Sedimentary lipids as indicators of depositional conditions in the coastal Peruvian upwelling regime

by

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ABSTRACT

This thesis assesses the utility of various sedimentary lipids as indicators of short-term changes in depositional conditions and sedimentary organic matter sources in the coastal upwelling regime off of Peru. A variety of lipids (n-alkanes, n-alkanols, C_{37} alkenones, hopanoids, keto-ols, lycopane, phytol, stenols, stanols, sterenes, and tetrahymanol) were quantified in Peru margin sediments from both the oxygen minimum zone (OMZ) and several near-shore locations. I discuss the utility of the lipid profiles, the alkenone-U^k_{37} "paleothermometer", the n-alkane CPI, and several stanol/stenol ratios as indicators of short-term changes in depositional conditions. This work also provides the first assessment of the influence of *Thioploca*, a genus of sulfur-oxidizing bacteria, on organic compound distributions in upwelling regime sediments.

The potential of the alkenone-U^k_{37} as a sedimentary marker for El Niño/ Southern Oscillation (ENSO) events was assessed by comparing the historical ENSO record with detailed U^k_{37} profiles for ^{210}Pb-dated cores from the OMZ. Sediments from the center of the OMZ sectioned at intervals ≤ the yearly sedimentation rate have the greatest potential for holding a U^k_{37} record of El Niño events. The U^k_{37} signals of individual El Niño events were substantially attenuated in the sediments examined, and periods of frequent ENSO activity (e.g., 1870-1891) were more readily identified than isolated ENSO events in periods of less frequent ENSO activity. Detailed depth profiles of the C_{37} alkenones in a core, SC3, from ≈253 m (O_2 <0.1 ml/l bottom water) suggest significant alkenone degradation and/or alteration (≈30%) in the 0-1 cm interval, despite the dysoxic depositional conditions. However, the similarity of the U^k_{37} values for the five 2 mm sections from 0-1 cm suggest that the U^k_{37} may be unaffected by the alkenone loss. Correlation between the C_{37} alkenone concentration profiles in two cores from ≈15°S collected nine years apart are consistent with the use of these compounds for "molecular stratigraphy."

The utility of sedimentary hydrocarbons and alcohols as indicators of short-term changes in depositional conditions was determined in core SC3 by (1) a multivariate factor analysis of the lipid data and (2) a consideration of individual source-specific biomarkers. In this core, profiles of odd-carbon-number n-alkanes (C_{25}-C_{33}) and even-carbon number n-alkanols (C_{24}-C_{28}) reflect changes in the input of terrigenous sediment relative to marine sediment during deposition, as indicated by the correlations between these lipids and inorganic indicators of terrigenous clastic debris. The n-alkane carbon preference index (CPI) provides a less-sensitive record of fluctuations in the terrestrial input than the concentration profiles of the individual n-alkanes and n-alkanols, and these lipids are *not* well-correlated with the historical El Niño record. The similarity of all the stenol profiles measured and the lack of concordance between these profiles and inorganic indicators of terrigenous input suggest that fluctuations in the abundance of higher plant stenols are obscured by the larger marine contribution of these compounds. Similarities between the profiles of total organic carbon (TOC) and cholestanol/cholesterol are consistent with stenol hydrogenation being influenced by the sediment redox conditions.

Profiles of sterols and sterol alteration products illustrate that the rapid downcore decreases in sterol concentrations do not simply represent conversion of sterols into other steroidal compounds, but must also involve steroid degradation and possibly formation of

non-solvent-extractable steroids. In OMZ sediments, the ratio [cholesterol alteration products] / [cholesterol + cholesterol alteration products] substantially increases from 0-4 cm, but at deeper depths, there is no systematic change in the ratio. This suggests that if there is a progressive conversion of cholesterol to these degradation products below 4 cm, then it is obscured by an equally rapid removal of these compounds from the sediments. Stenol profiles in surface sediments suggest a range of degradation rates for these compounds. Differential remineralization of steroids can cause the relative steroid abundances in ancient sediments to bear little resemblance to the relative abundances of the sterols from which these compounds were derived. This limits the use of steroids as indicators of the *relative importance* of the original organic matter inputs. However, important quantitative statements can be made concerning the depositional environment, based on the presence, rather than relative abundance, of certain steroids derived from specific sources.

In SC3, the downcore increase in burial time (100 cm ≈ 310 years b.p.) and the downcore changes in sediment chemistry did not result in accumulation of cholesterol alteration products from more advanced portions of the alteration pathways than are achieved in the 0-1 cm interval. The absence of cholest-4-ene, cholest-5-ene and cholestane suggests that cholestadiene reduction to cholestenes and cholestene reduction to cholestane do not begin to occur over the time scale and under the sedimentary conditions encountered in the surface 100 cm of Peru margin OMZ sediments.

Although the hopanoids found in the Peru sediments can be related relatively easily to compounds found in ancient sediments and oils, these hopanoids are not as useful as steroids for reconstruction of organic matter sources and paleoenvironmental conditions. This is because the bacterially-derived precursors of these compounds are generally not specific to any particular type of bacteria.

This thesis provides the first assessment of the influence of *Thioploca* on organic compound distributions in upwelling regime sediments. *Thioploca*, a genus of colorless, sulfur-oxidizing, filamentous bacteria, constitutes as much as 80% of the biomass in surface sediments from the OMZ. Since marine species of *Thioploca* have been found only in dysaerobic surface sediments of upwelling regimes, biomarkers for this organism may be useful in identifying similar depositional conditions in the sedimentary record. *Thioploca* (dry) was found to be ≈3.8-4.1 wt% lipid. Three fatty acids: *cis* 16:1Δ9, 16:0 and *cis* 18:1Δ11 accounted for 69-72% of this lipid. Hydroxy fatty acids, hopanoids and hydrocarbons were conspicuously absent from the *Thioploca*. This organism was found to contain cyclolaudenol, a C_{31} sterol with an unusual structure; diagenetic alteration products of this sterol may serve as markers for *Thioploca* input to sedimentary organic matter, and hence as markers for paleo-upwelling depositional environments in the sedimentary record. No quantitatively significant alteration products of cyclolaudenol were identified in the Peru surface sediments.

Thioploca was found to be 9-10 dry wt% protein, and the THAA composition of the *Thioploca* contained no unusual amino acids that might serve as *Thioploca* markers. The *Thioploca* THAA composition was similar to surface sediment from core SC3 (0-1 cm), but differed significantly from the THAA composition of surface sediments (0-3 cm) from the Peru margin analyzed in a previous study.

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CHAPTER 1

INTRODUCTION

1.1 General introduction

An interplay between rapid advances in analytical technology and new applications for organic geochemistry has spurred the tremendous expansion in organic geochemical research seen in the 1980's. One rapidly developing area has been the application of organic geochemistry to paleoenvironmental reconstruction, a subject previously treated primarily with techniques from geology, paleontology, and inorganic geochemistry. The work reported here assesses the utility of sedimentary lipids as indicators of short-term changes in depositional conditions in the coastal upwelling regime off Peru. This introduction describes both the geological significance of this depositional environment and the importance of this study.

1.2 The depositional environment of coastal Peru

Southeast trade winds along the Peru-Chile margin result in Ekman transport of surface water (<25 m depth) offshore, and this water is replaced by upwelling from <100 m. This eastern-boundary current system, called the Peru current, causes upwelling of variable intensity along the Peru-Chile margin, with the areas of strongest upwelling occurring between 4-6°S and 14-16°S (Zuta et al., 1975, Brockmann et al., 1980). Upwelling of nutrient-rich water in these areas stimulates extremely high primary productivity of 1-10 g C $m^{-2}d^{-1}$ (Ryther et al., 1971; Gagosian et al. 1980). Diatoms are the most abundant phytoplankton (species abundance varies seasonally and latitudinally; Guillen et al., 1973), and copepods are the dominant zooplankton (*Calanus*, *Eucalanus*, and *Centropages* spp.; Sandstrom, 1982). During normal upwelling, this area is one of the most productive fisheries in the world; production of the anchovy *Engraulis ringens* from this region has accounted for as much as 20% of global fish production yearly (Walsh, 1981).

Along the Peru coast, partial remineralization of organic matter in the water column and sediments results in an oxygen minimum zone (OMZ; O_2 <0.1 ml/l) which impinges on the continental margin from ≈75 to 500 m water depth (Fig. 2.1). During unusual hydrographic conditions, hydrogen sulfide has been reported in the OMZ (Dugdale et al., 1977), but dysoxic rather than anoxic conditions typically characterize the OMZ water column. Benthic macrofauna are essentially absent from surface sediments within the oxygen minimum, and as much as 80% of the benthic biomass consists of *Thioploca* , a genus of sulfur-oxidizing, filamentous bacteria (Gallardo, 1977; Rosenberg et al. 1983).

Depositional conditions along the coast vary latitudinally. From 6-10°S, the wide continental shelf (≈100 km) results in relatively shallow water depths under the area of highest productivity. As a result, surface sediments in this area are continuously reworked by the southward-flowing Peru undercurrent. Sediment reworking and slow basin subsidence in this region result in slow deposition of a coarse-grained, calcareous (>15 wt% $CaCO_3$) mud facies with TOC contents < 5 wt%. In contrast, the much narrower shelf (5-15 km) from 11-15°S places surface sediments out of reach of the Peru undercurrent, and sediments within the OMZ (outer shelf-upper slope) experience bottom current velocities near zero. The more quiescent depositional environment and the rapid basin subsidence from 11-15°S result in rapid accumulation (200-1000 cm/1000 years) of a fine-grained, diatomaceous mud (Scheidegger and Krissek, 1983; Suess and Killingley, 1987). These carbonate-poor sediments have TOC contents as high as 22 wt% (Repeta, 1989). Figure 1.1 A-G gives examples of some of the biogenic and inorganic debris present in OMZ sediments at 15°S.

The upwelling regime at ≈15°S, one of the most well-characterized portions of the Peru margin, was the source of most samples analyzed in this work. The Peruvian coast adjoining this area is a narrow, sparsely-vegetated, arid plain (< 0.8 cm/yr average precipitation; Johnson, 1976) bordered on the east by the Andes mountains and on the south by the Atacama desert. Because of low average continental runoff and high coastal primary productivity, the TOC of sediments deposited within the OMZ from 11-15°S is only minimally influenced by terrestrial input, although some higher plant debris can be found in the sediments (Fig. 1.1 F and 1.1 G). On the west, the continental slope is bordered by the Peru-Chile trench, marking the convergence of the Nazca and South American plates. The grade of the continental shelf is ≈1:10 (Henrichs and Farrington, 1984), and slumping has caused sedimentary hiatuses in some areas (DeVries and Schrader, 1981) of this seismically active margin. Sediments at 15°S have the highest rates of organic carbon accumulation reported for the Peru margin (Reimers and Suess, 1983b). At 15°S, Staresinic (1978) measured a carbon flux of 250 mg C $m^{-2}d^{-1}$ (≈ 6% of primary production) to sediment traps at 50 m water depth, and as much as 50-80% of this carbon accumulates in surface sediments (Henrichs and Farrington, 1984).

The Peru upwelling regime is regularly perturbed by El Niño events, climatic disturbances of variable intensity which last from several months to a year and affect the eastern tropical Pacific once every 2-10 years (Quinn et al., 1987). During El Niño conditions, relaxation of the strong southeast trade winds causes deepening of the thermocline, nutricline, and mixed layer along the Peru margin. Primary productivity then decreases, and prolonged El Niño events can cause widespread mortality of anchovy and

sea-bird populations (Barber and Chavez 1983, 1986). During El Niño conditions, sea-surface temperature, rainfall, and continental runoff typically increase (Deser and Wallace, 1987; Quinn et al., 1987). Recognition of a relationship between El Niño conditions and the Southern Oscillation (a measure of the difference in atmospheric pressure between the South Pacific subtropical high and the Indonesian equatorial low) has led to the term El Niño-Southern Oscillation (ENSO) to describe this entire climatic perturbation, and not simply the anomalous oceanographic conditions along the Peru coast. The ENSO phenomenon has been implicated in short-term climatic events that extend even beyond the Pacific basin (e.g., Philander, 1989). Although the term El Niño was originally used by Peruvian fishermen to refer simply to anomalously warm water off Peru, the term is now frequently used as an abbreviation for El Niño-Southern Oscillation.

1.3 The geologic importance of coastal upwelling

The organic geochemistry of the Peruvian upwelling regime has been the subject of numerous studies with very diverse goals. Because the present study draws on much of this previous research, I list here some of the diverse aims that have been proposed for geochemical investigations of this particular depositional environment.

The OMZ of the coastal Peruvian upwelling regime is a modern analog to the depositional environments of certain important petroleum source rocks, such as the Miocene Monterey Formation of the California Borderland (e.g., Soutar et al., 1981). Because organic matter alteration pathways in surface sediments ultimately affect kerogen type and eventual petroleum yield of a sediment (Tissot et al., 1974), there has been interest in characterizing the factors affecting organic matter alteration in these surface sediments. Furthermore, there has been interest in identifying biomarkers specific to this type of depositional environment which could be useful in identifying similar depositional conditions in the geologic record (e.g., Brassell and Eglinton, 1983; ten Haven et al., 1989).

Because of the high primary productivity along the Peru margin, the water column and sediments of this area have been studied to characterize the degradation of sterols (Gagosian et al., 1983a, 1983b; Smith et al., 1983), amino acids (Henrichs, 1980), carotenoids (Repeta and Gagosian, 1983, 1987; Repeta, 1989) and various other lipids (Wakeham et al., 1984). In addition, Peru margin sediments have been the subject of intense phosphorite research (Sandstrom, 1982; Baker and Burnett, 1988, and references therein), since this is one of the few areas in the world where Recent phosphorites occur and are presently being formed. Other studies of this region have assessed the relationship

Figure 1.1 A: Diatom frustules (*Coscinodiscus*; Dr. Diane Stoecker, personal communication) in sediment from core SC3, 8-9 cm, Station 4, 253 m water depth. The station location is shown in figure 2.1.

Figure 1.1 B: Amorphous organic matter in sediment from core SC3, 13-14 cm.

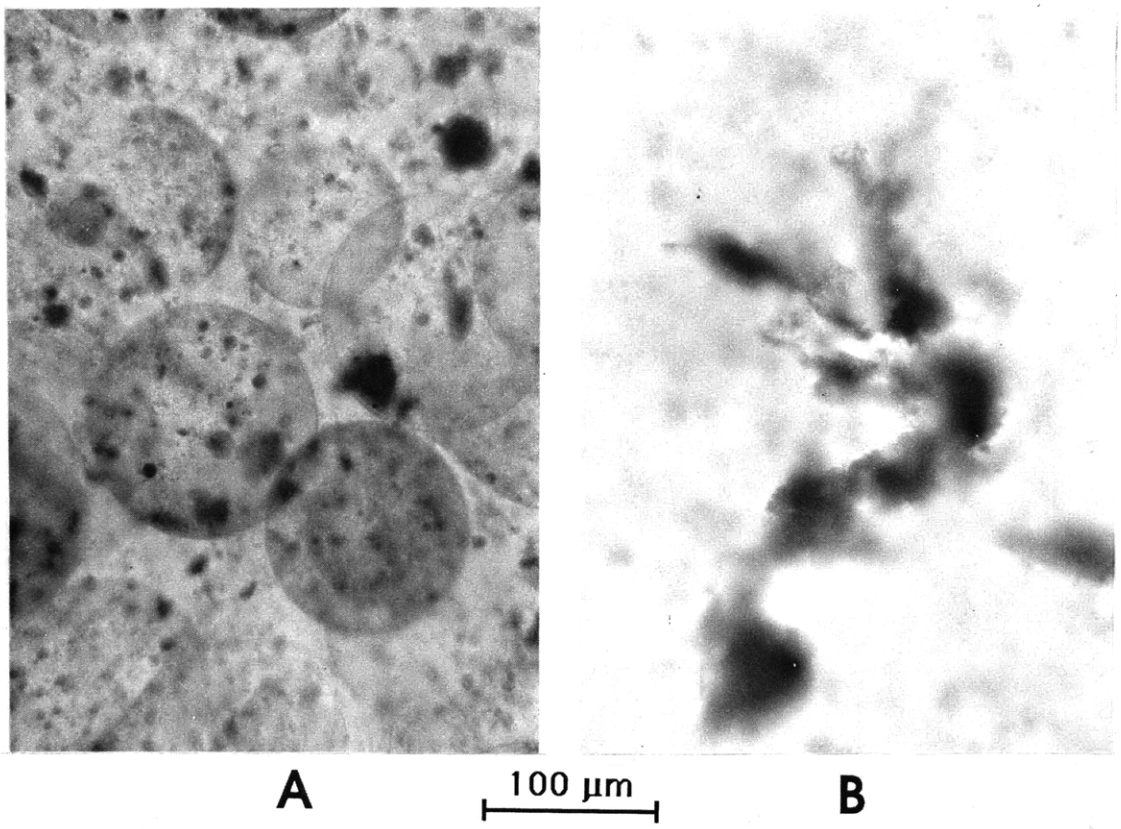
Figure 1.1 C: Rotalid-form benthic foram (*Cibicides* ?) in sediment from core SC3, 44-45 cm.

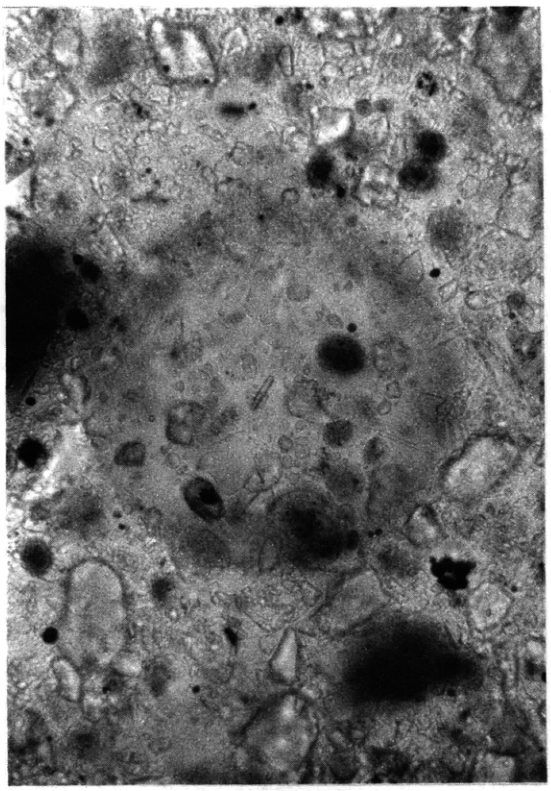
Figure 1.1 D: Benthic foram (*Bolivina*; Dr. W. Berggren, personal communication) in sediment from core SC3, 85-86 cm. *Bolivina* spp. are characteristic of low-oxygen, organic-rich sediments (Douglas, 1981).

Figure 1.1 E: Terrigenous clastic debris (angular fragments) and *Coscinodiscus* frustule in sediment from core SC3, 75-76 cm. This section of the core is unusually rich in terrigenous rock debris, as discussed in chapter 4.

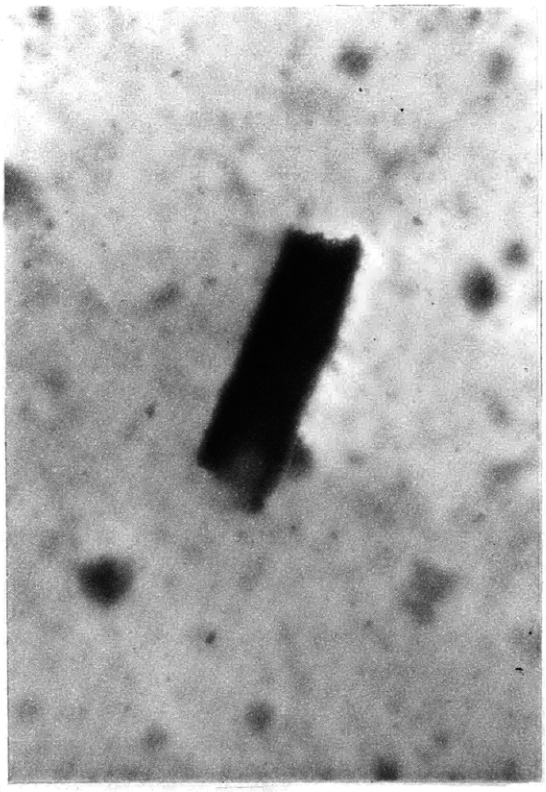
Figure 1.1 F: Higher plant fragment (?) in sediment from core SC3, 85-86 cm.

Figure 1.1 G: Macroscopic higher plant debris from surface sediment grab sample G39, station TT2D, 63 m water depth. The station location is shown in figure 2.1.


A
100 µm
B
C
D

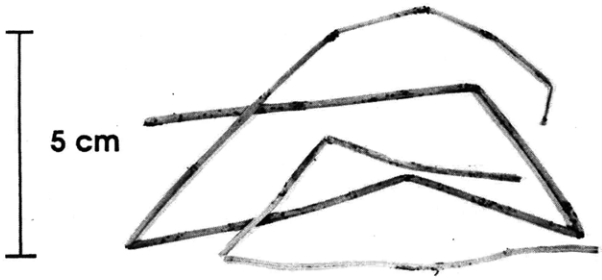


E 100 µm



F 100 µm

Higher plant debris from sediment grab sample G39, station TT2D, 63 m water depth



G

between carbon preservation, primary productivity, bottom-water oxygenation, and sedimentation rate (Reimers and Suess, 1983b; Calvert and Pedersen, 1990).

1.4 Previous work on paleoenvironmental records for this area

Previous efforts to derive paleoenvironmental records from Peru margin sediments have primarily dealt with >500 yr time scales and have attempted to identify only major changes in this environment. DeVries and Schrader (1981) and DeVries and Pearcy (1982) used changes in fish scale and diatom abundances in Peru margin surface sediments from 11-13°S (sedimentation rates ≤ 1 mm/yr) to construct a record of large-scale changes in the physical oceanography of that area since the Pleistocene. Reimers and Suess (1983a) proposed that profiles of the elemental and isotopic compositions of kerogen from these sediments reflect changes in circulation, upwelling, and bottom-water oxygenation during the last 16,000 years. Reimers and Suess (1983b) correlated changes in the climate and physical oceanography of this area since the Late Pleistocene with two depositional hiatuses and with changes in regional TOC accumulation. In 1987, the Peru margin at 11°S was the site of the Ocean Drilling Program leg 112, which sought to characterize the impact of Quaternary sea level changes on organic matter preservation and the location of the OMZ.

Interest in the El Niño phenomenon has provided substantial impetus for constructing much more detailed records of the Peruvian paleoclimate. Efforts to construct an historical record of El Niño events have included studies of ice stratigraphy in the Peruvian Andes (Thompson et al., 1984), flood deposits in northern coastal Peru (Wells, 1987), Peru margin sedimentary TOC profiles (Henrichs and Farrington, 1984), and Peru margin sedimentary alkenone profiles (Farrington et al., 1988).

1.5 The contribution of this study

Numerous sedimentary organic geochemical parameters have been proposed as indicators of paleodepositional conditions in coastal upwelling areas (e.g., Brassell and Eglinton, 1983). However, individual studies typically deal with only a few of these parameters, and many studies have not had access to very finely-sectioned, dated cores. As a result, it is frequently *not* possible to assess the relative utility of discrete organic geochemical indicators of depositional conditions. Furthermore, insufficient geochemical data for a set of samples can make it difficult to identify the correct data interpretation from among several possible scenarios. In this context, the work reported here has had two specific goals: (1) assessing the relative utility of a large number of sedimentary lipids as indicators of short-term changes in depositional conditions in the coastal upwelling regime off Peru, and (2) determining if the lipid geochemistry of these sediments records an

historical record of ENSO events that have affected this region. The second aim, a subset of the first, is of specific interest because identification of a sedimentary signature of ENSO events may lead to an extension of the historical ENSO record (Quinn et al., 1987), which would certainly be useful in studying the ENSO phenomenon.

Since the low dissolved oxygen concentrations in the OMZ inhibit bioturbation (Rhoads and Morse, 1971; Rosenburg et al., 1983; Henrichs and Farrington, 1984), sediments within the depth range of the OMZ may hold an undisturbed geochemical record of changes in depositional conditions. This study used finely-sectioned, dated cores from the OMZ to assess the utility of various sedimentary organic geochemical parameters as indicators of El Niño events and other short-term changes in the depositional environment. All analytical techniques are described in chapter 2. In chapter 3, I explore the utility of the sedimentary alkenone-U^k_{37} temperature record as an indicator of El Niño depositional conditions by comparing the historical ENSO record with U^k_{37} profiles for three cores from the OMZ. In chapter 4, I determine the usefulness of individual compounds as indicators of higher-plant input by comparing profiles of these lipids in core SC3 from the OMZ with inorganic indicators of terrigenous input; I examine the utility of terrigenous lipids as indicators of ENSO conditions, and I discuss the geochemical implications of numerous other lipid profiles in this core.

Chapter 5 explores the impact of early diagenesis on steroids and pentacyclic triterpenoids in core SC3. The remineralization and alteration of cholesterol and hopanols are examined as examples of steroid and hopanoid diagenesis. The degradation pathways of cholesterol in this very finely-sectioned core are compared with the sterol degradation pathways that have been proposed previously (e.g., Mackenzie et al., 1982) based on water column, surface sediment, and theoretical studies.

Chapters 6 and 7 provide the first assessment of the influence of *Thioploca* on organic compound distributions in upwelling regime sediments, and provide the first data on potential biomarkers for this organism. The filamentous bacteria, *Thioploca*, constitutes as much as 80% of the biomass in dysaerobic surface sediments (O_2 <0.1 ml/l bottom water) in the coastal upwelling regimes of Peru and Chile. Since marine species of *Thioploca* have been found only in dysaerobic surface sediments of upwelling regimes, biomarkers for this organism may be useful in identifying similar depositional conditions in the sedimentary record.

Chapter 8 reviews the conclusions of this thesis and discusses the application of these data to the study of ancient sediments from similar depositional environments including (1) ODP sediments from the Peru margin and (2) the Miocene Monterey Formation of the California Borderland. Chapters 3, 4, and 6 are presented in the format of journal articles

co-authored with my thesis advisors, Dr. John W. Farrington, and Dr. Daniel J. Repeta. Appendices 1 and 2 provide tables of the data used to make the thesis figures. Appendix 3 provides mass spectra of compounds discussed in chapters 3, 4, and 5.

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CHAPTER 2

METHODS

2.1 Sediment and *Thioploca* spp. sample collection

During July 1987, on the R/V *Moana Wave* cruise 87 leg 08 (PUBS I), Soutar-type box cores of sediment were collected from the center and edges of the OMZ in the Peru upwelling region near 11°S and 15°S. Following collection, the cores were immediately sectioned and frozen for subsequent analyses. Grab samples of surface sediment were collected using a Van Veen grab sampler and were also immediately frozen. Sampling station locations are shown in Fig. 2.1, and the samples collected at each station are listed in Table 2.1. X-rays of the 4 cores discussed in this thesis are shown in Fig. 2.2-2.5†.

Thioploca spp. were sieved from sediments collected from the OMZ; the sampling locations are listed in Table 2.1. Within minutes of sieving the sediments, individual strands of *Thioploca* were picked from the sieved material, rinsed in filtered seawater, aggregated into groups of strands, and frozen for subsequent analyses. The samples of picked and rinsed *Thioploca* appeared to be free of all other material based on examination with a binocular stereoscope.

2.2 Lipid extraction of samples and lipid analysis

The procedures and equipment used for lipid extraction differ only slightly from the procedures described by Farrington et al. (1988). Frozen samples were thawed, and homogenized by mixing with a solvent-rinsed stainless-steel spatula. Approximately 10-15 g of wet sediment were added to a 50 ml Corex centrifuge tube. Sufficient isopropanol was added to bring the volume to 50 ml, and then internal recovery standards were added ($C_{16}D_{32}$ n-alkane, $C_{24}D_{50}$ n-alkane, $C_{32}D_{66}$ n-alkane, C_{19}-n-alkan-2-one, C_{19} fatty acid methyl ester, and C_{21} free fatty acid). The tubes were sonic extracted for ≈10 min using a Tekmar sonic insertion probe disruptor. The tubes were centrifuged until sediment formed a pellet. The isopropanol was decanted into a 500 ml separatory funnel containing 60 ml of 1/6 saturated, hexane-extracted NaCl(aq) prepared from $KMnO_4$-distilled water. The sediment was re-extracted with ≈40 ml methanol-chloroform (1:1 v/v), and then ≈40 ml methanol-chloroform (1:3 v/v). After each extraction, the tubes were centrifuged and the supernates were combined in the separatory funnel. Lipids were partitioned into the

† The X-rays were produced by Jim Broda and co-workers in the WHOI Geology and Geophysics Department using a Philips K140Be Macrotank Portable Industrial X-ray Tubehead. Exposure was at 110Kv at small aperature in slow scan mode (15 cm/min).

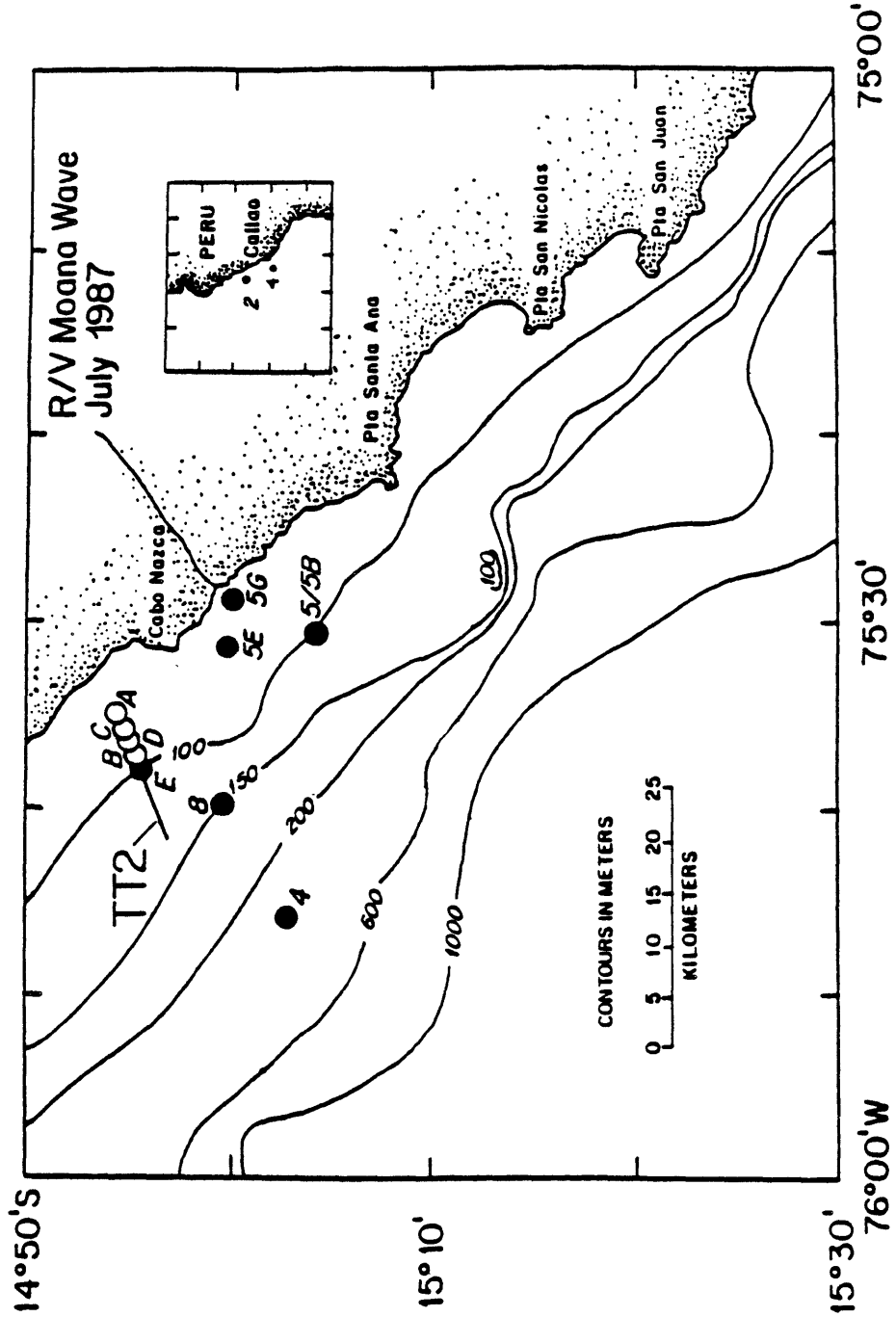

Figure 2.1: Station locations (R/V Moana Wave leg 87-08: PUBS I) where samples analyzed in this thesis were collected. The location of Station 2 is shown in the inset. Latitude and longitude divisions in the inset are 5°. The samples from each station are listed in Table 2.1. Stations from which samples were collected but not analyzed have not been included in this figure.

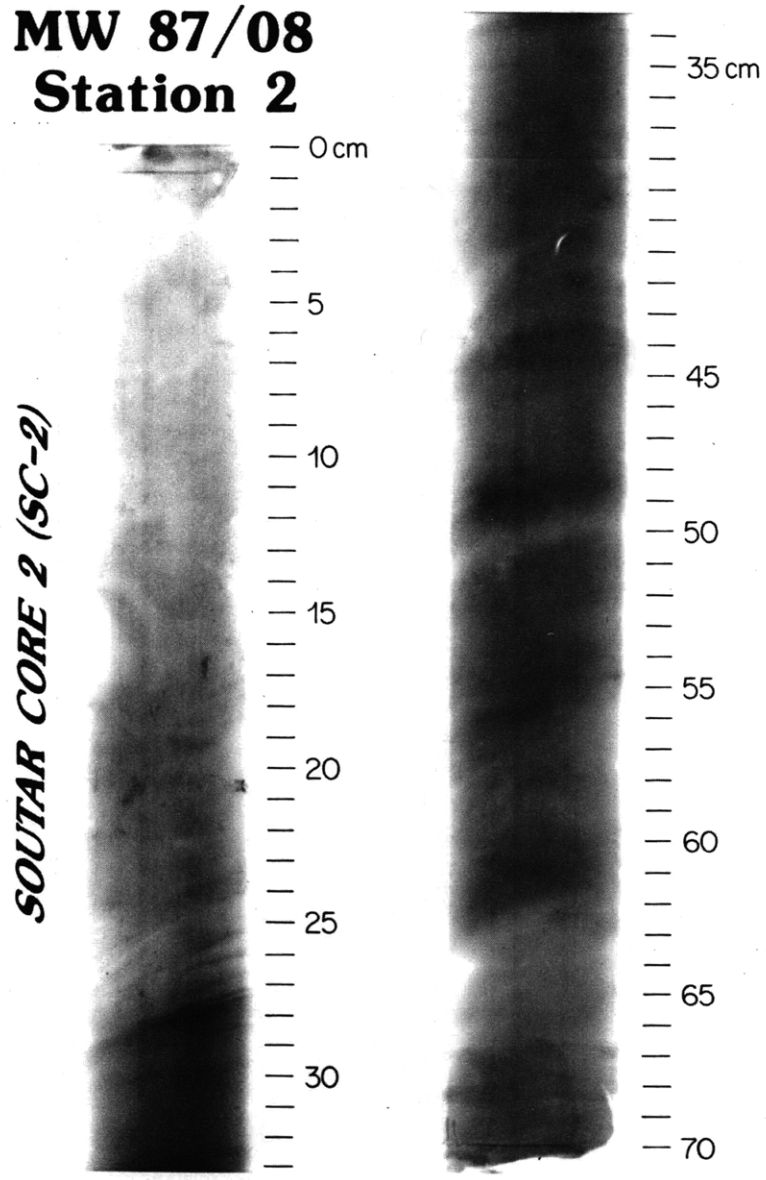

Figure 2.2: X-ray of core SC2 from Station 2, 255 m water depth.

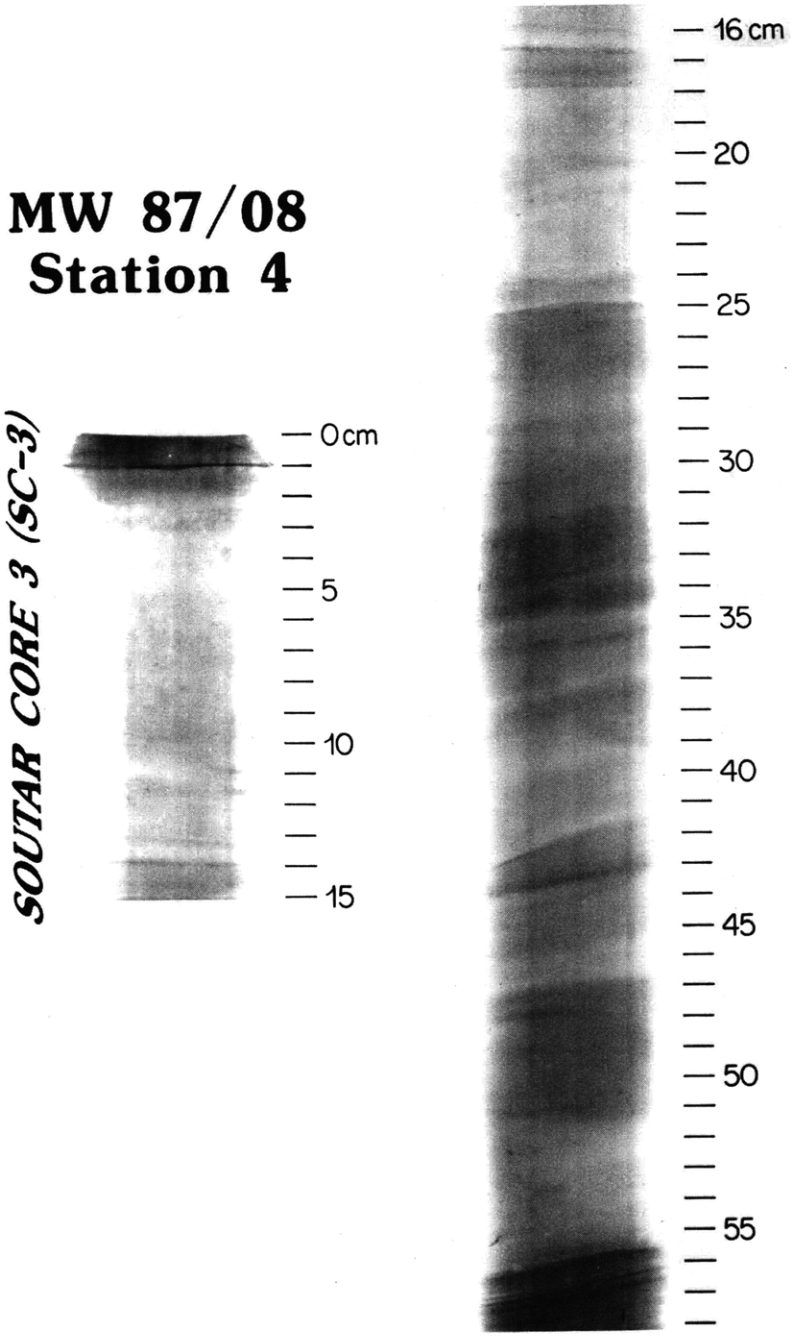

Figure 2.3: X-ray of core SC3 from Station 4, 253 m water depth.

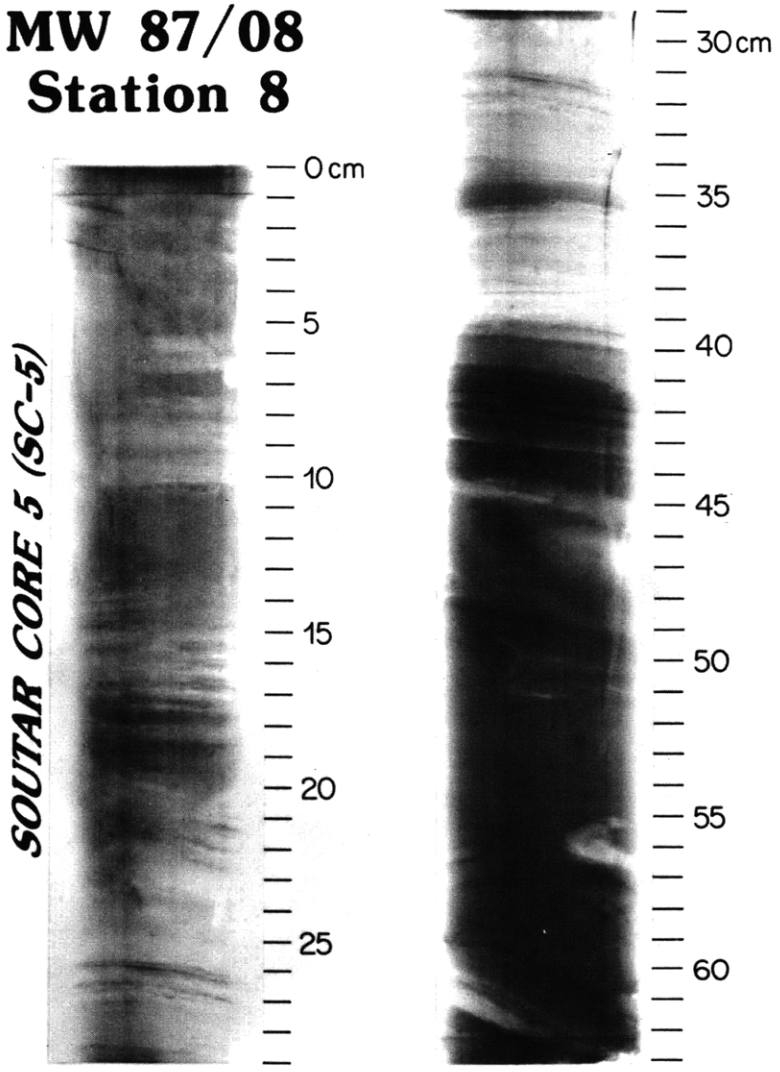

Figure 2.4: X-ray of core SC5 from Station 8, 135 m water depth.

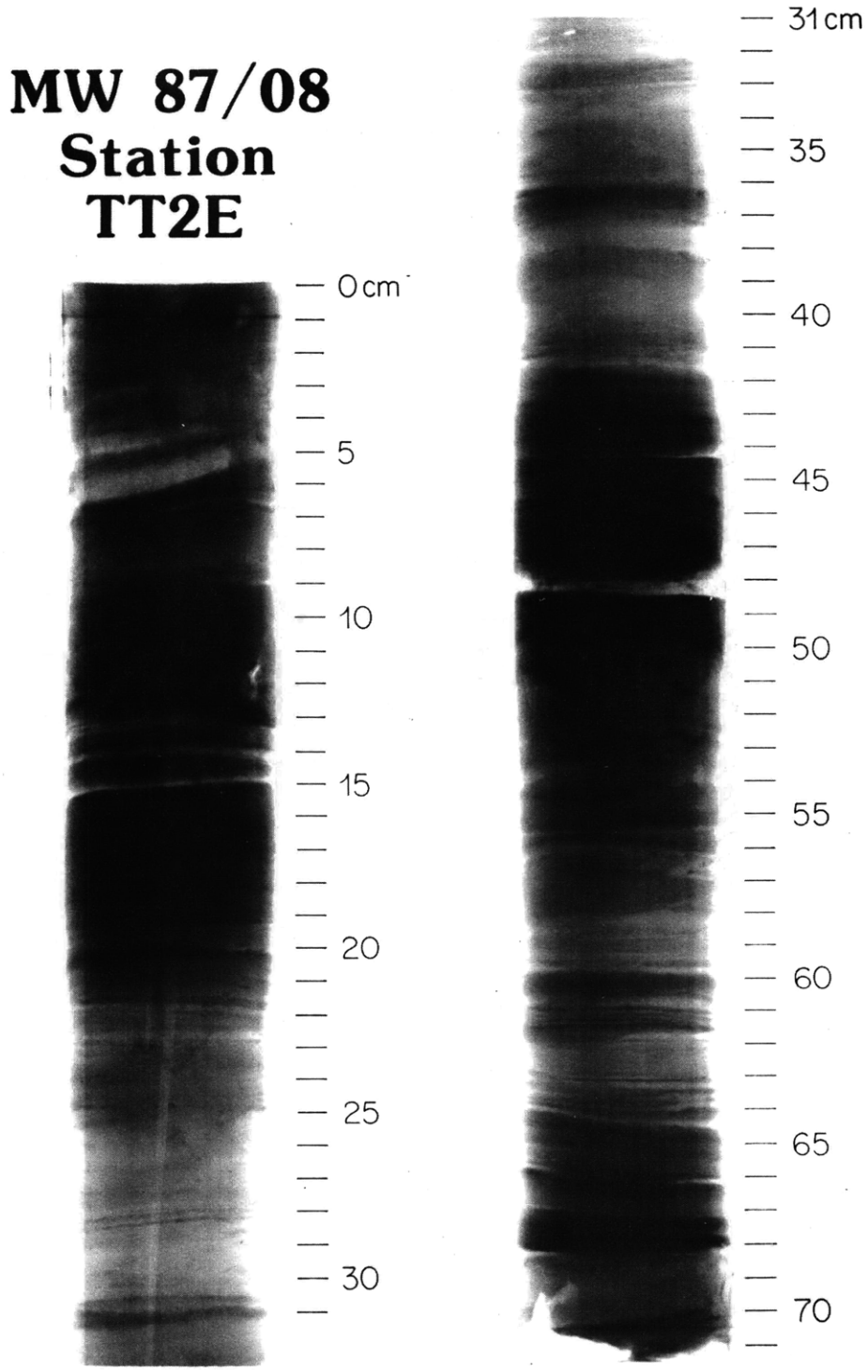

Figure 2.5: LEFT: X-ray of core BC9 (0-32 cm). RIGHT: X-ray of core SC7 (31-71 cm). Both cores are from Station TT2E, 105-110 m water depth. An X-ray of the surface of SC7 is not available.

TABLE 2.1
Sampling Locations

Sample	Sampling station	water depth	latitude	longitude
core SC2	2	255 m	11°04.21'S	78°03.14'W
core SC3	4	253 m	15°06.16'S	75°42.09'W
core SC5	8	135 m	14°59.96'S	75°39.23'W
core SC7	TT2E	105-110 m	14°56.62'S	75°36.81'W
grab G25	5G	30 m	15°00.4'S	75°27.8'W
grab G28	TT2A	25 m	14°54.03'S	75°35.20'W
grab G37	TT2C	50 m	transect on 15°S	
grab G39	TT2D	63 m	14°54.53'S	75°36.19'W
Thioploca #1	TT2E	100 m	14°54.20'S	75°36.81'W
Thioploca #2	5B	73-75 m	15°04.27'S	75°31.97'W
Thioploca #3	TT2D	63 m	14°54.53'S	75°36.19'W
Thioploca #6	8	140 m	14°59.96'S	75°39.23'W
Thioploca #15	5E	75 m	15°00.07'S	75°31.85'W

isopropanol/chloroform phase, which was drained into a 500 ml round-bottom flask containing ≈30 cc granular Na_2SO_4. The aqueous phase was re-extracted twice with 25 ml chloroform, which was added to the round-bottom flask. An additional 25 ml of chloroform was then added to the round-bottom flask to force additional water out of solution with the organic phase. The flask was then vigorously swirled for ≈1 min and allowed to stand for > 2 h to allow the Na_2SO_4 to dry the solution. The solution was then decanted into a glass funnel containing a glass wool plug and 25 cc of additional Na_2SO_4. The funnel was rinsed with 35 ml of additional chloroform, and the lipid extract was rotary evaporated to a small volume.

One-half of the total lipid extract (TLE) was separated into lipid classes by silica-gel column chromatography. The column consisted of a glass chromatographic column (0.9 cm x 35 cm , with a 300 ml reservoir) containing 7 g of 5% deactivated silica gel (BioRad-BioSil, 100-200 mesh) wet packed in hexane onto 2 cm of activated copper (previously activated with 2N HCl). The activated copper removes the elemental sulfur which would otherwise elute in Fraction 1. Fractionation was accomplished using the following elution scheme:

Fraction	Eluent	Compounds analyzed
1	20 ml Hexane	alkanes, some monoenes
2	20 ml Tol./Hex. (25:75 v/v)	polyunsaturated alkenes, aromatic hydrocarbons
3	20 ml Tol./Hex. (50:50 v/v)	polyunsaturated alkenes, aromatic hydrocarbons
4	20 ml EtOAc/Hex. (5:95 v/v)	fatty acid methyl esters (FAMEs)
5	20 ml EtOAc/Hex. (10:90 v/v)	ketones, FAMEs
6	20 ml EtOAc/Hex. (15:85 v/v)	n-alkanols, hopanols, 4-methyl sterols
7	20 ml EtOAc/Hex. (20:80 v/v)	4-desmethyl sterols, alkan-15-one-1-ols
8	20 ml EtOAc, 20 ml methanol	polar material not analyzed

The sample was loaded onto the column in hexane; the sample vial was rinsed with a small amount of each successive fraction, and these rinses were added to the column.

Fractions 1-7 were analyzed by high-resolution gas chromatography (GC) using a Carlo Erba 4160 gas chromatograph with an on-column injector and a J & W Scientific Durabond DB-5 30 m fused silica capillary column (0.32 mm I.D., 0.25 μm film thickness). Fractions 2 and 3 were combined prior to analysis. The GC program used for

fractions 1, 2+3, 4, 6, and 7 was: injection at 70°C, isothermal for 1 min, 3°/min to 250°, 4°/min to 310°, 6°/min to 320, isothermal for 13 min. The GC program used for fraction 5 was: injection at 100°C, isothermal for 1 min, 5°/min to 320°, isothermal for 15 min. Compound identifications were based on data from electron-impact gas chromatography-mass spectrometry (GC-MS) and/or chemical-ionization (methane) GC-MS and/or GC coelution with authentic standards; Table 2.2 indicates the method(s) used for identification of each compound. Appendix 3 contains mass spectra (from sediment extracts, not standards) of thirty-six of the compounds discussed in the text. Spectra of n-alkanes and n-alkanols are not included in this appendix, since they are readily available in most mass-spectral data bases. The GC-MS system was a Finnigan 4510 quadropole mass spectrometer interfaced to a Carlo Erba 4160 gas chromatograph with a DB5 column (described above) and helium as the carrier gas. GC-MS operating conditions were 50 eV ionization potential with the source at 100 °C with scanning rate from 50-650 amu per second.

The alcohols in fractions 6 and 7 were acetylated prior to GC analysis by (1) evaporating the solvent from the sample in a 4 ml vial, (2) adding 40 µl pyridine and 40 µl acetic anhydride, (3) sealing the vial under N_2 and leaving at room temperature for ≈16 h, (4) evaporating the reagents under an N_2 stream, and (5) rinsing the sides of the vial with methylene chloride and then evaporating the solvent under N_2.

After GC analysis of Fraction 1, the alkenes were removed from the fraction using a column of $AgNO_3$ impregnated (10%) silica gel (Aldrich,+200 mesh). The column consisted of 0.7 g silica gel dry packed into a glass disposable Kimble pasteur pipette (≈ 23 cm) plugged with glass wool. The column was pre-conditioned with 5 ml of hexane. The sample was loaded onto the column in hexane and was eluted with 4 ml of hexane. The sample was then re-analyzed by GC, and the n-alkanes were quantified. In some samples, the eluate of the $AgNO_3$ column contained an alkene, 22, 29, 30 trisnorneohop-13(18)ene, which was identified by comparison of the mass spectrum with published spectra (Sandstrom, 1982). This compound partially coelutes with C_{28} n-alkane under our analytical conditions; an important implication of this coelution is that when calculating the n-alkane carbon preference index (CPI, see chapter 4) of a sediment, the purity of the C_{28} n-alkane peak should be verified.

A known amount of D_{26}-dodecane was added to each fraction prior to GC analysis. Compounds were quantified by comparing the GC peak areas of the compounds of interest with the GC peak area of the D_{26}-dodecane. GC response factors relating the response of various compounds to the response of D_{26}-dodecane were measured with external standards and were generally very close to 1. A response factor of 1 was assumed in the

Table 2.2
Compounds Quantified in SC3

Compound	Identification	Some Major Sources	Reference
n-alkanes >C_{24}	1, 3	Higher plants	Eglinton and Hamilton (1967)
n-alkanols >C_{26}	1, 3	Higher plants	Eglinton and Hamilton (1967)
Alkan-15-one-1-ols	3	Planktonic cyanobacteria	Morris and Brassell (1987)
Phytol	1, 3	Chlorophyll-a	Volkman and Maxwell (1986)
C_{37} alkenones	3	Prymnesiophyceae	Marlowe et al (1984)
$C_{20:1}$ isoprenoid	3	Diatom?	
Lycopane	1, 2, 5	Phytoplankton?	
STEROLS:			
24-methylcholest-5, 22-dien-3ß-ol	1, 2	Diatoms	Gagosian et al. (1983)
24-methylcholest-5-en-3ß-ol	1, 2	Higher Plants	Volkman (1986)
Cholesterol	1, 2	Zooplankton	Gagosian et al. (1983)
Cholest-5,22-dien-3ß-ol	3	Diatoms Zooplankton	Gagosian et al. (1983)
Dinosterol (4, 23, 24-trimethylcholest-22en-3ß-ol)	3	Dinoflagellates	Boon et al. (1979)
24-ethylcholest-5-en-3ß-ol	1, 2	Higher plants Phytoplankton	Volkman (1986)
24-ethylcholest-5, 22-dien-3ß-ol	1, 2	Higher Plants Phytoplankton	Volkman (1986)
5α(H) analogs of Δ^5 stenols	2, 3	Stenol reduction Primary production	Nishimura and Koyama (1977)
STERENES:			
Cholest-3, 5-diene	3	Stenol alteration product	Wakeham et al. (1984)
Cholest-R, N, N-triene	4	Stenol alteration product	Wakeham et al. (1984)
14α(H)-1(10→6)-abeocholesta-5,7,9 (10)-triene	3	Stenol alteration product	Hussler and Albrecht (1983)
PENTACYCLIC TRITERPENOIDS:			
Homohopanol, bishomohopanol	3	Hopanoid alteration product	Rohmer et al. (1984)
Tetrakishomohopanol	4	Hopanoid alteration product	Rohmer et al. (1984)
17ß(H), 21ß(H)-homohopane	3	Hopanoid alteration product	Huc (1978)
Tetrahymanol	3	Protozoan?	Ten Haven et al. (1989)

[1] GC coelution with authentic standards.
[2] Electron impact GC-MS/ comparison with spectrum of authentic standard.
[3] Electron impact GC-MS/ comparison with published spectra.
[4] Electron impact GC-MS/ inspection of spectrum and comparison with spectra of similar compounds.
[5] Chemical ionization (methane) GC-MS/ comparison with spectrum of authentic standard.

quantification of unknown compounds and certain compounds for which authentic standards were not available. Duplicate extractions of three sediment samples suggest that the uncertainty in the lipid analyses is ± 4-5%. This is after all internal recovery standards have been normalized to recoveries of 100% (actual recoveries are almost always > 85%). The high precision of these analyses is also illustrated by a comparison of lipid data for the 15 sections of SC3subcore with the data for samples from the corresponding depth range in core SC3. The comparison between SC3subcore and SC3 is discussed in chapter 3 and illustrated in Fig 3.10A.

The silica gel, NaCl, Na_2SO_4, and glass wool were Soxhlet extracted with methanol/toluene 1:1 v/v for 24 h and then methylene chloride for 24 h. All solvents were Burdick and Jackson High Purity Solvents, except chloroform, which was Burdick and Jackson GC^2 brand solvent. The ethyl acetate was redistilled before use. Solvent purity was confirmed by running blanks of each lot of each solvent.The glassware used in the lipid extraction of samples and in the preparation of lipid fractions was washed with (1) Micro glassware cleaner (International Products Corp.) and water, (2) distilled water, (3) methanol, (4) acetone, (5) toluene, (6) hexane, and (7) methylene chloride. Analytical blanks of the lipid extraction procedure and the lipid fraction preparation were periodically run following exactly the same procedures as for a sample.

2.3 Sample dry weight calculation and CHN analyses

Sediment dry weights were determined by drying a weighed aliquot of wet sample at 110°C for 24 h and then correcting the dry weight for salts. Pore water was assumed to have a salinity of 3.5 wt %, and the following equation was used to calculate the salt-free sediment dry weight:

$$\text{Salt-free dry wt} = W * \left[([D/W] * 1.03627) - 0.03627\right]$$

W is the sediment wet weight, and D is the sediment dry weight including salt.

Sediment TOC measurements were performed on 2-5 mg of dried, ground, carbonate-free sediment that had been exposed to HCl vapors in a closed container for 48 hours. Sample weights used in the TOC calculation are for the dried sediment before the carbonate removal and were corrected for pore water salts. TOC measurements were made on a Perkin Elmer 2400 CHN analyzer in which the samples were combusted in pure oxygen at 925°C.

2.4 THAA, total carbohydrate and total protein analyses

Total hydrolyzable amino acid analyses : The THAA analysis technique is described in detail by Conway (1990), and is described here in brief. Frozen *Thioploca* samples were thawed, rinsed in twice-distilled water and dried at 60°C for 3 h. The dried samples were weighed on a Cahn 25 Automatic Electrobalance to ±2 μg, and were placed in 10 ml glass ampules with 1.0 ml of twice-distilled 6N HCl and known amounts of the non-protein amino acids γ-aminobutyric acid and norleucine as internal standards. The ampules were sealed under nitrogen after they were successively evacuated and then flushed with nitrogen six times. The samples were hydrolyzed at 110°C for 36 hours. The hydrolysates were lyophilized in Altech 5 ml microreaction vials. To ensure complete removal of water and HCl, the samples were reconstituted in 100 μl ethanolic solution ($EtOH:H_2O$:triethylamine (TEA) = 1:1:1) and re-lyophilized. Samples then were derivitized with 220 μl of phenolisothiocyanate (PITC) solution ($EtOH:H_2O$:TEA:PITC = 7:1:2:1) for 15 min. before being re-dried under vacuum. For HPLC analysis, the samples then were diluted in 500 μl of eluent A (see below) and passed through a 0.45 μm filter. The HPLC was equipped with a Varian 2010 dual head reciprocating pump, an Isco 2360 gradient programmer, and a Beckman Ultrapure ODS C_{18} reverse phase, high performance column equipped with a pre filter element and a C_{18} guard column. The column was maintained at 48°C with an Altech HPLC column water bath equipped with a Lauda K2/R constant temperature circulator. Two eluents were used in a gradient elution scheme: eluent A= 0.03M sodium acetate with 6.0% acetonitrile and 0.05% triethylamine (pH= 6.3; adjusted with acetic acid), eluent B= 50% H_20, 50% acetonitrile. Gradient usedwas: 0-15%B in 10 min, 15-35% B in 10 min, 35-80% B in 10 min, 80-100% B in 1 min, 100% B for 5 min, 100-0% B in 5 min, 100% A for 20 min. Compounds were detected by measuring absorbance at 254 nm with a Kratos spectroflow 757 absorbance detector. Amino acid identifications were by comparison with retention times of authentic standards. For comparison with the THAA data for *Thioploca*, a bulk protein assay of *Thioploca* was performed as described below.

Total protein and carbohydrate assays : A *Thioploca* sample was rinsed in doubly distilled water, dried at 60°C for 3 hours, homogenized with an agate mortar, and weighed on a Cahn 25 Automatic Electrobalance to ± 2 μg. This 4.032 mg sample was added to a homogenization tube along with 4.24 ml of doubly distilled water. One ml aliquots of the homogenized mixture were placed in four test tubes: two for protein assay, two for carbohydrate assay. For the protein assay, 4 ml of biuret reagent was added to both of the sample tubes and to a blank tube containing 1 ml of water. After one hour, the samples and

blank were filtered through a 0.25 μm syringe filter, and absorbance at 560 nm was measured using a Beckman DU-7 spectrophotometer. Calibration was with an external response curve using bovine serum albumin as a standard and was linear in the response range of the samples. The carbohydrate assay was done by the phenol-sulfuric acid method: 1 ml of 5% phenol and 5 ml of concentrated H_2SO_4 were added to both of the sample tubes and to a blank tube containing 1 ml of water. After 20 min, absorbance was measured at 490 nm. Calibration based on an external response curve using D-glucose as a standard, and was linear in the response range of the samples.

2.5 Analysis of total and supported ^{210}Pb in sediments

Excess ^{210}Pb profiles were determined using techniques and equipment described by Buesseler (1986). Samples were 7-12 g of dried, ground sediment; dry weights were corrected for salts. Total ^{210}Pb was determined by counting the 46.5 KeV γ-ray from ^{210}Pb decay. Supported ^{210}Pb was determined by counting the 352 KeV γ-ray from ^{214}Pb decay; excess ^{210}Pb was calculated as the difference between total and supported ^{210}Pb. Counting efficiencies were determined with pitchblende standards and, for the total ^{210}Pb measurements, were corrected for self absorption.

2.6 ICP analyses of elemental sediment composition

In sixteen sections of SC3, the abundances of a suite of elements (Al, Ti, Zr, Fe, P and Mn) were measured by inductively coupled plasma (ICP) spectroscopy after total sediment dissolution. Dissolved sediment samples were prepared by (1) combusting the sediments in air at 500°C for 24 h, (2) mixing the combusted sediment in a 1:4 weight ratio with $LiBO_2$ flux, (3) fusing the sediment-flux mixture at 1125°C for 15 min, and then (4) dissolving the fusion in 1M HCl. This procedure is described in greater detail by Govindaraju and Mevelle (1987), and the ICP analytical technique is described in detail by Bankston (1988).

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CHAPTER 3

THE ORGANIC GEOCHEMISTRY OF PERU MARGIN SURFACE SEDIMENTS-I. A COMPARISON OF THE C_{37} ALKENONE AND HISTORICAL EL NIÑO RECORDS

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Abstract: The alkenone-U^k_{37} "paleothermometer" has potential as a sedimentary marker for El Niño/ Southern Oscillation (ENSO) events in the Peru upwelling regime. We assessed this potential by comparing the historical ENSO record with detailed U^k_{37} profiles for ^{210}Pb-dated cores from the Peru margin oxygen minimum zone (OMZ). Sediments with the greatest potential for holding a sedimentary U^k_{37} record of El Niño events are sediments from the center of the OMZ sectioned at intervals ≤ the yearly sedimentation rate. The U^k_{37} signals of individual El Niño events were substantially attenuated in the sediments we examined, and periods of frequent ENSO activity (e.g., 1870-1891) were more readily identified than isolated ENSO events in periods of less frequent ENSO activity. Detailed depth profiles of the C_{37} alkenones in a core from ≈253 m (O_2 <0.1 ml/l bottom water) suggest significant alkenone degradation and/or alteration (≈30%) in the 0-1cm interval, despite the dysoxic depositional conditions. However, the similarity of the U^k_{37} values for the five 2 mm sections from 0-1 cm suggests that the U^k_{37} may be unaffected by the alkenone loss. Correlation between the C_{37} alkenone concentration profiles in two cores from ≈15°S collected nine years apart are consistent with the use of these compounds for "molecular stratigraphy."

INTRODUCTION

During normal upwelling, extremely high primary productivity (1-10 gC $m^{-2}d^{-1}$) characterizes the Peruvian coastal upwelling regime between 11°and 15°S (RYTHER et al., 1971; GAGOSIAN et al., 1980). Organic matter remineralization in the water column and sediments results in an oxygen minimum zone (OMZ; O_2 <0.1 ml/l) impinging on the Peru margin from ≈75 to 500 m water depth (Fig. 1). Since the low dissolved oxygen concentrations in the OMZ inhibit bioturbation (RHOADS and MORSE, 1971; ROSENBURG et al., 1983; HENRICHS and FARRINGTON, 1984; McCAFFREY et al., 1989), sediments within the depth range of the OMZ may hold an undisturbed geochemical record of changes in depositional conditions.

The Peru upwelling regime is regularly perturbed by El Niño Southern Oscillation (ENSO) events, climatic disturbances of variable intensity which last from several months to a year and affect the eastern tropical Pacific once every 2-10 years (QUINN et al., 1987). During ENSO conditions, the thermocline, nutricline, and mixed layer deepen along the Peru margin; primary productivity decreases (BARBER and CHAVEZ, 1983, 1986), and sea-surface temperature, rainfall, and continental runoff typically increase (DESER and WALLACE, 1987; QUINN et al., 1987). The historical record of El Niño occurrences in the eastern tropical Pacific extends to ≈ 450 years b.p., with good documentation for only

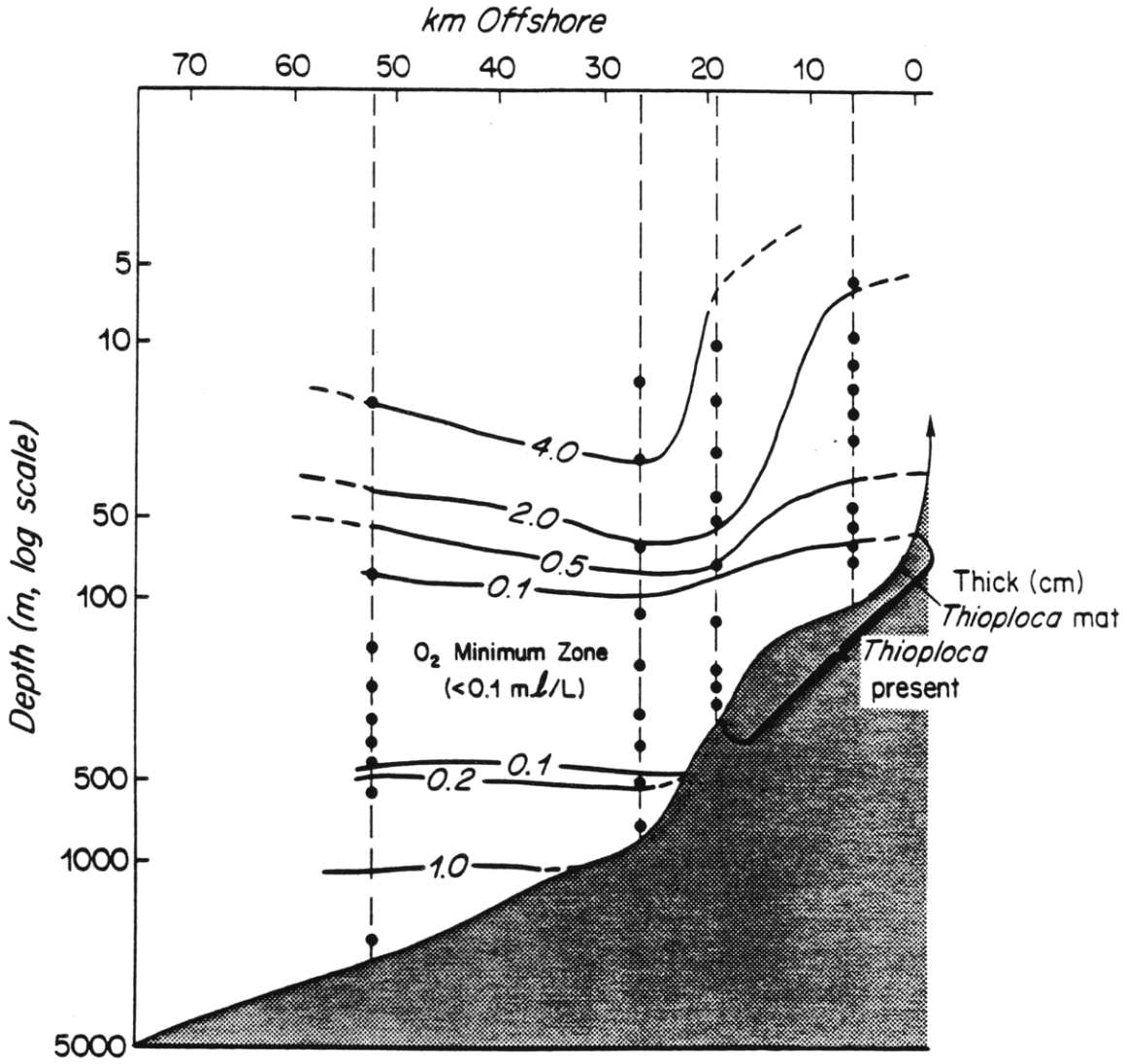

Figure 1: Dissolved O_2 transect from the Peru upwelling area, 15°S (from cruise report for R/V Moana Wave 87/08-PUBS I).

the most recent 200 years (QUINN et al., 1987). A longer history of El Niño events would be useful in studying the El Niño phenomenon, and a range of methods have been proposed for identifying an extended ENSO record [including studies of ice stratigraphy in the Peruvian Andes (THOMPSON et al., 1984) and flood deposits in northern coastal Peru (WELLS, 1987)]. The organic geochemistry of marine sediments from the Peru margin OMZ might hold a detailed ENSO record since depositional conditions in coastal Peru change dramatically during El Niño events.

VOLKMAN et al. (1980a) and MARLOWE et al. (1984) found that planktonic algae of the class Prymnesiophyceae produce C_{37} methyl ketones with two, three and four double bonds (all *trans*; RECHKA and MAXWELL, 1988), and MARLOWE et al. (1984) noted that the average degree of unsaturation increases with decreasing growth temperature. By establishing a correlation between the $\delta^{18}O$ of shells of the foraminifera *Globigerinoides sacculifer* and the U^k_{37}[1] ratio in a core from the Kane Gap, BRASSELL et al. (1986) showed that sedimentary alkenone profiles can provide information on changing sea-surface temperature (SST). PRAHL and WAKEHAM (1987) calibrated the alkenone-temperature relationship using cultures of *Emiliania huxleyi*, and found that the culture temperature is linearly proportional to U^k_{37}. From a comparison of the U^k_{37} of sediment trap samples with SST, PRAHL and WAKEHAM (1987) showed that their U^k_{37} -temperature calibration is also applicable to the marine environments they investigated. This calibration was refined by PRAHL et al. (1988) and reported as: $U^k_{37} = 0.034T+0.039$, with temperature, T, as °C. The alkenone-U^k_{37} has potential as a sedimentary marker for El Niño/ Southern Oscillation (ENSO) events because sea-surface temperature is elevated in the Peru upwelling regime during ENSO conditions by 2-12°C (QUINN et al., 1987). In sediments from the OMZ, the U^k_{37} may provide an especially useful alternative to the carbonate-$\delta^{18}O$ method of SST reconstruction since sediments from the OMZ are typically carbonate-poor diatomaceous oozes[2].

