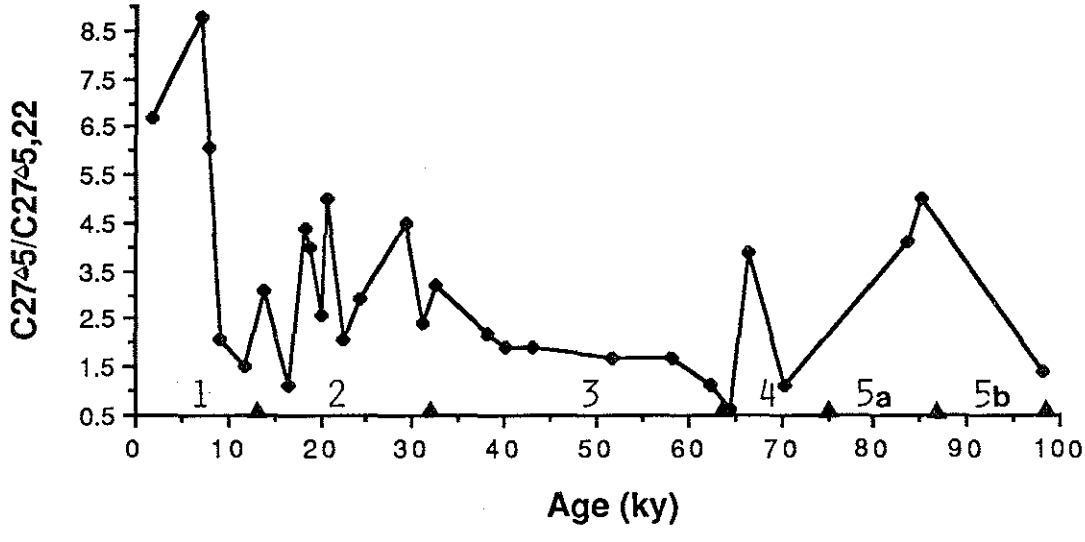
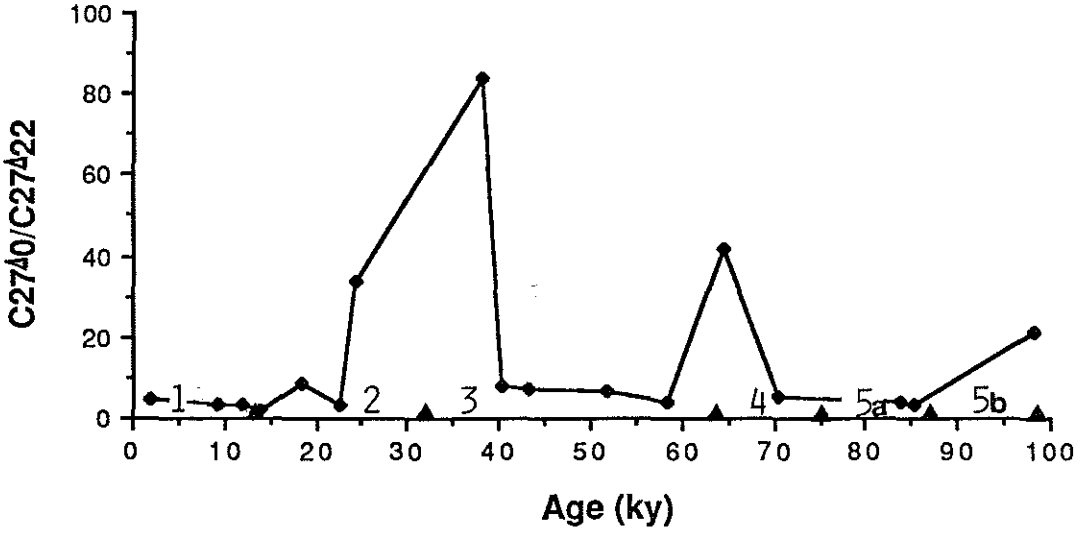

C27Δ5/C27Δ5,22
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
0
10
20
30
40
50
60
70
80
90
100
Age (ky)
1
2
3
4
5a
5b

Fig. 4.14 Cholestan-3ß-ol/cholest-22-en-3ß-ol/($C_{27}\Delta^0/C_{27}\Delta^{22}$) ratio time series.

Fig. 4.15 Cholest-5-en-3ß-ol/2752 ($C_{27}\Delta^5/C_{27}\Delta^{5,22}$) ratio time series.


C27Δ0/C27Δ22
100
80
60
40
20
0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

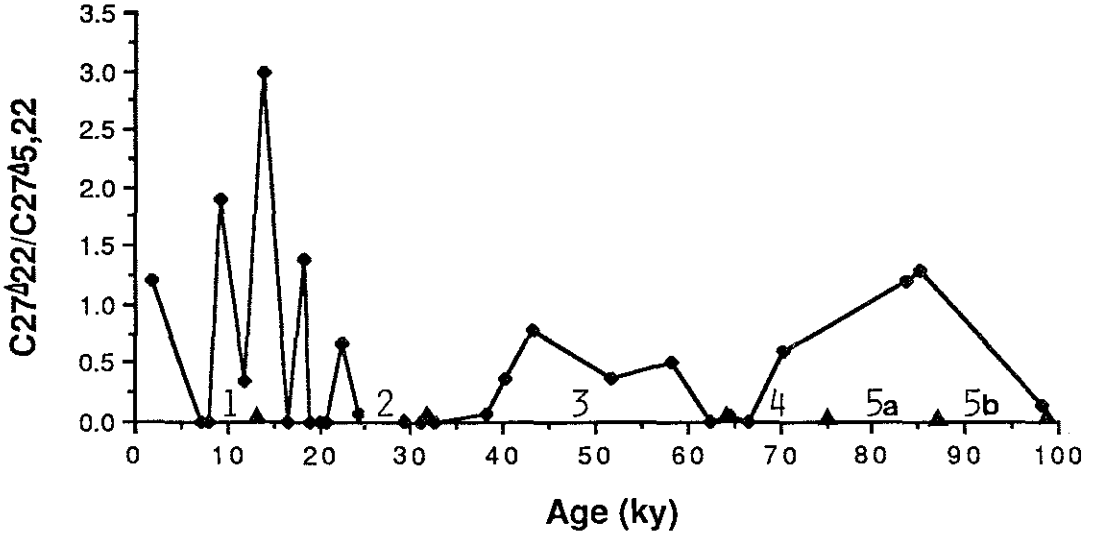
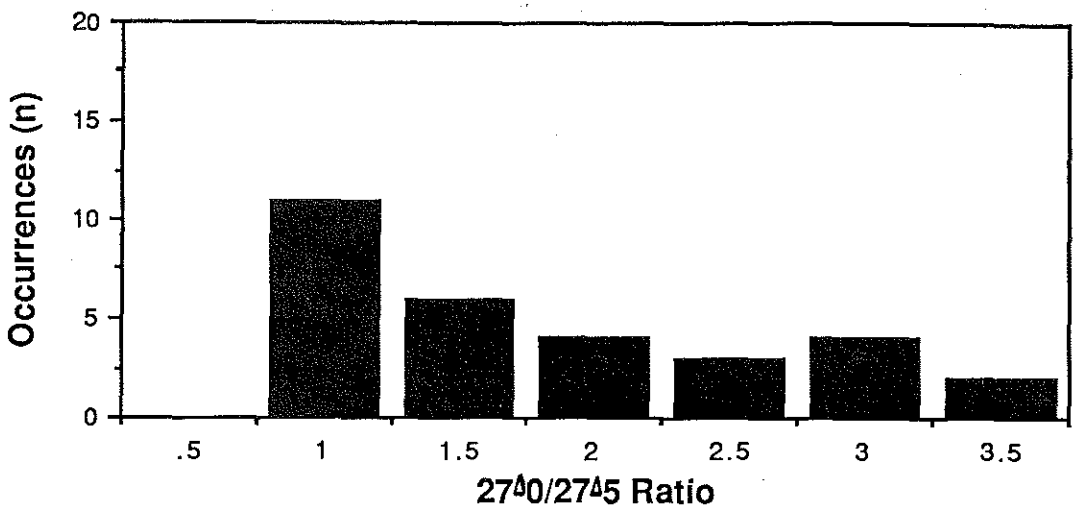

C27Δ22/C27Δ5,22
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1
2
3
4
5a
5b
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

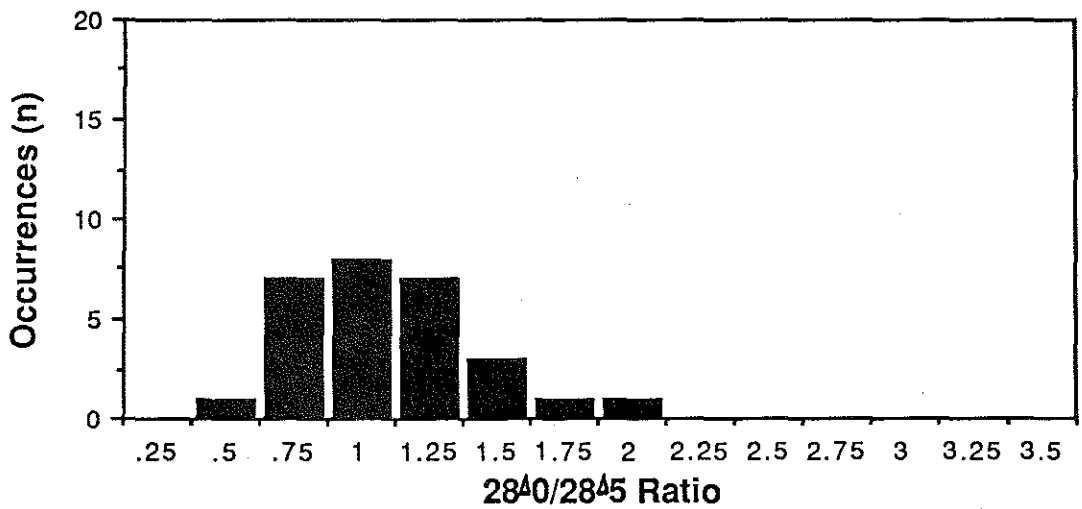
Fig. 4.16 Histograms of stanol/stenol (Δ^0/Δ^5) ratios in DSDP 619.

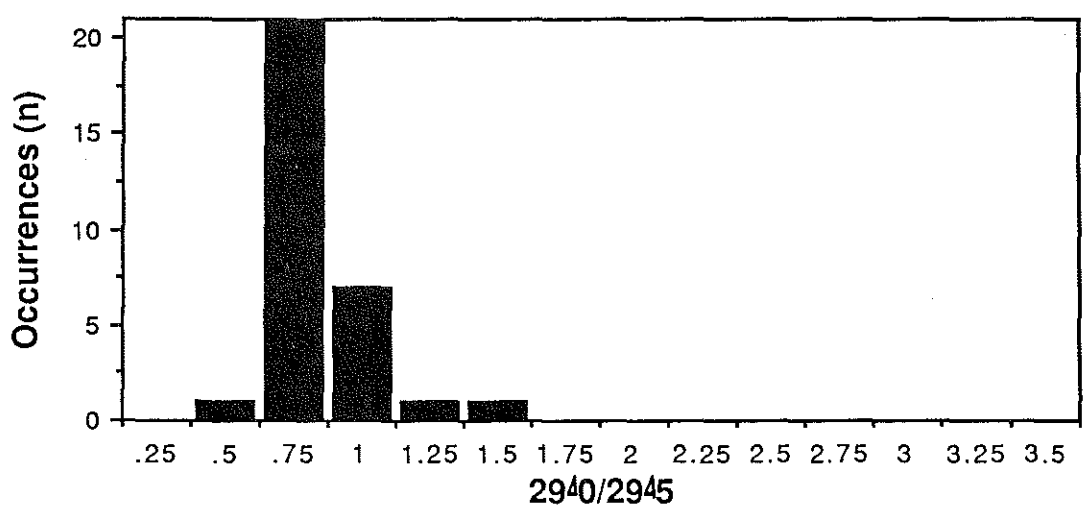
a. Cholestan-3ß-ol/cholest-5-en-3ß-ol ($C_{27}\Delta^0/C_{27}\Delta^5$)

b. 24-methylcholestan-3ß-ol/24-methylcholest-5-en-3ß-ol ($C_{28}\Delta^0/C_{28}\Delta^5$).

c. 24-ethylcholestan-3ß-ol/24-ethylcholest-5-en-3ß-ol ($C_{29}\Delta^0/C_{29}\Delta^5$.)


Occurrences (n)
20
15
10
5
0
.5
1
1.5
2
2.5
3
3.5
27Δ0/27Δ5 Ratio


Occurrences (n)
20
15
10
5
0
.25
.5
.75
1
1.25
1.5
1.75
2
2.25
2.5
2.75
3
3.25
3.5
28Δ0/28Δ5 Ratio


Occurrences (n)
20
15
10
5
0
.25
.5
.75
1
1.25
1.5
1.75
2
2.25
2.5
2.75
3
3.25
3.5
29Δ0/29Δ5

the greatest range (4.0 - 0.5) of the three sterol classes, with its maximum frequency of occurrence in the 0.5 - 1.0 range (Fig. 4.16.a). The 24-methylcholestan-3ß-ol/24-methylcholest-5-en-3ß-ol ($C_{28}\Delta^0$/-$C_{28}\Delta^5$) ratios span the range from 0.25 to 2, with a nearly Gaussian distribution and a maximum in the 0.75 - 1.0 range (Fig. 4.16.b). The 24-ethylcholestan-3ß-ol/24-ethylcholest-5-en-3ß-ol ($C_{29}\Delta^0/C_{29}\Delta^5$) ratios span the range from 0.25 to 1.5 with most (87°/$_o$) of the ratios occurring in the 0.50-0.75 range (Fig. 4.16.c).

The higher average ($\pm 1\sigma$) stanol/stenol ratios of the C_{27}-sterols (1.6 $\pm$ 0.8, n=30) than the C_{28} sterols (0.98 $\pm$ 0.31, n=30), and the C_{29}-sterols (0.68 $\pm$ 0.18, n=31) suggests the following order of susceptibility to diagenetic transformation: $C_{27} > C_{28} > C_{29}$. This conclusion assumes that the C_{27} to C_{29} stanol/stenol pairs started with approximately the same initial ratio. This assumption is supported by many observations of C_{27} to C_{29} stanol/stenol ratios which typically fall in the range of 0.1-0.2 in organisms (Nishimura and Koyama, 1976 and 1977) and in seawater samples (Gagosian and Heinzer, 1979). The C_{29}-sterols appear to be the least susceptible to reduction of all the sterols examined, and the $C_{29}\Delta^0/C_{29}\Delta^5$ pair is the only one which is still apparently undergoing transformation in the Pigmy Basin time series. Since the C_{27} and C_{28} stanol/stenol pairs show no significant temporal increase and they have higher values than most biological sources (~0.1-0.2), the C_{27} and C_{28} sterols are presumed to have attained their observed degree of transformation before ~2 kybp (the beginning of these time series), perhaps prior to burial.

CONCLUSIONS

The 4-desmethylsterol data collected for combined organic biomarker and $\delta^{13}C$-C_{org} analyses (Chapter 3) were evaluated for the potential occurrence of sterol double bond (Δ^5, Δ^{22}) reductions . The sedimentary records of four possible product/precursor ratios from each of the 3 classes of C_{27} to C_{29} 4-desmethylsterols were examined for temporal trends. Only the Δ^5 reductions of the C_{29}-sterols (24-ethylcholest-5-en-3ß-ol and 24-ethylcholesta-5,22-dien-3ß-ol) appeared to be significant in DSDP 619. The positive correlation of 24-ethylcholestan-3ß-ol/24-ethylcholest-5-en-3ß-ol ($C_{29}\Delta^0/C_{29}\Delta^5$) ratios with paired $\delta^{13}C$-C_{org} values (as well as age) was consistent with a combined diffferential hydraulic particle sorting and molecular transformation mechanism. A long-term source change of 24-ethyl-cholestan-3ß-ol relative to 24-ethylcholest-5-en-3ß-ol seems a less probable explanation for these results since both sterols are predominantly of a terrigenous origin in the Pigmy Basin. The frequency distributions of stanol/stenol (Δ^0/Δ^5) ratios of the C_{27} to C_{29} 4-desmethylsterols indicate that the relative degree of transformation by class increases in the order: $C_{27} > C_{28} > C_{29}$. Since the product/precursor ratios of the C_{27}- and C_{28}-sterols show no significant increase with age, they appear to have attained this degree of transformation before ~2kybp. However, differential rates of competing reactions of both the precursor and products may have obscured these simple transformation ratio records.

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Table 4.1.

Sterol Ratio Time Series Data
Pigmy Basin, D.S.D.P. 619

Sample Number[a]	Depth (mbs)	Age (ky)	$\delta^{13}C_{org}$ (o/oo PDB)	$\frac{C_{29}^{0}\ \Delta^{5}}{C_{29}\ \ C_{29}}$	$\frac{C_{29}^{22}\ \Delta^{5,22}}{C_{29}\ \ C_{29}}$	$\frac{C_{29}^{5}\ \Delta^{5,22}}{C_{29}\ \ C_{29}}$	$\frac{C_{29}^{0}\ \Delta^{22}}{C_{29}\ \ C_{29}}$	$\frac{C_{28}^{0}\ \Delta^{5}}{C_{28}\ \ C_{28}}$
1	1.61	1.9	-24.1	0.80	n.d.	n.d.	16.0	0.70
2	2.62	3.1	-22.6	0.59	0.57	5.7	5.9	1.30
4	4.48	5.3	-24.3	0.46	2.00	10.0	2.3	n.d.
5	5.98	7.1	-24.5	0.62	0.39	3.1	4.9	0.93
6	6.84	8.1	-24.6	0.66	0.40	2.9	4.8	0.43
7[b]	7.79	9.2	-23.8	1.10	0.87	2.8	3.6	1.30
9	10.07	11.9	-25.7	0.54	0.42	4.4	5.7	0.64
10	13.13	13.9	-24.7	0.62	0.45	4.3	6.0	1.80
12	18.80	16.5	-24.9	0.80	0.62	2.4	3.3	0.98
14	23.03	18.3	-25.7	0.60	0.39	4.1	6.3	1.60
15	24.58	19.0	-25.5	0.52	0.40	3.3	4.2	0.83
16	27.08	20.1	-25.7	0.54	0.41	3.1	4.1	0.84
17F	28.20	20.6	-25.7	0.64	0.47	2.9	4.0	1.10
18	32.33	22.4	-25.9	0.52	0.64	2.8	2.3	0.76
19F	36.63	24.3	-25.4	0.56	0.44	3.3	4.2	0.78
21F	47.76	29.3	-25.9	0.68	0.47	4.2	6.1	0.56
22	51.96	31.1	-26.0	0.58	0.48	4.6	5.7	0.80
23F	56.89	32.6	-26.5	0.64	0.51	4.9	6.0	0.71
24	60.98	35.9	-26.1	0.78	0.53	4.6	6.6	0.61
25F	65.26	38.2	-26.2	0.66	0.44	4.9	7.3	1.10
26	68.78	40.2	-26.0	0.54	0.49	4.6	5.0	0.55
28	74.30	43.2	-25.8	0.63	0.61	5.4	5.5	0.91
31F	89.58	51.7	-26.3	0.54	0.46	5.2	6.0	0.50
34	101.53	58.3	-25.0	0.76	0.52	3.5	5.1	0.72
35F	108.78	62.3	-24.7	0.62	0.52	4.5	5.4	1.10
36	114.46	64.4	-22.8	0.82	0.69	2.9	3.4	1.10
37F	118.38	66.5	-25.7	0.60	0.38	3.7	5.8	1.00
38	127.98	70.3	-24.8	0.78	0.70	4.2	4.7	1.10
42	147.31	83.8	-23.2	0.75	0.57	3.5	4.7	1.30
43	148.39	85.1	-22.8	0.71	0.58	3.8	4.6	n.d.
47F[b]	158.24	98.2	-22.2	1.40	0.74	3.0	5.7	1.10

[a]"F" denotes samples frozen upon collection; all other samples were obtained from D.S.D.P. refrigerated storage five months later.
[b]Sample may be from an interval of possible sediment density flows.