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[1]BRASSELL et al. (1986a) defined U^k_{37} as $(C_{37:2}-C_{37:4})/(C_{37:2}+C_{37:3}+C_{37:4})$. PRAHL and WAKEHAM (1987) defined a new parameter, $U^{k'}_{37} = (C_{37:2})/(C_{37:2}+C_{37:3})$, which omitted $C_{37:4}$, a compound not biosynthesized in significant quantities at temperatures >15°C (PRAHL and WAKEHAM 1987). For the range of temperatures found in Peru, U^k_{37} and $U^{k'}_{37}$ are essentially identical. Except when referring to BRASSELL et al. (1986), we define U^k_{37} with the $U^{k'}_{37}$ definition.

[2]Since organic matter remineralization is an acid producing process, the carbonate-poor nature of OMZ sediments is accentuated by carbonate dissolution from organic matter remineralization.

In this study, we assess the impact of ENSO events on the alkenone-U^k_{37} sediment record by comparing the historical record of ENSO events with detailed U^k_{37} and alkenone concentration profiles in two ^{210}Pb-dated cores from the OMZ center (255 m at 11°04.21'S; 253 m at 15°06.16'S) and one ^{210}Pb-dated core from the landward edge of the OMZ (≈105 m, 14°56.62'S). Numerous previous studies have contributed substantially to the understanding of the biogeochemistry of lipids in the water column and surface sediments of the Peru upwelling area (e.g., GAGOSIAN et al., 1983a,b; REPETA and GAGOSIAN, 1983, 1987; SMITH et al., 1983a,b; VOLKMAN et al., 1983, 1987; WAKEHAM et al., 1984; FARRINGTON et al., 1988; McCAFFREY et al., 1989; REPETA, 1989; TEN HAVEN et al., 1990). In addition, the Peru margin at 11°S was recently the site of the Ocean Drilling Program leg 112, which sought to characterize the impact of Quaternary sea level changes on organic matter preservation and the location of the OMZ. However, FARRINGTON et al. (1988) is the only previous study to interpret lipid profiles of Peru sediments in light of the historical record of ENSO occurrences. Their work showed a qualitative correspondence between the historical ENSO record and the alkenone U^k_{37} profile in a ^{210}Pb-dated surface core from the center of the OMZ (268 m, 15°09'S), but they did not have sufficient sampling resolution to discern whether the sediment record resolves specific ENSO events or simply records an average temperature of much longer periods (e.g., 10-20 years). Our more detailed investigation of the resolution of the sedimentary U^k_{37} record was made possible by collection of longer, more finely-sectioned cores (0.2-1.0 cm sections) and by the occurrence of the intense 1982-83 ENSO event four years prior to our sediment sampling.

EXPERIMENTAL

During July 1987, on R/V *Moana Wave* cruise 87 leg 08 (PUBS I), Soutar-type box cores of sediment were collected from the center and edges of the OMZ (Fig. 1) in the Peru upwelling region near 11°S and 15°S. Three cores were analyzed in this study. Cores SC2 and SC3 were collected from the OMZ center (255 m, 11°04.21S; 253 m, 15°06.16'S respectively). Core SC7 was collected from the landward edge of the OMZ (105 m, 14°56.62'S). Following collection, the cores were immediately sectioned and frozen for subsequent analyses. The procedures and equipment used for lipid extraction of sediments and lipid analyses are described in detail by FARRINGTON et al. (1988); the techniques can be *summarized* as follows. Frozen samples were thawed, nonadecan-2-one was added as an internal recovery standard, and samples were sonic extracted successively with isopropanol, methanol-chloroform (1:1 v/v), and methanol-chloroform (1:3 v/v). Lipids

were partitioned into isopropanol/chloroform by addition of $NaCl_{(aq)}$. One-half of the total lipid extract (TLE) was separated into lipid classes by silica-gel column chromatography. The alkenone fraction was analyzed by high-resolution gas chromatography (GC) using a Carlo Erba 4160 gas chromatograph equipped with an on-column injector and a J & W Scientific Durabond DB-5 30m fused silica capillary column. The GC was programmed 100-320°C at 5° min^{-1} and held at 320°C for 15 min. Compound identifications were based on comparison of electron-impact gas chromatography-mass spectrometry (GC-MS) spectra with published alkenone spectra (DE LEEUW et al., 1980; MARLOWE et al., 1984; RECHKA and MAXWELL, 1988). The GC-MS system was a Carlo Erba 4160 gas chromatograph, with a DB5 column and helium as the carrier gas, interfaced to a Finnigan 4510 quadropole mass spectrometer. Sediment dry weights were determined by drying a weighed aliquot of wet sample at 110°C for 24 h and then correcting the dry weight for salts (pore water was assumed to have a salinity of 3.5 wt %). Duplicate extractions indicate that the uncertainty of the reported alkenone concentrations is ± 5-8%. However, since the U^k_{37} is a compound ratio, it is subject to a much smaller analytical error than the absolute alkenone concentrations, and we have repeatedly found that duplicate extractions of a given sample yield U^k_{37}-temperatures of ± 0.2°C (using the temperature calibration of PRAHL et al., 1988; see above).

Excess ^{210}Pb profiles were determined using techniques and equipment described by BUESSELER (1986). Samples were 7-12 g of dried, ground sediment; dry weights were corrected for salts. Total ^{210}Pb was determined by counting the 46.5 KeV γ-ray from ^{210}Pb decay. Supported ^{210}Pb was determined by counting the 352 KeV γ-ray from ^{214}Pb decay; excess ^{210}Pb was calculated as the difference between total and supported ^{210}Pb. Counting efficiencies were determined with pitchblende standards and, for the total ^{210}Pb measurements, were corrected for self absorption.

Sediment TOC measurements were performed on 2-5 mg of dried, ground, carbonate-free sediment that had been exposed to HCl vapors in a closed container for 48 h. Sample weights used in the TOC calculation are for the dried sediment before the carbonate removal and were corrected for pore water salts. TOC measurements were made using a Perkin Elmer 2400 CHN Elemental Analyzer.

RESULTS AND DISCUSSION

We present two discussions as a background for the presentation of our U^k_{37} data. (1) Since a comparison of the historical ENSO record with the sedimentary organic geochemistry depends on accurate core dating, we first discuss our ^{210}Pb-derived sediment

accumulation rates and compare them with rates reported for 12°S and 15°S by other studies. (2) Then, as a basis for interpretation of our U^k_{37} data, we provide a theoretical discussion of the relationship between the sedimentary U^k_{37}, the sedimentation rate, and the sediment sampling interval.

SEDIMENT ACCUMULATION RATES

We recognize explicitly that due to the non-steady-state nature of deposition in this environment our ^{210}Pb-derived estimates of sediment accumulation rates are averages that are not necessarily applicable to depositional periods of < 5-10 years. Nevertheless, as we will demonstrate, valuable insights into the sediment geochemistry and stratigraphic record can be gained using these average accumulation rates. Our ^{210}Pb-derived sediment accumulation rates for the three cores are discussed below and are compared with sediment accumulation rates previously reported for this area (Table 1). In each core, excess ^{210}Pb activity in the surface sediment was 10-20 times higher than supported ^{210}Pb activity, which was low and relatively constant within each core (SC3 = 4.5 ± 0.8 dpm/g [mean ± st. dev.]; SC2 = 4.0 ± 0.85 dpm/g; SC7 = 1.9 ± 0.13 dpm/g).

The excess ^{210}Pb data for SC2 (255 m, 11°04.21'S) from 2-12 cm (Fig. 2) yields a sediment accumulation rate for this interval of 0.47 cm/yr (from the best exponential fit; R =0.95). The excess ^{210}Pb in the 0-1 cm section, however, is significantly higher than would be predicted from the 2-12 cm fit, and may represent a very recent change in sedimentation rate. A discontinuity in the excess ^{210}Pb profile at 12 cm suggests slower sedimentation below 12 cm, or a disconformity at that depth (e.g., from slumping), or a substantial resuspension and transport event. Additional ^{210}Pb data for deeper sections would be needed to distinguish between these possibilities. Because the porosity does not change significantly over the depth range of the SC2 ^{210}Pb profile, a correction for sediment compaction was not made. Our data for SC2 are in good agreement with accumulation rates reported by KOIDE and GOLDBERG (1982) for a core from 194 m, 12°S. They calculated sediment accumulation rates of 0.34 cm/yr (^{210}Pb-derived) and 0.37 cm/yr (^{228}Th/^{232}Th-derived), and their ^{210}Pb profile indicated a change in sedimentation rate to 0.15 cm/yr below 10 cm.

We analyzed SC3 (253 m, 15°06.16'S) for excess ^{210}Pb to 55 cm (Fig. 3). Over this depth range, sediment compaction in SC3 is significant, and dry wt/wet wt increases by more than a factor of 2 (Fig. 4). Therefore, the excess ^{210}Pb profile for SC3 (Fig. 3) is shown as a function of total sediment accumulation (mg dry wt/ cm^2) rather than depth. The best exponential fit (R =0.983) to the data from 0-55 cm (Fig. 4) yields a sediment accumulation rate of 41.1 mg cm^{-2}yr^{-1}. For the surface sediment porosity (salt-free dry wt/

wet wt= 0.0595 for 0-1 cm) this sediment accumulation rate corresponds to 0.75 cm/yr, but for the porosity at 50-51 cm (salt-free dry wt/ wet wt =0.1341) this accumulation rate corresponds to 0.38 cm/yr. Our sediment accumulation rates for SC3 compare favorably with rates reported by HENRICHS and FARRINGTON (1984) for a core (KNSC6) from the OMZ center (268 m, 15°09'S); they report ^{210}Pb-derived sedimentation rates (corrected for compaction) of 1.1 cm/yr for 0-25 cm and 0.3 cm/yr for 25-50 cm. Sediment accumulation rates of similar magnitude (^{210}Pb-derived =0.32 cm/yr; ^{228}Th/^{232}Th-derived =0.37 cm/yr) were also reported by KOIDE and GOLDBERG (1982) for a core from 183 m, 14°39'S, and their ^{210}Pb profile indicated a change in sedimentation rate to 0.15 cm/yr below 10 cm.

The third core we examined, SC7 , was collected from the landward edge of the OMZ (105 m) at 14°56.62'S (21 km from SC3). Because the porosity does not change significantly over the 0-15 cm depth range of the ^{210}Pb profile, a correction for sediment compaction was not made, and the SC7 ^{210}Pb profile is shown as a function of depth (Fig. 5). The data for 0-15 cm indicate an average sediment accumulation rate of 0.6 cm/yr; however, the constant excess ^{210}Pb activity from 4-10 cm and from 12-15 cm (Fig. 5) suggests that these intervals were either deposited very rapidly or bioturbated subsequent to deposition. Because SC7 was deposited at the OMZ edge, changes in the location of the upwelling plume may have periodically caused this core to lie outside the OMZ (Fig. 1), where bottom-water oxygenation would have made bioturbation possible. HENRICHS and FARRINGTON (1984) also found an irregular ^{210}Pb profile for a core they collected from the same region (90 m, 15°02.9'S), for which they proposed a similar interpretation.

From the ^{14}C ages of two sections per core, KIM and BURNETT (1988) calculated sediment accumulation rates of 0.028, 0.18, and 0.049 cm/yr for three cores from ≈15°S (387 m, 133 m, and 86 m water depth). These rates are 2-20 times lower than our ^{210}Pb-derived rates for this area. KIM and BURNETT also calculated higher rates (0.16, 0.36, and 0.31 cm/yr, respectively) from the excess ^{210}Pb profiles of these cores. In other papers (BURNETT et al., 1988; FROELICH et al., 1988), Burnett and coworkers use the ^{210}Pb-derived sedimentation rates for these cores as the best estimate of the rate of sediment accumulation. KIM and BURNETT (1988), however, proposed that the excess ^{210}Pb profiles were the result of mixing of ^{210}Pb-rich surface sediment into deeper, ^{210}Pb-depleted sediment, and they suggested that the correct sediment accumulation rates are given by the ^{14}C results. Because our study depends significantly on the interpretation of our ^{210}Pb data, we comment in detail on KIM and BURNETT's interpretation of their data and offer an alternative explanation for the discordance between their ^{14}C and ^{210}Pb-derived sediment accumulation rates.

Table 1
Sedimentation Rates for 11°, 12°, and 15°S in the Peru upwelling regime

Study	Core Location	Water Depth(m)	Dating Method	Sed. Rate (cm/yr)	Applicable depth (cm)†
This study (SC7)	14°56.62'S 75°36.81'W	105	^{210}Pb	0.61	(0-15)
(SC2)	11°04.21'S 78°03.14'W	255	^{210}Pb	0.47	(2-12)
(SC3)	15°06.16'S 75°42.09'W	253	^{210}Pb	(41.1 mg $cm^{-2}yr^{-1}$)*	(0-55)
Henrichs and Farrington (1984)	15°09'S 75°34'W	268	^{210}Pb	1.1 0.3	(0-25) (25-50)
Koide and Goldberg (1982)	12°02'S 77°43'W	194	^{210}Pb	0.34 0.15	(0-10) (>10)
			$^{228}Th/^{232}Th$	0.37	(0-7)
	14°38.9'S 76°103'W	183	^{210}Pb	0.32 0.15	(0-13) (>13)
			$^{228}Th/^{232}Th$	0.37	(0-7)
Kim and Burnett (1988)	12°05.0'S. 77°39.5'W	183	^{210}Pb	0.23	(<20)
			^{14}C	0.069	
	15°16.9'S 75°23.9'W	387	^{210}Pb	0.16	(≈7-31)
			^{14}C	0.028	
	15°15.7'S 75°23.5'W	133	^{210}Pb	0.36	(<30)
			^{14}C	0.18	
	15°12.4'S 75°19.9'W	86	^{210}Pb	0.31	(>6)
			^{14}C	0.049	

†Regression through the ^{210}Pb data in this depth range yielded the given sedimentation rate.
*In SC3, the sediment accumulation rate (as cm/yr) varies with the degree of sediment compaction from 0.75 cm/yr at 0-1 cm depth to 0.38 cm/yr at 50-51 cm depth.

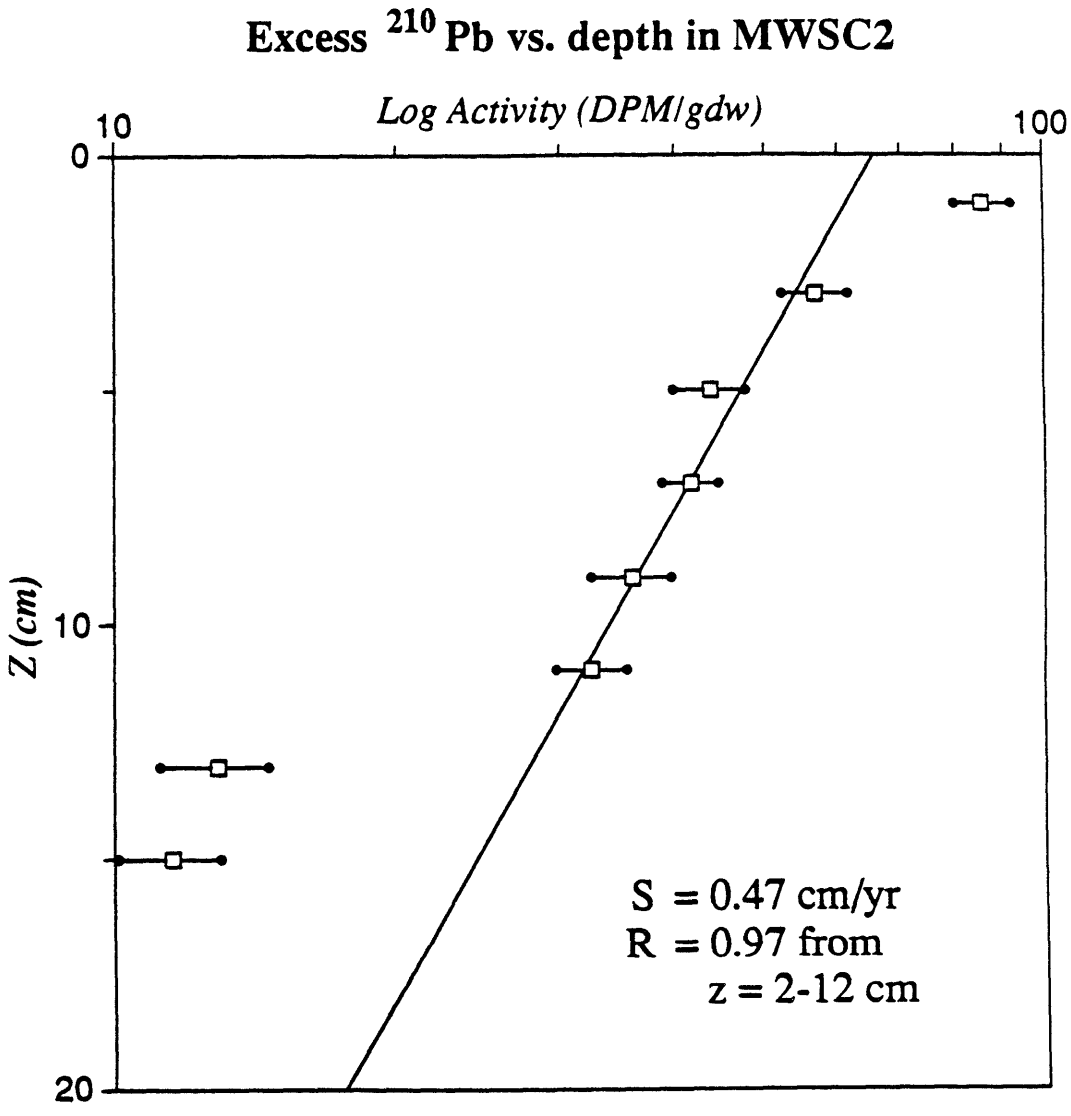


Figure 2: Log excess ^{210}Pb activity vs depth in SC2. Best exponential fit using data from 2-12 cm is shown.

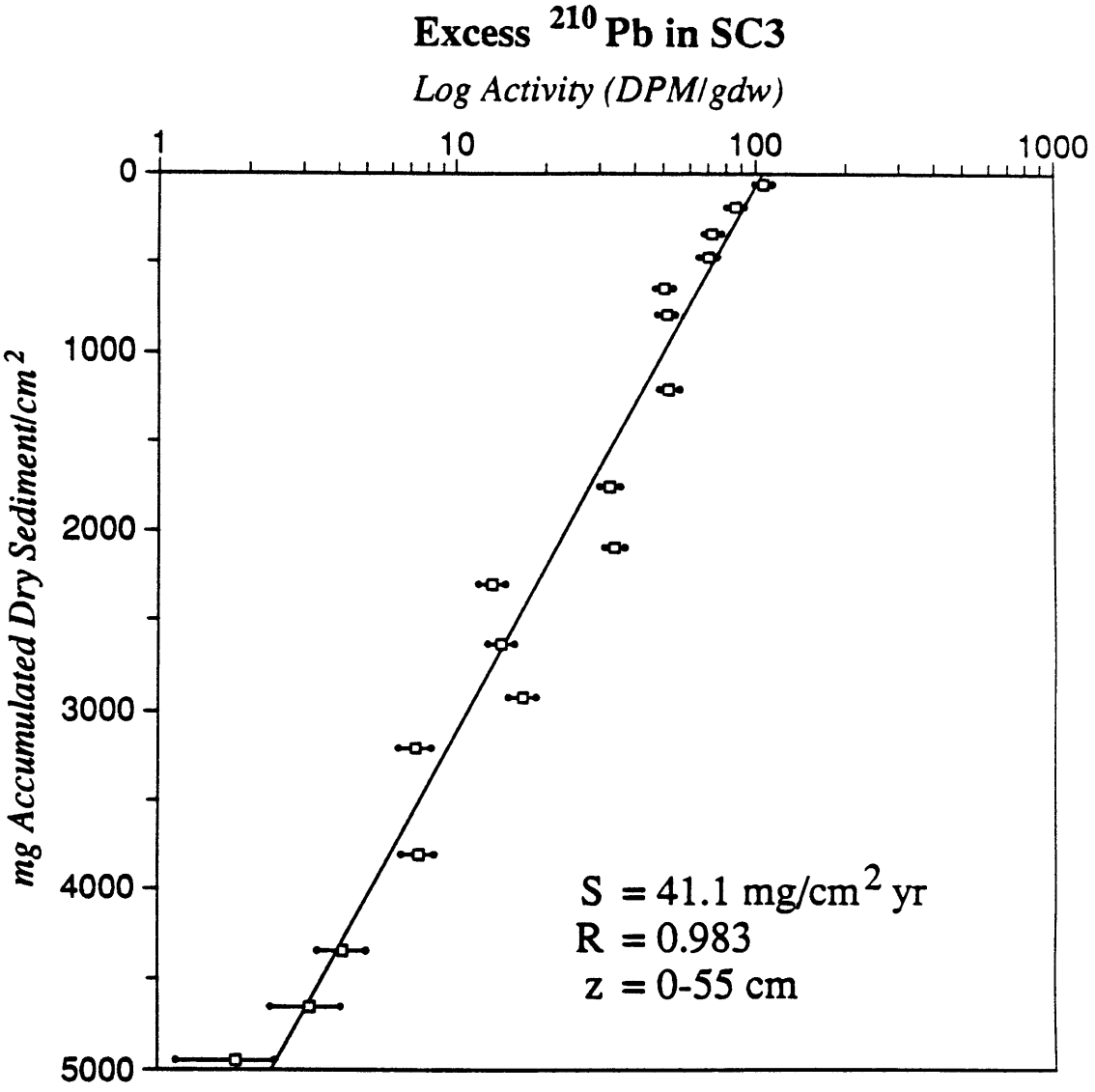


Figure 3: Log excess ^{210}Pb activity vs total sediment accumulation (mg dry wt/cm^2) in SC3.

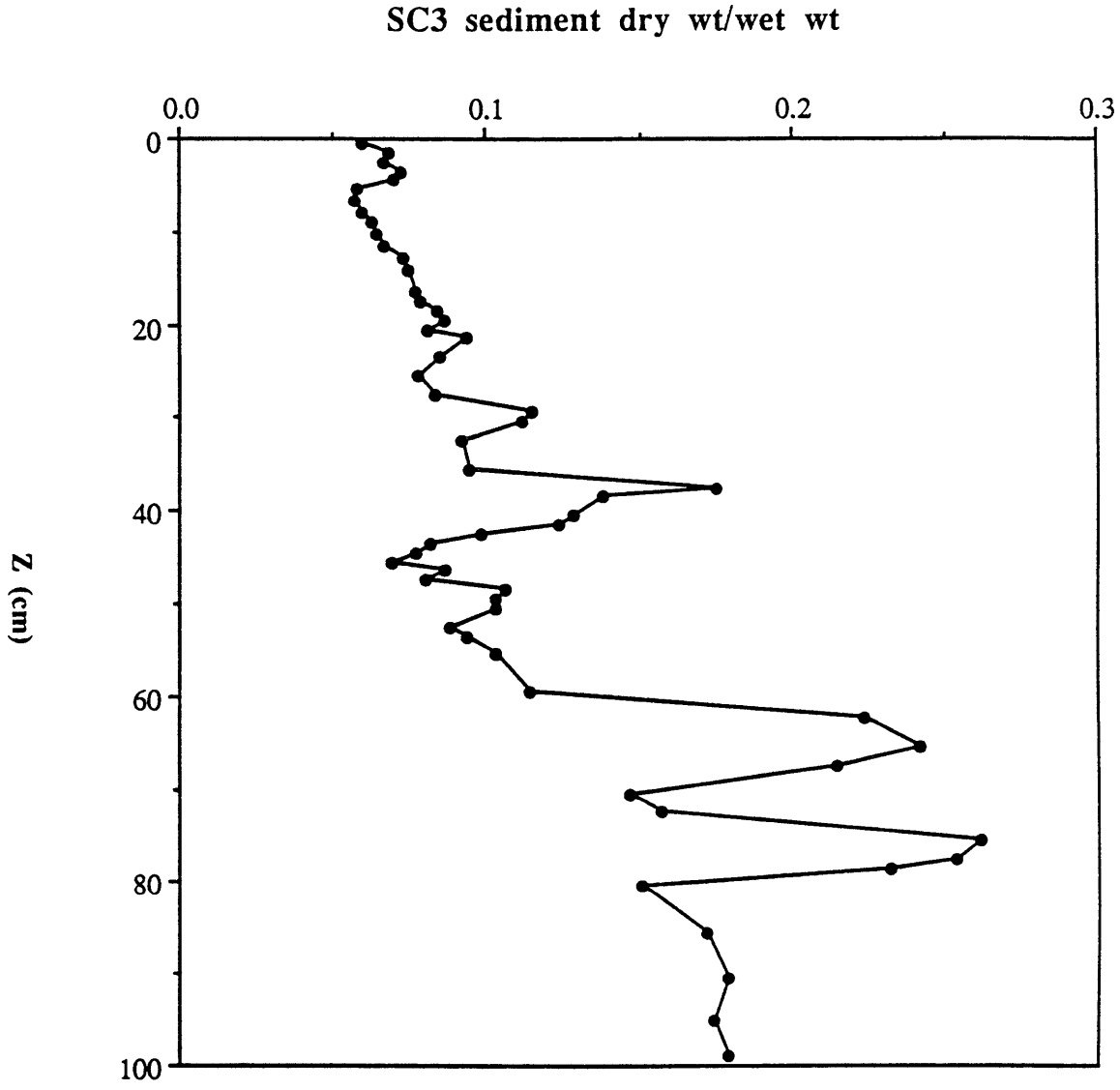


Figure 4: Sediment dry weight/wet weight in SC3. Dry weights have been corrected for salt content assuming a pore-water salinity of 3.5%.

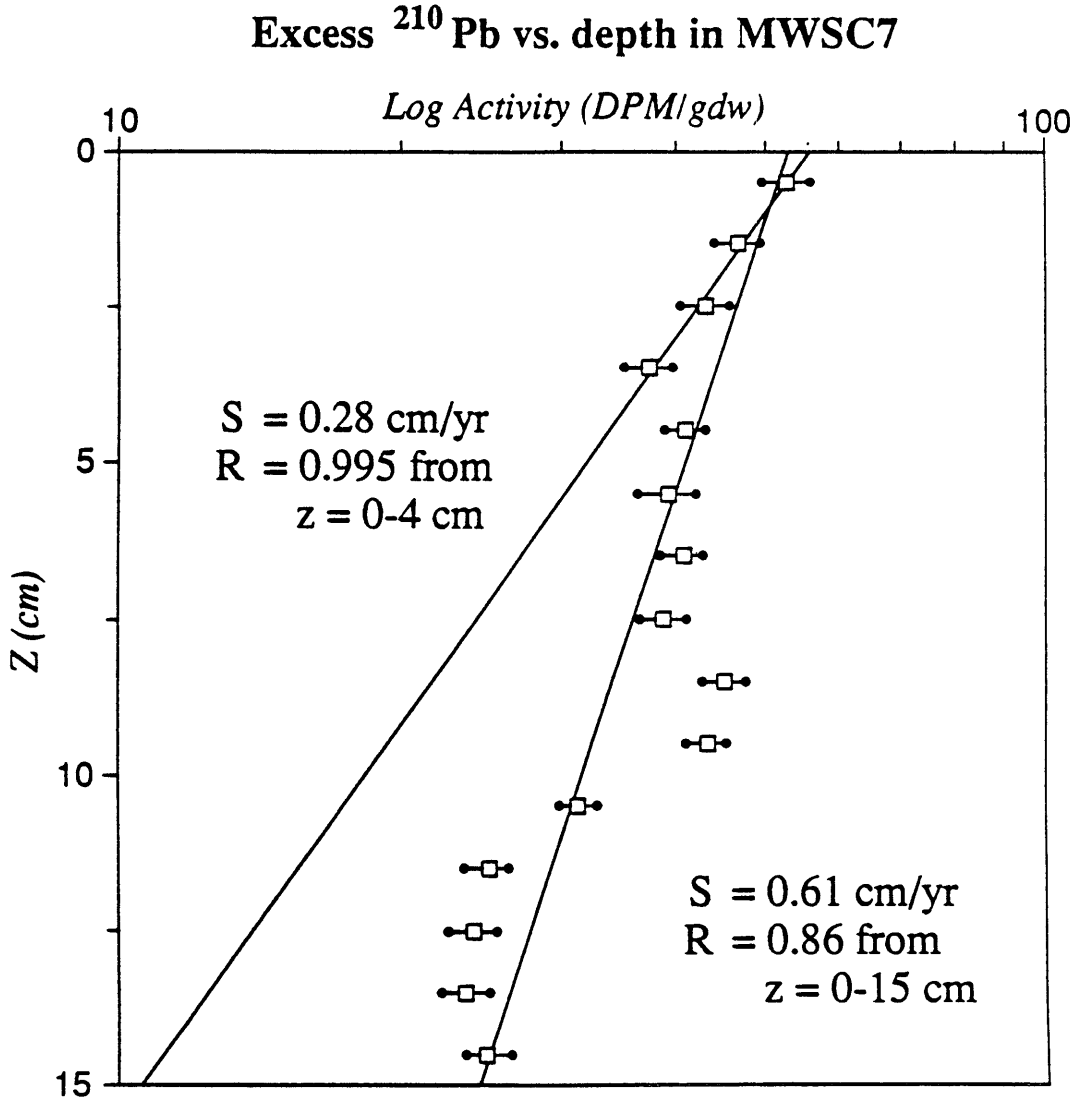


Figure 5: Log excess ^{210}Pb activity vs depth in SC7. Best exponential fits from 0-4 cm and from 0-15 cm are shown.

KIM and BURNETT's cores from ≈15°S (Table 1) were collected in the depth range of the OMZ (Fig. 1) where bioturbation is inhibited (ROSENBERG et al., 1983; HENRICHS and FARRINGTON, 1984). KIM and BURNETT report excess ^{234}Th ($t_{1/2}$=24.1days) in the top 5 cm of the core from 133 m (although the activity at 5 cm, 11± 16 dpm/g, is not significant) and the top 10 cm of the core from 387 m; this suggests physical admixing of the top 5-10 cm. However, they report that these cores are laminated below 15 cm and 12 cm, respectively. Excess ^{210}Pb in these cores extends to 40 cm, as deep as sediments were analyzed. Given the sedimentation rates (^{14}C-derived) which they propose for these cores (0.028 and 0.18 cm/yr) and the fact that excess ^{210}Pb would be detectable only for ≈6 half lives (130-140 years), it is unlikely that mixing could have distributed excess ^{210}Pb throughout the cores without destroying the sediment laminations.

Furthermore, KOIDE and GOLDBERG (1982) note that the agreement between the ^{210}Pb and $^{228}Th/^{232}Th$ chronologies (despite the very different half lives) for their cores from 12°02'S (194 m) and 14°39'S (183 m) suggests that bioturbation did not significantly influence their ^{210}Pb or $^{228}Th/^{232}Th$ profiles. KOIDE and GOLDBERG's ^{210}Pb chronologies for these cores were corroborated by their data for ^{238}Pu and $^{239}Pu+^{240}Pu$. Their ^{210}Pb chronology places the advent of SNAP ^{238}Pu (from atmospheric fallout from the SNAP-9A satellite) in the 12°02'S core at the expected time (≈1964 for the southern hemisphere). In the 14°39'S core, the ^{210}Pb and $^{228}Th/^{232}Th$ chronologies place the advent of SNAP ^{238}Pu approximately 3-8 years early, suggesting bioturbation of only the surface 0.5-1.4 cm at the advent of ^{238}Pu deposition.

It is probable that KIM and BURNETT (1988) calculated lower sedimentation rates from the ^{14}C data than from the ^{210}Pb data because they overestimated the ^{14}C activity of primary production. To calculate a radiocarbon age for a single sample (rather than a profile), the $^{14}C/^{12}C$ ratio (corrected for isotopic fractionation) is needed for both the sample at present and the sample *when deposited.* Most of the dissolved inorganic carbon (DIC) in the mixed layer of the eastern tropical Pacific is upwelled from 50-80 m, and, as a result, the mixed layer DIC would be expected to have an "apparent age" relative to modern activity of 500-800 years (Druffel, personal communication); new production would appear at least that old *at the time of deposition.* Furthermore, the apparent age of the DIC in the water column mixed layer is a function of the ^{14}C activity both of the upwelled DIC and of the atmospheric DIC added to the mixed layer; therefore, the apparent age of modern primary production, although old, is less than the apparent age of primary production before the advent of nuclear weapons testing. KIM and BURNETT's ^{14}C and ^{210}Pb-derived sedimentation rates indicate that their ^{14}C-dated core sections predate weapons testing; therefore, the apparent age of these samples when deposited was probably even

higher than the 500-800 year age of modern productivity. The high "apparent age" of the original primary production probably accounts for most of the ^{14}C age of some of KIM and BURNETT's samples, since four of the six ^{14}C ages reported for their 15°S cores are less than 800 yrs.

A THEORETICAL DISCUSSION OF THE SEDIMENTARY U^k_{37} RECORD

A theoretical consideration of the relationship between the sedimentary U^k_{37}, the sedimentation rate, and the sediment sampling interval is useful as a basis for interpretation of our U^k_{37} data. When the sectioning interval of a core is >50% of the width of the sediment deposited during an ENSO, then, depending on the location of section boundaries, there may be no core section that contains only an ENSO time interval. The inclusion of an ENSO time interval in a section with sediment deposited either before or after the ENSO will attenuate the ENSO temperature signal not simply as a linear average of the ENSO and non-ENSO temperatures, but rather as a weighted average of the alkenone concentrations in the ENSO and non-ENSO sediment. This distinction may result in greater attenuation of an ENSO temperature signal, since the 5-20 fold reduction in primary productivity typically associated with an ENSO event (Barber and Chavez 1983, 1986) is probably accompanied by a decrease in Prymnesiophyte productivity. Cocolithophore populations are known to have declined off the coast of Paita, Peru (5°S) after the onset of the 1982-1983 ENSO in September, 1982 (CHAVEZ, 1985, as reported in MITCHELL-INNES and WINTER, 1987). Furthermore, the correlation between sedimentary TOC and C_{37} alkenone concentrations in Peru margin sediments (this study; FARRINGTON et al., 1988) suggests lower Prymnesiophyte productivity during El Niño conditions.

The fraction (**X**) of the ENSO U^k_{37} signal attenuated (i.e., the fraction lost) by mixing with non-ENSO sediment can be calculated as:

$$X = \frac{U_e - U_o}{U_e - U_n} = \frac{U_e - \left[\dfrac{A_e + A_n}{\dfrac{A_e}{U_e} + \dfrac{A_n}{U_n}}\right]}{U_e - U_n} \qquad \text{Eq. 1}$$

where $U_o = U^k_{37}$ in a homogenized sediment sample containing both ENSO and non-ENSO sediment, $U_e = U^k_{37}$ of the material produced during the ENSO, $U_n = U^k_{37}$ of material produced during normal upwelling, $A_e = C_{37:2}$ alkenone (ng/g sediment) contributed to the sample from ENSO sediment, and $A_n = C_{37:2}$ alkenone (ng/g sediment)

contributed to the sample from non-ENSO sediment. A value of X=0 would correspond to no attenuation of the ENSO signal, while a value of X=1 would correspond to complete attenuation of the ENSO signal by mixing with non-ENSO sediment. This equation can be simplified exactly to:

$$X = \frac{\frac{A_n}{A_e}}{\frac{A_n}{A_e} + \frac{U_n}{U_e}} \qquad \text{Eq. 2}$$

Equation 2 indicates that the fraction by which the ENSO signal is attenuated, X, increases both as A_n/A_e increases and as the actual ENSO temperature signal increases (i.e., as U_n/U_e decreases). However, as shown in Fig. 6, signal attenuation is much more strongly controlled by A_n/A_e than by U_n/U_e. Three factors control A_n/A_e: (1) the width of the sediment sectioning interval relative to the sedimentation rate, (2) the width of the sediment mixed layer relative to the sedimentation rate, and (3) the difference in Prymnesiophyte productivity between ENSO and non-ENSO periods of deposition. Figure 6 illustrates that, although the attenuation of an ENSO signal in a core section increases rapidly with increasing A_n, the rate of signal attenuation with respect to increasing A_n/A_e continually decreases. Therefore, although an ENSO signal is attenuated ≈30% for an A_n/A_e value of 0.5, it is attenuated only ≈80% for an A_n/A_e value ten times as large. Very strong ENSO events (using the intensity classification of QUINN et al., 1987) exhibit SST anomalies of 7-12°C (i.e. the 1982-83 ENSO) which should be easily detectable even with 80% signal attenuation.

In contrast to very strong ENSO events, weak and moderate events (SST anomalies of <3°C) would be difficult to identify conclusively unless the sectioning interval was sufficiently small so as to strongly limit A_n/A_e. In areas subject to even moderate bioturbation (i.e., a mixed layer width >50% of the width of the signal of interest), the large signal attenuation would probably make it difficult to identify the signature of individual weak and moderate events regardless of the sectioning interval. These implications of Eq. 2 also have applications beyond this study and should be considered before seeking to identify other short-term SST fluctuations in the sedimentary U^k_{37} record.

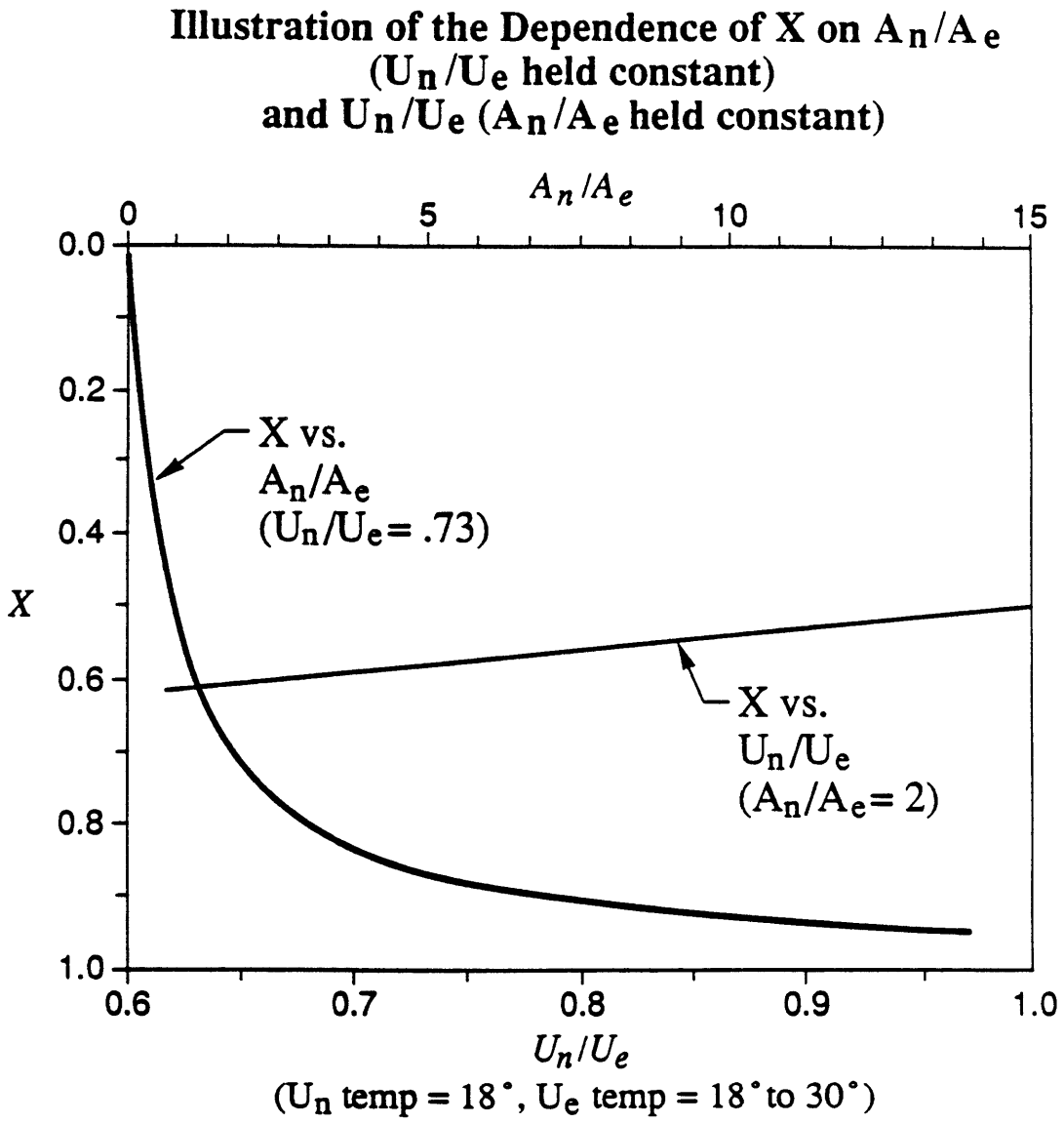


Figure 6: Illustration of the dependence of X (see equation 2) on A_n/A_e (U_n/U_e held constant) and U_n/U_e (A_n/A_e held constant). X is the fraction of the U^k_{37} ENSO signal attenuated by mixing with non-ENSO sediment . X =0 when none of the signal is attenuated. X =1 when the signal is completely lost due to mixing with non-ENSO sediment .

THE U^k_{37} RECORD OF CORES SC2, SC3 AND SC7

To determine if the sedimentary U^k_{37} signature of a very strong ENSO event can be identified in sediments from the Peru OMZ, we looked for the U^k_{37} signature of the 1982-83 ENSO in the surface 15 cm of the three ^{210}Pb-dated cores (SC2, SC3, and SC7). The U^k_{37} record of SC3 was then examined for older ENSO signals (to 100 cm) to compare with both the historical ENSO record (QUINN et al., 1987) and the U^k_{37} profile reported by FARRINGTON et al. (1988) for a core collected in 1978 (KNSC6) several km further north. We analyzed a total of 92 sections from the three cores. Our core-top data are shown in Fig. 7a-c, and the deeper profile for core SC3 is shown in Fig. 8. From the U^k_{37} profiles, we calculated paleo-temperature profiles using the temperature-U^k_{37} calibration equation of PRAHL et al. (1988): $U^k_{37} = 0.034T+0.039$. Although it is possible that this calibration does not exactly define the U^k_{37} -temperature relationship for our field area, we present our data as temperatures, rather than as U^k_{37} values, so that the magnitudes of *fluctuations* in the U^k_{37} profiles will be more accessible to visual interpretation and comparison with the SST record. It is reassuring to note, however, that the temperatures calculated for our 15°S cores (SC3 and SC7) do fall within the range of temperatures (16-19.7°C) found at 15°S during three hydrographic surveys of this area [February-March 1978, GAGOSIAN et al. (1980); March-April 1981, GAGOSIAN et al. (1983c); July 1987, FARRINGTON, unpublished data]. A continuous history of the actual SST at 15°S is not available.

Core SC2 was collected from the OMZ center (255 m at 11°04.21'S) and was sectioned at 0.25-2.0 cm intervals. The SC2 U^k_{37} profile (Fig. 7A) is characterized by a temperature maximum at 3.0-2.5 cm which corresponds to deposition during the 1982-83 ENSO. As discussed in the previous section, the ^{210}Pb data for SC2 (Fig. 2) suggest a sedimentation rate of ≈0.47 cm/yr; this close to the core top, we cannot distinguish this rate from the 0.55 cm/yr rate that would place deposition of the observed temperature maximum at 1982-1983. The 1.7° temperature maximum is one data point (0.5 cm) wide, as one would expect from the short duration (≈1.5 years) of the ENSO event. This maximum is substantially larger than the analytical error (± 0.2°C, see Experimental).

There is certainly a significant component of non-ENSO sediment in the 3.0-2.5 cm section of SC2. The actual temperature anomaly associated with the 1982-83 ENSO was 7-12°C (QUINN et al., 1987); if the 1.7° temperature maximum at 3.0-2.5 cm represents the 1982-83 ENSO, then Eq. 2 indicates that (for a normal upwelling temperature of 18°C) the alkenones produced during the ENSO contribute only 21-30% of the total alkenones in the section (i.e. An/Ae = 2.3-3.7). This is probably because the sectioning interval is wider than than the ENSO signal. The sedimentation rate during the ENSO was probably

reduced due to lower primary productivity, but this cannot be confirmed from the ^{210}Pb profile, since the duration of this decrease in sedimentation would have been too short to observe using the 2 cm sectioning interval of the ^{210}Pb profile.

The TOC values in the top 6 cm of SC2 are extremely high and relatively constant (19.2 - 22.4 dry wt% TOC; REPETA, 1989). These values are very similar to the TOC values for bulk plankton from tows in the Peru upwelling area (13.7-22.9 dry wt% TOC; LIBES, 1983), which suggests that SC2 contains almost entirely marine (rather than terrigenous) detritus. The lack of terrigenous detritus in SC2 may explain why the TOC for the 3.0-2.5 cm section corresponding to the 1982-83 ENSO does not differ substantially from the TOC in the overlying or underlying core sections. If terrigenous input is small and bottom water dysoxia remains constant, then an ENSO-induced decrease in primary productivity translates into a lower sedimentation rate, not a decrease in sedimentary TOC (MÜLLER and SUESS, 1979).

Core SC3 was collected at 15°06.16'°S at approximately the same depth as SC2 (253 m vs. 255 m). The U^k_{37} profile for core SC3 (sectioned at 1·cm intervals) rises ≈ 1.0°C from 5-4 cm and is constant from 4-0 cm (Fig. 7B). When the temperature profile for all 100 cm of SC3 is considered (Fig. 8), the temperature rise from 5-4 cm seems more significant, since there are only three other rapid temperature increases of similar or greater magnitude in the entire core. The ^{210}Pb-derived sedimentation rate of 41.1 mg cm^{-2} yr^{-1} for SC3 surface sediments places the 1982-83 ENSO event at a depth of 4-3 cm. The temperature rise from 5-4 cm may, therefore, represent a very attenuated signal of the 1982-83 El Niño. To determine if the 1 cm width of the sectioning interval in SC3 was causing attenuation of a larger U^k_{37} increase in the 5-0 cm depth range, we analyzed 15 sections (0.2-0.5 cm intervals) in the top 5 cm of a subcore ($SC3_{sub}$) of SC3. The temperatures of the 0-2 mm and 2-4 mm sections in $SC3_{sub}$ were slightly lower than the temperature for the 0-1 cm section in SC3, and were equal to the U^k_{37} -temperature of the suspended floc (Fig. 7B) which was filtered from the water overlying the sediment-water interface of SC3. Below 4 mm, the temperature profile for $SC3_{sub}$ was essentially the same (Fig. 7B) as for SC3. The temperature increase from 5-4 cm in SC3 occurs ≈0.5 cm shallower in $SC3_{sub}$. This offset is due to subcore compaction that occurred during collection, as evinced by the depression of the sediment-water interface we observed in the subcore (6 cm diameter) relative to the interface in the surrounding sediments.

The presence of an undisturbed *Thioploca* bacterial mat on SC3 suggests that the top of the core was not lost during collection. The U^k_{37} increase from 5-4 cm and the homogeneity of the U^k_{37} profiles of SC3 and $SC3_{sub}$ from 4-0 cm suggest that the 1982-83 ENSO signal may have been distributed over the top 4 cm of SC3 by physical mixing of

the surface sediments. The lower U^k_{37} temperature of the SC3 surface floc and of the top 4 mm of $SC3_{sub}$ suggests that the most recent sediment has been less influenced by mixing with the ENSO signal.

FARRINGTON et al. (1988) demonstrated a qualitative correlation between the broad U^k_{37} maximum in KNSC6 and the number of strong and very strong ENSO events that occurred between 1860 and 1930 (using ENSO strength classification and chronology of QUINN et al., 1978). In Fig. 9, we compare the historical ENSO record (from QUINN et al., 1987) with the alkenone temperature record for 0-100 cm in SC3, a core much more finely sectioned than KNSC6. The time scale for SC3 was calculated from the ^{210}Pb-derived sediment accumulation rate of 41.06 mg $cm^{-2}yr^{-1}$. ENSO events are plotted as four years in duration as a first approximation of sediment mixing. This figure suggests qualitative similarities between the historical ENSO record and the SC3 alkenone temperature record. The correspondence between the records seems best for periods when El Niño events are more common (e.g., 1870-1891, 1685-1725), and during these periods, the sedimentary alkenone record may record "packets" of El Niño events (rather than specific events).

There are several possible explanations for the lack of a better correlation between the sedimentary record and specific ENSO events. As discussed above, the resolution of the sedimentary El Niño record is a function of the width of the sectioning interval, the width of sediment mixed layer at the time of deposition, and the quality of the core dating. The lack of a substantial difference between the U^k_{37} profile of SC3 and the much more finely sectioned subcore of SC3 suggests that the resolution of the sedimentary U^k_{37} profile would not necessarily be improved by a finer sectioning interval. Although there is little bioturbation in the OMZ, the surficial *Thioploca* bacterial mat may contribute to formation of a nephaloid-like layer in which the most recently deposited sediment can be physically admixed by bottom currents. Alternatively, reduction in alkenone deposition during ENSO events may be so substantial as to significantly augment the attenuation resulting from even minor admixing of ENSO sediment with sediment deposited during normal upwelling.

Uncertainty in the dating of SC3 below 55 cm may account for some of the discrepancy between the historical and sedimentary records. The ^{210}Pb-derived sedimentation rate for SC3 is the average accumulation rate for 0-55 cm, and in constructing Fig. 9, we have assumed that this rate is also applicable to the 55-100 cm section. The dry wt/wet wt in SC3 (Fig. 4) increases regularly over most of the depth range of the ^{210}Pb profile (0-55 cm), but there are two significant peaks in dry wt/wet wt between 60 and 80 cm depth. Deposition of these two intervals may have been more or less rapid than the sediment accumulation rate determined for 0-55 cm, and, as a result, the

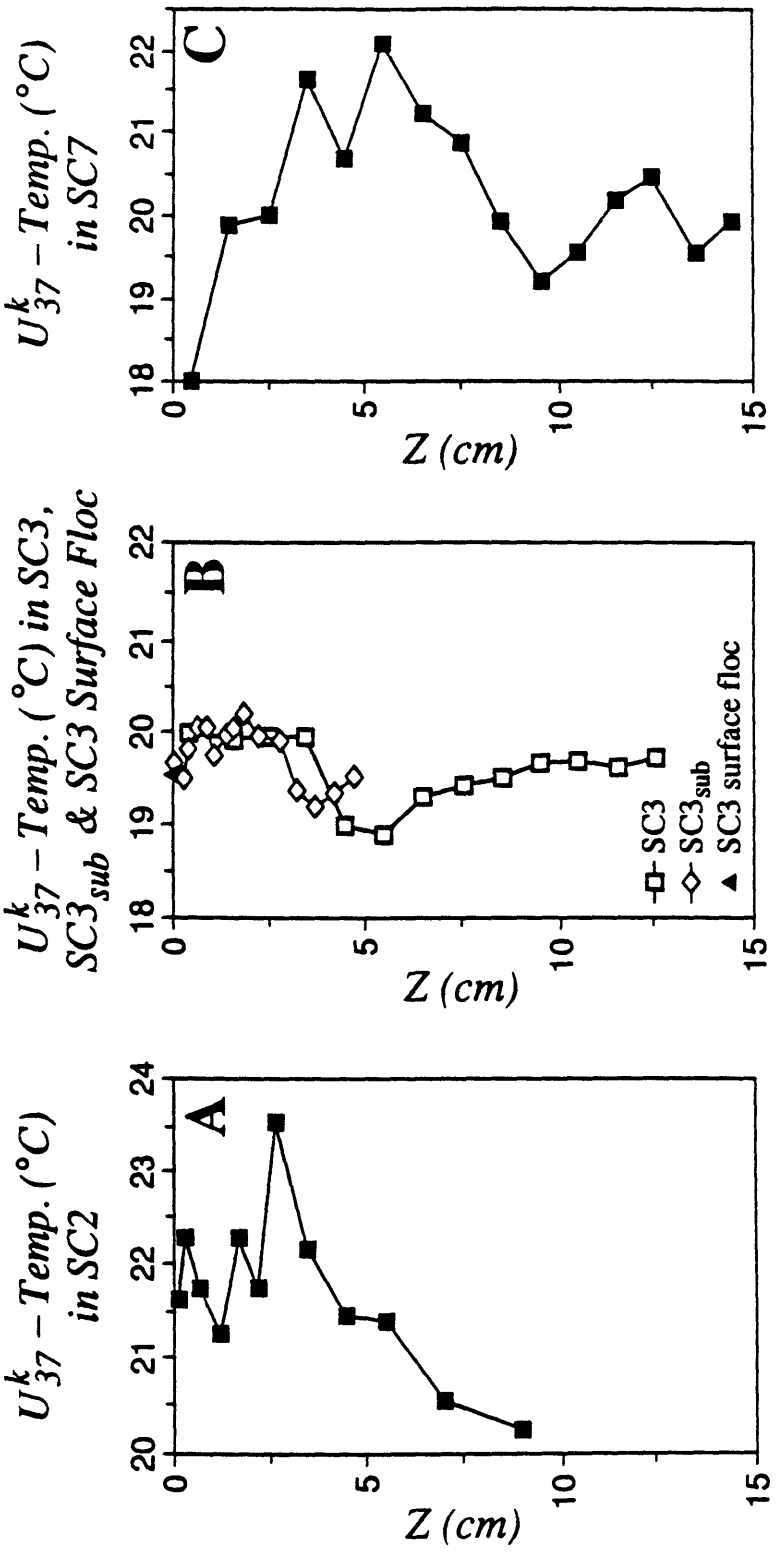


Figure 7: (A) U^k_{37} -temperature profile of SC2. (B) U^k_{37} -temperature profiles of SC3, $SC3_{sub}$ and SC3 surface floc. (C) U^k_{37} -temperature profile of SC7.

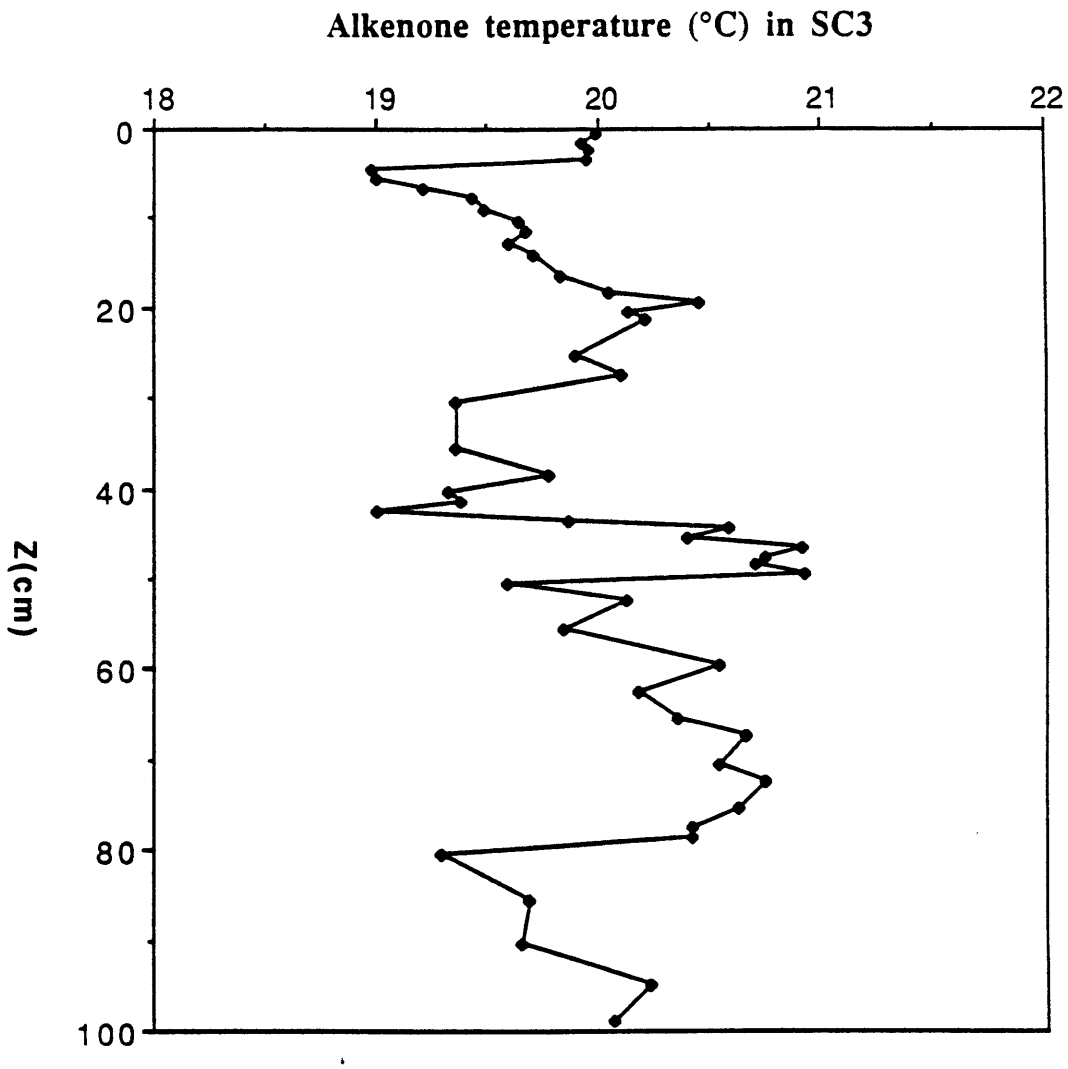


Figure 8: The U^{k}_{37}-temperature profile of SC3.

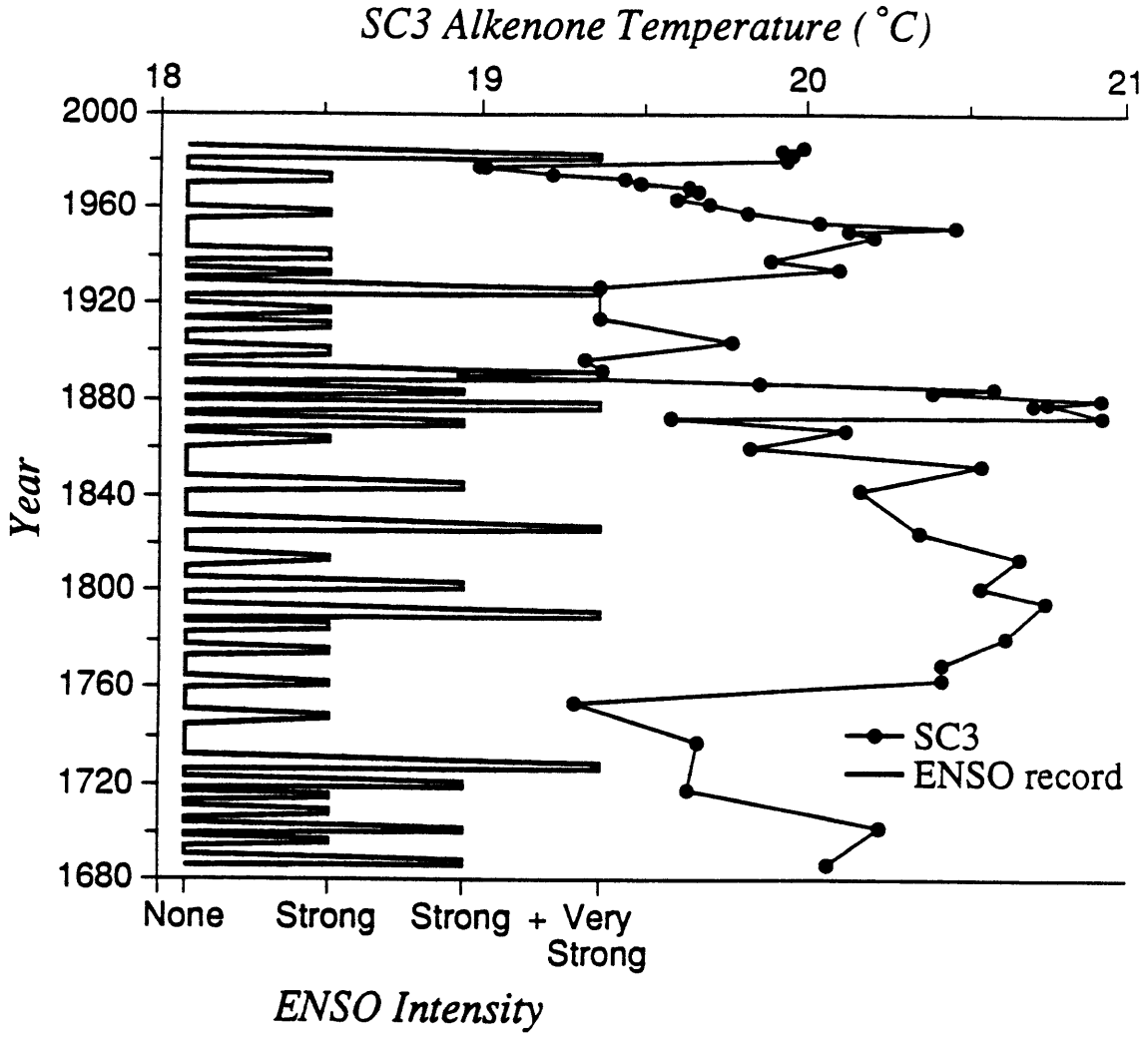


Figure 9: Comparison of the alkenone temperature record in SC3 with the historical ENSO record compiled by QUINN et al (1987),who define 'Very Strong' events as having SST anomalies of 7-12°C, 'Strong' events as having anomalies of 3-5°C, and 'Strong+' events as being intermediate in intensity between Strong and Very Strong. The time scale for SC3 was calculated from the ^{210}Pb-derived sedimentation rate of 41.06 mg $cm^{-2}yr^{-1}$. ENSO events are plotted as being 4 years long to account for sediment mixing.

chronology for this section of the core is less certain. The sum of the width of these peaks, however, is only ≈12 cm; therefore, even a factor of two difference in the sedimentation rate for these intervals relative to the rest of the core would result in an error of only ≈30 years in the chronology for the section of the core below 60 cm.

The third core examined, SC7, had a far more variable U^k_{37}-temperature record (Fig. 7C) than SC3. We attribute this variability to the location of SC7 at the landward edge of the OMZ (105 m), an area more affected by changes in the intensity and location of the upwelling plume than is the center of the OMZ where SC3 was collected. This interpretation is supported by the excess ^{210}Pb profile for SC7 (Fig. 5) which, as mentioned above, suggests a variable sedimentation rate and/or episodic bioturbation. In addition, REPETA (1989) found extensive pigment degradation in SC7 suggesting significant sediment reworking. Sediment reworking may also explain the significantly lower TOC in SC7 relative to SC3; the section of SC7 we analyzed for C_{37} alkenones (0-14 cm) was 3.9-4.2 wt% TOC (REPETA, 1989) whereas we found 9.0-12.0 wt% TOC in the same interval of SC3. FARRINGTON et al. (1988) also found a much more variable U^k_{37} record in a core from the edge of the OMZ (KNSC4) compared with a core (KNSC6) from the OMZ center. The instability of the depositional environment of SC7 and the lack of a good ^{210}Pb chronology for this core prevents interpretation of the U^k_{37} record of this core with respect to the historical SST/ ENSO record.

ALKENONE LOSS DURING EARLY DIAGENESIS

Since sedimentary organic matter remineralization is typically most intense near the sediment-water interface (WESTRICH and BERNER, 1984; MIDDLEBURG, 1989), surface-sediment alkenone profiles provide one indicator of the impact of diagenesis on sedimentary alkenone concentrations. Unless alkenone deposition during sedimentation of the 0-6 mm interval of $SC3_{sub}$ was substantially higher (30%) than at any other time during deposition of the 100 cm core, our data for the C_{37} alkenone concentrations in $SC3_{sub}$ suggest significant post-depositional loss (≈30%) of alkenones in the surface 1 cm (Fig. 10a, b). The surface point in the SC3 profile (0-1 cm) is lower than the average of the five points in this interval in $SC3_{sub}$; this may represent analytical error associated with this one point in SC3. However, with the exception of that point, alkenone concentrations in SC3 correlate well with the average of concentrations in the equivalent intervals of $SC3_{sub}$.

The decrease in the $SC3_{sub}$ alkenone profile may be the result of significant alkenone remineralization, despite the dysoxic depositional conditions. An intriguing alternative is that the alkenone decrease in $SC3_{sub}$ may be the result of formation of organic sulfur compounds by reaction of the alkenone double bonds with inorganic sulfur species.

SINNINGHE DAMSTÉ et al. (1989) identified C_{37} and C_{38} organic sulfur compounds in the Cretaceous Jurf ed Darawish Oil Shale which they attributed to incorporation of inorganic sulfur species into C_{37} and C_{38} alkenones or alkenes. Furthermore, C_{37} and C_{38} alkylthiophenes have been found frequently in sediment bitumens and immature oils (personal communication, J. W. de Leeuw). In the sediments we examined, inorganic sulfur species may have been available for sulfur quenching at very shallow sediment depths, since FOSSING (1990) found that dissolved O_2 in sediments from the OMZ decreased to zero by 2 mm at the time our cores were collected. Although organic sulfur compounds have been found in recent, unconsolidated sediments (e.g., RULLKÖTTER et al., 1988), an assessment of the possibility of sulfur quenching of alkenones in $SC3_{sub}$ must await a study of the sedimentary organic sulfur compound distribution very near the sediment-water interface (i.e., 0-1 cm) of the OMZ.

At MANOP Site C (1°N 140°W) in the eastern tropical Pacific, PRAHL et al. (1990) noted that the alkenone concentrations in surface sediments were ≈1/3 the concentrations found in sediment trap material collected 500 m above bottom. This finding suggested alkenone degradation in the water column and/or at the sediment/water interface. In contrast, for the Peru margin at 15°S, VOLKMAN et al. (1983) found that the alkenone flux to sediment traps was similar to the estimated alkenone accumulation rate in a core from the same area. However, VOLKMAN et al. (1983) could easily have missed alkenone loss of the magnitude we observed in $SC3_{sub}$, since they suggested an uncertainty of as much as ± 50% in the alkenone accumulation rate for their core, and their sediment trap data represent very short (12 h) periods of deposition not necessarily representative of the average flux. Feeding experiments with the copepod *Calanus helgolandicus* (VOLKMAN et al., 1980b) indicated that the alkenones may be unaffected by zooplankton grazing. Therefore, if there is alkenone degradation in $SC3_{sub}$, it may occur as a result of microbial degradation independent of gut bacterial activity.

PRAHL et al. (1989) report aerobic alkenone degradation >85% over ≈8 Kyr in a turbidite sequence from the north-east Atlantic but report little degradation in a lower, unoxidized portion of the turbidite. Since our core, $SC3_{sub}$, was deposited in the center of the OMZ under dysoxic conditions (0_2 <0.1 ml/l), the alkenone decrease in $SC3_{sub}$ initially seems at odds with data from PRAHL et al. (1989a); however, the alkenone loss in $SC3_{sub}$ is in an interval corresponding to ≈1 year of deposition, suggesting that the alkenone loss which occurs in the OMZ sediments is relatively rapid, and may not be observed in alkenone profiles of more slowly sedimented or more widely sectioned cores. This is illustrated by the alkenone concentration profiles for 0-100 cm of SC3 (Fig. 10b) which if considered alone would give no indication of the alkenone concentration decrease

suggested by $SC3_{sub}$. If alkenone degradation and/or alteration in surface OMZ sediments is a general phenomenon, then this limits the use of the sedimentary alkenone distributions in the OMZ as a quantitative record of Prymnesiophyte paleoproductivity. Fluctuations in alkenone concentration profiles may, perhaps, provide *qualitative* information on changes in Prymnesiophyte productivity, if the extent of alkenone loss in surface sediments can be assumed to be relatively constant during deposition and initial incorporation into the sediment record.

The influence of diagenesis on the sedimentary U^k_{37} depends not on the resistance of alkenones to degradation or alteration, but rather on the rate of degradation (or alteration) of $C_{37:2}$ relative to $C_{37:3}$. The U^k_{37} values for the five 2 mm sections from 0-1 cm of $SC3_{sub}$ and for the surface floc of SC3 (Fig. 7b) scatter within a narrow range (0.5°C), suggesting that the U^k_{37} may be unaffected by the alkenone loss This interpretation of the surface U^k_{37} data is tentative since diagenetic alteration of the U^k_{37} in the surface 1 cm could have been obscured by a coincidental change (due to changing SST) of equal magnitude but opposite direction in the U^k_{37} of the originally deposited material.