Table 4.1. (continued)

Sample Number	$^{22}_{28}\Delta^{14}C$ ^{5,22}	$^{5}_{28}\Delta^{14}C$ $^{5,22}_{28}$	$^{0}_{28}\Delta^{14}C$ $^{22}_{28}$	$^{0}_{27}\Delta^{14}C$ $^{5}_{27}$	$^{22}_{27}\Delta^{14}C$ $^{22}_{27}$	$^{5}_{27}\Delta^{14}C$ $^{5,22}_{27}$	$^{0}_{27}\Delta^{14}C$ $^{22}_{27}$
1	0.79	2.30	2.10	0.84	1.20	6.70	4.7
2	1.10	1.70	2.09	1.20	n.d.	n.d.	n.d.
4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	0.58	0.90	1.40	0.78	<0.01	8.80	n.d.
6	0.87	0.93	0.46	1.00	<0.01	6.10	n.d.
7[b]	2.10	1.60	0.99	3.10	1.90	2.10	3.4
9	0.72	0.97	0.86	0.72	0.35	1.50	3.2
10	0.55	0.76	2.50	2.10	3.00	3.10	2.1
12	1.50	1.00	0.67	1.90	<0.01	1.10	n.d.
14	0.75	0.75	1.60	2.80	1.40	4.40	8.9
15	0.68	0.79	0.96	0.75	<0.01	4.00	n.d.
16	0.81	0.77	0.79	0.92	<0.01	2.60	n.d.
17F	0.71	0.59	0.95	0.97	<0.01	5.00	n.d.
18	1.10	0.59	0.40	0.94	0.68	2.10	3.0
19F	0.76	0.77	0.78	0.78	0.07	2.90	34.0
21F	0.74	1.80	1.30	1.10	<0.01	4.50	n.d.
22	0.72	1.20	1.40	0.93	<0.01	2.40	n.d.
23F	0.67	1.20	1.30	0.94	<0.01	3.20	n.d.
24	0.90	1.80	1.20	1.30	n.d.	n.d.	n.d.
25F	0.80	1.20	1.60	3.30	0.08	2.20	84.0
26	0.62	1.50	1.40	1.60	0.36	1.90	8.1
28	0.78	2.00	2.30	2.90	0.79	1.90	7.0
31F	0.54	1.50	1.40	1.50	0.37	1.70	6.7
34	0.67	1.10	1.20	1.20	0.51	1.70	3.9
35F	0.56	1.20	2.30	2.00	<0.01	1.10	n.d.
36	2.60	1.60	0.67	2.90	0.04	0.59	42.0
37F	0.52	0.72	1.40	1.90	<0.01	3.90	n.d.
38	1.02	1.20	1.20	2.70	0.60	1.10	5.1
42	0.85	0.62	0.91	1.20	1.20	4.10	4.0
43	0.61	0.55	n.d.	0.91	1.30	5.00	3.5
47F[b]	1.75	1.70	1.10	2.20	0.14	1.40	21.1

[c]Ages of samples 1-47F were linearly interpolated from isotope (sub)stage boundaries 1-5b. Ages of samples 48F-55 were linearly interpolated between substage boundary 5b and an assumed core bottom age of 105ky (Williams and Kohl, 1986); high abundances of quartz sand, shallow water benthic foraminifera, and lack of datable horizons indicated sediment density flows through this interval (Kohl, 1986; Williams and Kohl, 1986).

n.d. = not defined because denominator was below detection limit of ~3 ng/gds.

CHAPTER 5

ALKENONE MOLECULAR STRATIGRAPHY IN AN OCEANIC ENVIRONMENT AFFECTED BY GLACIAL MELTWATER AND/OR FLUVIAL EVENTS

ABSTRACT

The sedimentary record of a ratio (U^{K}_{37}) of long chain (C_{37}-C_{39}) unsaturated alkenones is a useful indicator of glacial-interglacial climatic change in the Late Quaternary northern Gulf of Mexico where a planktonic foraminiferal $\delta^{18}O$-$CaCO_3$ record is complicated by meltwater and/or fluvial events (Williams and Kohl, 1986). Application of a laboratory temperature calibration of the U^{K}_{37} ratio (Prahl and Wakeham, 1987) to a Pigmy Basin hydraulic piston core record (DSDP 619) suggested that the minimum glacial surface mixed layer (SML) temperature was 8±1°C colder than the Holocene high SML temperature of 25.6±0.5°C. This predicted glacial-interglacial U^{K}_{37}-temperature difference was significantly larger than the differences predicted by either the foraminiferal $\delta^{18}O$ or foraminiferal assemblage temperature methods (0.8-2.0°C). This large difference may be caused by Prymnesiophyte assemblage changes in this area in response to climatically-induced hydrographic changes. Interglacial periods may be dominated by pelagic Prymnesiophyte assemblages, while glacial periods may be dominated by neritic assemblages. The correlation of U^{K}_{37} ratio with the sedimentary organic carbon composition ($\delta^{13}C$-C_{org}) is consistent

with the predominance of preserved input of erosive terrigenous organic carbon during glacial stages in the northern Gulf of Mexico when sea level was as much as 150m lower than in the present interglacial stage. Marine organic carbon burial dominated in warmer interglacial stages 1 and 5a-b.

INTRODUCTION

The oxygen isotopic composition ($\delta^{18}O$) of foraminiferal shell carbonates is one of the most widely used stratigraphic methods in Quaternary paleoceanography. The $\delta^{18}O$ of biogenic carbonates is predominantly a function of the isotopic composition and temperature of the ambient water in which the carbonate-producing organism grew its shell (Shackleton and Opkyke, 1973; Duplessy, 1978; Shackleton, 1987). A large proportion (~75°/$_{o}$) of the glacial-interglacial $\delta^{18}O$ variations in foraminiferal records is attributable to glacial ice volume variations; the remainder is attributed to local temperature changes (Shackleton, 1967; Labeyrie et al., 1986; Chappell and Shackleton, 1986; Shackleton, 1987). These results are either concordant with or partially derived from the altitudes of dated coral terraces and equilibrium continental ice sheet models (Broecker, 1982; Chappell and Shackleton, 1986; Shackleton, 1987).

For most of the area of the global ocean, the stable oxygen isotopic (^{18}O and ^{16}O) composition of seawater is sufficiently well-mixed that foraminiferal $\delta^{18}O$ records can be stratigraphically correlated. However, some areas of the ocean, such as the northern Gulf of Mexico, are not isotopically well-mixed because of local

sources of fluvial and/or meltwater input. Melting of the Laurentide ice sheet on the North American continent near the end of isotope stage 2 caused negative excursions up to ~2.4°/$_{oo}$ in $\delta^{18}O$ values of planktonic foraminiferal carbonate (Kennett and Shackleton, 1975; Emiliani et al., 1978; Leventer et al., 1982; Fillon and Williams, 1984; Williams, 1984; Williams and Kohl, 1986). In fact, average annual discharge of the Mississippi River into the Gulf of Mexico during the Laurentide ice sheet melting at the close of stage 2 was calculated to have been 1.8 to 4.0 times larger than the largest historically recorded flood, with probable annual peak floods twice as large (Emiliani et al., 1978). Thus, in areas affected by episodic glacial meltwater and/or fluvial events, the ability to correlate planktonic $\delta^{18}O$ records with open oceanic records will be diminished.

Brassell et al. (1986a) observed in deep-sea sediments of the eastern equatorial Atlantic Ocean that a ratio of long chain C_{37} unsaturated alkenones (U^K_{37}) correlated well with the oxygen isotopic composition of planktonic foraminiferal carbonates. Preliminary temperature-controlled laboratory culture experiments with Emiliani huxylei and alkenone analysis of contemporary water column particles supported the suggestion that a concentration ratio of di- and triunsaturated C_{37} alkenones (U^K_{37} = [37:2]/([37:2] + [37:3])) was a function of the ambient water temperature in which Prymnesiophyte plankton grew. With temperature-controlled batch culture experiments, Prahl and Wakeham (1987) showed that the U^K_{37} ratio of Emiliani huxleyi alkenones was linearly related to the ambient water temperature in which the Prymnesiophyte alga grew, and

thereby calibrated the U^{K}_{37}-temperature relationship for this organism.

In addition to the observation that the U^{K}_{37} ratio may be predominantly a function of the ambient water temperature, the unsaturation ratio is apparently well preserved relative to $CaCO_3$ in some deep-sea environments. Brassell et al. (1986a) found that the U^{K}_{37} ratio covaried with planktonic foraminiferal $\delta^{18}O$ for a large proportion (~550ky) of a 13 m (~1My) gravity core recovered from the Kane Gap region of the eastern equatorial Atlantic. In some lengths of the core, foraminiferal shells were absent, presumably dissolved. The alkenones, however, were preserved through those intervals of carbonate dissolution and the U^{K}_{37} ratio was also proposed to be useful as a molecular stratigraphic index where standard foraminiferal $\delta^{18}O$ stratigraphy was unavailable.

Since the northern Gulf of Mexico had a Late Quaternary sequence of meltwater and/or fluvial events which complicated the foraminiferal carbonate $\delta^{18}O$ records (Kennett and Shackleton, 1975; Emiliani et al., 1978; Leventer et al., 1982; Fillon and Williams, 1984; Williams, 1984; Williams and Kohl, 1986), we have investigated the utility of the U^{K}_{37} ratio as a molecular stratigraphic and paleothermometric indicator in such marine environments.

METHODS

Samples

The samples used in this study were from a 208.7m hydraulic piston core collected from the D/V Glomar Challenger (Leg 96, Site 619) in

the Pigmy Basin (27°11.61'N, 91°24.54'W) in the northern Gulf of Mexico. Sampling of this sediment core was described in detail elsewhere (Chapter 2).

Alkenone Analysis

The procedures for the extraction, separation, and analysis of the alkenones were previously described (Chapter 3). Briefly, the alkenones were sonically extracted with $(CH_3)_2CHOH$ and $CHCl_3$:CH_3OH (1:1) from 10±2g wet sediment samples. 2-Nonadecanone was used as an interval recovery standard for the alkenones. Gas chromatographic analysis was performed on a Carlo Erba 2150 gas chromatograph with a Varian Vista 401 Chromatography Data System. Forty ketone analyses gave 84±7.6°/$_{oo}$ (C = 9.0°/$_{oo}$, where the variance C ≡ 100σ/$\overline{X}$) recovery of the ketone standard. A triplicate analysis of the U^K_{37} ratio gave a variance of 1.5°/$_{oo}$. Structural determinations were based on gas chromatographic retention times and computerized gas chromatographic/mass spectrometric (C-GC-MS) analyses of samples and comparison with published mass spectra.

Sedimentary Organic Carbon Isotopic Analysis

Sedimentary organic carbon isotopic analysis ($\delta^{13}C$-C_{org}) was previously described (Chapter 2). All $\delta^{13}C$-C_{org} values are given relative to the Chicago PDB isotopic standard.

Chronostratigraphy

The chronostratigraphy used in this study is based on the isotope (sub)stage boundary ages of Shackleton and Imbrie (1973) assigned to the DSDP 619 Globeriginoides ruber oxygen isotope record by Williams

and Kohl (1986). Ages were estimated by linear interpolation between (sub)stage boundaries. Additional chronostratigraphic constraints for DSDP 619 include planktonic foraminiferal zonal boundaries (Z/Y, Y/X) (Kohl, 1986), a phytoplanktonic boundary (Constance and Parker, 1986) and a volcanic ash layer (Y8) correlated by major-element chemistry to a major eruption of the Guatemalan Lake Atitlan Caldera (Ledbetter, 1986).