MOLECULAR STRATIGRAPHY

The depth profiles of alkenones, organic carbon, and U^k_{37} reported by FARRINGTON et al. (1988) for core KNSC6 are reasonably well-correlated with these parameters in our core SC3 collected from a similar water depth (268 m vs. 253 m), nine years later, several km further south. The correlation between KNSC6 and SC3 is most striking for the alkenone concentration and TOC profiles (Fig. 11a and b). We have offset the KNSC6 profiles downward 7 cm with respect to the SC3 profiles to account for the sedimentation that occurred during the nine years between collection of the two cores (as indicated by the ^{210}Pb-derived sediment accumulation rate for SC3). In Fig. 12, we compare the U^k_{37} -temperature profiles for KNSC6 and SC3. Using our current GC conditions, we re-analyzed several of the KNSC6 alkenone samples analyzed by FARRINGTON et al. (1988), and we found no significant deviations from the originally reported U^k_{37} values for this core. The significantly higher temperatures attained in the KNSC6 profile relative to the SC3 profile may stem either from differences in the physical oceanography (i.e., SST) or Prymnesiophyceae species distribution between the two coring locations. The former possibility is supported by remote sensing which has previously shown the irregularity of SST in the upwelling plume along the Peru coast (e.g., MOODY et al., 1981). There is as yet no evidence to suggest differences in the alkenone-temperature relationship between Prymnesiophyte species, but we cannot rule out

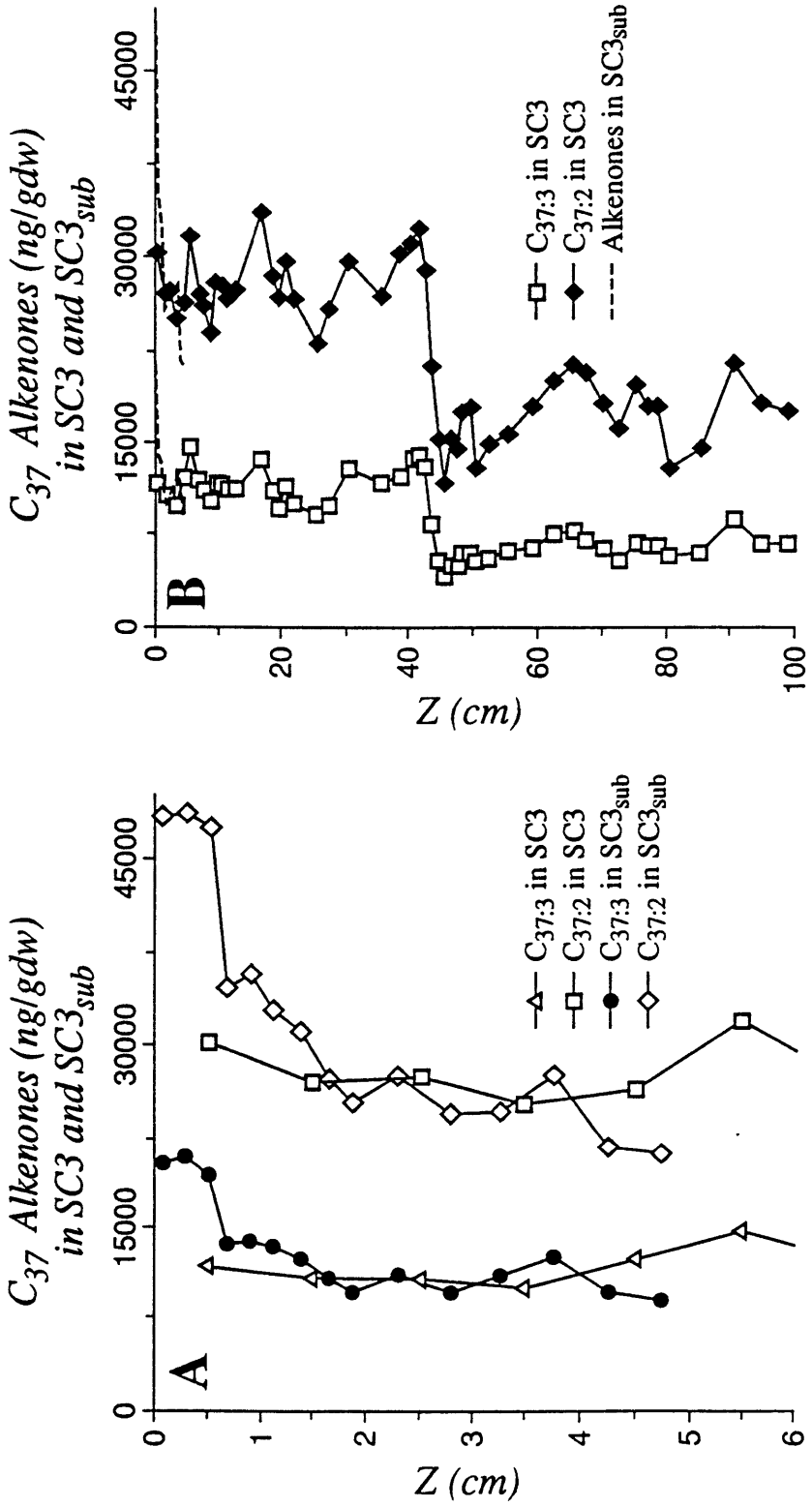
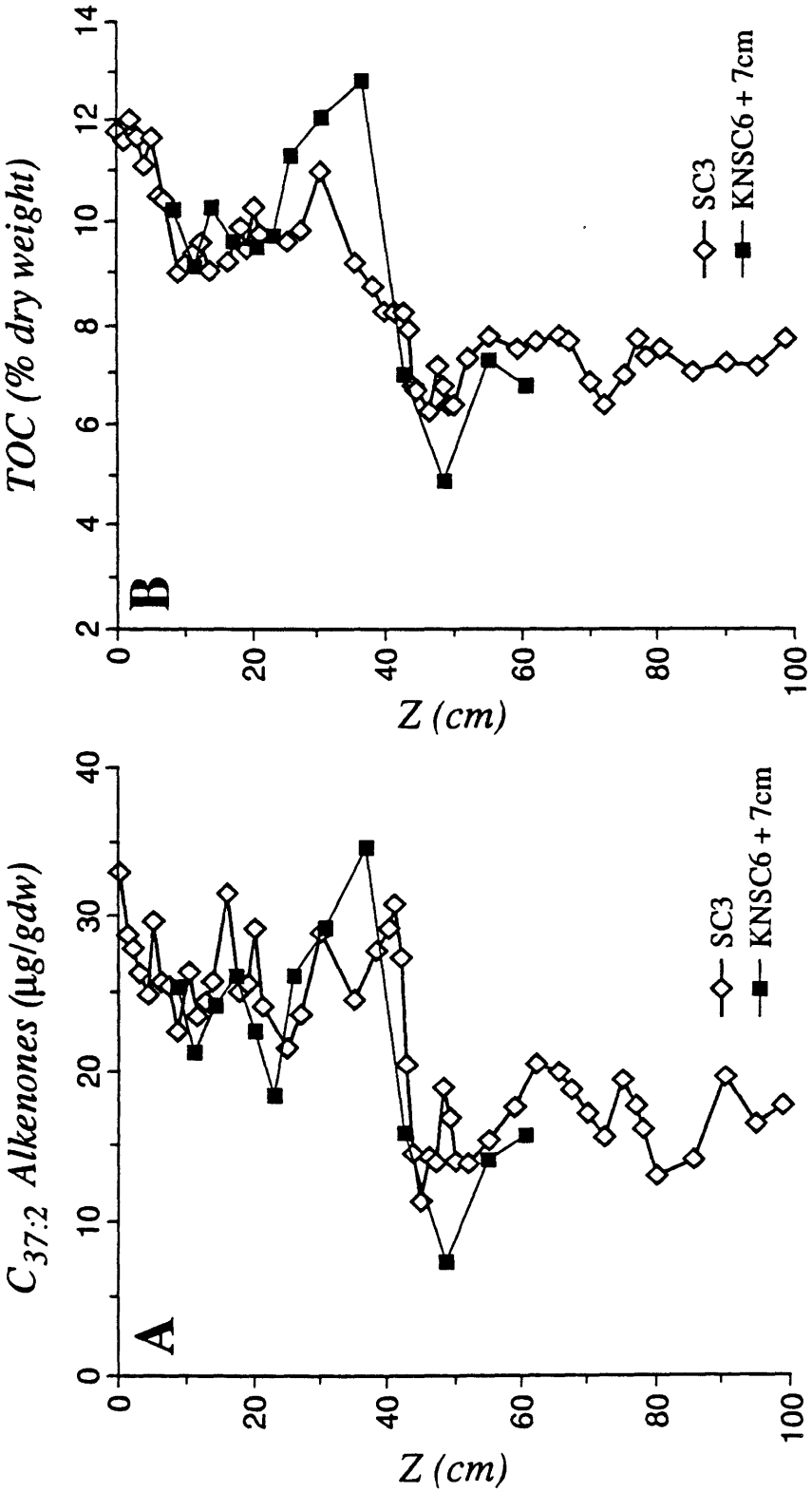


Figure 10: C_{37} alkenone concentrations in SC3 and $SC3_{sub}$ (A) 0-6 cm, (B) 1-100 cm. The 100 cm scale illustrates how the alkenone loss in $SC3_{sub}$ could easily be missed in a more widely sectioned core.

Figure 11: (A) Comparison of the $C_{37:2}$ alkenone profile of SC3 with the $C_{37:2}$ alkenone profile of KNSC6 (FARRINGTON et al., 1988). (B) Comparison of the TOC profile of SC3 with the TOC profile of KNSC6. The KNSC6 profiles have been offset 7 cm downward to account for deposition between the collection times of the two cores.


B
TOC (% dry weight)
Z (cm)
SC3
KNSC6 + 7cm
A
$C_{37:2}$ Alkenones (µg/gdw)
Z (cm)
SC3
KNSC6 + 7cm

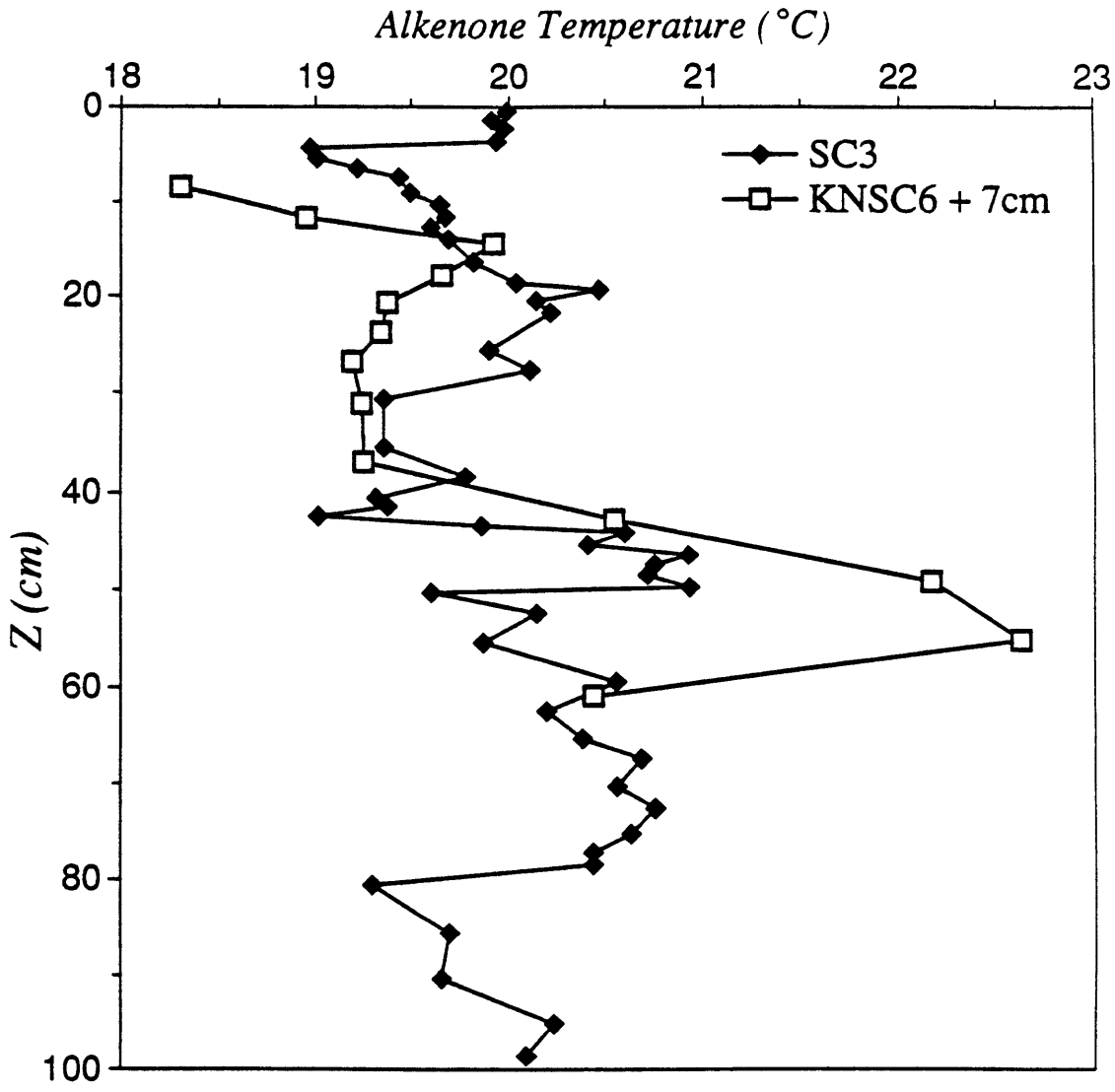


Figure 12: Comparison of the U^k_{37}-temperature profile of SC3 with the U^k_{37}-temperature profile of KNSC6 (FARRINGTON et al., 1988). The KNSC6 profile has been offset 7 cm downward to account for deposition between the collection times of the two cores.

the possibility of spatial heterogeneity of species composition and accompanying differences in the U^k_{37} of the alkenones delivered to the sediments at the two locations.

The correlation between KNSC6 and SC3 observed in the depth profiles of alkenones, organic carbon, and U^k_{37} provides substantial support for the proposal implicit in many organic geochemical studies of sediments and explicitly stated by others (REED and MANKIEWICZ, 1975; BRASSELL et al., 1986) that the composition of organic matter at the molecular level can be used as an effective tool for cross-correlation of stratigraphic units. We are in the process of obtaining additional lipid compound data from the cores of the 1987 R/V *Moana Wave* cruise to provide a more extensive evaluation of the molecular stratigraphy concept as applied to modern sediments.

CONCLUSIONS

• The sedimentary U^k_{37} signals of individual El Niño events were substantially attenuated; periods of frequent ENSO activity (e.g., 1870-1891) were more readily identified in the sediment record than isolated ENSO events in periods of less frequent ENSO activity. A very attenuated U^k_{37} signal from the very strong 1982-83 ENSO was observed at a depth of 3.0- 2.5 cm in a core (SC2) from the OMZ center, ≈11°S. This suggests that individual, very strong El Niño events (SST anomalies of 7-12°C) can potentially be identified in the sediment record using the sedimentary U^k_{37}.

• The resolution of the El Niño record is a function of the width of the sediment mixed layer at the time of deposition, the core sectioning interval, and the quality of the core dating. A consideration of how the sedimentary U^k_{37} signal from an ENSO is attenuated by mixing with non-ENSO sediment (Eq. 2) illustrates that even moderate sediment bioturbation would probably prevent detection of individual El Niño events of weak or moderate intensity (SST anomalies of <3°C). This result should be considered before seeking to identify other short-term SST fluctuations in the sedimentary U^k_{37} record.

• Temperatures calculated from the U^k_{37} of Peru sediments using the calibration of PRAHL et al., (1988) are within the range of sea surface temperatures previously reported for this area.

• Concentrations of the C_{37} alkenones decrease ≈30% in the surface 1 cm of core $SC3_{sub}$ (≈253 m; O_2 <0.1 ml/l bottom water), suggesting significant alkenone degradation and/or alteration (perhaps by sulfur quenching) in this interval. However, the similarity of the U^k_{37} values for the five 2 mm sections from 0-1 cm and for the surface floc of SC3 (Fig. 7b) suggest that the U^k_{37} may be unaffected by the alkenone loss.

• Correlation between the C_{37} alkenone, TOC, and U^k_{37} profiles in two cores from ≈15°S collected nine years apart (SC3 and KNSC6) provide substantial support for the concept of "molecular stratigraphy," the idea that the composition of organic matter at the molecular level can be used as an effective tool for cross correlation of stratigraphic units.

• The ^{210}Pb-derived sedimentation rates for our cores are consistent with previously published sedimentation rates with the exception of ^{14}C-derived rates reported by KIM and BURNETT (1988). It is probable that KIM and BURNETT calculated lower sedimentation rates from their ^{14}C data because they overestimated the ^{14}C activity of primary production.

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CHAPTER 4

THE ORGANIC GEOCHEMISTRY OF PERU MARGIN SURFACE SEDIMENTS-II. PALEOENVIRONMENTAL IMPLICATIONS OF HYDROCARBON AND ALCOHOL PROFILES

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Abstract: We assess the utility of sedimentary hydrocarbons and alcohols as indicators of short-term changes in depositional conditions in the coastal Peruvian upwelling regime at 15°S. The distribution of 35 lipids (n-alkanes, n-alkanols, hopanols, keto-ols, lycopane, phytol, stenols, stanols, sterenes, and tetrahymanol) in a 1 m dated core from 253 m water depth are interpreted by: (1) a multivariate factor analysis, and (2) a consideration of individual source-specific biomarkers. Profiles of odd-carbon-number n-alkanes (C_{25}-C_{33}) and even-carbon-number n-alkanols (C_{24}-C_{28}) reflect changes in the input of terrigenous sediment relative to marine sediment during deposition, as indicated by the correlations between these lipids and inorganic indicators of terrigenous clastic debris. The n-alkane carbon preference index (CPI) provides a less-sensitive record of fluctuations in the terrestrial input than the concentration profiles of the individual n-alkanes and n-alkanols, and these lipids are *not* well-correlated with the historical El Niño record. The similarity of all the stenol profiles measured and the lack of concordance between these profiles and inorganic indicators of terrigenous input suggest that fluctuations in the abundance of higher-plant stenols are obscured by the larger marine contribution of these compounds. Similarities between the profiles of total organic carbon (TOC) and cholestanol/cholesterol are consistent with stenol hydrogenation being influenced by the sediment redox conditions.

INTRODUCTION

In this report, we assess the utility of various sedimentary hydrocarbons and alcohols as indicators of short-term changes in depositional conditions in the coastal Peruvian upwelling regime at 15°S. During normal upwelling, primary productivity at 15°S is extremely high (1-10 gC $m^{-2}d^{-1}$; RYTHER et al., 1971; GAGOSIAN et al. 1980a). Partial remineralization of this organic matter in the water column and at the sediment-water interface intensifies an oxygen minimum zone (OMZ; O_2 <0.1 ml/l) that impinges on the Peru margin from ≈75 to 500 m water depth. The low oxygen concentrations in the OMZ inhibit sediment bioturbation (McCAFFREY et al., 1989, 1990 and references therein); therefore, sediments deposited within the OMZ may hold an undisturbed geochemical record of depositional conditions. The Peruvian upwelling regime is regularly perturbed by El Niño Southern Oscillation (ENSO) events, climatic disturbances of variable intensity which last from several months to a year and affect the eastern tropical Pacific once every 2-10 years (QUINN et al., 1987). During ENSO conditions, the thermocline, nutricline, and mixed layer deepen along the Peru margin; primary productivity decreases (BARBER and CHAVEZ, 1983, 1986), and sea-surface temperature, rainfall, and continental runoff

typically increase (QUINN et al., 1987). Previously, we reported a correlation between periods of frequent ENSO activity and elevated alkenone-U^k_{37} temperatures in a Peru margin core, SC3, from the OMZ (McCAFFREY et al., 1990).

Since continental runoff from Peru increases during ENSO conditions, a sedimentary record of terrigenous lipid input to Peru margin sediments has potential as an indicator of past El Nino events. However, identification of a signature of higher plant input to these sediments is complicated by (1) the existence of marine sources of many lipids abundant in higher plants, and (2) the small magnitude of higher-plant input to these sediments relative to marine input. Odd-carbon-number n-alkanes and even-carbon-number n-alkanols are abundant in the epicuticular waxes of higher plants (e.g., EGLINTON and HAMILTON, 1967; TULLOCH, 1976), but are also produced in small concentrations by some phytoplankton and bacteria (VOLKMAN et al, 1983, and references therein). The most abundant stenols in most higher plants (VOLKMAN, 1986) are 24-ethylcholest-5-en-3ß-ol and 24-ethylcholest- 5, 22-dien-3ß-ol, but these compounds are also produced by certain phytoplankton. 24-ethylcholest-5-en-3ß-ol is the dominant stenol in the diatom *Asterionella glacialis* (VOLKMAN, 1986), the Prymnesiophyte *Pavlova lutheri* (LIN et al., 1982), and two red tide flagellates (NICHOLS et al., 1987). C_{29} stenols have been found in smaller concentrations in chlorophytes (VOLKMAN, 1986) and diatoms of the genus *Thalassiosira* (VOLKMAN and HALLEGRAEFF, 1988), a genus abundant in the Peru upwelling area. Therefore, odd-carbon-number n-alkanes, even-carbon-number n-alkanols, and C_{29} stenols in marine sediments cannot be assumed *a priori* to be markers for terrestrial input.

In order to distinguish the relative importance of marine and terrigenous sources of specific lipids in these sediments, we performed a multivariate factor analysis (e.g., JÖRESKOG et al., 1976; MARDIA et al., 1979) of the concentrations of 35 lipids and TOC in 50 sections of a core from the center of the Peru margin OMZ [core SC3, the core McCAFFREY et al. (1990) used to compare the C_{37} alkenone and historical ENSO records]. A variety of lipids were included in the factor analysis: n-alkanes, n-alkanols, hopanols, keto-ols, lycopane, phytol, stenols, stanols, sterenes, and tetrahymanol. The factors resulting from the multivariate analysis are interpreted here in light of the down-core profiles of the factor scores and the reported sources of the specific compounds. The identification of a terrigenous factor is confirmed by comparing profiles of lipids highly loaded on this factor with inorganic indicators of terrigenous input, including (1) the sedimentary abundances of Al, Ti, Zr and Fe and (2) the sediment dry weight/wet weight ratio.

EXPERIMENTAL

Core SC3 (100 cm) was collected from the OMZ center (253 m, 15°06.16'S, 75°42.09'W) in the Peru upwelling region, using a Soutar-type box corer during the R/V *Moana Wave* cruise 87 leg 08 (PUBS I, July 1987). Following collection, the core was immediately sectioned and frozen for subsequent analyses. X-ray imaging demonstrated that SC3 is laminated, and ^{210}Pb dating of this core suggests a sedimentation rate of 41.1 mg cm^{-2} yr^{-1} (McCAFFREY et al., 1990; 100 cm ≈ 310 years before 1987). We measured 40 lipids in 50 sections of the core. These lipids were chosen from a variety of compound classes (alkanes, alkenes, alcohols, ketones, and keto-ols), and represent input from phytoplankton, zooplankton, bacteria, nekton, and terrestrial higher plants, although many of the compounds are produced by more than one source. Table 1 lists the major reported source(s) for each compound; some of the lipids have no known source, but were included in the lipid factor analysis in the hope that the factor loadings would provide insight into their sources. Surface sediment from progressively shallower water depths of 135 m, 100 m, 50 m, 30 m, and 25 m (from near the mouth of the Rio Grande, ≈ 15°S) were collected using a Van Veen grab sampler and were analyzed to provide one measure of the influence of terrestrial input on the sedimentary lipids.

The procedures and equipment used for lipid extraction and analyses are described by FARRINGTON et al. (1988); the techniques can be summarized as follows. Frozen samples were thawed, internal recovery standards were added ($C_{16}D_{32}$ n-alkane, $C_{24}D_{50}$ n-alkane, $C_{32}D_{66}$ n-alkane, and C_{19} n-alkan-1-one), and samples were sonic extracted successively with isopropanol, methanol-chloroform (1:1 v/v), and methanol-chloroform (1:3 v/v). Lipids were partitioned into isopropanol/chloroform by addition of $NaCl_{(aq)}$. One-half of the total lipid extract (TLE) was separated into lipid classes by silica-gel column chromatography. Alkenes were removed from the alkane fraction using a column of $AgNO_3$ impregnated (10%) silica gel. The alcohol fractions were derivatized with pyridine and acetic anhydride to form the acetates. All sample fractions were analyzed by high-resolution gas chromatography (GC) using a Carlo Erba 4160 gas chromatograph with a J & W Scientific Durabond DB-5 30 m fused silica capillary column (0.32 mm i.d., 0.25 μm film thickness) and an on-column injector. The GC program used for the hydrocarbon and alcohol fractions was: injection at 70°C, isothermal for 1 min, 3°/min to 250°, 4°/min to 310°, 6°/min to 320, isothermal for 13 min. The program used for the ketone fraction was: injection at 100°C, isothermal for 1 min, 5°/min to 320°, isothermal for 15 min. Compound identifications were based on data from electron-impact gas chromatography-mass spectrometry (GC-MS) and/or chemical-ionizaion (methane) GC-MS and/or GC coelution with authentic standards; Table 1 indicates the method(s) used for identification of each

Table 1
Compounds Quantified in SC3

Compound	Identification	Some Major Sources	Reference
n-alkanes >C_{24}	1, 3	Higher plants	Eglinton and Hamilton (1967)
n-alkanols >C_{26}	1, 3	Higher plants	Eglinton and Hamilton (1967)
Alkan-15-one-1-ols	3	Planktonic cyanobacteria	Morris and Brassell (1987)
Phytol	1, 3	Chlorophyll-a	Volkman and Maxwell (1986)
C_{37} alkenones	3	Prymnesiophyceae	Marlowe et al (1984)
Lycopane	1, 2, 5	Phytoplankton?	
STEROLS:			
24-methylcholest-5, 22-dien-3ß-ol	1, 2	Diatoms	Gagosian et al. (1983)
24-methylcholest-5-en-3ß-ol	1, 2	Higher Plants	Volkman (1986)
Cholesterol	1, 2	Zooplankton	Gagosian et al. (1983)
Dinosterol (4, 23, 24-trimethylcholest-22en-3ß-ol)	3	Dinoflagellates	Boon et al. (1979)
24-ethylcholest-5-en-3ß-ol	1, 2	Higher plants Phytoplankton	Volkman (1986) Volkman and Hallegraeff (1988)
24-ethylcholest-5, 22-dien-3ß-ol	1, 2	Higher Plants Phytoplankton	Volkman (1986)
5α(H) analogs of Δ^5 stenols	2, 3	Stenol reduction Primary production	Nishimura and Koyama (1977)
STERENES:			
Cholest-3, 5-diene	3	Stenol alteration product	Wakeham et al. (1984)
Cholest-R, N, N-triene	4	Stenol alteration product	Wakeham et al. (1984)
14α(H)-1(10→6)-abeocholesta-5,7,9 (10)-triene	3	Stenol alteration product	Hussler and Albrecht (1983)
PENTACYCLIC TRITERPENOIDS:			
Monohydroxy hopanols ($C_{31,32}$)	3	Hopanoid alteration product	Rohmer et al., (1984)
C_{34} monohydroxy hopanol	4	Hopanoid alteration product	Rohmer et al., (1984)
17ß(H), 21ß(H)-homohopane	3	Hopanoid alteration product	Huc (1978)
Tetrahymanol	3	Protozoan?	Ten Haven et al. (1989) Harvey and McManus (1990) H. R. Harvey, pers. com. to JWF, 5/23/90

[1] GC coelution with authentic standards.
[2] Electron impact GC-MS/ comparison with spectrum of authentic standard.
[3] Electron impact GC-MS/ comparison with published spectra.
[4] Electron impact GC-MS/ inspection of spectrum and comparison with spectra of similar compounds.
[5] Chemical ionization (methane) GC-MS/ comparison with spectrum of authentic standard.

compound. The GC-MS system was a Finnigan 4510 quadrapole mass spectrometer interfaced to a Carlo Erba 4160 gas chromatograph with a DB5 column and helium as the carrier gas. The principal components factor analyses of the lipid distributions were performed using Systat version 3.2 statistics software run on a Macintosh SE personal computer; the matrices factored were correlation matrices calculated from absolute concentrations (not relative abundances) of the lipids in the sediments. A varimax rotation (JÖRESKOG et al., 1976; MARDIA et al., 1979) was used on the resulting factors.

Sediment dry weights were determined by drying a weighed aliquot of wet sample at 110°C for 24 hours and then correcting dry weight for salts (pore water was assumed to have a salinity of 3.5 wt %). Sediment TOC measurements were performed on 2-5 mg of dried, ground, carbonate-free sediment that had been exposed to HCl vapors in a closed container for 48 hours. Sample weights used in the TOC calculation are for the dried sediment before the carbonate removal and were corrected for pore water salts. TOC measurements were made on a Perkin Elmer 2400 CHN analyzer in which the samples were combusted in pure oxygen at 925°C. In 16 sections of SC3, the abundances of Al, Ti, Zr, and Fe were measured by inductively coupled plasma (ICP) spectroscopy after total sediment dissolution. Dissolved sediment samples were prepared by (1) combusting the sediments at 500°C for 24 h, (2) mixing the combusted sediment in a 1:4 weight ratio with $LiBO_2$ flux, (3) fusing the sediment-flux mixture at 1125°C for 15 min, and then (4) dissolving the fusion in 1 M HCl. This procedure is described in greater detail by Govindaraju and Mevelle (1987), and the ICP analytical technique is described in detail by Bankston (1988).

RESULTS AND DISCUSSION

I. MULTIVARIATE ANALYSIS

Principal component factor analysis is a multivariate statistical technique that creates variables which are independent linear combinations of the original variables in a data set. By reducing the number of original variables to a smaller number of independent variables (factors), this technique reduces the "redundancy" in a data set and highlights fundamental differences between groups of variables. Principal component factor analysis has been applied to a variety of organic geochemical data including methylphenanthrene distributions in coals (KVALHEIM et al., 1987), kerogen pyrolysis products (e.g., ØYGARD et al., 1988; EGLINTON et al., 1989), and lipid distributions in oils (HUGHES et al., 1985; ZUMBERGE et al, 1987) and ancient sediments (BRASSELL et al., 1986; MELLO et al., 1988). However, this technique has only occasionally been applied to lipid distributions in Recent samples (SHAW and JOHNS, 1986; SICRE et al.,

1988; HOSTETTLER et al., 1989). With the appropriate axes rotation, the concentration of a lipid common to more than one source can theoretically be partitioned between each of the factors representing a source of the lipid. Therefore, factor analysis of lipid data is complementary to the biomarker approach, because the use of biomarkers has frequently been limited by the identification of multiple sources for many lipids.

We performed a principal components factor analysis of the data for 35 lipids (Table 2) and TOC in 50 sections of SC3. Five factors explaining 91.31% of the variance in the data were retained, and Table 2 lists the compound loadings (following a varimax rotation). Depth was not a variable in the factor analysis, and the downcore plots of the factor scores are shown in Fig. 1. The significance of each of these factors is discussed below. Tables of the 1800 lipid and TOC concentrations used in the factor analysis are available upon request (appendix 3 in this thesis).

Factor 1- marine lipids

Factor 1 accounts for 35.47% of the variance, and we propose that it represents the input of marine lipids from the overlying water column. Many of the stenols with high loadings on this factor (i.e., 24-methylcholest-5,22-dien-3ß-ol, cholesterol, and dinosterol) have planktonic sources (GAGOSIAN et al., 1983). Phytol, the esterifying alcohol in chlorophyll-a, can obviously be phytoplankton-derived.

Two compounds highly loaded on Factor 1, tetrahymanol (gammaceran-3ß-ol) and lycopane (2, 6,10, 14, 19, 23, 27, 31-octamethyldotriacontane), have no reported marine source. Tetrahymanol in marine sediments is believed to have a planktonic source (TEN HAVEN et al., 1989; VENKATESAN, 1989; HARVEY and McMANUS, 1990) since this compound is produced by fresh-water protozoa of the genus *Tetrahymena*. The high loading of tetrahymanol on factor 1 with compounds of known planktonic origin is consistent with a planktonic source for tetrahymanol. Two sources have been proposed for lycopane in marine sediments: hydrogenation of acyclic carotenoids (KIMBLE et al., 1974) and *de novo* synthesis by methanogenic bacteria (BRASSELL et al., 1981). Lycopane in SC3 probably does *not* originate from carotenoid hydrogenation, since acyclic carotenoids are essentially absent in Peru-margin sediments (REPETA and GAGOSIAN, 1987). The surface maximum in the lycopane profile (Fig. 2A) suggests that methanogenic bacteria are not the source of the lycopane either. Pore-water sulfate at the station where SC3 was collected is not completely reduced until ≈150 cm (FOSSING et al., 1990); therefore, it is unlikely that there is significant methanogenisis in SC3, especially near the surface of the core. The lycopane profile of another core, SC7, from closer to shore (100 m water depth, 14°56.62'S) is also characterized by a surface maximum, suggesting that the surface

lycopane maximum in SC3 is not unusual. In SC7 (1 cm sectioning intervals), lycopane decreases regularly from 1040 ng/gdw (0-1 cm) to 390 ng/gdw (3-4 cm).

The lycopane in SC3 and SC7 may be from a presently-unidentified phytoplankton. The fresh-water, green microalga *Botryococcus braunii* has been found to produce significant concentrations of other acyclic isoprenoid hydrocarbons (MAXWELL et al., 1968; COX et al., 1973), including tetradehydrolycopane (METZGER and CASADEVALL, 1987). A planktonic source of lycopane in SC3 is consistent with the loading of lycopane on factor 1 with C_{27} stenols, C_{28} stenols, and phytol, compounds with unequivocally planktonic sources, and with tetrahymanol, a compound of probable planktonic origin. A planktonic lycopane source, rather than a bacterial source, is also consistent with the finding of FREEMAN et al. (1990) that the carbon isotopic composition of lycopane ($\delta^{13}C$ = -20.9 °/∞) from the Messel Shale is substantially heavier than the carbon isotopic composition of bacterial lipids (hopanoids) in the same sediments.

The downcore plot of the factor 1 scores (Fig. 1) decreases sharply near the surface, reflecting diagenetic alteration and/or degradation of lipids near the sediment-water interface. Since only the first few cm have high scores of factor 1, we factored the data set again, excluding the first 3 cm, to determine how the composition and importance of this factor would be affected. When 0-3 cm are excluded, factor 1 accounts for 45.54% of the variance, and has a similar composition to factor 1 in the 0-100 cm analysis. Table 3 lists the compound loadings on each of the factors in the 3-100 cm factor analysis, following a varimax rotation; Fig. 3 shows the downcore plots of the factor scores. In the 3-100 cm factor analysis, factor 1 scores exponentially decrease away from the sediment-water interface, again reflecting the effects of diagenetic alteration and/or degradation near the top of the core. However, the "rate constant" for loss of factor 1 in the 3-100 cm analysis (Fig. 3) is lower than for factor 1 in the 0-100 cm analysis (Fig 1). This is consistent with the model of MIDDLEBURG (1989) which proposes that organic matter degradation in sediments can be described by first-order kinetics with a rate parameter that continually decreases following deposition.

The C_{37} alkenones, compounds produced by phytoplankton of the class Prymnesiophyceae (MARLOWE et al., 1984) are much more highly loaded on factor 1 in the 3-100 cm analysis than in the 0-100 cm analysis. This is because the alkenones do not show the rapid decrease below the sediment-water interface characteristic of the lipids highly loaded on factor 1 in the 0-100 cm analysis. The stability of the alkenone concentrations below the sediment-water interface may be caused by greater resistance of the alkenones to degradation. McCAFFREY et al. (1990) report that in a more finely

Table 2
Compound loadings[1] on 5 factors explaining 91.31% of variance in 50 sections of core SC3 from 0-100 cm

FACTOR	1	2	3	4	5
% of total variance explained	35.47	16.80	18.76	6.40	13.89
Compound	**Loadings:**				
Cholesterol	**0.973**	0.114	-0.063	0.085	0.080
24-methylcholest-5, 22-dien-3ß-ol	**0.970**	0.143	-0.057	0.082	0.090
24-ethylcholest-5-en-3ß-ol	**0.947**	0.145	0.105	0.134	0.174
Phytol	**0.943**	0.015	0.144	0.081	0.146
24-methylcholest-22-en-3ß-ol	**0.937**	0.116	0.169	0.052	0.259
5α-cholestan-3ß-ol	**0.927**	0.099	0.194	0.057	0.283
24-ethylcholest-5, 22-dien-3ß-ol	**0.892**	0.117	0.275	0.129	0.288
24-methylcholest-5-en-3ß-ol	**0.891**	0.014	0.245	0.083	0.321
Tetrahymanol	**0.845**	0.108	0.382	0.018	0.299
24-ethylcholest-22-en-3ß-ol	**0.833**	0.071	0.379	0.171	0.321
C_{28} n-alkan-1-ol	**0.796**	0.433	0.146	-0.140	0.166
Lycopane	**0.775**	0.134	0.404	-0.062	0.409
Dinosterol	**0.740**	0.122	0.588	0.003	0.260
Total Organic Carbon (TOC)	0.509	0.142	0.614	0.069	0.453
C_{26} n-alkan-1-ol	0.665	**0.710**	-0.056	-0.047	-0.118
C_{29} n-alkane	-0.040	**0.967**	0.134	0.097	0.061
C_{27} n-alkane	-0.002	**0.932**	0.004	0.060	0.306
C_{33} n-alkane	0.203	**0.850**	0.197	0.124	0.340
C_{31} n-alkane	0.163	**0.845**	0.231	0.104	0.351
C_{24} n-alkan-1-ol	0.484	**0.763**	0.025	-0.262	-0.131
C_{25} n-alkane	0.310	0.655	0.100	0.060	0.616
F5 hopanol[2]	-0.168	0.242	**0.896**	0.067	0.107
C_{32} hopanol	0.176	0.268	**0.871**	-0.161	0.115
C_{31} hopanol	0.461	0.109	**0.790**	-0.094	0.264
14α(H)-1(10→6)-abeocholesta-5,7,9 (10)-triene	0.088	-0.280	**0.786**	0.266	-0.066
$C_{37:3}$ alkenone	0.217	0.296	**0.702**	0.220	0.375
$C_{37:2}$ alkenone	0.259	0.358	0.665	0.274	0.346
Cholest-3, 5-diene	0.461	-0.022	0.615	-0.259	0.316
Cholest-R, N, N-triene	0.418	0.004	0.588	0.048	0.434
C_{30} triterpenoid[3]	0.144	-0.449	0.573	0.432	-0.009
C_{30}-alkan-15-one-1-ol	0.103	0.037	0.363	**0.895**	0.118
C_{32}-alkan-15-one-1-ol	0.162	0.123	-0.107	**0.866**	-0.001
C_{32} n-alkane	0.334	0.187	0.321	-0.026	**0.822**
C_{30} n-alkane	0.336	0.348	0.313	-0.034	**0.791**
C_{24} n-alkane	0.472	0.156	0.181	0.127	**0.786**
C_{26} n-alkane	0.440	0.325	0.161	0.077	**0.785**

[1]Loadings > 0.7 are shown in bold-face type.
[2]C_{32} monohydroxy hopanoid of unknown structure in ketone fraction. See text.
[3]C_{30} monounsaturated triterpenoid of unknown structure. See text.

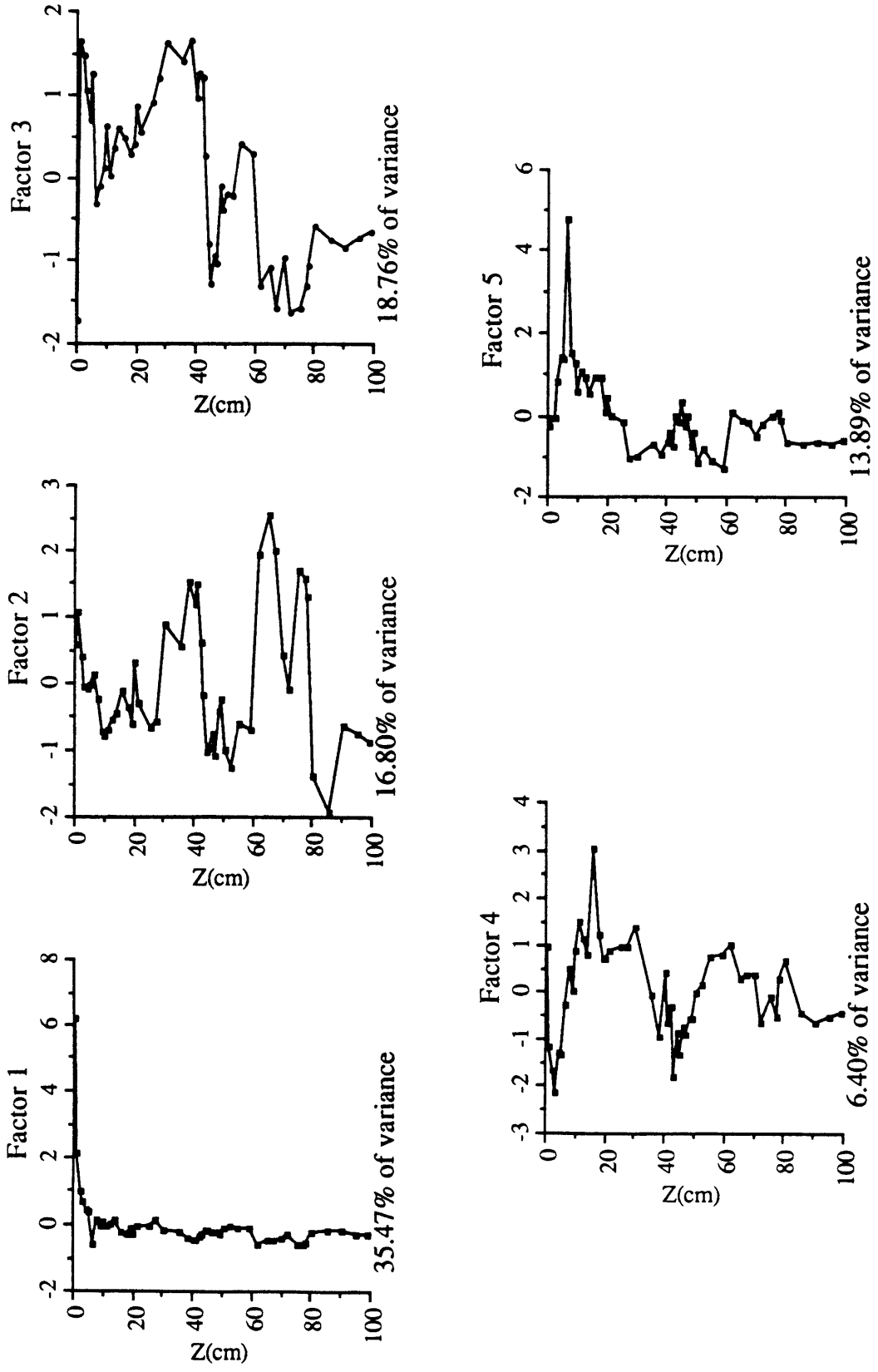

Figure 1: Downcore plots of factor scores in SC3 for 0-100 cm factor analysis.

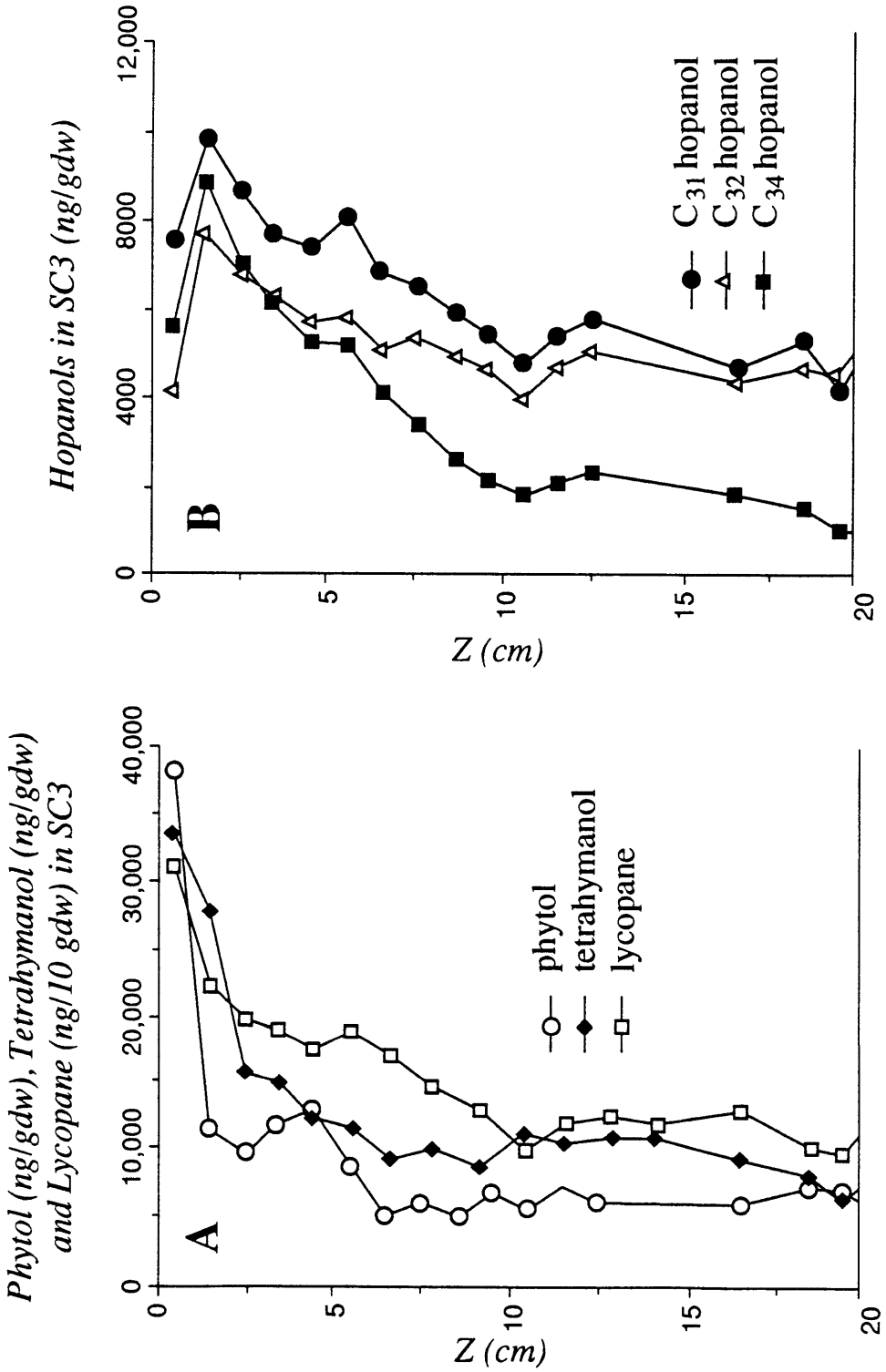

Figure 2: (A) Phytol, tetrahymanol, and lycopane in SC3, 0-20 cm. (B) Monohydroxy hopanols in SC3, 0-20 cm.

Table 3
Compound loadings[1] on 5 factors explaining 91.13% of variance in 47 sections of core SC3 from 3-100 cm

FACTOR	1	2	3	4	5
% of total variance explained	45.54	19.86	13.35	6.63	5.76
Compound	**Loadings:**				
Cholesterol	**0.949**	0.052	0.197	0.078	0.140
24-methylcholest-22-en-3ß-ol	**0.942**	0.084	0.248	0.042	0.108
24-methylcholest-5,22-dien-3ß-ol	**0.933**	0.229	0.150	0.067	0.070
Tetrahymanol	**0.927**	0.051	0.291	0.109	0.025
5α-cholestan-3ß-ol	**0.925**	0.028	0.281	0.056	0.196
Lycopane	**0.915**	0.149	0.236	-0.045	0.061
24-methylcholest-5-en-3ß-ol	**0.896**	-0.138	0.186	0.174	0.173
Phytol	**0.874**	-0.062	0.236	0.056	-0.255
24-ethylcholest-5,22-dien-3ß-ol	**0.873**	0.075	0.398	0.162	0.152
C_{32} n-alkane	**0.863**	0.249	-0.058	0.020	0.354
Total Organic Carbon (TOC)	**0.857**	0.184	0.320	0.151	-0.001
24-ethylcholest-22-en-3ß-ol	**0.843**	0.011	0.418	0.221	0.115
24-ethylcholest-5-en-3ß-ol	**0.841**	0.127	0.399	0.200	0.188
Dinosterol	**0.797**	0.084	0.565	0.018	-0.018
Cholest-R, N, N-triene	**0.775**	-0.054	0.265	0.194	0.155
Cholest-3, 5-diene	**0.764**	-0.003	0.273	-0.189	-0.152
C_{30} n-alkane	**0.754**	0.394	0.040	-0.022	0.457
C_{24} n-alkane	**0.733**	0.169	0.060	0.058	0.596
C_{31} hopanol	**0.701**	0.090	0.637	-0.075	0.005
C_{26} n-alkane	0.695	0.365	-0.029	0.070	0.551
$C_{37:3}$ allkenone	0.592	0.299	0.603	0.165	0.199
$C_{37:2}$ alkenone	0.561	0.358	0.576	0.237	0.174
C_{28} n-alkan-1-ol	0.587	**0.724**	-0.075	-0.112	-0.123
C_{26} n-alkan-1-ol	-0.126	**0.952**	0.000	-0.020	-0.195
C_{29} n-alkane	-0.064	**0.936**	0.210	0.097	0.162
C_{27} n-alkane	0.046	**0.925**	0.021	0.063	0.331
C_{24} n-alkan-1-ol	-0.088	**0.890**	0.022	-0.239	-0.219
C_{33} n-alkane	0.305	**0.886**	0.050	0.206	0.168
C_{31} n-alkane	0.293	**0.858**	0.147	0.130	0.242
C_{25} n-alkane	0.399	0.681	0.089	-0.001	0.569
F5 hopanol[2]	0.420	0.281	**0.794**	0.108	0.003
C_{32} hopanol	0.464	0.251	**0.779**	-0.159	0.010
14α(H)-1(10→6)-abeocholesta-5,7,9 (10)-triene	0.27	-0.332	**0.762**	0.227	-0.048
C_{32}-alkan-15-one-1-ol	-0.009	0.097	-0.079	**0.913**	0.007
C_{30}-alkan-15-one-1-ol	0.254	0.021	0.344	**0.877**	0.066
C_{30} triterpenoid[3]	0.385	-0.410	0.425	0.426	-0.247

[1]Loadings > 0.7 are shown in bold-face type.
[2]C_{32} monohydroxy hopanoid of unknown structure in ketone fraction. See text.
[3]C_{30} monounsaturated triterpenoid of unknown structure. See text.

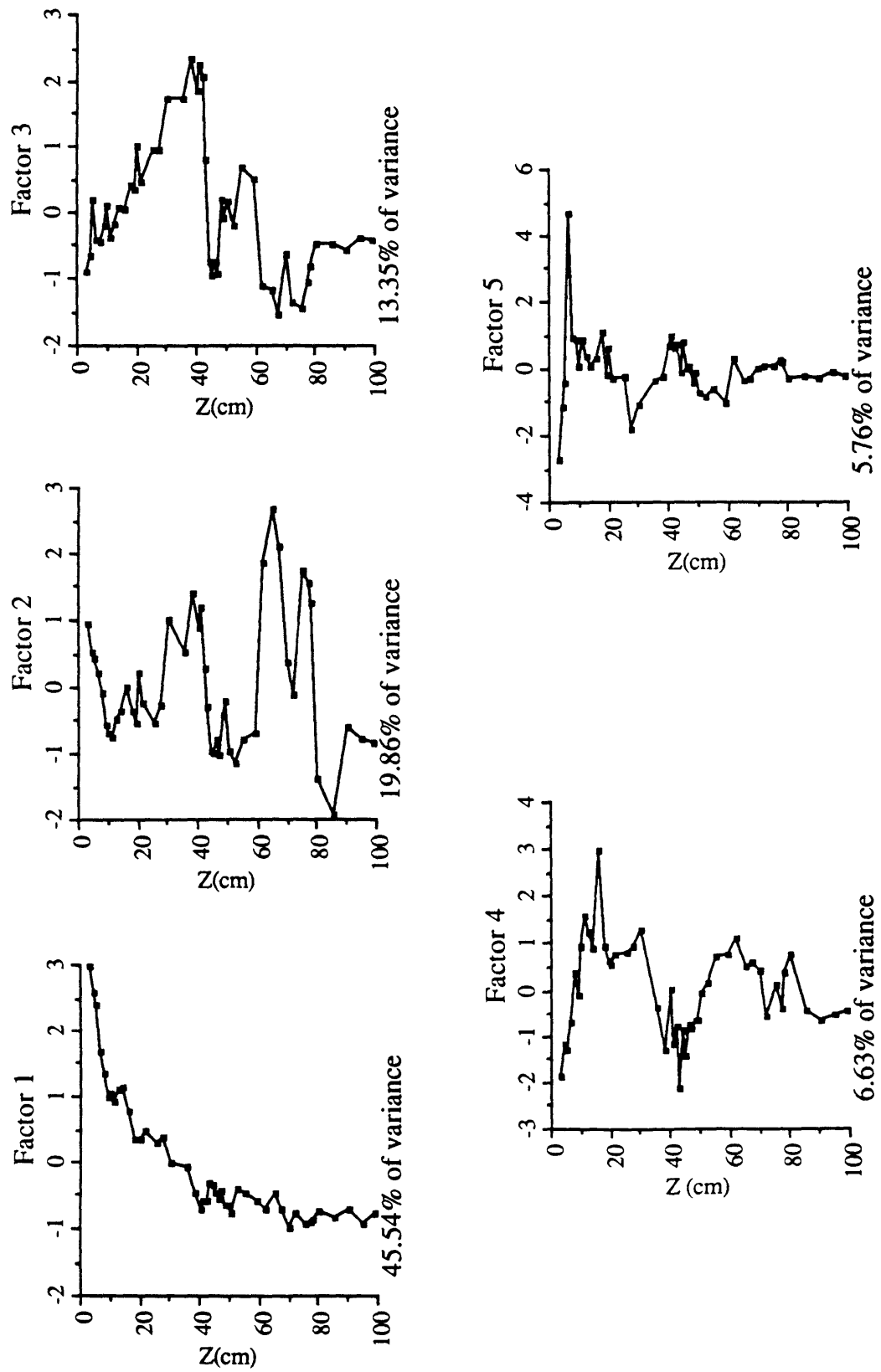

Figure 3: Downcore plots of factor scores in SC3 for 3-100 cm factor analysis.

sectioned subcore of this core, the alkenones are substantially more abundant (30%) in the surface 6 mm than at deeper depths; this is not apparent in the data presented here because of the wider (1 cm) sectioning interval. The significant loading of the alkenones on factor 3 is discussed below.

Factor 2- terrigenous lipids

Compounds with the highest loadings on factor 2 in both the 0-100 cm and 3-100 cm factor analyses are odd-carbon-number n-alkanes and even-carbon-number n-alkanols (Fig. 4). These compounds are abundant in the epicuticular waxes of higher plants (e.g., EGLINTON and HAMILTON, 1967; TULLOCH, 1976), but are also produced in small concentrations by some phytoplankton and bacteria (VOLKMAN et al, 1983, and references therein). Therefore, odd-carbon-number n-alkanes and even-carbon-number n-alkanols in SC3 cannot be assumed *a priori* to be markers for terrestrial input.

We assessed the relative importance of terrestrial and marine sources of n-alkanes and n-alkanols in SC3 by comparing the profiles of these biomarkers with several inorganic indicators of the sedimentary abundance of terrigenous rock and mineral debris. We measured Al, Ti, Zr and Fe in 16 sections of SC3, and their profiles are extremely well-correlated (Fig. 5). These elements are sedimentary markers for terrigenous clastic material. Aluminosilicates are the primary source of sedimentary Al, and detrital heavy minerals, such as rutile and zircon, are a major source of sedimentary Ti and Zr. Fe is abundant in detrital mafic minerals, and is also present in aluminosilicates, albeit in lower concentrations. Profiles of these elements are also well-correlated in SC3 with the sediment dry weight/wet weight ratio (abbreviated as C_S for sediment "concentration of solids"), another inorganic marker for the input of terrigenous detritus to the sediments (Fig. 6). Although C_S also increases with sediment compaction, sharp fluctuations in the C_S profile reflect fluctuations in the relative abundance of terrigenous and marine sediment, because terrigenous rock and mineral debris is typically more dense than the diatomaceous ooze that comprises most of the marine detritus.

We calculated an aluminosilicate profile for SC3 by assuming an average Al concentration in the aluminosilicates of 12 wt %. This aluminosilicate profile is probably a good approximation of the actual profile, since clays of the smectite and illite groups (>80 % of the fluvial clay at 15°S; SCHEIDEGGER and KRISSEK, 1982) and K-feldspar are ≈10 wt % Al, while plagioclase is 10-20 wt % Al. In Fig. 7 discussed below, we compare the C_{29} n-alkane and C_{26} n-alkanol profiles with the aluminosilicate profile rather than directly with the elemental profiles so that the approximate magnitude of the fluctuations in

the terrigenous component of the sediment is more accessible to visual comparison with the biomarker profiles.

n-alkanes and n-alkanols: Even-carbon-number n-alkanols (C_{24}-C_{28}) and odd-carbon-number n-alkanes (C_{25}-C_{33}) are well-correlated with both wt% aluminosilicates in SC3 and the C_s profile (Fig. 7). This suggests that (1) factor 2 represents primarily terrestrial input to SC3 and (2) downcore fluctuations in these lipid profiles reflect changes in the magnitude of input and not simply changes in the efficiency of preservation.

Since the TOC in Peru margin sediments is primarily marine-derived, biomarker/TOC ratios for terrigenous compounds should increase when the sedimentary input of the terrigenous biomarkers increases relative to the sedimentary input of marine organic matter. The TOC-normalized profiles of the even-carbon-number n-alkanols and the odd-carbon-number n-alkanes in SC3 are, in fact, well-correlated with Al (Fig. 8); this further suggests a terrestrial origin of these compounds in SC3. For comparison, Fig. 9 illustrates that there is no correlation between the TOC-normalized profile of dinosterol (a biomarker for marine dinoflagellate input to the sediments; BOON et al., 1979) and Al, an expected result since dinosterol is *not* terrigenous in origin.

The abundance of odd-carbon-number n-alkanes relative to even-carbon-number n-alkanes in a sample can provide another indicator of the source of these lipids. One measure of the odd/even predominance is the n-alkane carbon preference index:

$$\text{CPI} = \frac{(2*\Sigma\text{odd carbon numbers } C_{25} \text{ to } C_{33})}{(\Sigma\text{even carbon numbers } C_{24} \text{ to } C_{32} + \Sigma\text{even carbon numbers } C_{26} \text{ to } C_{34})}$$

The n-alkane CPI of higher-plant epicuticular waxes ranges from 3 to >20 (calculated from data in EGLINTON and HAMILTON, 1967; and TULLOCH, 1976), whereas the CPI for bacterial and phytoplankton n-alkanes is generally closer to 1 (CLARK and BLUMER, 1967; VOLKMAN et al., 1983, and references therein). We calculated the CPI of our samples using the concentration of C_{30} n-alkane for both C_{30} n-alkane and C_{28} n-alkane in the CPI equation. This was done because 22, 29, 30 trisnorneohop-13(18)-ene was present in some of our samples and partially coelutes with C_{28} n-alkane under our analytical conditions. In samples not containing the trisnorneohopene, C_{30} n-alkane and C_{28} n-alkane are similar in concentration. Substitution of C_{30} n-alkane for C_{28} n-alkane in the CPI equation allows calculation of the CPI for samples in which the C_{28} n-alkane is obscured by the trisnorneohopene. This hopene was *not* removed by $AgNO_3$-impregnated silica (a

generally effective method for separating alkenes from alkanes), perhaps because the double bond is between tertiary carbons.

The CPI profile for SC3 (Fig. 10A) increases from ≈ 3 near the surface to ≈ 8 at 39 cm. From 39-100 cm, the CPI fluctuates from 6-8. The abundances of the odd n-alkanes relative to one another also changes downcore. In the surface of the core, C_{29} n-alkane and C_{31} n-alkane are the dominant homologs and the C_{29} n-alkane/C_{31} n-alkane ratio ≈0.8-0.9; with increasing depth, C_{29} n-alkane becomes more abundant than C_{31} n-alkane (Fig. 10B). To assess the influence of terrestrial n-alkanes on the CPI and C_{29}/C_{31} ratio of SC3, we analyzed surface sediments collected at progressively shallower water depths: 253 m (core SC3), 135 m, 100 m, 50 m, 30 m, and 25 m. The 30 m sample was taken from 15°00.4'S, near the mouth of the Rio Grande river. The 50 m and 25 m samples were collected from further north (14°54'S). Compared with the sediments from the OMZ, the near-shore samples (50 m, 30 m, and 25 m) had both a higher CPI and a higher C_{29}/C_{31} ratio. Figure 11 shows the n-alkane CPI vs the C_{29}/C_{31} ratio for all the sediments analyzed. These data suggest that the sedimentary n-alkanes represent mixing of a marine end-member and terrestrial end-member. If the terrestrial and marine n-alkanes are assumed to have a CPI of 10 and 1 respectively, then the surface sediment of SC3 (CPI≈ 3-4) would have a marine n-alkane component of ≈ 67-78%. In contrast, the sections of SC3 with the highest CPI (≈ 8) would have a marine n-alkane component of only ≈ 22%.

The CPI increase from 0-39 cm in SC3 is probably due to the selective degradation of the low-CPI marine component of these n-alkanes relative to the high-CPI, more refractory, higher-plant component of these compounds. Several studies (AIZENSHTAT et al., 1973; PRAHL et al., 1980; VOLKMAN et al., 1983) have suggested that terrestrial lipids may be more resistant than marine lipids to post-depositional degradation, perhaps due to the association of the higher-plant lipids with refractory biopolymers. One consequence of the selective degradation of the marine n-alkanes is that the n-alkane CPI profile for SC3 (Fig. 10) does not record the major fluctuations in the aluminosilicate and C_s profiles (i.e., at 65 cm and 75 cm) recorded by the n-alkane and n-alkanol profiles (Fig. 7-8). The insensitivity of the CPI profile to fluctuations in the relative terrestrial input arises because changes in the abundance of terrestrial n-alkanes can only change the sediment CPI if non-terrestrial n-alkanes with a different CPI are also present in the sediment.

It is interesting to note that the n-alkanols are much more highly loaded on factor 2 in the 3-100 cm factor analysis (Table 3) than in the 0-100 cm factor analysis (Table 2); this is because these compounds show a significant concentration decrease in the first few cm (Fig. 7B) analogous to the compounds highly loaded on factor 1. This decrease may be due

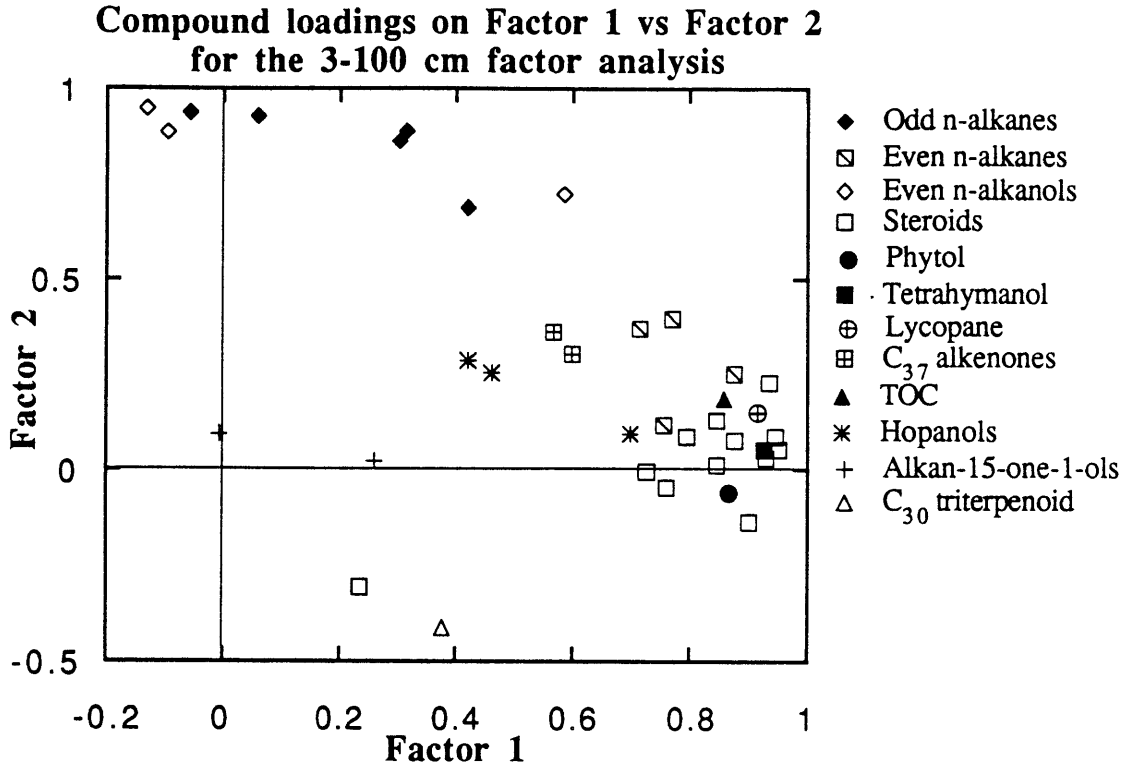

Figure 4: Compound loadings on factor 1 vs factor 2 for the 3-100 cm factor analysis. The steroid with the low loading on factor 1 is the anthrosteroid, 14α(H)-1(10→6)-abeocholesta-5,7,9 (10)-triene.

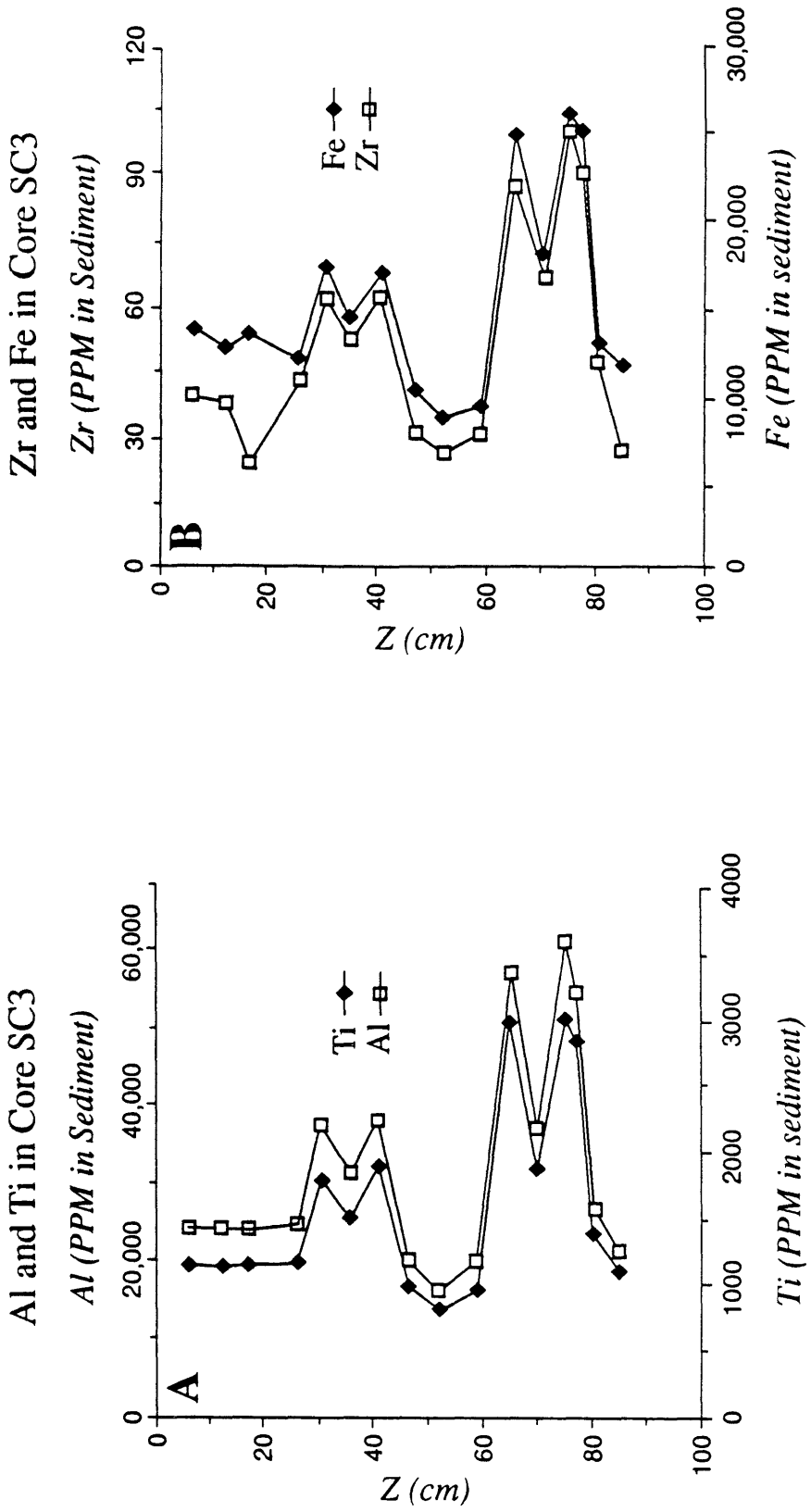

Figure 5: (A) Al and Ti in SC3. (B) Zr and Fe in SC3.