RESULTS AND DISCUSSION

U^K_{37} Time Series

The U^K_{37} time series from the Pigmy Basin (DSDP 619) is presented in Fig. 5.1. The U^K_{37} ratio generally decreases from a high value of 0.85 in interglacial oxygen isotope stage 5a to a low value of 0.63 near the isotope stage 2/3 boundary and then increases to a high value of 0.89 in the latter part of isotope stage 1. Interglacial stages 5a and 1 have the highest values observed in this core at 0.81 and 0.89, respectively. The four lowest U^K_{37} values which occurred were in glacial isotope stages 2, 3, and 4--0.62 in stage 4, 0.65 and 0.63 in stage 3, and 0.65 in stage 2. On an isotope stage-averaged basis, interglacial substage 5a had the highest U^K_{37} value of 0.85 (n=1), stage 4 had a lower value of 0.74±0.10 (±1σ, n=4), stage 3 had an even lower value of 0.68±0.04 (n=7) which equaled that of stage 2 (0.68±0.03, n=11), and interglacial stage 1 had an average of 0.77±0.08 (n=7). These trends and average values reproduce the gross glacial-to-interglacial cold and warm trends of global climate characterized by more typical planktonic foraminiferal

$\delta^{18}O$ records.

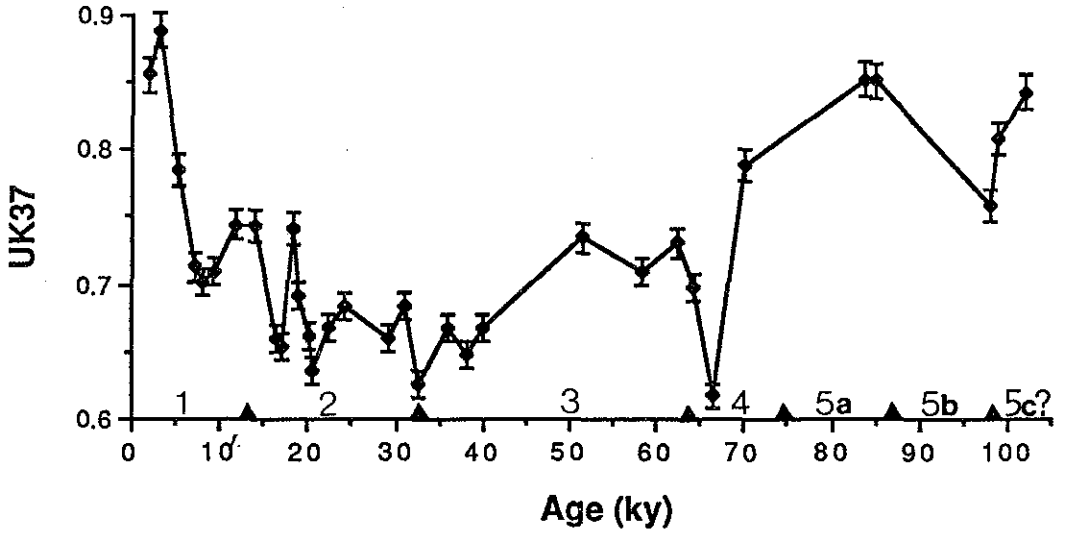
Two foraminiferal oxygen isotopic records are reproduced below the Pigmy Basin U^{K}_{37} record for comparison. The Globigerinoides sacculifer $\delta^{18}O$ record from the Caribbean Sea (P6304-7; 15°06'N, 69°38'W, 3929 m; Emiliani et al., 1972; Broecker, 1974)(Fig. 5.2) is a rather typical open ocean record. Interglacial isotope stages 1 and 5 have $\delta^{18}O$ values which are ~1.8°/$_{oo}$ depleted in ^{18}O relative to glacial isotope stage 2. The $\delta^{18}O$ values change relatively continuously in time, rather than as an episodic series of $\delta^{18}O$ maxima and minima. The oxygen isotopic record of Globigerinoides ruber from the Pigmy Basin (DSDP 619)(Fig. 5.3), by contrast, was characterized by a series of episodic $\delta^{18}O$ minima (Williams and Kohl, 1986). The cause of the episodic minima was argued to be the input of ^{18}O depleted water from continental ice melting and/or fluvial events. Meltwater events in the northern Gulf of Mexico which caused large negative $\delta^{18}O$ deviations from typical open oceanic values have been previously reported in a number of investigations (Kennett and Shackleton, 1975; Emiliani et al., 1978; Leventer et al., 1982; Fillon and Williams, 1984; Williams, 1984). The establishment of a correlation between the U^{K}_{37} ratio and the Pigmy Basin G. ruber $\delta^{18}O$ record was not attempted because the data were unpaired and the $\delta^{18}O$ record was discontinuously episodic.

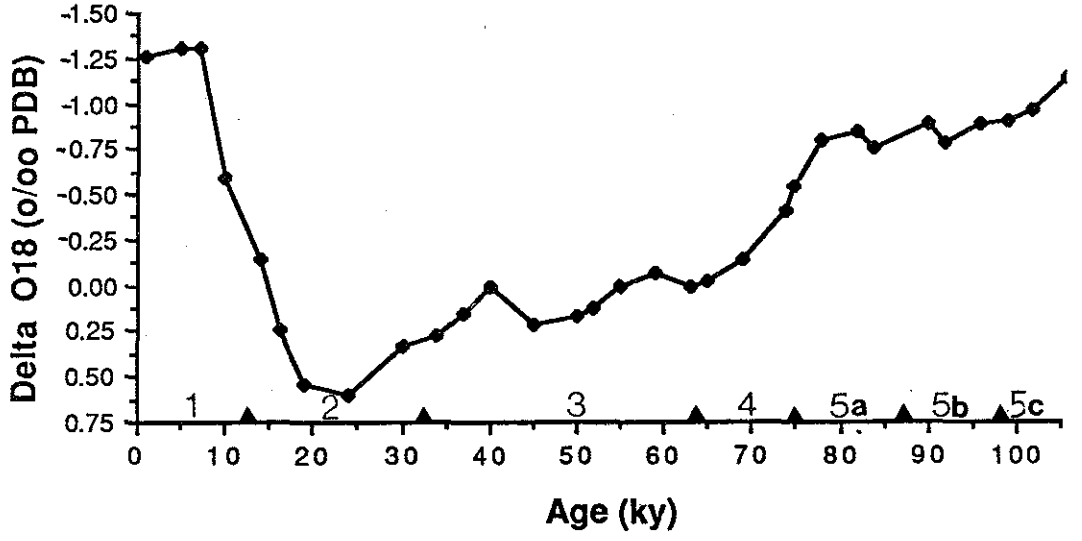
The potential advantage of U^{K}_{37} molecular stratigraphy in marine environments susceptible to freshwater runoff is that the U^{K}_{37} ratio is considered to be predominantly a function of ambient water temperature. By contrast, the oxygen isotopic composition of

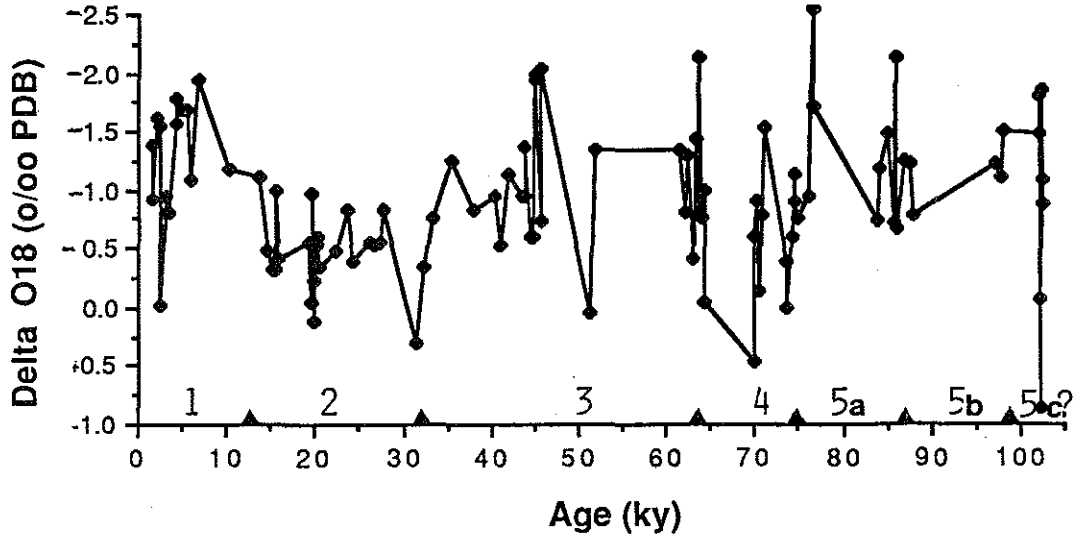
Figure 5.1. Time series of U^{K}_{37} ratio ([37:2]/([37:2]+[37:3])] values in Pigmy Basin DSDP Core 619, in which 37:2 and 37:3 are di- and triunsaturated C_{37} alkenones, respectively.

Figure 5.2. Oxygen isotopic ($\delta^{18}O$) record of Globigerinoides sacculifera from the Caribbean Sea (core P6304-7; 15°06'N, 69°38'W) (Emiliani, 1972).

Figure 5.3. Oxygen isotopic ($\delta^{18}O$) record of Globigerinoides ruber from Deep Sea Drilling Project Core 619 in the Pigmy Basin in the northern Gulf of Mexico (Williams and Kohl, 1986). The chronostratigraphy is discussed in text.


UK37
0.9
0.8
0.7
0.6
1
2
3
4
5a
5b
5c?
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


Delta O18 (o/oo PDB)
-1.50
-1.25
-1.00
-0.75
-0.50
-0.25
0.00
0.25
0.50
0.75
1
2
3
4
5a
5b
5c
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


Delta O18 (o/oo PDB)
-2.5
-2.0
-1.5
-1.0
-0.5
0.0
0.5
-1.0
1
2
3
4
5a
5b
5c?
0
10
20
30
40
50
60
70
80
90
100
Age (ky)

foraminiferal carbonates is both a function of the ambient water's temperature and oxygen isotopic composition.

Whereas the Pigmy Basin U^K_{37} record is qualitatively smoother and less episodic in nature, more similar to the G. sacculifer record from the Caribbean Sea, the Pigmy Basin G. ruber $\delta^{18}O$ record is punctuated by episodic freshwater runoff (negative $\delta^{18}O$) events. Since most stratigraphic techniques rely on the ability to match events (e.g., $\delta^{18}O$ maxima and minima, and isotope stage inflection points), the use of U^K_{37} molecular stratigraphy should allow additional stratigraphic constraints where $\delta^{18}O$ records are complicated by episodic glacial meltwater and/or fluvial events.

The U^K_{37} Surface Mixed Layer Temperature

Surface mixed layer (SML) temperatures for waters overlying the Late Quaternary Pigmy Basin were calculated using the laboratory culture U^K_{37}-temperature calibration of Prahl and Wakeham (1987). With temperature-controlled batch cultures of the Prymnesiophyte alga, Emiliani huxleyi, they determined that a linear least squares regression of U^K_{37} values on culture temperature gave the following temperature calibration equation: $U^K_{37} = 0.033T + 0.043$ ($r = 0.997$, $n = 20$). The present limits on the measurement of the U^K_{37} ratio give a potential accuracy of ±0.5°C in determining water temperatures from the U^K_{37} ratio.

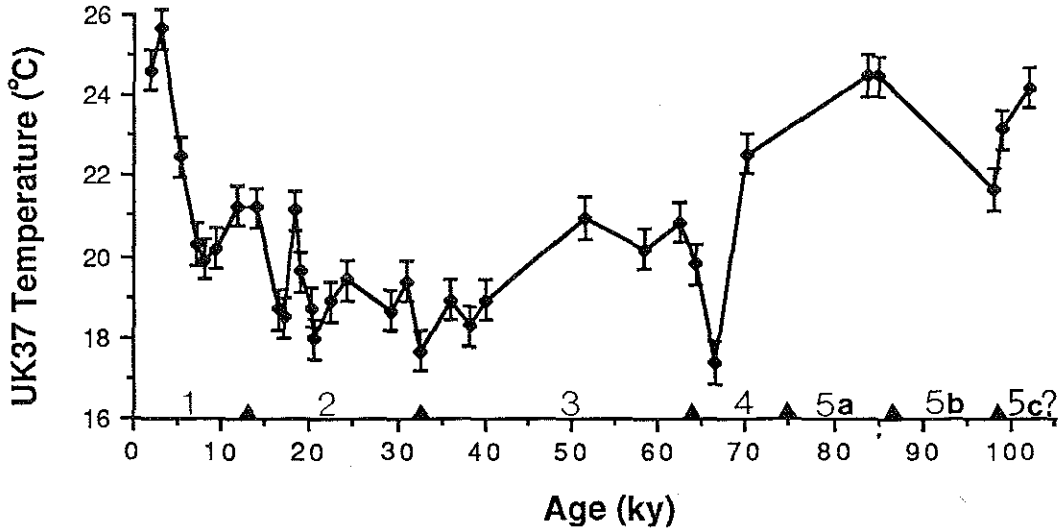
The surface mixed layer temperature time series (Fig. 5.4) is analogous to the U^K_{37} time series since SML temperature is linearly related to the U^K_{37} ratio. In general, the SML temperature (±0.5°C) decreases from 24.5°C in interglacial substage

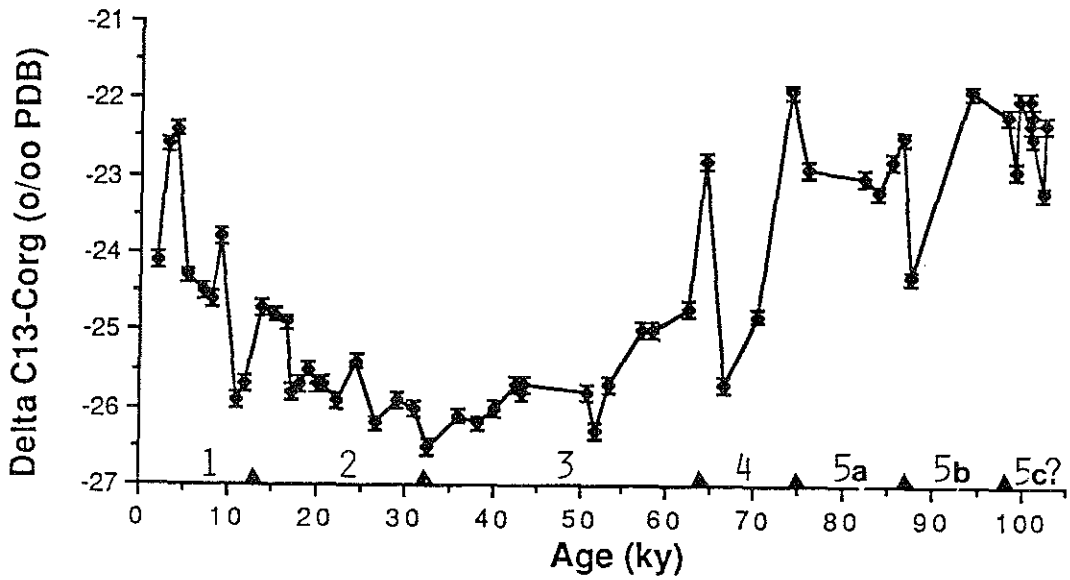
5a to 17.7°C near the stage 2/3 boundary, then increases to a stage 1 maximum of 25.6°C. Glacial isotope stage 4 has a minimum SML temperature of 17.4°C as low (±0.5°C) as the lowest value observed in isotope stages 2-3 (17.7°C). Glacial stage 4 was previously characterized by sea surface temperatures as cold as glacial stage 2 (Emiliani, 1972). For comparison, present-day annual average sea surface temperature overlying the Pigmy Basin is ~24.5-25.5°C (Robinson, et al., 1979). The U^{K}_{37} temperature suggests a maximal glacial-to-interglacial increase of ~8±1°C in the northern Gulf of Mexico, corresponding favorably to a 5-6°C increase in Caribbean surface water suggested on the basis of planktonic foraminiferal $\delta^{18}O$ values (Emiliani, 1972). The presumed oxygen isotopic composition of average glacial ice in the latter calculation, however, caused an overestimate of the actual temperature change (Shackleton, 1967). Although CLIMAP (1976) transfer function sea surface temperatures correlate well with U^{K}_{37} temperatures for the Kane Gap Region of the eastern equatorial Atlantic (Brassell et al., 1986; Prahl and Wakeham, 1987), a glacial-to-interglacial August temperature difference of less than 2°C was suggested for the Gulf of Mexico. Paleotemperature sea surface maps produced by application of foraminiferal assemblage-temperature transfer function methods showed maximum glacial-interglacial temperature changes of only ~1-2°C and a glacial seasonal temperature contrast of ~6.5°C in the northern Gulf of Mexico (Brunner, 1982), only about two-thirds of the present seasonal contrast of 9±1°C (Robinson, et al., 1979).

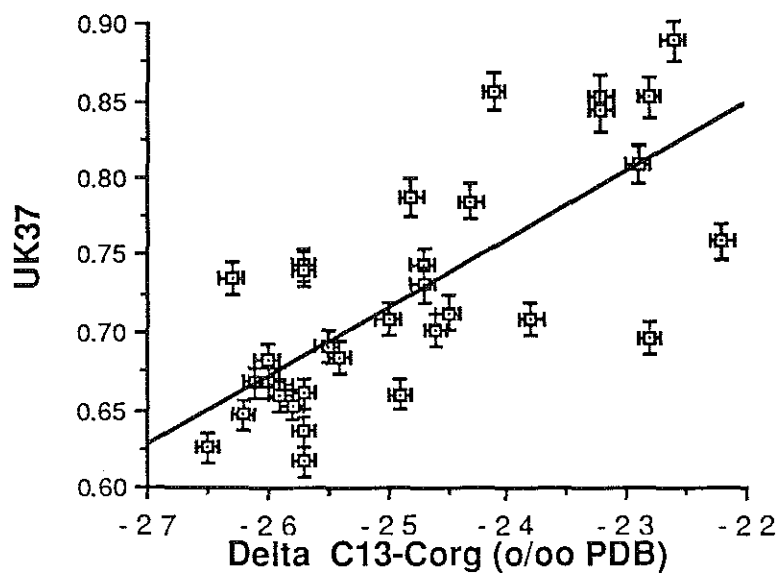
Figure 5.4. Surface mixed layer temperatures calculated from U^{K}_{37} values in Pigmy Basin Core DSDP 619, using Prahl and Wakeham's (1987) U^{K}_{37}-temperature relationship: $U^{K}_{37} = 0.033T + 0.043$.

Figure 5.5. Time series of the carbon isotopic composition of sedimentary organic carbon ($\delta^{13}C\text{-}C_{org}$) of DSDP 619 in the Pigmy Basin, showing relatively positive (marine) values in interglacial stages and relatively negative (terrigenous) values in glacial stages.

Figure 5.6. Cross correlation plot of paired U^{K}_{37} ratios and sedimentary organic carbon isotopic compositions ($\delta^{13}C\text{-}C_{org}$). A least squares linear regression line is superimposed ($U^{K}_{37} = 0.044 \bullet \delta^{13}C\text{-}C_{org} + 1.8$; $P<0.0001$, $r^2 = 0.56$, $n = 33$).


UK37 Temperature (°C)
26
24
22
20
18
16
1
2
3
4
5a
5b
5c?
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


Delta C13-Corg (o/oo PDB)
-21
-22
-23
-24
-25
-26
-27
1
2
3
4
5a
5b
5c?
0
10
20
30
40
50
60
70
80
90
100
Age (ky)


UK37
0.90
0.85
0.80
0.75
0.70
0.65
0.60
-27
-26
-25
-24
-23
-22
Delta C13-Corg (o/oo PDB)

Potential Causes for Discrepant Temperature Differences

Two explanations for the large temperature differences predicted by the U^{K}_{37} and foraminiferal $\delta^{18}O$ and assemblage temperature methods are possible. Firstly, Prymnesiophyte depth and temperature habits and community composition may vary with long-term climatic and/or seasonal changes, resulting in a biased sedimentary record of greater apparent glacial-interglacial SML temperatures than actually occurred on average. Alternatively, the foraminiferal assemblage- and foraminiferal $\delta^{18}O$-temperature methods may also suffer analogous climatic and/or seasonal biases which could cause an underestimation of the actual surface water temperature. The relative merits of the foraminiferal assemblage-, foraminiferal $\delta^{18}O$-, and U^{K}_{37}-temperature estimation methods applied in the northern Gulf of Mexico are examined here.

The glacial-interglacial temperature difference in the water overlying the Pigmy Basin can be estimated with the DSDP 619 G. ruber $\delta^{18}O$ record (Williams and Kohl, 1986) (Fig. 3) and knowledge of the foraminiferal species' water column and seasonal distribution, the biogenic calcite $\delta^{18}O$-temperature relationship (~1°/$_{oo}$ $\delta^{18}O$ per 4°C), and an estimate of the glacial-interglacial ice volume effect on the oxygen isotopic composition of seawater . The year-round occurrence and depth habits of planktonic foraminifera (as well as ambient temperature and seawater $\delta^{18}O$ composition) are essential environmental factors contributing to their usefulness as upper water column temperature indicators. Some planktonic foraminiferal species only occur during certain seasons of the year

which may result in a seasonally-biased sedimentary foraminiferal $\delta^{18}O$ record (Deuser et al., 1981). A series of net tows over five days in the Panama Basin revealed the vertical stratification of planktonic foraminiferal communities in the upper water column and indicated that there were characteristic temperature ranges for given species (Fairbanks et al., 1982). G. ruber was found to calcify mainly in the upper 25 to 37.5 meters of the Panama Basin surface waters. In the Sargasso Sea, G. ruber occurred throughout the year and calcified their shells in the upper 25m of the water column (Deuser et al., 1981). The sedimentary record of G. ruber $\delta^{18}O$ values should be the best foraminiferal record of the combined effects of glacial ice volume changes and upper water column variations (Deuser, 1987). Subtracting the 1.1-to-1.3‰ ice volume signal from a representative glacial-interglacial $\delta^{18}O$ change (~1.5‰) in the Pigmy Basin leaves a 0.2-0.4‰ difference that can be attributed to the surface water temperature change. This $\delta^{18}O$ difference corresponds to a 0.8-1.6°C temperature difference, comparing well with the foraminiferal assemblage estimate of 1-2°C (Brunner, 1982) and to the small ($\leq$2°C) variations predicted by the CLIMAP (1976) reconstruction of tropical and subtropical temperatures.