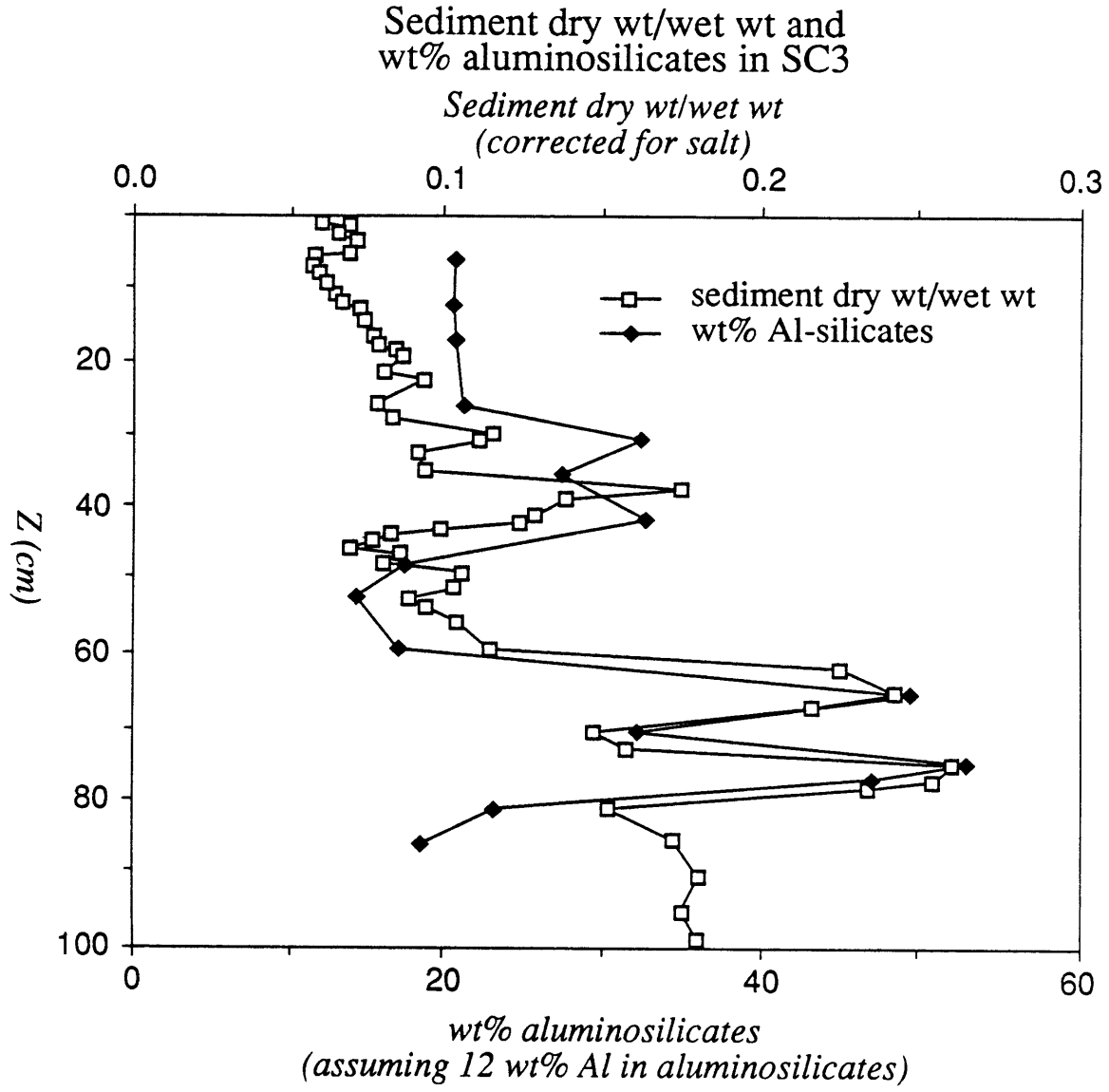

Figure 6: Sediment dry wt/wet wt and wt% aluminosilicates in SC3.

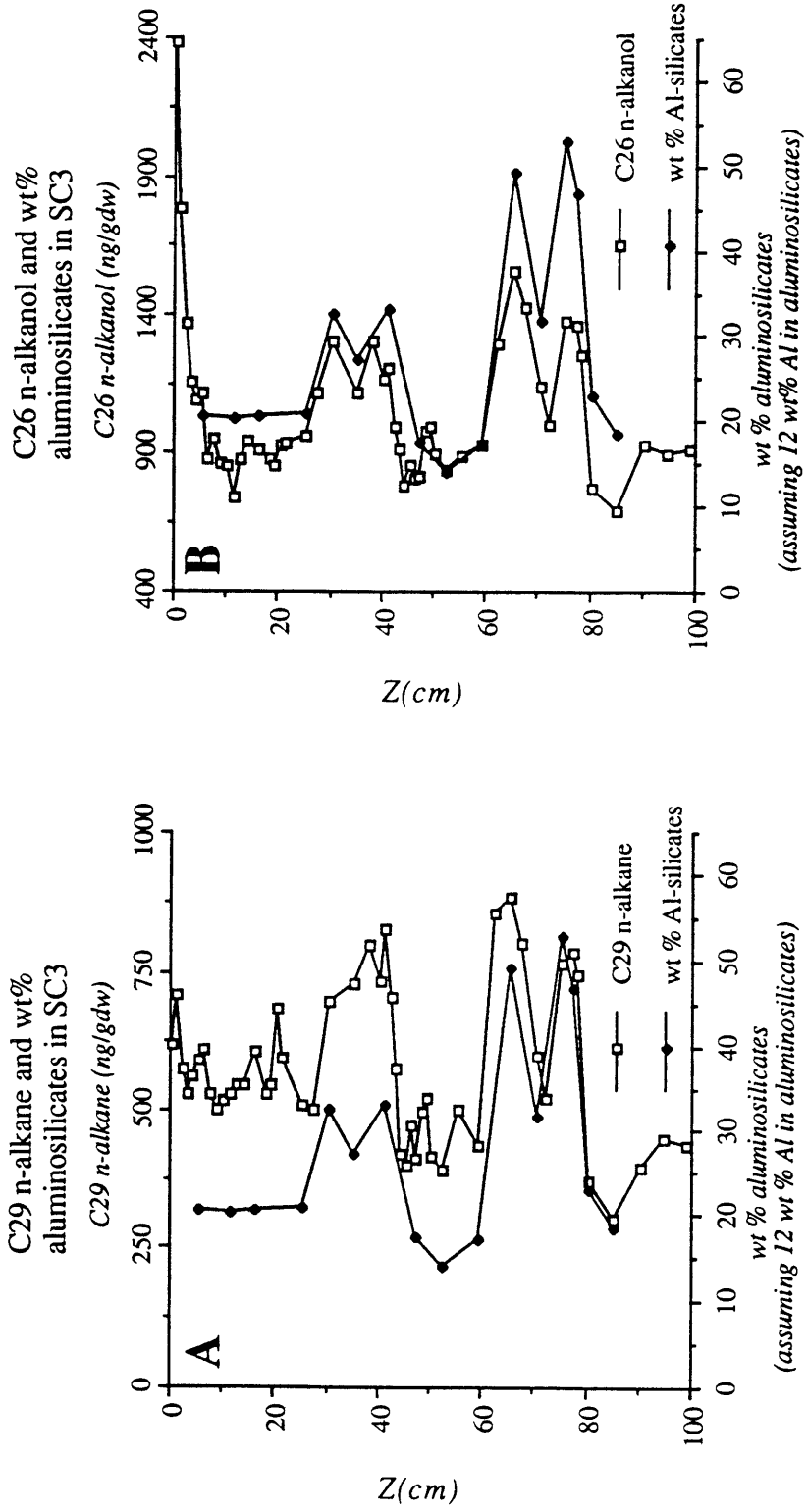

Figure 7: (A) C_{29} n-alkane and wt% aluminosilicates vs depth in SC3. C_{29} n-alkane and wt% aluminosilicates are correlated at R = 0.82, n=16. (B) C_{26} n-alkanol and wt% aluminosilicates vs depth in SC3. C_{26} n-alkanol and wt% aluminosilicates are correlated at R =0.89, n=16.

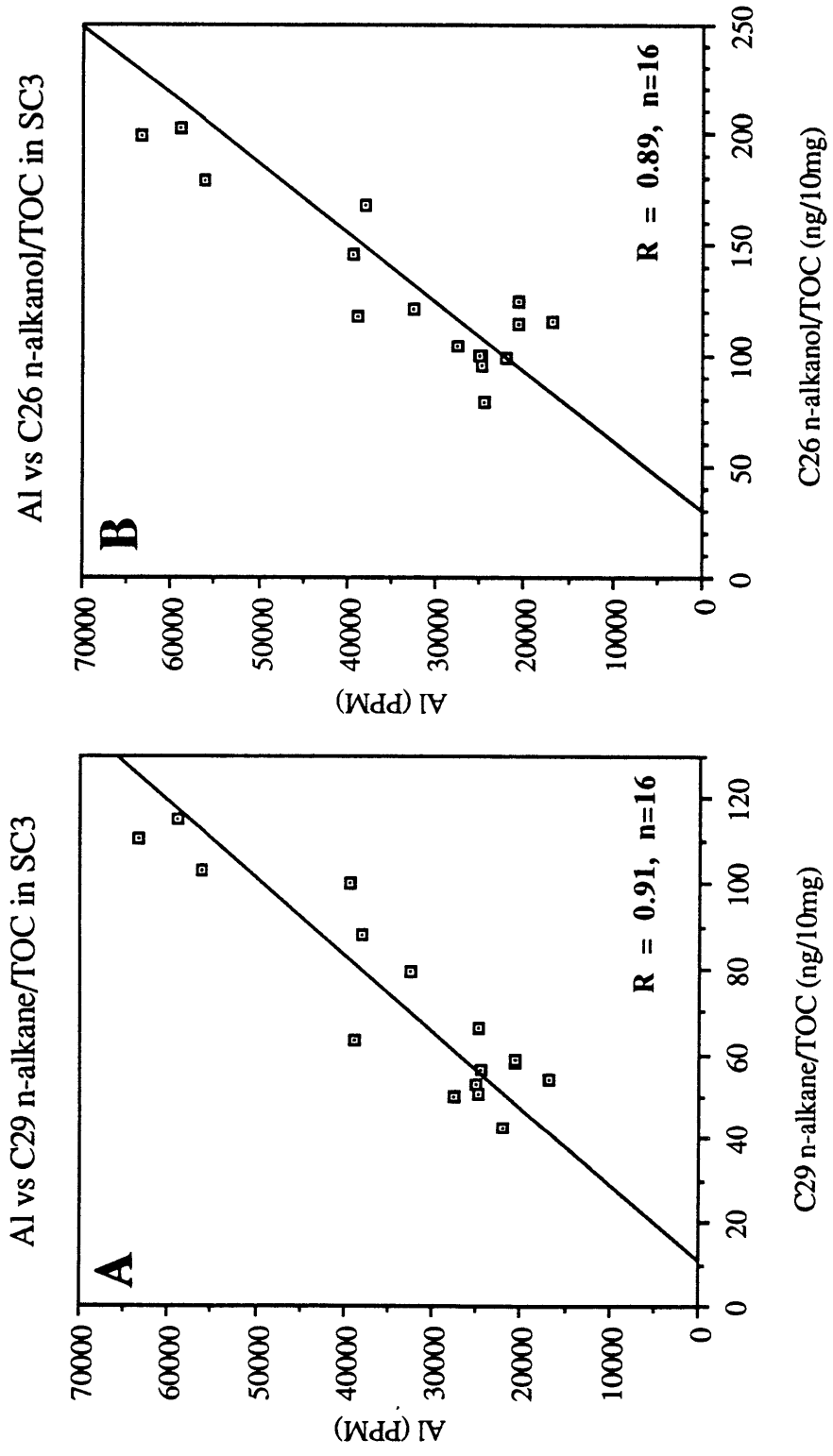

Figure 8: (A) Al vs C_{29} n-alkane/TOC in SC3. (B) Al vs C_{26} n-alkanol/TOC in SC3.

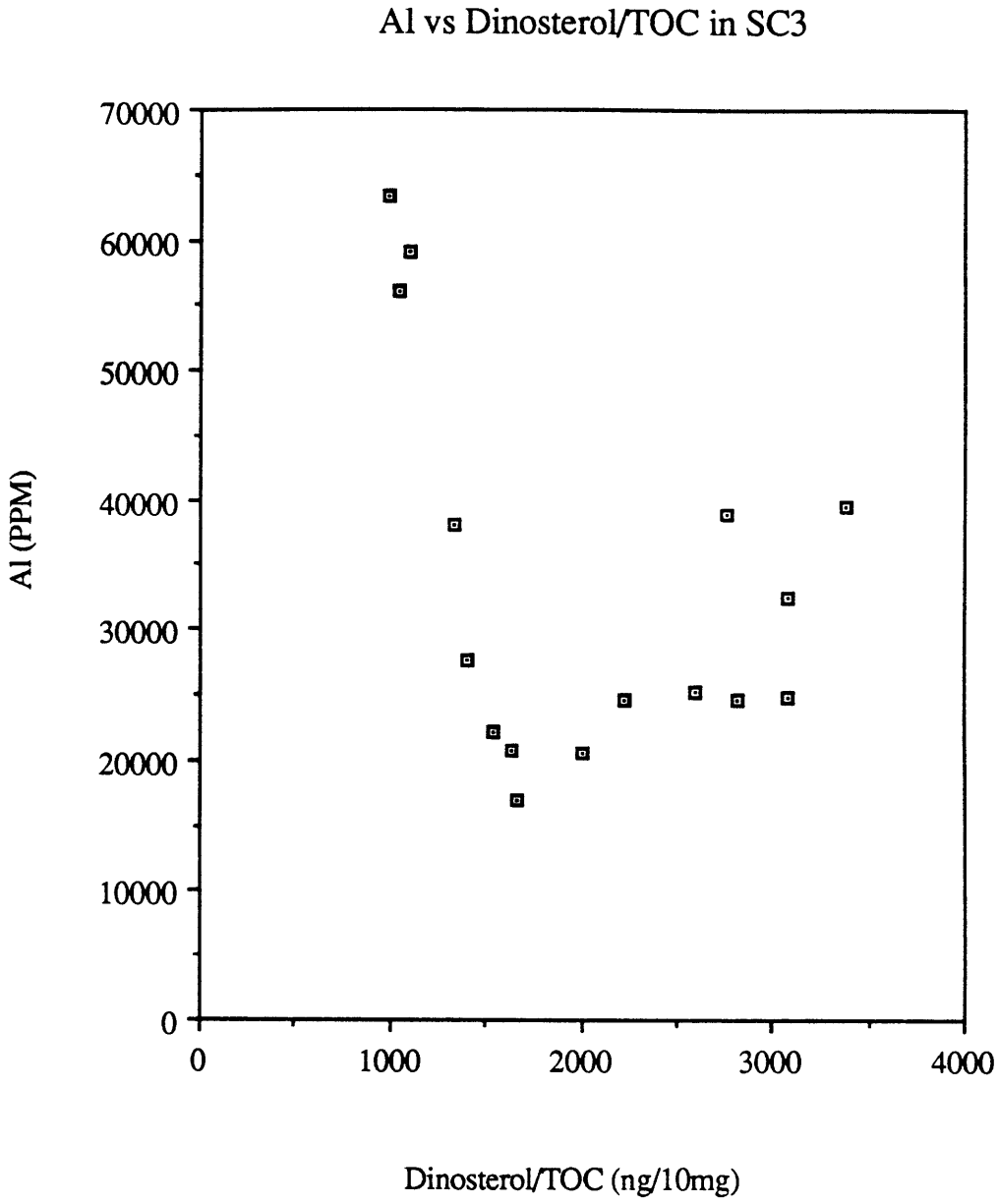

Figure 9: Al vs Dinosterol/TOC in SC3. There is essentially no correlation. The best linear fit through the data has a *negative* slope, and R= 0.4., n= 16.

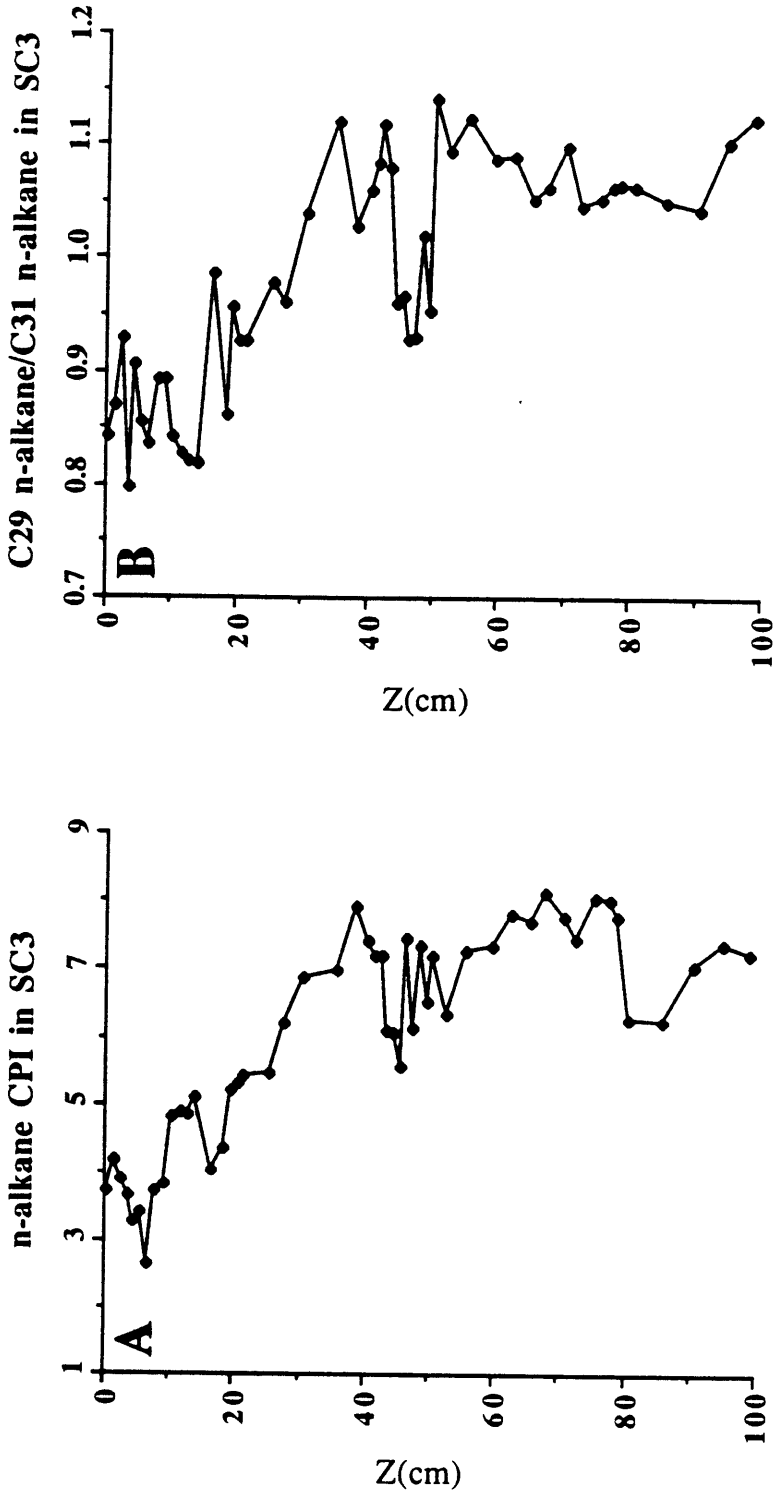

Figure 10: (A) The n-alkane CPI in SC3. (B) C_{29} n-alkane/C_{31} n-alkane in SC3.

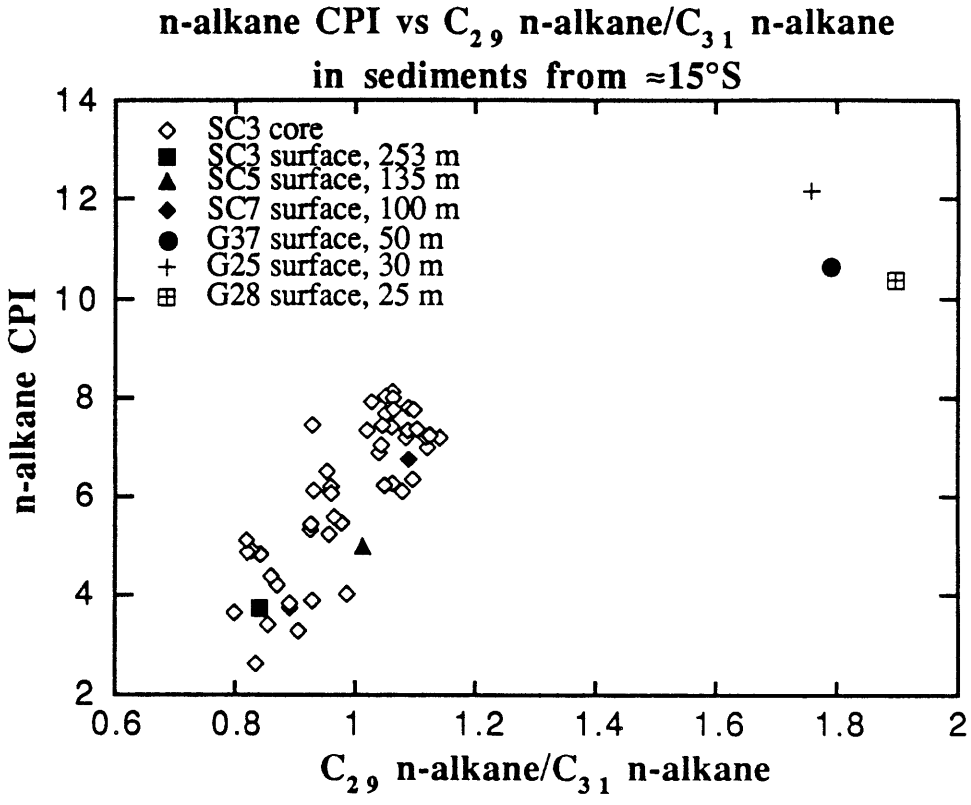

Figure 11: The n-alkane CPI vs C_{29} n-alkane/C_{31} n-alkane in sediments from ≈ 15°S.

to more efficient degradation of these alcohols near the sediment-water interface. Alternatively, it may be the result of degradation of a marine component of the n-alkanols in the surface few cm and the preferential preservation of a higher-plant component of these compounds.

Sterols: Although the 24-R epimers of 24-ethylcholesterol, 24-ethylcholest-5,22-dien-3ß-ol, and 24-methylcholesterol (ß-sitosterol, stigmasterol, and campesterol, respectively) are characteristic of higher plants, our analytical techniques do not resolve the 24-R and S epimers. However, a primarily marine origin of these compounds in SC3 is suggested by the high loadings of these stenols on factor 1 with marine stenols such as 24-methylcholest-5,22-dien-3ß-ol, dinosterol and cholesterol (Fig. 4). The lack of correlation between the aluminosilicate profile and all the stenol profiles further suggests a marine source of these lipids. These data indicate that the contribution of stenols from higher plants in SC3 is obscured by a much larger marine contribution of these compounds. VOLKMAN et al. (1987) also proposed a marine origin for 24-ethylcholesterol in Peru surface sediments from closer to shore (core BC7, 85 m), but suggested that the marine component may be substantially degraded by 4 cm, leaving higher-plant-derived stenols at deeper depths. In contrast, our data for SC3 (253 m) suggest that throughout the 100 cm of the core, all the stenols we measured have a primarily marine source. The higher-plant stenols in SC3 are evidently sufficiently low in abundance so that selective degradation of the marine contribution of these compounds does not result in primarily higher-plant stenols at depth in the core.

SCHEIDEGGER and KRISSEK (1983) proposed that zooplankton and nekton play a crucial role in terrigenous sediment deposition off coastal Peru by ingesting fine-grained terrigenous debris in the water column and excreting this material as rapidly-sinking fecal pellets. An implication of this proposal is that terrigenous sediment deposition depends both on the sediment input from the continent and on marine primary production which controls zooplankton and nekton abundances (SCHEIDEGGER and KRISSEK, 1983). The lack of correlation between marine and terrigenous markers in SC3 is *not* inconsistent with this scenario and may be the result of two processes: (1) unusually intense terrestrial input events, whether they are dust storms or episodes of runoff, may deliver to the sea surface clastic debris with a larger mean grain size which can rapidly settle without incorporation into fecal pellets, and (2) enhanced input of continental sediment dilutes the concentration of concomitantly deposited marine markers.

Factors 3, 4, and 5

The compounds loaded most highly on factor 3 are monohydroxy hopanols and a B-ring monoaromatic anthrosteroid [14α(H)-1(10→6)-abeocholesta-5,7,9 (10)-triene], an alteration product of cholesterol (HUSSLER and ALBRECHT, 1983). The compound moderately loaded on factor 3 and listed as "C_{30} triterpenoid" in Table 2 and Table 3 is a C_{30} hydrocarbon of unknown structure. The electron impact mass spectrum [MS: 218 (100%), 205 (24.3%), 177 (12.6%), 189 (12.1%), 163 (9.4%), M^+= 410 (4.7%), and 395 (1.5%)] indicates rings+double bonds = 6. This compound is the most abundant lipid >C_{25} in the alkene fraction of most sections of SC3.

The C_{31} and C_{32} hopanols are homohopane-31-ol and bishomohopane-32-ol, previously identified by VOLKMAN et al. (1987) in sediments from this area. The compound highly loaded on factor 3 and listed as "F5 hopanol" in Table 2 and Table 3 is a C_{32} monohydroxy hopanol present in the ketone-containing fraction (Fraction 5, FARRINGTON et al, 1988) of the lipid extract, the fraction eluting from the silica gel column immediately prior to the fraction containing the other hopanols. The mass specrum of the underivitized alcohol is similar to bishomohopane-32-ol, but unlike that compound the acetate derivative is not formed by reaction with acetic anhydride and pyridine; this hopanol may be bishomohopane-22-ol, since alcohols at tertiary carbons are less susceptible to acetylation with these reagents. In surface sediments, we also found a C_{34} hopanol (tetrakishopane-34-ol ?) previously unreported in these sediments; the acetate derivative has the electron impact mass spectrum: 191 (100%), 305 (57.4%), 227 (29.9%), 369 (8.9%), 245 (5.6%) 526 (2.84%), 466 (1.1%), and 511 (0.96%). This compound was not included in the factor analysis because it rapidly decreased in abundance with depth (Fig. 2B) and was not detected below 50 cm.

Hopanoids are ubiquitous in marine and lacustrine sediments (OURISSON et al., 1979, 1987; QUIRK et al., 1984) and are biosynthesized by many bacteria as well as a few plants (certain tropical trees, grasses, and ferns) and lichens (OURISSON et al., 1979). Because of the restricted occurrence of these compounds in plants, hopanoids in marine sediments are typically attributed to bacterial input and alteration of bacterial precursors (OURISSON et al., 1987). The monohydroxy hopanols measured in SC3 have not been found in significant concentrations in bacteria and are probably alteration products of polyhydroxy hopanoids, such as bacteriohopanetetrol (ROHMER et al., 1980, 1984), which are abundant lipids in many bacteria. In contrast to the compounds loaded on factor 1, the hopanols have no significant decrease from 0-1 cm of SC3, and have a subsurface maximum at 1-2 cm (Fig. 2B). This difference between the hopanols and the planktonic markers is attributed to a substantial post-depositional input of polyhydroxy hopanoids

from bacteria in the sediment. The hopanols in SC3 are significantly correlated with TOC ($r = 0.79$ for C_{31} hopanol and TOC, $n=50$), suggesting a dependence of sedimentary bacterial biomass on the quantity of available substrate (sedimentary TOC).

The profile of the C_{27} anthrosteroid [14α(H)-1(10→6)-abeocholesta-5,7,9 (10)-triene] in SC3 is remarkably constant from 0-43 cm (mean ± st. dev.= 973 ± 154 ng/gdw). The proposed precursor to this compound is a cholestatriene or cholestadiene (BRASSELL et al., 1984). The cholestenes measured in SC3 are most abundant near the top of the core, steadily decrease in concentration with depth, and load highly on factor 1 in the 3-100 cm analysis. Therefore, the constancy of the C_{27} anthrosteroid profile and the consequent loading of this lipid on factor 3 may indicate that (1) formation of the C_{27} anthrosteroid from a sterene occurs primarily in the water column and/or at the sediment-water interface and (2) very little of the C_{27} anthrosteroid degrades following deposition. Formation of C_{29} anthrosteroids (which were not detected in the Peru sediments) from C_{29} sterenes may occur over a longer time scale, as suggested by data for DSDP sediments from the San Miguel Gap (BRASSELL et al., 1984). The 14α configuration of the C_{27} anthrosteroid in the Peru sediments rules out the possibility that the compound represents input of ancient organic matter from the continent, since isomerization at C-14 occurs relatively quickly during diagenesis (RULLKÖTTER and WELTE, 1983; BRASSELL et al., 1984).

The significant loading of the C_{37} alkenones on factor 3 (0.645-0.687) is a result of the correlation of the alkenones with TOC, and the lack of a substantial decrease in the alkenone concentration immediately below the sediment-water interface. This is illustrated by the lower loading of these compounds on factor 3, and the higher loadings of these compounds on factor 1, when 0-3 cm are excluded from the analysis (Table 3).

The only compounds highly loaded on factor 4 are the C_{30} and C_{32} alkan-15-one-1-ols first identified by DE LEEUW et al. (1981). These compounds are widespread in marine sediments (MORRIS and BRASSELL, 1988), and the only source that has been suggested is the planktonic cyanobacterium *Aphamizomenon flos-aquae*, in which MORRIS and BRASSELL (1988) found alkan-1,15-diols. If planktonic cyanobacteria are the source of these compounds in SC3, then the lack of correlation between these compounds and the planktonic markers in factor 1 may be due to differences in the timing of blooms of cyanobacteria and other primary producers. Unfortunately, we are unaware of any data on cyanobacteria distributions in this environment. The lack of correlation between the alkan-15-one-1-ols and the planktonic markers in factor 1 may also partially be the result of greater resistance of the keto-ols to degradation. This is illustrated by the downcore increase in the alkan-15-one-1-ol concentrations relative to the stenol concentrations. In the 0-1 cm section, the sum of the C_{30} and C_{32} alkan-15-one-1-ols is

<7% of the sum of the five stenols measured; this value increases to a maximum of 230% in the 75-76 cm section.

In the 0-100 cm factor analysis, factor 5 is composed primarily of even-carbon-number n-alkanes and explains 13.89% of the variance. However, in the 3-100 cm factor analysis, these compounds are loaded on factor 1, and factor 5 (5.76% of the variance) has no highly loaded compounds. This difference between the two factor analyses stems from the greater resistance of these alkanes to degradation when compared with the other compounds loaded on factor 1. A significant marine source of even-carbon-number n-alkanes is consistent with the low-CPI planktonic and bacterial n-alkanes which we have suggested are present in this core.

II. TERRIGENOUS MARKERS AND THE ENSO RECORD: AEOLIAN VS. FLUVIAL INPUT

Continental runoff from the coastal Peruvian desert typically is low, but substantially increases during most El Niño events (QUINN et al., 1987; DESSER and WALLACE, 1987). Terrigenous biomarkers, therefore, have potential as sedimentary indicators of El Niño conditions. However, the historical El Niño record is not well-correlated with the odd-carbon-number n-alkanes or even-carbon-number n-alkanols in SC3 (Fig. 12). Although the two maxima centered at 65 cm and 75 cm in the n-alkane and n-alkanol profiles (Fig. 3, factor 2) may be related to the two very strong ENSO events of 1791 and 1828 (Fig. 12), there is no correlation in the rest of the core between the ENSO record and these compounds. During the period of greatest ENSO activity from 1870-1891, there is actually a minimum in the n-alkane and n-alkanol concentration profiles. If continental runoff is the source of these compounds, then the lack of correlation between these lipids and the historical El Niño record may indicate that sediment from runoff is not delivered directly to the OMZ. Terrigenous sediment may initially be deposited closer to shore, and may reach the OMZ only as a result of subsequent resuspension and off-shore transport. Furthermore, REIMERS and SUESS (1983) proposed that a portion of the terrigenous sediment deposited at 15°S may be advected from further north and deposited at 15°S due to the weakening of the Peru undercurrent caused by the southward narrowing of the Peru shelf.

The lack of a correlation between the historical El Niño record and the n-alkanol, n-alkane, and aluminosilicate profiles may also indicate that the terrigenous source of these compounds in SC3 is aeolian transport from the continent rather than continental runoff. SCHNEIDER and GAGOSIAN (1985) measured n-alkanol and n-alkane concentrations in aerosols from 10-100 km off the coast of Peru at ≈15°S. Their data suggests that aerosol

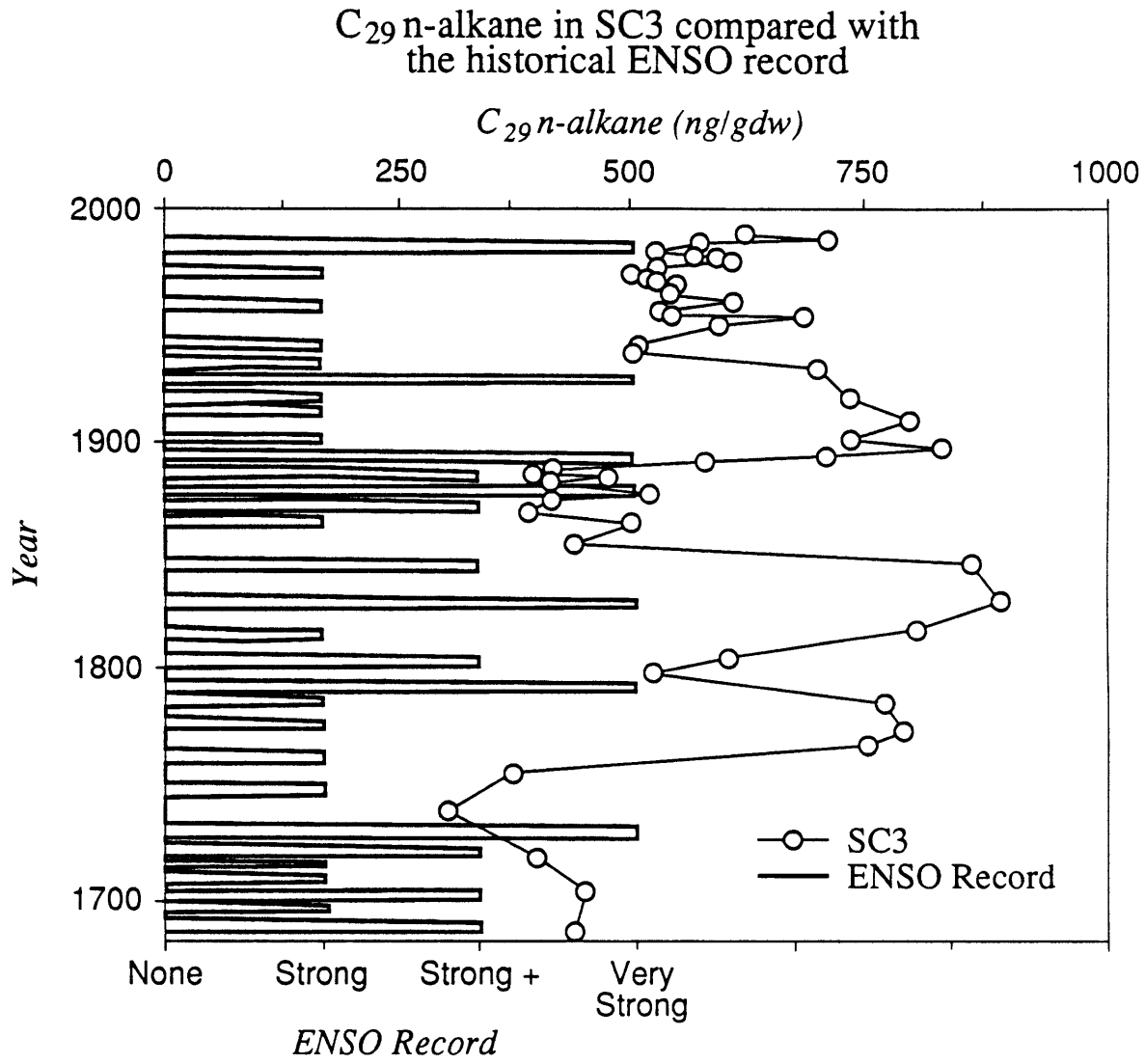

Figure 12: Comparison of the C_{29} n-alkane profile in SC3 with the historical ENSO record compiled by QUINN et al. (1987),who define 'Very Strong' events as having SST anomalies of 7-12°C, 'Strong' events as having anomalies of 3-5°C, and 'Strong+' events as being intermediate in intensity between Strong and Very Strong. The time scale for SC3 was calculated from the ^{210}Pb-derived sedimentation rate of 41.06 mg $cm^{-2}yr^{-1}$. ENSO events are plotted as being 4 years long to account for sediment mixing.

input could account for the entire inventory of long-chain n-alkanes and n-alkanols in SC3 if aerosols are a significant source of terrigenous sediment in this core. We converted the concentration units that SCHNEIDER and GAGOSIAN (1985) used (μg lipid/m^3 of air) into units of μg lipid/g Al, by using the value of 116 ±7 ng Al /m^3 air reported by RAEMDONCK and MAEHAUT (1986) for an aerosol collected from 14-12°S along the Peru coast. SCHNEIDER and GAGOSIAN (1985) report C_{29} n-alkane ≈140 pg/m^3, which can be converted to 1210 ±70 μg C_{29} n-alkane/ g Al aerosol. In the SC3 sediments analyzed for Al, the C_{29} n-alkane concentrations are 12-24 μg/g Al. If the Al in these samples is entirely aerosol-derived, then (using the value of 1210 ±70 μg C_{29} n-alkane/ g Al aerosol) only 1-2% of the C_{29} n-alkane associated with the aerosols would have to survive transport through the water column to account for the entire C_{29} n-alkane inventory in these sediments.

Fluvial sediments and aeolian dusts from the Peru coast have equivalent mineralogies (SCHEIDEGGER and KRISSEK, 1982). In addition, the direction of offshore oceanic sediment transport is coincident with dust trajectories (SCHEIDEGGER and KRISSEK, 1982). As a result, the relative importance of aeolian and runoff sources of terrigenous detritus to coastal Peruvian sediments is difficult to determine. SCHEIDEGGER and KRISSEK (1983) estimated the terrigenous detritus input from continental runoff to coastal Peruvian sediments (10°-14°S) and determined a value close to their estimate of terrigenous sediment accumulation over this area; however, these estimates have substantial uncertainties. It is possible that a significant fraction of the sedimentary terrigenous detritus at 15°S has an aerosol origin, given the arid coastal conditions (precipitation < 0.8 cm/ yr at 15°S; JOHNSON, 1976), the significant mineral aerosol concentration (RAEMDONCK and MAEHAUT, 1986), and the low average continental runoff (SCHEIDEGGER and KRISSEK, 1982). Furthermore, aerosol input to coastal sediments may be greater at 15°S than it is further north, since precipitation along the Peru coast decreases progressively to the south (JOHNSON, 1976).

III. PALEOENVIRONMENTAL IMPLICATIONS OF STANOL/STENOL RATIOS

The stanol/stenol ratio in sediments (stanol referring to saturation of the ring system, not the side chain) may hold a record of changes in the redox conditions of surface sediments. NISHIMURA and KOYAMA (1977) examined the stanol/stenol ratios in four lakes, and found the highest ratios in the two anoxic lakes, lower ratios in a seasonally anoxic lake, and the lowest ratios in a year-round oxic lake. They proposed that in anoxic sediments the stanol/stenol ratio is a function of the rate of stenol reduction to stanols which they suggested was controlled by the surface-sediment redox conditions. GAGOSIAN et

al. (1980b) supported this conclusion and reported substantially lower stanol/stenol ratios in oxic sediment from the western North Atlantic than in anoxic sediment from the Black Sea and Walvis Bay. The stanol/stenol ratio in oxic sediments may also be affected by selective degradation of stenols relative to stanols (NISHIMURA and KOYAMA, 1977); however, this process is not as significant in anoxic sediments, where stenol hydrogenation is rapid relative to stenol degradation (GASKELL and EGLINTON, 1976; NISHIMURA and KOYAMA, 1977).

For each of the Δ^5 stenols measured in SC3, we determined profiles of the 5α(H)-stanol/ stenol ratio. With the exception of the 24-ethylcholest-22-en-3ß-ol/24-ethylcholest-5,22-dien-3ß-ol ratio, the other ratios increase by factors of 2-4 from 0 to 4 cm (i.e., Fig. 13 and 14). Comparison of these data with data for a core from ≈15°S deposited under more oxic depositional conditions (core BC7, VOLKMAN et al., 1987) suggests that the high stanol/stenol values in SC3 are the result of stenol reduction caused by reducing depositional conditions. In BC7, VOLKMAN et al. (1987) report very little down-core variation in stanol/stenol ratios. Their data for cholestanol and cholesterol correspond to a stanol/stenol ratio ranging from 0.22 (0-1 cm) to 0.28 (16-19 cm), with the highest value, 0.57, occurring at 8-9 cm. The water depth of BC7, 85 m, is either outside of or on the upper edge of the OMZ (which may fluctuate in lateral extent), while SC3 was collected from 253 m, the OMZ center. FOSSING (1990) found that at the time SC3 was collected, pore-water dissolved O_2 in the OMZ decreased to zero by 2 mm sediment depth. This difference in depositional environment is reflected in the much lower TOC in BC7 (2-4 wt %) than in SC3 (6-12 wt %). The differences between the sampling locations of SC3 and BC7 suggest that the higher stanol/stenol values in SC3 are probably the result of stenol hydrogenation in SC3 which occurred under more reducing conditions than existed in BC7.

Below the first few cm of SC3, the cholestanol/cholesterol ratio is correlated with the sedimentary TOC (Fig. 13). The correlation of TOC with the stanol/stenol ratio implies a relationship between the TOC and the efficiency of the stenol hydrogenation. A significant difference between the cholestanol/cholesterol profile and the TOC profile is that the increase in TOC from 47 to 30 cm is ≈10 cm shallower than the increase in the cholestanol/cholesterol ratio from 55 to 40 cm. The 10 cm offset in the TOC and cholestanol/cholesterol profiles may be explained if deposition of higher TOC sediments resulted in more reducing conditions to 10 cm below the sediment-water interface. The TOC correlation with cholestanol/cholesterol cannot be the result of TOC-induced changes in the sedimentary redox potential (E_H), since below 2 mm sediment depth (oxygen decreases to zero at 2 mm; FOSSING, 1989) sulfate is the dominant electron acceptor

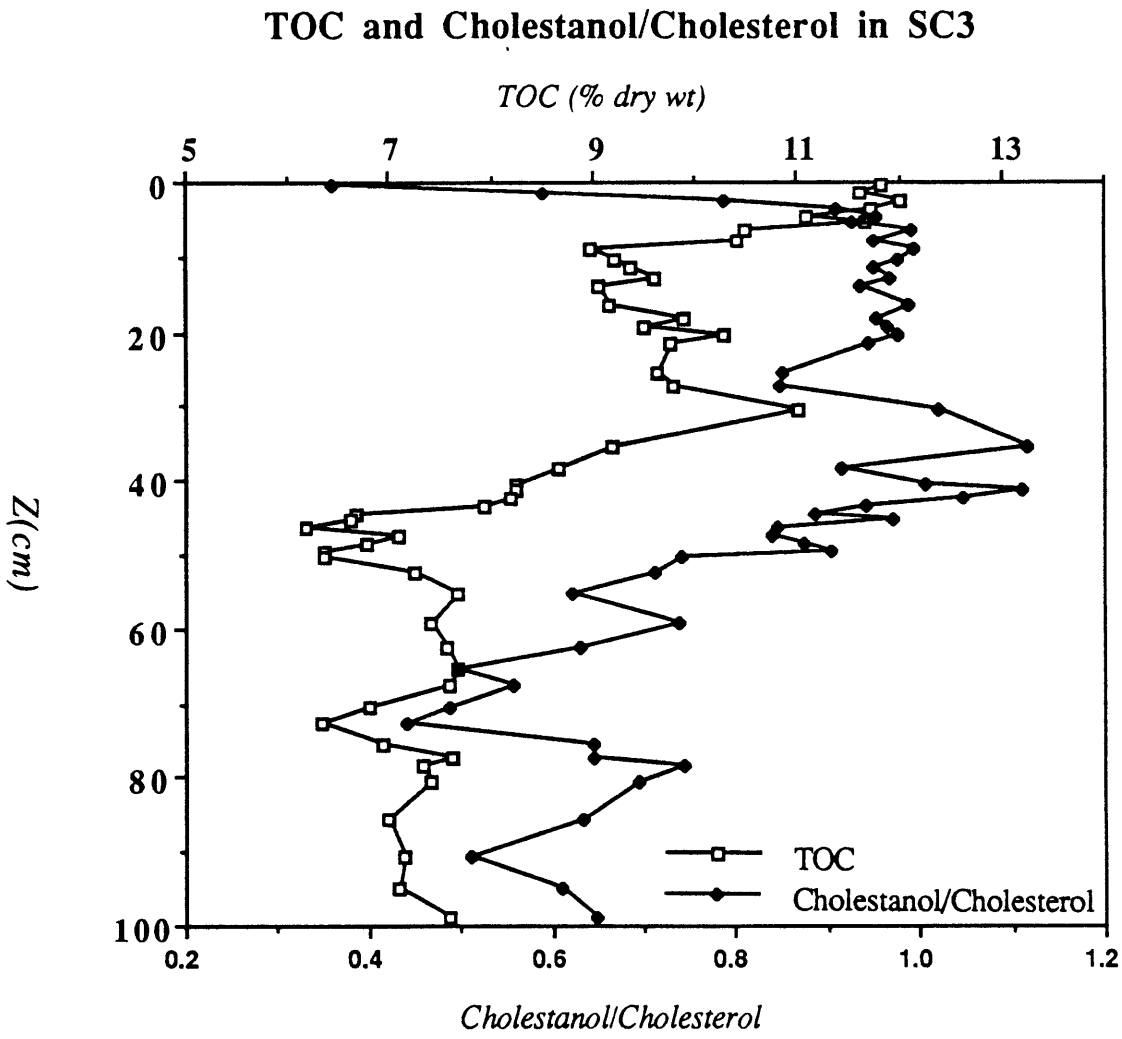

Figure 13: TOC and cholestanol/cholesterol in SC3.

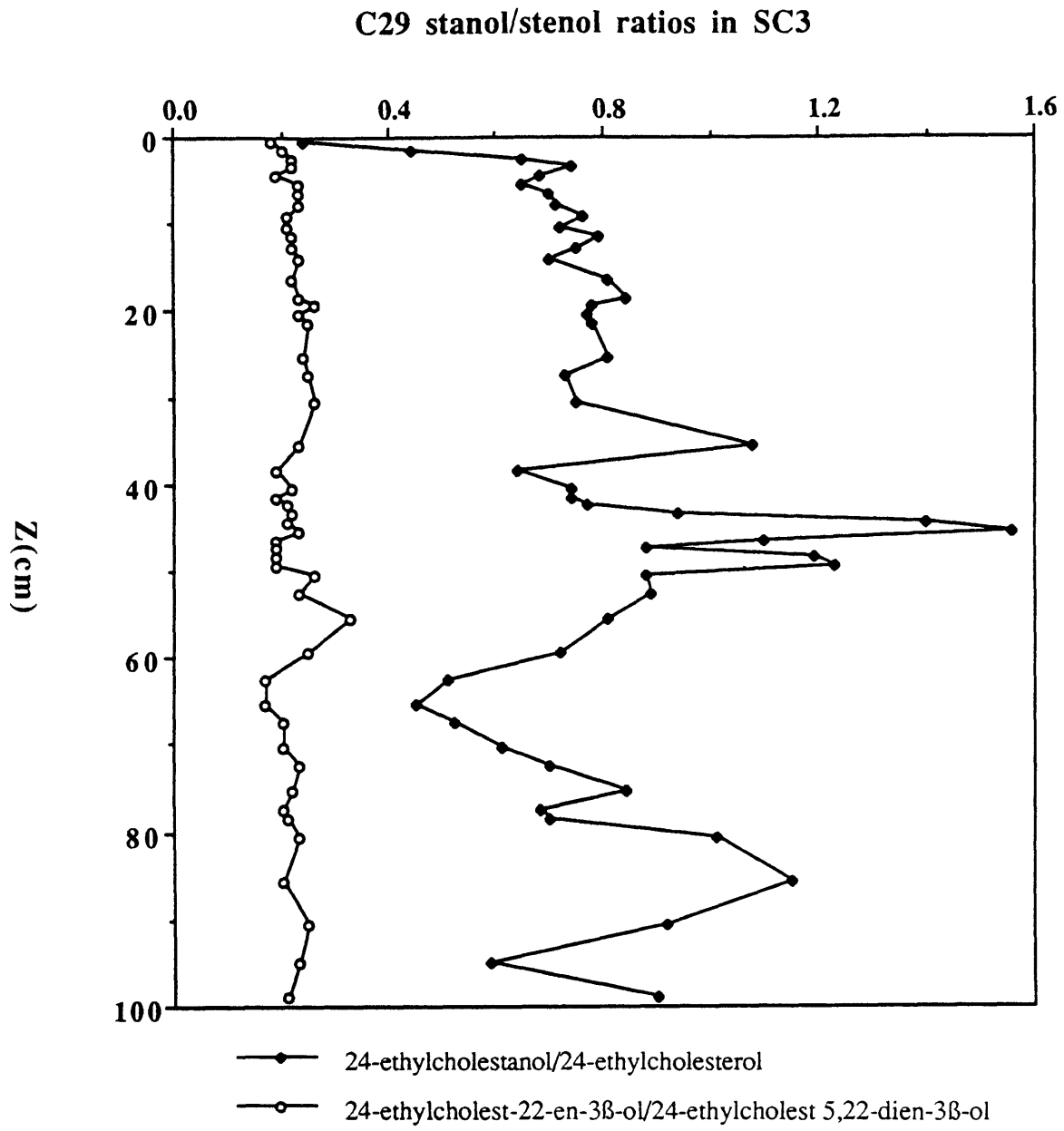

Figure 14: C_{29} stanol/stenol ratios in SC3.

throughout the 100 cm of SC3. Therefore, the TOC correlation with cholestanol/cholesterol suggests that a reductant proportional to TOC is involved in the stenol hydrogenation.

The profile of the 24-ethylcholestanol/ 24-ethylcholesterol ratio in SC3 (Fig. 14) is characterized by a maximum from 42-49 cm. In the ^{210}Pb chronology for SC3, 42-49 cm corresponds to 1870-1891 a period of frequent El Nino activity; this section also corresponds to a maximum in the alkenone-U^k_{37} temperature profile (McCAFFREY et al., 1990), an additional indicator of El Niño. This sediment interval is a minima in the TOC and aluminosilicate profiles and has an unusual abundance of centric diatom (*Coscinodiscus*) frustules, which are the dominant sedimentary component in this section. The high 24-ethylcholestanol/ 24-ethylcholesterol ratio may be the result of selective degradation of the stenol relative to the stanol during reworking of this section under more oxic depositional conditions induced by the ENSO activity. This scenario is consistent with (1) the low absolute concentrations of 24-ethylcholestanol and 24-ethylcholesterol in this section, and (2) our finding of very high 24-ethylcholestanol/ 24-ethylcholesterol ratios (1.2-4.5) in the more oxic surface sediments we analyzed from outside the OMZ (25 m, 30 m and 50 m water depth). The lack of a maximum in the cholestanol/cholesterol ratio (Fig. 13) in this section indicates that 24-ethylcholestanol may also have been relatively more abundant than the other stanols at the time of deposition, perhaps as a result of an unusual constellation of plankton during this period.

The 24-ethylcholest-22-en-3ß-ol/24-ethylcholest-5,22-dien-3ß-ol ratio is remarkably constant ($\approx$ 0.20) throughout almost the entire core (Fig. 14). This observation is in striking agreement with the finding of NISHIMURA (1978) that during a 340 day anaerobic incubation experiment in lake sediments "no conversion of stigmasterol [24R-ethylcholest-5, 22-dien-3ß-ol] into stanol was observed" while cholesterol, campesterol and ß-sitosterol were significantly reduced to stanols. The constancy of this stanol/stenol ratio in SC3 is enigmatic, considering the variability in the other stanol/stenol ratios.

CONCLUSIONS

A principal components factor analysis of 35 lipids and TOC in 50 sections of a core from the OMZ of the Peru margin at 15°S yielded five factors explaining 91.31% of the variance in the data. The composition of the factors and the downcore plots of the factor scores have implications for the utility of these lipids as indicators of (1) certain depositional conditions and (2) sources of sedimentary organic matter. Specific conclusions include the following:

• Factor 1 primarily represents input of planktonic lipids to the sediment, including phytol, stenols, and tetrahymanol. The high loading of lycopane on this factor suggests that

the primary sedimentary input of lycopane is from the water column. The surface maximum in the lycopane profile is not consistent with a source from sedimentary methanogenic bacteria. Therefore, lycopane cannot be assumed to be a marker for organic matter input from methanogenic bacteria.

• Factor 2 consists primarily of odd-carbon-number n-alkanes and even-carbon-number n-alkanols. The correlation of these lipids with Al, Ti, Zr, Fe and sediment dry wt/ wet wt indicate that downcore fluctuations in factor 2 reflect fluctuations in the input of terrigenous sediment relative to marine sediment. The loading of the C_{29} stenols onto factor 1 and the lack of concordance between the C_{29} stenols and the inorganic indicators of terrigenous input suggest that the small actual contribution of stenols from higher plants to SC3 is obscured by the marine contribution of these stenols. Therefore, n-alkanes and n-alkanols may provide a better record of higher-plant input than is provided by C_{29} stenols in areas of high primary productivity and low higher-plant input, such as the Peru margin.

• Factor 3 consists primarily of monohydroxy hopanols. Differences between profiles of hopanols (factor 3) and planktonic markers (factor 1) near the sediment-water interface probably reflect the lack of a post-depositional input of the plankton markers and the substantial post-depositional input of the bacterial hopanols. The hopanols are well-correlated with TOC, a reflection of the linkage between sedimentary bacterial biomass and the quantity of available substrate. The high loading of a C_{27} B-ring monoaromatic anthrosteroid on this factor may suggest that this compound is formed in the water column and/or near the sediment-water interface and is resistant with respect to degradation.

• Factor 4 consists of C_{30} and C_{32} alkan-15-one-1-ols, which may be from planktonic cyanobacteria. These compounds are not well-correlated with any of the other lipids measured. In addition, the alkan-15-one-1-ols appear to be significantly more resistant to degradation than the planktonic markers loaded on factor 1.

•The n-alkane CPI profile for SC3 provides a less-sensitive record of fluctuations in the terrestrial input than the concentration profiles of the individual n-alkanes and n-alkanols. The profiles of long-chain n-alkanes and long-chain n-alkanols are *not* well-correlated with the historical El Niño record; in SC3, these compounds probably do not provide a record of continental runoff, but may represent either aeolian input from the continent or input of resuspended near-shore sediment originally derived from continental runoff.

• Similarities between the profiles of TOC and cholestanol/cholesterol suggests that a reductant proportional to TOC is involved in the stenol hydrogenation. The offset observed between the TOC profile and the cholestanol/cholesterol profile suggests that changes in the

redox conditions at the sediment surface affect the stanol/stenol ratio as much as 10 cm into the underlying sediments.

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CHAPTER 5

THE IMPACT OF DIAGENESIS ON STEROID AND PENTACYCLIC TRITERPENOID BIOMARKER APPLICATIONS

5.1 Introduction

As much as 90% of the primary production in the Peru upwelling area at 15°S is remineralized in the water column (Lee and Cronin, 1982; Henrichs and Farrington, 1984). Furthermore, pore-water nutrient profiles (Henrichs and Farrington, 1984) and sulfate reduction rates (Fossing, 1990) demonstrate that much of the organic matter reaching sediments in the OMZ is remineralized within several years of deposition, despite the bottom-water dysoxia and the lack of benthic macrofauna. Fossing (1990) reports that at 15°S the rate of sulfate reduction in OMZ sediments is equivalent to remineralization of 9-29% of the primary production, with more than 50% of the sulfate reduction occurring from 0-20 cm where core SC3 was collected (253 m water depth). As discussed in the previous chapter, the distribution of lipids in surface sediments of the OMZ is profoundly altered during early diagenesis, and many compounds (such as stenols, phytol, tetrahymanol, lycopane, and C_{20} and C_{25} acyclic isoprenoid alkenes) rapidly decrease in concentration downcore.

Numerous studies have sought to understand the rapid concentration decreases of sedimentary organic constituents near the sediment-water interface. Berner (1980) and Westrich and Berner (1984) proposed the "multi-G model," which states that sedimentary organic matter consists of several components each of which decay by first order kinetics, but with different decay constants. According to this model, concentration profiles consist of several superimposed first-order decay profiles. With increasing depth in the sediment, the organic matter components with the lowest rates of decay become a progressively more important part of the total organic matter. Middleburg (1989) carried this model to the extreme, by proposing the equivalent of a G model with an infinite number of components. Middleburg (1989) suggested that rapid decreases in sedimentary organic matter concentrations with increasing depth result from a continuous decrease in the average decay rate of the organic matter with increasing time. Although organic matter profiles calculated with these models accurately mimic the observed organic matter concentration decreases in sediments, a physical interpretation of these concentration decreases is more speculative. One interpretation is that some organic matter is more resistant to degradation because of its form (e.g., Henrichs and Doyle, 1986); as discussed in chapter 4 with regard to terrigenous lipids, compounds associated with complex biopolymers may be more resistant to remineralization than the same compounds associated with a less refractory matrix.

Whatever the cause of the rapid post-depositional loss of lipids in SC3, this loss illustrates that even in sediments from the OMZ, post-depositional alteration and remineralization of compounds may, on a time scale of several years, result in the almost complete loss of some biomarkers which are abundant near the sediment-water interface. Unless stable alteration products of these compounds can be identified in the sediments, the paleoenvironmental information associated with these compounds is lost with their degradation.

In this chapter, the distribution of cholesterol and cholesterol alteration products in SC3 is discussed in detail as an example of the effects of early diagenesis on the distribution of sedimentary steroids. Steroid and pentacyclic triterpenoid diagenesis in surface sediments is then discussed with regard to the utility of these compounds as sedimentary indicators of organic matter source and paleoenvironmental conditions.

5.2 Stenol loss during early diagenesis

Gagosian et al. (1983) calculated that the fraction of stenol primary production preserved in sediments at 15°S is approximately twice the fraction of TOC preserved and 1.5 times the fraction of amino acids preserved. Nevertheless, stenol degradation is quite intense; Gagosian et al. (1983) estimated that only 10-50% of the stenols produced in the euphotic zone (≈0-14 m) at 15°S are exported to deeper depths, primarily by incorporation into anchovy and zooplankton fecal pellets and zooplankton molts and carcasses. Furthermore, only 5-20% of the original stenol production reaches 52 m water depth, and only 1.5-6% of the original stenols survive diagenesis in surface sediments (Gagosian et al., 1983). A rapid decrease in the concentration of solvent-extractable steroids below the sediment-water interface is a widespread phenomenon that has been found in a range of sedimentary environments (Lee et al., 1980). Sterols in SC3 decreased in concentration (Fig. 5.1) approximately exponentially from 0-4 cm (≈6 years of deposition, as indicated by ^{210}Pb dating); the best exponential fits to the sterol profiles from 0-4 cm yielded first order decay rates (Table 5.1) ranging from a low of 0.145 yr^{-1} for dinosterol to a high of 0.536 yr^{-1} for cholesterol. Stenol concentrations below 4 cm decreased less rapidly (Fig. 5.2), and TOC-normalized concentrations varied by less than a factor of 2 from 10-100 cm.

The rapid decrease in stenol concentrations in the surface sediments of SC3 is the result of (1) stenol alteration to other steroidal compounds, (2) stenol remineralization, and possibly (3) the formation of bound steroids* from free stenols. The relative importance of each of these processes is discussed below.

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* The term "bound steroids" is used here to refer to steroids not extracted from organic matter using the ultrasonic solvent extraction method described in chapter 2.

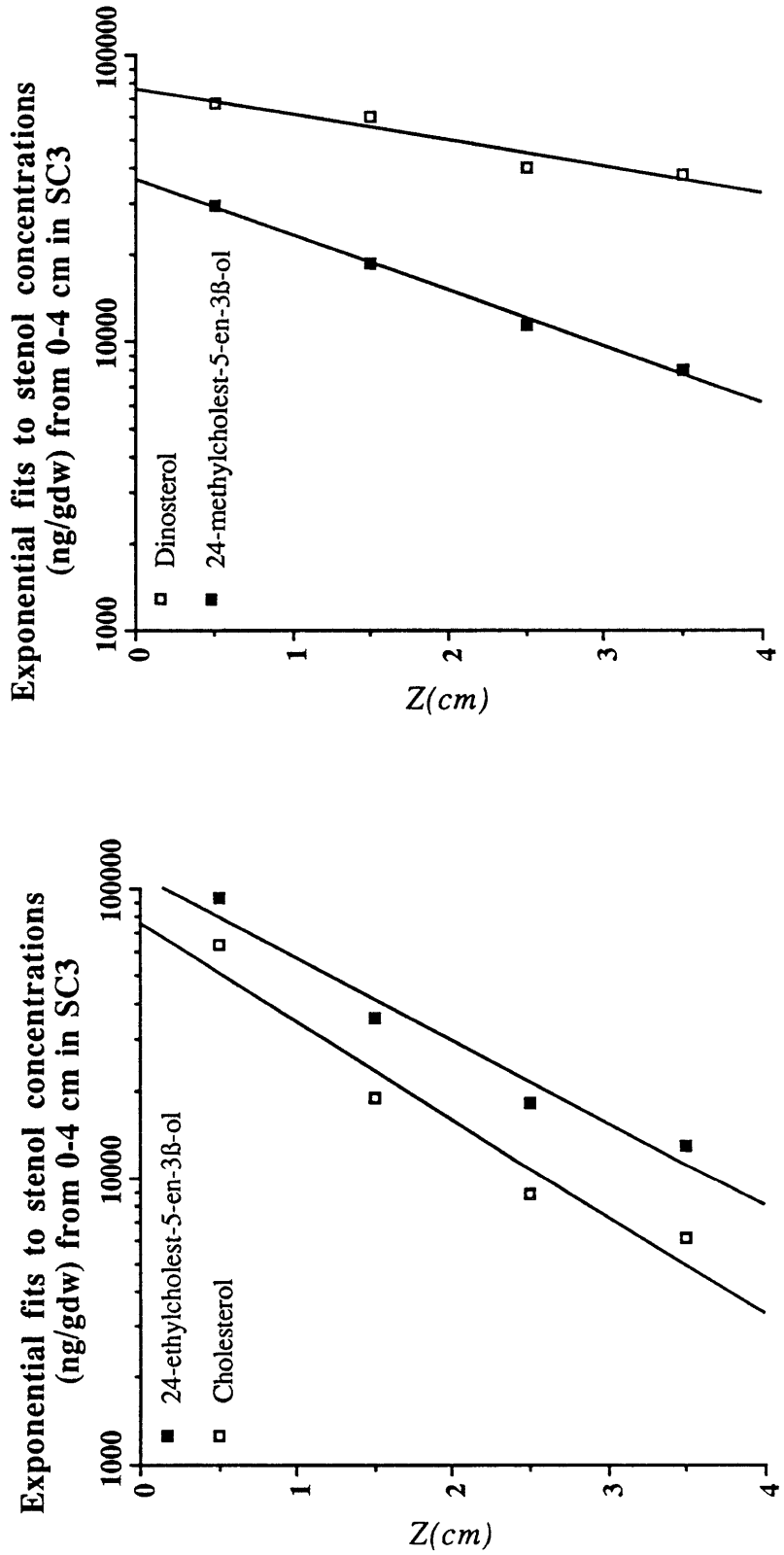

Figure 5.1: Exponential fits to stenol concentrations (ng/gdw) from 0-4 cm in SC3. Table 1 gives the rates of decay indicated by these fits.

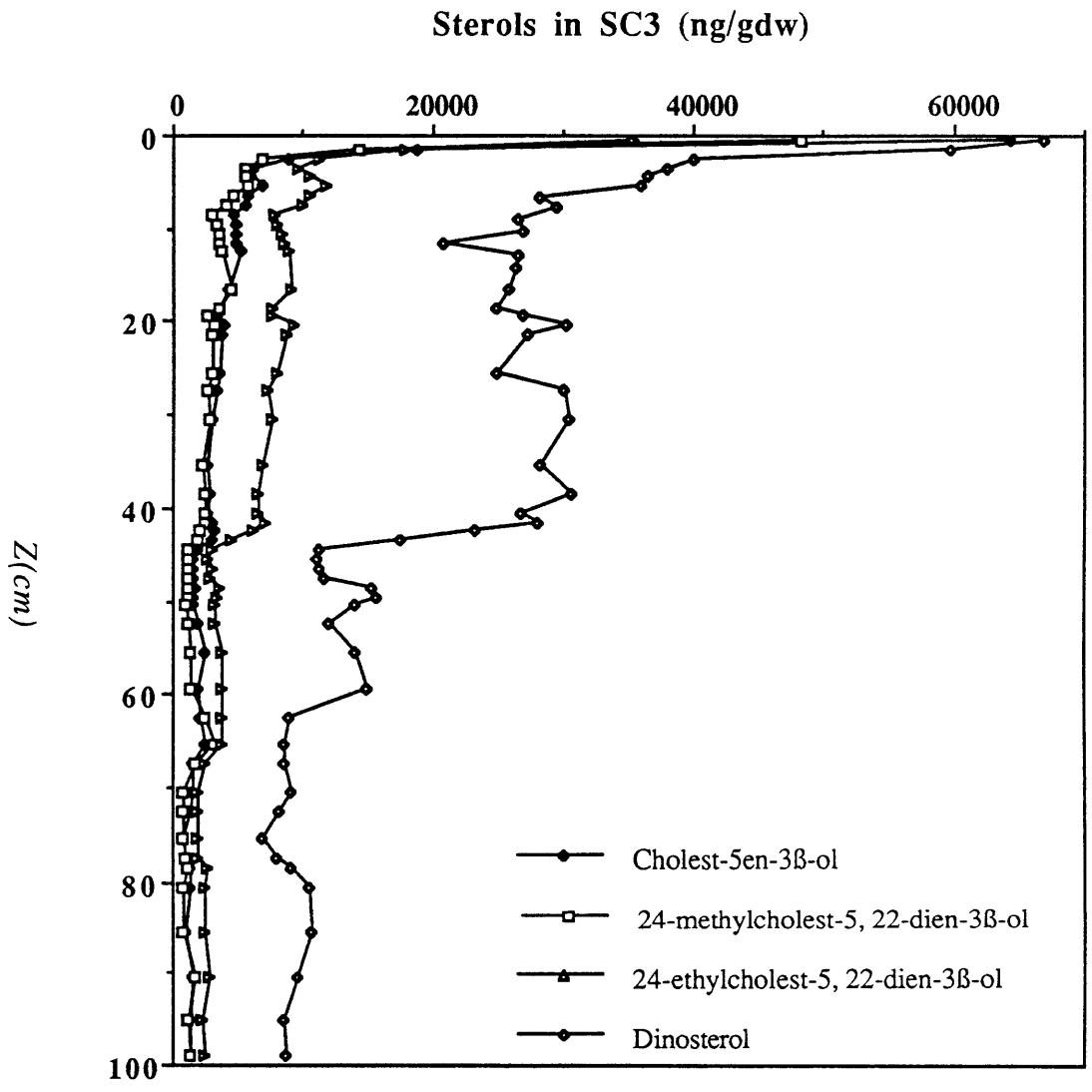

Figure 5.2: Concentration profiles (ng/gdw) of selected stenols in SC3.

Table 5.1
First-order decay rates of stenols from 0-4 cm in SC3

The accumulation rate for SC3 is 41.06 mg/cm^{2}yr (see chapter 3); using the average value of dry wt/wet wt for 0 - 4 cm calculated from appendix 1, the average sedimentation rate can be calculated to be 0.69 cm/yr from 0-4 cm. Using this sedimentation rate, the exponential fits to the stenol concentrations from 0-4 cm correspond to the following first-order rates of decay (λ):

Stenol	λ (yr^{-1})	R^2 of fit
Cholesterol	0.54	0.94
24-methylcholest-5, 22-dien-3ß-ol	0.50	0.91
Cholest-5, 22-dien-3ß-ol	0.49	0.92
24-ethylcholest-5-en-3ß-ol	0.45	0.96
24-methylcholest-5-en-3ß-ol	0.31	0.995
24-ethylcholest-5, 22-dien-3ß-ol	0.30	0.93
Dinosterol	0.15	0.91

The alteration of cholesterol to other steroidal compounds

The 4-desmethylsteroids are biosynthesized as stenols and, to a lesser extent, as stanols (Nishimura and Koyama, 1977). Although thermally immature ancient sediments may contain sterols (e.g., Cretaceous DSDP sediments, Comet et al., 1981) or sterenes (e.g., Miocene Monterey Shale, Giger and Schaffner, 1981), steroids occur only as steranes and aromatic compounds in more thermally mature ancient sediments and oils. Many of the precursor-product relationships relating biologically produced sterols to "geosteroids" found in ancient sediments have been elucidated by numerous studies summarized by Mackenzie et al. (1982), de Leeuw and Baas (1986), and de Leeuw et al. (1989). Three discrete alteration pathways can be distinguished for 4-desmethyl Δ^5 stenols, and these are shown in Fig. 5.3: (I) formation of a 3, 7-diol by oxidation of C-7, and subsequent formation of cholestatrienes and cholestatriene alteration products, (II) dehydration of the alcohol to form cholestadienes and cholestadiene alteration products, and (III) oxidation of the alcohol to cholestenone, followed by formation of cholestanone, cholestanol, cholest-2-ene and cholestane. The alteration pathways proposed for formation of geosteroids, such as polyaromatic compounds, during catagenesis are not shown. The six alteration products of cholesterol which have been found in SC3 are indicated in Fig. 5.3 by circles around the compound numbers. The exact locations of the double bonds in the cholesta-N, N, N- triene (compound 12) found in SC3 are not known. The GC-MS spectrum of this compound is spectrum II in appendix 3.