In the northern Gulf of Mexico, both the foraminiferal assemblage (Brunner, 1982) and $\delta^{18}O$-temperature methods suggest relatively small (0.8-2°C) glacial-interglacial temperature differences, the U^{K}_{37} record of the Pigmy Basin suggest a much larger change of 8±1°C. An 8°C temperature increase would cause an ~2‰ $\delta^{18}O$ increase in foraminiferal carbonates. With the additional ice volume

effect of 1.1-1.3°/$_{oo}$, the composite glacial-interglacial signal would be ~3.1-3.3°/$_{oo}$, approximately twice the amplitude observed in the Pigmy Basin record.

The temporal variations in foraminiferal $\delta^{18}O$ records and evidence from continental geology support large glacial-interglacial variations in continental ice volume. Shackleton (1967) showed that a planktonic foraminiferal $\delta^{18}O$ record paralleled that of benthic species in the Carribean Sea. He concluded that it would be improbable that the temperatures of both the surface and deep waters of the ocean underwent nearly the same variations. The predominant cause of the glacial-interglacial oxygen isotopic time variation was argued to be the waxing and waning of continental glaciers. The volume of ice contained within the glaciers calculated using the elevations of paleo-shorelines (25-50 x 10^6 km^3) delineated by coral reef terraces and equilibrium shape models of continental glaciers (50 x 10^6 km^3) constrained by geological remnants of ice margins were near the estimate (60 x 10^6 km^3) calculated using the benthic foraminiferal $\delta^{18}O$ record with 1.6°/$_{oo}$ attributable to ice volume variations (Broecker, 1982). Later, combined analyses of dated coral terraces and highly resolved foraminiferal $\delta^{18}O$ records showed that although ice volume changes dominated (~75°/$_{o}$) the glacial-interglacial $\delta^{18}O$ record, a smaller, but significant (~25°/$_{o}$) portion of variations in the $\delta^{18}O$ record was attributable to deep-sea temperature changes (Chappell and Shackleton, 1986; Shackleton, 1987). Using recent estimates of foraminiferal $\delta^{18}O$ variations attributable to glacial-interglacial ice volume

(1.1°/$_{oo}$ in the Norwegian Sea, Labeyrie et al., (1987); 1.3°/$_{oo}$ in the eastern tropical Pacific, calculated by Mix and Pisias (1988) from Chappell and Shackleton (1986); versus 1.6°/$_{oo}$, used by Broecker, 1982), a revised estimate of glacial ice volume (40-50 x 10^6 km^3) falls within the range (25-50 x 10^6 km^3) predicted by continental geological evidence.

Considering the convergent lines of evidence which support large glacial-interglacial oxygen isotopic variations (1.1-1.3°/$_{oo}$) in foraminiferal records caused by ice volume changes, the relatively smaller temperature estimates (0.8-2°C) from $\delta^{18}O$ and foraminiferal assemblage methods for the northern Gulf of Mexico seem more plausible than the larger U^K_{37} ratio temperature estimate (8±1°C).

The phytoplanktonic sources of alkenones and the source organisms' water column distribution are two significant factors which affect the U^K_{37} ratio of the alkenones that they produce. These factors may have caused the discrepancy between the U^K_{37} and foraminiferal temperature methods. Unlike sedimentary foraminiferal $\delta^{18}O$ records which are typically monospecific, a U^K_{37} record may be composed of alkenones produced by a variety of different species of the class Prymnesiophyceae (Marlowe et al., 1984; Marlowe et al., 1986). To date, the U^K_{37} ratio temperature method has generally been applied in pelagic environments (Brassell, et al., 1986a, Brassell, et al., 1986b), where Prymnesiophyte assemblages are often dominated by Emiliani huxleyi (Okada and Honjo, 1973; Honjo and Okada, 1974; Okada and McIntyre, 1977). The laboratory U^K_{37}-temperature calibrations are based on Emiliani huxleyi cultures (Brassell, et al., 1986a; Prahl

and Wakeham, 1987), while preliminary monoculture evidence suggests that the U^K_{37}-temperature relationship may have some species dependence (Marlowe, 1984). Within the Prymnesiophyceae, some alkenone-producing phytoplankton species bear coccoliths (e.g. Emiliani huxleyi), while others do not (Marlowe et al., 1984). More than 100 species of coccolithophorids have been listed in the Pacific and Atlantic Oceans (Okada and Honjo, 1973; Honjo and Okada, 1974; Okada and McIntyre, 1977) and in the marginal seas of the west Pacific Ocean and the Red Sea (Okada and Honjo, 1975), so that there are numerous potential alkenone-source organisms. In a 200m deep transect from 50°N to 15°S at 155°W in the Pacific Ocean, the distribution of many coccolithophorids was highly structured with both latitude and depth (Okada and Honjo, 1973). Many species distributions were separated by characteristic temperature ranges. Some areas with high temperature gradients had distinct species variations over small (~10m) depth intervals. By contrast to the spatially-structured and highly diverse pelagic coccolithophorid distribution, the distribution of neritic coccolithophorids was sporadic and its species diversity was comparatively low (Honjo and Okada, 1975). The coccolithophorid Gephyrocapra oceanica dominated the flora of the marginal seas, while Emiliani huxleyi, typically ubiquitous in pelagic environments, was relatively rare. In the California Current system of the southern California Borderlands, four coccolithophorid assemblages characteristic of different local water masses occurred within distances as small as 100 km (Winter, 1985).

The diversity of potential alkenone-producing Prymnesiophytes,

their depth and temperature habits, their potentially species dependent U^{K}_{37}-temperature relationship, and the Late Quaternary regional hydrography of the northern Gulf of Mexico may have contributed to the apparently large glacial-interglacial SML temperature differences (~8°C) in the DSDP 619 U^{K}_{37} record. When global sea level was lowered by ~150m in the last glacial period, the northern Gulf of Mexico would arguably be more hydrographically neritic than during interglacial periods. The sedimentation rate was ~3 times higher in glacial isotope stage 2 than in either interglacial (sub)stages 1 and 5a-b (Williams and Kohl, 1986; Chapter 2). A low salinity, high turbidity plume of Mississippi River outflow water was hypothesized to have moved nearer the Pigmy Basin in glacial periods and to have retreated in interglacial periods (Chapters 2 and 3). If coccolithophorid assemblages respond to the same environmental factors during the last 100 ky as they do presently, climatically-induced hydrographic (neritic versus pelagic) changes may have resulted in coccolithophorid (and other Prymnesiophyte) assemblage changes. The change in the hydrographic character of the northern Gulf of Mexico may have favored a pelagic coccolithophorid assemblage dominated by shallow-dwelling (warmer water) species in interglacial intervals, and deeper-dwelling (colder-water) species in glacial intervals. This scenario would account for the good correspondence of the late isotope stage 1 U^{K}_{37} temperature (25.6°C) with the contemporary average sea surface temperature (~25°C) overlying the Pigmy Basin and the discrepancy between the U^{K}_{37} temperature method (8°C) and the oxygen isotope and foraminiferal assemblage temperature method (1-2°C).

If this scenario is correct, then the U^{K}_{37} ratio may not accurately reflect the chronological record of upper water column temperature in areas subject to large hydrographic and Prymnesiophyte assemblages variations, like marginal seas. In the Pigmy Basin core, the U^{K}_{37} ratio time series probably records the combined effects of varying Prymnesiophyte assemblages and their respective temperatures (at depth) of alkenone synthesis.

The strong qualitative correspondence between U^{K}_{37}-temperature and a typical planktonic foraminiferal $\delta^{18}O$ record (Figs. 5.1 and 5.2) suggests that the U^{K}_{37} ratio may be a useful stratigraphic index in ocean environments potentially subject to climatically-induced Prymnesiophyte species assemblage changes. If Prahl and Wakeham's (1987) E. huxleyi U^{K}_{37}-temperature equation is applicable to neritic as well as pelagic assemblages of Prymnesiophytes, the Pigmy Basin U^{K}_{37} record may largely (75-88°/$_{o}$) represent the time-varying temperature (at depth) at which the bulk of preserved alkenones are biosynthesized, plus the smaller (12-25°/$_{o}$) sea surface temperature variation. Instead of simply recording surface mixed layer temperatures, the combined effects of glacial-interglacial variations in (1) average temperature of alkenone biosynthesis, (2) species assemblage composition, and (3) hydrography may amplify the sedimentary U^{K}_{37} signal. This amplified U^{K}_{37} signal may be a useful stratigraphic indicator in marine environments subject to climatically-induced Prymnesiophyte assemblage changes, like marginal seas.

U^{K}_{37} Ratios and Sedimentary Organic Carbon Isotopic Composition

A comparison of the U^{K}_{37} ratio and the sedimentary organic isotopic composition ($\delta^{13}C$-C_{org}) (Figs. 5.1, 5.4, and 5.5) suggests that they may be related phenomena. High U^{K}_{37} values which occur in interglacial stages in the Pigmy Basin generally correspond to high $\delta^{13}C$-C_{org} values; lower values for the U^{K}_{37} ratio and $\delta^{13}C$-C_{org} are characteristic of glacial stages. A linear regression of paired U^{K}_{37} ratios and $\delta^{13}C$-C_{org} values from the Pigmy Basin (Fig. 5.6) shows that these properties are significantly correlated ($P<0.0001$, $r^2 = 0.56$, $n = 33$).

The connection between the U^{K}_{37} ratio and sedimentary carbon isotopic composition may be due to global glacial-interglacial climatic change. During interglacial periods (e.g. (sub)stages 5a-b) when sea surface temperatures were somewhat elevated relative to those of glacial periods and pelagic Prymnesiophytes may have dominated the local assemblages, sea level was high, covering most of the continental shelf. Marine organic matter dominated the preserved record of organic matter input in the Pigmy Basin, as indicated by $\delta^{13}C$-C_{org} (Fig. 5.5), N/C, and total C_{37-39} alkenone/C_{org} measurements (Chapters 2 and 3). As the global climate cooled, large volumes of ice accumulated on the continents, lowering sea level as much as 150 m (Shackleton, 1967; Broecker, 1982; Chappell and Shackleton, 1986; Shackleton, 1987). The U^{K}_{37} ratio of the Pigmy Basin decreased, perhaps due lower ambient water temperatures and the presence of a neritic assemblage of Prymnesiophytes. The lowered sea level resulted in increased sedimentation rates (Williams and Kohl,

1986) and the erosion of terrigenous organic matter into the hemipelagic Pigmy Basin, as indicated by $\delta^{13}C$-C_{org} (Fig. 5.5), N/C, and 24-ethylcholesterol/C_{org} measurements (Chapters 2 and 3). As global climate warmed, sea level increased, and a pelagic Prymesiophyte assemblage may have returned to the waters overlying the Pigmy Basin, the U^K_{37} values increased and marine organic matter again dominated the preserved record of organic matter deposition.

CONCLUSIONS

The application of a ratio of long chain unsaturated alkenones (U^K_{37}) for molecular stratigraphy shows potential useful application in Quaternary marine environments that are locally influenced by freshwater (meltwater and/or fluvial) runoff events. A significant discrepancy exists between the glacial-interglacial upper water column temperature differences obtained with the U^K_{37}-temperature method (8±1°C) and the foraminiferal $\delta^{18}O$ and foraminiferal assemblage temperature methods (~0.8-2.0°C). Considering (1) the concordant results between the foraminiferal $\delta^{18}O$ and assemblage temperature methods, (2) the mutual agreement of three methods of glacial ice volume estimation (equilibrium continental ice sheet models, raised coral terraces, and foraminiferal $\delta^{18}O$ records) which constrain foraminiferal $\delta^{18}O$ temperature calculations, and (3) the sensitivity of some Prymnesiophyte assemblages to hydrographic conditions, it is tentatively concluded that the U^K_{37} ratio is more useful as a stratigraphic, than a paleothermometric, indicator in marine environments like marginal

seas. The combined use of both $\delta^{18}O$ and U^{K}_{37} stratigraphic techniques may allow improved stratigraphic control and give Prymnesiophyte assemblage- and depth-dependent paleothermometric information about neritic environments.

The U^{K}_{37} ratio and sedimentary organic carbon isotopic composition ($\delta^{13}C$-C_{org}) in the Quaternary Pigmy Basin are significantly related. The relationship may exist because both organic geochemical properties are influenced by variations in global climate. The U^{K}_{37} ratio appears to have been affected by variations in surface mixed layer temperature and, possibly, Prymnesiophyte assemblage composition, while $\delta^{13}C$-C_{org} variations were apparently dominanted by sea level changes. Higher interglacial U^{K}_{37} ratios and higher sea level in the northern Gulf of Mexico were accompanied by a predominance of marine organic carbon burial while lower glacial U^{K}_{37} ratios and sea level co-occurred with a predominance of terrigenous organic carbon burial.

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TABLE 5.1

TIME SERIES OF U^{K}_{37}, SURFACE MIXED LAYER TEMPERATURE, AND $\delta^{13}C$-C_{org}

Sample Number[a]	D.S.D.P. Identification[b]	Depth (mbs)	Age[c] (ky)	U^{K}_{37} Ratio	SML Temp. (°C)	$\delta^{13}C_{org}$ (°/₀₀PDB)
1	1-1:58-63	1.61	1.9	0.856	24.6	-24.1
2	1-2:9-14	2.62	3.1	0.889	25.6	-22.6
4	1-3:45-50	4.48	5.3	0.785	22.5	-24.3
5	1-4:45-50	5.98	7.1	0.713	20.3	-24.5
6	1-4:131-136	6.84	8.1	0.701	19.9	-24.6
7	1-5:76-81	7.79	9.2	0.709	20.2	-23.8
9	1-7:4-9	10.07	11.9	0.744	21.3	-25.7
10	3-2:10-15	13.13	13.9	0.743	21.2	-24.7
12	3-5:128-132	18.80	16.5	0.660	18.7	-24.9
13	4-1:10-15	20.33	17.1	0.653	18.5	-25.8
14	4-2:130-135	23.03	18.3	0.741	21.1	-25.7
15	4-3:135-140	24.58	19.0	0.691	19.6	-25.5
16	4-5:85-90	27.08	20.1	0.661	18.7	-25.7
17F	4-CC:10-16	28.20	20.6	0.636	18.0	-25.7
18	5-2:90-95	32.33	22.4	0.667	18.9	-25.9
19F	5-CC:5-12	36.63	24.3	0.684	19.4	-25.4
21F	6-CC:5-10	47.76	29.3	0.659	18.7	-25.9
22	7-2:113-118	51.96	31.1	0.683	19.4	-26.0
23F	7-CC:5-10	56.89	32.6	0.626	17.7	-26.5
24	8-2:45-50	60.98	35.9	0.668	18.9	-26.1
25F	8-CC:2-8	65.26	38.2	0.647	18.3	-26.2
26	9-1:5-10	68.78	40.2	0.668	18.9	-26.0
31F	11-2:5-10	89.58	51.7	0.735	21.0	-26.3
34	12-3:90-95	101.53	58.3	0.709	20.2	-25.0
35F	13-2:5-10	108.78	62.3	0.731	20.8	-24.7
36	13-4:123-128	114.46	64.4	0.697	19.8	-22.8
37F	14-2:5-10	118.38	66.5	0.617	17.4	-25.7
38	15-2:5-10	127.98	70.3	0.788	22.6	-24.8
42	17-2:8-13	147.31	83.8	0.853	24.6	-23.2
43	17-2:116-121	148.39	85.1	0.852	24.5	-22.8
47F	18-CC:0-5	158.27	98.2	0.759	21.7	-22.2
48F	19-1:47-53	165.60	99.2	0.809	23.2	-22.9
54	22-1:50-55	187.83	102.2	0.843	24.2	-23.2

Table 5.1 (continued)

[a]"F" denotes samples frozen upon collection; all other samples were obtained from D.S.D.P. refrigerated storage five months later.
[b](Core-Section:Interval in cm)
[c]Ages of samples 1-47F were linearly interpolated from isotope (sub)stage boundaries 1-5b. Ages of samples 48F-55 were linearly interpolated between substage boundary 5b and assumed core bottom age of 105ky (Williams and Kohl, 1986); high abundances of quartz sand, shallow water benthic foramifera, and lack of datable horizons indicated sediment density flows through this interval (Kohl, 1986; Williams and Kohl, 1986).

CHAPTER 6

GENERAL SUMMARY

The combined analyses of four types of organic geochemical measurements gave insight into the glacial-to-interglacial climatic effects on the sources and deposition of sedimentary organic matter in the Pigmy Basin in the northern Gulf of Mexico. The combined analyses of bulk parameters allowed the determination that there were two major sources of sedimentary organic matter in the Pigmy Basin. The use of both bulk and trace organic geochemical analyses allowed the investigation of problems that could not be addressed by either type of measurement alone. The establishment of linear relationships between organic biomarker compounds (normalized to sedimentary organic carbon) and sedimentary organic carbon isotopic composition shows that selected biomarker compounds can be used to a first approximation to characterize bulk sedimentary organic matter sources in this environment. Analyses in other sedimentary environments would test the generality of these relationships. Some of the organic biomarkers have the additional useful quality of being quite source specific which allows a better characterization of organic matter sources and perhaps the environment from which they came. Terrigenous and marine carbon isotopic end-members were derived from selected biomarker/C_{org} versus $\delta^{13}C$-C_{org} analyses and were used to differentiate marine and terrigenous C_{org} records from a total organic carbon record. Quantitative analyses of C_{org}

concentration, sedimentary organic carbon isotopic composition , N/C ratios, and organic biomarker concentration measurements allowed the following observations on organic matter deposition in the Late Quaternary Gulf of Mexico:

1. Paired analyses of $\delta^{13}C$-C_{org} and N/C of Pigmy Basin sediments show that the composition of the organic matter is a mixture of C_3-photosynthetic terrigenous and marine organic components. Other hypotheses to explain the glacial-to-interglacial $\delta^{13}C$-C_{org} increase since the Last Glacial Maximum in the Pleistocene Gulf of Mexico include temperature-dependent fractionation of carbon isotopes by phytoplankton, mixing of C_3 and C_4 terrigenous plant material, and sedimentary diagenesis of sedimentary organic carbon. The two former hypotheses are unlikely because they would require approximately constant (marine and terrigenous, respectively) N/C ratios with variable $\delta^{13}C$-C_{org} values while a linear $\delta^{13}C$-C_{org} versus N/C relationship with a significant (non-zero) slope is observed. Sedimentary diagenesis is an improbable explanation since it would require an unprecedented, large (3-6°/$_{oo}$) and time-vaying degree of carbon isotopic fractionation for deep sea sedimentary environments.

2. The correspondence between the $\delta^{13}C$-C_{org} and N/C time series and glacial-interglacial climatic cycles chronicled in the Pigmy Basin confirm Sackett's (1964) hypothesis of climatically-controlled mixing of eroded terrigenous organic carbon and phytoplanktonic-produced marine organic carbon composing the sedimentary organic carbon in the Quaternary northern Gulf of Mexico.

3. The simultaneous evaluation of C_{org} concentrations and $\delta^{13}C$-C_{org} measurements, and $\delta^{13}C$-C_{org} end-members (from paired $\delta^{13}C$-C_{org} and lipid biomarker analyses) allow calculation of terrigenous C_{org} and marine C_{org} concentrations.

4. The net accumulation rate of total sedimentary organic carbon is the sum of the net accumulation rates of eroded terrigenous organic carbon and contemporaneous primary production of marine organic carbon minus sedimentary remineralization. The average rate of total sedimentary organic carbon burial is 2.6 ± 1.3 times higher in glacial stages 2 to 4 than in interglacial (sub)stages 1 and 5a-b.

5. Average (±1σ) terrigenous C_{org} concentrations are 1.4 ± 1.1 times higher in glacial stages 2 to 4 than in interglacial (sub)stages 1 and 5a-b. The average net accumulation rate of terrigenous organic carbon was 3.7 ± 3.1 times higher in isotope stages 2 to 4 than in interglacial stages 1 and 5a-b. The higher accumulation rates of terrigenous organic carbon in stages 2 to 4 are presumably due to higher continental (shelf and estuarine) erosion rates caused during lowered sea level stands of glacial periods.