Wakeham et al. (1984) reported cholest-2-ene and cholesta-3,5-diene in suspended particulate matter in the eastern tropical North Pacific. *All* of the cholesterol alteration products found in SC3 could be identified in the 0-1 cm section, illustrating that these compounds can be formed in the water column and/or at the sediment-water interface during the most initial stages of diagenesis. It is interesting that in SC3 the downcore increase in burial time (100 cm ≈ 310 years b.p.) and the downcore changes in sediment chemistry did not result in accumulation of cholesterol alteration products from more advanced portions of the alteration pathways than are achieved in the 0-1 cm interval. Specifically, the absence of cholest-4-ene, cholest-5-ene and cholestane suggests that cholestadiene reduction to cholestenes and cholestene reduction to cholestane do not occur on the time scale and under the sedimentary conditions represented by SC3. De Leeuw et al. (1989) presented compelling theoretical and empirical evidence that cholest-5-ene is produced by the selective reduction of cholest- 3, 5-diene, rather than by isomerization of cholest-2-ene (previously proposed; e.g., Mackenzie et al., 1982; McEvoy and Maxwell,

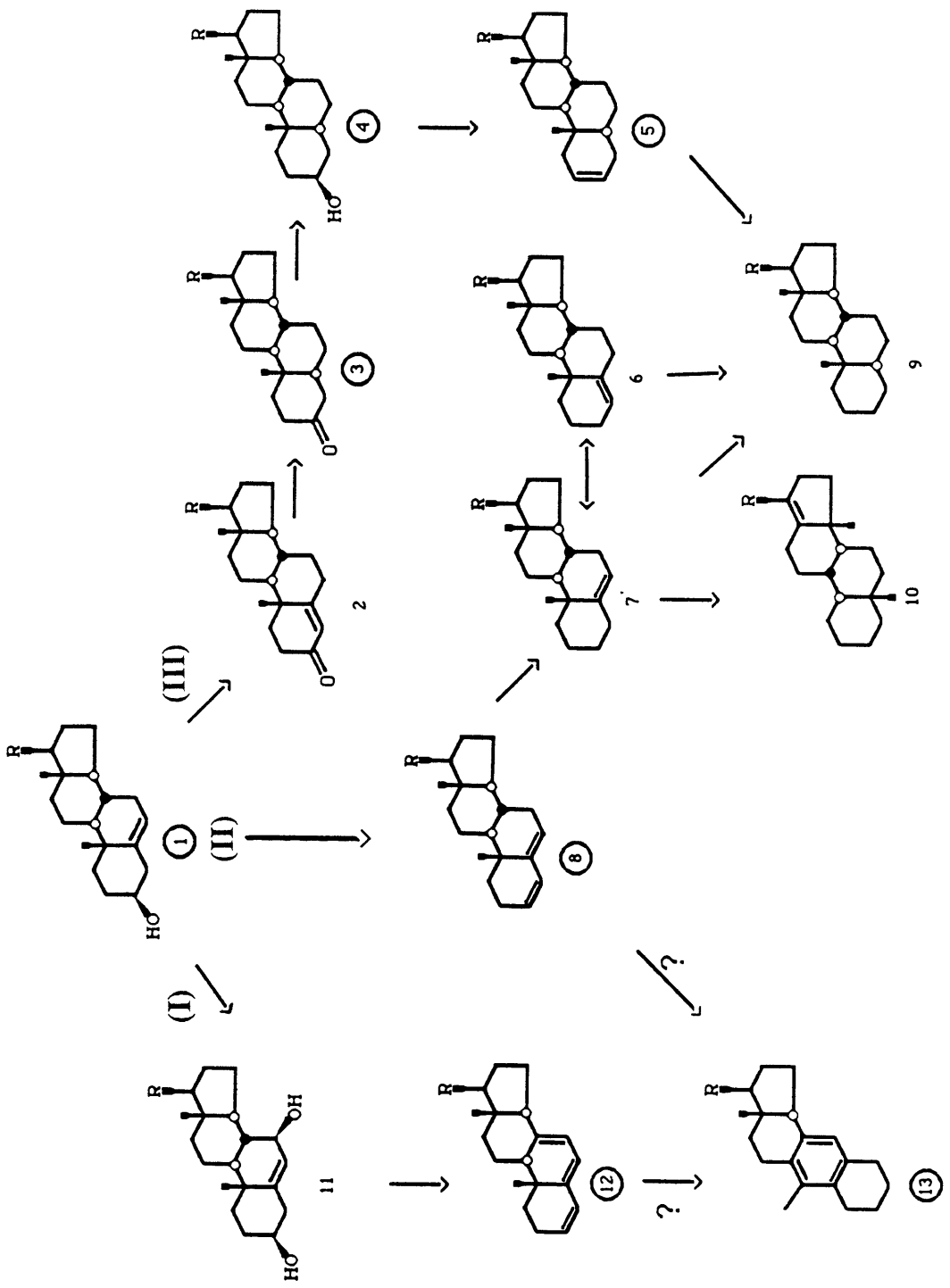

Figure 5.3: Diagenetic alteration pathways of 4-desmethyl Δ^5 stenols. Circled compound numbers indicate the cholesterol derivatives [R= 2-(6-methylheptane)] found in SC3. In SC3, the unsaturations in the cholestatriene (compound 12) are nuclear, but the exact double bond locations are uncertain (GC-MS spectrum II, appendix 3).

1983) which would necessitate an unstable secondary carbocation intermediate. Cholest-4-ene is then formed by the isomerization of cholest-5-ene; neither of these compounds are present in SC3. GC-MS inspection of the cholestane elution time in the alkane chromatogram (as determined by prior co-injection with an authentic standard) indicated that cholestane was not present even in trace amounts in the 0-1 cm and 98-100 cm sections. The GC traces of the other 48 sections of SC3 also revealed no substantial peaks at the cholestane elution time. Studies of DSDP sediments (e.g., Rullkötter et al., 1981; Rullkötter and Welte, 1983) have shown that progressive reduction of sterenes to steranes under average geothermal gradients is not complete until burial to several hundred meters. The data for SC3 show that in these sediments this reduction does not even begin in the surface 1 m.

The cholesta-N, N, N-triene is the only cholesterol alteration product found in SC3 which is not found throughout the core. Most abundant at the top of the core, this compound decreases in concentration to ≈ 0 by ≈ 65 cm. Compound 13 in Fig. 5.3, 14α(H)-1(10→6)-abeocholesta-5,7,9 (10)-triene (hereafter, C_{27} anthrosteroid) is the only cholesterol alteration product found in SC3 which has also been found in ancient sediments (DSDP sediments of various ages ranging from Recent to Cretaceous, Hussler and Albrecht, 1983; Brassell et al., 1984; ten Haven et al., 1990). As discussed in chapter 4, the profile of the C_{27} anthrosteroid is remarkably constant from 0-43 cm (mean ± st. dev.= 973 ± 154 ng/gdw). The proposed precursor to this compound is a cholestatriene or cholestadiene (Brassell et al., 1984). Since the cholestenes measured in SC3 are most abundant near the top of the core, the constancy of the C_{27} anthrosteroid profile may indicate that (1) formation of the C_{27} anthrosteroid from a sterene occurs primarily in the water column and/or at the sediment-water interface and (2) very little of the C_{27} anthrosteroid degrades following formation. The presence of only the 14α[H] isomer of the C_{27} anthrosteroid rules out the possibility that this compound represents input of ancient organic matter from the continent, since isomerization at C-14 occurs relatively quickly during diagenesis (Rullkötter and Welte, 1983; Brassell et al., 1984).

The only other anthrosteroid found in SC3 was a C_{28} tetraunsaturated compound [GCMS spectrum XXXV in appendix 3]. Ten Haven et al. (1990) identified an anthrosteroid with the same mass spectrum in ODP sediments from the Peru margin and suggested that the compound contained all nuclear double bonds. However, I suggest that the extra unsaturation is at C-22 and M/e 294 = cleavage of the 22-23 bonds. Therefore, I suggest that the compound is 24-methyl, 14α(H)-1(10→6)-abeocholesta-5,7,9 (10), 22-tetraene, which may be derived from a sterene derived from brassicasterol (24-methylcholesta-5, 22-dien-3ß-ol), an abundant sterol in surface sediments from this area.

Since C_{29} anthrosteroids were not detected in the Peru sediments (but have been found in ancient DSDP sediments, Brassell et al., 1984), formation of C_{29} anthrosteroids from C_{29} sterenes may occur over a longer time scale than formation of the C_{27} and C_{28} compounds found in SC3.

Figure 5.4 shows the absolute concentrations and relative abundances of cholesterol and cholesterol alteration products in the 0-1 cm and 98-100 cm intervals of SC3. This figure illustrates the tremendous decrease below the sediment-water interface in the abundance of cholesterol and cholestanol relative to the other cholesterol alteration products. However, most of the change in the relative abundances of cholesterol and the cholesterol alteration products occurs in the surface few cm. The ratio: [cholesterol alteration products] / [cholesterol + cholesterol alteration products] substantially increases from 0-4 cm (Fig. 5.5*), but at deeper depths, there is no systematic change in this ratio, which varies from 0.7-0.8 from 5-100 cm. This figure suggests that if there is a progressive conversion of cholesterol to these compounds below 4 cm, then it is obscured by an equally rapid removal of these alteration products from the sediments.

Figures 5.6 and 5.7 show the profile in SC3 of C_{TOT}, the sum of the concentrations of cholesterol, 5α-cholestanol, cholesta-3, 5-diene, cholesta-N, N, N-triene, and the C_{27} anthrosteroid. C_{TOT} decreases ≈75% from 0-3 cm, with most of this decrease representing loss of cholesterol and cholestanol. This figure further illustrates that the rapid decrease in the cholesterol profile near the sediment-water interface does not simply represent conversion of cholesterol into steroid degradation products, but must also involve steroid degradation and possibly formation of bound steroids.

Remineralization of stenols

In chapter 4, the rapid increase in the CPI from 0 to ≈40 cm in SC3 was explained as the result of rapid remineralization of marine-derived n-alkanes. Furthermore, it was noted that lycopane rapidly decreases in concentration below the sediment-water interface in cores SC3 and SC7. Because these saturated hydrocarbons do not possess functional groups which can facilitate cross linking into macromolecular organic matter, the post-depositional

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* Cholest-2-ene, which was only quantified in the 0-1 cm and 98-100 cm sections, was not included among the alteration products in Fig. 5.5. Cholest-2-ene, C_{28} n-alkane, and 22, 29, 30-trisnorneohop-13(18)-ene (which all occur in lipid Fraction 1) coelute under our GC analytical conditions. However, as described in chapter 2, $AgNO_3$-treated silica gel can be used to remove most alkenes, including cholest-2-ene from this fraction. Therefore, cholest-2-ene was quantified in the 0-1 and 98-100 cm intervals (Fig. 5.4) as the difference between the concentration of this peak in Fraction 1 and the concentration of this peak in the $AgNO_3$-treated Fraction 1. In these two core sections, cholest-2-ene is more than four times as abundant as the sum of C_{28} n-alkane and 22, 29, 30-trisnorneohop-13(18)-ene. This was confirmed by GC-MS analysis of these samples.

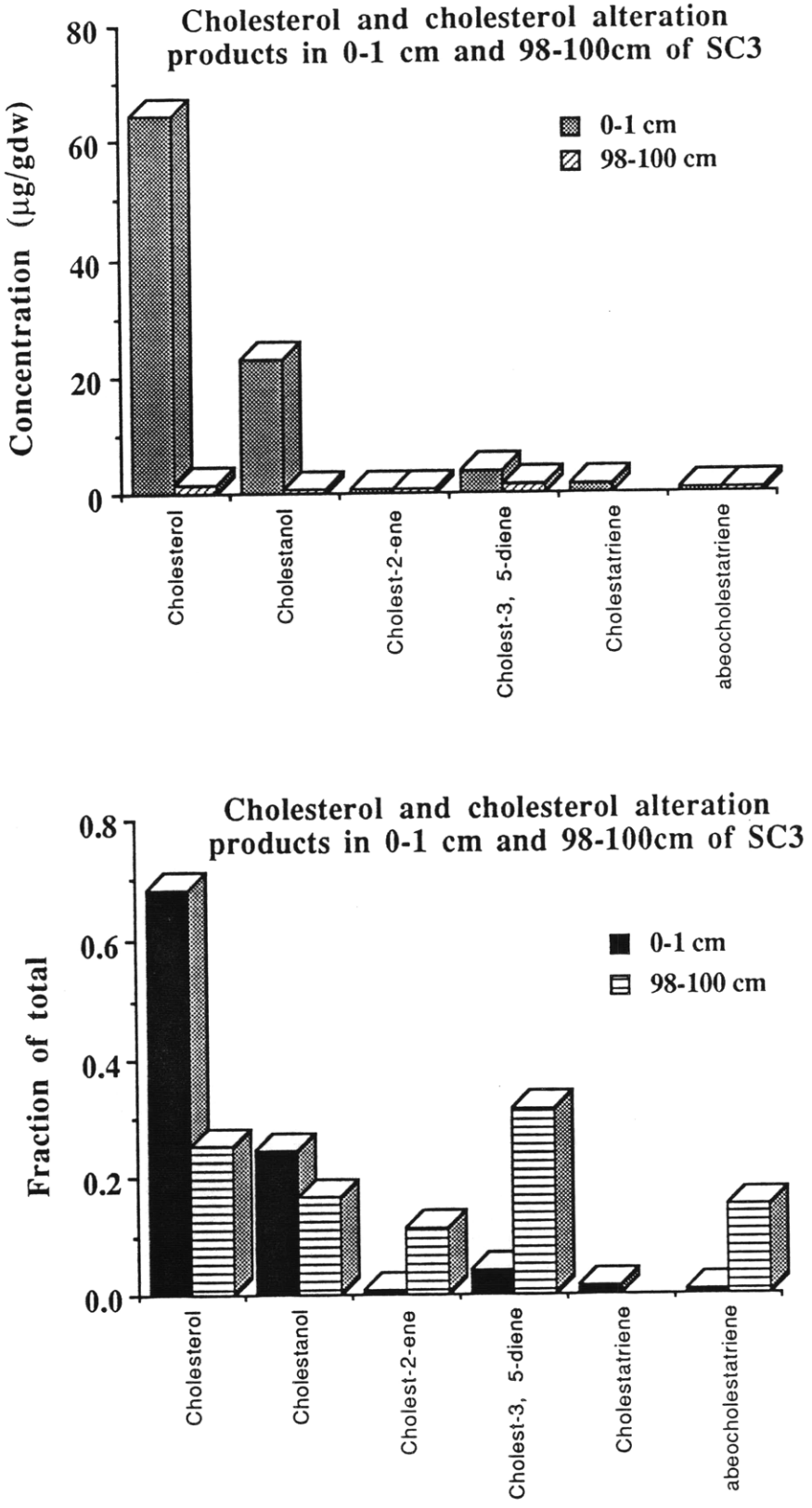


Figure 5.4: (A) Concentrations (µg/gdw) of cholesterol and cholesterol alteration products in 0-1 cm and 98-100 cm of SC3. (B) Cholesterol and cholesterol alteration products, shown as fraction of total, in 0-1 cm and 98-100 cm of SC3.

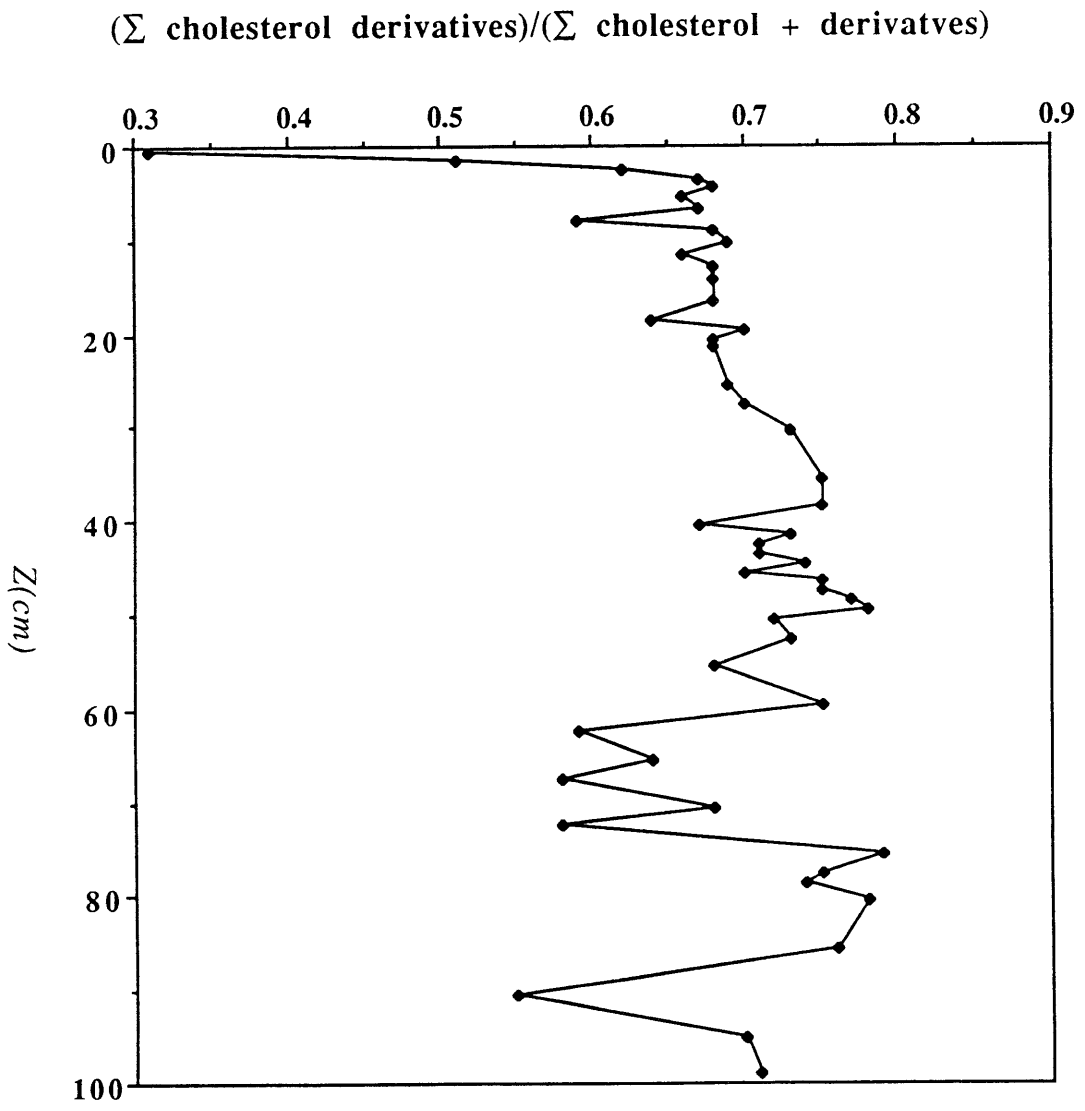


Figure 5.5: The ratio [5α-cholestanol + cholesta-3,5-diene + cholestatriene + abeocholestatriene] / [cholesterol + 5α-cholestanol + cholesta-3,5-diene + cholestatriene + abeocholestatriene] in SC3.

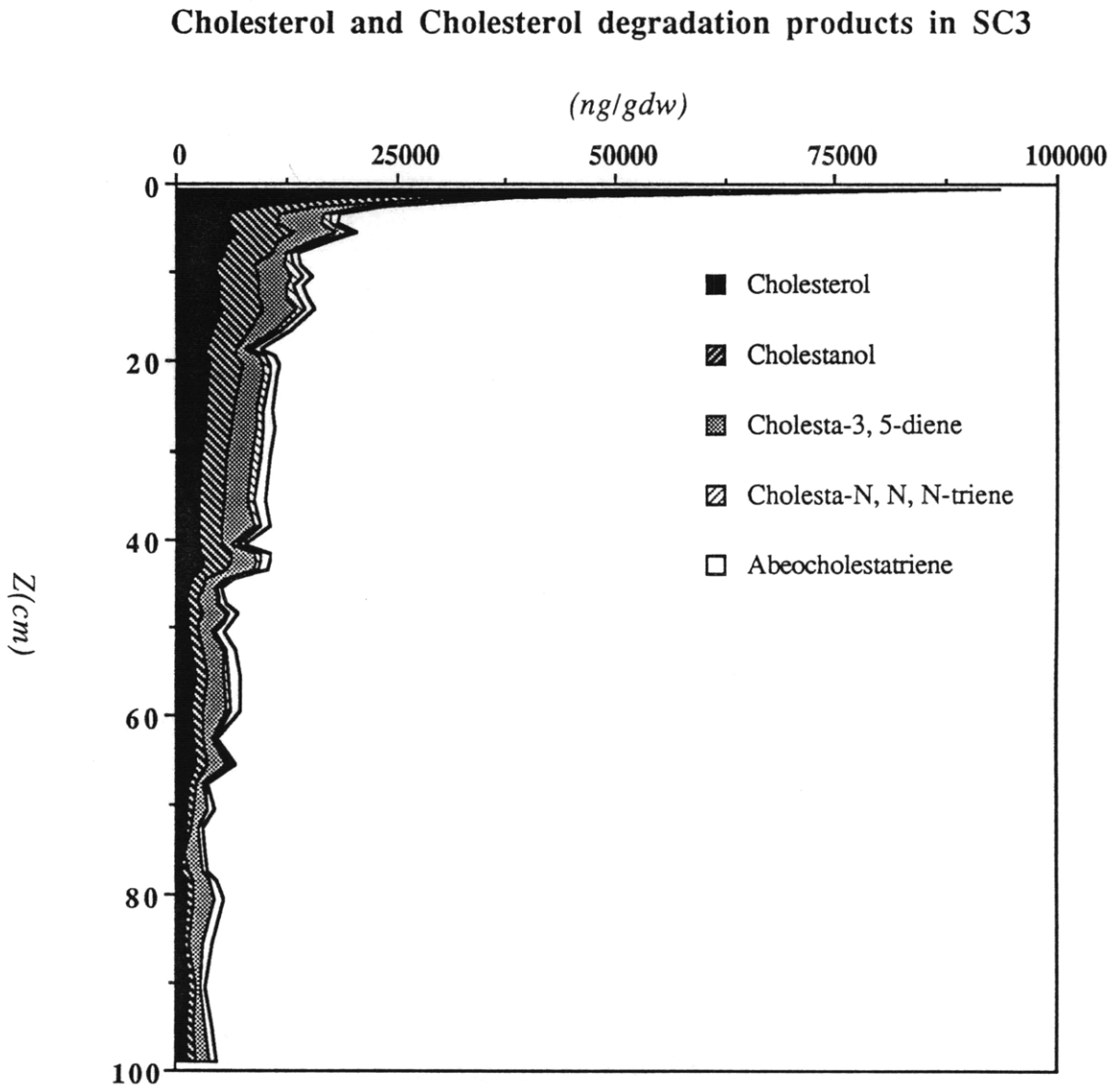


Figure 5.6: Concentration profiles of cholesterol and cholesterol degradation products in SC3, 0-100 cm.

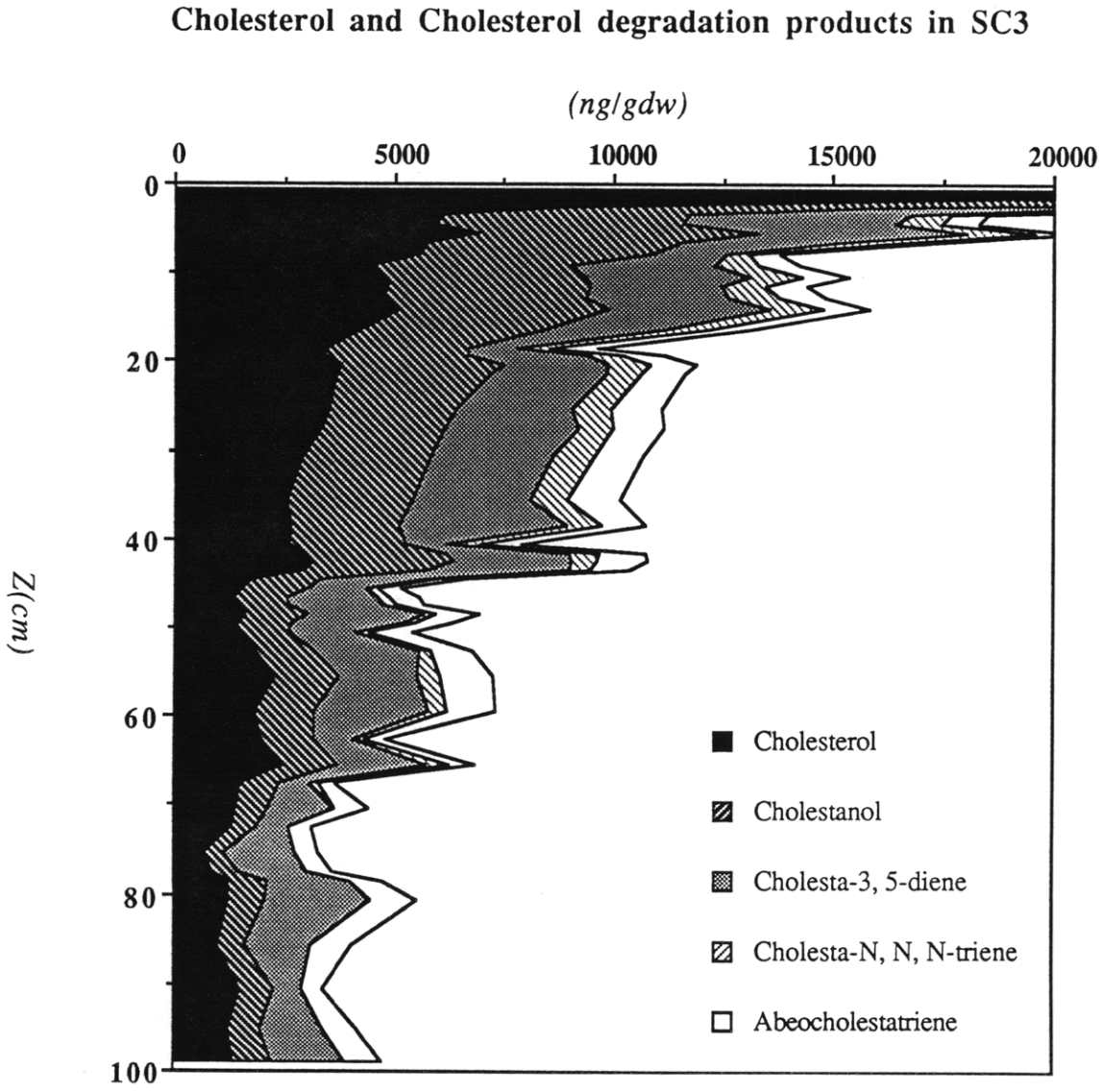


Figure 5.7: Detail of Figure 5.6.

loss of n-alkanes and lycopane is probably the result of degradation, rather than formation of bound compounds. Much of the post-depositional loss of stenols from the sediments must also be the result of degradation. Because of the alcohol moiety, stenols should be even more susceptible to microbial degradation than alkanes. The rapid loss of stenols which has been observed in the Peru margin water column (Gagosian et al., 1983), without a concomitant increase in bound stenol concentrations, further suggests that these compounds can be readily degraded.

Harvey et al. (1988) found that dinosterol is unaffected by passage through the gut of the copepod *Calanus helgolandicus*, whereas cholesterol is readily incorporated by this organism; they attributed the lack of both dinosterol uptake and dinosterol degradation to the absence of nuclear unsaturations in this compound. The differential loss of stenols from core SC3 (Table 5.1) is probably a result of both differences in the stenol structures and differences in the organic matter matrix with which the stenols are associated. The organic matter matrix associated with each stenol is partially a function of the respective sources of these steroids. The degradation and transformation of steroids in SC3 are probably primarily biologically mediated processes. However, since dissolved oxygen decreases from <0.1 ml O_2/l at the sediment surface to zero by a depth of ≈ 2 mm (Fossing, 1990), biological mediation of stenol degradation in SC3 was probably limited to fermenting bacteria.

Formation of bound stenols from free stenols

Bound steroids in organic tissues and surface sediments are primarily steryl esters (i.e., Lee et al., 1979). In ancient sediments, steroids may be bound by sulfide or polysulfide linkages to asphaltenes or kerogen (i.e., Sinninghe Damsté, 1989). Lee et al. (1980) noted that both ester-bound sterols and solvent-extractable sterols in Black Sea sediments decrease in concentration with depth. Degradation of organic matter containing ester-bound sterols could result in a post-depositional *release* of solvent-extractable sterols, but there are no data to indicate that *formation* of ester-bound sterols from free sterols occurs in sediments (de Leeuw et al., 1983). Nishimura (1977) studied the formation of bound sterols in lake sediment; with increasing depth, Nishimura found a constant stanol/stenol ratio in bound sterols but a sharply increasing stanol/stenol ratio in extractable sterols, suggesting no conversion of free sterols to bound form. Furthermore, Nishimura (1977) found no formation of bound cholesterol from free cholesterol during a 1200 day sediment incubation experiment.

At some point during the diagenesis of marine sediments, reduced inorganic sulfur species (such as H_2S and/or elemental sulfur) from sulfate reduction form steroid

thiophenes and also cross-link sterols or sterenes to macromolecular organic matter by aliphatic sulfide or polysulfide bridges. Steroids with thiophene side chains have been observed in crude oils (Sinninghe Damsté et. al., 1987, 1988, 1989), and pyrolyses of asphaltenes and kerogens have yielded alkylthiophenes presumed to be derived from bound steroids (Sinninghe Damsté et. al., 1988, 1989). Production of steranes from Raney-Ni desulfurization of asphaltenes and kerogens (Sinninghe Damsté et. al., 1990) indicates that steranes are bound to these substances by sulfide and/or polysulfide groups. However, the importance of sulfur cross-linking of stenols into a bound form as a sink for free stenols in *surface* sediments from the Peru margin OMZ is difficult to assess because of the uncertain time scale on which inorganic sulfur is incorporated into organic matter in general and steroids in particular. Mossmann et al. (1990) showed that sulfur is incorporated into Peru margin kerogen and bitumen in the surface 15 m of ODP leg 112 core 680 (250 m water depth, 11°S) and core 686 (450 m water depth, 11°S), but their data did not allow an assessment of the importance of this process near the sediment-water interface. Formation of bound steroids by sulfur cross-linking may occur more or less rapidly than total sulfur incorporation into organic matter, but there are presently no data with which to assess the importance of this process in these sediments.

5.3 Implications of stenol loss for biomarker applications

The implications of the stanol/stenol ratios in SC3 are discussed in detail in chapter 4, and are not repeated here.

In the study of ancient sediments and oils, interest in steroid distributions can be divided into three discrete areas: (1) use of the steroid distributions in oils and sediments as characteristic "fingerprints" for correlating oils with source rocks (e.g., Seifert, 1977), (2) reconstruction of the thermal history of a sediment (the "time-temperature" history) based on the progress of isomerization and/or aromatization reactions of steroids (e.g., Beaumont et al., 1985), and (3) use of sedimentary steroid distributions as indicators of the original organic matter source and/or depositional environment (e.g., Moldowan et al., 1990). Stenol degradation during early diagenesis obviously does not affect (1), and it also does not affect (2) which deals with steroid hydrocarbon *ratios* in maturing sediments, and is independent of the concentrations of the original sterols. However, stenol degradation during early diagenesis can have substantial implications for (3).

Table 1 and Fig. 5.2 illustrate that all stenols do not degrade at the same rate in the OMZ sediments. Differential remineralization of steroids can cause the relative abundances of steroid alteration products in an ancient sediment to bear little resemblance to the relative abundances of the original steroids from which these compounds were derived (Volkman et

al., 1987). This limits the use of steroids as indicators of the *relative importance* of the original organic matter inputs. For example, one method that has been proposed for estimating the importance of terrestrial organic matter input to surface sediments is based on the use of ternary plots of the abundances of C_{27}, C_{28} and C_{29} steroids (e.g., Huang and Meinschein, 1979); differential remineralization of these compounds would make it difficult to use a ternary plot of data from recent sediments to interpret a similar diagram for ancient sediments. An entirely different application of relative steroid abundances to paleoenvironmental questions was suggested by Brassell et al. (1984). They suggested that the relative abundances of steroids derived from a common steroid precursor may be a function of the microbial activity in the original depositional environment. Therefore, ratios of these co-genetic compounds, or their alteration products in ancient sediments, may provide information concerning the original depositional conditions. Such an application of relative steroid abundances in an ancient sediment may be less affected by differential rates of lipid remineralization in surface sediments, since the compounds in question have a common source.

At present the most quantitative statements that can be made concerning depositional conditions using sedimentary steroids are based on the presence, rather than relative abundance, of certain steroids derived from specific sources. For instance, compelling data has been put forward to suggest that C_{30} sedimentary 24-n-propylcholestanes are molecular fossils characteristic of marine algal input (Moldowan et al., 1990). This discovery presents an important tool for distinguishing marine and lacustrine sediments in the geologic record, based simply on the *presence* of these compounds.

Identification of sulfur-containing and sulfur-bound steroids in oils, asphaltenes and kerogens highlights the possibility that factors which control the availability in sediments of inorganic reduced sulfur species may affect the final form in which sedimentary steroids appear in ancient sediments and oils. Factors controlling the abundance in sediments of reduced inorganic sulfur species include, but are not limited to, primary production, bottom water oxygenation, sedimentation rate, and sediment iron content (i.e., Berner, 1984). Since this study has not dealt with sulfur-containing compounds, a detailed discussion of the potential impact of various sedimentary conditions on the availability of inorganic reduced sulfur species for steroid quenching in sediments is beyond the scope of this work.

5.4 Pentacyclic triterpenoid diagenesis

Fern-7-ene and tetrahymanol (Structures I and II, Fig. 5.8) were the only pentacyclic triterpenoids other than hopanoids identified in SC3. Fern-7-ene has been found in numerous surface sediments, including ODP sediments from the Peru upwelling regime

(ten Haven et al., 1990) and DSDP sediments from the upwelling regime off Northwest Africa (ten Haven et al., 1989b). Other fernenes are known to be produced by the anaerobic photosynthetic bacterium *Rhodomicrobium vannielii* (Howard, 1980), and fern-7-ene probably has a bacterial source in these sediments as well. As discussed in detail in chapter 4, the tetrahymanol in SC3 is probably phytoplankton-derived. This compound is beleived to be the precursor to gammacerane (II, Fig. 5.8), a triterpane common in ancient sediments and oils (ten Haven et al., 1989a; Venkatesan, 1989).

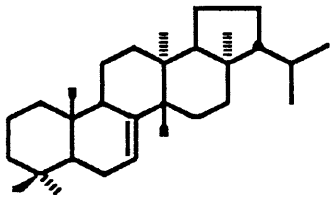
Seven hopanoids were identified in SC3 (Table 5.2). Hopanoids are ubiquitous in marine and lacustrine sediments (Ourisson et al., 1979, 1987; Quirk et al., 1984) and are biosynthesized by many bacteria as well as a few plants (certain tropical trees, grasses, and ferns) and lichens (Ourisson et al., 1979). Because of the restricted occurrence of these compounds in plants, hopanoids in marine sediments are typically attributed to bacterial input and alteration of bacterial precursors (Ourisson et al., 1987). In a survey of ≈ 100 strains of bacteria from a range of taxonomic groups, Rohmer et al. (1984) noted that ≈ 50% contained hopanoids. They found that these lipids are not present in archaebacteria or purple sulfur bacteria but may be as concentrated as 0.1- 2 mg/gdw in many other procaryotes. Bacterial hopanoids are predominantly polyhydroxy hopanols with extended side chains, such as bacteriohopanetetrol (III, Fig. 5.8), but the C_{30} hopanoids diploptene [hopan-22(29)-ene] and diplopterol (hopan-22-ol) are also present in almost all hopanoid-containing bacteria (Rohmer et al., 1984). Hopanoids, like steroids, are present in thermally mature ancient sediments and oils only as alkanes and aromatic compounds. However, the diagenetic alteration pathways relating bacterial hopanoids to "geohopanoids" found in ancient sediments are less well-defined than the steroid alteration pathways discussed above.

Table 5.2 lists (1) the pentacyclic triterpenoids identified in SC3 and (2) references reporting these compounds in similar sediments. The structures of these compounds are given in Fig. 5.8, and the mass spectra are shown in appendix 3. With the exception of the C_{34} hopanol, tetrakishomohopan-34-ol, all of these compounds have previously been identified in marine sediments. Tetrakishomohopan-34-ol, probably has not been reported previously because of the late GC elution time of this compound (≈ 87.5 min when run as the acetate under the analytical conditions described in chapter 2). The hopanols quantified in SC3 have not been found in significant concentrations in bacteria and are probably alteration products of polyhydroxy hopanoids (Rohmer et al., 1980, 1984) with longer side chains, such as bacteriohopanetetrol (III, Fig 5.8). The 17ß(H), 21ß(H)-homohopane in SC3 is probably an alteration product of homohopan-31-ol. Neohop-13(18)-ene has been identified in the anaerobic photosynthetic bacterium *Rhodomicrobium vannielii* (Howard,

Table 5.2
Pentacyclic triterpenoids identified in core SC3

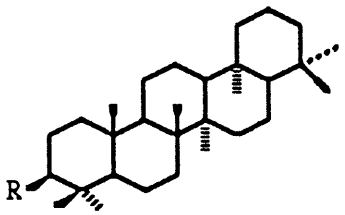
Compound	Related sediments in which the compound has been found	Reference
Fern-7-ene	Peru ODP sediments (≈11°S)	ten Haven et al. (1990)
	DSDP sediments from North-west African upwelling regime	ten Haven et al. (1989b)
Tetrahymanol	"ubiquitous" in marine surface sediments	ten Haven et al. (1989a) Venkatesan (1989)
Homohopan-31-ol	Peru surface sediments (≈15°S)	Volkman et al., (1987)
Bishomohopan-32-ol	Peru surface sediments (≈15°S)	Volkman et al., (1987)
Tetrakishomohopan-34-ol		None
17ß(H), 21ß(H)-homohopane	Peru ODP sediments (≈11°S)	ten Haven et al. (1990)
	Neogene DSDP sediments from the California Borderland	Rullkötter et al. (1981)
Neohop-13(18)-ene	Neogene DSDP sediments from the California Borderland	Simoneit and Mazurek (1981) Rullkötter et al. (1981)
22, 29, 30-trisnorneohop-13(18)-ene	Peru surface sediments (≈15°S)	Sandstrom (1982)
22, 29, 30-trisnorhop-17(21)-ene	Peru surface sediments (≈15°S) Namibian surface sediments	Sandstrom (1982)

(I)



Fern-7-ene

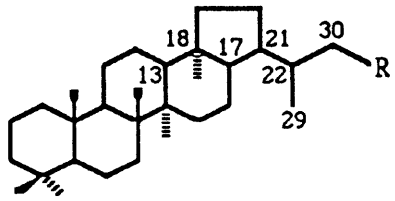
(II)



R=OH (Tetrahymanol)

R=H (Gammacerane)

(III)



R= CH_3 (Homohopane)

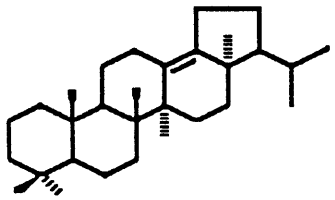
R= CH_2OH (Homohopan-31-ol)

R= CH_2CH_2OH (Bishomohopan-32-ol)

R= $CH_2CH_2CH_2CH_2OH$ (Tetrakishomohopan-34-ol)

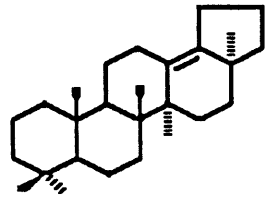
R= 2, 3, 4, 5-tetrahydroxypentane (Bacteriohopanetetrol)

(IV)



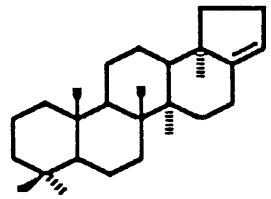
Neohop-13(18)-ene

(V)



22, 29, 30- trisnorneohop-13(18)-ene

(VI)



22, 29, 30- trisnorhop-17(21)-ene

Figure 5.8: Structures of selected pentacyclic triterpenoids discussed in text.

1980) and probably has a bacterial source in the Peru sediments as well. The trisnorhopenes found in SC3 are discussed below.

Hopanoids in ancient sediments

The hopanoids found in SC3 are likely precursors of several compounds found in ancient sediments and oils. With sediment maturation, the 17ß(H) biological configuration of hopanoids isomerizes to the thermodynamically more stable 17α(H) configuration (van Dorsselaer et al., 1977). The hopanes, 17α(H), 21ß(H)-homohopane, 17α(H), 21ß(H)-bishomohopane, and 17α(H), 21ß(H)-tetrakishomohopane have been found in crude oils (Seifert and Moldowan, 1978), and are probably formed by isomerization of the 17ß(H) alkanes formed by dehydration and subsequent saturation of the monohydroxy hopanols found in SC3. The alkanes 17α(H), 21ß(H)-22, 29, 30-trisnorhopane and 18α(H), 21ß(H)-22, 29, 30-trisnorneohopane occur nearly ubiquitously in crude oils (Seifert and Moldowan, 1978). A biological source for trisnorhopanoids has not been found; Seifert and Moldowan (1978) proposed that trisnorhopanes in crude oils arise from the early diagenetic cleavage of the 21-22 bond (Fig. 5.8) in hopanoids with a functionalized side chain. The trisnorhopenes in the Peru margin sediments (V and VI, Fig 5.8) almost certainly are unsaturated intermediates in this conversion of bacterially-produced hopanoids to the trisnorhopanes found in ancient sediments and oils. As noted by Sandstrom (1982), the presence of these trisnorhopenes in OMZ surface sediments suggests that, at least in this environment, the side chain cleavage reaction proceeds at a very early stage of diagenesis.

Although the hopanoids found in the Peru sediments can be related relatively easily to compounds found in ancient sediments and oils, these hopanoids are not as useful as steroids for reconstruction of organic matter sources and paleoenvironmental conditions. This is because the bacterially-derived precursors of these triterpenoids are generally not specific to any *particular* type of bacteria. Although hopanoids are absent from archaebacteria and certain groups of eubacteria (such as purple sulfur bacteria), the taxonomically diverse procaryotes that do produce hopanoids tend to produce a widespread and non-specific group of these compounds (Rohmer et al., 1984). Therefore, the primary application of hopanoids to the study of ancient sediments has thus far been limited to (1) use of these compounds for oil-source rock and oil-oil correlations, and (2) use of the extent of hopanoid isomerization and aromatization reactions for reconstruction of sediment thermal histories (i.e., Beaumont et al., 1985).

An unusual hopanoid, 17α(H), 18α(H), 21ß(H)-28, 30-bisnorhopane, with no known biological precursor, occurs in a few ancient sediments including the Miocene

Monterey Formation of the California Borderland, where this compound is extremely abundant (as much as 26 μg/ gdw, Seifert et al., 1978; Katz and Elrod, 1983; Curiale et al., 1985; Requejo and Halpern, 1989). The Monterey Formation is thought to have been deposited in a coastal upwelling regime analogous to that now present along the Peru margin (i.e., Soutar et al., 1981; Williams, 1984), yet no diagenetic precursor for the bisnorhopane could be identified in the Peru margin sediments. This finding is enigmatic, considering the high abundance of the bisnorhopane in the Monterey, and suggests the possibility is that this compound is derived from a natural product of a now-extinct organism. Applications of findings from the Peru sediments to the study of the Monterey Formation are discussed further in chapters 6 and 8.

5.5 Conclusions

• Stenol profiles in surface sediments suggest a range of degradation rates for these compounds. Differential remineralization of steroids can cause the relative steroid abundances in an ancient sediment to bear little resemblance to the relative abundances of the original steroids from which these compounds were derived. This limits the use of steroids as indicators of the *relative importance* of organic matter sources. However, important quantitative statements can be made concerning the depositional environment, based on the presence, rather than relative abundance, of certain steroids derived from specific sources.

• The rapid decrease below the sediment-water interface of C_{TOT}, the sum of cholesterol and cholesterol alteration products, illustrates that the rapid downcore decrease in the cholesterol concentration does not simply represent conversion of cholesterol into stenol alteration products, but must also involve steroid degradation and possibly formation of bound steroids.

• The ratio [cholesterol alteration products] / [cholesterol + cholesterol alteration products] substantially increases from 0-4 cm, but at deeper depths, there is no systematic change in the ratio. This suggests that if there is a progressive conversion of cholesterol to these degradation products below 4 cm, then it is obscured by an equally rapid removal of these compounds from the sediments.

• In SC3, the downcore increase in burial time (100 cm ≈ 310 years b.p.) and the downcore changes in sediment chemistry did not result in accumulation of cholesterol alteration products from more advanced portions of the alteration pathways than are achieved in the 0-1 cm interval. The absence of cholest-4-ene, cholest-5-ene and cholestane suggests that cholestadiene reduction to cholestenes and cholestene reduction to cholestane

occur over time scales and under sedimentary conditions not encountered in the surface 100 cm of Peru margin OMZ sediments.

• Although the hopanoids found in the Peru sediments can be related relatively easily to compounds found in ancient sediments and oils, these hopanoids are not as useful as steroids for reconstruction of organic matter sources and paleoenvironmental conditions. This is because the bacterially-derived precursors of these compounds are generally not specific to any particular type of bacteria.

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CHAPTER 6

GEOCHEMICAL IMPLICATIONS OF THE LIPID COMPOSITION OF *THIOPLOCA* SPP. FROM THE PERU UPWELLING REGION -15°S.

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Abstract-*Thioploca*, a genus of colorless, sulfur-oxidizing, filamentous bacteria, constitutes as much as 80% of the biomass in dysaerobic surface sediments (O_2<0.1 ml/l bottom water) in the coastal upwelling regimes of Peru and Chile. The lipid composition of *Thioploca* collected from sediments from the oxygen minimum zone in the Peru upwelling region near 15°S is presented here, and we provide the first assessment of the influence of *Thioploca* on organic compound distributions in upwelling regime sediments. Since marine species of *Thioploca* have been found only in dysaerobic surface sediments of upwelling regimes, biomarkers for this organism may be useful in identifying similar depositional conditions in the sedimentary record. *Thioploca* (dry) was found to be ≈3.8-4.1 wt% lipid. Three fatty acids: *cis* 16:1Δ9, 16:0 and *cis* 18:1Δ11 accounted for 69-72% of this lipid. Hydroxy fatty acids, hopanoids and hydrocarbons were conspicuously absent from the *Thioploca*. The *Thioploca* was found to contain cyclolaudenol, a C_{31} sterol with an unusual structure; diagenetic alteration products of this sterol may serve as markers for *Thioploca* input to sedimentary organic matter, and hence as markers for paleo-upwelling depositional environments in the sedimentary record.

INTRODUCTION

Thioploca, a genus of colorless, sulfur-oxidizing bacteria, consists of bundles of filaments encased in a common, whitish-yellow mucilaginous sheath as much as several cm long and 500 μm wide (Larkin and Strohl, 1983; Maier and Gallardo, 1984) . Marine species of *Thioploca* have been found only in dysaerobic surface sediments (O_2 <0.1 ml/l bottom water) of coastal upwelling regimes, including coastal Peru and Chile (Gallardo, 1977; Maier and Gallardo, 1984; Henrichs and Farrington, 1984; Gallardo, 1985), and Walvis bay, Southwest Africa (Morita et al., 1981). In the coastal upwelling regimes off Peru and Chile, where the low oxygen waters of the Peru-Chile Subsurface Countercurrent impinge on the surface sediments, *Thioploca* constitutes as much as 80% of the biomass (Gallardo, 1977; Rosenberg et al., 1983; Maier and Gallardo, 1984; Gallardo, 1985) and, therefore, has a significant impact on the organic geochemistry of these sediments.

Some aspects of the lipid composition of *Thioploca* collected from the oxygen minimum zone in the Peru upwelling region near 15°S are presented here, and we provide the first assessment of the influence of *Thioploca* on organic compound distributions in upwelling regime sediments. These data are of interest for several reasons:

(1) The environmental specificity of *Thioploca* makes biomarkers for this organism potentially useful in identifying similar depositional conditions in the sedimentary record.

(2) Since some ancient sediments deposited in coastal upwelling regimes (such as the Miocene Monterey Formation of the California Borderland) are important petroleum source rocks (e.g., Hunt, 1979; Katz and Elrod, 1983), markers for *Thioploca* could aid in future studies of the relative importance of oxic vs. suboxic conditions during petroleum source rock deposition in upwelling environments.

(3) The occurrence of abundant fossilized bacterial mats in the Monterey Formation led Katz and Elrod (1983) to suggest *Thioploca* as a possible source for a diagenetic precursor to the unusual bisnorhopane [17α(H), 18α(H), 21ß(H)-28, 30-bisnorhopane] present in many Monterey oils and sediment bitumens (Philp, 1985; Katz and Elrod, 1983), but, as discussed below, our data indicate that this is unlikely.

(4) The abundant fossilized bacterial mats in the Monterey Formation have also led to the suggestion (Williams and Reimers, 1983; Williams, 1984) that sulfur-oxidizing bacterial mats in these environments may be an important kerogen precursor; our characterization of the lipid composition of these organisms is a necessary first step for future investigations of this possibility.

EXPERIMENTAL

Thioploca has never been successfully cultured; therefore, samples for lipid analyses had to be collected from the field. *Thioploca* was sieved from sediments collected from the oxygen minimum zone in the Peru upwelling region near 15°S, during July 1987, on leg 08 of the R/V *Moana Wave* cruise 87 (PUBS I), as part of a continuing study of early diagenesis of organic matter in the Peru upwelling region (Volkman et al., 1983; Henrichs and Farrington, 1984; Farrington et al., 1988). The relevant sampling locations are given in Table 1. Within minutes of sieving the sediments, individual strands of *Thioploca* were picked from the sieved material, rinsed in clean seawater, aggregated into groups of strands, and frozen for subsequent analyses. The samples of picked and rinsed *Thioploca* appeared by examination with a binocular stereoscope to be free of all other material, and as is discussed below, this is also suggested by the absence from the *Thioploca* samples of a suite of lipids characteristic of the surface sediments in the study area. Soutar-type box cores of sediment were collected from the oxygen minimum zone, and *Thioploca* was present in the surface sediments. These cores were immediately sectioned at 1 cm intervals and frozen for subsequent analyses.

The lipid composition of two samples ("THIO#1" and "THIO#2") of *Thioploca* collected 17 km apart (Table 1) and the lipid composition of surface sediments were determined using gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). The procedures and equipment used for lipid extraction, column

chromatography, fatty acid derivitization, gas chromatography, and gas chromatography mass spectrometry (GC-MS) of samples were the same as previously described (Farrington et al., 1988) and can be briefly *summarized* as follows:

Frozen samples were thawed, internal recovery standards were added, and samples were sonic extracted successively with isopropanol, methanol-chloroform (1:1 v/v) and methanol-chloroform (1:3 v/v); lipids were partitioned into isopropanol/chloroform by addition of $NaCl_{(aq)}$. One half of the total lipid extract (TLE) was separated into lipid classes by silica gel column chromatography. One fourth of the original TLE of each sample was treated with 0.5N KOH in methanol to saponify the esterified fatty acids. Fatty acids were converted to fatty acid methyl esters (FAMEs) by reaction with 10% BCl_3-methanol and separated from the other lipids in the TLE using silica gel column chromatography. All sample fractions were analyzed by high resolution gas chromatography (GC) with a J & W Scientific Durabond DB-5 30 m fused silica capillary column and an on-column injector. Identification of individual FAMEs was by comparison of the GC retention times with authentic standards. Compound identifications were confirmed by electron impact GC-MS analyses, using conditions described in the legend of Fig. 1. The *cis* configuration of the double bond in 16:1Δ9 and 18:1Δ11 (Table 1) was determined by matrix isolation gas chromatography Fourier transform infrared spectroscopy (MI-GC-FTIR).

Thioploca and sediment dry weights were determined by drying an aliquot of each sample at 110°C for 24 h and then correcting the aliquot dry weight for salts (brine in the samples was assumed to have a salinity of 3.5 wt%). The weight of total lipids extracted from the *Thioploca* samples was determined by passing 1/4 of the original TLE through an activated copper column (to remove elemental sulfur). The resulting solvent-lipid mixture was evaporated to a small volume under an N_2 stream and then transferred to a 10 mg, tared, solvent-rinsed, aluminum CAHN balance pan, where the remaining solvent was evaporated and the residues weighed on a CAHN 25 Automatic Electrobalance to $\pm$ 2 μg.

The solvent-extracted residue of one of the *Thioploca* samples (THIO#2) was heated with refluxing 6N KOH in methanol/water (1:1 v/v) for 2 h to determine the quantitative importance of additional lipids bound to the solvent-extracted residues by ester linkages. The insoluble *Thioploca* residues from this KOH extraction were then heated with refluxing 6N HCL for 6 h under nitrogen to liberate any addition lipids that may have been bound to the *Thioploca* residues by amide or ether linkages.

Nitrogen and carbon stable isotope analysis of one *Thioploca* sample was performed for us (Dr. Brian Fry's laboratory; Marine Biological Laboratory, Woods Hole) on a Finigan 2540 magnetic deflection MS. Three *Thioploca* samples were analyzed by

Pyrolysis GC, and the pyrolysis products (peak P2) of one of these samples were analyzed by EI GC-MS. The pyrolysis GC-MS procedure was the same as that described in detail by Tarafa et al. (1987).

RESULTS AND DISCUSSION

LIPIDS LIBERATED BY SOLVENT EXTRACTION

The total lipids from solvent extraction of the *Thioploca* samples were found to be 3.8-4.1 dry wt% of the samples (Table 1). The lipid extracts contained very low n-alkane concentrations (indistinguishable from the analytical blanks). Total fatty acids collectively constituted 2.7-3.1 dry wt% of the *Thioploca* (Table 1). Three fatty acids: *cis* 16:1Δ9, 16:0 and *cis* 18:1Δ11 accounted for 95-96 % of the total fatty acids and 69-72% of the total lipid content of the *Thioploca* extracts (Table 1). In most species of bacteria (other than archaebacteria) fatty acids account for 2-8 dry wt% (Asselineau, 1966); therefore, the values determined for *Thioploca* are not unusual. The most commonly reported mono-unsaturated fatty acids in bacteria are, in fact, 16:1Δ9 and 18:1Δ11 (Perry et al., 1979; Parkes and Taylor, 1983; Gillan and Johns, 1986). Given the high concentrations of these monoenoic straight-chain acids in *Thioploca*, the absence of large concentrations of branched acids (e.g. i15:0, a15:0, i17:0, a17:0) is not surprising, since bacteria with high concentrations of monoenoic acids typically do not produce large concentrations of branched acids (Gillan and Johns, 1986; Goossens et al., 1986).

The fatty acids: 16:1Δ9, 16:0 and 18:1Δ11 are also the most abundant fatty acids in surface sediments from the study area (Table 1, and Farrington et al., 1988). Since abundances of *Thioploca* ranging from ≈100-1000 g/m^2 (wet wt., concentrated near the sediment-water interface) are common in sediments from the OMZ of the Peru-Chile upwelling regimes (Gallardo, 1977; Rosenburg et al., 1983; Gallardo, 1985), the high concentrations of 16:1Δ9, 16:0 and 18:1Δ11 in *Thioploca* suggest that *Thioploca* may be an important source of these compounds in the sediments. However, a quantitative assessment of the importance of *Thioploca* as a source of these fatty acids in the sediments would require data on average rates of *Thioploca* organic matter synthesis in these sediments. The fatty acid distribution in surface sediments of core SC7 is shown in Table 1 and includes fatty acids from sources other than *Thioploca*. A detailed discussion of fatty acid biogeochemistry in sediments of this region is in preparation.

Cyclolaudenol (24-methyl-9,19-cyclolanost-25-en-3ß-ol), an unusual 4,4-dimethyl C_{31} sterol with a 9,19 cyclopropyl ring (Fig. 1B) was found in the *Thioploca* samples in concentrations ≈82 µg/gdw and accounted for >95% of the sterols in the *Thioploca*

extracts (≈0.21% of the total lipids). The cyclolaudenol was identified by coelution with an authentic standard, and by comparison of the mass spectrum of the compound (Fig. 1A) with the mass spectrum of the authentic standard (Fig. 1B). Although, prior to 1967, sterols had not been identified in procaryotes (Bird et al., 1971), there have been several reports since that time of sterols in bacteria (see Kohl et al., 1983 for a review). Bouvier et al. (1976) has reported significant concentrations of 4,4-dimethyl and 4α-methyl sterols in *Methylococcus capsulatus*, and has reported that sterol biosynthesis in this bacterium is blocked at the level of 4 -methyl sterols. *Thioploca* is another example of a bacterium that contains a 4,4-dimethyl sterol, but does not accumulate 4-desmethyl sterols. The lack of 4-desmethyl sterols, however, cannot be generalized to all bacteria, since Kohl et al. (1983) identified a substantial concentration of cholest-8(9)-en-3ß-ol in *Nannocystis exedens*. Although 4-desmethyl sterols have also been found in several cyanobacteria (De Souza and Nes, 1968; Reitz and Hamilton, 1968), Ourisson et al. (1987) concluded that the low levels of the common 4-desmethyl sterols found in cyanobacteria were probably found as a result of sample contamimation.

It is interesting to note that cycloartanol (9,19-cyclolanost-3ß-ol), a sterol very similar to cyclolaudenol, has been reported in significant concentrations in sediments from the laminated cyanobacterial mat sequence in the Solar Lake adjacent to the Gulf of Aqaba (Boon, 1984; Edmunds and Eglinton, 1984), and in sediments from a cyanobacterial mat (Cardoso et al., 1978) from the Persian Gulf coast of Abu Dhabi (United Arab Emirates). These studies did not identify the source of the cycloartanol in these sediments, but the presence of the similar sterol, cyclolaudenol, in *Thioploca* suggests that the cycloartanol in the cyanobacterial mat sediments may also have a bacterial source.

Ourisson et al. (1979) and others have noted that many hopanoids, or their diagenetic precursors, may serve as bacterial biomarkers. However, the hopanoids present in the Peru surface sediments (Volkman et al., 1987; Farrington , unpublished data) are apparently not derived from the *Thioploca*, since hopanoids (with molecular wt. <650 amu) were *not* found among the alkane, fatty acid (esterified or free), ketone, or alcohol fractions of the *Thioploca* extracts. In addition, the absence of hopanoids in the *Thioploca* suggests that, contrary to previous suggestions (Katz and Elrod, 1983), *Thioploca* is probably not a source for a diagenetic precursor to the unusual bisnorhopane [17α(H), 18α(H), 21ß(H)-28, 30-bisnorhopane] present in many Monterey oils and sediment bitumens. Steroids and hopanoids are biosynthesized by different pathways from the cyclization of squalene; Ourisson et al. (1979) suggested that steroid biosynthesis is evolutionarily more advanced than hopanoid biosysnthesis, and they noted that steroid-producing bacteria typically do not

Table 1
Lipid data from solvent extracts of *Thioploca* (THIO#1 and THIO#2) and surface sediments (0-1 cm) of Soutar core SC7. Stable isotope data for whole *Thioploca*.

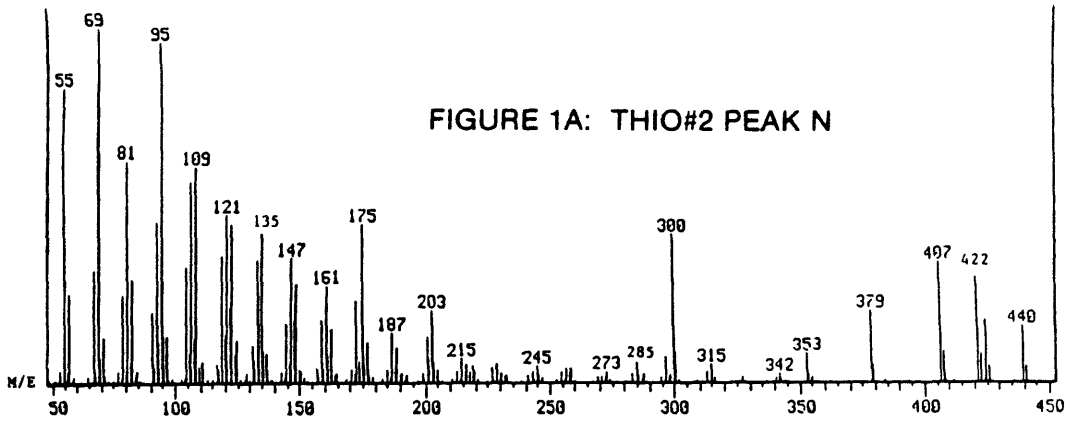
	THIO #1	THIO#2	SC7(0-1cm)
Sampling location LON:	75°36.81'W	75°31.97'W	75°36.81'W
LAT:	14°54.20'S	15°.04.27'S	14°56.62'S
Water depth	100 m	73-75 m	105-110 m
Sample size extracted† (dry)	19.2 mg	14.0 mg	1600 mg
Total lipids (% dry wt)	4.1	3.8	
$\delta^{13}C$ (relative to PDB)†	----	-21.8±0.05 °/∞	----
$\delta^{15}N$ (relative to air)†	----	+4.8 ±0.1 °/∞	----
Cyclolaudenol (µg/gdw)	83.5	80.5	1.26
Total Fatty Acids (µg/gdw)	30800	27300	870
Fatty Acids (as % of total)			
14:1Δ9	0.015	0.036	0.247
14:0	0.627	0.635	7.78
*iso*15:0	0.526	0.778	3.59
*anteiso*15:0	0.370	0.605	4.14
15:0	0.270	0.195	2.01
*iso*16:0	0.048	0.109	2.04
cis*-16:1Δ9	**42.5**	**40.3**	**16.9**
16:0	**17.3**	**18.0**	**18.7**
*anteiso*17:0	0.158	0.148	2.25
17:0	0.182	0.174	1.11
18:4	0.045	0.065	1.21
*iso*18:0/18:3¥	0.049	0.041	1.21
18:1Δ9/18:2¥	0.468	0.303	8.42
cis*-18:1Δ11	**36.0**	**37.8**	**15.2**
18:0	0.906	0.543	2.86
20:5	§	§	4.61
20:1Δ11	0.098	0.102	1.86
20:0	0.060	0.038	0.643
22:6	§	§	0.624
22:1Δ13	0.046	§	0.260
22:0	0.050	0.019	0.551
23:0	0.023	§	0.141
24:1Δ15	§	§	0.221
24:0	0.074	0.046	1.21
25:0	0.024	§	0.132
26:0	0.050	0.046	0.907
27:0	§	§	0.208
28:0	0.026	0.017	0.359
29:0	§	§	0.216
30:0	0.034	§	0.374

†Isotopic measurments of Thio#2 were performed on a 1.3mg (dry) whole (unextracted) *Thioploca* sample.

*Double bond geometry determined by GC-FTIR.

¥ Compounds separated by "/" coelute, and value presented is a sum of their concentrations.

§ Concentrations <4.5µg/gdw.



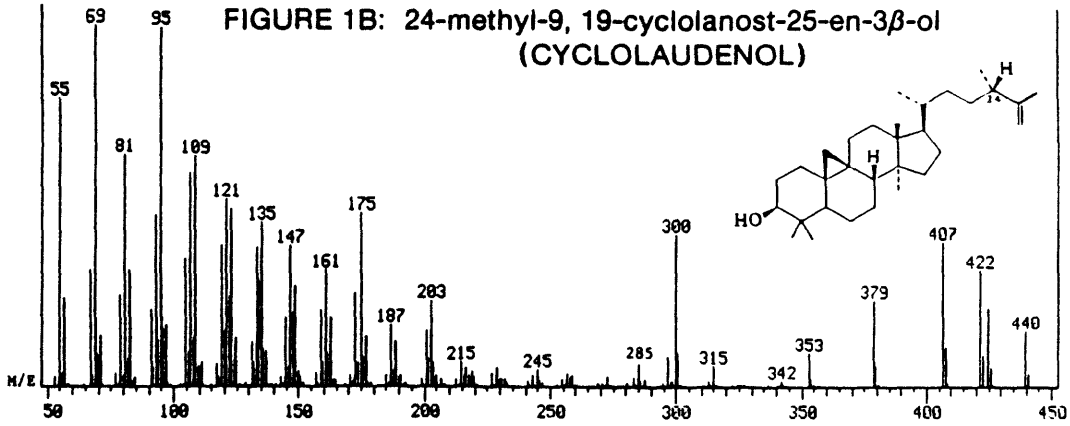


FIGURE 1: (A) Electron impact mass spectrum of compound N in sample THIO#2. (Finnigan 4500 quadropole mass spectrometer interfaced to a Carlo Erba 4160 gas chromatograph utilizing a column of the same type as that used in the GC analyses and helium as the carrier gas). GCMS injections were on-column at 70°C and the GC was programmed at 3.5°C/min to 260°C and at 4°C/min to 310°C. GCMS operating conditions were 50eV ionization potential with the source at 100°C and electron multiplier voltage at 950 volts with scanning rate from 50-650 amu per second. (B) Electron impact mass spectrum of authentic standard of cyclolaudenol; GCMS conditions were same as above, except that the electron multiplier voltage was 1000 volts. The mass spectra of compound N in THIO#1 and THIO#2 were the same.

produce hopanoids. Therefore, given the presence of the cyclolaudenol in the *Thioploca*, the absence of hopanoids is perhaps not surprising.

It may be possible to use cyclolaudenol and/or the products of its diagenetic alteration as markers for *Thioploca* input to sedimentary organic matter. The potential of cyclolaudenol and its diagenetic alteration products as *Thioploca* -specific biomarkers is enhanced by the restricted terrestrial sources of this sterol (reported by Akihisa et al. [1986] in *Musa sapientum* [Banana peel]; in the latex and stem of *Euphorbia caudicifolia* [Govardhan et al., 1984]; in maize [Goodwin, 1977]; and in the rhizomes of a fern, *Polypodium vulgare* [Ghisalberti et al. , 1969]). To the best of our knowledge, cyclolaudenol has not been reported previously in marine or lacustrine organisms or sediments. Volkman et al. (1987) did not report cyclolaudenol among the sterols in a Peru sediment core, "BC7", taken shoreward of the oxygen minimum zone and hence outside the zone of *Thioploca* occurrence. Smith et al. (1983) did not report cyclolaudenol among the sterols in Peru surface sediments from further north at 12°S; Smith et al. did not mention the presence of *Thioploca*, and therefore their core may have been taken from a less oxygen-depleted area outside the zone of *Thioploca* occurrence. Alternatively, since these studies were not looking for cyclolaudenol, its occurrence may have been overlooked. Thus far, our data for the sedimentary distribution of cyclolaudenol is preliminary, since under our analytical conditions partial coelution of cyclolaudenol with another, more abundant steroid in the sediments requires quantitation of cyclolaudenol by GC-MS. Our analyses of sediments from 0-1 cm , 4-5 cm and 8-9 cm of Soutar core 7 (SC7) indicate that the cyclolaudenol concentration in this core decreases rapidly with depth. Analysis of sediment from 45-51 cm in SC6, a core from the oxygen minimum zone at 15°S recovered in 1978 (Henrichs and Farrington, 1984) indicates the presence of cyclolaudenol, albeit in trace quantities. We cannot distinguish at this time whether or not the decrease in cyclolaudenol concentration with depth in SC7 is due to early diagenic transformation (the hypothesis that we favor) or is due to variations in the abundance of *Thioploca* at the time of deposition. If cyclolaudenol (rather than its transformation products) is to be used as a biomarker for *Thioploca*, it may be necessary to use mass selective detection to identify the compound among the other more abundant steroids in sediments. However, many potential diagenetic alterations of cyclolaudenol, such as loss of the alcohol function (by formation of the sterone or 2-3 sterene), saturation of the 25-ene, or opening of the 9-19 cyclopropyl ring, would lead to unique products which may also have significant potential as markers for *Thioploca*.

Thioploca has never been successfully cultured, but analyses of naturally grown samples, such as those used in this study, would be necessary for a study of the impact of

Thioploca on sedimentary geochemistry even if cultured samples were available, since the lipid composition of cultured bacteria can be a function of the culturing conditions (Oliver and Colwell, 1973). It is unlikely that the cyclolaudenol identified in our *Thioploca* samples represents contamination of the samples by sedimentary organic matter. The careful sampling procedure has already been discussed. In addition, if contamination by sedimentary organic matter were the source of the cyclolaudenol, then the lipids in Table 2, which are examples of lipids far more abundant than cyclolaudenol in the sediments from the study area (this work, and Farrington et al., 1988), should have also been detected in the *Thioploca* extracts, *but were not*. The absence of these lipids from the *Thioploca* suggests that the lipid composition of the *Thioploca* samples reflects that of the *Thioploca* itself.