6. Average marine C_{org} concentrations are only 0.43 ± 0.26 as high in glacial stages 2 to 4 as in interglacial isotope (sub)stages 1 and 5a-b. However, the highest average net accumulation rates of marine organic carbon occurred in glacial stages 4 and 2, largely because of the sedimentation rate differences. After a model-dependent compensation for the differential effects of sedimentation rates on marine organic carbon preservation, the glacial stage 2 values nearly equaled those of interglacial substages 1 and 5a-b. The combined analyses of marine and

terrigenous organic carbon concentrations and net accumulation rates suggests that a nutrient-bearing, low salinity plume of the Mississippi River may have advanced and retreated over the Pigmy Basin as sea level fell and rose, respectively, in the Quaternary northern Gulf of Mexico.

7. The combined analyses of selected organic biomarker compounds, sedimentary carbon isotopic composition, and sedimentary organic carbon concentrations allowed general paleoceanographic reconstructions of glacial and interglacial modes of organic matter deposition in the Late Quaternary Pigmy Basin.

8. Linear least squares regressions of biomarker/C_{org} ratios on $\delta^{13}C$-C_{org} values with first-order C_{org} remineralization kinetics approximated idealized diagenetic models for organic carbon-normalized terrigenous and marine biomarker sedimentary records on the time scale of 2-100 ky. Processes (including C_{org} remineralization, hydraulic particle sorting, source changes, biomarker degradation, and differential marine and terrigenous organic carbon remineralization rates) which cause divergences from the simple biomarker/C_{org} versus $\delta^{13}C$-C_{org} linear relationship may limit the application of this simple diagenetic model. More sophisticated modelling techniques would account for more of the variance than this simple model.

9. The organic carbon-normalized concentrations of total C_{37-39} alkenone/C_{org} were significantly linearly related to sedimentary organic carbon isotopic composition, indicating that they were useful tracers of marine organic carbon on the 2-100 ky time scale. Interglacial isotope (sub)stages 5a-b, 1 and 2 were generally characterized by higher total C_{37-39} alkenone/C_{org} values than the

intervening stages 4-2, with two local maxima succeeding isotopic stages 4 and 2.

10. A time-varying residual trend from the total C_{37-39} alkenone/C_{org} versus $\delta^{13}C$-C_{org} linear regression was consistent with the occurrence of two processes. The general decreasing trend with time was attributed to organic carbon remineralization. Episodic extrema may be attributed to source changes (i.e., time-varying total C_{37-39} alkenone/marine C_{org} ratios).

11. The application of a ratio of long chain unsaturated alkenones (U^K_{37}) for molecular stratigraphy shows potential useful application in Quaternary marine environments that are locally influenced by freshwater (meltwater and/or fluvial) runoff events. A significant discrepancy exists between the glacial-interglacial upper water column temperature differences between the U^K_{37}-temperature method (8±1°C) and the foraminiferal $\delta^{18}O$ and foraminiferal assemblage temperature methods (~0.8-2.0°C). Considering (1) the concordant results between the foraminiferal $\delta^{18}O$ and assemblage temperature methods, (2) the mutual agreement of three methods of glacial ice volume estimation (equilibrium continental ice sheet models, raised coral terraces, and foraminiferal $\delta^{18}O$ records) which constrain foraminiferal $\delta^{18}O$ temperature calculations, and (3) the sensitivity of some Prymnesiophyte assemblages to hydrographic conditions, it is concluded that the U^K_{37} ratio may be a useful stratigraphic, but probably not a paleothermometric indicator in marine environments like marginal seas which may be subject to climatically-induced Prymnesiophyte assemblage changes and freshwater runoff events.

12. The U^{K}_{37} ratio and sedimentary organic carbon isotopic composition ($\delta^{13}C$-C_{org}) in the Quaternary Pigmy Basin are significantly related. The relationship may exist because both organic geochemical properties are influenced by variations in global climate. The U^{K}_{37} ratio appears to have been affected by variations in surface mixed layer temperature and, perhaps, Prymnesiophyte assemblage composition, while $\delta^{13}C$-C_{org} variations were apparently dominated by sea level changes. Higher, interglacial U^{K}_{37} ratios and higher sea levels in the northern Gulf of Mexico were accompanied by a predominance of marine organic carbon burial while lower glacial U^{K}_{37} ratios and sea levels co-occurred with a predominance of terrigenous organic carbon burial.

13. The time-varying residual trend from the 24-ethylcholesterol/C_{org} versus $\delta^{13}C$-C_{org} linear regression was consistent with the occurrence of a number of processes causing divergences from a simple mixing relationship. The general skewed sinusoidal trend in the residual time series was consistent with sedimentary organic carbon remineralization. Large, positive 24-ethylcholesterol/C_{org} residuals above the C_{org} remineralization trend in the ~20-65 kybp interval may have been caused by hydraulic particle sorting. This hypothesis was supported by clastic sedimentological results which showed coarser particle deposition in the Pigmy Basin during near the glacial maximum than in interglacial stages. Climatically-induced floral source changes may also have contributed to or caused the positive residual trend. Episodic extrema were attributed to source changes.

14. The organic carbon-normalized concentration of 24-ethylcholesterol/C_{org} was significantly related to sedimentary organic carbon isotopic composition, indicating that it was a useful terrigenous organic matter tracer in the 2-100 ky Pigmy Basin sedimentary record. Interglacial isotope stages 5a-b and 1 were characterized by lower 24-ethylcholesterol/C_{org} values than during the intervening stages 4-2, with a local maximum near the glacial-intergalcial stage 2/1 boundary.

15. Four other desmethylsterols (cholesterol, 22-dehydrocholesterol, brassicasterol, and campesterol) and the nC_{26-32}even fatty alcohols were also significantly related to sedimentary organic carbon isotopic composition. Their residual trends were similar to that for 24-ethylcholesterol/C_{org}. The residuals may be attributed to C_{org} remineralization, hydraulic particle sorting, and/or floral source changes.

16. Eight other 4-desmethylsterols ($C_{27-29}\Delta^{22}$-, $C_{27 \text{ and } 29}\Delta^{5,22}$-, and $C_{27-29}\Delta^{0}$-4-desmethylsterols) when normalized to C_{org} followed the general trend of 24-ethylcholesterol/C_{org}, but were insignificantly related to sedimentary organic carbon isotopic composition. The similarity to the 24-ethylcholesterol/C_{org} record suggested that some portion of these 4-desmethylsterols also had a terrigenous origin. Sedimentary diagenesis, hydraulic particle sorting, and source changes may have contributed to the statistical insignificance of these biomarker compounds as quantitative tracers of organic matter determined by a linear least squares model.

17. For 4-desmethylsterols there was an absence of marine biomarker/C_{org} characteristics (positive slope and $\delta^{13}C$-C_{org} intercept $\cong$ 19±2°/oo PDB) relative to $\delta^{13}C$-C_{org}, despite the fact that most of the sterols examined had both terrigenous and marine sources. These observations implied that terrigenous sterols were better preserved than marine sterols. The apparent differential diagenetic labilities of terrigenous and marine 4-desmethylsterols suggested that sedimentary sterol records may be biased in favor of terrigenous sterol preservation.

18. The 4-desmethylsterol data collected for combined organic biomarker and $\delta^{13}C$-C_{org} analyses were evaluated for the potential occurrence of sterol double bond (Δ^5, Δ^{22}) reductions . The sedimentary records of four possible product/precursor ratios from each of the 3 classes of C_{27-29}-4-desmethylsterols were examined for temporal trends. Only the Δ^5-hydrogenations of the C_{29}-sterols (24-ethylcholest-5-en-3ß-ol and 24-ethylcholesta-5,22-dien-3ß-ol) appeared to be significant in DSDP 619. The positive correlation of 24-ethylcholestan-3ß-ol/24-ethylcholest-5-en-3ß-ol ($C_{29}\Delta^0/C_{29}\Delta^5$) ratios with paired $\delta^{13}C$-C_{org} values (as well as age) was consistent with a combined diffferential hydraulic particle sorting and molecular transformation mechanism. A long-term source change of 24-ethyl-cholestan-3ß-ol relative to 24-ethylcholest-5-en-3ß-ol seems a less probable explanation for these results since both sterols are predominantly of a terrigenous origin in the Pigmy Basin.

19. The frequency distributions of stanol/stenol (Δ^0/Δ^5) ratios of the C_{27-29}-4-desmethylsterols indicate that the relative degree of

transformation by class increases in the order: $C_{27} > C_{28} > C_{29}$. Since the product/precursor ratios the C_{27}- and C_{28}-sterols show no significant increase with age, they appear to have attained this degree of transformation before ~2kybp. However, differential rates of competing reactions of both the precursor and products may have obscured these transformation ratio records.

This research has demonstrated the power of combined organic geochemical analyses to discern sources and processes of organic matter deposition in a deep-sea sedimentary environment. With a method to determine marine and terrigenous C_{org} and the proper global sampling strategy, we may begin to constrain the glacial-interglacial transfer of organic carbon between major reservoirs. Given the locally-varying physical responses of the earth to long-term climatic change, sedimentary organic matter distribution may have a distinct regional character, as we are beginning to learn. However, even if marine C_{org} can be differentiated from terrigenous C_{org} in sedimentary records, their relationship to the original sedimentary organic matter input is still not well understood. This unresolved problem remains a major challenge for organic geochemists. Non-steady state diagenetic modelling of organic matter degradation may be part of the solution.

If the C/P ratio of buried sedimentary organic matter increases with sedimentation rate, then the glacial-interglacial variation in sedimentation rates may affect the atmospheric partial pressure of CO_2. Generally higher glacial erosion rates on the continental platforms and higher sedimentation rates in marine environments would release more P per unit C to the water column, fertilizing the ocean.

The biological fixation of C and P could contribute to the glacial decrease in atmospheric pCO_2 since more P relative to C would be removed from the surface ocean, decreasing the pCO_2. Hence the measurement of bulk organic geochemical properties in Quaternary research may have considerable value.

The processes which cause the deviations (residuals) in organic biomarker/C_{org} versus $\delta^{13}C$-C_{org} regressions should be investigated more thoroughly. The long-term residual trends for organic carbon-normalized biomarker concentrations were considered to be mainly due to faster C_{org} remineralization than organic biomarker degradation. This hypothesis could be evaluated further by comparing individual biomarker diagenetic tranformations in a nearly steady state sedimentary environment with respect to sedimentary organic carbon remineralization, or by developing more sophisticated non-steady state models for environments like the Pigmy Basin. Characterization of the process of differential hydraulic particle sorting in ancient sedimentary environments would benefit from paired sedimentological and organic geochemical analyses which could potentially show the distribution of selected biomarkers with characteristic grain sizes. Spikes in the organic geochemical records (e.g., marine and terrigenous C_{org}, alkenones/C_{org}, and 24-ethylcholest-5-en-3ß-ol/C_{org}) could be better characterized by high temporal resolution sampling, for example, during the time of meltwater events. Characterization of mechanisms such as short-term phenomena may contribute to understanding the mechanism of long-term climatic change. The carbon isotopic composition of individual organic biomarker compounds promises to more specifically discern their