LIPIDS LIBERATED BY BASE EXTRACTION AND ACID EXTRACTION

The solvent-extracted residues of one of the *Thioploca* samples (THIO#2) were treated with refluxing 6N KOH in methanol/water (1:1 v/v) for 2 h to determine the quantitative importance of additional lipids bound to the solvent-extracted residues by ester functional groups. The only additional lipids liberated by this technique were a small amount of fatty acids (14:0, 15:0, 16:1, 16:0, 18:1 and 18:0); the total additional fatty acids liberated were ≈400 μg/gdw, or ≈1.6% of the total fatty acids liberated by solvent extraction alone

The insoluble *Thioploca* residues from this KOH extraction were then heated with refluxing 6N HCl for 6 h under nitrogen to liberate any addition lipids (frequently referred to as "tightly bound" lipids) that may have been bound to the *Thioploca* residues by amide or ether linkages. Goossens et al. (1986) and Mendoza et al. (1987) note the abundance of hydroxy fatty acids in many bacteria and report that hydroxy fatty acids are efficiently extracted from bacterial and sedimentary organic matter only by strong acid treatment or heating at high temperatures with base (Kawamura and Ishiwatari, 1984). Goossens et al. propose that the tightly bound nature of the hydroxy fatty acids results from these compounds being bound by amide linkages to the insoluble biopolymeric residues. Our acid treatment of the *Thioploca* residue released no measurable quantities of hydroxy fatty acids (4 μg/gdw would have been detectable). The fact that these compounds would have been recovered by our procedure was confirmed by the good recoveries (>85%) of hydroxy fatty acid standards ($C_{16}\alpha$-OH FAME and $C_{14}\alpha$-OH FAME) refluxed with acid under similar conditions as the *Thioploca* residue and worked up with the same procedure as was the *Thioploca* acid extract. The acid extract of the *Thioploca* residues did contain small amounts of 14:0, 15:0, 16:1, 16:0, 18:1 and 18:0 fatty acids; the total additional fatty

Table 2
Examples of lipids (µg/gdw) more abundant than cyclolaudenol in sediments from the OMZ (core SC7) but not detected in *Thioploca* (THIO#1 and THIO#2): evidence that cyclolaudenol in the *Thioploca* is not from contamination by sediments

	THIO #1	THIO#2	SC7(0-1cm)¥
Cyclolaudenol	83.5	80.5	1.26
Cholesterol	§	§	29.2
Dinosterol	§	§	22.2
$C_{37:2}$ Alkenone	§	§	5.41
$C_{37:3}$ Alkenone	§	§	3.09
branched $C_{20:1}$*	§	§	2.84

¥ Farrington et al., 1988 report similar concentrations for the alkenones and branched $C_{20:1}$ compound in surface sediments from this region.
§ Not detected. Concentrations of 3µg/gdw would be detectable for the *Thioploca* samples.
* 2,6,10-trimethyl-7-(3-methyl-butyl)-dodecene

acids liberated were ≈400 μg/gdw, or ≈1.5% of the total fatty acids liberated by solvent extraction alone.

THIOPLOCA PYROLYSIS GC

Pyrolysis GC of three *Thioploca* samples and pyrolysis GC-MS of one *Thioploca* sample were performed both to provide information on lipid moieties which may not have been detected by our extraction/analytical procedures and to determine the kinds of lipid moieties that thermal degradation of *Thioploca* -synthesized organic matter could potentially generate. Compounds in the low temperature pyrolysis peak, P1 (≈6.5mg/g ash wt. of *Thioploca*), are largely the products of thermal distillation, and were not analyzed by GC-MS. Only the C_7 -C_{24} pyrolysis products in the high temperature, or P2 peak (total P2 ≈ 20.0 mg/g ash wt. of *Thioploca*; P2 temperature range≈ 360-500 °C; T_{max}≈470°C) were analyzed by GC-MS.

Most of the compounds found in P2 , including alkyl benzenes, phenols, indoles and other nitrogen containing compounds, were probably the products of carbohydrate and protein pyrolysis (Boon, 1984). This agrees with the low lipid concentration (<5 dry wt. %) found in the *Thioploca* extracts discussed above (Table 1). Lipids in P2 included hexadecanoic acid (16:0 ≈ 7.6 μg/g ash wt. of *Thioploca*), which was probably derived from esters, since esters can pyrolyze to the acid + an alk-1-ene. The much lower abundance of 16:0 in the pyrolysate compared to the *Thioploca* solvent extracts may partially reflect the lower abundance in the *Thioploca* of bound 16:0 relative to unbound 16:0 illustrated by a comparison of the results of the solvent and base extractions discussed above. Low concentrations of several branched and unbranched alkanes were also found in P2 (total alkanes ≈ 0.1 mg/g ash wt. of *Thioploca*). These alkanes eluted from the GC between n-C_{11} and n-C_{18}, but the similarity of EI mass spectra of many branched acyclic alkanes prevents us from precisely identifying these compounds from GC-MS data alone. Alkanes are generally not subject to rearrangement during pyrolysis; therefore, the origin of the branched alkanes is not clear, given the lack of branched compounds (other than a small amount of *iso* and *anteiso* fatty acids) in the lipid extracts. Sulfur-containing compounds (including thiophenes) were also identified in the pyrolysate; however, interpretation of the presence of these compounds is complicated by the abundant intracellular elemental sulfur in *Thioploca* (several wt%), since Schmid (1986) has demonstrated that elemental sulfur can react with organic matter when heated to form compounds such as thiophenes.

THE CARBON AND NITROGEN ISOTOPIC COMPOSITION OF *THIOPLOCA*

Since *Beggiotoa*, a genus of sulfur-oxidizing bacteria which is a member of the same family (Beggiatoaceae) as *Thioploca*, has been found to fix isotopically light N_2 (Nelson et al., 1982), it has been suggested that *Thioploca* may also fix nitrogen (Libes, 1983) with a light isotopic signature that could potentially be used to trace the input of *Thioploca* -synthesized organic matter to sediments. Although Maier and Gallardo (1984) disputed their findings, Morita et al. (1981) suggested that *Thioploca* is a methylotroph; the possibility of *Thioploca* existing as a methylotroph suggested to us that the carbon isotopic signature of *Thioploca* might also be sufficiently light as to have utility in quantifying the contribution of *Thioploca* to sedimentary organic matter. However, our determination of the carbon and nitrogen isotopic composition of a *Thioploca* sample (Table 1) suggested that the isotopic composition of the *Thioploca* is not sufficiently different from the average values for marine phytoplankton (Libes, 1983) to contribute to a quantification of the contribution of *Thioploca* to sedimentary organic matter.

CONCLUSIONS

• *Thioploca* (dry) was found to be ≈3.8-4.1 wt% lipid. Three fatty acids: *cis* 16:1Δ9, 16:0 and *cis* 18:1Δ11 accounted for 69-72% of this lipid.

• The absence of hopanoids (with molecular wt <650 amu) in the *Thioploca* suggests that, contrary to previous suggestions, *Thioploca* is probably not a source for a diagenetic precursor to the unusual bisnorhopane [17α(H), 18α(H), 21ß(H)-28, 30-bisnorhopane] present in many Monterey oils and sediment bitumens.

• Cyclolaudenol and/or its degradation products may be usable as markers for input of *Thioploca*- synthesized organic matter to the sedimentary record. Markers for *Thioploca* could aid in paleoenvironmental reconstruction, and could aid in characterizing the relative importance of oxic vs. suboxic conditions during petroleum source rock deposition in upwelling environments.

• Hydroxy fatty acids in the C_{12}+ molecular weight range and n-alkanes in the C_{14}-C_{37} molecular weight range were not present in the solvent, base or acid extracts of the *Thioploca*.

• Pyrolysis GC-MS of *Thioploca* (peak P2) revealed primarily carbohydrate and protein pyrolysis products. Lipid moieties included low concentrations of hexadecanoic acid and several branched and unbranched alkanes. Sulfur-containing pyrolysis products were found, but their significance is difficult to interpret, because of the unknown effects during pyrolysis of the large elemental sulfur content of *Thioploca*.

• The carbon and nitrogen isotopic composition of a *Thioploca* sample ($\delta^{13}C$ = -21.8 ± 0.05°/∞; $\delta^{15}N$= +4.8 ± 0.1°/∞) suggests that in *Thioploca* these parameters are insufficiently different from the average isotopic composition of marine phytoplankton to contribute to a quantification of the input of *Thioploca* to sedimentary organic matter.

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CHAPTER 7

OTHER ASPECTS OF THE ORGANIC GEOCHEMISTRY OF *THIOPLOCA* SPP.

7.1 Introduction

The potential of cyclolaudenol as a biomarker for *Thioploca* is diminished by the apparently rapid degradation of this compound in surface sediments; however, elucidation of the degradation pathway of this compound may identify a stable alteration product of cyclolaudenol which can serve as a *Thioploca* marker. In this chapter, I discuss some simple alteration products of cyclolaudenol which I searched for in surface sediments from the OMZ. In addition, I briefly discuss some intriguing compounds that Bac (1990), Brassell and co-workers have found in ancient sediments and have suggested may be alteration products of a C_{30} -cyclosterol similar to cyclolaudenol.

In the second part of this chapter, I discuss the total hydrolyzable amino acid (THAA) composition of *Thioploca*. The high benthic biomass of *Thioploca* spp. in many parts of the OMZ of the Peru upwelling region has led to the suggestion that *Thioploca* may be an important source of organic nitrogen to these sediments (Libes, 1983; Henrichs et al., 1984). I investigated the THAA composition of *Thioploca* to assess the importance of *Thioploca* as a source of sedimentary THAA in the OMZ and to determine if these bacteria produced any unusual amino acids that might be used as biomarkers for *Thioploca*.

7.2 Cyclolaudenol degradation

7.2.1 Cyclolaudenol degradation during early diagenesis

Figure 7.1 shows several possible simple alterations of cyclolaudenol which, by analogy with degradation pathways of other steroids, might be expected to occur in surface sediments. As noted in chapter 6, Edmunds and Eglinton (1984) found cycloartanol (9,19-cyclolanost-3ß-ol), a sterol very similar to cyclolaudenol, in sediments from the Solar Lake (north-east Sinai). The only other 4,4-dimethyl sterol they identified in these sediments was cycloartanone, which was more abundant than cycloartanol. This is intriguing since, as discussed in chapter 5, an important degradation pathway of 4-desmethyl sterols (Fig. 5.3) is:

stenol→stenone→stanone→stanol→sterene

Although cycloartanol is a 4,4-dimethyl sterol with a saturated ring-system, the identification of cycloartanone in the Solar Lake sediments suggested that cycloartanol might also degrade to a stanone. Furthermore, the similarity of cyclolaudenol to cycloartanol suggested that the cyclolaudenol in Peru sediments might degrade to a sterone as well. I examined the ion chromatogram of M/e= 438 (the molecular ion of

cyclolaudenone) in the sterone fraction of several Peru sediment extracts. Only minor 438 peaks were found. To identify if one of these peaks was cyclolaudenone, I synthesized a cyclolaudenone standard from cyclolaudenol. This allowed determination of the GC retention time of this compound and acquisition of a mass spectrum of authentic cyclolaudenone.

7.2.2 Synthesis of cycloartenone and cyclolaudenone

Cholestanone, cycloartenone (9, 19-cyclolanost-24-en-3-one), and cyclolaudenone were prepared individually by a Jones oxidation of the respective sterols. The cholestanone and cycloartenone were prepared as tests of the derivitization technique. Jones Reagent was prepared by dissolving 26.72 g chromic trioxide in a solution of 23 ml concentrated H_2SO_4 in 77 ml water ($KMnO_4$-distilled). Forty µg of sterol in 500 µl of acetone were added to a 4 ml vial containing a teflon-coated stir-bar. While stirring this solution, ≈10 µl of Jones Reagent was added. The resulting solution was stirred for 1 h, and then 500 µl of saturated $NaCl_{(aq)}$ and 500 µl of hexane were added. This mixture was stirred vigorously for 20 min. The organic phase was transferred to a second vial, and the aqueous phase was re-extracted with an additional 500 µl of hexane which was also transferred to the second vial. The hexane was evaporated under a stream of N_2 to ≈500 µl . To titrate any residual acid, ≈500 µl of 2% $NaHCO_{3(aq)}$ was added to the hexane and was stirred for 20 min. The aqueous phase was removed, and 500 µl of distilled water was added to the hexane and stirred for 20 min. The aqueous phase was removed and granular Na_2SO_4 was added to the hexane to remove residual water. The organic phase was then transferred to another vial and dried under N_2. The yield of this derivitization was ≈ 75%, and only one product (the sterone) was formed in each reaction.

The difference between the GC retention times of the cycloartenol and cycloartenone and the difference between the retention times of the cyclolaudenol and cyclolaudenone were similar to the difference between the retention times of cholestanol and cholestanone. This suggests that formation of the cycloartenone and cyclolaudenone did not result in opening of the cyclopropyl ring which would substantially change the geometry of the B-C ring juncture and hence the GC retention time. The mass spectra of the cycloartenone and cyclolaudenone are shown in Fig. 7.2. A comparison of these spectra with the spectrum of cyclolaudenol (Fig. 6.1) allows a tentative identification of some of the major fragments in the cyclolaudenol spectrum (Fig. 7.3). The proposed origin of M/e =300 in Fig. 7.3 is consistent with (1) the presence of this ion in the spectra of both cyclolaudenone and cyclolaudenol and (2) the presence of M/e = 286 in the spectra of cycloartenone and cycloartenol.

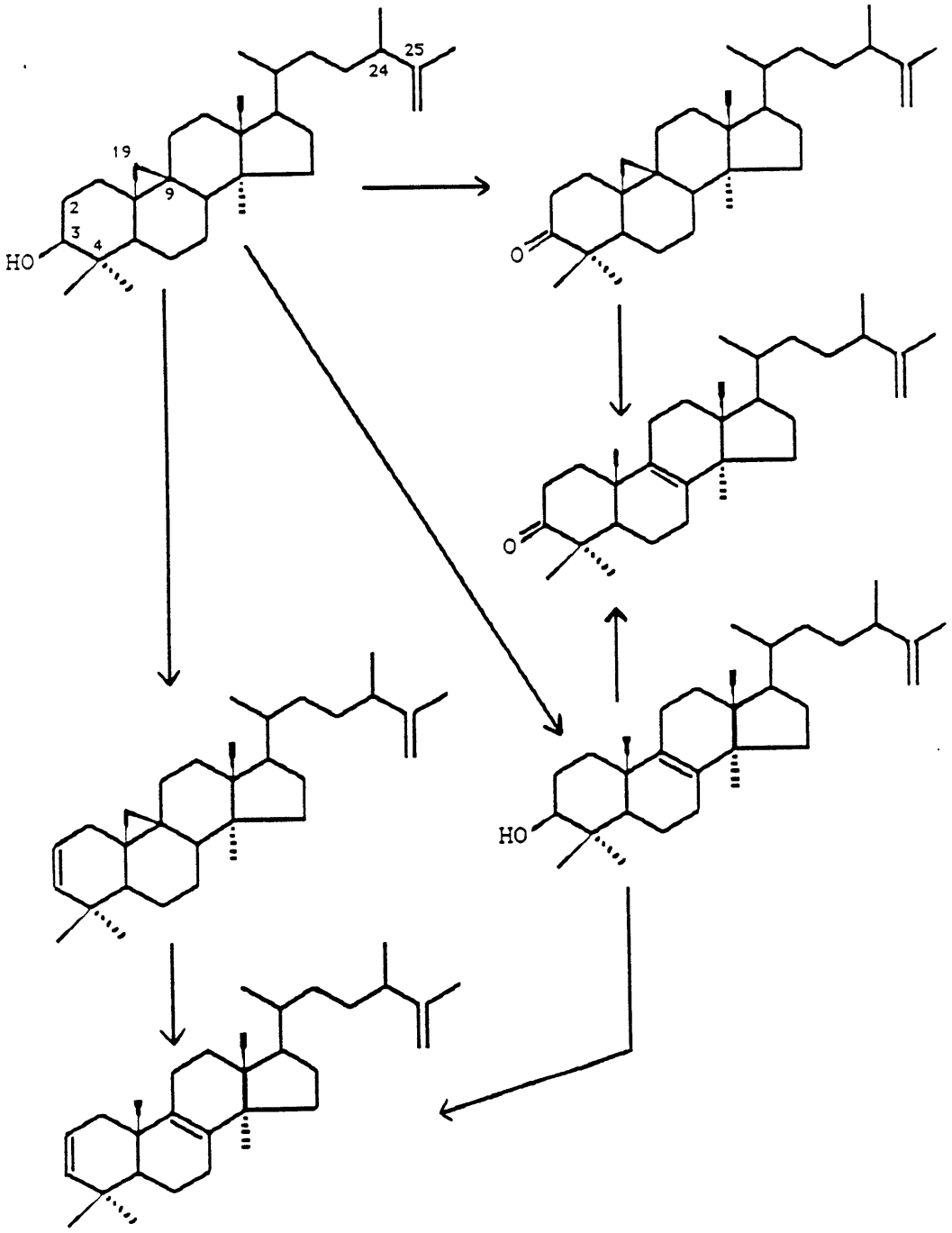


Figure 7.1: Potential simple alterations of cyclolaudenol during early diagenesis.

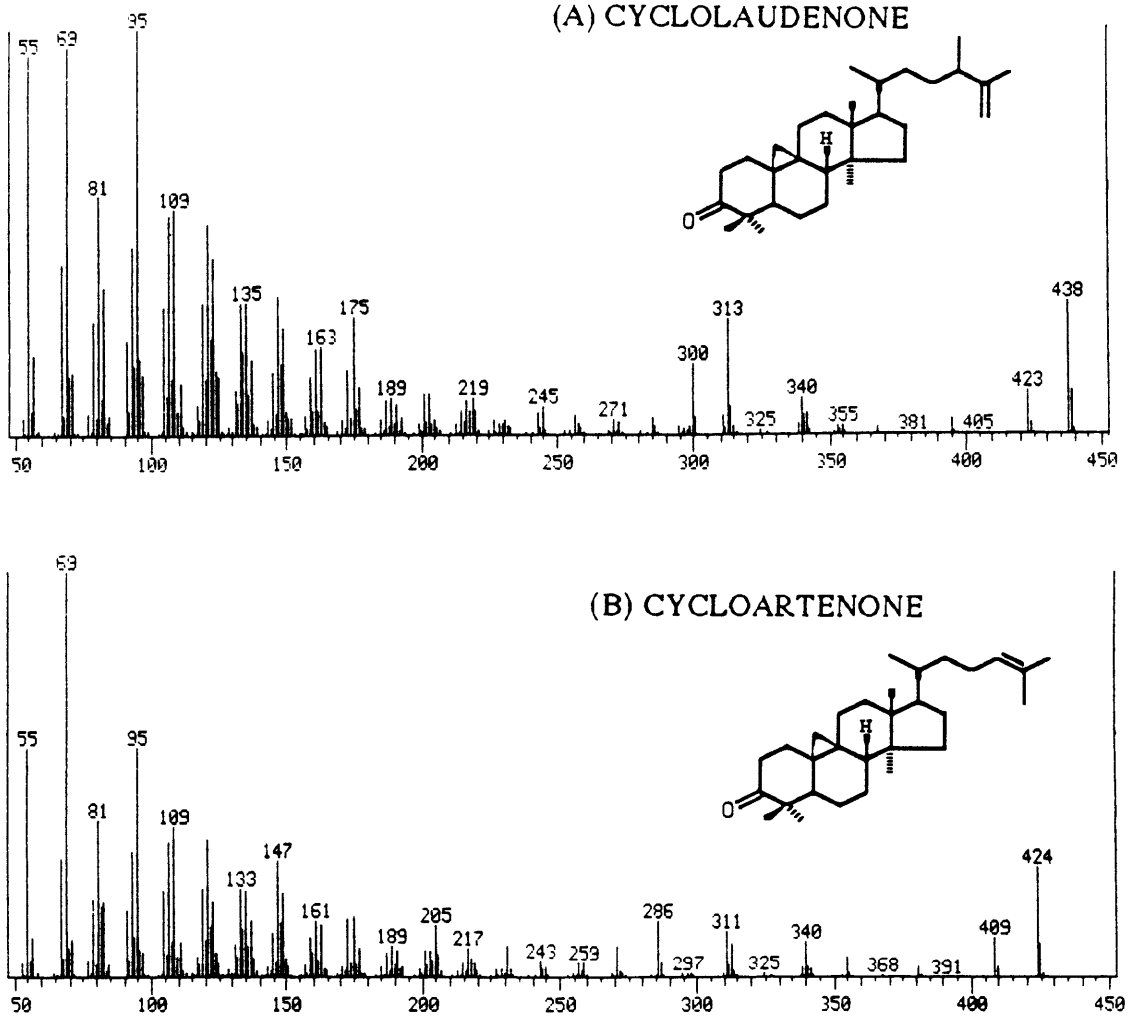
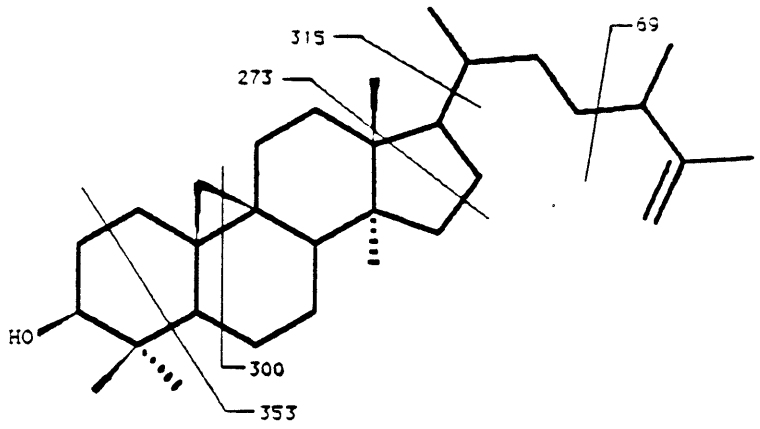
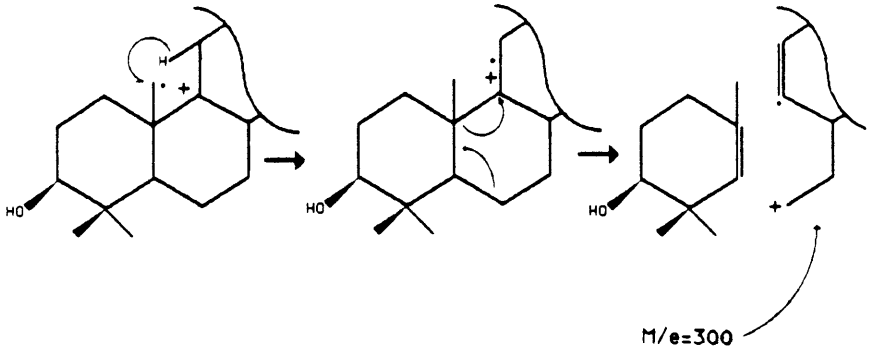


Figure 7.2: (A) Mass spectrum of cyclolaudenone. (B) Mass spectrum of cycloartenone.

Cycloiaudenol
24-Methyl-9,19-cycloianost-25-en-3ß-ol



Formation of M/e=300:



Formation of M/e= 422 and M/e= 407.

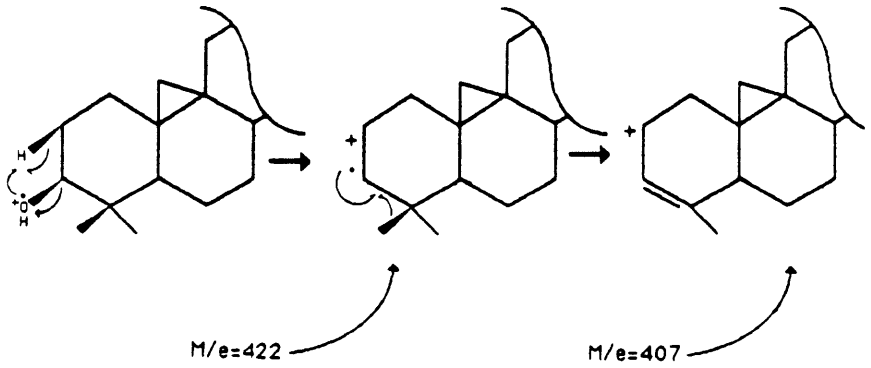


Figure 7.3: Possible origins of some major ions in the cycloiaudenol mass spectrum.

7.2.3 The long-term fate of cyclolaudenol

Comparison of the cyclolaudenone spectrum and retention time with GCMS data from the sterone fraction of surface sediments from the OMZ (core SC7, 100 m; core KNSC6, 268 m) suggested that this compound was not present in significant quantities in these sediments; therefore, this compound is probably not a significant alteration product of cyclolaudenol in these sediments. Furthermore, ion chromatograms of the molecular ions of the other potential cyclolaudenol alteration products shown in Fig 7.1 suggested that only trace quantities of these compounds could be present in the extracts of the sediments investigated. Cyclolaudenol may undergo a series of rapid alterations in the sediments, with none of the initial alteration products accumulating. Another intriguing possibility is that cyclolaudenol, or an alteration product of this compound, is converted into a bound form, perhaps by addition to the double bond in the side-chain or addition to the double bond that would result from dehydration of the alcohol.

Although the long-term diagenetic fate of cyclolaudenol is unknown, the recent work of Bac (1990) and Brassell (personal communication) suggests a possible diagenetic fate of a cyclosterol similar to cyclolaudenol. Bac and Brassell identified an unusual set of C_{30} 4,4-dimethyl steroids (similar to dammaraene) in the late-Cretaceous Moreno Formation of the San Joaquin Basin, California. They propose (Brassell, personal communication) that these compounds may be alteration products of a C_{30} cyclosterol, such as cycloartanol, which has undergone opening of the cyclopropyl ring and a series of methyl migrations. An intriguing, unanswered question is whether or not the sterol precursor of the these compounds was a natural product of the same kind of bacterial mat that left fossilized remains in the Miocene Monterey Formation of the same basin (Williams, 1984).

7.3 THAA, total protein, and total carbohydrate in *Thioploca* spp.

Henrichs et al. (1984) determined the composition of THAA in sediments from five cores from the Peru upwelling region at 15°S. Three of these cores (water depths of 92, 268, and 506 m) were taken from the OMZ and contained *Thioploca* in the surface sediments. The other two cores were taken outside the OMZ (1428 m and 5300 m) and did not contain *Thioploca*. Henrichs et al. (1984) found neither a trend in THAA composition down the cores, nor a significant difference between the THAA compositions of the *Thioploca* -containing sediments and sediments from outside the OMZ. Therefore, determination of the THAA composition of *Thioploca* could potentially distinguish between two possibilities: (1) if the THAA composition of *Thioploca* were similar to the sediments, then *Thioploca* could represent a significant source of the sedimentary THAA, but simply

not have a distinctive signature with respect to the amino acids analyzed by Henrichs et al.(1984), or (2) if the THAA composition of *Thioploca* differed substantially from the sedimentary THAA composition, then *Thioploca* is probably not a major source of THAA in OMZ sediments. Unfortunately, the data for the THAA composition of six *Thioploca* samples and two sediments analyzed in this study do not clearly indicate which of these scenarios is more likely.

The THAA compositions of the *Thioploca* samples (Table 7.1) were very similar and contained no unusual amino acids that might be used as biomarkers for this organism. The THAA composition of *Thioploca* was similar to surface sediment from core SC3 (Fig 7.4). However, as shown in Fig. 7.5, the relative amounts (mole %) of six amino acids differ significantly between the sediment samples analyzed by Henrichs et al. (1984) and the samples analyzed in this study. The samples I analyzed contained relatively more leucine and isoleucine and relatively less glycine, threonine, serine and asparagine than the sediments analyzed by Henrichs et al. (1984). This difference between the THAA compositions of the sediment analyzed in this study and those reported by Henrichs et al. (1984) may be an artifact of differences in analytical methodologies between the two studies. The present study used the HPLC technique described in chapter 2, and Henrichs et al. (1984) measured the amino acids by GC as N-heptafluoro-butyryl-n-butyl esters. Alternatively, differences between the two studies may be real, and the sediment analyzed in this study (SC3, 0-1 cm) may differ from sediments analyzed by Henrichs et al. (1984) because the narrowest surface sediment interval analyzed by Henrichs et al. (1984) was 0-3 cm.

In Table 7.1, the *Thioploca* and sediment THAA data are compared with the THAA composition of another sulfur-oxidizing bacteria, *Thiomicrospira crunogena* (Conway, 1990), two other marine bacteria, *Chromobacterium* and *Desulfovibrio* (Henrichs, 1980), and "mixed marine plankton" (Prahl and Meuhlhausen, 1989). Glutamic acid, glycine, alanine, valine, and leucine are the most common amino acids in these samples, as in a large number of other organisms (Conway, 1990). Lysine is relatively abundant in the *Thioploca* samples (10 %).

Wt % protein from the biuret assay of the *Thioploca* was 20.5%. Wt% protein from THAA quantification was 8.1, 9.1 and 12.6%. The phenol-sulfuric acid assay of the *Thioploca* indicated that carbohydrates were 11.9%, but this assay may underestimate the abundance of certain complex carbohydrates, such as mucopolysaccarides (Conway, 1990).

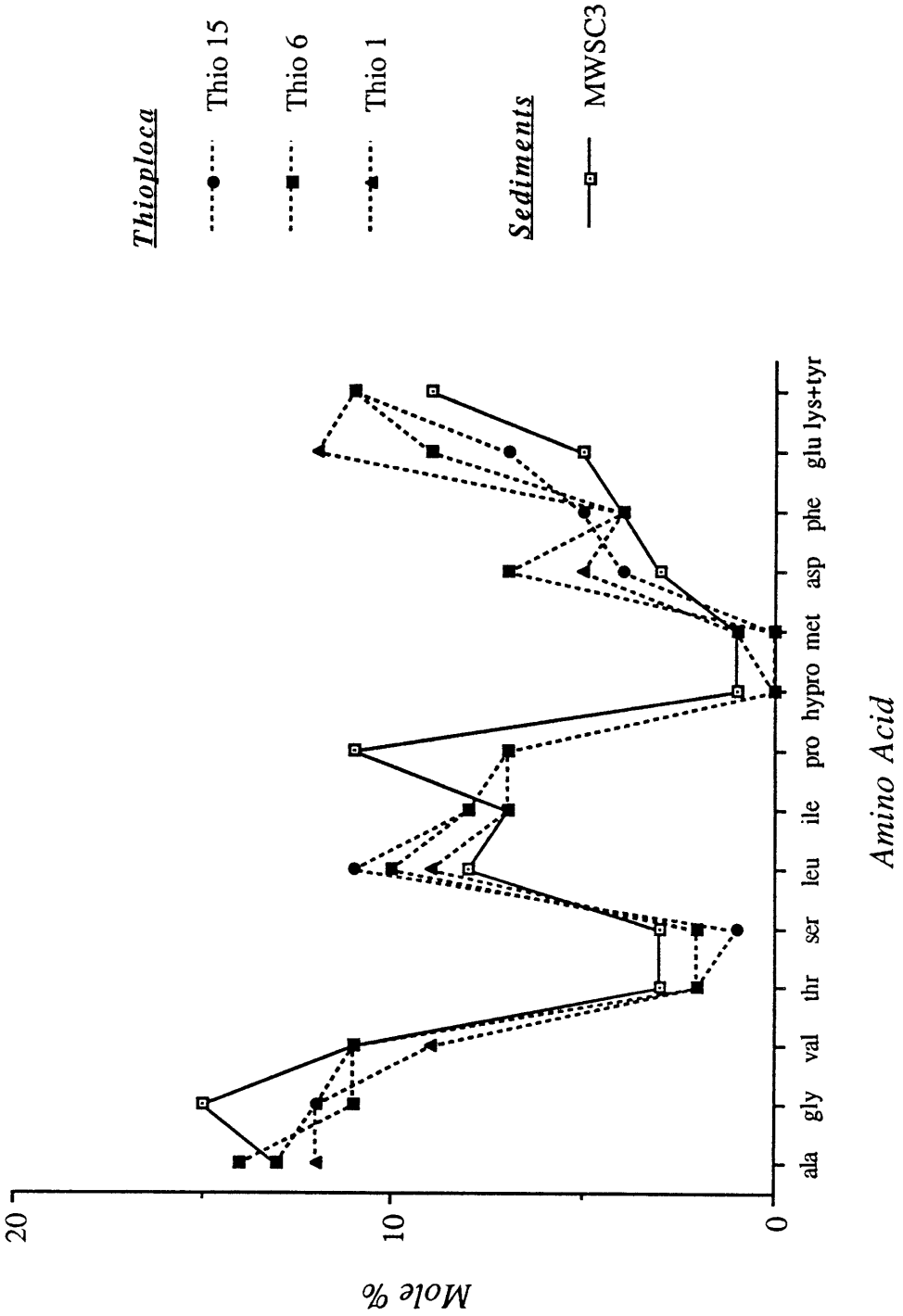


Figure 7.4: THAA in surface sediment from core SC3 and in *Thioploca* samples from three stations (locations in Table 2.1). Data for each *Thioploca* sample is the average of two discrete hydrolyses and analyses of the homogenized sample. The mole % values were calculated using only the amino acids analyzed by Henrichs et al. (1984) to facilitate a comparison with their data in Fig. 7.5. The complete analyses of the *Thioploca* samples are given in Table 7.1.

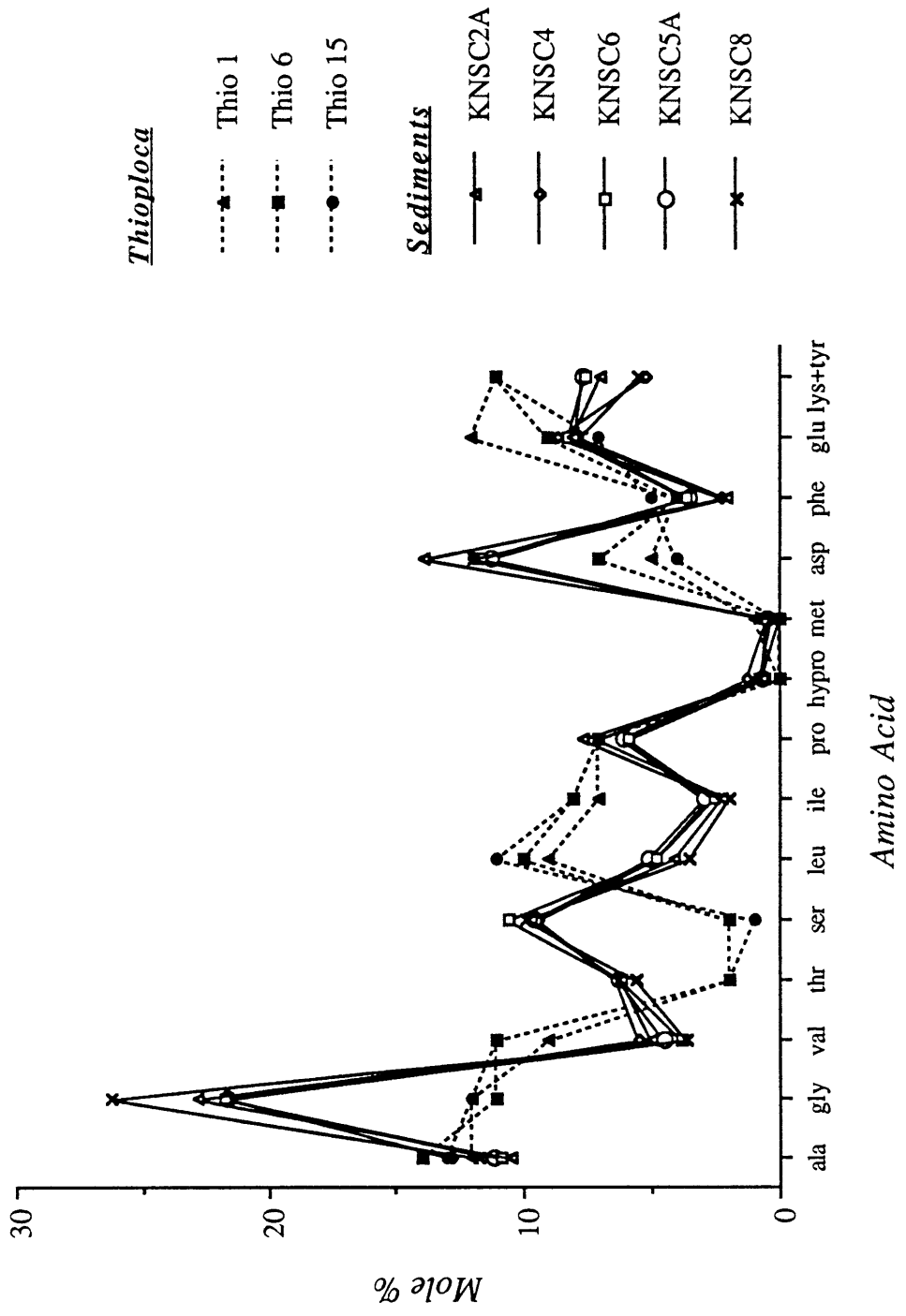


Figure 7.5: THAA in *Thioploca* samples compared with THAA data reported by Henrichs et al. (1984) for Peru surface sediments. The mole % values for the *Thioploca* samples were calculated using only the amino acids analyzed by Henrichs et al. (1984) to facilitate a comparison with their data.

Table 7.1
Comparison of the THAA composition (Mole%) of *Thioploca*, several marine bacteria, and "mixed marine plankton"

Amino Acid	*Thioploca* sample #1	*Thioploca* sample #6	*Thioploca* sample #15	*Thiomicrospira crunogena*[1]	*Desulfovibrio*[2]	*Chromobacteria*[3]	Mixed plankton[4]
Asp	5	7	4	1	8.7	8.3	10
Glu	12	9	7	1	9.9	11	12
Ser	2	2	1	1	9.4	9.5	5
Gly	12	11	12	10	13	11	14
His	1	1	1	0	§	§	2
Arg	4	4	5	4	§	§	5
Thr	2	2	2	3	6.1	6.7	6
Ala	12	14	13	16	12	12	10
Pro	7	7	7	19	4.4	3.5	4
Val	9	11	11	16	7.8	9	6
Met	1	0	0	1	0.8	§	2
Cys	0	0	0	3	§	§	1
Ile	7	8	8	7	4.4	3.6	4
Leu	9	10	11	9	5.8	6.1	7
Phe	4	4	5	4	3.7	3.4	3
Try	1	0	0	0	§	§	0
Lys	10	10	10	3	11.4 *	10.6*	6
Tyr	1	1	1	0	*	*	3

[1]A gram-negative sulfur-oxidizing marine bacterium. Data from Conway (1990).
[2]Data from Henrichs (1980), does not include free amino acids.
[3]Data from Henrichs (1980), does not include free amino acids.
[4]Calculated from data in Prahl and Meuhlhausen (1989).
§Concentration unknown, not measured.
*Lysine and Tyrosine are summed.

7.4 Conclusions

• No quantitatively significant alteration products of cyclolaudenol were identified in the Peru surface sediments. Standards of cycloartenone and cyclolaudenone were synthesized and the mass spectra of these compounds allow identification of some of the major ions in the cyclolaudenol mass spectrum. The identification of a group of 4,4 - dimethyl steroids in the late Cretaceous Moreno Formation by Bac (1990) has led to the suggestion that these compounds may be alteration products of a cyclosterol similar to cyclolaudenol.

• *Thioploca* was found to be 9-10 dry wt% protein, and the THAA composition of the *Thioploca* contained no unusual amino acids that might serve as *Thioploca* markers. The *Thioploca* THAA composition was similar to surface sediment from core SC3, but differed significantly from the THAA composition of surface sediments from the Peru margin analyzed by Henrichs et al. (1984). Differences between the THAA compositions of sediments analyzed in the two studies may be an artifact of differences in the analytical methodologies or may be a result of differences in the width of the surface sediment sections analyzed in the two studies.

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CHAPTER 8

GENERAL SUMMARY AND IMPLICATIONS FOR THE STUDY OF ANCIENT SEDIMENTS

8.1 Introduction

Interest in the El Niño phenomenon has provided substantial impetus for constructing detailed records of the Peruvian paleoclimate. Because the coastal Peruvian ecosystem and depositional conditions are severely impacted by El Niño events, Peru margin sediments may yield an organic geochemical record of past ENSO occurrences. Interest in the organic geochemistry of these sediments has also been motivated by recognition of the coastal Peruvian OMZ as a modern analog to the depositional environments of certain important petroleum source rocks (e.g., Demaison and Moore, 1980). Because organic matter alteration pathways in surface sediments ultimately affect kerogen type and eventual petroleum yield of a sediment, there are important applications for an understanding of the factors affecting organic matter alteration in these sediments. Furthermore, recognition of the potential of organic geochemistry for paleoenvironmental reconstruction has led to a search for biomarkers specific to this type of depositional environment which could be used to identify similar depositional conditions in the geologic record (e.g., Brassell and Eglinton, 1983; ten Haven et al., 1989, 1990).

Numerous sedimentary organic geochemical parameters have been proposed as indicators of paleodepositional conditions in coastal upwelling areas (e.g., Brassell and Eglinton, 1983). However, individual studies typically deal with only a few of these parameters, and many studies have not had access to very finely-sectioned, dated cores. As a result, it is frequently *not* possible to assess the relative utility of discrete organic geochemical indicators of depositional conditions. In this context, the work reported here has had two specific goals: (1) assessing the relative utility of a large number of sedimentary lipids as indicators of short-term changes in depositional conditions and organic matter sources in coastal Peru, and (2) determining if the lipid geochemistry of these sediments records an historical record of ENSO events that have affected this region. The second aim, a subset of the first, is of specific interest because identification of a sedimentary signature of ENSO events may lead to an extension of the historical ENSO record (Quinn et al., 1987), which would certainly be useful in studying the ENSO phenomenon.

8.2 Specific conclusions

I assessed the potential of the alkenone-U^k_{37} "paleothermometer" as a sedimentary marker for ENSO events by comparing the historical El Niño record with detailed U^k_{37} profiles for ^{210}Pb-dated cores from the Peru margin OMZ. Sediments from the center of the OMZ sectioned at intervals ≤ the yearly sedimentation rate have the greatest potential for holding a U^k_{37} record of ENSO occurrences. The U^k_{37} signals of individual El Niño events were substantially attenuated in the sediments examined, and periods of frequent ENSO activity (e.g., 1870-1891) were more readily identified than isolated ENSO events in periods of less frequent ENSO activity. Detailed depth profiles of the C_{37} alkenones in a core from ≈253 m (O_2 <0.1 ml/l bottom water) suggest significant alkenone degradation and/or alteration (≈30%) in the 0-1 cm interval, despite the dysoxic depositional conditions. However, the similarity of the U^k_{37} values for the five 2 mm sections from 0-1 cm suggests that the U^k_{37} may be unaffected by the alkenone loss.

Correlation between the C_{37} alkenone concentration profiles in two cores from ≈15°S collected nine years apart is consistent with the use of these compounds for molecular stratigraphy. It may be possible to use other sedimentary lipids for molecular stratigraphic correlations as well, since not only the alkenone profiles, but also the TOC profiles of these two cores are well-correlated.

The utility of sedimentary hydrocarbons and alcohols as indicators of short-term changes in depositional conditions was assessed. The distribution of 35 lipids (n-alkanes, n-alkanols, hopanols, keto-ols, lycopane, phytol, stenols, stanols, sterenes, and tetrahymanol) in a 1 m dated core from 253 m water depth were interpreted by: (1) a multivariate factor analysis, and (2) a consideration of individual source-specific biomarkers. Profiles of odd-carbon-number n-alkanes (C_{25}-C_{33}) and even-carbon-number n-alkanols (C_{24}-C_{28}) reflect changes in the input of terrigenous sediment relative to marine sediment during deposition, as indicated by the correlations between these lipids and inorganic indicators of terrigenous clastic debris. The n-alkane carbon preference index (CPI) provides a less-sensitive record of fluctuations in the terrestrial input than the concentration profiles of the individual n-alkanes and n-alkanols, and these lipids are *not* well-correlated with the historical El Niño record. The similarity of all the stenol profiles measured and the lack of concordance between these profiles and inorganic indicators of terrigenous input suggest that fluctuations in the abundance of higher-plant stenols are obscured by the larger marine contribution of these compounds. Similarities between the profiles of total organic carbon (TOC) and cholestanol/cholesterol are consistent with stenol hydrogenation being influenced by the sediment redox conditions.

Profiles of sterols and sterol alteration products illustrate that the rapid downcore decreases in sterol concentrations do not simply represent conversion of sterols into other steroidal compounds, but must also involve steroid degradation and possibly formation of bound steroids. In core SC3, the ratio [cholesterol alteration products] / [cholesterol + cholesterol alteration products] substantially increases from 0-4 cm, but at deeper depths, there is no systematic change in the ratio. This suggests that if there is a progressive conversion of cholesterol to these degradation products below 4 cm, then it is obscured by an equally rapid removal of these compounds from the sediments. Stenol profiles in surface sediments suggest a range of degradation rates for these compounds. Differential remineralization of steroids can cause the relative steroid abundances in an ancient sediment to bear little resemblance to the relative abundances of the original sterols. This limits the use of steroids as indicators of the *relative importance* of the original organic matter inputs. However, important quantitative statements can be made concerning the depositional environment, based on the presence, rather than relative abundance, of certain steroids derived from specific sources.

In SC3, the downcore increase in burial time (100 cm ≈ 310 years b.p.) and the downcore changes in sediment chemistry did not result in accumulation of cholesterol alteration products from more advanced portions of the alteration pathways than are achieved in the 0-1 cm interval. The absence of cholest-4-ene, cholest-5-ene and cholestane suggests that cholestadiene reduction to cholestenes and cholestene reduction to cholestane occur over time scales and under sedimentary conditions not encountered in the surface 100 cm of Peru margin OMZ sediments.

Although the hopanoids found in the Peru sediments can be related relatively easily to compounds found in ancient sediments and oils, these hopanoids are not as useful as steroids for reconstruction of organic matter sources and paleoenvironmental conditions. This is because the bacterially-derived precursors of these compounds are not specific to any particular type of bacteria.

The lipid composition of *Thioploca,* a genus of sulfur-oxidizing, filamentous bacteria from the Peru margin OMZ is presented here, with the first assessment of the influence of *Thioploca* on organic compound distributions in upwelling regime sediments. Since marine species of *Thioploca* have been found only in dysaerobic surface sediments of upwelling regimes (where they may constitute as much as 80% of the benthic biomass), biomarkers for this organism may be useful in identifying similar depositional conditions in the sedimentary record. *Thioploca* (dry) was found to be ≈3.8-4.1 wt% lipid. Three fatty acids: *cis* 16:1Δ9, 16:0 and *cis* 18:1Δ11 accounted for 69-72% of this lipid. Hydroxy fatty acids, hopanoids and hydrocarbons were conspicuously absent from the *Thioploca*. This

bacteria was found to contain cyclolaudenol, a C_{31} sterol with an unusual structure; diagenetic alteration products of this sterol may serve as markers for *Thioploca* input to sedimentary organic matter, and hence as markers for paleo-upwelling depositional environments in the sedimentary record. No quantitatively significant alteration products of cyclolaudenol were identified in the Peru surface sediments.

Thioploca was found to be 9-10 dry wt% protein, and the THAA composition of the *Thioploca* contained no unusual amino acids that might serve as *Thioploca* markers. The *Thioploca* THAA composition was similar to surface sediment from core SC3 (0-1 cm), but differed significantly from the THAA composition of surface sediments (0-3 cm) from the Peru margin analyzed by Henrichs et al. (1984). Differences between the THAA compositions of the sediments analyzed in these studies may be an artifact of differences in the analytical methodologies or may be a result of differences in the width of the surface sediment sections analyzed in the two studies.

8.3 The application of these findings to the study of ancient sediments

The sediments studied in this thesis were deposited over short time scales (≈300 yrs), and much of the preceding discussion has dealt with assessing the utility of organic geochemical parameters as indicators in these sediments of recent, short-term changes in depositional conditions and organic matter source. However, these results have significant implications for the study of ancient sediments as well. Chapter 5 has discussed the implications of steroid diagenesis for the study of ancient sediments, and chapter 6 has discussed the potential of *Thioploca* biomarkers for identification of paleoupwelling environments in the geologic record. A consideration of the utility of this thesis for the study of ancient sediments suggests the following comments as well.

Sediment compaction: Ancient sediments typically have undergone greater compaction than the surface sediments analyzed here. As a result, the smallest time intervals which can be sampled in ancient sediments from a similar depositional environment may be substantially longer than in the surface sediments characterized here. In SC3 (253 m water depth, ≈15°S) the sediment dry wt/wet wt ratio (dry wt corrected for dissolved salts) increases from ≈ 0.06 at 0-1 cm to ≈ 0.18 at 100 cm (Fig. 3.4). In ODP leg 112 sediments from a similar water depth (Hole 680, 252.5 m water depth, ≈11°S) the dry wt/wet wt ratio increases irregularly downcore and averages ≈ 0.5 from 60 m to 100 m (Suess et al., 1988). If a sediment interval 1 cm wide with an initial dry wt/wet ratio of 0.06 is compressed (with loss of only pore water) until the dry wt/wet wt ratio reaches 0.5, the sediment interval width would decrease from 1 cm to ≈ 0.12 cm (assuming a pore water density equivalent to seawater, ≈1.024 g/cm^3). Therefore, the minimum time scale of

the processes which can be investigated in the ODP sediments buried deeper than several meters may be an order of magnitude longer (decades) than for sediments analyzed in this thesis (years). The loss of sampling resolution resulting from sediment compaction may have especially important implications for certain biomarker applications. For example, as discussed in chapter 4, for a given concentration of C_{37} alkenones in a sediment, a sedimentary U^k_{37} signal is exponentially attenuated as sediment deposited either before or after the signal is included in a sediment sample.

Diagenesis and biological evolution: Brassell and Eglinton (1983) noted that the utility of specific biomarkers for the interpretation of ancient sediments depends on two assumptions: (1) that the compounds are either not affected by diagenetic alteration or have unique, identifiable alteration products, and (2) that the biological sources of these compounds have not substantially changed since the sediments were deposited. The susceptibility of the biomarkers to microbial, clay-catalyzed, and catagenic alteration controls the conditions and time span under which (1) is valid. The history of biological evolution controls the time span under which (2) is valid. The implications of compound degradation for biomarker applications have been discussed for the C_{37} alkenones (section 3.5), for n-alkanes (section 4.2), and for stenols (chapter 5).

The history of the evolution of alkenone biosynthesis has implications for the use of these compounds as paleothermometric indictors in ancient sediments. In Recent sediments, the C_{37} alkenones are thought to come primarily from the cosmopolitan marine coccolithophorid, *Emiliania huxleyi* (Marlowe et al., 1984; Prahl et al., 1988). Although this organism first appears in the geologic record ≈ 250,000 y.b.p. (McIntyre, 1970), the C_{37} alkenones have also been found in substantially older sediments. Based on the assemblage of nanofossils, Marlowe et al., (1990) suggested that the alkenones in these older sediments were produced by other genera in the same family (Gephyrocapsaceae) as *Emiliania*. Because the U^k_{37}-temperature relationship has only been calibrated for *E. huxleyi* (Prahl et al., 1988), the applicability of this calibration to sediments predating *E. huxleyi* is uncertain. However, a correlation between the relative alkenone unsaturation in these sediments and the temperature of alkenone biosynthesis is likely, given the proposed biochemical role of these compounds (Marlowe et al., 1984) in modulating membrane fluidity in response to changing temperature. A correlation between U^k_{37} and paleotemperature in ancient sediments is also suggested by the observation of Brassell (1989) that a decrease in the U^k_{37} of sediments at the Eocene/ Oligocene boundary is synchronous with the global oceanic cooling suggested by the $\delta^{18}O$ of foraminiferal carbonate.

For sediments pre-dating *E. huxleyi*, the use of alkenones for reconstruction of *quantitative* temperature profiles will require (1) calibration of the U^k_{37}-temperature relationship that existed for the Gephyrocapsaceae in older sediments (perhaps by comparison of U^k_{37} and carbonate $\delta^{18}O$ records), and (2) characterization of the diagenetic fate of the alkenones (Brassell, 1989). In Recent sediments, the C_{37} alkenones produced by Prymnesiophytes occur as a mixture of di-, tri- and tetra- unsaturated compounds. However, the earliest appearances of each of these compounds in the geologic record are not contemporaneous. The earliest reported occurrence of the $C_{37:4}$ alkenone is Pleistocene (Marlowe et al., 1990), whereas the earliest occurrences of the $C_{37:3}$ and $C_{37:2}$ alkenones are Eocene (Marlowe, 1984) and Mid-Cretaceous (Farrimond et al., 1987) respectively. The differences in the timing of the first appearances of these compounds are probably the result of evolution of alkenone biosynthesis in these algae (Farrimond et al., 1987; Marlowe et al., 1990) and suggest that Eocene sediments (the oldest containing both $C_{37:2}$ and $C_{37:3}$ alkenones) may be the oldest with potential for alkenone paleothermometry.

Terrigenous markers and ancient sediments: The finding of terrigenous biomarkers in the Peru margin OMZ sediments (chapter 4) suggests that the sedimentary distribution of these compounds may provide a record of terrigenous input to the sediments, despite the paucity of coastal vegetation. Terrigenous biomarker profiles in ancient sediments probably have utility as indicators of *fluctuations* in the abundance of terrigenous inputs. However, the selective preservation of higher plant biomarkers (e.g., long-chain n- alkanes) relative to marine markers observed in SC3 (this study) and elsewhere (Aizenshtat et al., 1973; Prahl et al., 1980; Volkman et al., 1983) indicates that the biomarker distributions in ancient sediments probably do not reflect the original *absolute concentrations* of the terrestrial and marine organic matter inputs. In addition, when increasing sediment maturity results in petroleum generation, the utility of n-alkane concentration profiles as indicators of terrigenous input greatly decreases. This is because thermal cracking of n-alkanes from kerogen not only increases the bitumen n-alkane concentrations, but also decreases the n-alkane CPI, since n-alkanes from thermal cracking of kerogen have a CPI $\approx$ 1 (e.g., Hunt , 1979). Therefore terrestrial markers measured in the Peru margin sediments, n-alkanes and n-alkanols, have applicability as terrigenous indicators only in thermally immature ancient sediments.

The Miocene Monterey Formation: In the Middle Miocene, bioturbated calcareous shales were forming under oxic depositional conditions in the California Borderland. Then, $\approx$14 m.y.b.p. (Middle Miocene), this depositional environment radically changed as formation of the Antarctic ice sheet lowered sealevel and initiated an oceanic cooling. This cooling increased atmospheric thermal gradients which increased wind stress and

intensified coastal upwelling in the California Borderland (Summerhays, 1981). In this changed environment, laminated, siliceous, organic-rich diatomites and siliceous shales, now comprising the upper Monterey Formation, were deposited within a well-developed OMZ. Recent interest in this formation stems largely from its position as one of the most important petroleum source rocks of the United States west coast (e.g., Kruge, 1986). Because the coastal upwelling regime in which these siliceous sediments were deposited is analogous to the present coastal upwelling regime along Peru (e.g., Soutar et al., 1981; Williams, 1984), studies of modern Peru sediments are frequently suggested as a tool for interpreting the Monterey. As discussed below, this thesis has several implications for the study of this formation.

In thermally immature sections of the Monterey, alkenone paleothermometry may provide a record of changes in the relative intensity of upwelling. Such a record may have molecular stratigraphic utility in correlating time equivalent sections of the Monterey. Furthermore, since deposition of the Monterey was affected by both changes in the physical oceanography and tectonic events (e.g., wrench-fault basin formation; Graham and Williams, 1985) alkenone paleothermometry may be useful for distinguishing the sedimentary signature of upwelling events from changes in organic matter preservation caused by changes in basin geometry and/or bottom water oxygenation. I am unaware of any studies that have attempted to identify these lipids in pre-Quaternary sediments from the California Borderland.

Williams (1984) noted that fossil bacterial mats "occur commonly in siliceous sediments of the Miocene Monterey Formation in the San Joaquin Valley, where they coat bedding planes of thinly laminated diatomites, siliceous shales, and porcelanites." Furthermore, she notes that in terms of total organic carbon, "mat laminated rocks comprise the richest [petroleum] source rock lithotype in the Monterey Formation of the San Joaquin Valley." The fossilized bacterial mats, however, are probably not the cause of the high organic carbon content of these sediments. *Thioploca* is found under low oxygen conditions, which are also conducive to organic matter preservation (Demaison and Moore, 1980). Therefore, the high organic content of the source rocks containing the fossilized bacterial mats may have more to do with the low-oxygen depositional conditions than with the presence of bacterial mats in the depositional environment.

The composition of *Thioploca* (chapters 6 and 7) suggests that the primary impact of *Thioploca* on petroleum source-rock formation may be the physical effects of *Thioploca* on sediment accumulation rather than the input of *Thioploca*-synthesized organic matter. *Thioploca* is not more lipid-rich (chapter 6) than marine detritus from the water column (e.g., Wakeham et al., 1984). Furthermore, the fatty acids, *cis* 16:1Δ9, 16:0 and *cis*

18:1Δ11, which account for most (69-72%) of the *Thioploca* lipid material, are not more abundant in the Peru sediments than many lipids not produced by *Thioploca* , such as 4-desmethylstenols and C_{37} alkenones. These bacteria, however, do have a substantial physical impact on the sediments, because of the mat structure the *Thioploca* form near the sediment-water interface. By physically stabilizing surface sediments, this mat may inhibit sediment resuspension (Grant and Bathmann, 1987) in a manner analogous to plant roots inhibiting soil erosion. As noted by Williams (1984), these bacteria may also physically affect sedimentation as a result of particles adhering to the mucilaginous bacterial sheaths, a well-known mechanism by which cyanobacterial stromatolites (Williams, 1984) and *Beggiatoa* bacterial mats (Grant and Bathmann, 1987) affect sedimentation in shallower depositional environments.

The occurrence of abundant fossilized bacterial mats in the Monterey Formation led Katz and Elrod (1983) to suggest *Thioploca* as a possible source for a diagenetic precursor to the unusual bisnorhopane [17α(H), 18α(H), 21ß(H)-28, 30-bisnorhopane] abundant in many Monterey oils and sediment bitumens (Seifert et al., 1978; Katz and Elrod, 1983; Curiale et al., 1985; Requejo and Halpern, 1989). However, *Thioploca* is certainly not the source of this compound, since hopanoids are not present in *Thioploca* (chapter 6). As discussed in chapter 5, no diagenetic precursor for the bisnorhopane could be identified in the Peru margin sediments either, an enigmatic finding considering the high abundance of the bisnorhopane (as much as 26 μg/ gdw; Seifert et al., 1978) in the Monterey. One possibility is that this compound is derived from a natural product of a now-extinct organism.

The Monterey Formation is characterized by extremely sulfur-rich kerogens, and is as much as 8 to 14 wt% S in some basins (Orr, 1986). Type II-S kerogens [Type II kerogens with a $S_{org.}/C$ ratios (mol/mol) > 0.04; Orr, 1986] are found not only in the Monterey, but also in a small number of other formations, including the Phosphoria (Montana), Serpiano (Switzerland), Jurf ed Darawish (Jordan), and Brown Limestone (Gulf of Suez) formations. These sulfur-rich kerogens are of particular interest because they generate oil at lower thermal maturities and with higher asphaltene and resin contents than sulfur-poor Type II kerogens (Walker et al., 1983; Orr, 1986; Tannenbaum and Aizenshtat, 1985), a phenomenon which has been attributed to the lower activation energy needed for cleavage of sulfur-sulfur and sulfur-carbon bonds than for cleavage of carbon-carbon bonds (Orr, 1986; Sinninghe Damsté et al., 1989).

Three depositional conditions facilitate the eventual formation of a sulfur-rich kerogen (Orr, 1986). The environment must be marine, because of the need for a sulfur source (sulfate). In addition, the level of primary productivity and/or the physical oceanography of

the basin must result in anoxic sediments and microbial sulfate reduction. Furthermore, the sediments typically must be poor in terrigenous clastic debris, since iron (derived primarily from rock detritus) competes with organic matter as a sedimentary sink for sulfur (Gransch and Posthuma, 1974). In the Peru upwelling regime, the presence of (1) high productivity, (2) an OMZ which impinges on the sediments, and (3) an arid coastline with low terrigenous input, results in sulfur-rich kerogen formation. Mossmann et al. (1990) found kerogen S concentrations as high as 12 wt% in ODP sediments from the Peru margin. Furthermore, Mossmann et al. (1990) showed that sulfur is incorporated into Peru margin kerogen and bitumen in the surface 15 m of ODP leg 112 core 680 (250 m water depth, 11°S) and core 686 (450 m water depth, 11°S), suggesting "that early diagenetic reactions exert a major control on the ultimate sulfur content of kerogen." Unfortunately, their data did not allow an assessment of the importance of this process near the sediment-water interface.

By oxidizing H_2S to elemental sulfur, the *Thioploca* in Peru surface sediments may significantly affect the sedimentary sulfur content. *Thioploca* contains abundant intracellular sulfur granules (Maier and Gallardo, 1984), and *Beggiatoa*, a genus of filamentous, sulfur-oxidizing bacteria in the same family as *Thioploca*, is known to be as much as 20 wt% elemental sulfur (Nelson and Castenholz, 1981). Grant and Bathmann (1987) reported that elemental sulfur produced by *Beggiatoa* mats enrich the sulfur content of coastal marine surface sediments from Nova Scotia by a factor of five relative to sediments underlying the mat. With increasing depth of burial, the elemental sulfur produced by the *Thioploca* in Peru surface sediments is apparently again reduced to sulfide; Mossmann et al. (1990) found that in Peru margin ODP sediments elemental sulfur decreases with depth, and >95% of the total sedimentary sulfur is bound in pyrite and kerogen. However, by oxidizing H_2S to elemental sulfur, *Thioploca* may significantly decrease the loss of reduced sulfur from the sediments by H_2S diffusion and, in this way, increase the fraction of the reduced sulfur that eventually is bound into pyrite and kerogen.

8.4 Future research

This thesis highlights the potential of several areas of research for further developing applications of biomarkers to the interpretation of upwelling regime sediments. Some of these areas, briefly discussed below, include (1) delineation of the time scale on which there is sulfur cross-linking of lipids into high-molecular-weight organic matter, (2) characterization of the isotopic composition of individual lipid profiles, (3) determination of the stereochemistry of certain lipids, and (4) investigation of the distribution of high molecular weight lipids (C_{40}-C_{100}) in these sediments.

Chapters 3 and 5 noted that an assessment of the geochemical implications of lipid remineralization requires a better understanding of the time scale on which there is sulfur cross-linking of lipids into high-molecular-weight organic matter. Some of the lipids most labile with respect to degradation (e.g., polyunsaturated fatty acids, alkenes, and, to a lesser extent, alcohols) would probably be the compounds most susceptible to sulfur-cross linking. Since many of these lipids are thought to degrade rapidly near the sediment-water interface (e.g., Farrington et al., 1990), the timing of sulfur cross-linking may be of critical importance in determining the preservation of these compounds. If this process occurs soon after deposition (within several cm of the sediment-water interface), then we may presently underestimate the relative importance of many compounds in defining the lipid signature of depositional conditions preserved in the sediment kerogen.

The advent of gas chromatography-isotope-ratio-mass-spectrometry (e.g., Freeman et al., 1990) has provided a potentially very powerful tool for assessing the importance of various lipid sources in a sediment. This potential is illustrated by the discussion in chapter 4 of the relative importance of terrestrial and marine sources of n-alkanes, n-alkanols, and stenols. Because $\delta^{13}C$ values of terrestrial lipids are substantially lighter (as much as 8 °/∞) than the $\delta^{13}C$ values of the same compounds from a marine source, downcore plots of the isotopic composition of a lipid could provide an independent assessment of downcore changes in the relative importance of these sources of the compound. In addition, by determining the covariance of the isotopic composition of specific lipids, one may use this technique to assess whether or not specific lipids have a common source (Freeman, 1989).

Determination of the stereochemistry of certain lipids may further elucidate the sources of these compounds in sediments. For instance, in chapter 4 it was noted that higher plants and phytoplankton both produce 24-alkyl-substituted sterols, albeit with different stereochemistries at C-24. The 24-R and S epimers of these compounds have identical mass spectra and coelute under the GC conditions used here. However, if the peak containing both epimers could be collected in sufficient quantity (perhaps by HPLC), the configuration at C-24 could be determined by NMR. Downcore profiles of the relative abundances of these epimers could then provide information on changes in the relative importance of terrestrial and marine sources of these compounds. Determination of the stereochemistry of lipids with no known source, such as lycopane (chapter 4), might constrain the possible sources of these compounds as well. For instance, it was noted in chapter 4 that carotenoid reduction has been suggested as a source for sedimentary lycopane. If lycopane, which has six chiral centers, were shown to be optically active (like other acyclic isoprenoids, such as phytol), then a source from carotenoid reduction would be unlikely, since such a reduction would probably not be stereospecific. Determination of

the optical activity of individual compounds, such as lycopane, in a lipid mix should be possible by gas chromatography-vibrational circular dichroism techniques currently under development (Daniel Repeta, personal communication).

Another area of research relevant to the work presented here concerns the characterization of high-molecular-weight lipids (>C_{40}) in these sediments. The advent of high-temperature gas chromatogaphy-mass spectrometry (HTGC-MS) has presented the possibility of identifying and quantifying lipids in the C_{40}-C_{100} range, compounds not previously measurable by GC-MS (e.g., Carlson et al., 1989). With increasing carbon number, the potential source-specificity of a compound increases, which suggests that this technique may provide a wealth of new, very source-specific, biomarkers.

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APPENDIX 1- DATA FOR CORE SC3

All lipid concentrations are in ng/gdw. Depth (cm) is for middle of core secion.

DEPTH	dry wt/wet wt*	%TOC	%N	C/N (mol/mol)	C24 n-alkane	C25 n-alkane	C26 n-alkane	C27 n-alkane	C29 n-alkane
0.5	0.0595	11.82	1.59	8.7	89.3	174	90.4	244	618
1.5	0.0682	11.61	1.61	8.4	56.9	137	66.3	267	708
2.5	0.0666	12.00	1.55	9.0	46.3	115	63.2	212	574
3.5	0.0723	11.73	1.19	11.5	51.0	114	65.4	212	530
4.5	0.0699	11.10	1.26	10.3	58.5	131	63.0	211	562
5.5	0.0574	11.68	1.38	9.9	57.8	123	59.3	224	589
6.6	0.0570	10.49	1.37	8.9	98.8	208	113.0	327	609
7.9	0.0590	10.41	1.21	10.0	67.4	127	63.6	211	530
9.1	0.0626	8.97	1.02	10.3	61.4	122	56.8	197	500
10.4	0.0640	9.20	1.07	10.0	58.4	103	49.9	177	516
11.6	0.0667	9.37	1.16	9.4	58.0	113	53.2	198	527
12.9	0.0725	9.60	1.08	10.4	52.0	118	63.8	197	545
14.1	0.0744	9.06	1.03	10.3	51.8	110	55.5	207	543
16.5	0.0765	9.17	1.17	9.1	53.3	117	57.6	221	605
18.5	0.0836	9.88	1.12	10.3	61.6	116	58.5	199	529
19.5	0.0863	9.50	1.18	9.4	43.8	99	41.5	183	545
20.5	0.0806	10.28	1.06	11.3	44.9	124	56.7	232	683
21.5	0.0936	9.76	1.07	10.6	41.5	102	46.6	195	592
25.5	0.0779	9.62	1.12	10.0	52.5	108	51.9	201	508
27.5	0.0831	9.79	1.19	9.6	37.0	91	37.9	177	500
30.5	0.1115	11.02	1.26	10.2	39.2	117	49.0	242	697
35.5	0.0938	9.19	1.17	9.2	41.0	115	45.2	246	727
38.5	0.1381	8.67	1.21	8.4	37.7	129	45.2	275	795
40.5	0.1286	8.25	1.11	8.7	44.5	120	41.5	249	730
41.5	0.1237	8.25	1.10	8.7	47.6	141	49.3	278	826
42.5	0.0978	8.19	1.03	9.3	37.6	115	41.1	231	702
43.5	0.0812	7.94	0.91	10.2	47.0	114	45.9	199	575
44.5	0.0768	6.67	0.81	9.6	36.7	87	32.6	146	419
45.5	0.0690	6.62	0.75	10.3	47.0	96	46.0	160	397
46.5	0.0859	6.19	0.71	10.2	32.4	86	32.6	162	473
47.5	0.0796	7.10	0.79	10.5	35.0	86	34.9	155	412
48.5	0.1057	6.77	0.76	10.4	34.9	93	33.9	197	497
49.5	0.1030	6.36	0.71	10.4	37.6	98	41.9	189	522
50.5	0.1027	6.35	0.73	10.1	27.1	83	30.2	149	413
52.5	0.0879	7.25	0.83	10.2	30.7	81	34.1	146	390
55.5	0.1026	7.67	0.88	10.2	28.5	92	33.4	174	498
59.5	0.1137	7.42	0.88	9.8	26.7	86	31.8	161	436
62.5	0.2235	7.56	0.88	10.0	41.0	132	53.0	309	854
65.5	0.2415	7.67	0.92	9.7	41.9	145	53.1	335	884
67.5	0.2145	7.59	0.87	10.2	39.4	128	47.2	306	800
70.5	0.1467	6.81	0.77	10.3	32.9	108	38.8	225	598
72.5	0.1570	6.33	0.73	10.1	28.7	94	35.3	204	519
75.5	0.2610	6.94	0.79	10.2	35.2	125	49.3	295	766
77.5	0.2532	7.61	0.87	10.2	37.3	126	47.8	304	783
78.5	0.2316	7.33	0.82	10.4	38.1	122	45.6	281	744
80.5	0.1503	7.41	0.81	10.7	26.1	70	32.2	144	371
85.5	0.1717	7.00	0.75	10.9	20.8	54	22.4	99	299
90.5	0.1790	7.15	0.76	11.0	23.5	76	28.9	154	396
95.0	0.1741	7.09	0.77	10.7	24.4	83	27.5	152	448
99.0	0.1792	7.60	0.87	10.2	26.0	81	31.8	164	435

*dry wt was corrected for interstitial salt assuming a pore-water salinity of 3.5%.

DEPTH	C30 n-alkane	C31 n-alkane	C32 n-alkane	C33 n-alkane	C34 n-alkane	CPI	Homohopane	Lycopane	Branched C20:1*
0.5	126	735	104	283	119	3.7	153	3000	9740
1.5	137	814	131	317	68	4.2	155	2220	7300
2.5	108	618	98	274	118	3.9	148	2010	6050
3.5	120	663	127	251	55	3.7	133	1920	4850
4.5	138	620	139	272	82	3.3	141	1780	4360
5.5	133	689	145	248	100	3.4	160	1900	8040
6.6	204	729	189	260	100	2.6	159	1730	7600
7.9	111	594	113	238	46	3.7	139	1470	7310
9.1	102	561	96	208	52	3.8	141	1280	6350
10.4	79	612	69	213	60	4.8	113	991	3180
11.6	80	636	76	229	57	4.9	132	1190	5630
12.9	79	664	83	236	62	4.9	134	1230	5220
14.1	80	663	73	239	60	5.1	135	1180	5670
16.5	116	613	114	254	38	4.0	157	1280	5830
18.5	97	615	87	234	31	4.4	144	1010	3620
19.5	79	570	68	219	36	5.2	145	969	1940
20.5	102	738	86	276	33	5.3	181	1170	2120
21.5	85	639	74	238	28	5.4	152	955	1570
25.5	69	519	48	201	35	5.5	163	1080	1530
27.5	59	521	50	204	31	6.2	168	1060	1270
30.5	75	670	54	248	27	6.9	198	1240	567
35.5	72	649	57	239	34	7.0	180	1220	420
38.5	83	773	46	273	18	7.9	242	959	
40.5	72	688	58	256	22	7.4	192	919	
41.5	90	763	54	267	18	7.2	206	1060	
42.5	75	628	45	210	12	7.2	158	1010	
43.5	71	533	46	186	14	6.1	131	1000	
44.5	54	436	38	150	13	6.1	103	784	
45.5	52	411	35	143	17	5.6	92	733	
46.5	47	509	38	168	13	7.5	103	620	
47.5	52	443	39	151	17	6.1	100	687	
48.5	56	487	29	177	12	7.3	145	818	
49.5	61	547	45	190	19	6.5	140	748	
50.5	39	362	30	134	12	7.2	118	797	
52.5	43	356	31	133	16	6.4	124	800	
55.5	50	443	35	169	13	7.2	152	946	
59.5	42	401	30	149	16	7.3	156	958	
62.5	82	784	57	299	20	7.8	198	734	
65.5	89	841	66	322	23	7.7	229	759	
67.5	75	753	52	295	21	8.1	211	678	
70.5	58	544	38	218	16	7.8	168	697	
72.5	54	497	37	195	15	7.5	143	633	
75.5	73	728	52	289	19	8.0	184	663	
77.5	74	736	56	284	18	8.0	203	695	
78.5	71	700	56	276	19	7.8	221	701	
80.5	43	350	31	141	17	6.3	126	779	
85.5	35	285	26	113	13	6.2	119	475	
90.5	39	380	38	151	14	7.0	165	693	
95.0	45	406	32	152	14	7.4	129	381	
99.0	42	387	31	147	14	7.2	157	530	

*2,6,10-trimethyl-7-(3-methyl-butyl)-dodecene

C27 anthro-steroid†	C30 triterpenoid	Cholesta-3, 5-diene	Cholesta-R,N,N-triene	Cholesta-N,N,N-triene	C37:3 alkenone	C37:2 alkenone	Uk37
781	3510	3970	2060	1350	11640	30110	0.719
1180	3520	5120	4690	2200	10650	26910	0.716
839	3920	5100	2630	1500	10740	27290	0.718
850	3940	5030	2060	881	9890	25040	0.717
838	3230	4850	2070	1030	12120	26290	0.684
928	3000	4720	2650	1530	14550	31680	0.685
959	2510	3550	2340	1320	11920	26810	0.692
701	3070	1680	977	488	11170	26040	0.700
927	3930	3280	1720	1000	10130	23820	0.702
1060	4920	3720	3310	1200	11540	27810	0.707
938	4450	2980	2840	1030	11360	27510	0.708
1050	4680	3240	3040	1190	11130	26640	0.705
1040	5100	3640	3340	1220	11260	27430	0.709
949	7420	2740	1350	967	13520	33590	0.713
1110	4070	1070	1390	740	11030	28390	0.720
961	6030	2770	898	769	9698	26800	0.734
1060	5970	2390	1580	947	11310	29580	0.723
1010	6550	2610	923	769	9987	26500	0.726
1150	7940	2590	1580	904	9161	23000	0.715
1130	8760	3060	1110	811	9890	25730	0.722
1090	5640	2770	1600	937	12990	29660	0.695
1190	4670	2650	1550	867	11600	26730	0.697
1020	3150	3800	1060	794	12290	30260	0.711
938	1240	928	1480	756	13500	30900	0.696
1060	2500	2830	1060	686	13890	32100	0.698
1140	2270	2660	1120	602	13230	28830	0.685
893	2580	3230	871	433	8386	20950	0.714
676	2780	2360	597	300	5404	15280	0.739
546	1560	1350	713	275	4255	11640	0.732
659	2730	2110	566	269	5080	15240	0.750
624	3020	2150	559	292	4960	14420	0.744
976	4400	2660	591	272	6001	17350	0.743
874	4000	2580	571	245	5943	17840	0.750
985	4460	1520	592	296	5438	12990	0.705
943	5630	2430	566	274	5638	14720	0.723
1200	2840	1780	1090	521	6216	15500	0.714
1080	3590	2590	717	440	6435	18080	0.737
467	810	858	238	276	7599	20000	0.725
571	444	2040	679	538	7767	21110	0.731
381	664	708	202	192	7176	20590	0.742
802	1870	1540	408		6494	18240	0.737
510	1270	723	158		5492	15980	0.744
525	352	1660	403	348	6882	19600	0.740
571	581	1570	385	355	6524	17930	0.733
702	1160	1880	488	391	6542	17980	0.733
1060	3320	2390	582		5743	13080	0.695
976	2850	1520	352		6016	14600	0.708
457	1360	625	125		8861	21380	0.707
756	2500	1410	405		6819	18130	0.727
809	3000	1690	475		6823	17650	0.721

†14∂(H)-1(10—6)-abeocholesta-5,7,9 (10)-triene

DEPTH	Tetrahymanol	C31 hopanol	C32 hopanol	F5 hopanol	C34 hopanol	Phytol	C22 n-alkanol
0.5	33700	7600	4210	1470	5580	38200	1590
1.5	28100	9860	7620	4880	8820	11600	1300
2.5	16000	8670	6820	5100	7040	9860	
3.5	15200	7770	6310	4610	6180	11900	
4.5	12500	7420	5780	4230	5300	13100	
5.5	11800	8120	5890	4920	5190	8880	
6.6	9350	6880	5120	4770	4100	5220	
7.9	10100	6530	5430	4180	3350	5990	904
9.1	8860	5890	4940	3630	2600	5180	922
10.4	11000	5410	4640	3810	2120	6720	852
11.6	10400	4750	4000	3360	1820	5550	803
12.9	10700	5390	4680	3540	2100	7120	
14.1	10700	5730	4960	3670	2270	6020	
16.5	9150	4640	4360	4620	1760	5950	856
18.5	7900	5260	4630	4280	1440	7040	845
19.5	6220	4140	4470	3970	996	6680	798
20.5	7570	5240	5390	4520	1000	5480	910
21.5	6700	4930	4950	3760	1150	6520	861
25.5	6120	5650	5030	4760	1140	7110	863
27.5	7210	5110	4780	4770	718	7980	930
30.5	7390	7310	6890	5390	807	5180	1080
35.5	6640	6340	6470	5090	575	6320	1040
38.5	6460	6890	7170	5430	500	3970	950
40.5	5780	6640	6580	5390	553	4000	969
41.5	6400	6700	6790	5070	567	3220	
42.5	5740	5800	6530	4850	501	3250	832
43.5	4170	4750	5820	3720	448	3520	973
44.5	2270	3130	4050	2560	186	3500	568
45.5	2160	3070	4190	2480		2830	
46.5	1850	2880	3570	2480	269	3150	579
47.5	2120	2520	3080	2560	167	3020	492
48.5	2540	3860	4020	3400		3310	609
49.5	2520	3880	4230	2970		2810	639
50.5	2480	4320	3660	3800		3430	457
52.5	2550	4410	3870	3210		4350	504
55.5	3400	5700	4970	4680		6830	614
59.5	3400	5040	4590	4230		4600	591
62.5	2310	2920	3550	3620		2370	824
65.5	2030	3080	3710	3440		1560	976
67.5	1500	2180	2860	3110		2080	827
70.5	1500	2550	3260	2890		1310	546
72.5	1120	1260	2370	2350		2480	570
75.5	1200	1240	2780	2440		931	764
77.5	1460	1990	3190	2880		1900	801
78.5	1600	2520	3610	3100		2100	833
80.5	1460	2290	3380	2700		1920	501
85.5	1470	2150	1720	2680		2050	456
90.5	2080	4150	3410	2810		1450	651
95.0	1530	2470	3170	2890		1560	553
99.0	1460	2580	2820	3220		1570	551

DEPTH	C24 n-alkanol	C26 n-alkanol	C28 n-alkanol	Dinosterol	cholest-5, 22-dien-3ß-ol	Cholesterol	24-methylcholest 5,22 dien-3ß-ol	24-methylcholest 5-en-3ß-ol
0.5	1920	2380	4350	66900	18800	64300	48300	29800
1.5	1670	1780	4300	59800	5850	18800	14300	18600
2.5	1710	1370	2290	39900	2800	8850	6810	11400
3.5	1460	1150	2590	37900	2250	6140	5600	8010
4.5	1390	1090	1600	36400	2110	5920	5470	8580
5.5	1280	1120	1620	36000	2360	6900	5750	9630
6.6	1080	878	1440	28100	1950	5770	4640	8990
7.9	1110	949	1340	29500	1720	5590	4080	8770
9.1	999	863	1310	26600	1340	4520	2910	7210
10.4	970	857	1180	26900	1360	4730	3380	7550
11.6	935	740	862	20900	1330	4860	3460	8170
12.9	980	879	1070	26600	1340	4760	3530	8060
14.1	1030	943	1200	26400	1450	5110	3760	8610
16.5	1060	915	1190	25800	1320	4240	3600	7530
18.5	1020	876	1180	24900		3440	2990	5420
19.5	988	859	946	26800		3400	2650	4290
20.5	1150	932	1040	30300		3800	3180	4590
21.5	1070	933	976	27300		3720	3000	4670
25.5	1100	962	987	24900		3480	2890	4960
27.5	1190	1120	1030	30100		3330	2650	4620
30.5	1370	1300	1300	30400		2910	2750	3110
35.5	1200	1110	1440	28200		2580	2150	4530
38.5	1430	1300	1430	30600		2680	2440	2570
40.5	1290	1160	1180	26700		2640	2430	3000
41.5	1440	1200	1150	28000		2920	2310	3300
42.5	1320	991	958	23200		3120	2050	4040
43.5	1290	913	822	17500		2990	1920	3500
44.5	1080	784	848	11300		1770	1050	2550
45.5	1110	858	689	11000		1540	1080	2800
46.5	1030	808	822	11200		1390	1060	1660
47.5	1010	815	691	11600		1430	1090	1830
48.5	1230	977	845	15300		1620	1160	1660
49.5	1270	997	900	15600		1390	1130	1250
50.5	1190	897	692	14000		1510	964	1440
52.5	1110	836	680	12000		1850	1090	3520
55.5	1080	884	773	14000		2320	1270	7260
59.5	1210	927	710	14900		1850	1210	2730
62.5	1400	1300	1390	8830		1980	2410	1130
65.5	1730	1550	1680	8440		2470	3110	1450
67.5	1560	1430	1560	8510		1540	1630	864
70.5	1280	1140	983	9090		1430	798	1520
72.5	1170	1000	925	8030		1320	747	1220
75.5	1490	1380	1380	6870		686	679	383
77.5	1350	1360	1350	7950		904	834	466
78.5	1350	1250	1230	8980		1240	1110	1020
80.5	883	777	642	10400		1240	822	1820
85.5	828	692	518	10700		984	667	1380
90.5	1130	927	888	9590		1540	1570	1160
95.0	1050	897	824	8420		1240	1100	1190
99.0	997	913	902	8670		1360	1280	1110

DEPTH	24-ethylcholest 5,22 dien-3ß-ol	24-ethylcholest 5-en-3ß-ol	cholest-22-en-3ß-ol	cholestanol	24-methylcholest 22-en-3ß-ol	24-methyl-cholestan-3ß-ol	24-ethylcholest 22-en-3ß-ol
0.5	35500	93000	7940	23100	15100	10900	6390
1.5	17800	35400	3010	11100	6930	7060	3540
2.5	11200	18300	1540	6960	4330	5650	2510
3.5	9540	13000	1310	5580	4100	4490	2120
4.5	10500	15400	1410	5640	4100	4820	2040
5.5	11800	17900	1510	6400	4000	5900	2720
6.6	10540	15800	1080	5730	3580	5040	2370
7.9	9960	15400	976	5310	3150	4970	2270
9.1	7740	12100	819	4500	2510	3950	1630
10.4	7970	14400	833	4630	2580	4220	1680
11.6	8220	13700	833	4610	2480	4410	1830
12.9	8410	13900	805	4600	2540	4530	1840
14.1	8760	16000	864	4790	2700	4600	2000
16.5	9020	13200	666	4200	2640	4250	2010
18.5	7500	10400		3270	2480	3500	1720
19.5	7580	10200		3280	2040	3480	2000
20.5	9240	12500		3710	2450	4010	2100
21.5	8750	10900		3510	2510	3650	2210
25.5	8010	9770		2960	1950	3170	1930
27.5	7220	9720		2820	1780	2780	1810
30.5	7540	11900		2970	1990	2690	1950
35.5	6870	8870		2880	2200	2850	1580
38.5	6370	11800		2460	1670	2060	1180
40.5	6370	9540		2650	1740	2400	1410
41.5	6940	10500		3240	2060	2760	1340
42.5	6060	10200		3260	1950	2950	8080
43.5	4480	6820		2810	726	2380	998
44.5	2870	2390		1560	1120	1300	608
45.5	2580	2190		1490	1030	1350	602
46.5	2940	2430		1170	976	1020	557
47.5	2770	3010		1200	815	1020	517
48.5	3520	2740		1420	1020	1140	680
49.5	3360	2250		1260	856	969	647
50.5	3080	3150		1120	616	978	806
52.5	3060	3650		1320	968	1220	697
55.5	3740	5600		1450	1210	1640	1230
59.5	3710	5710		1370	990	1240	943
62.5	3630	5870		1240	1030	675	630
65.5	3630	5360		1230	963	820	634
67.5	2400	3410		859	830	587	478
70.5	1770	2940		697	484	537	362
72.5	1770	2730		581	608	600	402
75.5	1770	2070		443	364	413	390
77.5	1860	2650		583	530	436	373
78.5	2540	3710		923	638	629	540
80.5	2450	3140		860	608	868	571
85.5	2320	2400		622	591	785	465
90.5	2740	3280		785	771	759	681
95.0	2220	2860		758	604	658	507
99.0	2340	2790		883	681	723	501

DEPTH	24-ethyl-cholestan-3β-ol	C30 n-alkan-15-one-1-ol	C32 n-alkan-15-one-1-ol
0.5	22300	9960	8640
1.5	15700	8200	6120
2.5	12000	6990	4590
3.5	9620	5220	3570
4.5	10500	6780	4840
5.5	11600	6110	4350
6.6	11000	8330	5690
7.9	10900	9760	7110
9.1	9220	8720	6160
10.4	10300	10500	7250
11.6	10800	11600	8310
12.9	10400	10800	7860
14.1	11200	10100	7160
16.5	10700	16500	10200
18.5	8770	11800	6420
19.5	7920	9600	6120
20.5	9720	10100	5670
21.5	8480	10300	6180
25.5	7950	11800	5750
27.5	7110	11300	6190
30.5	8920	11590	9140
35.5	9570	8760	5010
38.5	7480	8620	3120
40.5	7050	9130	6680
41.5	7800	6570	4560
42.5	7860	8070	5020
43.5	6390	4160	2760
44.5	3350	5820	4910
45.5	3430	4700	3990
46.5	2680	5750	4740
47.5	2650	5550	4270
48.5	3270	6200	5000
49.5	2760	6180	5290
50.5	2760	7410	6410
52.5	3270	7420	6950
55.5	4520	10300	7840
59.5	4120	10200	8520
62.5	2970	9680	8280
65.5	2410	8380	7530
67.5	1780	7620	7410
70.5	1790	7800	7320
72.5	1900	5320	4550
75.5	1750	6420	6570
77.5	1800	5740	5150
78.5	2580	7820	7100
80.5	3160	8560	8100
85.5	2750	6240	4400
90.5	3000	5910	5070
95.0	1690	5770	4820
99.0	2500	5650	5100

SC3 elemental analyses after total sediment dissolution:

DEPTH	Al ppm	Ti ppm	Zr ppm	Fe ppm	P ppm	Mn ppm
5.5	24700	1150	40.1	13800	1450	150
10.5	24500	1140	39.1	12900	1420	151
17.5	24700	1160	24.9	13700	1470	170
25.5	25200	1190	44.1	12400	1670	156
30.5	38900	1780	63.1	17600	1610	221
35.5	32600	1500	53.3	14600	1620	187
41.5	39500	1910	63.6	17100	1820	227
47.5	20800	978	31.5	10400	716	120
52.5	16900	838	27.7	8840	639	107
59.5	20700	966	31.9	9520	1010	121
65.5	59100	3000	88.4	24900	1490	352
70.5	38000	1860	66.5	17900	1460	215
75.5	63300	3010	100.7	25800	1340	355
77.5	56200	2830	90.5	25000	1460	357
80.5	27600	1390	47.8	12900	878	174
85.5	22100	1110	27.4	11800	1330	163

SC3 210-Pb Analyses:

Depth (cm)	calculated overlying sediment(mg	Excess 210Pb (dpm/g)	Excess + error (dpm/g)	Excess - error (dpm/g)
0.97	59	107	114	101
2.92	196	85.9	91.5	80.4
4.92	342	72.7	77.4	68.1
7.34	471	71.3	75.8	66.7
11.06	661	49.8	53.1	46.5
13.44	797	51.1	54.6	47.5
17.5	1220	51.7	55.3	48.0
23.5	1750	32.8	35.1	30.5
27.5	2090	34.0	36.4	31.6
29.5	2300	13.1	14.6	11.7
32.5	2630	14.1	15.6	12.7
35.5	2930	16.6	18.1	15.0
37.5	3210	7.11	7.95	6.27
41.5	3810	7.35	8.26	6.45
47.5	4340	4.1	4.90	3.31
50.5	4660	3.17	3.99	2.35
53.5	4950	1.78	2.43	1.13

SC3subcore

DEPTH	C37:3 alkenone	C37:2 alkenone	Uk37
0.1	20170	48590	0.707
0.3	20620	48760	0.703
0.5	19180	47660	0.713
0.7	13380	34490	0.720
0.9	13750	35450	0.721
1.125	13350	32770	0.711
1.375	12160	30950	0.718
1.625	10560	27180	0.720
1.875	9610	25390	0.725
2.3	10770	27340	0.717
2.8	9700	24360	0.715
3.25	10590	24410	0.697
3.75	12310	27560	0.691
4.25	9342	21400	0.696
4.75	8879	20980	0.703

APPENDIX 2- DATA FOR CORE SC2, SC5, SC7 and Grab samples
All lipid concentrations are in ng/gdw. Depth listed is for middle of core section

Grab samples:	C24 n-alkane	C25 n-alkane	C26 n-alkane	C27 n-alkane	C28 n-alkane	C29 n-alkane	C30 n-alkane	C31 n-alkane	C32 n-alkane	C33 n-alkane	C34 n-alkane
G25	18.9	153	32.1	392	68.2	807	46.3	459	23.7	154	7.49
G28	5.4	29.6	10.5	89.6	24.9	276	16.6	145	8.33	45.8	3.58
G37	26.7	152	53.5	500	141	1700	105	949	50.7	278	15.90

Grab samples:	dry wt/ wet wt	Wt% C	Wt%N
G25	0.663	0.45	0.02
G28	0.680	0.37	0.02
G37	0.529	0.82	0.09

SC2 210-Pb analyses:

Depth (cm)	Excess 210Pb (dpm/g)	Excess + error (dpm/g)	Excess - error (dpm/g)
1	86	92.1	80.02
3	57	61.7	52.34
5	43.7	47.6	39.8
7	41.7	44.7	38.8
9	36	39.5	32.6
11	32.5	35.4	29.7
15	11.5	12.9	10
13	12.8	14.5	11.1

SC5 210-Pb analyses:

Depth (cm)	Excess 210Pb (dpm/g)	Excess + error (dpm/g)	Excess - error (dpm/g)
2.5	72	76.3	67.6
3.5	57.71	61.2	54.2
4.5	55.2	58.5	51.9
5.5	58.4	61.9	54.9
6.5	43.3	46.1	40.6
7.5	41.5	44	38.9
8.5	24.4	26	22.9
9.5	19.8	21.2	18.4
10.5	24	26	22
11.5	21.2	22.8	19.5

SC7 210-Pb analyses:

Depth (cm)	Excess 210Pb (dpm/g)	Excess + error (dpm/g)	Excess - error (dpm/g)
0.5	52.7	55.8	49.7
1.5	46.7	49.3	44.1
2.5	43.1	45.8	40.5
3.5	37.4	39.7	35.2
4.5	40.9	42.9	38.9
5.5	39.2	41.9	36.4
6.5	40.7	42.8	38.6
7.5	38.9	41	36.8
8.5	45	47.3	42.8
9.5	43.1	45.3	40.9
10.5	31.4	33	29.8
11.5	25	26.3	23.6
12.5	24.1	25.6	22.6
13.5	23.6	25	22.2
14.5	24.9	26.4	23.5

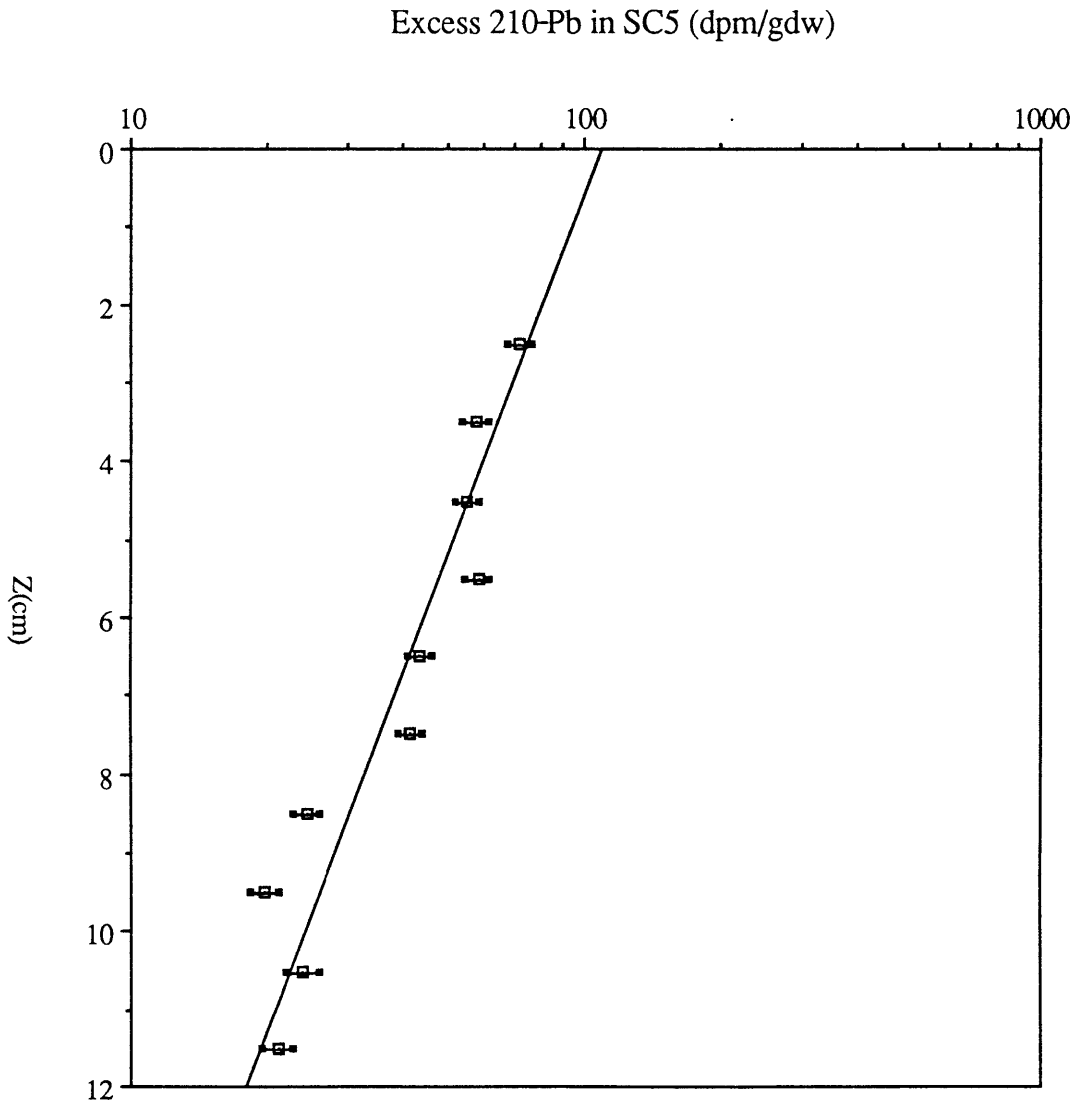


Figure A2.1: Excess ^{210}Pb profile for core SC5. The best exponential fit to these data (2-12 cm; n=10) yields a sedimentation rate of 0.206 cm/yr.

APPENDIX 3- SELECTED MASS SPECTRA OF COMPOUNDS DISCUSSED IN TEXT

This appendix contains mass specra of thirty-six compounds discussed in the text. All of the spectra included are from GC-MS analyses of sediment lipid extracts *and are not from standards*. Table 2.2 lists the method(s) used to identify the individual compounds. The GC-MS operating conditions are described in chapter 2. The compounds are listed in order of increasing carbon number. Derivatized compounds are listed with compounds having the carbon number of the underivatived form (i.e., cholesterol acetate is listed with the C_{27} compounds not the C_{29} compounds). Spectra **XXXV** and **XXXVI** (24-methyl-14α(H)-1(10→6)-abeocholesta-5, 7, 9 (10), 22-tetraene and fern-7-ene) are listed out of order with respect to carbon number.

When an ion chromatogram does not have an intensity maximum at the same time as the other ions in a spectrum, the ion is idicated by a '*'. Although a background subtraction routine was used, these ions represent either background contamination of the spectrum or partial coelution of another compound with the compound of interest.

Some comments on these spectra include the following:

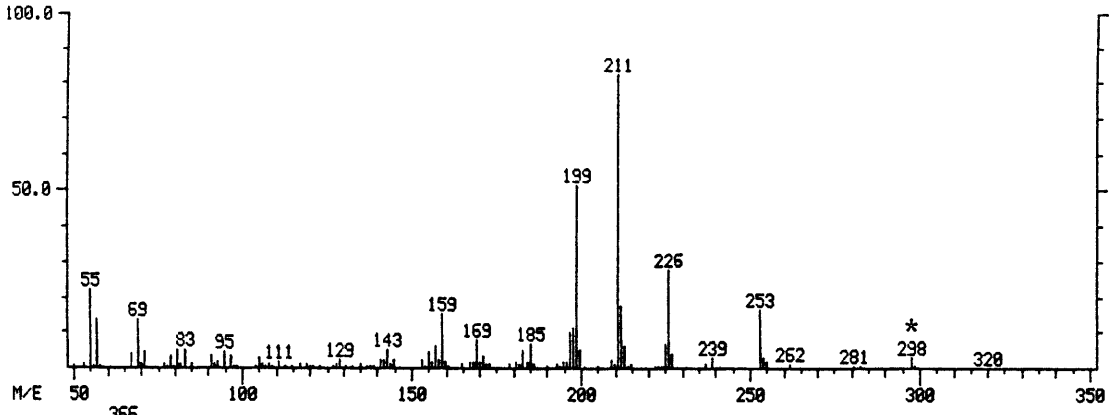
Spectrum (**I**) is an excellent match with that with that of the authentic standard reported by Hussler and Albrecht (1983) [chapter 4 references].

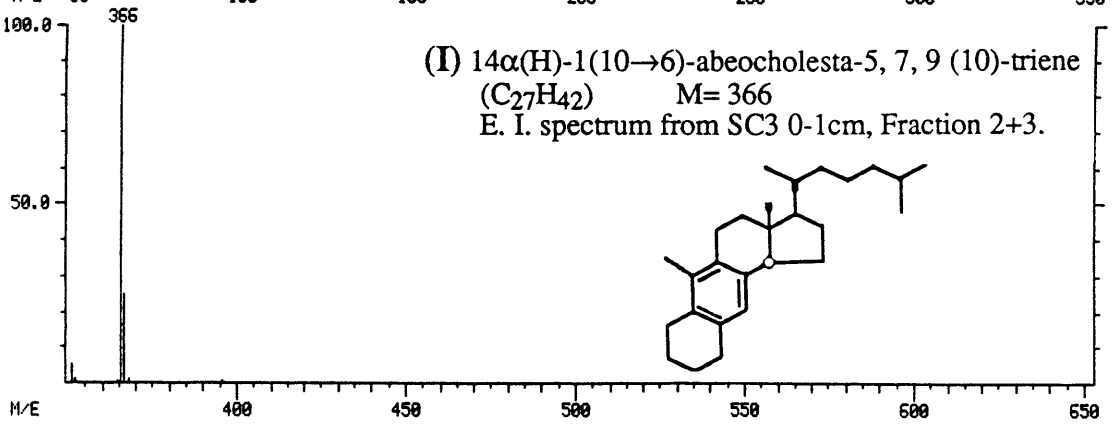
The spectra of the trisnorhopenes (**V and VI**) are excellent matches with spectra reported by Sandstrom (1982)[chapter 1 references].

The ion M/z= 316 in the spectrum (**VII**) of cholest-2-ene arises from a retro-Diels Alder loss of butadiene, and distinguishes cholest-2-ene from cholest-4-ene and cholest-5-ene. Spectrum (**VII**) is an excellent match with the spectrum of the authentic standard run on the WHOI instrument.

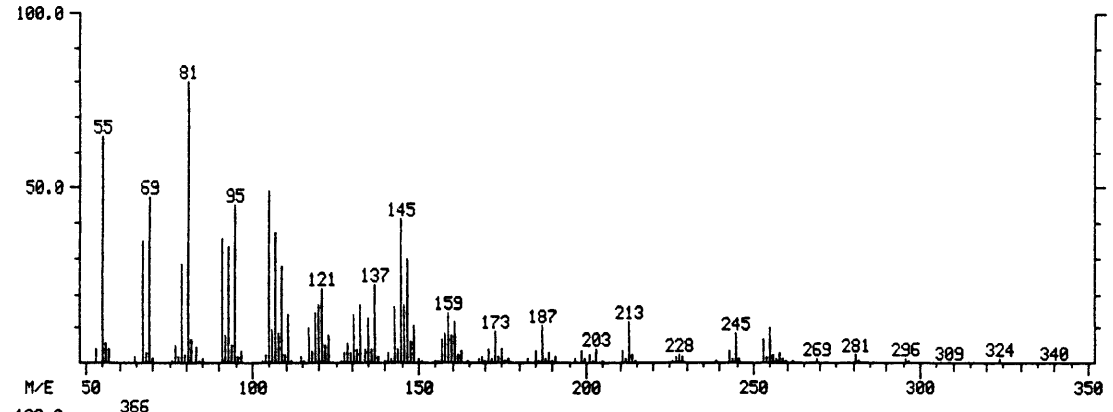
The ion M/z= 298 in spectra (**XXIV and XXIX**) of the alkan-15-one-1-ols results from a McLafferty rearrangement at the ketone and is the equivalent of M/z = 328 in the TMS spectrum reported by de Leeuw et al. (1981) [chapter 4 references].

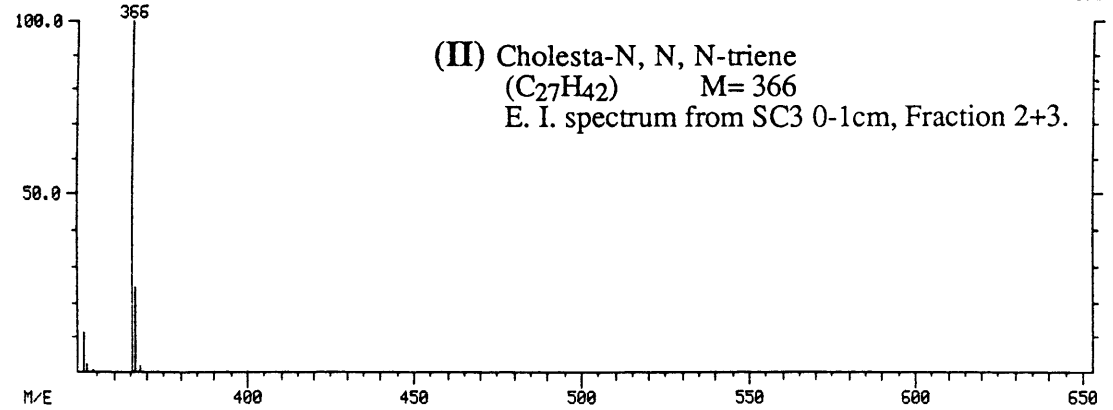
The neohop-13(18)-ene spectrum (**XXV**) is an excellent match with the spectra reported by Simoneit and Mazurek (1981) and Howard (1980)[chapter 5 references]. The 17ß(H), 21ß(H)-homohopane spectrum (**XXVI**) is an excellent match with the spectrum reported by Huc (1978).



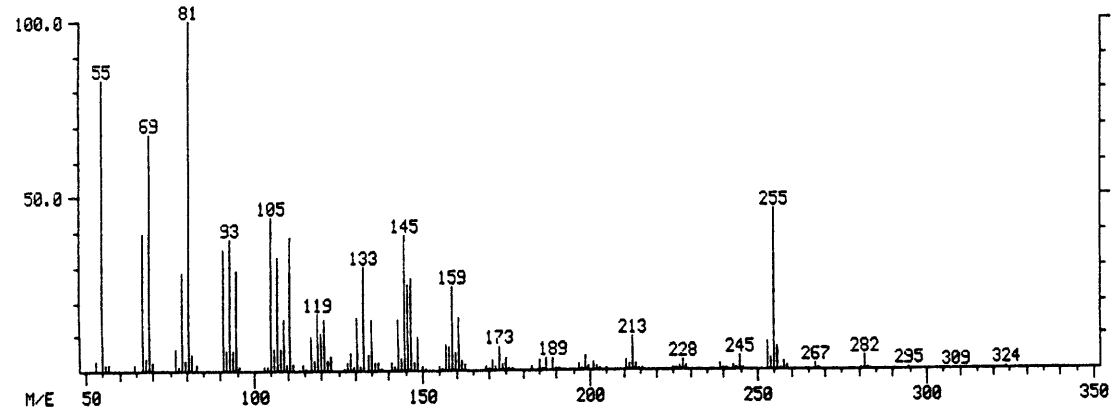


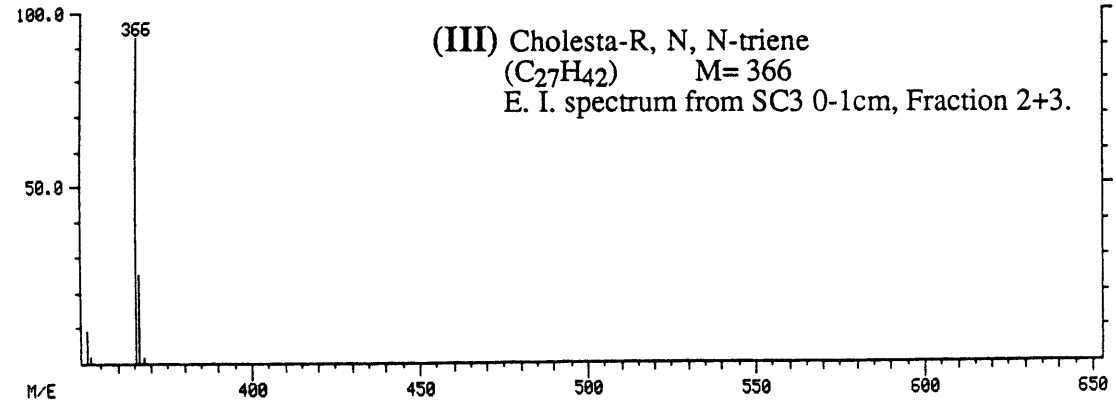
(I) 14α(H)-1(10→6)-abeocholesta-5, 7, 9 (10)-triene
($C_{27}H_{42}$) M= 366
E. I. spectrum from SC3 0-1cm, Fraction 2+3.



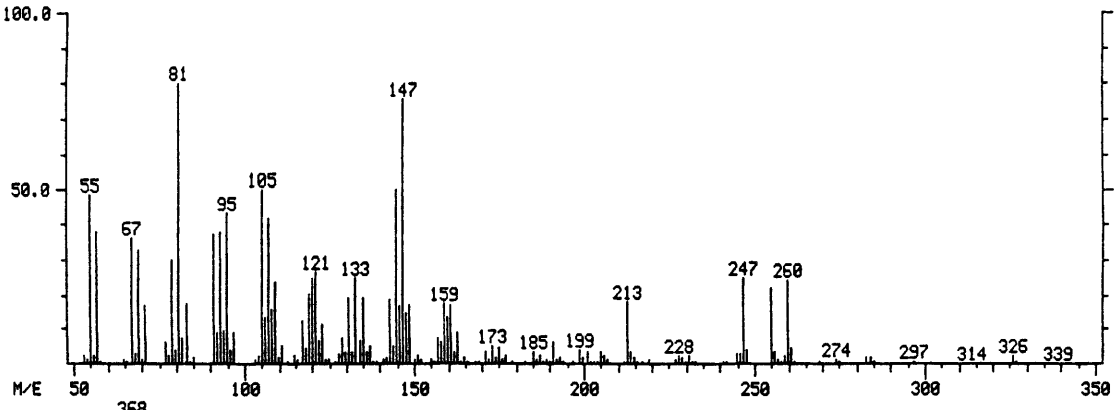


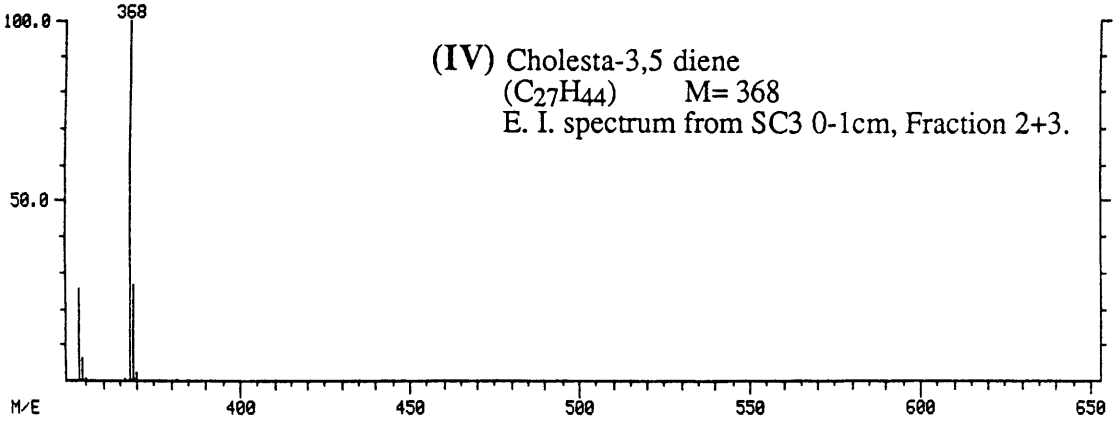
(II) Cholesta-N, N, N-triene
($C_{27}H_{42}$) M= 366
E. I. spectrum from SC3 0-1cm, Fraction 2+3.



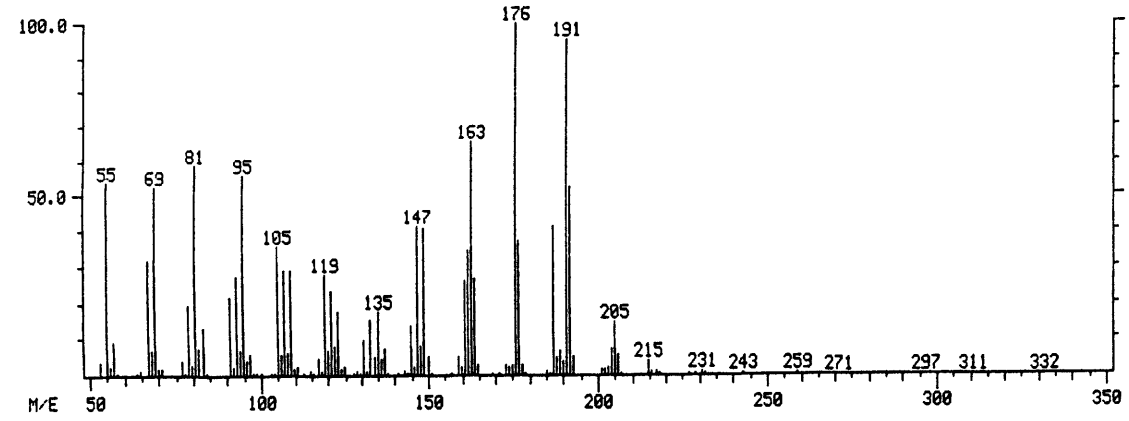


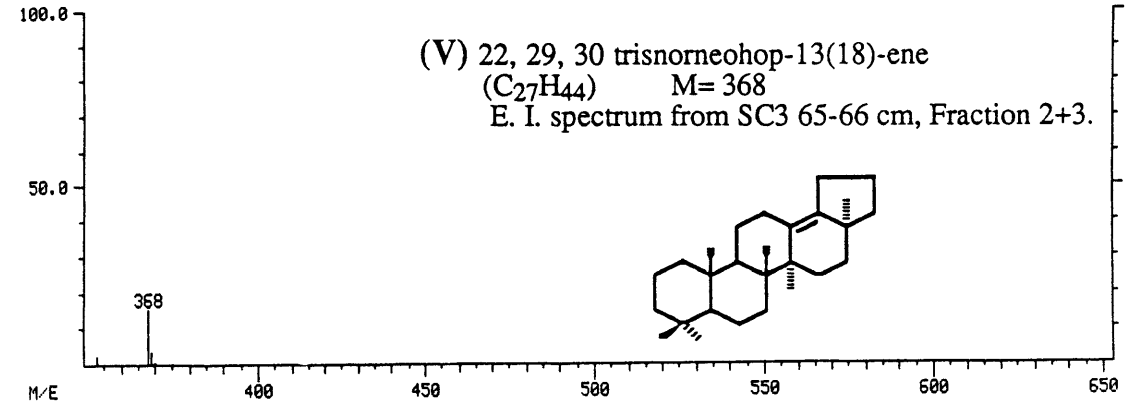
(III) Cholesta-R, N, N-triene
($C_{27}H_{42}$) M= 366
E. I. spectrum from SC3 0-1cm, Fraction 2+3.



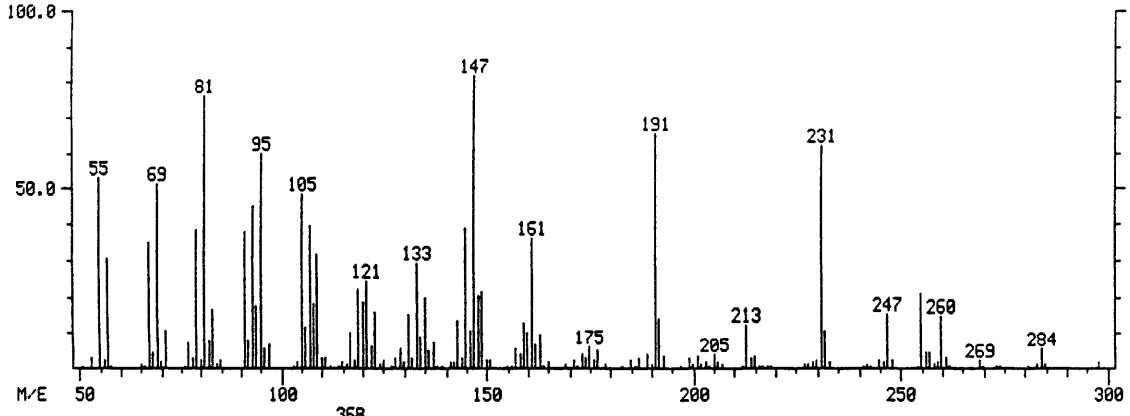


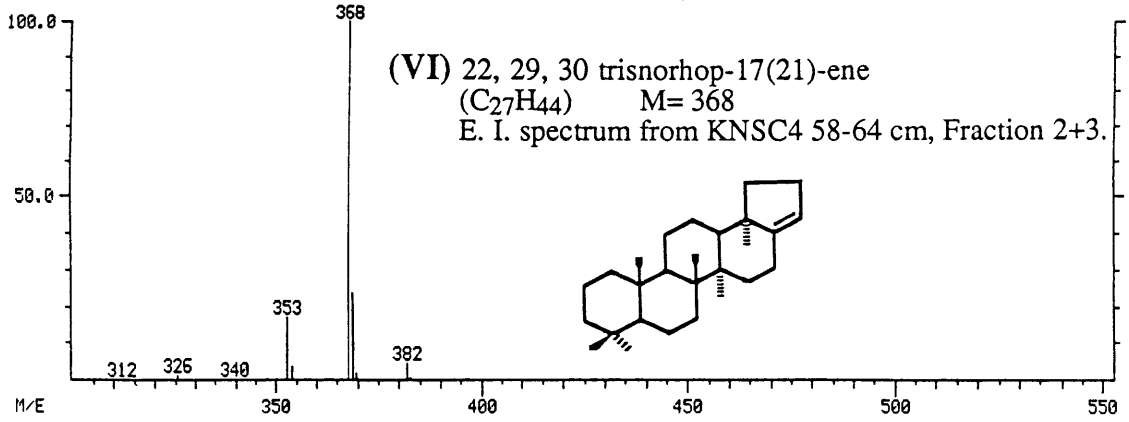
(IV) Cholesta-3,5 diene
($C_{27}H_{44}$) M= 368
E. I. spectrum from SC3 0-1cm, Fraction 2+3.



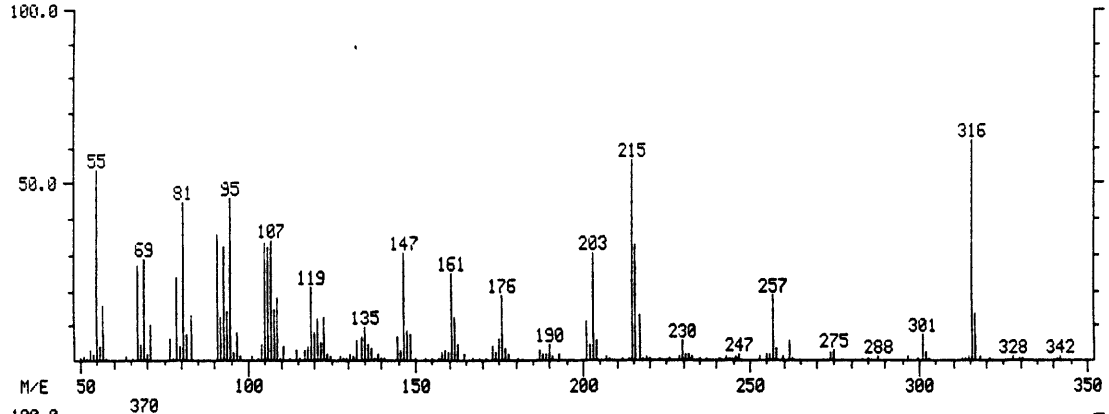


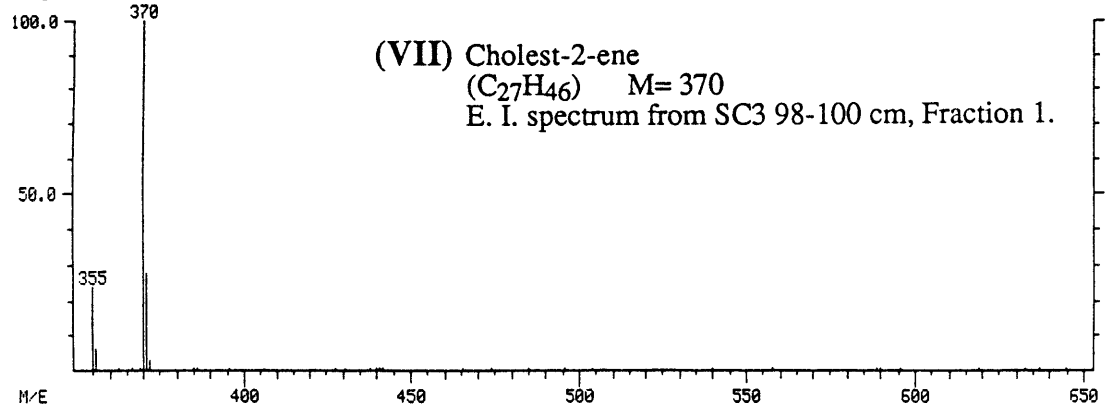
(V) 22, 29, 30 trisnorneohop-13(18)-ene
($C_{27}H_{44}$) M= 368
E. I. spectrum from SC3 65-66 cm, Fraction 2+3.



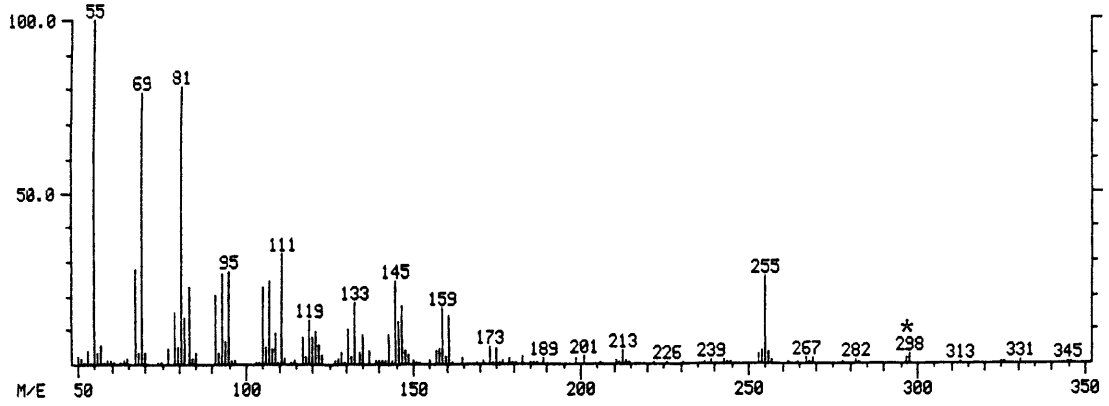


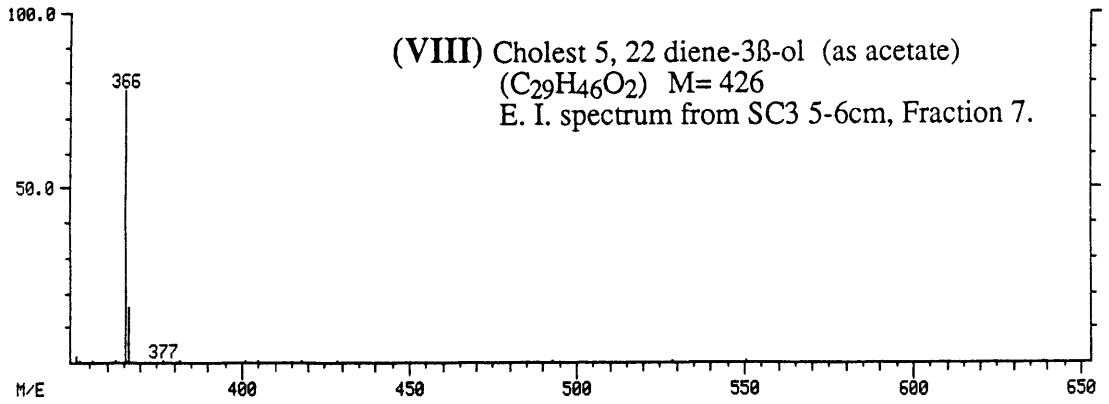
(VI) 22, 29, 30 trisnorhop-17(21)-ene
($C_{27}H_{44}$) M= 368
E. I. spectrum from KNSC4 58-64 cm, Fraction 2+3.



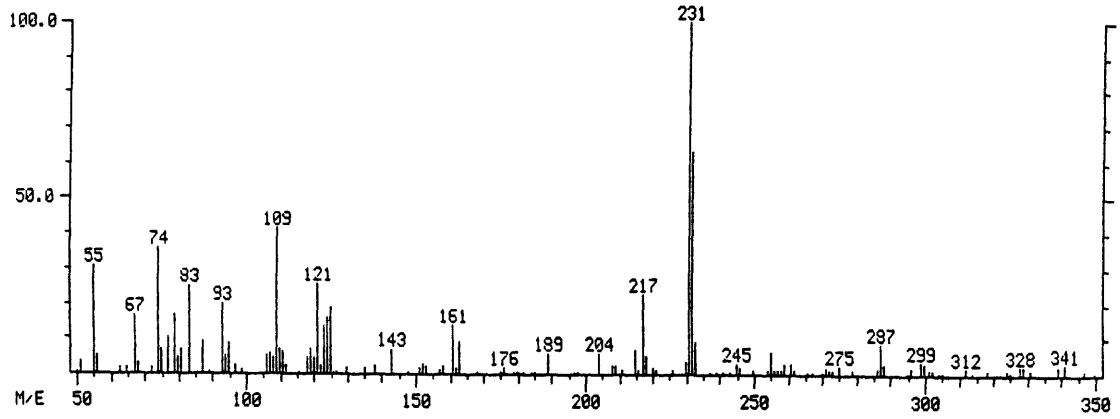


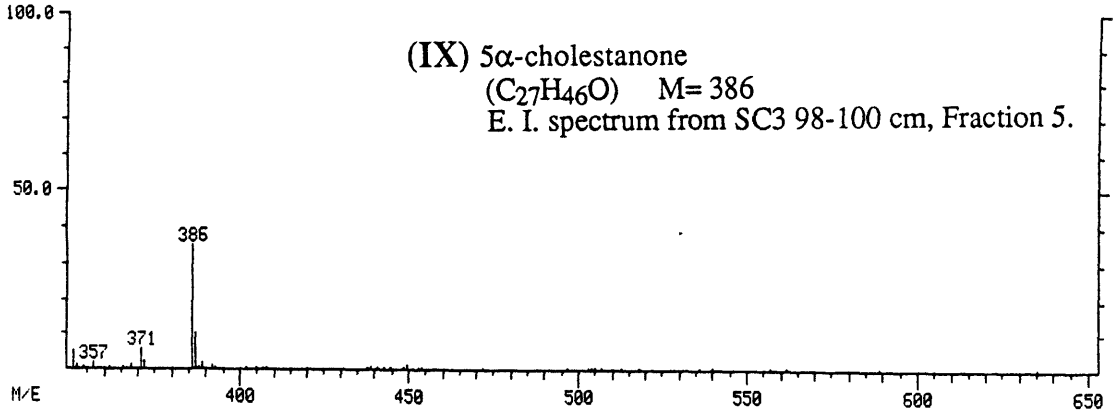
(VII) Cholest-2-ene
($C_{27}H_{46}$) M= 370
E. I. spectrum from SC3 98-100 cm, Fraction 1.



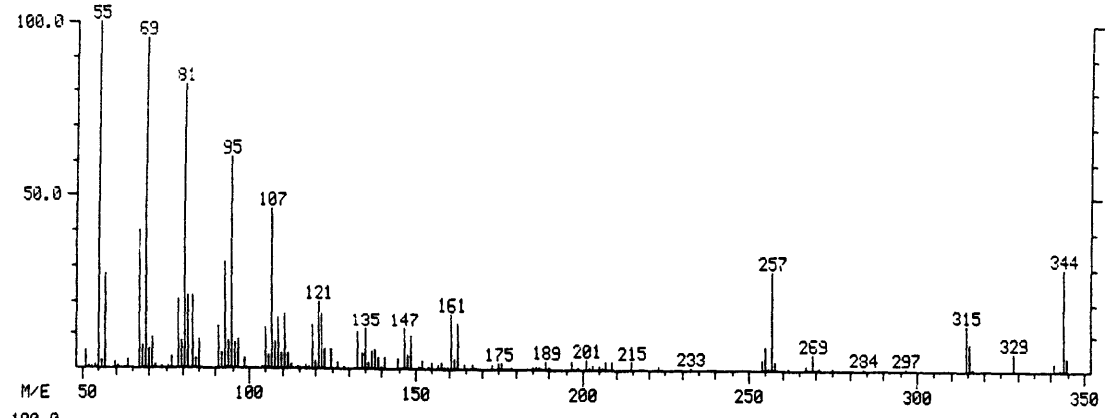


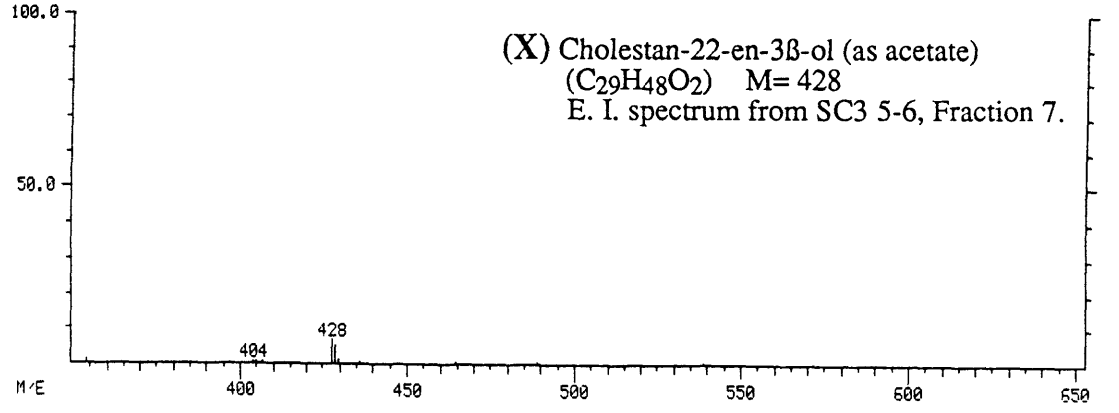
(VIII) Cholest 5, 22 diene-3ß-ol (as acetate)
($C_{29}H_{46}O_2$) M= 426
E. I. spectrum from SC3 5-6cm, Fraction 7.



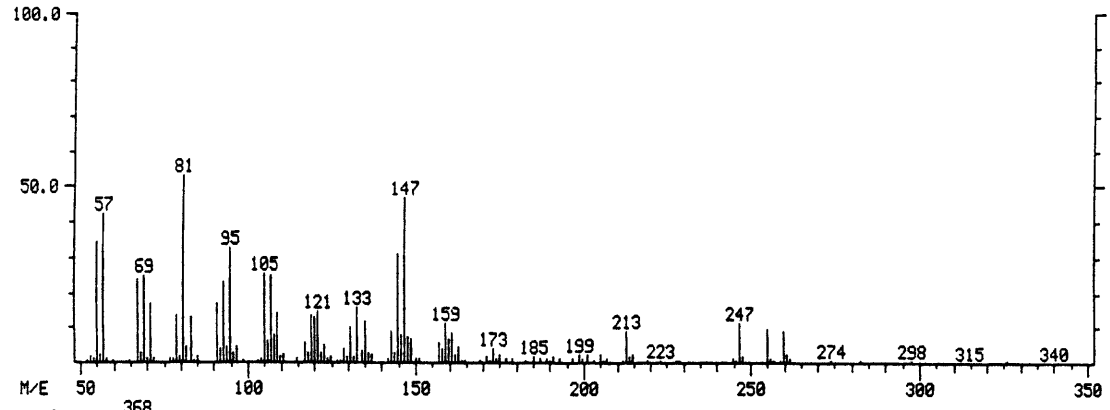


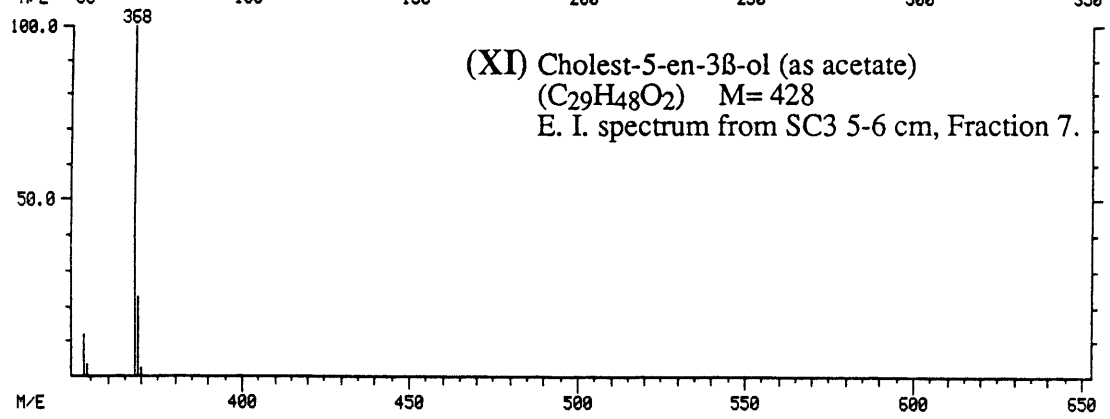
(IX) 5α-cholestanone
$(C_{27}H_{46}O)$ M= 386
E. I. spectrum from SC3 98-100 cm, Fraction 5.



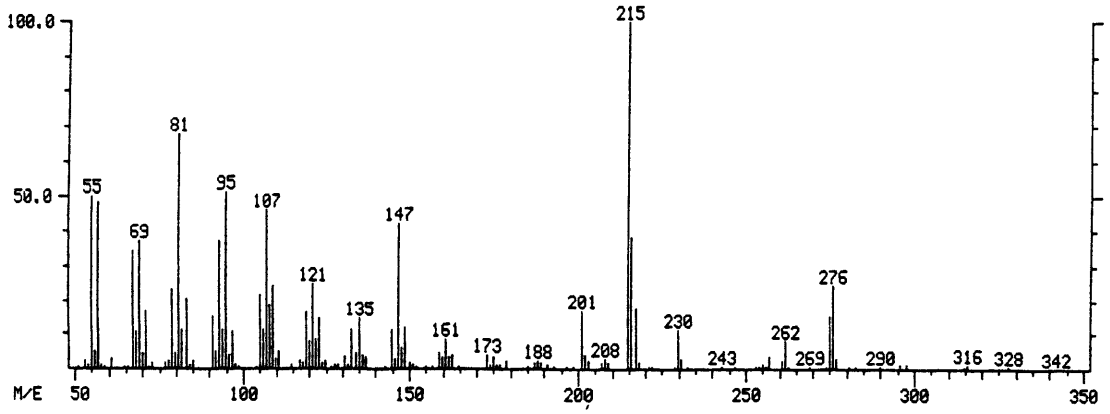


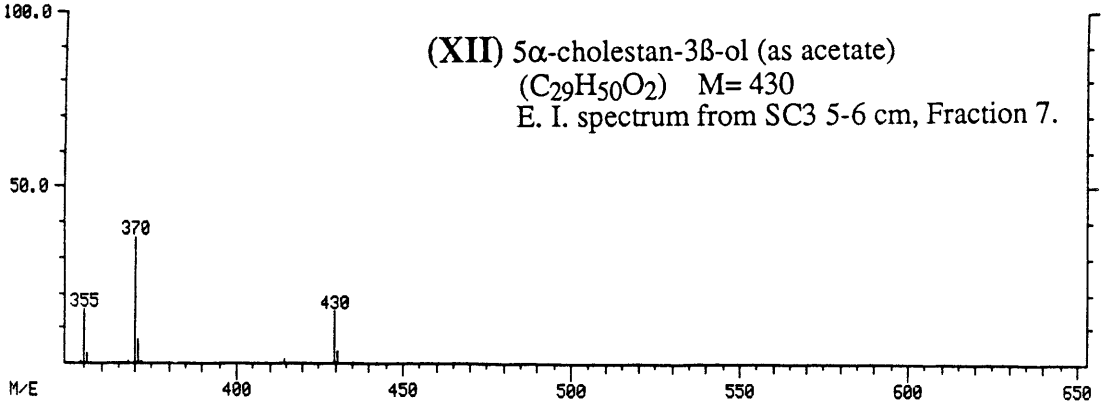
(X) Cholestan-22-en-3ß-ol (as acetate)
$(C_{29}H_{48}O_2)$ M= 428
E. I. spectrum from SC3 5-6, Fraction 7.



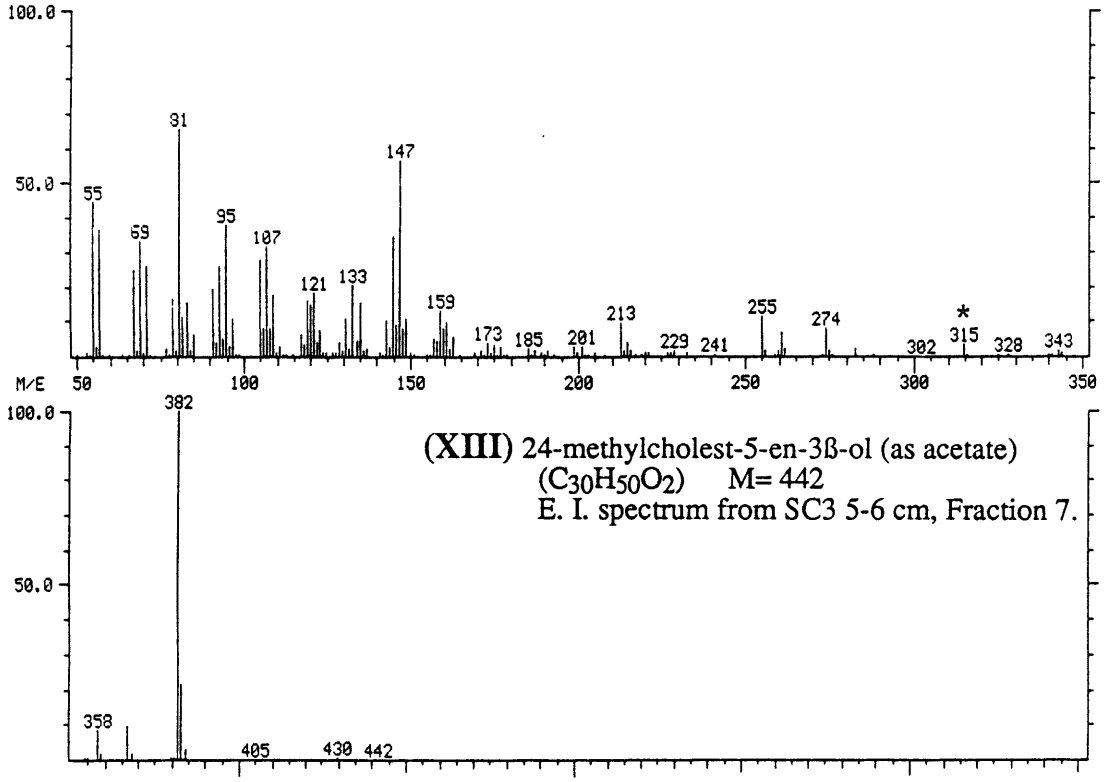


(XI) Cholest-5-en-3ß-ol (as acetate)
($C_{29}H_{48}O_2$) M= 428
E. I. spectrum from SC3 5-6 cm, Fraction 7.

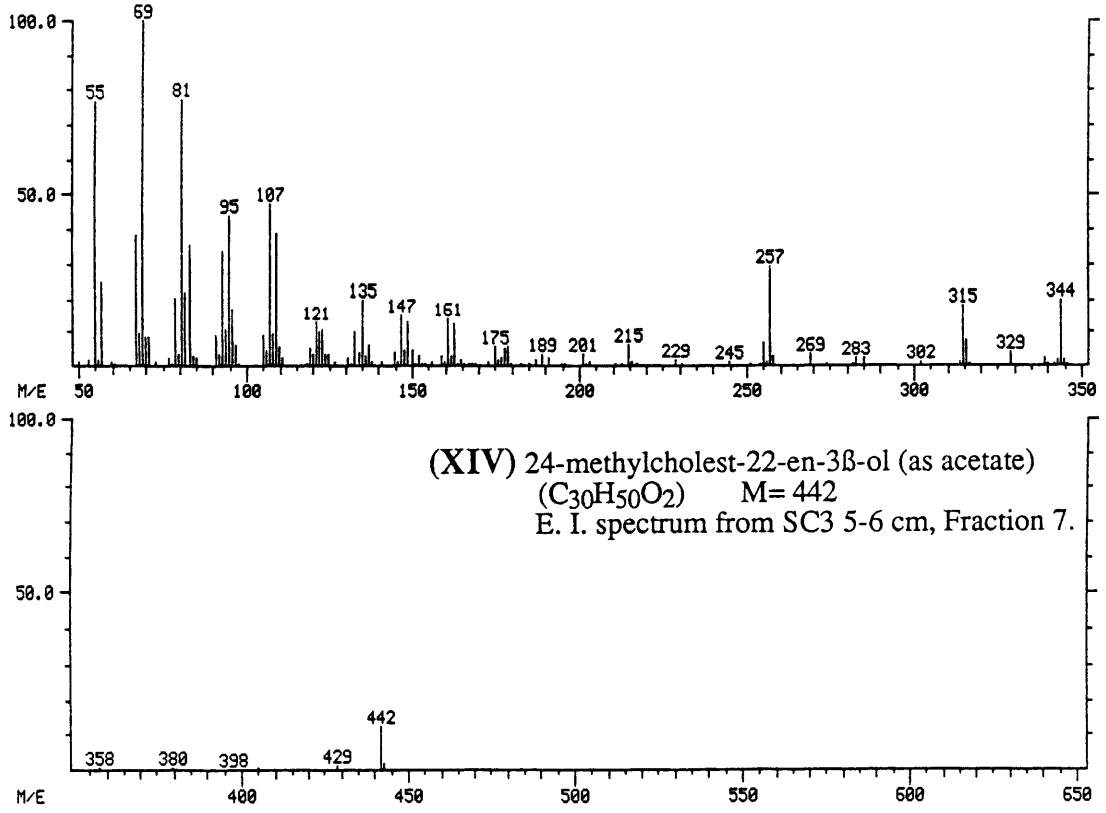




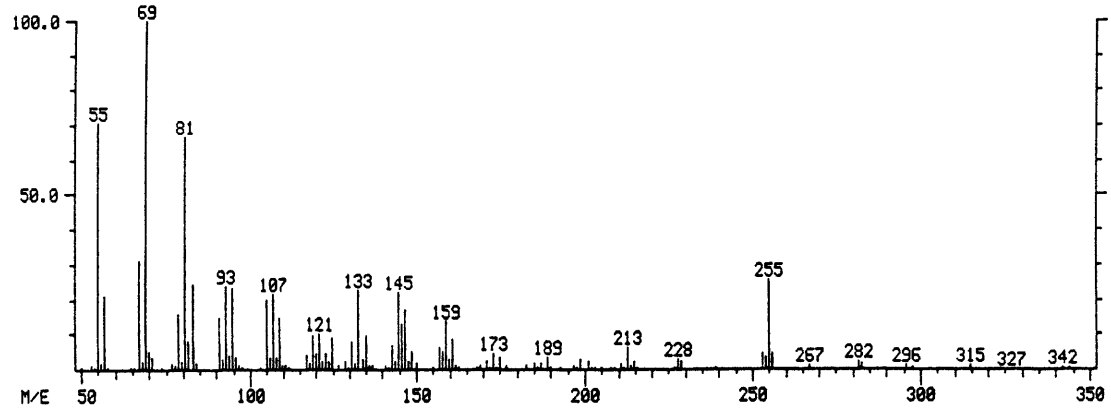
(XII) 5α-cholestan-3ß-ol (as acetate)
($C_{29}H_{50}O_2$) M= 430
E. I. spectrum from SC3 5-6 cm, Fraction 7.

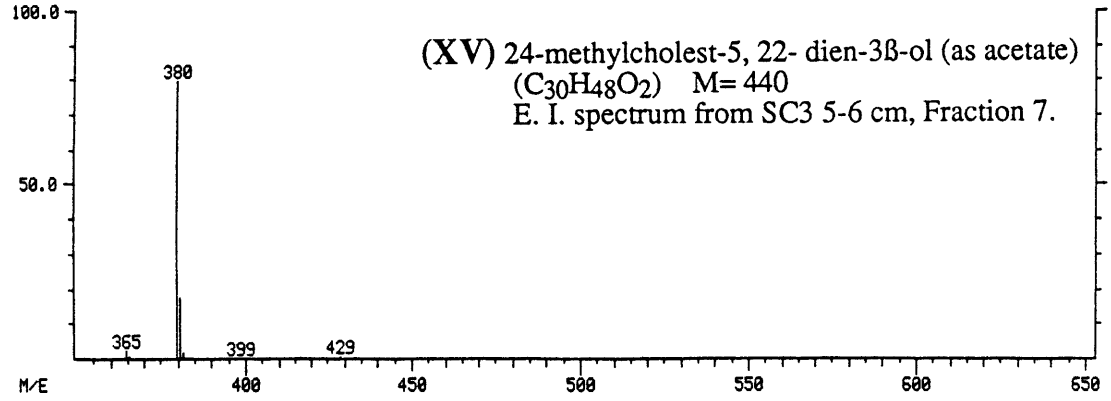


(XIII) 24-methylcholest-5-en-3ß-ol (as acetate)
($C_{30}H_{50}O_2$) M= 442
E. I. spectrum from SC3 5-6 cm, Fraction 7.

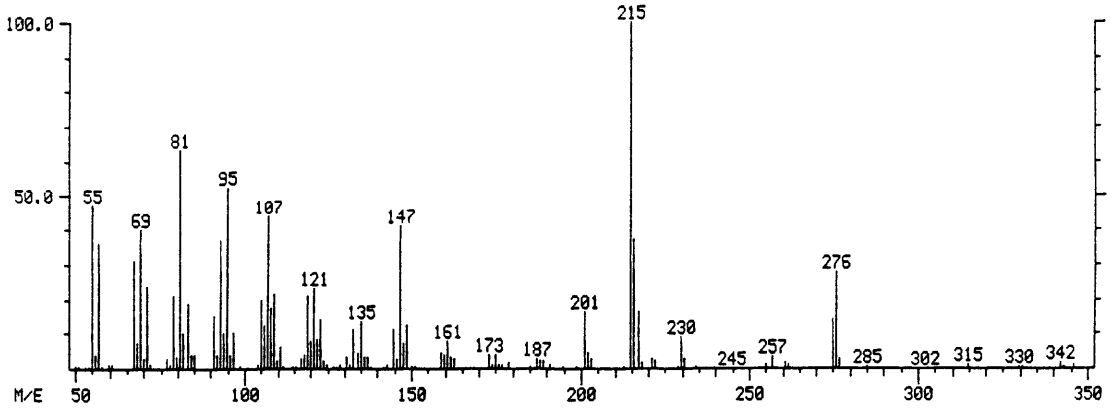


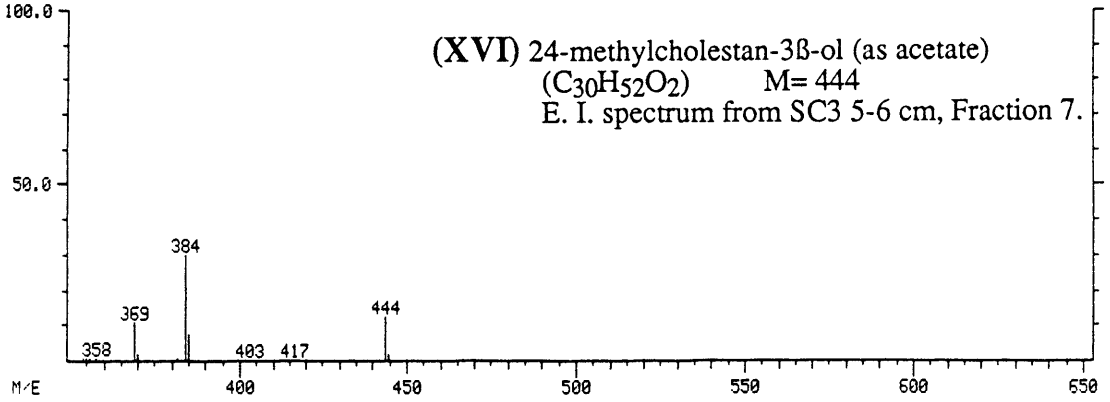
(XIV) 24-methylcholest-22-en-3ß-ol (as acetate)
($C_{30}H_{50}O_2$) M= 442
E. I. spectrum from SC3 5-6 cm, Fraction 7.



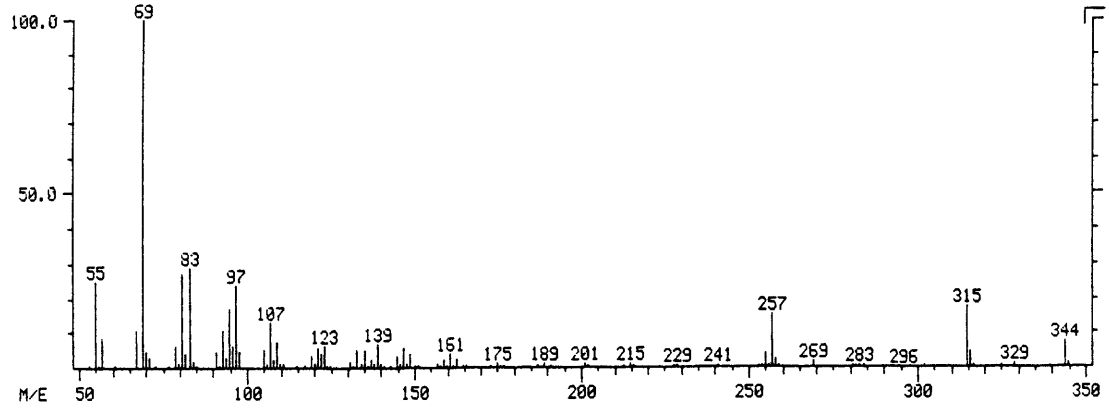


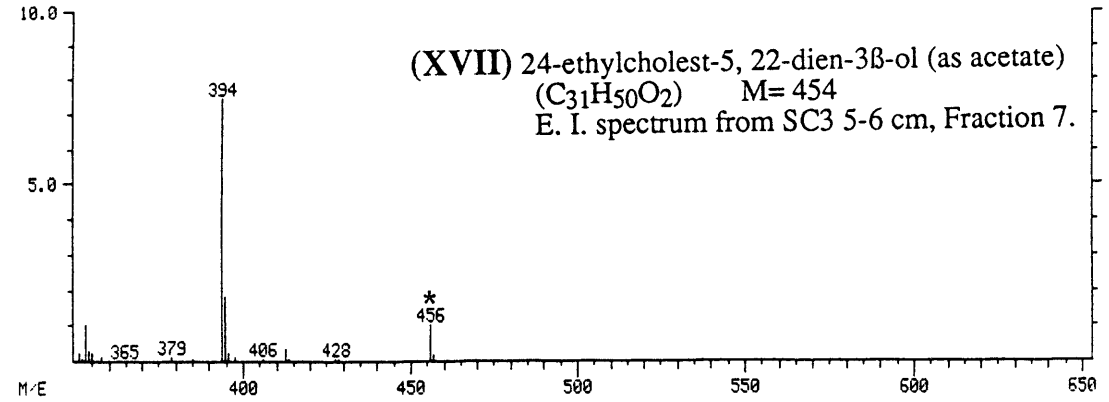
(XV) 24-methylcholest-5, 22- dien-3ß-ol (as acetate)
($C_{30}H_{48}O_2$) M= 440
E. I. spectrum from SC3 5-6 cm, Fraction 7.



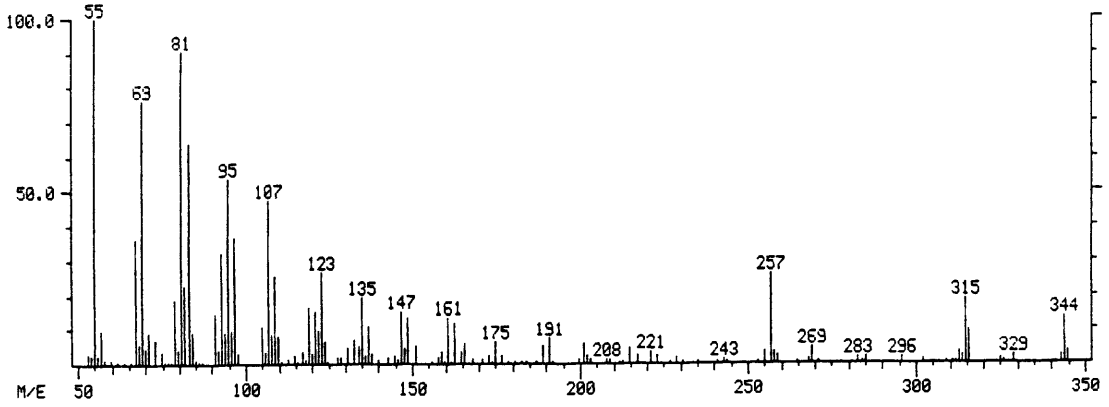


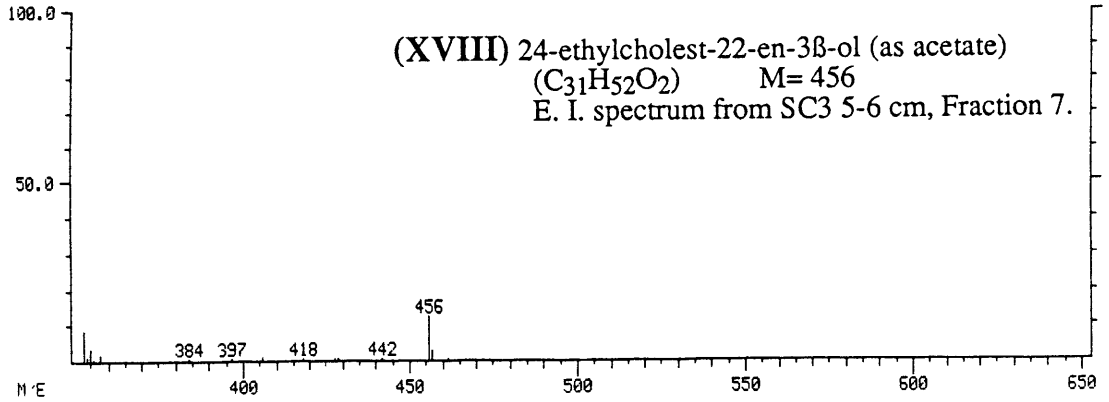
(XVI) 24-methylcholestan-3ß-ol (as acetate)
($C_{30}H_{52}O_2$) M= 444
E. I. spectrum from SC3 5-6 cm, Fraction 7.



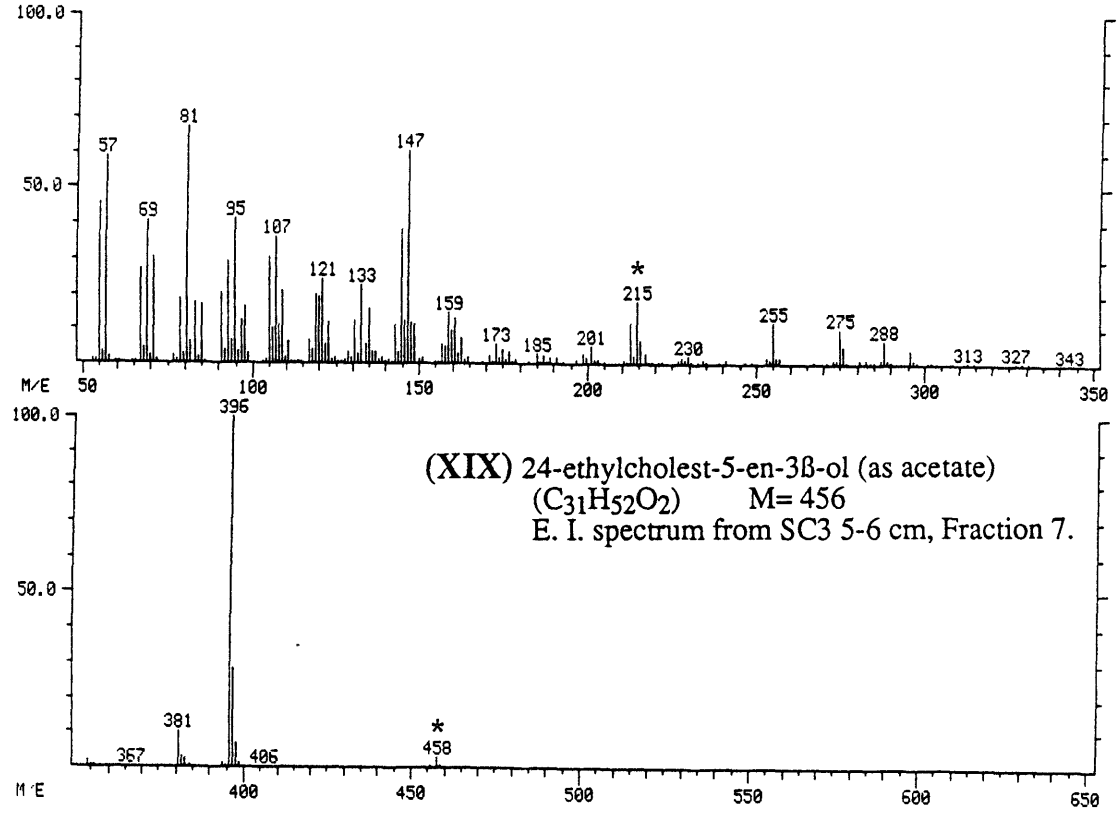


(XVII) 24-ethylcholest-5, 22-dien-3ß-ol (as acetate)
($C_{31}H_{50}O_2$) M= 454
E. I. spectrum from SC3 5-6 cm, Fraction 7.

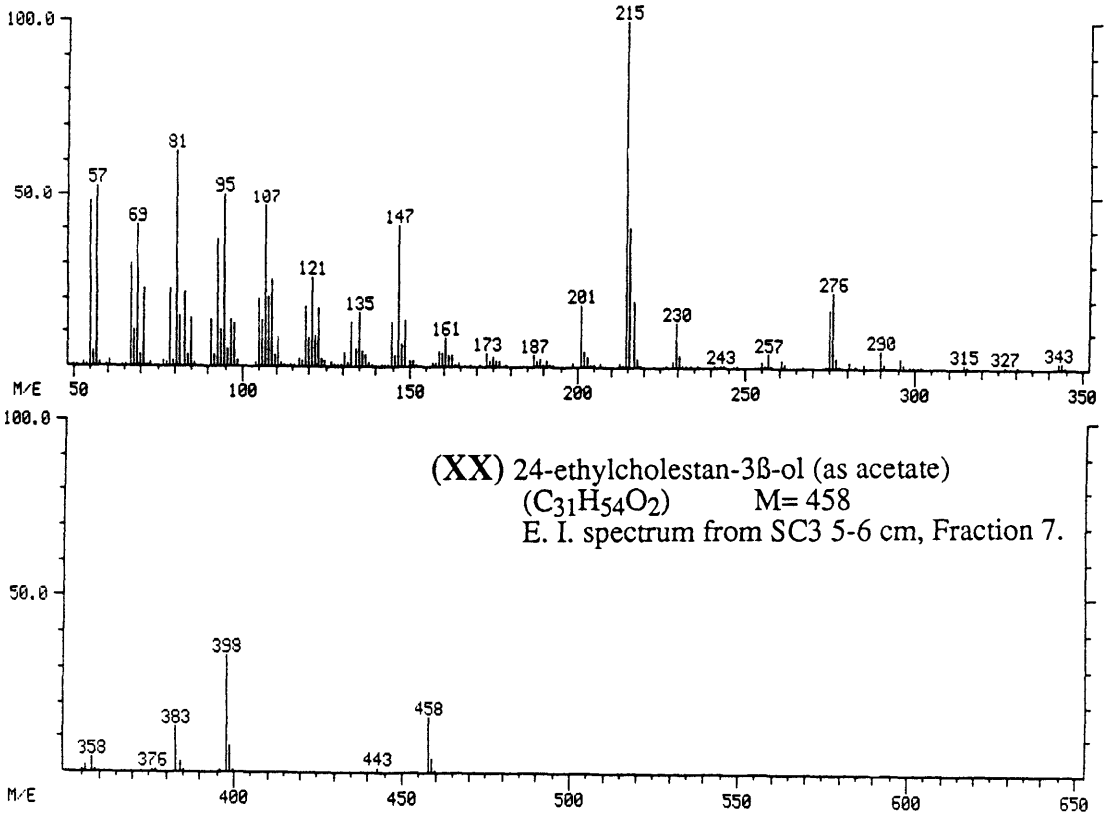




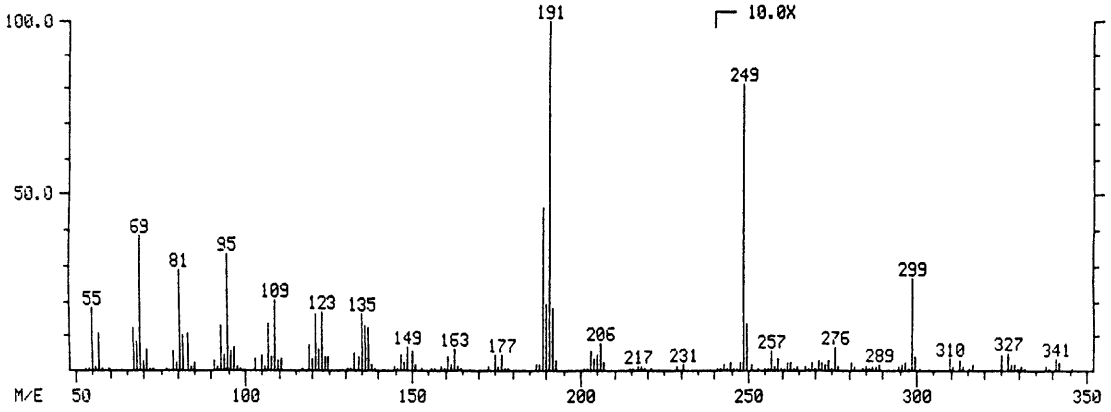
(XVIII) 24-ethylcholest-22-en-3ß-ol (as acetate)
($C_{31}H_{52}O_2$) M= 456
E. I. spectrum from SC3 5-6 cm, Fraction 7.

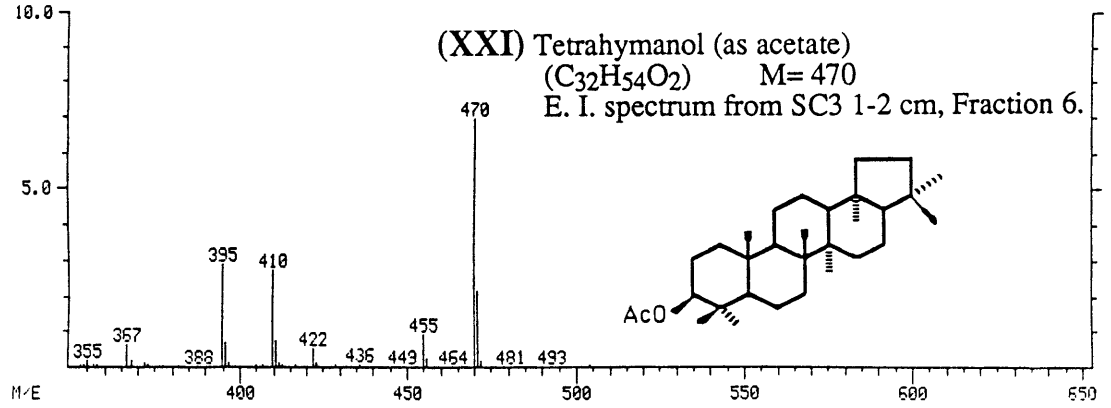


(XIX) 24-ethylcholest-5-en-3ß-ol (as acetate)
$(C_{31}H_{52}O_2)$ M= 456
E. I. spectrum from SC3 5-6 cm, Fraction 7.

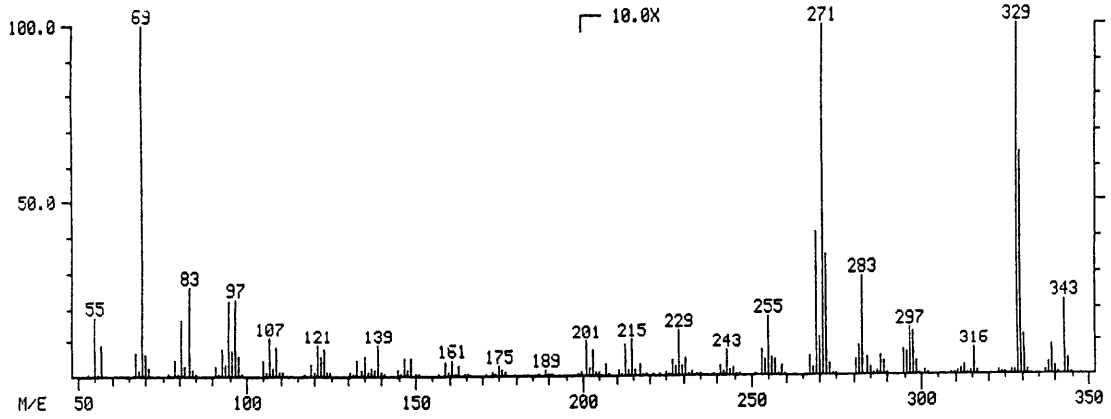


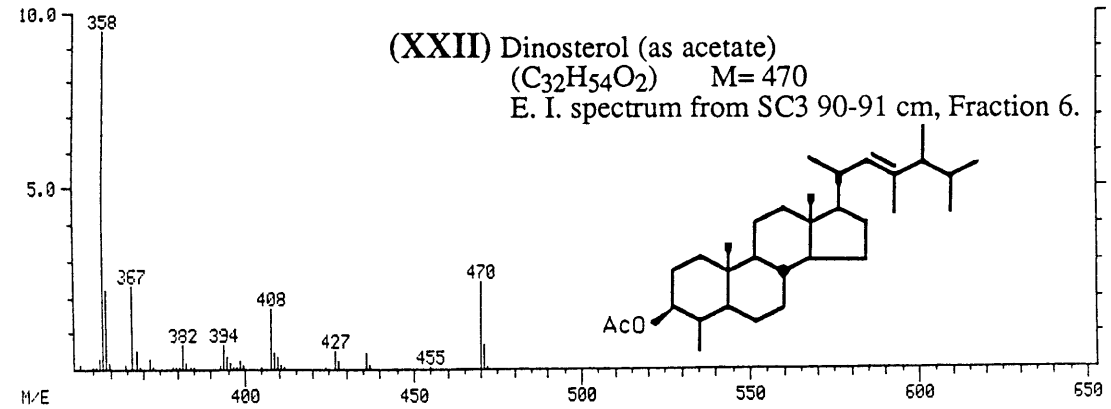
(XX) 24-ethylcholestan-3ß-ol (as acetate)
$(C_{31}H_{54}O_2)$ M= 458
E. I. spectrum from SC3 5-6 cm, Fraction 7.



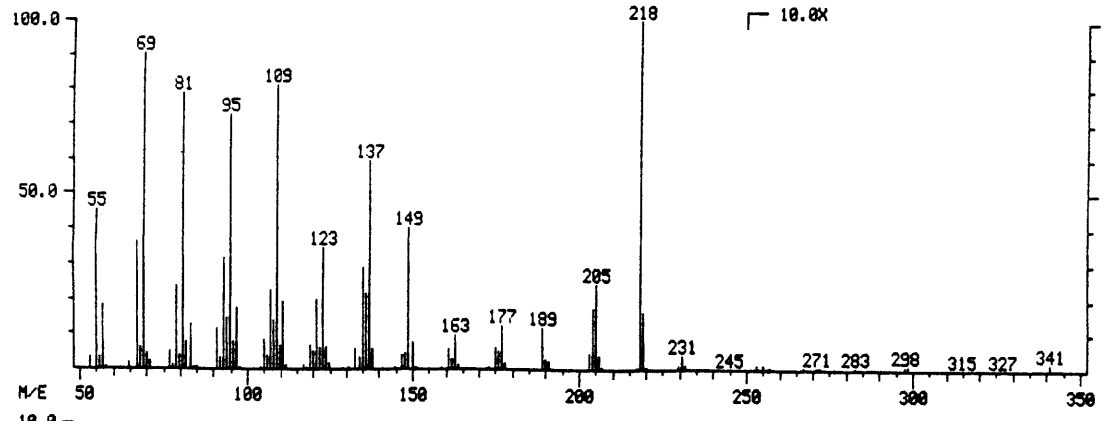


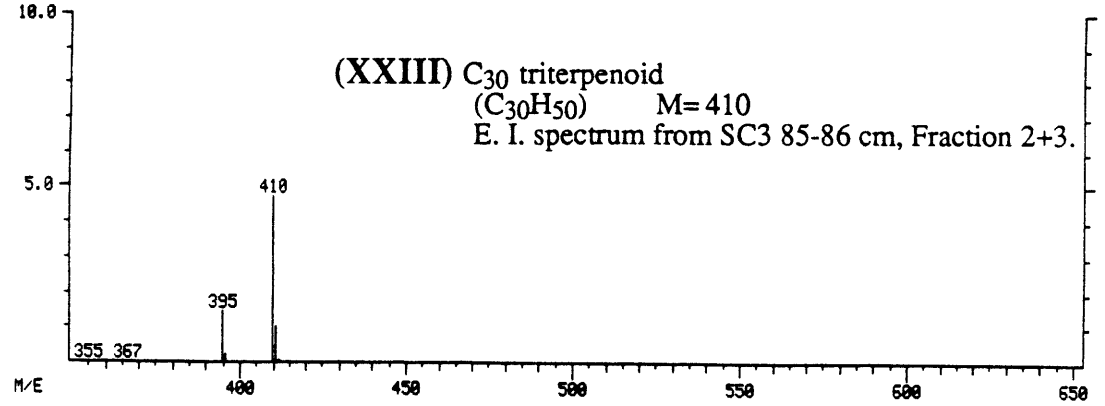
(XXI) Tetrahymanol (as acetate)
($C_{32}H_{54}O_2$) M= 470
E. I. spectrum from SC3 1-2 cm, Fraction 6.



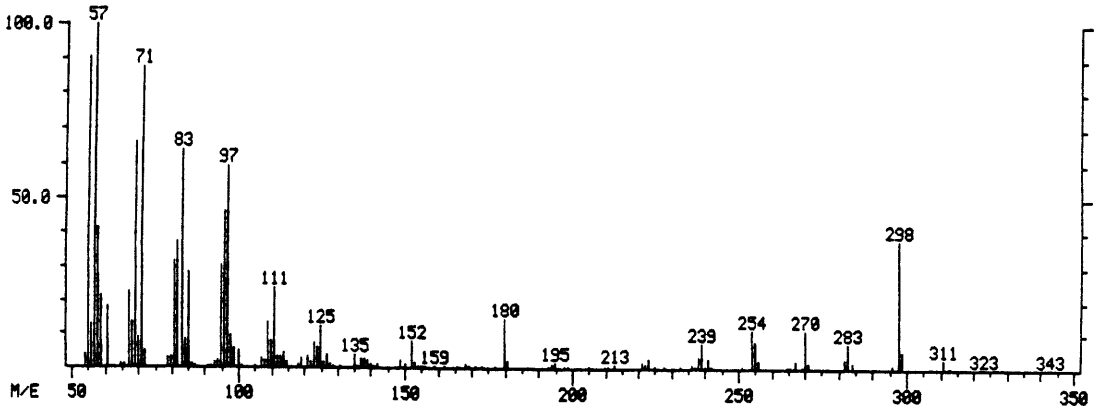


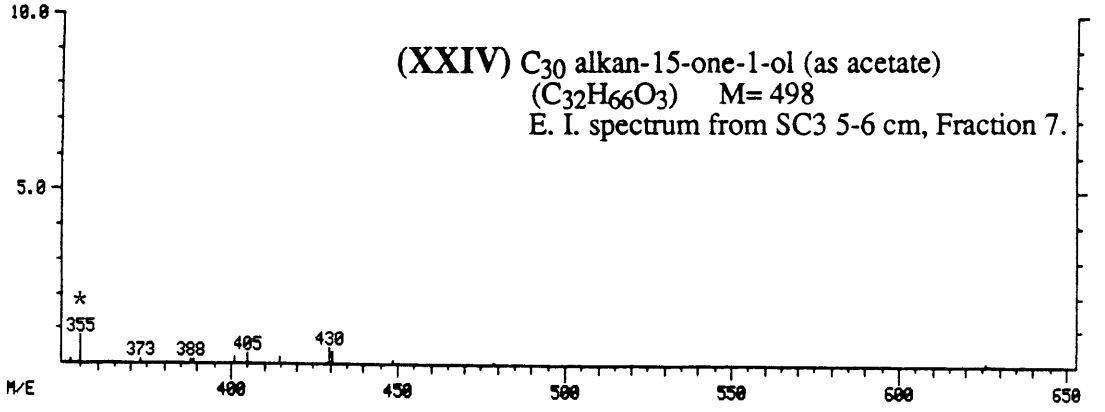
(XXII) Dinosterol (as acetate)
($C_{32}H_{54}O_2$) M= 470
E. I. spectrum from SC3 90-91 cm, Fraction 6.



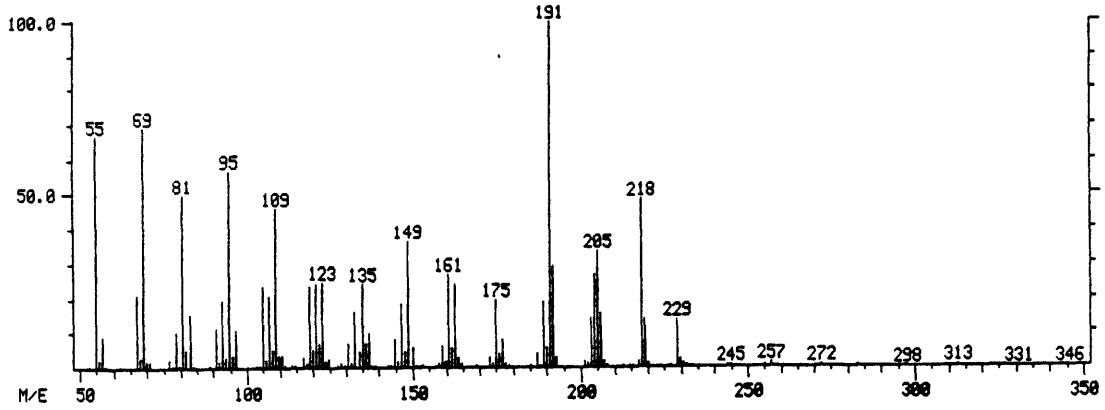


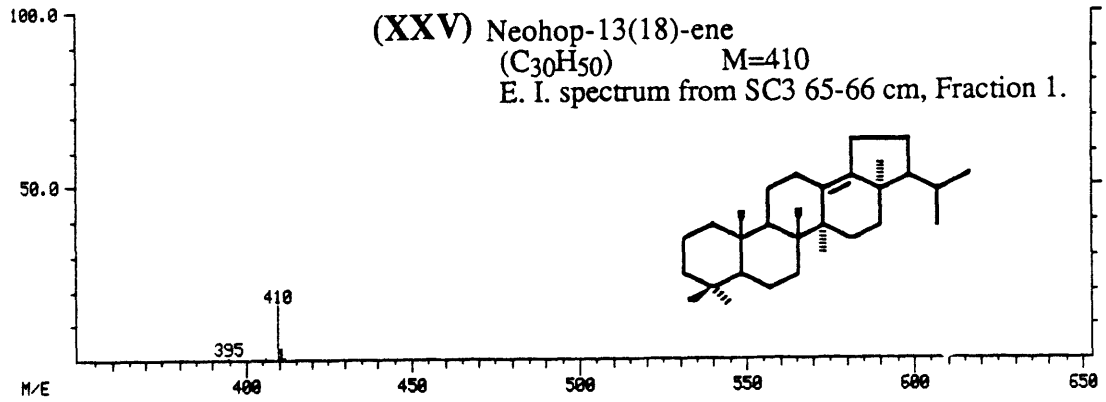
(XXIII) C_{30} triterpenoid
($C_{30}H_{50}$) M= 410
E. I. spectrum from SC3 85-86 cm, Fraction 2+3.



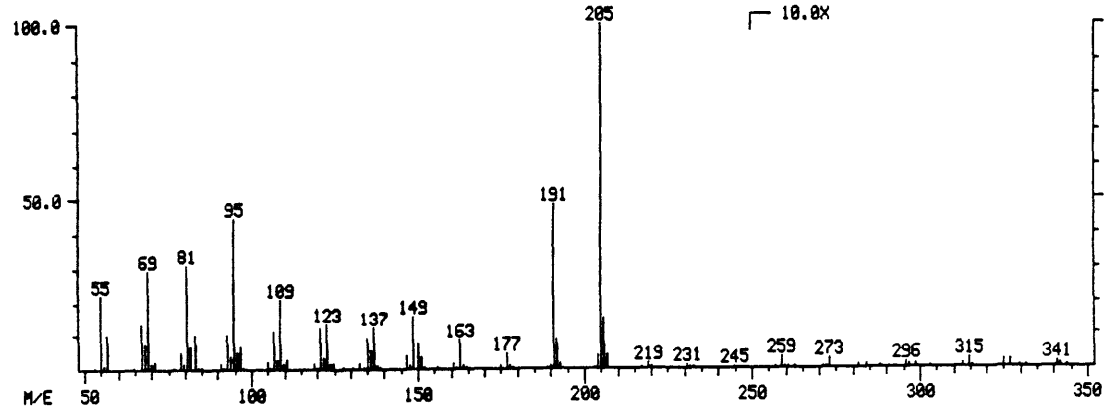


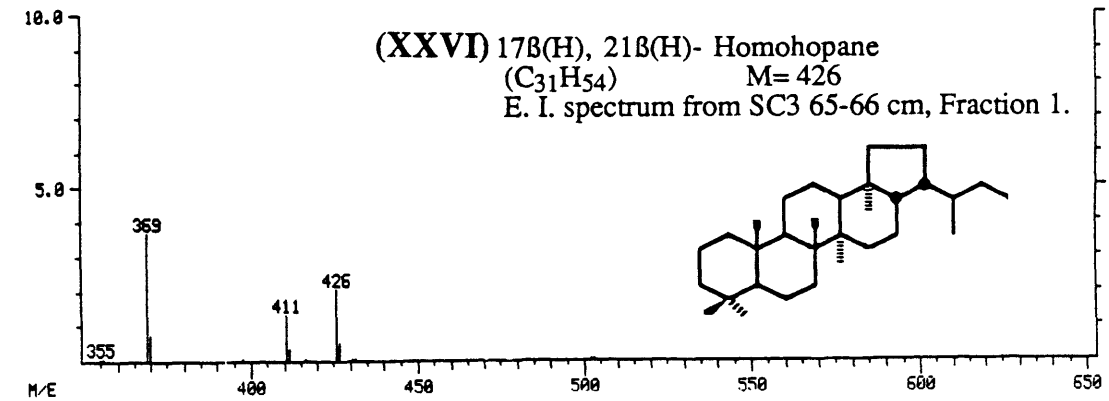
(XXIV) C_{30} alkan-15-one-1-ol (as acetate)
($C_{32}H_{66}O_3$) M= 498
E. I. spectrum from SC3 5-6 cm, Fraction 7.



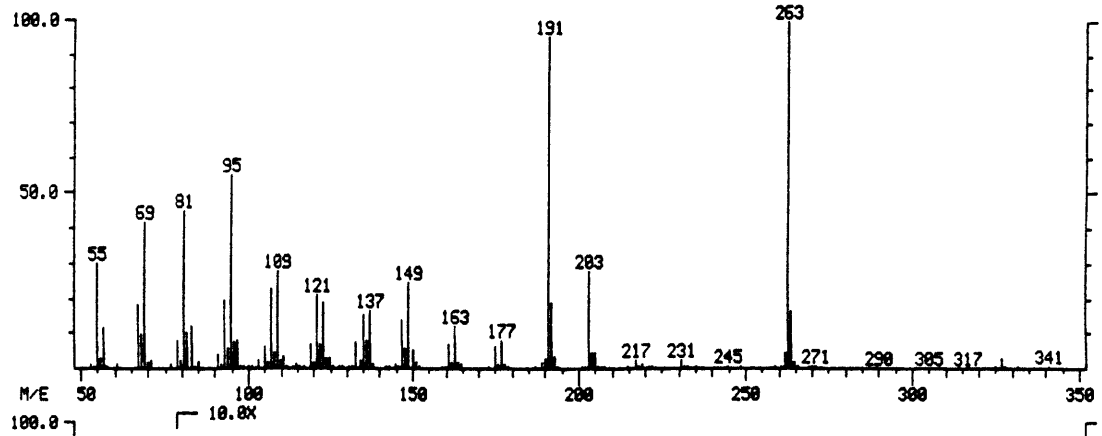


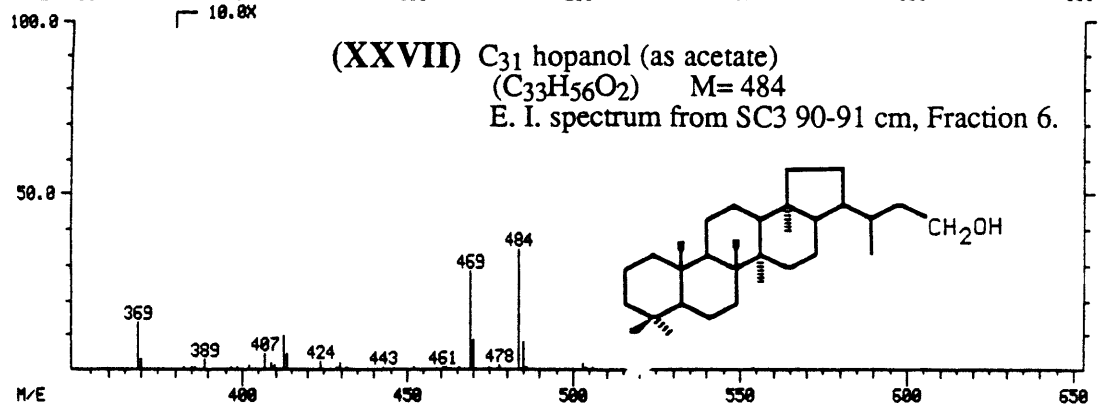
(XXV) Neohop-13(18)-ene
$(C_{30}H_{50})$ M=410
E. I. spectrum from SC3 65-66 cm, Fraction 1.



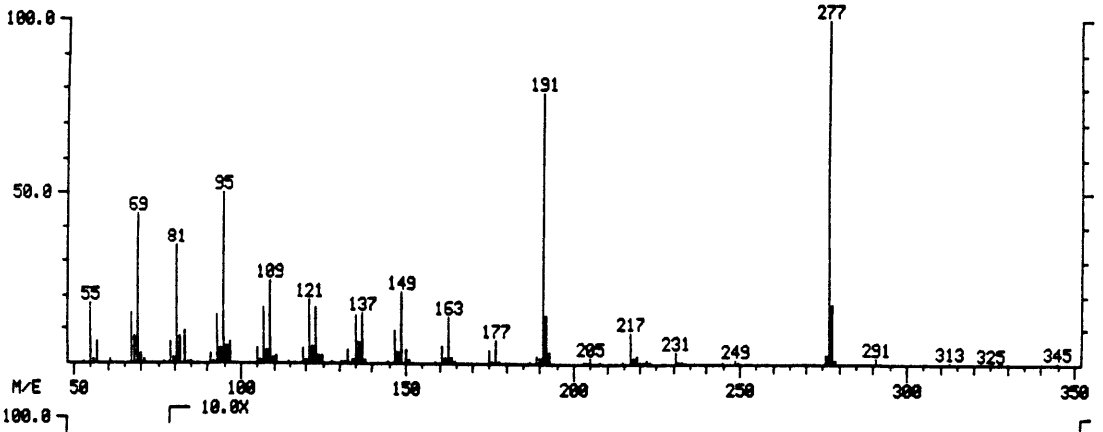


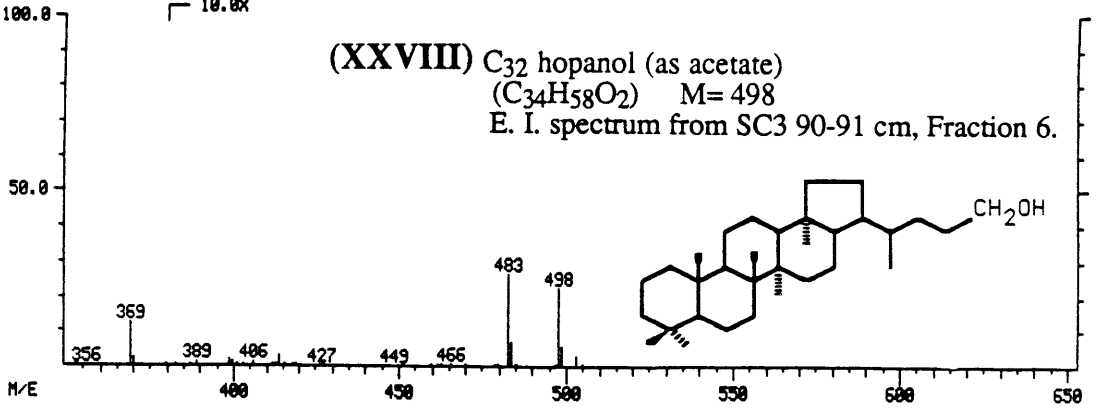
(XXVI) 17ß(H), 21ß(H)- Homohopane
$(C_{31}H_{54})$ M= 426
E. I. spectrum from SC3 65-66 cm, Fraction 1.



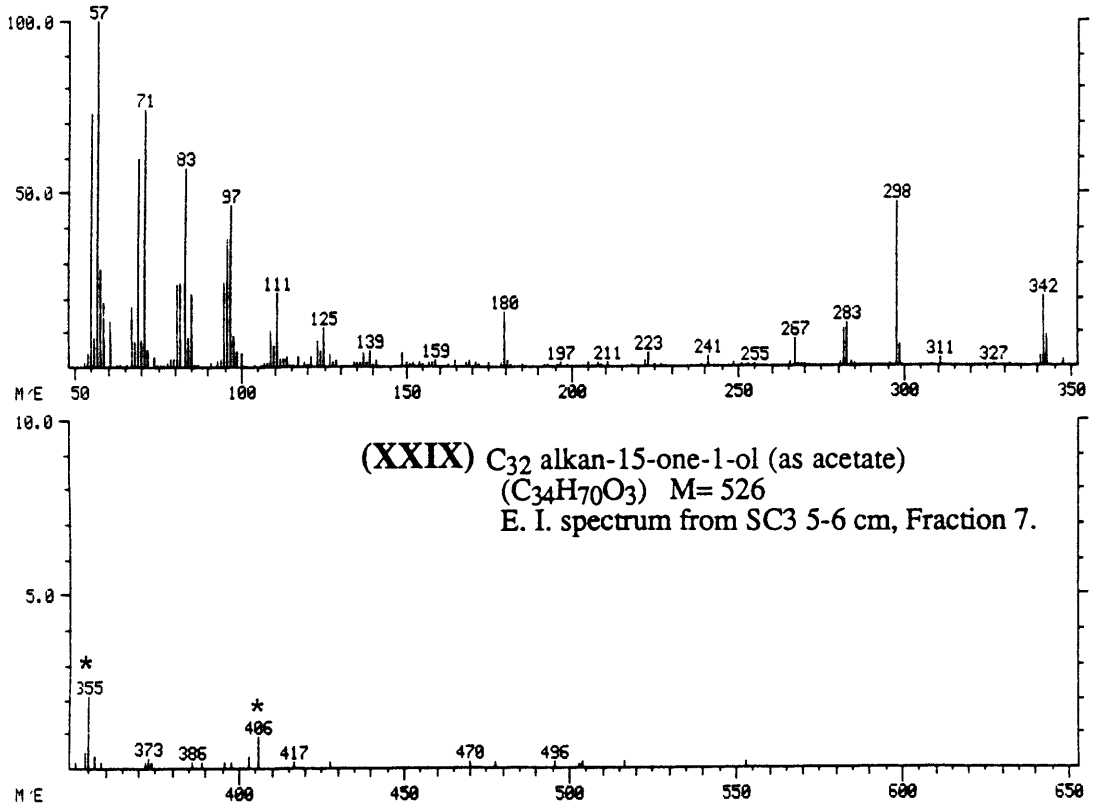


(XXVII) C_{31} hopanol (as acetate)
($C_{33}H_{56}O_2$) M= 484
E. I. spectrum from SC3 90-91 cm, Fraction 6.

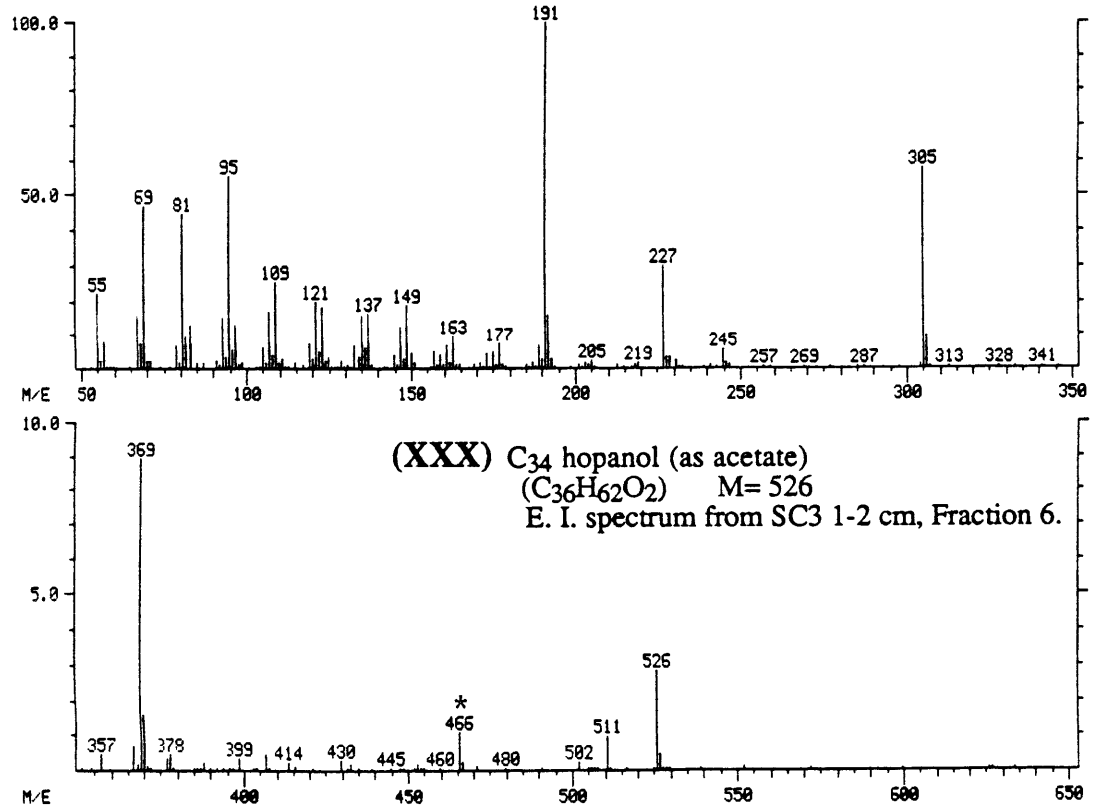




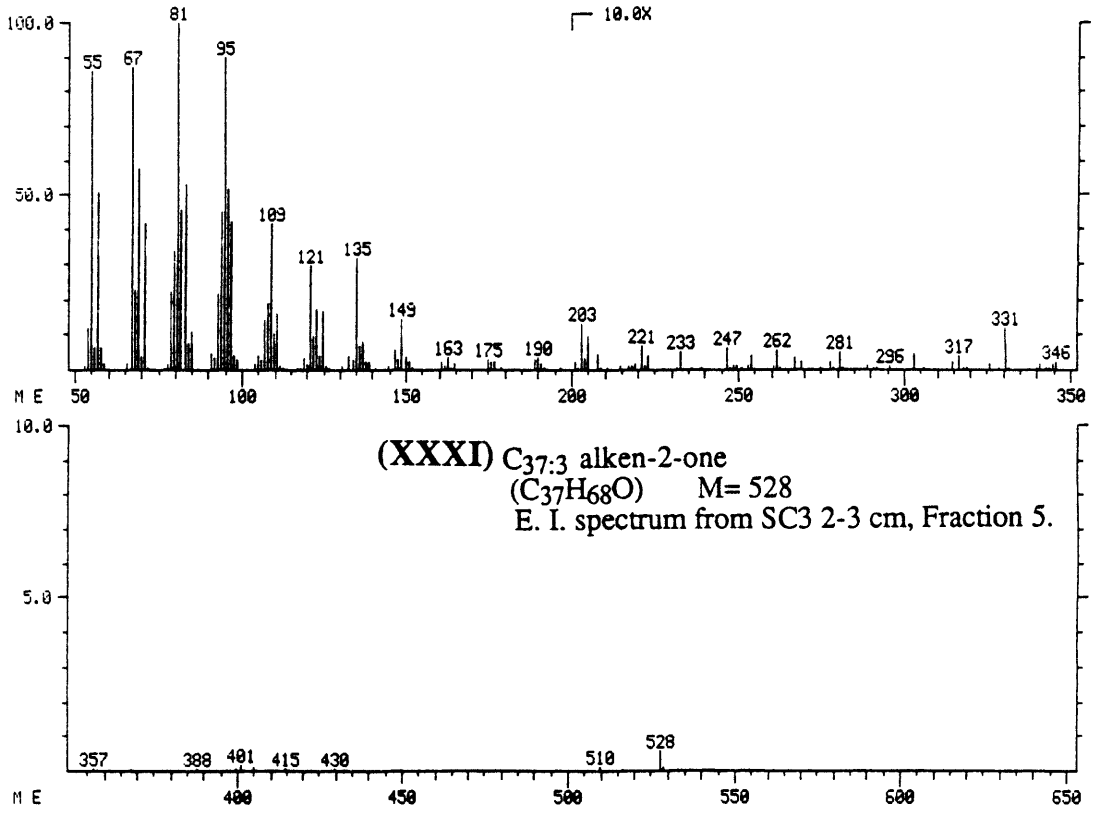
(XXVIII) C_{32} hopanol (as acetate)
($C_{34}H_{58}O_2$) M= 498
E. I. spectrum from SC3 90-91 cm, Fraction 6.



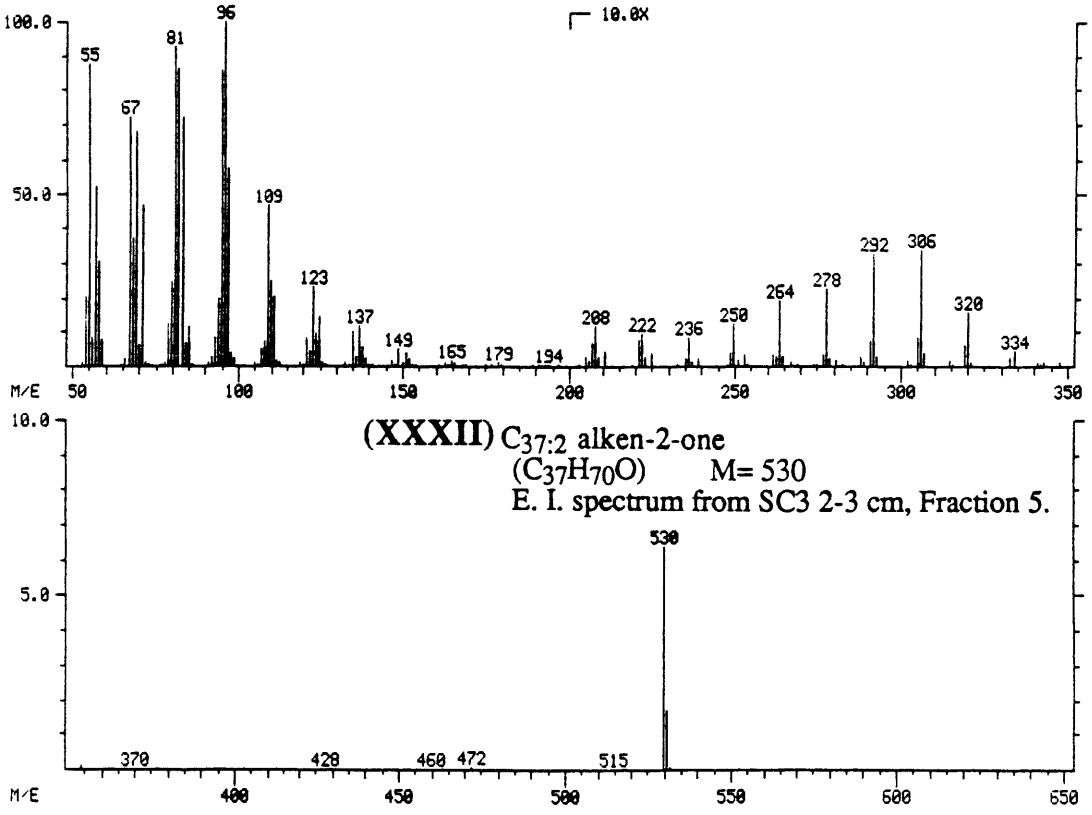
(XXIX) C_{32} alkan-15-one-1-ol (as acetate)
($C_{34}H_{70}O_3$) M= 526
E. I. spectrum from SC3 5-6 cm, Fraction 7.



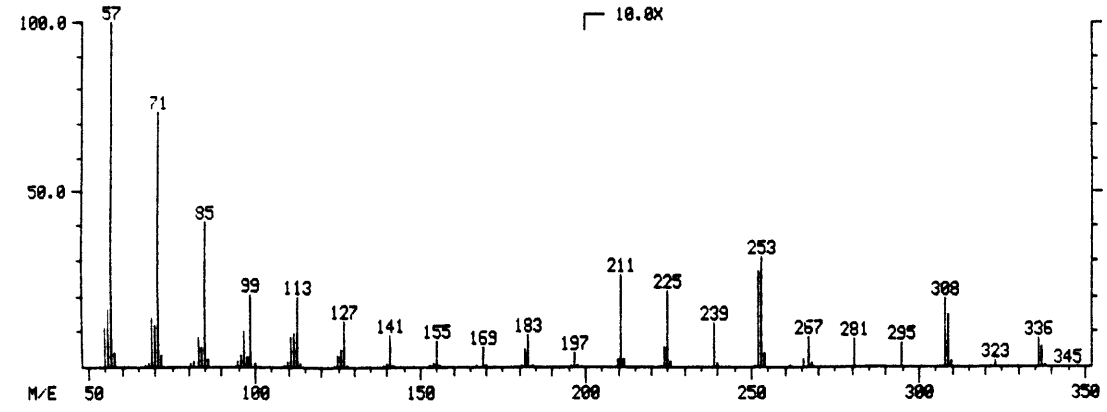
(XXX) C_{34} hopanol (as acetate)
($C_{36}H_{62}O_2$) M= 526
E. I. spectrum from SC3 1-2 cm, Fraction 6.

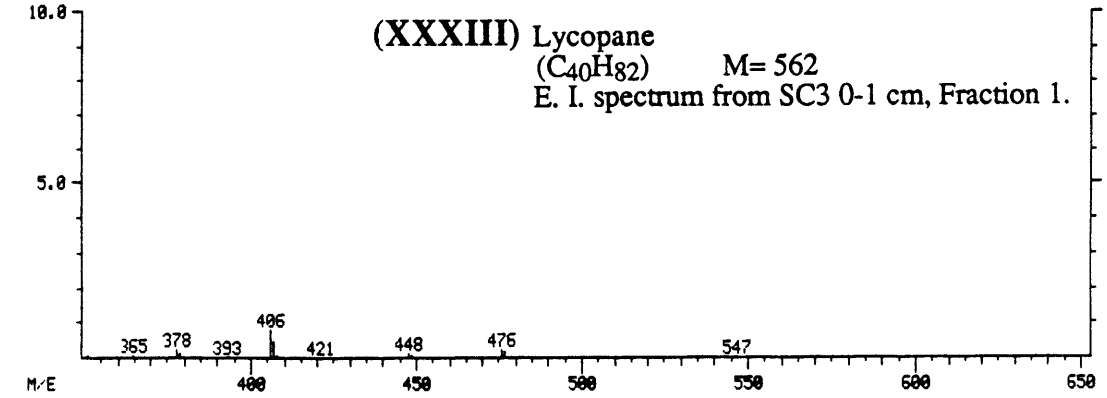


(XXXI) $C_{37:3}$ alken-2-one
($C_{37}H_{68}O$) M= 528
E. I. spectrum from SC3 2-3 cm, Fraction 5.

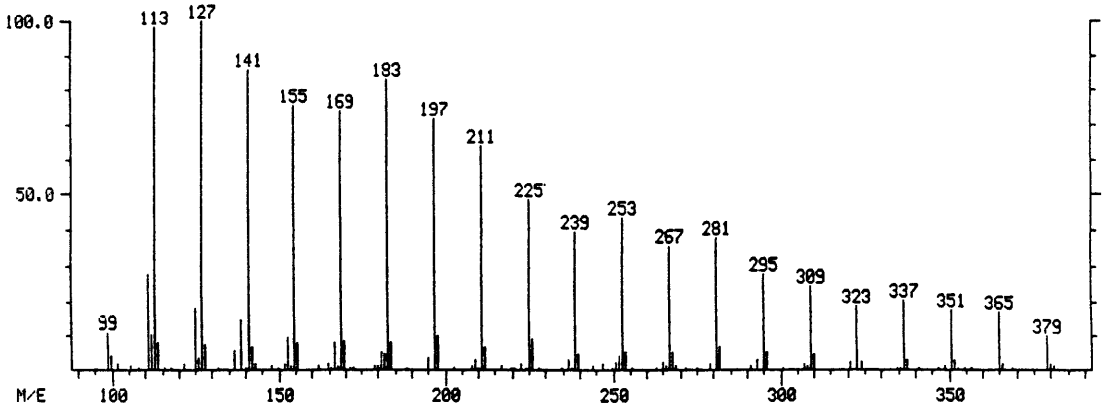


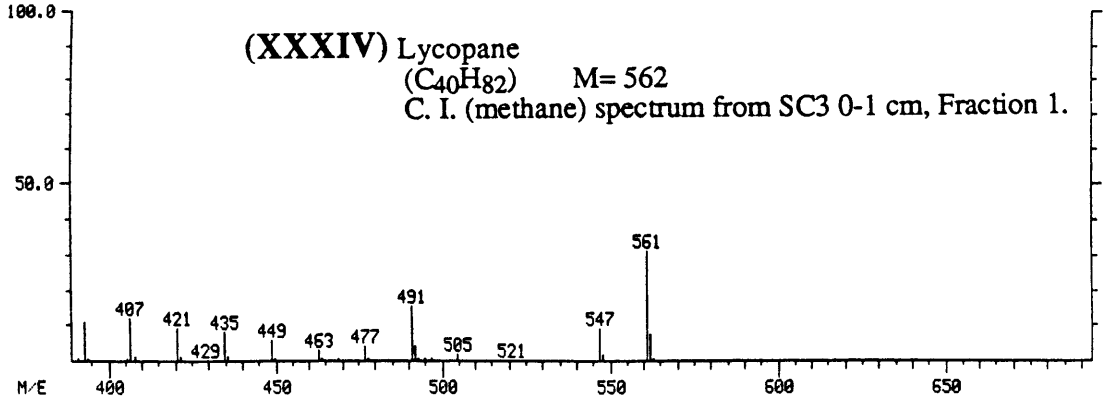
(XXXII) $C_{37:2}$ alken-2-one
($C_{37}H_{70}O$) M= 530
E. I. spectrum from SC3 2-3 cm, Fraction 5.



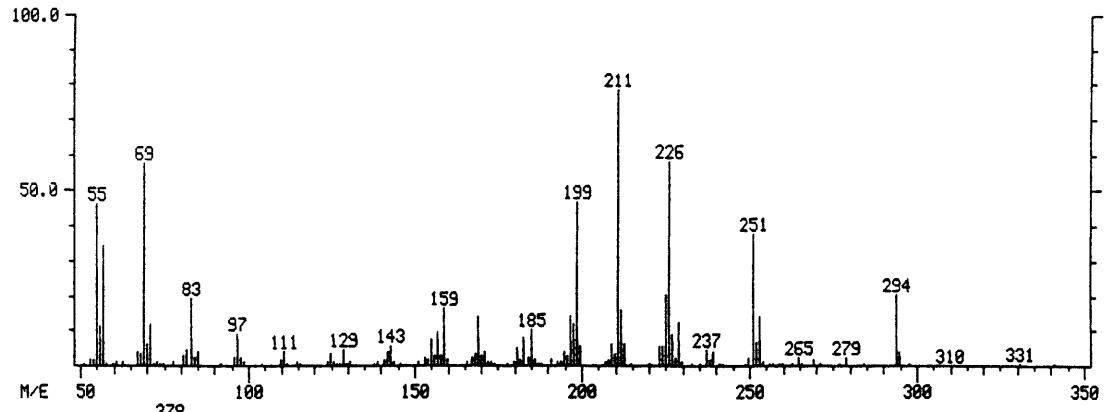


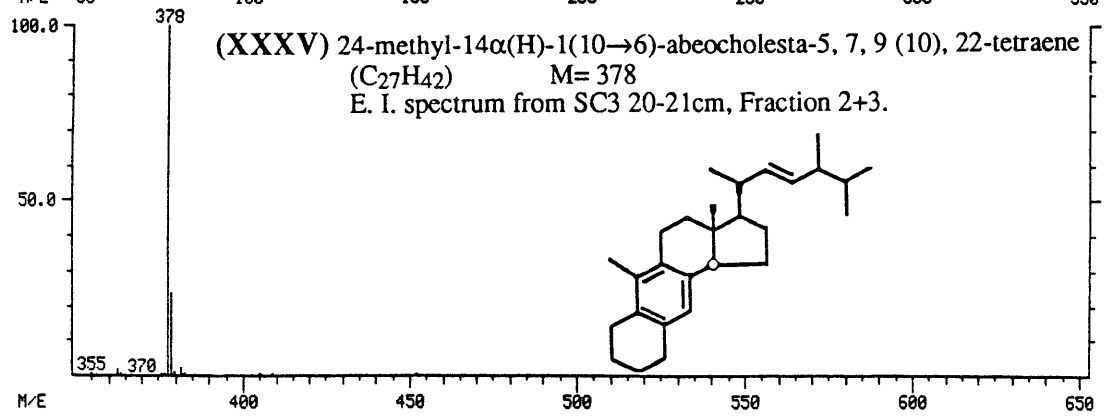
(XXXIII) Lycopane
($C_{40}H_{82}$) M= 562
E. I. spectrum from SC3 0-1 cm, Fraction 1.



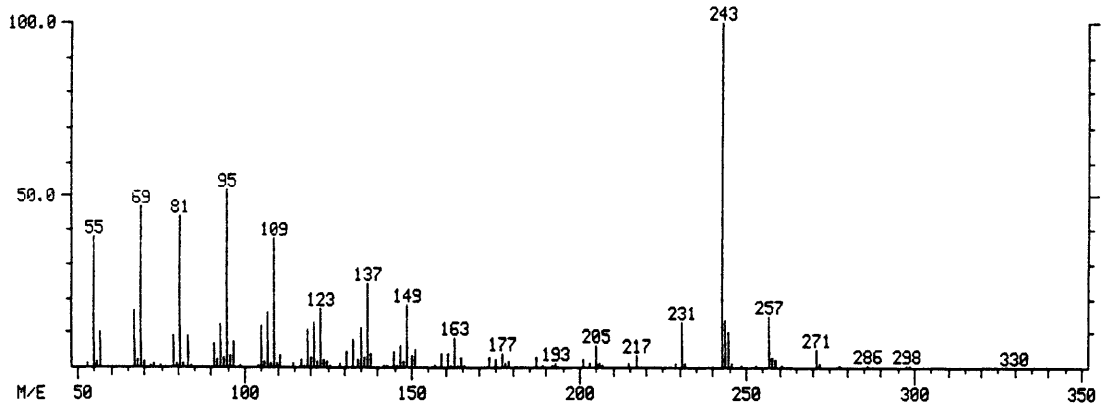


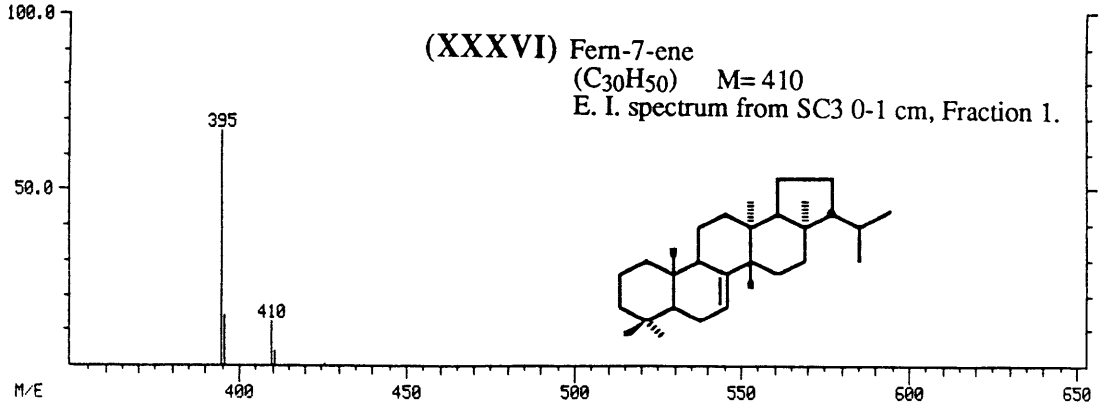
(XXXIV) Lycopane
($C_{40}H_{82}$) M= 562
C. I. (methane) spectrum from SC3 0-1 cm, Fraction 1.





(XXXV) 24-methyl-14α(H)-1(10→6)-abeocholesta-5, 7, 9 (10), 22-tetraene
($C_{27}H_{42}$) M= 378
E. I. spectrum from SC3 20-21cm, Fraction 2+3.





(XXXVI) Fern-7-ene
($C_{30}H_{50}$) M= 410
E. I. spectrum from SC3 0-1 cm, Fraction 1.

BIOGRAPHICAL NOTE

The author was born on Long Island, New York, on May 16, 1963, and lived in upstate New York until 1969, when his family moved to La Jolla, California. He attributes his interst in oceanography to frequent family trips to the Scripps aquarium and to the beautiful beaches he has lived near. In 1977, his family moved to Charleston, South Carolina, where he attended high school. The author's interest in geology dates to a summer job at Union Texan Petroleum in Houston, Texas during 1981. The author did his undergraduate work at Harvard University from 1981 to 1985, and graduated Magna Cum Laude With Highest Honors from the Geology Department. His interest in geochemistry was initiated as a result of interactions with Dr. H. D. Holland, his undergraduate thesis advisor and friend. The author enjoys SCUBA diving, the beach, Italian food, and most movies.

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